The Potential and Challenges of Drop-in Biofuels

A Report by IEA Bioenergy Task 39

AUTHORS:

Sergios Karatzos
University of British Columbia, Canada

James D. McMillan
National Renewable Energy Laboratory, USA

Jack N. Saddler
University of British Columbia, Canada

Report T39-T1 July 2014

iea
Energy Technology
Network

The Potential and Challenges of Drop-in Biofuels

Report prepared by:

Sergios Karatzos
University of British Columbia, Canada

James D. McMillan
National Renewable Energy Laboratory, USA

Jack N. Saddler
University of British Columbia, Canada

First electronic edition produced in 2014

A catalogue record for this Report is available from the British Library.

ISBN: 978-1-910154-07-6 (electronic version)

Published by IEA Bioenergy

Disclaimer

THE POTENTIAL AND CHALLENGES OF 'DROP-IN' BIOFUELS

EXECUTIVE SUMMARY

This report was commissioned by IEA Bioenergy Task 39 with the goal of providing a background to the topic, an assessment of technical approaches being developed and an overview of anticipated challenges in large scale commercialization of so called "drop-in" biofuels. For the purposes of this report, "drop-in" biofuels are defined as "liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure".

The global petroleum industry is expected to require increasing amounts of hydrogen in the coming years to upgrade crude oil feedstocks of declining quality (i.e., increasingly heavier and more sour), particularly in areas where especially heavy oils are being sourced such as Venezuela and Alberta. For the foreseeable future, much of this hydrogen is likely to be derived from natural gas. At the same time, there will also be increasing demand for hydrogen to deoxygenate biomass (carbohydrates and lignin) to produce drop-in hydrocarbon biofuels.

Oil refineries use hydrogen to upgrade low grade crude oil by removing sulfur and other heteroatom impurities (hydrotreating) and by "cracking" longer oil carbon chains to shorter chains while also enriching them with hydrogen (hydrocracking). One result of these hydrogen-consuming processes (collectively known as hydroprocessing) is to elevate the hydrogen to carbon ratio of low grade crude oils. The hydrogen to carbon ratio in petroleum feedstocks is a good indicator of their quality for fuel production since a high sulfur content as well as the presence of long and condensed carbon chains (e.g., in coal) reduce the H/C ratio. As detailed in the main body of the report, the H/C ratio can be visualized as a staircase in which the more "steps" that have to be climbed up the "H/C staircase", the more hydrogen inputs and processing efforts are required to elevate the H/C ratio to the level required for higher grade liquid gasoline, diesel and jet transportation fuels. Non-hydrogen-consuming processes such as catalytic or thermal cracking can also improve the H/C ratio of petroleum feeds by removing carbon in the form of tars and char (coke). However, this approach consumes feedstock and reduces yields and so is generally avoided, particularly when crude oil prices are high.

It is also evident that a majority of evolving drop-in biofuel technologies require hydrogen (H_2) inputs or other chemical reduction processes to upgrade oxygen-rich carbohydrate, lignin or lipid feedstocks to hydrogen-rich hydrocarbons that are functionally equivalent to petroleum-derived liquid fuels. As detailed in the report, a variation of the hydroprocessing step will likely be common to many drop-in biofuel technology platforms, with imported hydrogen used to remove oxygen (in the form of H_2O) from oxygenated lignocellulose intermediates or lipid feedstocks. Alternatively, non-hydrogen consuming processes (whether chemical or biological) will have to oxidize significant amounts of feedstock carbon in order to produce the required hydrogen or alternative reducing power carriers (e.g., nicotinamide adenine dinucleotide phosphate or NADPH). However, these alternative routes to deoxygenation are generally less attractive as they can consume a significant amount of the feedstock. After adjusting for the oxygen content of the biomass feedstock, the hydrogen to carbon ratio, H_{eff}/C, can be defined as a relevant metric for drop-in biofuel processes. Highly oxygenated biomass feedstocks such as sugar molecules have a H_{eff}/C ratio of 0 whereas the target for drop-in biofuels is approximately 2, similar to the H/C ratio of diesel. Most biomass feedstocks (sugars, biomass, lignin) have a low H_{eff}/C ratio and are thus situated near the bottom steps of the H/C staircase. Biomass feedstocks thus need to "climb" more steps than fossil feedstocks to reach the chemically reduced state of diesel, jet and gasoline fuels. Even low grade fossil feedstocks such as coal ($H/C = 0.5$) contain a substantially higher H_{eff}/C ratio than most biomass feedstocks. A notable exception are the biomass lipid fractions and other renewable oleochemical types of feedstocks, which contain much lower levels of oxygen and have an H_{eff}/C ratio of about 1.8 and are thus much farther up the H/C staircase and more readily suited for conversion to drop-in biofuels.

There are several ways to produce drop-in biofuels that are oxygen-free and functionally equivalent to petroleum transportation fuels. These are discussed within three major sections of the report and include: oleochemical processes, such as the hydroprocessing of lipid feedstock from either oil crops, algae or tallow; thermochemical processes, such as the thermal conversion of biomass to fluid intermediates (gas or oil) which are then catalytically upgraded/hydroprocessed to hydrocarbon fuels; and biochemical processes, such as the biological conversion of biomass (sugars or cellulosic materials) to longer chain alcohols and hydrocarbons. A fourth category is also briefly described that includes "hybrid" thermochemical/biochemical technologies such as fermentation of synthesis gas and catalytic reforming of sugars/carbohydrates.

To date, oleochemical based processes have been the main supplier of the drop-in biofuels that have been evaluated for commercial application by sectors such as aviation. These processes require a simple hydroprocessing step to catalytically remove oxygen from the fatty acid chains present in the lipid feedstock to convert them to diesel-like hydrocarbon mixtures. This technology is well developed, is maturing and entails relatively low technological risk and low capital expenditure compared to other emerging drop-in biofuel production routes. Most lipid feedstocks have relatively low oxygen content (11% mass) and thus require lower hydrogen inputs to be upgraded to liquid transportation fuels. However, the feedstock is generally costly and available in limited supply, as vegetable oils such as palm and rapeseed are currently priced in the range of USD $500-$1200/t (or $12-30/GJ) compared to approximately USD $75-$125/t (oven dry basis, or $3.75-6.25/GJ) for lignocellulosic biomass, and their supply is often limited by competition from other value-added end users (e.g., food and cosmetics industries). There are also ongoing challenges regarding the sustainable production of vegetable oils as production is relatively land use and resource intensive. Although "food-vs.-fuels" concerns and related debate are likely to continue, several companies are operating commercial oleochemical feedstock-to-biofuels facilities around the world, including Neste Oil (Finland, Rotterdam, Singapore) and Dynamic Fuels (Louisiana, USA).

The various thermochemical methods currently being assessed for biofuel production have their origins in the ancient process of "burning" biomass in the absence of oxygen to make charcoal, a higher calorific value product. Thermochemical processing conditions can be optimized to influence the ratio of the three main products of bio-oil, synthesis gas and char. The two main routes to drop-in biofuels are through pyrolysis and gasification. Fast pyrolysis (essentially treating biomass at 500 °C for a few seconds) has been studied in detail since the early 1980s and bio-oil yields of up to 75 wt% can typically be obtained from various biomass feedstocks. Although there are a few, niche high value markets for bio-oil components, such as food flavouring (Barbeque flavour), today pyrolysis liquids are primarily considered for use in stationary power generating facilities such as the proposed 720 tpd Pyrogrot facility in Sweden. Bio-oils can also be upgraded to drop-in biofuels although this requires significant hydrogen inputs. While these hydrogen inputs can be generated from the biomass feedstock itself, this process is inefficient when compared to sourcing hydrogen from an external source such as natural gas. The pyrolysis platform requires large amounts of hydrogen gas inputs which represent a large proportion of both capex and opex in a stand-alone facility. It has been estimated that sourcing external hydrogen from an oil refinery can reduce the capex of a pyrolysis drop-in biofuel facility by ca. 40% and the opex by ca. 15% (Jones et al. 2009). Pyrolysis platforms also have great potential to leverage oil refineries in order to reduce biofuels production capital and operating costs. The major saving will in part be a result of sourcing hydrogen from the oil refinery directly. However, it is estimated that current US refinery hydrogen capacity of 3 billion standard cubic feet per day, would need to be tripled to meet the 2022 US RFS cellulosic advanced biofuel mandate of 15 billion gallons (57 billion L) using pyrolysis platform-derived diesel/gasoline blendstock. Although existing hydrocracking units (downstream in a refinery) can co-process petroleum and hydrotreated pyrolysis oils (HPO), this practice is not yet commercial and it comes with challenges related to adapting the catalyst design to accommodate two disparate feedstocks (HPO and petroleum). A case study where Haldor Topsoe (the world's biggest manufacturer of petroleum refinery catalysts) performed trials on industrial hydrocrackers using various biofeeds identified several challenges to catalytic "co-processing" of biofeed blends with petroleum. Although further upstream insertion points have been suggested, such as at the vacuum distillation tower, these alternative processing strategies can only be used with minimally processed pyrolysis oils which can contain large amounts of refinery contaminants such as oxygen and inorganics. Two of the major challenges constraining development of pyrolysis derived drop-in biofuels are the availability of low cost sustainable hydrogen and the technological advances needed to adapt hydrotreating catalysts to bio-oil feedstocks. Various companies such as Canada's ENSYN have operated pilot plants for several years and KiOR recently completed a 49 million litre per year (MLPY) or 13 million gallon per year (MGPY) commercial facility in the US.

The other major thermochemical route to drop-in biofuels is through gasification. Gasification of biomass or bio-oil produces synthesis gas ("syngas", comprised of mostly H_2 and CO), which is primarily used to fuel stationary heat and power facilities such as the 8 MW bio-power station in Gussing, Austria. Syngas can also be upgraded (catalytically condensed) to drop-in liquid biofuels via the Fischer-Tropsch process (FT), which has its origins in the 1920s in Germany when access to oil was problematic. Since the 1980s, South Africa's Sasol converts coal syngas into diesel at the CtL Secunda facility which has a capacity of 160,000 barrels of diesel per day. A variation of the FT process is used in the world's largest natural gas-to-liquids facility (Shell's Pearl GtL facility in Qatar, completed in 2011) to produce 140,000 barrels of diesel per day. However, biomass derived syngas is less energy dense than natural gas and it contains more impurities and a lower H/C ratio. As a result, biomass syngas needs to be enriched in hydrogen and cleaned of the impurities such as tars, nitrogen and other heteroatoms that can deactivate synthesis catalysts. Hydrogen is typically produced from the syngas itself by a process known as the "water-gas shift" reaction. However, this reaction consumes feedstock carbon and thus reduces the overall biomass-to-fuel yields. Alternatively, as is being proposed by companies such as Sundrop

Biofuels in the US, the hydrogen can be derived from natural gas. Generally, gasification technologies entail high capital costs to both gasify the biomass and convert the resulting syngas to Fischer-Tropsch liquids or partially oxygenated liquid hydrocarbon products such as mixed alcohols. To benefit from economies of scale, these types of facilities usually have to be constructed at large scales. The capital cost estimates for a first-of-kind gasification-based facility are in the region of USD $600-900 million. Several companies are pursuing gasification platform routes to drop-in biofuels such as Forest BtL Oy in Finland, which has licensed Choren's Carbo-V technology and intends to complete a 129 million litre per year (MLPY) {or 34 million gallon per year MGPY} facility by 2016.

The capital costs of both the oleochemical and thermochemical processes could be reduced by leveraging existing process units available in petroleum refineries. Oil refineries are complex facilities comprised of the many unit operations needed to fractionate and upgrade diverse crude oil feedstocks. Upgrading entails a number of intertwined processes such as cracking (breaking heavy hydrocarbon chains to lighter ones), naptha reforming (creating aromatic molecules necessary for gasoline blends) and hydrotreatment (mainly used to remove sulfur before fuel blendstock finishing). The dilemma in trying to identify refinery insertion points for renewable feedstock drop-in biofuel intermediates is to what extent should the intermediate be upgraded (deoxygenated) prior to insertion and to what extent should the refinery be adapted to accept less-upgraded, oxygen-containing biofeed intermediates. The challenges of processing biofeeds in an oil refinery are significant, as has been demonstrated by previous industrial trials using less problematic renewable feedstocks such as fatty acids containing relatively low amounts of oxygen (11% oxygen). The oxygen content of biofeeds translates to corrosion of metallurgy and extensive coking of catalyst surfaces as well as downstream contamination risks and requirements for venting of oxygenated gases (CO, CO_2 and H_2O). Strategies to mitigate these challenges include limiting the blending rate of biofeeds in petroleum feeds and favouring insertion points towards the end of refinery processing, both of which lower the risk of downstream contamination with biomass oxygenates, inorganics and tars. Hydroprocessing units situated at the end of the oil refining process are suitable for drop-in biofuel leveraging. All of the drop-in biofuel processes proposed to date entail some form or degree of capital intensive and hydrogen-consuming hydroprocessing (especially pyrolysis and hydrotreated ester and fatty acids (HEFA) platforms). Refineries can be leveraged by drop-in biofuel facilities in order to utilize existing hydroprocessing facilities and also to source low cost fossil feedstock derived hydrogen. Still, even with this lower risk co-location strategy, there are significant challenges that need to be resolved such as matching the scale, siting and catalyst design for two distinctly different feedstocks (bulky and reactive solid biomass versus relatively inert petroleum liquids (crude oil)).

Biological routes form the third category of drop-in biofuel technologies. These include metabolic pathways that convert highly oxygenated, low H_{eff}/C, sugars to high energy density molecules such as butanol (e.g. Gevo, Butamax), farnesene (e.g. Amyris) and fatty acids (e.g. LS9). The metabolic processes involved in biologically deoxygenating carbohydrates to drop-in fuel molecules are energy-intensive and they are usually employed by the microorganisms when under stress and as mechanisms to store energy or build defence barriers (e.g. lipid layers). In industrial practice, this generally translates to biological systems with low volumetric productivities and less stable metabolic pathways. These so-called advanced fermentation pathways are not as efficient as conventional sugar-to-ethanol industrial fermentation systems. A key advantage of biological compared to thermochemical routes, is their ability to produce relatively pure molecular streams with predictable chemistry that can be readily functionalized (chemically). Thus this route can take advantage of the rapidly growing value-added chemicals and polymers markets. These markets consist mostly of organic diacids and dialcohols (butanediol, succinic acid etc.) which have lower H_{eff}/C ratios than hydrocarbon-like drop-in biofuels. Thus they are "easier" to produce with fewer processing efforts and fewer hydrogen inputs. In the near term, it is likely that the biological platform will exploit the higher margins that can be achieved in value-added biochemical markets rather than fuel markets. Various business intelligence organisations have estimated significant growth for these bio-based chemicals over the coming decade (e.g. ca. 20%/year to reach 50 million metric tonnes by 2020). Until these lucrative chemical markets are saturated, there will be little incentive for biological conversion companies to produce biofuels.

A fourth category of “hybrid platforms” combines elements of the categories described earlier. These include fermentation of syngas (example, LanzaTech), alcohol-to-jet (example, BYOGY), acid-to-ethanol (example, Zeachem), and aqueous phase reforming (example, Virent). Each of these technologies has certain advantages such as improved utilization of feedstock carbon (Zeachem, LanzaTech) or use of commodity bio-feedstock such as sugar and ethanol coupled with ‘low risk’ and rapid catalytic reforming (BYOGY, Virent). Disadvantages include mass transfer issues such as the slow diffusion of gases into aqueous fermentation broths and the difficulty of isolating organic acids from fermentation mixtures. Catalyst issues such as the low tolerance of current reforming catalysts to oxygenated feedstocks are also a challenge, as are feedstock and capital intensity to provide hydrogen for catalytic reduction of acids, alcohols or other oxygenated products to de-oxygenated saturated hydrocarbons.

While tremendous technical progress and commercialization activity have taken place over the past several years, only relatively small amounts of drop-in biofuels functionally equivalent to petroleum-derived transportation fuels are commercially available today. In the same way conventional (so-called "first generation") bioethanol from sugar and starch was used to establish the infrastructure and "rules" for subsequent production and use of advanced (so-called "second generation") bioethanol, it is likely that oleochemical derived drop-in biofuels will initially be used to establish the markets and procedures for use of drop-in biofuels. This is exemplified by the many Hydrotreated Vegetable Oil (HVO)-based biofuel flight trials and refinery processing trials undertaken over the last few years and by the recent ASTM approval of oleochemical derived jet fuel blendstocks. However, significant expansion of the oleochemical platform will be limited by the cost, availability and sustainability of food grade (vegetable oil) or animal oil/fat based feedstocks. The challenge of developing emerging thermochemical based drop-in technologies can be viewed as analogous to cellulosic ethanol, which uses more plentiful, non-food lignocellulosic biomass as feedstock but entails larger technology risks and higher capital costs. In this context, thermochemical technologies are well positioned to account for a considerable component of drop-in biofuel capacity growth over the near-to-midterm. This is primarily because biochemical and hybrid based drop-in biofuel processes typically provide lower yields of higher value oxygenated intermediates (e.g. organic dialcohols and diacids) that can command higher value in the rapidly growing bio-based chemicals markets. It is also likely that future biorefineries will utilize biomass in much the same way that current petroleum refineries use crude oil by converting the raw feedstock into a diverse range of fuels and chemicals products in a single highly integrated facility. However, it is probable that larger sized thermochemical based facilities will primarily focus on converting biomass feedstocks to commodity scale drop-in biofuels and bioenergy products while somewhat smaller scale biochemical or algal platform based facilities will convert sugar, biomass or syngas feedstocks to specific higher value non-commodity products such as farnesene, butanediol, succinic acid, butanol or oils for use in more lucrative biobased chemicals markets (e.g., cosmetics, food additives, lubricants, etc.). Regardless, for all of these technologies, hydrogen sourcing will play a major role in future commercialization of drop-in biofuel platforms.

Contents

Tables

Figures

CHAPTER 1: BACKGROUND – BIOFUELS & PETROLEUM INDUSTRY

Biofuels are currently being developed as renewable alternatives to fossil derived transportation fuels with the hope of achieving environmental and socioeconomic benefits such as reduced GHG emissions, employment generation and energy security. Bioethanol and biodiesel are the main commercially available biofuels and currently contribute about ~2% by volume of global transportation fuel demand (US EIA, 2013). However, these fuels are chemically and functionally different from petroleum-derived fuels and they thus do not make full use of the existing petroleum processing and distribution infrastructure. As infrastructure components, such as vehicle engines, fueling stations, refineries, etc., are very expensive to change, it is recognised that it would simplify biofuels production and usage growth if biofuels could be readily "dropped-into" the existing infrastructure (petroleum distribution and refining, fuel specifications, etc.) and be functionally equivalent to current petroleum-derived fuels. However, as will be described in more detail, it is likely that producing such "drop-in" biofuels will require more complex processing infrastructure and higher processing inputs, most notably hydrogen (H_2) inputs, than today's predominant bioethanol and biodiesel biofuels. Consequently, greater techno-economic challenges will probably be encountered when trying to achieve cost competitive routes to drop-in biofuels

Hydrogen is a key input not only for drop-in biofuel producers (e.g. hydrotreated vegetable oils) but also for other sectors, most notably the Oil & Gas sectors, which have to upgrade crude oil of ever declining quality to meet the needs of a growing market for more refined and lighter petroleum products. In the future, drop-in biofuel producers may have to compete for hydrogen resources with the petroleum sector as well as the ammonia fertilizer industry.

1.1 Biofuels rationale

Unstable and rising petroleum prices, the finite nature of the resource, as well as concerns about fossil fuel emissions and dependence on politically unstable regions for transportation fuel imports are among the major motivations for pursuing biofuels. Biofuels are arguably the most likely near term renewable alternative to petroleum fuels, with some forms of transportation that cannot be easily electrified (such as long distance trucking, shipping and aviation) having this approach as the only alternative.

Rising oil prices have been a major motivator in finding alternatives to fossil based transportation fuels, with the OPEC oil crises of the 1970's stimulating several counties to look into alternative, renewable biofuels. However, as oil prices decreased in the 1980's (Figure 1-1), the interest and research support into biofuels largely decreased, although countries such as Brazil and the United States continued to try to commercialise conventional (so-called "first generation") biofuels, primarily bioethanol from sugars and starches (grains) and biodiesel from plant crop seed oils. Investment in advanced (so-called "second generation") biofuels produced from non-food feedstocks increased in the early 2000s due to a combination of factors such as increasing awareness of the role of transport derived carbon emissions in climate change and increasing dependence on crude oil imports to Europe and North America. The availability and price of these crude oil imports is increasingly uncertain for a variety of reasons such as geopolitical conflict and political uncertainty. More recently, despite the discovery of new unconventional Oil & Gas resources, the IEA forecasts that the price of oil will remain high over the coming decades while demand for biofuels is expected to further increase and play a major role in meeting ambitious GHG emission reduction targets globally. According to the most likely future policy scenarios ("current" and "new" policies scenarios) described in IEA's 2012 Word Energy Outlook (Figure 1-1), the price of oil is expected to rise to above USD $120/barrel by 2035, and in the absence of new policy action it is projected to climb to almost USD $150/barrel by 2035 (IEA, 2012b).

In this backdrop of expensive petroleum through to 2035, biofuels are well positioned to become a significantly larger contributor to the global energy landscape. According to the IEA's "blue map" scenario, biofuels could provide 27% of total transport fuel by 2050 (IEA, 2011b). If this production level of biofuel could be achieved it would avoid the production of 2.1 gigatonnes of CO_2 emissions per year compared to if this amount of petroleum-derived fuels were used (IEA, 2011b).

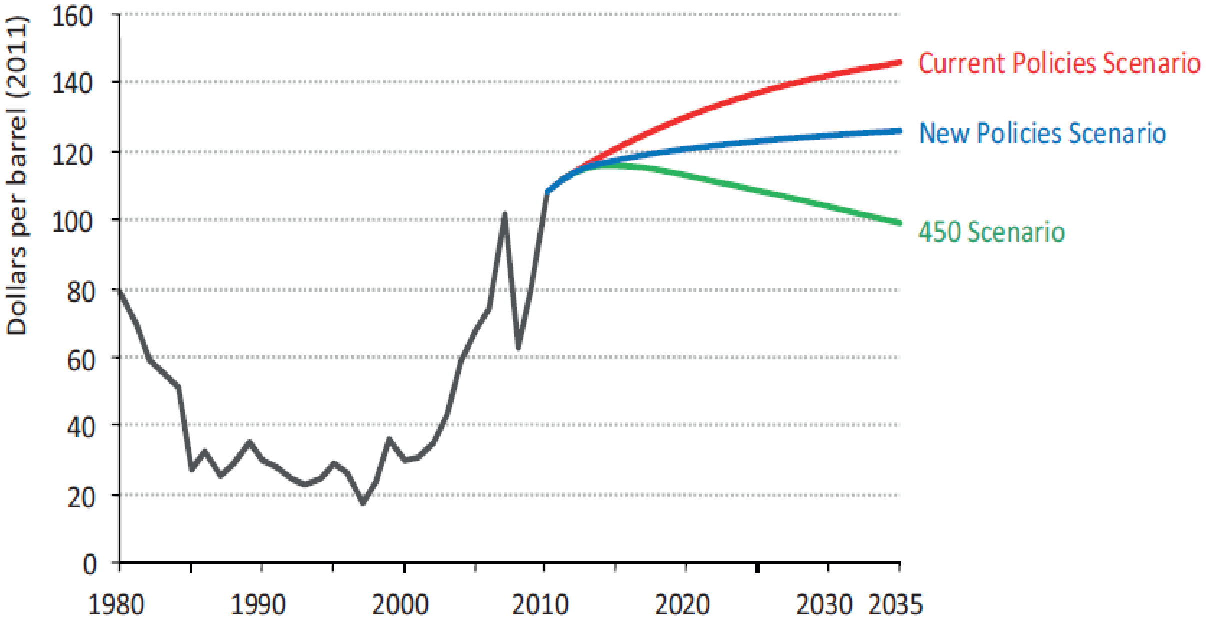


Figure 1-1: Average IEA crude oil price
(Source: IEA, 2012)

1.2 Current biofuels

Conventional (or what others have termed "first generation") food crop-based biofuels such as bioethanol from sugar or starch and biodiesel from oilseed, waste oil or tallow are currently the only commercially available large-scale biofuels. Of the 89 million barrels per day (mbpd) of liquid fuels produced globally in 2011, 1.9 mbpd were conventional biofuels (US EIA, 2012). Biofuel production has grown almost exponentially over the last decade (Figure 1-2) with bioethanol providing the vast majority of this biofuel which is predominantly produced in the USA and Brazil. Recent IEA estimates project global biofuel production to more than double by 2035 (to ca. 4.5 mbpd) over 2011 production levels (IEA, 2012b). The majority of the growth in biofuels over the last decade has come from the US and to a lesser extent Brazil. Together Brazil and the USA currently account for three quarters of world total biofuel production and close to 90% of global bioethanol production (U.S. EIA, 2010). The world's third biggest biofuel producer is the European Union. In contrast to the US and Brazil, the EU produces mostly biodiesel (>80% of total biofuel production volume) with lesser amounts of bioethanol.

The historical policy, market and infrastructure parameters that made these countries leaders in biofuel development are relevant to current efforts to develop "drop-in" biofuels.

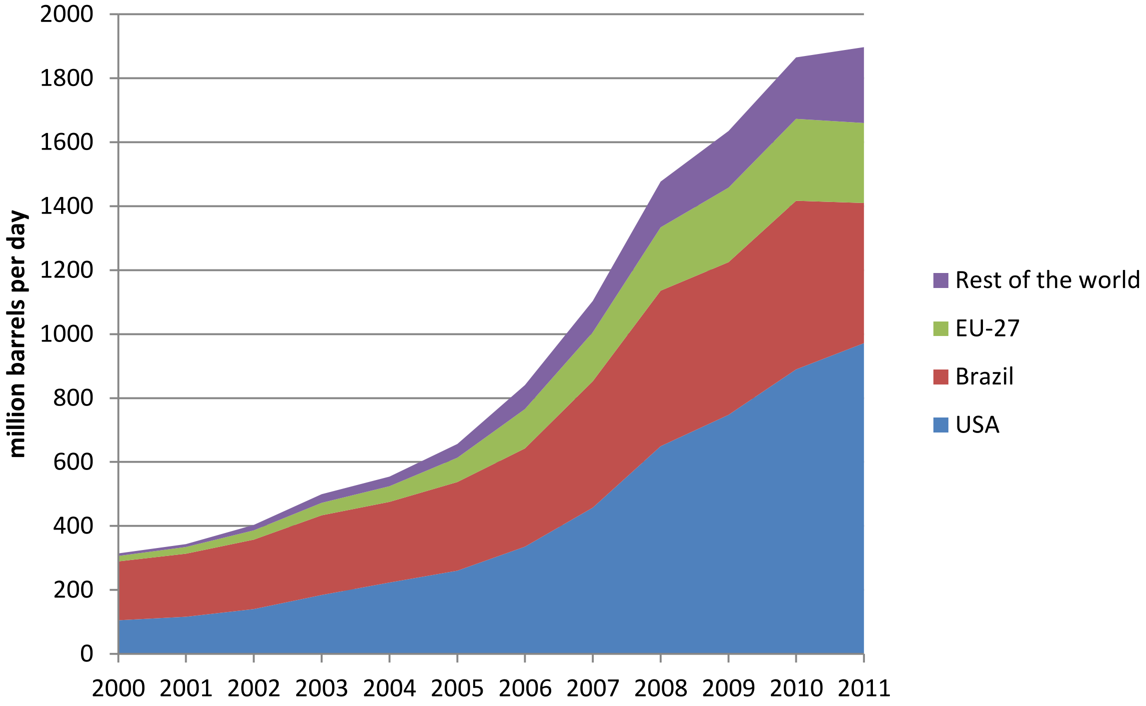


Figure 1-2: Historic biofuel production volumes
(Source: data from US EIA, 2012)

1.2.1 Ethanol

In 2011 the world produced 1,493,000 bpd of bioethanol fuel with the US producing 908,000 bpd (or 60% of global), Brazil 392,000 bpd (or 25% of global) and the EU 72,000 bpd (or 5% of global) (US EIA, 2011).

The USA is currently the world's largest ethanol producer**.** Significant production and use of bioethanol began in the USA in the early 1980s with the main driver being energy security concerns arising from the rapid increases in global petroleum prices during the 1970s and 1980s (Tyner, 2008). Another driver that promoted corn ethanol in the USA was (and still is) the strong campaigns aimed at gaining political support for expanding markets and revenues for the corn and bioethanol industries. Federal as well state government measures such as direct funding of partnerships, research funds, tax incentives and renewable fuel mandates were developed to help the then emerging corn ethanol industry (Mabee, 2007). These US policies, variations of which are still in force, were successful in developing the rapid increase in ethanol production over the last few decades. Leveraging on an efficient and highly productive corn industry especially in the US Midwest where corn growing is favoured by both agronomic and geo-climatic factors, these ethanol supporting policies helped the US become the current world leader in bioethanol production volume, surpassing Brazil beginning in 2004.

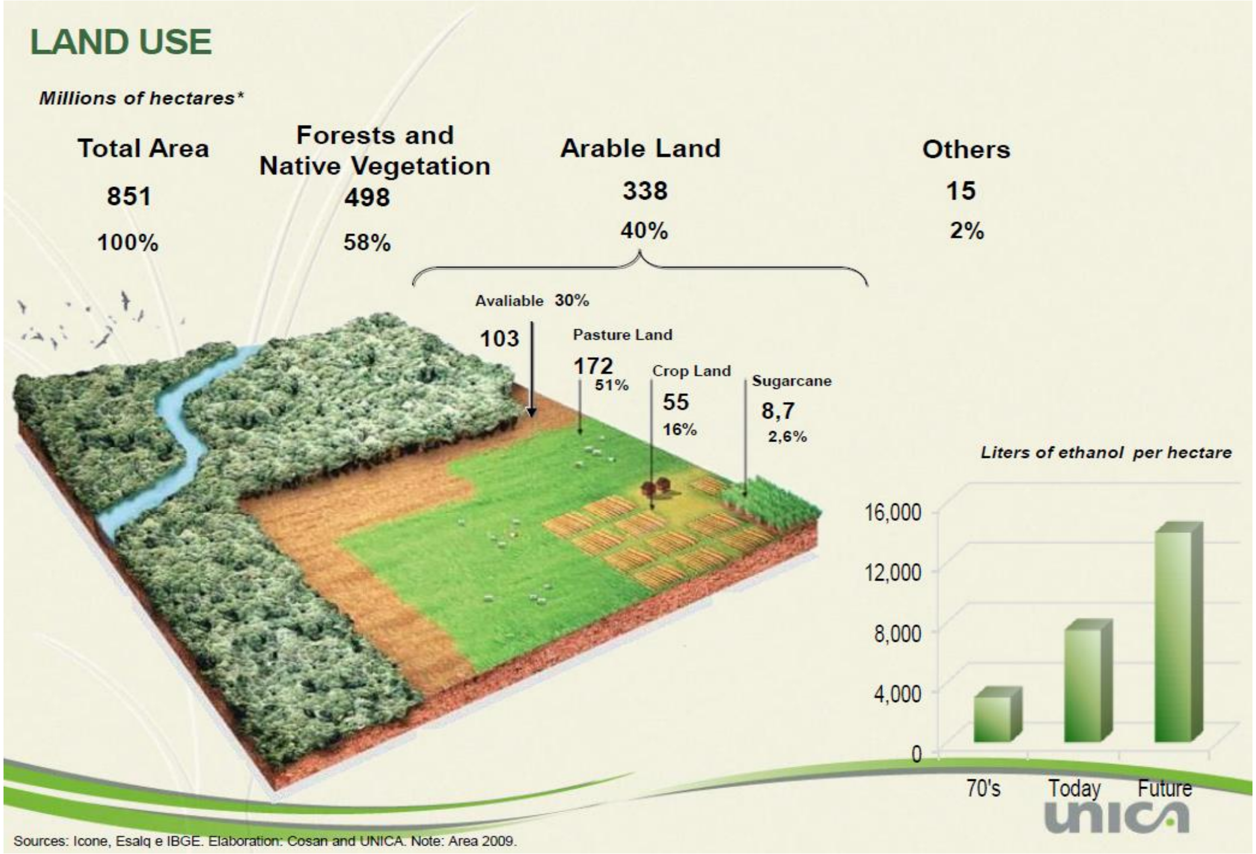
Current US biofuel policies are derived from the Energy Independence and Security Act of 2007 and the associated Renewable Fuel Standard (RFS). In July 2012 the updated RFS known as "RFS2" came into effect and stipulated an aggregate of 36 billion gallons (136 billion L) per year of renewable transportation fuel to be used by 2022. Conventional biofuel (essentially corn grain derived ethanol) is expected to provide a large portion of this mandate, reaching a plateau of 15 billion gallons (57 million L) per year by 2015. Advanced biofuels (biomass derived diesel, cellulosic biofuels and non-cellulosic advanced biofuels) are expected to make up the balance by providing, by 2022, a total of 21 b gallons of the 36 b gallons per year, with 16 b of these advanced biofuel gallons derived from cellulosic feedstocks. RFS2 requires biofuels to achieve minimum life-cycle GHG emission reductions relative to petroleum fuels. If the biofuel LCA demonstrates less than 20% GHG emission reduction compared to the fossil fuel it displaces it will not be eligible to qualify as a contribution towards the RFS mandate obligations. If the LCA shows a GHG reduction between 20% and 49%, the biofuel is eligible to count towards the 15 b gallon conventional fuel obligation (However, this "mandate" is already close to saturated by the existing corn ethanol industry). Finally, if the biofuel LCA indicates a relative GHG savings of 50% or higher, it is considered advanced biofuel counting towards the 21 b gallon mandate. Although the RFS's annually increasing advanced biofuels volume targets are currently behind schedule, there are ongoing efforts to achieve the ultimate 21 billion gallons per year advanced biofuel goals by 2022 (Schnepf & Yacobucci, 2013). Interestingly, Brazilian sugarcane ethanol and, more recently, sweet sorghum ethanol (grown and distilled in the US using renewable power) have been assessed and qualified to be classified as advanced biofuels, despite the fact that they are "food" based. This is primarily due to their more favorable life cycle GHG emission profiles (Schnepf & Yacobucci, 2013).

Excise taxes in the form of VEETC (Volumetric Ethanol Excise Tax Credit) were enacted in 2004 by the "American Jobs Creation Act". Under this scheme, blenders can claim tax breaks of $0.5 USD/gal ($0.13 USD/L) of ethanol and $1 USD/gal ($0.26 USD/L) of biodiesel (0.5 USD/gal if made from waste oils). These tax credits represented a major source of financial support for the growth of the US biofuels industry. However, these have expired at the end of 2012.

Pure ethanol cannot be used as unblended fuel in most current automobile vehicle engines without modifications. One exception is Brazil, where, as will be discussed in the next paragraph, Flexi-fuel Vehicles (FFVs) which can use neat hydrous ethanol (~E95) are abundant. Another exception are the E85 FFVs that have been designed to use up to 85% by volume anhydrous ethanol. A relatively small number of E85 vehicles are currently on the road, mostly in the EU and the US. As an example, about 7 million E85s vehicles were in use in the US in 2012, out of a total light duty vehicle fleet of more than 150 million. The use of ethanol at blend rates beyond 10% may also pose infrastructure compatibility issues with the rest of the petroleum distribution and processing network. More detail on this incompatibility of ethanol fuels is provided in Section 1.4.1. The bottom line is that ethanol is not viewed as a fully "infrastructure compatible" fuel in countries other than Brazil. In the US, for example, blending of ethanol with gasoline is usually limited to 10% by volume (E10) for regular non-FFVs (flexible fuel vehicles) and this blending limit is regulated by the EPA (US EPA, 2013). As this blending limit effectively caps ethanol consumption, it has also been called the "blend wall". Although the EPA has recently permitted the use of 15% ethanol by volume for vehicles manufactured in year 2001 or later, the entire light duty vehicle fleet is not approved to use this higher blend.

Brazil, the second largest ethanol producer, has the world's oldest and most established biofuel program. In 1975, triggered by the 1970's OPEC oil crisis, the Brazilian military led a government initiated campaign named "National Alcohol Program Proalcool" to make Brazil independent of foreign oil imports and provide a stable internal demand for its growing sugarcane industry. The program involved subsidies and incentives for sugarcane ethanol while the government also signed agreements with automobile manufacturers to help them create a market for vehicles running on pure (hydrous) ethanol. The campaign was initially so successful that a decade later, in 1985, 100% of new cars sold ran only on ethanol fuel. However, a few years later due to sugar prices increasing and crude oil prices decreasing the Brazilian bioethanol industry entered a challenging period. Between the late 1980s and 1999 when the price of hydrated alcohol was not regulated, ethanol use and ethanol-powered car sales decreased substantially. In response the government introduced ethanol blending mandates (22-25%) and deregulatory decrees to try to keep the ethanol industry afloat. As petroleum prices increased during the 2003-2008 period and as E100 FFVs were gradually introduced, ethanol has established itself as a major component of the Brazilian transportation fuel infrastructure. The success of the Proalcool program in Brazil is evident in that the sugarcane industry now accounts for 3.5% of GDP and 3.6 million jobs, with ethanol production consuming about 50% of Brazil's total sugar feedstock (This latter percentage varies depending on the relative commodity prices of sugar and ethanol) (de Almeida et al., 2008).

Today there are no direct subsidies for ethanol production in Brazil, though there is a degree of preferential treatment for ethanol as compared to gasoline. Ethanol faces no excise tax while federal duties are much lower than those for gasoline ($0.26 vs $0.01 per litre). State enforced fuel VAT is also lower for ethanol than gasoline in most ethanol producing states such as São Paolo. De Almeida et al. (2008) estimate that ethanol enjoys tax incentives of about USD 1 billion per year and that the Proalcool program cost around 16 billion for the period of 1979 up until the mid-1990's (these numbers are much lower than historical US government support for corn ethanol) (Sorda et al., 2010). In 2012, ethanol accounted for 50% market share of the gasoline-powered vehicle fleet in Brazil, with E25 mandatory across the country and hydrous ethanol (~E95) widely available too.



Sources: Icone, Esalq e IBGE. Elaboration: Cosan and UNICA. Note: Area 2009.

Figure 1-3: Brazilian sugarcane land use and ethanol productivity
(Source: Sawaya Jank, 2011)

The Brazilian sugarcane industry is well positioned to expand without clearing forest land or displacing pastures (Figure 1-3) according to UNICA (Brazilian Association of Sugarcane Producers). The current average yield of ethanol (about 7000 L/ha, as shown in Figure 1-3) is expected to continue to increase. As depicted in Figure 1-3, out of the 338 m ha of arable land, 30% is unutilized and potentially available for sugarcane plantations expansion. Sugar cane production currently occupies only 2.6% of Brazil's arable land.

The EU accounts for about 5% of global ethanol production using mainly grain starch and beet sugar as feedstocks. The EU has a strong policy push for biofuels as discussed in section 1.2.2. During the summer of 2013, the capacity of EU ethanol production increased with the commissioning of Vivergo Fuels Ltd.'s large wheat-to-ethanol plant in Hull, United Kingdom. This 420 MMly (110 MMgy) facility cost about $450 million to build and is a joint venture between AB Sugar, BP and DuPont Industrial Biosciences.

The remaining 10% of global ethanol volume production occurs in countries outside the EU, US and Brazil including, China (39,000 bpd in 2011), Thailand (9,000 bpd in 2011), Australia (7,500 bpd in 2011), and other countries mainly in Asia and Oceania (US EIA, 2011).

1.2.2 Biodiesel

The EU is the world's leading biodiesel producer. Of the 0.4 mbpd of biodiesel produced globally in 2011, around 0.2 million were produced in the EU (US EIA, 2012). The US, Brazil and Argentina follow the EU and each produce about 0.05-0.06 mbpd of biodiesel (US EIA, 2012). Following Rudolf Diesel's model engine which ran for the first time in Augsburg, Germany in 1893 using biodiesel as a fuel, biodiesel has been the predominant biofuel used in Europe's transportation sector, primarily because of the high proportion of diesel cars in Europe. Other factors that have also contributed to this European preference are that vegetable oil and animal fats (the biodiesel raw materials) are more regionally available than starch or sugar (the bioethanol raw materials) coupled with the ease of scaling down oilseed presses and methesterification units, which makes biodiesel production relatively well suited to the more decentralized and small scale nature of European agriculture.

Biodiesel is typically comprised of fatty acid methyl esters (FAMEs) derived from vegetable oils (and animal fats) which, like starch and sugar, compete with food and feed markets. Biodiesel use is typically limited by blend limits (maximum of 7% biodiesel blend with petroleum diesel). Use of pure biodiesel

(B100) requires engine modifications to avoid maintenance and cold flow performance problems (Knothe, 2011).

Europe’s biodiesel and bioethanol policies are primarily derived from the EU Renewable Energy Directive (RED, 2009/28/EC). In April 2009, the European parliament endorsed the RED and a binding target of 10% renewable energy use in transport (mainly to be met by biofuels) in 2020. In the same directive, the minimum GHG saving requirements were specified (35% initially and 50% starting from 2017) as well as other sustainability criteria such as no feedstock from protected habitats and other territories of ecological value. Biofuel tax incentives or mandated biofuel market shares were to be set by national governments and they differ from one European country to another. Recently the EU Parliament voted for a 6% by volume cap on food-derived biofuels while setting a separate 2.5% target to incentivize non-food biofuels, made from waste products and lignocellulosic biomass. The inclusion of indirect land use (iLUC) factors in accounting for a fuel’s carbon footprint post-2020 has also been proposed by the EU Parliament (van Noorden, 2013). This 6% cap and the inclusion of iLUC factors have however not been agreed upon between the EU Parliament and the Council (EU member state governments). A decision on these biofuel policies has created a “deadlock” over the last year or so and negotiations were still continuing as of 30 May 2014 (Euractiv, 2014).

1.2.3 Biomass-derived biofuels

The use of food products such as sugar and vegetable oils as raw materials for the manufacturing of biofuels has raised concerns about this increased use detrimentally driving higher prices for food/feed. The use of woody or grassy fibers (lignocellulosic biomass) is viewed as a more acceptable route for further growing the production of renewable liquid fuels. Such lignocellulosic materials (“biomass”) are more abundant and have good potential to provide higher fuel yields per unit of land area than food crops. With continued development, conversion of biomass feedstocks can be made to be less costly and to achieve lower carbon emission intensity than oilseed, starch or sugar crops. Historic price fluctuations have been much higher for food feedstocks than for lignocellulosic feedstocks. For example, although sugar and palm oil prices have fluctuated considerably since 1995 (Figure 1-4), over this same time period the price for biomass, such as hardwood logs, has been much more stable.

The main fibrous biomass feedstocks being considered for biofuels are crop residues (corn stover, wheat straw, sugarcane bagasse, etc.), herbaceous energy crops (miscanthus, switchgrass, cardoon, etc.), wood derived materials such as sawmill and forest residues and fast-rotation forestry species such as polar and willow.

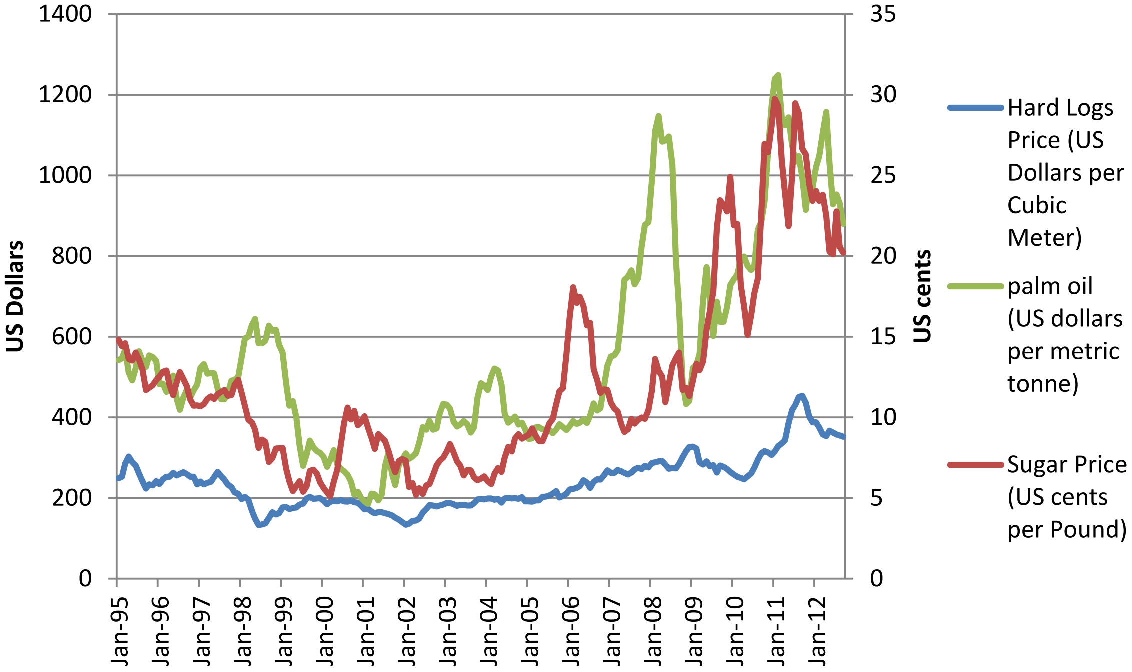


Figure 1-4: Price fluctuation of food vs cellulosic biofuel feedstocks
(Data from indexmundi 2013: http://www.indexmundi.com/commodities/)

The conversion of fibrous biomass (lignocellulose) to liquid fuels is achieved by two main process pathways, thermochemical and biochemical. Thermochemical processes aim at converting the bulky solid biomass to an energy dense liquid using combinations of pressure, temperature and catalysts during the conversion processes. Biochemical processes aim at biologically converting the biomass first to sugars then to a liquid fuel molecule such as ethanol. This latter type of process typically involves the integrated process steps of pretreatment, enzymatic hydrolysis, biological conversion (e.g., fermentation) and concentration. The pretreatment step (chemical and/or physical) allows fractionation of the lignin, hemicellulose and cellulose, and increases the accessibility of the cellulose to hydrolyzing agents such as enzymes. The sugars in the resulting enzymatic hydrolyzate are then fermented to ethanol or butanol or biologically converted to other liquid fuel molecules (e.g., farnesene), which are then separated (recovered) by distillation, liquid-liquid separation, membranes or other means.

However, while many thermochemical and biochemical routes to cellulosic biofuels are available, the processing of fibrous feedstocks to fuel grade products requires more energy and resources than does conventional biofuels (Sims et al., 2008).

As is discussed in more detail below, "drop-in" biofuels are expected to demonstrate the same functional properties as petroleum-derived fuels. These types of "drop-in" biofuels can be produced from cellulosic biomass via thermochemical conversion, from lipid feedstocks via hydrotreatment, or from sugars and alcohols via biological or chemical catalysis. Examples of such biofuels include Fischer-Tropsch liquids (FT liquids), hydrotreated pyrolysis oils (HPOs), and hydrotreated vegetable oils (HVOs). More recently, biochemical pathways, such as sugar conversion to drop-in or close to drop-in hydrocarbon molecules have also been developed and proposed as candidate technologies for hydrocarbon biofuel production. Companies such as Amyris and LS9 have engineered microorganisms to convert sugar to "diesel-like" molecules. Currently, these drop-in biofuel processes are largely at the research and demonstration stages although several large scale HVO facilities are being built and operated by companies such as Neste Oil and Dynamic Fuels while a commercial scale pyrolysis and upgrading facility was recently built and commissioned by the company KiOR.

1.3 Definition of drop-in biofuels

Conventional biofuels have a distinct chemical nature and so they can be accurately defined by their chemical composition alone. For example, bioethanol is ethanol and biodiesel is a fatty acid methyl ester (FAME). In contrast drop-in biofuels generally consist of a mixture of many different types of hydrocarbons, the properties of which, just like petroleum fuels, is typically characterized by the mixtures' functional characteristics such as distillation profile, viscosity, acidity, etc. A true drop-in biofuel should be able to be readily "dropped in" to the existing petroleum infrastructure and be handled in much the same way as petroleum fuels without requiring significant infrastructure adjustments.

In this vein, and considering the diversity of drop-in biofuel processes and product options, the following definition is used throughout this report to provide a functional representation of what is meant by a drop-in biofuel:

“Drop-in biofuels are liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure”

It should be noted that petroleum itself can sometimes contain up to 2 wt% oxygen (infrequently, even more) (Speight, 2006). The term “petroleum-derived blendstocks (fuels)” is used to describe the gasoline (petrol), diesel, jet and other types of commercial transportation fuel blendstocks as well as their refinery precursors that are currently processed in existing refineries, pipelines or anywhere upstream of a blending terminal in the petroleum supply chain.

1.4 Reasons for the increasing interest in Drop-in biofuels

Drop-in biofuels are currently attracting considerable attention. Some of the reasons are directly or indirectly related to challenges to further increasing the markets for ethanol and biodiesel biofuels such as their likely blend wall and supply constraints. Drop-in biofuels are better positioned as they avoid blend wall concerns and also potentially make better use of existing infrastructure (current inventory of petroleum refineries, supply channels and liquid fuel powered combustion engines).

1.4.1 Blend walls

As mentioned earlier, bioethanol and biodiesel cannot be used in a neat form in conventional automobile engines (without modifications and tuning) and they are not fully fungible with existing petroleum fuels. As a result, there are limits on the blending levels of these biofuels with petroleum fuels, with these limits stipulated and regulated by governments after consultation with automobile manufacturers and oil companies. With the exception of Brazil’s FFVs and US and EU E85 vehicles, most jurisdictions outside of Brazil blend ethanol at levels that do not exceed 10% by volume (E10). The blending rate for biodiesel generally varies between 2% and 20% by volume. This blend wall has, in part, limited the growth of biofuels and in the US in particular, these ethanol blend wall volumes have already been reached (Tyner, 2010). To confuse matters further, the RFS ethanol mandate currently stipulates consumption of ethanol volumes at levels above what can be used without breaking the E10 blend wall. Short of buying ethanol that they cannot sell, gasoline blenders have resorted to buying the ethanol permit equivalent (Renewable Identification Numbers) from non-obligated parties. This RIN trading has given rise to an unregulated futures market which resulted in the recent, unprecedented surge in the market price of US RFS's ethanol RINs from under USD $0.10/gallon ($0.026/L) to over US $1/gallon ($0.26/L). This has triggered increased tensions between RFS-obligated oil companies and the US Environmental Protection Agency (Schnepf & Yacobucci, 2013). Although one solution to resolve the blend wall constraint would be the wider use of E85 flexi-fuel vehicles (FFVs), as shown by Tyner and Viteri (2010), E85 penetration cannot grow fast enough to provide a fleet that could absorb all the "over-the-blend wall" amounts of ethanol that could be produced in the US. If there was enough economical drop-in biofuel production in the US, such blend wall-related issues would be avoided.

1.4.2 Energy density, aviation and other long distance transportation sectors

Aside from blend wall limitations in gasoline and diesel automobiles, there are transportation modes where conventional biofuels cannot be used, or their use is not favoured. Aviation is the most salient example of a transportation sector that can only use drop-in biofuels since ethanol and biodiesel do not fulfill key jet fuel requirements such as stringent cold flow viscosity and energy density specifications. Since jet engines cannot be readily "electrified" they are uniquely dependent on biofuels for renewable fuel alternatives. In addition, the aviation industry's requirements for affordable and renewable jet fuels are becoming ever more pressing, as the industry has committed to GHG emission reductions amidst increasing oil prices and increasing demand for air travel. Examples of such aviation biofuel commitments include (not an exhaustive list):

- European Commission's "European Advanced Biofuels Flight path" initiative is a roadmap with clear milestones to achieve an annual production of two million tonnes of sustainably produced biofuel for aviation by 2020.
- US Federal Aviation Administration's (FAA) aviation biofuel goal to use 1 billion gallons (3.8 million L) of renewable jet fuel per year from 2018 onwards (Hileman et al., 2009)
- Various non-binding strategic targets for reducing aviation's carbon footprint via private airline carriers such as Lufthansa and Alaska Airlines as well as international aviation alliances such as the IATA (IATA, Dec 2013) and SAFUG (SAFUG, Dec 2013).
- KLM Airlines in collaboration with Air France, Argos and Spring Associates recently (2009) formed SkyNRG, a major international broker of available bio-jet fuels.
- Regional organisations/consortia for the development of aviation biofuels such as the Sustainable Aviation Fuels Northwest (SAFN) in the US and the Brazilian coalition of academic, government and commercial partners: Aliança Brasileira para Biocombustiveis de Aviação (ABRABA).

More details on drivers behind the need for developing aviation biofuels are described in a recent IEA Bioenergy Task 40 report (Rosillo-Calle et al., 2012) as well as a report by the Air Transport Action Group (ATAG, 2012), a report by the Sustainable Aviation Fuels Northwest initiative (SAFN, 2011) and the Aviation biofuels website of the European Biofuels Technology Platform. Other long distance and non-electrifiable transportation modes such as marine shipping and long distance trucking are also better suited to using drop-in biofuels than conventional biofuels. It should be noted that these sectors are expected to represent much of the transportation fuel demand growth over the next decade or so (IEA, 2012). As discussed in more detail in Section 1.8.2, it is expected that regulations will be tightened on maximum sulfur content allowed in marine and road fuels. Consequently, biomass derived drop-in biofuels (and other biofuels) that exhibit low sulfur content will also look more attractive.

1.4.3 Energy security and crude oil prices

As explained in the IEA's "blue map" scenario (IEA, 2011b) biofuels are projected to account for 27% of total global transportation fuel demand by 2050. This ambitious target will be difficult to reach using only conventional biofuels such as ethanol and biodiesel.

1.4.4 Infrastructure incompatibility

Due to the chemical nature of bioethanol and biodiesel they have to be delivered and blended through separate distribution channels as they are incompatible with much of the petroleum infrastructure such as pipelines and storage tanks. Thus alternative channels must be used such as truck, rail or barge and this adds to the cost and carbon footprint of biofuels. The majority of the petroleum distribution infrastructure, such as pipelines, tanks, and related equipment is composed of low carbon and low alloy steels, and controlling rust and corrosion is of primary importance. Pipelines run petroleum products in batches which follow one after the other as shown in Figure 1-5. These batches follow specific sequences in order to avoid cross contamination. Between batches, a small amount of co-mingled product, known as interface or transmix, is generated and is normally segregated for refractionation to diesel and gasoline or returned to a refinery for processing. In this regard pipelines are vulnerable to contamination which can carry over from batch-to-batch. Biodiesel, for example, is reactive with pipeline metallurgy and it can adhere to the surfaces of pipeline walls, potentially contaminating subsequent petroleum batches. Jet fuels are particularly sensitive to biodiesel ester contaminants. As a general rule, any potential biofuel that might be transported through petroleum pipelines must be non-corrosive and hydrophobic. Most pipeline networks have engineering features in place to remove contaminating water (Bunting et al., 2010). An ideal drop-in biofuel would have similar (to petroleum) non-corrosive, non-reactive and non-hydrophilic functional properties so that it can fully utilize the existing, substantial, pipeline network for its distribution.

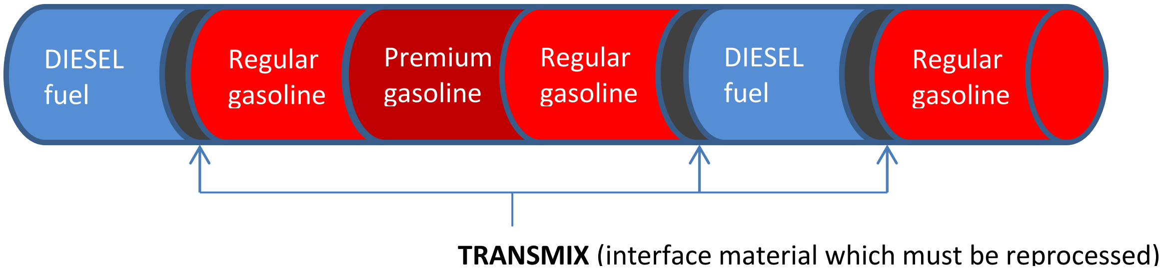


Figure 1-5: Typical sequence of petroleum products flow through a pipeline
(Source: adapted from API, 2001)

1.5 Properties of petroleum and drop-in biofuels

As defined earlier, drop-in biofuels must be functionally equivalent to current gasoline, diesel, jet and related fossil derived transportation fuels. This functional equivalence implies that drop-in biofuels must meet certain bulk properties such as miscibility with petroleum fuels, compatibility with fuel performance specifications, good storability, transportability with existing logistics structures and usability within existing engines (vehicles, jet planes etc.). Chemically, a drop-in biofuel could also be defined as a biomass-derived liquid hydrocarbon that has a low oxygen content, low water solubility and a high degree of carbon bond saturation. The exact specifications of these fuels will be determined by various physicochemical properties such as viscosity, carbon number, boiling point range, freezing point, flash point, aromatic content and others. Of these various properties the carbon number and boiling point range (shown in Figure 1-6) are the most commonly used parameters to distinguish between gasoline (light distillate), diesel and jet fuels (middle distillates). Gasoline is typically used in spark ignition engines and comprises a mixture of C4-C12 hydrocarbons with a 20-40% aromatic content. Diesel is primarily used in compression engines and it contains C10-C22 hydrocarbons with a 25% aromatic content. Aviation fuel is a mixture of C8-C16 with a maximum of 25% aromatic content and a range of stringent specifications such as very low freezing point (-40 C), thermal stability and low viscosity at low temperatures (Hileman et al., 2009). Marine fuel is a lower quality and lower cost fuel that is derived from the heavier distillates of refineries which contain very long carbon chains and low or no phenolics. The quality of marine fuels is measured with viscosity and density indexes (similarly to crude oil) rather than boiling point ranges (Vermeire, 2012).

Regarding biofuel properties and as shown in Figure 1-6, ethanol falls within the boiling point and carbon number range of gasoline fuels but it is only partly blendable with gasoline without the need for engine modification such as in flexifuel vehicles. Similarly biodiesel fits the properties of diesel fuel but it is again only partly blendable. As far as jet fuel properties are concerned, neither ethanol nor biodiesel fall within the narrow carbon number range of jet fuels and thus (as stated earlier) these fuels are not suited for aviation. While there are about a dozen other properties that have to be met by fuels in order to qualify for ASTM certification[1] as usable in existing engines, the oxygen content (or H/C ratio) and carbon number range can be considered as the minimum, most basic characteristics that have to be met.

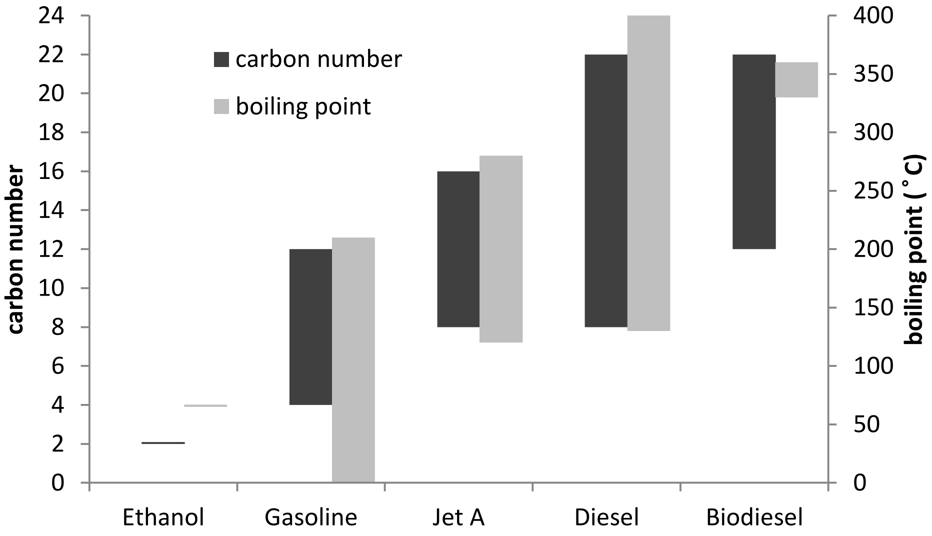


Figure 1-6: Carbon number and boiling point range of commercial transportation fuels
Source: (Hileman, Ortiz, Bartis, & Wong, 2009)

---

[1] For #2 Diesel Fuel for example, the ASTM standard contains the following parameters:
Particulate Contamination by Filtration, BP Distribution, Ash, Carbon, Hydrogen and Nitrogen, Carbon Residue, Cloud Point, Acid and Base Number, Color, Cold Filter Plugging Point, Copper Corrosion, Density, Distillation, Flash Point, Heat Content, Hydrocarbon Type, Lubricity (HFRR), Pour Point, Sulfur Content, Vicosity, Kinematic, Water and Sediment, High Temp Stability (Source: www.astm.org)

1.6 The Oxygen challenge

The greatest challenge for drop-in biofuels to meet the physicochemical properties of petroleum-based transportation fuels is decreasing the high oxygen content of biomass derived biofuels**.** Oxygen is present in biomass in various chemical functional groups such as esters, ethers and hydroxyl groups. While this oxygen content is potentially valuable for metabolic processes and for the production of some value added chemicals, it is highly undesirable for drop-in biofuels. As shown in Figure 1-7, biodiesel and bioethanol are only partially deoxygenated and this is one of the main reasons why these conventional biofuels are not fully compatible with existing petroleum infrastructure. These oxygenated functional groups can react with refinery and pipeline metallurgy as well as with biofuel components to form gums acids and other impurities often at the detriment of biofuel storability/stability (Pearlson, 2011; Bridgwater, 2012).

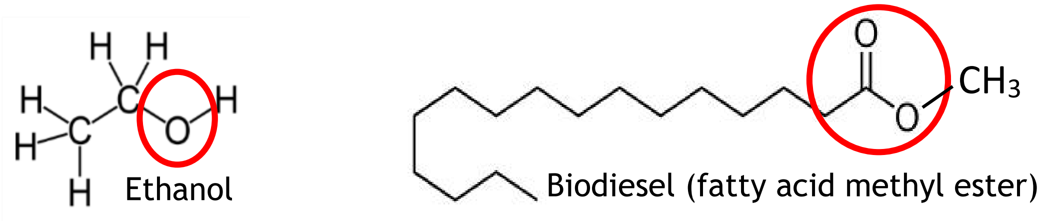


Figure 1-7: Current commercial biofuels and their oxygen content

Compatibility and reactivity are not the only reasons why it is important to deoxygenate biofuels. The oxygen in biofuels reduces their energy density. This in turn determines the size of a vehicle's fuel tank which in turn determines travel range for all modes of transportation. As shown in Figure 1-8, with increasing oxygen content, expressed as the molar ratio of oxygen to carbon (O/C) in the fuel molecule, the energy density of biofuels and biomass processing intermediates decreases linearly.

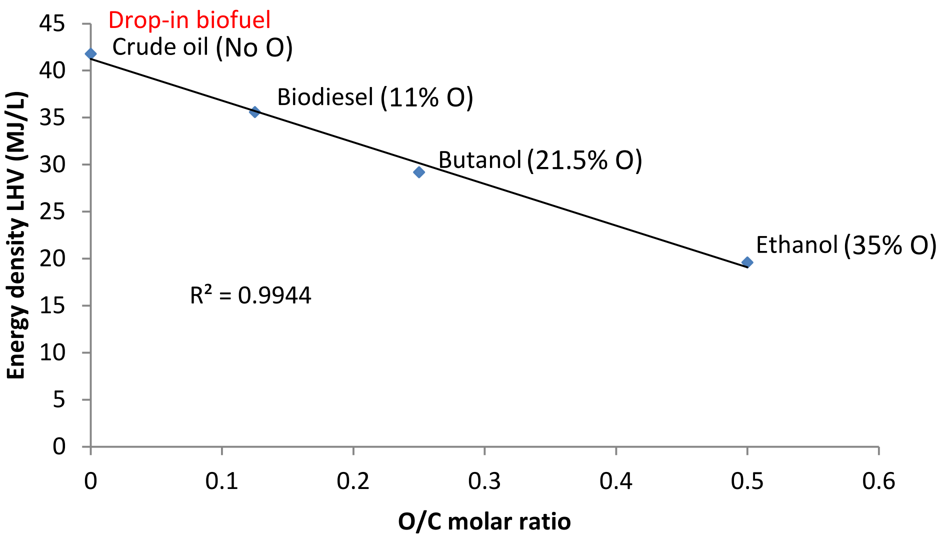


Figure 1-8: The effect of oxygen content on the energy density of liquid fuels
Data from ORNL, 2013

1.7 Deoxygenation of biomass

1.7.1 The Hydrogen -Biomass feedstock dilemma (or trade-off)

Deoxygenation of biomass intermediates is essential for the production of drop-in biofuels and it is primarily achieved by two main chemical reduction processes, hydrodeoxygenation (HDO) and decarboxylation (DCO). During hydrodeoxygenation the hydrogen present in the biomass intermediates (or supplied externally) is oxidized and oxygen is removed as water (H_2O) while in decarboxylation the carboxyl group carbon is oxidized and the oxygen is removed as carbon dioxide. While in practice these two processes take place simultaneously, certain conditions favour one reaction over the other. The HDO process is typically favoured when hydrogen can be readily accessed from an external source (e.g. hydrogen gas derived from natural gas) while, in the absence of hydrogen, the DCO route is favoured (NSF, 2011; Pearlson, 2011). When the DCO process is used, feedstock carbon is lost by oxidation and, as a result, the yield of the process is reduced. When hydrogen inputs are imported in the HDO process, although the yields are generally higher, the cost and sustainability of the imported hydrogen has to be assessed. These two alternative routes are simplified in Figure 1-9. The deoxygenation can be carried out either biologically or thermo-chemically. However, the trade-off between hydrogen inputs and process yields remains unchanged. In either of these two drop-in biofuel processes, the ultimate objective is not only to deoxygenate biomass intermediates but to also enrich them in hydrogen and thus elevate their low H/C ratio to the level of finished petroleum transportation fuels (H/C of about 2).

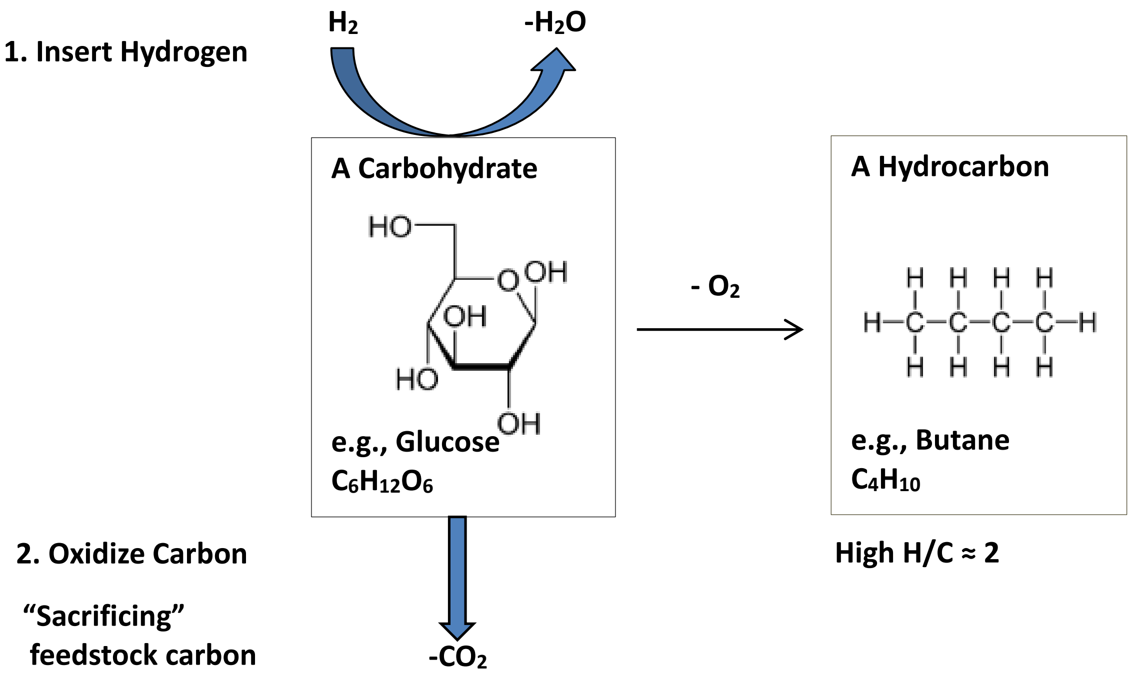


Figure 1-9: Simplified representation of carbohydrate deoxygenation mechanisms

1.7.2 The Hydrogen to Carbon ratio

The hydrogen to carbon ratio (H/C ratio) is used in the petroleum and coal industry to indicate how hydrogen rich and energy dense are various fossil feedstocks. In the production of drop-in biofuels one of the main objectives is to elevate the low H/C ratio of the biomass feedstock to that of diesel, jet and gasoline fuels which have H/C ratios close to 2. During combustion, the oxygen within the biomass consumes hydrogen and thus reduces its effective H/C ratio. Thus, using a biomass feedstock where the main elemental components are hydrogen carbon and oxygen, the H/C ratio must account for the relatively high level of oxygen (in contrast to petroleum feedstocks which contain practically no oxygen) as each oxygen atom consumes two hydrogen atoms to form a water molecule (H_2O) that contributes no energy to the combustion system (Vennestrøm et al., 2011). Thus, the "effective" H/C ratio for oxygenated biomass feedstocks, H_{eff}/C, is calculated by Equation 1.

$$\mathbf{H_{eff}/C} = \frac{n(H)-2n(O)}{n(C)}$$ where n=number of atoms of each element

Equation 1: The Effective Hydrogen to Carbon ratio

Highly oxygenated and hydrogen-poor biomass intermediates such as sugar and cellulosic biomass have low H_{eff}/C ratios. Glucose has an H_{eff}/C ratio of zero meaning that all hydrogen in the substrate is consumed by its abundant oxygen atoms. When the most common biofuel intermediates as well as target drop-in diesel molecules are listed along with their H_{eff}/C ratios in a “staircase” depiction, (Figure 1-10) it is apparent that, the wider the gap between H_{eff}/C of a feedstock and a target product molecule, the more processing and hydrogen input efforts (“steps”) that have to be taken to reach a target drop-in biofuel H/C situated at the top of the staircase. Thus, for example, a lipid feedstock used by the oleochemical drop-in biofuel platform will be favoured over a lignocellulosic biomass feedstock for drop-in biofuel production (Forsberg, 2009).

Although the “staircase” and H_{eff}/C concept (depicted in Figure 1-10) are useful "rules of thumb" to help assess the suitability of "biomass materials" as feedstocks for drop-in biofuels, these concepts need to also consider biomass intermediates that are rich in both hydrogen and oxygen. These types of intermediates include monoalcohols such as ethanol and butanol which, although they have a H_{eff}/C ratio of 2, are still too oxygenated to be considered as drop-in biofuels. Other intermediates such as lignin, although less oxygenated than sugars, are still several steps away from the drop-in H_{eff}/C target of 2. Typically, alcohol feedstocks have been used in in less conventional processes such as alcohol-to-jet fuel processes (discussed further in Chapter 5). In these processes, although the alcohols benefit from a high H_{eff}/C ratio they still need to be further deoxygenated (e.g. by using more hydrogen inputs) in order to produce hydrocarbons that are oxygen-free and suitable as drop-in biofuel blendstocks. It should also be noted that if these alcohol and lignin feedstocks are derived from biomass they will also require some type of pre-processing before they are available.

As the source, sustainability and cost of hydrogen will likely play an important role in any future drop-in biofuel sector it is worth discussing how hydrogen is currently produced and used in the oil and gas based industries.

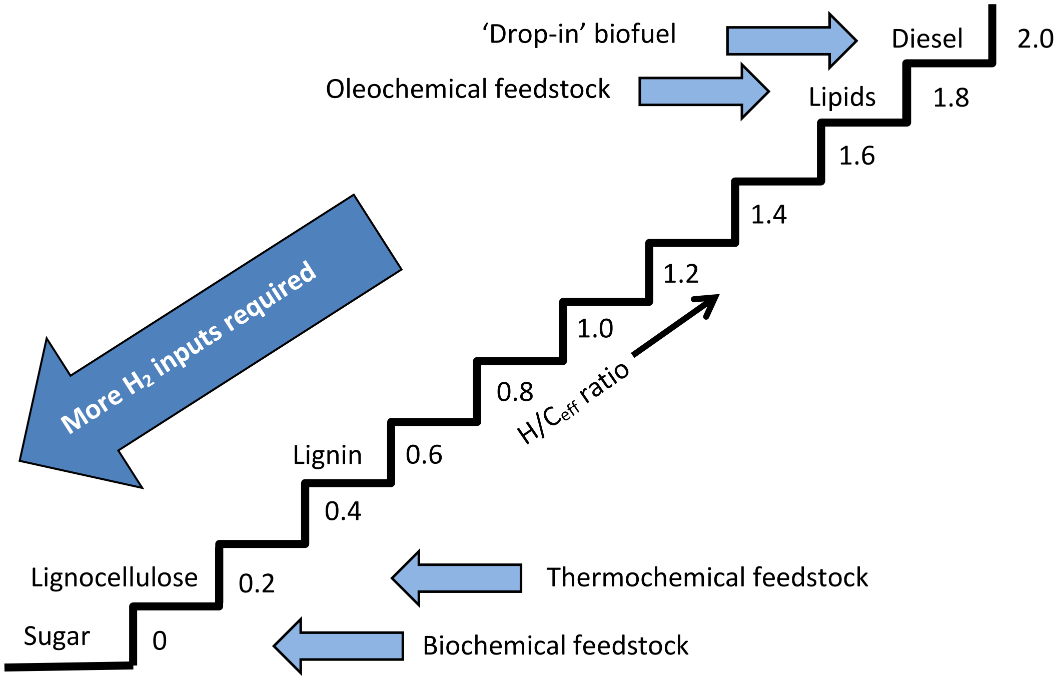


Figure 1-10: The effective Hydrogen to Carbon ratio "staircase"

1.8 Hydrogen in the petroleum Industry

It is apparent that the commercialization of drop-in biofuels will be heavily dependent on the availability and price of hydrogen (H_2) inputs in order to elevate biomass H/C ratios. Thus, it is important to better understand the market trends and potential competition for this key resource. The current major global use of industrial grade hydrogen is for petroleum refining and ammonia fertilizer production. In the petroleum industry hydrogen is used to decontaminate (desulfurize and "denitrogenize") crude oil and to upgrade ("crack") heavy oils to make lighter fuel products. Currently, and for the foreseeable future, the petroleum industry is and will be constrained by hydrogen availability due to the increasing need for hydrogen to upgrade crude oils of decreasing quality to satisfy market demand for increasingly pure and light petroleum products.

1.8.1 Declining quality of crude oil

Crude oil is not a homogeneous or consistent feedstock. Petroleum quality varies considerably between regions and over the lifetime of a reserve. The density (expressed as the "American Petroleum Institute

(API) index") and sulfur content (expressed as % wt) are the most commonly quoted crude oil quality parameters and they are viewed as approximate estimations of carbon content and energy content (heating value). Good quality oil is characterized as "light" (low density, high API) and "sweet" (low sulfur content) (Bunting et al., 2010).

Recent trends show crude oil feedstock decreasing in quality over time as it averages sourer (high sulfur) and heavier indices. For example, over the last 15 years, US refineries have been processing increasingly heavy and sour crude oil. For the oil industry, these trends translate to higher energy use and GHG emissions per unit of crude oil processed. In the US, the average energy consumption per crude oil processed has increased by more than 50% from 2001 to 2011 (S&T2, 2013). This trend of decreasing crude oil quality is expected to continue and, as shown in Figure 1-11, any forecasted growth in global oil reserves to the year 2020 has been projected to come from sour, heavy or acidic (high total acid number or TAN) crudes (US EIA, 2006). It is likely that refiners will have to adapt by utilizing more complex unit operations and using higher energy and hydrogen inputs to process these crudes

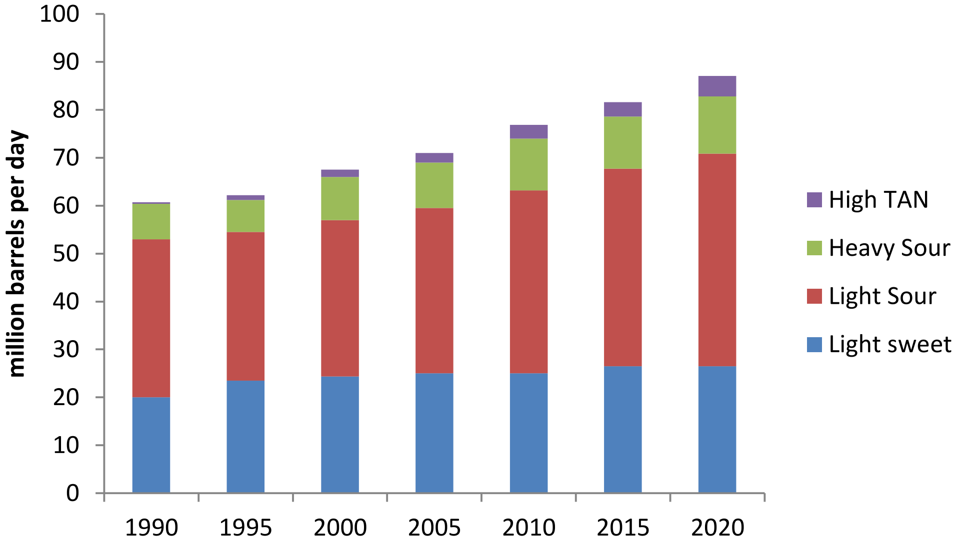


Figure 1-11: Purvin & Gertz forecast for world crude oil quality
(Source: data from US EIA, 2006)

Oil refineries upgrade heavy crude oil to light products (such as naphtha) by hydrocracking the heavier distillates, thus increasing the hydrogen input requirements of the refining facility. Cracking of heavy petroleum fractions can also be performed in catalytic crackers, which require no hydrogen inputs.

ISBN: 978-1-910154-07-6 (electronic version)

However, catalytic crackers convert a significant proportion of the feedstock to tar residues which translates to lower conversion yields. Thus, this approach is not favoured, especially when crude oil prices are high (generally above $60/bbl) (US EIA, 2007). This hydrogen vs yield dilemma has also been discussed in the context of upgrading biomass to drop-in fuels and it will be an interesting, common challenge for both petroleum and biomass refineries. (Oil refining operations are described in further detail in Section 1.9).

Oil sands are among the heaviest crudes currently being processed within the global pool of petroleum reserves. Oil sands are relatively “young” oil deposits that are tightly trapped between geological sediments. They comprise a mixture of heavy bitumen oil and sand that requires high energy inputs to process – for extraction, separation and refining – to finished fuels. To give some sense of the scale of operations for oil sands utilization, Alberta’s production is projected to increase from a current level of approximately 1.5 million barrels/day of synthetic crude oil (*cf.* world daily demand is 90 million barrels (IEA, 2011)) to 3.5 million barrels a day by 2020 (Alberta Government, 2007). From an emissions’ perspective, oil sands extraction and refining result in significantly higher impacts than does the production of conventional liquid petroleum fuels. According to the US National Energy Technology Laboratory, Canadian Oil sands WTT (well to tank) GHG emissions amount for about 34 kg CO_2 equivalent/ MMBtu LHV (Low Heating Value) diesel, which is more than double that of the benchmark crude oil WTI (Western Texas Intermediate) (Gerdes & Skone, 2009).

Coal to liquid (CtL) conversion to make transportation fuel is another fossil-based alternative that has been used during situations where access to petroleum has been restricted. CtL has been categorised as the production of Synthetic Liquid Hydrocarbons (SLH), indicating that these liquid hydrocarbons have been synthesized from non-liquid hydrocarbon sources (e.g. coal or natural gas). This technology can produce functional equivalents to jet, diesel and gasoline and relies on catalytically condensing syngas to hydrocarbon liquids, a process widely known as Fischer-Tropsch (FT) synthesis. The liquids resulting from the FT process vary in properties and the process can be optimised to produce products fitting gasoline jet or diesel fuel specifications. The chemistry of these liquids differs from traditional petroleum fuels in that they contain fewer aromatics and therefore are generally better suited for blending with heavier distillates (diesel and jet) than gasoline.

The company South Africa Synthetic Oil Ltd. (Sasol) is the world’s largest CtL manufacturer with extensive experience stretching back to the 1950s as a consequence of South Africa having abundant coal and limited petroleum resources (Bauen et al., 2009). In their Ctl process, coal is gasified and the resulting gas (syngas) catalytically condensed to liquid fuels. Sasol's coal-to-liquid plant in Secunda, South Africa has increased production up to its current processing capacity of 40 million metric tonnes of coal per year being used to produce approximately 150,000 barrel oil equivalents (on an energy basis) of liquid hydrocarbon fuels per day. In 2009, after a 7 year certification process, ASTM approved Sasol's semisynthetic jet fuel blends (containing 50% coal-derived and 50% petroleum-derived) (Bauen et al., 2009).

In a related area, the US Navy and Air Force both have prioritized the procurement of Synthetic Liquid Hydrocarbons (SLH) as a means to reduce reliance on petroleum imports (SAFN, 2012). In 2006, the US Air Force initiated testing of FT-jet fuel blends in all aircraft types. However, the Energy Independence Security Act of 2007 banned the procurement of fuels that are more carbon intensive (higher GHG emissions) than existing petroleum fuels. This Act essentially precluded coal-derived FT liquids from US vehicles due to their high GHG emissions (Bauen et al., 2009). Unless options such as Carbon Capture and Storage (CCS) can be employed, low-emissions biomass-derived SLH will likely be only alternative fuel choice using this type of conversion technology.

It is likely that unconventional sources of refinery feedstock such as heavy oil, oil sands and coal liquefaction will increase the environmental and economic costs of producing current transportation fuels. These "less than ideal" fossil feedstocks are generally hydrogen deficient and, just like biomass feedstocks, have much lower hydrogen to carbon ratios than "high quality crudes" such as Saudi Arabian light and sweet. Similarly to the previously described "staircase" arrangement, fossil feedstocks can also be compared for their relative processing and hydrogen requirements with an H/C staircase (Figure 1-12). Coal, which has an H/C ratio of about 0.5 requires 3 times more hydrogen inputs than do lighter crudes which have an H/C ratio of about 1.5 (Forsberg, 2005). These numbers indicate that there is a near linear relationship between H/C ratio and hydrogen requirements regardless of the type of feedstocks to be converted to finished fuels. This linear relation is a recognised rough-rule-of-thumb used by the petroleum refining industry but it has to be adapted to account for the presence of heteroatoms such as sulfur and nitrogen, which, just like oxygen, consume hydrogen during upgrading and refining (Forsberg, 2005).

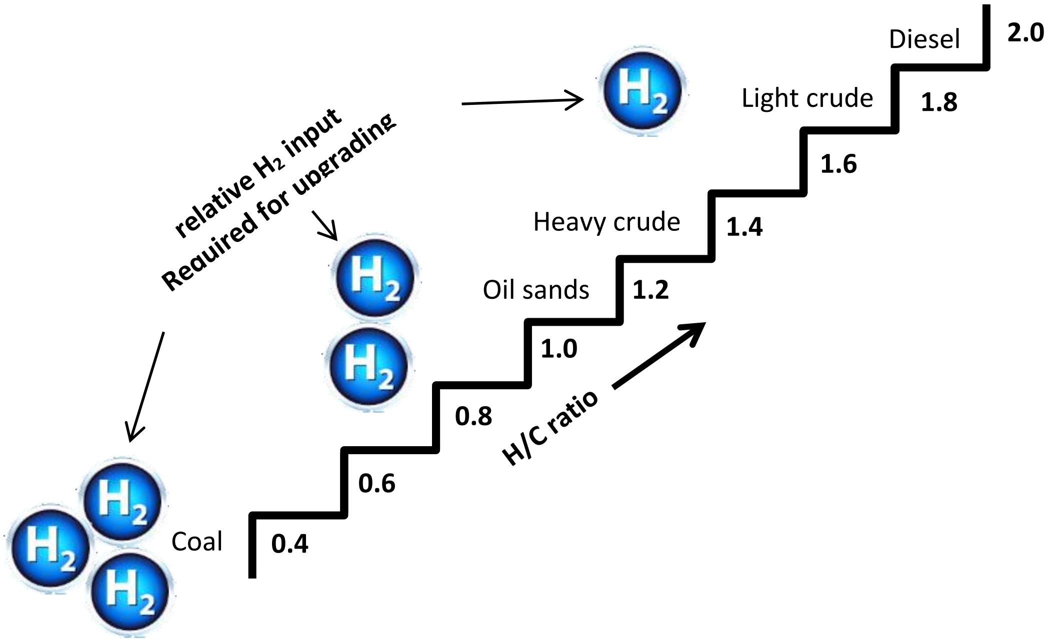


Figure 1-12: The hydrogen to carbon "staircase" for fossil fuel feedstocks

1.8.2 Demand for low sulfur and light petroleum products

As petroleum reserves become heavier and sourer, an opposing trend is occurring in petroleum markets where increasingly light and low-sulfur products are in demand. Globally, light products and particularly middle distillates (the main blendstock for jet fuel and diesel) are in increasingly higher demand than heavier fractions such as fuel oil and bunker fuels. The increase in demand for prime quality transportation fuels is mainly a result of the increased demand for long distance transportation fuels (in non-OECD countries in particular) and the tightening sulfur emission regulations in road and marine transport (in OECD countries especially).

While electric and natural gas vehicles are proposed as alternatives to petroleum-based light duty vehicles, these alternatives are not viable for longer distance transportation modes such as air travel and shipping. These latter, more inelastic and oil-dependent sectors are also where most of future petroleum fuel demand growth is expected to occur. Another long distance transportation mode that is projected to grow is truck/lorry freight transport, particularly in emerging non-OECD (Organization for Economic Cooperation and Development) economies such as China and India. In these countries domestic trade is now growing faster than export trade and goods are increasingly transported by road rather than by air or sea (IEA, 2012).

The petroleum feedstock used to make diesel fuels as well as higher grade heating oil and bunker fuels is the “middle distillates” petroleum fractions. Demand for middle distillates, more commonly called gasoil, is expected to grow exponentially over the next few decades as current fuel substitution trends increase, including fuel switching from gasoline to diesel, from heating oil to natural gas/electricity and from bunker fuels to higher quality marine gasoil. All of these trends, sometimes collectively referred to as the “dieselification” trend, favour increased diesel and gasoil production. According to the IEA (2011), gasoil alone accounts for almost 40% of total forecast growth in oil demand through to 2016 while its share of total petroleum product demand will climb steadily to 30% by the same year. The overall tendency for markets to grow mostly around the middle part of the barrel (middle distillates) is illustrated in Figure 1-13, where the demand growth for middle distillates is clearly evident. In aggregate, this growth represents 46% of the total demand growth through to 2017. During the same time period, heavy fuel oil demand is expected to show no or negative growth.

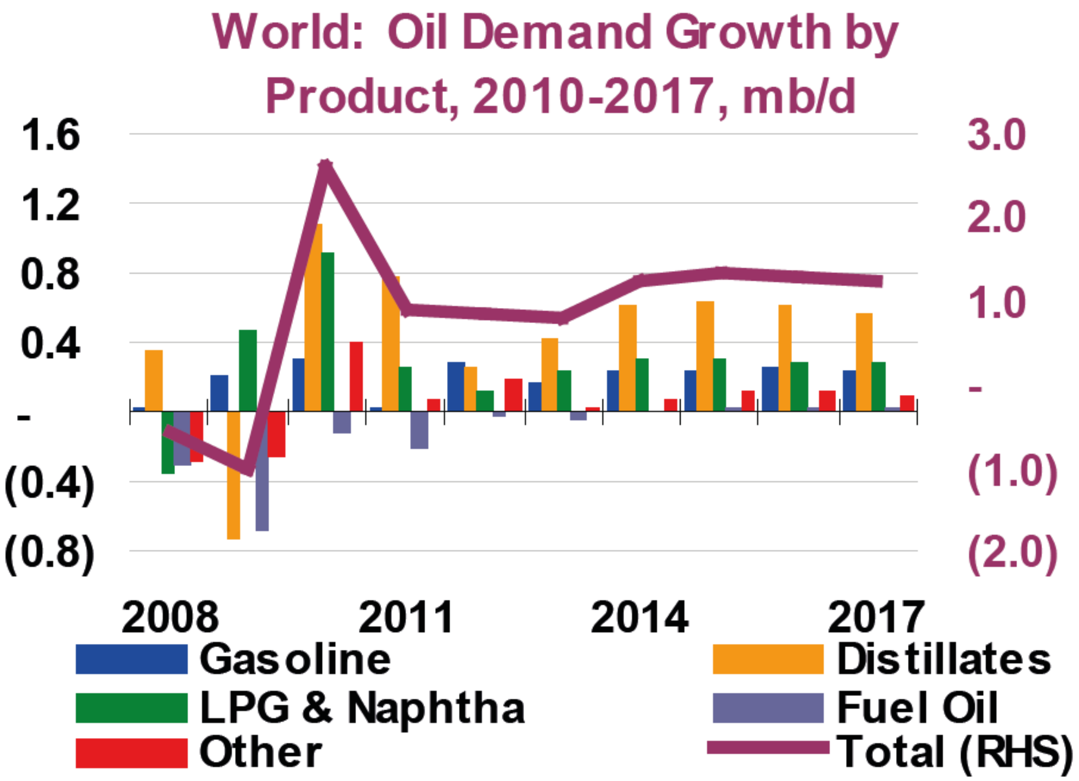


Figure 1-13: World oil demand by product, 2010-2017

(Source: IEA, 2012b)
Tightening fuel emission regulations are the second factor that will drive increased demand for light and low sulfur petroleum fractions as opposed to heavier and more sour fractions. Sulfur emission limits continue to be reduced, particularly for road and marine transport applications (IEA, 2011a; IMO, 2012). Bunker fuels, once thought of as the refining sector's "sink hole" for the lowest quality refinery fractions, are now also tightly regulated for their sulfur emissions by the UN's International Maritime Organization (IMO), as described in the International Convention for the Prevention of Pollution from Ships (MARPOL). MARPOL's Annex VI, in force since 2010, has focused on the establishment of "Sulfur Emission Control Areas" (SECAs) in high traffic European jurisdictions such as the Baltic and North Seas. Other SECAs have been designated in North America (in effect since August 2012) and even more are expected to be introduced in high shipping traffic hot spots in South American and the Pacific Rim (IEA, 2011a; IMO, 2012). In practice this means that, when operating within a SECA, a ship must only burn low sulfur fuels. Annex VI has been ratified by 63 countries, which account for some 90% of the gross tonnage of the world's merchant fleet. The fuel sulfur content limits under MARPOL are currently 1 wt% in SECAs and 3.5% outside SECAs. These limits are to be further decreased over the next decade to 0.1% in SECAs by 2015 and to 0.5% worldwide by 2020-2025, to the extent of sufficient availability of compliant low sulphur fuels (IEA, 2011a; IMO, 2012).

Sulfur emission control is also being applied to road transport as indicated by the fuel specification trends in national fuel standards, particularly in the EU and the US. In the EU, the specifications for maximum allowable sulfur in diesel (EN 590) dropped from 2000 ppm in 1994 to 10 ppm in 2009. Similar trends have been observed in the US where, as shown in Figure 1-14, maximum allowable sulfur contents of fuels have dropped over the last decade from hundreds to thousands of ppm down to only a few ppm for all types of gasoline and diesel fuels (US EIA, 2006).

Interestingly, the aviation sector has always been exempt from fuel emission regulations and the sulfur limits in aviation fuels can be as high as 3000 ppm although, in practice, jet fuel sulfur levels currently average only about 600 ppm worldwide (King, 2012). On the other hand, a recent analysis concluded that although desulfurizing jet fuels would reduce health impacts, it would increase these fuels' climate impact (because of removing cooling sulfate particles) and thus the costs and benefits came out to be broadly even (Gilmore et al., 2011). It is also likely that low maximum sulfur specifications for all other fuels will at least indirectly affect the sulfur content of jet fuels. For example high-sulfur jet fuel suppliers may have to find alternative distribution systems if pipeline operators, concerned about sulfur contamination to diesel and gasoline, stop accepting high-sulfur fuels (US EIA, 2006).

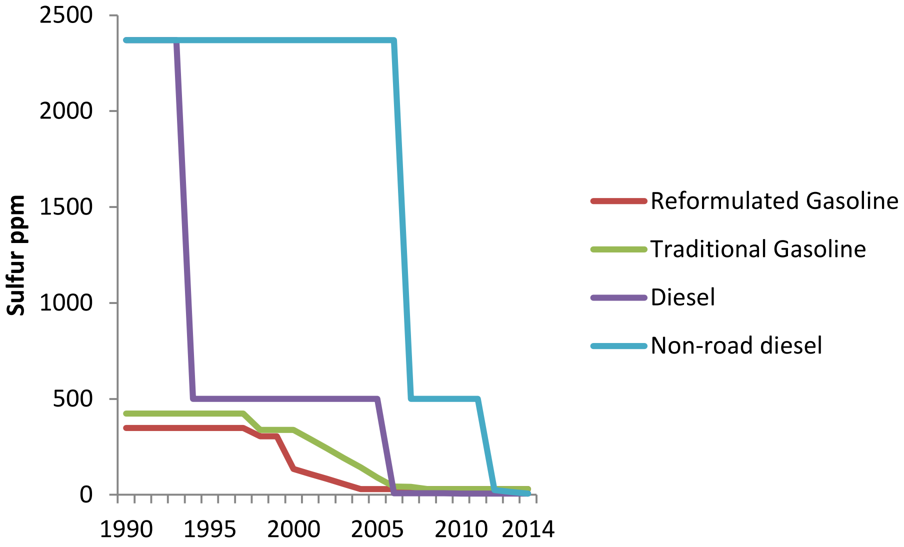


Figure 1-14: Sulfur Content Specifications for U.S. Petroleum Products, 1990-2014
(Source: US EIA, 2006)

In summary, the combination of declining crude oil quality and increasing demand for lighter and more refined petroleum based fuels will create a need for increased, global crude oil upgrading capacity. As a result and as described in the next section, large amounts of hydrogen are going to be required.

1.9 Oil refining basics (emphasis on hydrotreating and hydrocracking)

As oil refineries will increasingly have to adapt to hydrogen consuming processes, the following section provides a brief overview of oil refining basics with emphasis on hydrotreatment and hydrocracking and their role in removing sulfur from sour crude oils and in "cracking" heavy crudes to lighter products.

1.9.1 Crude oil

Crude oil is organic material which has been converted to a carbon-rich liquid over millions of years, under conditions of high temperature/pressure in between geological sediments. It comprises a mixture of hundreds of hydrocarbon molecules ranging in size (1 to 300 carbon atoms) and structure. In terms of structure, the hydrocarbon molecules that constitute crude oil are generally classified as:

- Paraffins (e.g., *n*-octane, *n*-cetane, C_nH_{2n+2})

- Isoparaffins (or branched alkanes, e.g., isocetane, C_nH_{2n+2})
- Olefins (e.g., ethene, C_nH_{2n})
- Cyclic paraffins (cycloalkanes or naphthenes are alkanes containing one or more saturated carbon atom rings)
- Aromatics (hydrocarbons containing one or more benzene rings)

Impurities such as sulfur, nitrogen and metals are also present in crude oil.

1.9.2 Oil refining

Oil refining refers to a complex system of industrial processes which converts crude oil to fuel grade liquids and value-added products such as chemicals and polymers/plastics. The simplest refinery process can be thought of as one where crude oil is heated and the different fractions collected and cooled to form (from lightest to heaviest) liquefied petroleum gas, gasoline, naphtha, kerosene, gas oil and fuel oil. The conversion entails a number of processes which fall under the three main categories of distillation, upgrading and blending. As simplified in Figure 1-15, and starting from the left side of the figure, a "generic" oil refinery consists of a distillation unit, which fractionates crude oil into product streams (also known as "cuts") according to their boiling point ranges. The lighter cuts (lower boiling point fractions) such as naphtha and "straight run gasoline" are typically used for gasoline grade fuels while the extremely light, mostly gaseous cuts (shown as "light ends" in Figure 1-15) are used for more value-added products. For example, light olefins (e.g., ethylene) and light aromatics (e.g., xylene) which are recovered near the top of the distillation column, are precursors to a number of high value polymer and plastics such as polyethylene and polyurethane. The middle streams from the distillation tower (after desulfurization) such as kerosene and gas oil are used for jet and diesel fuels respectively. These middle streams are also collectively known as "middle distillates". The heavier, higher boiling point streams go to residual fuel (which forms part of marine and heating fuel blends) or are sent to cracking facilities such as hydrocracking and Fluid Catalytic Cracking (FCC) units, to be upgraded to lighter, higher value products. The vacuum distillation tower is able to process extremely heavy residue into lighter, FCC feed and to heavier, coker feed. Cokers yield lighter FCC feed and very heavy and dense coke suitable as combustion fuel and typically used for power generation (US EIA, 2007).

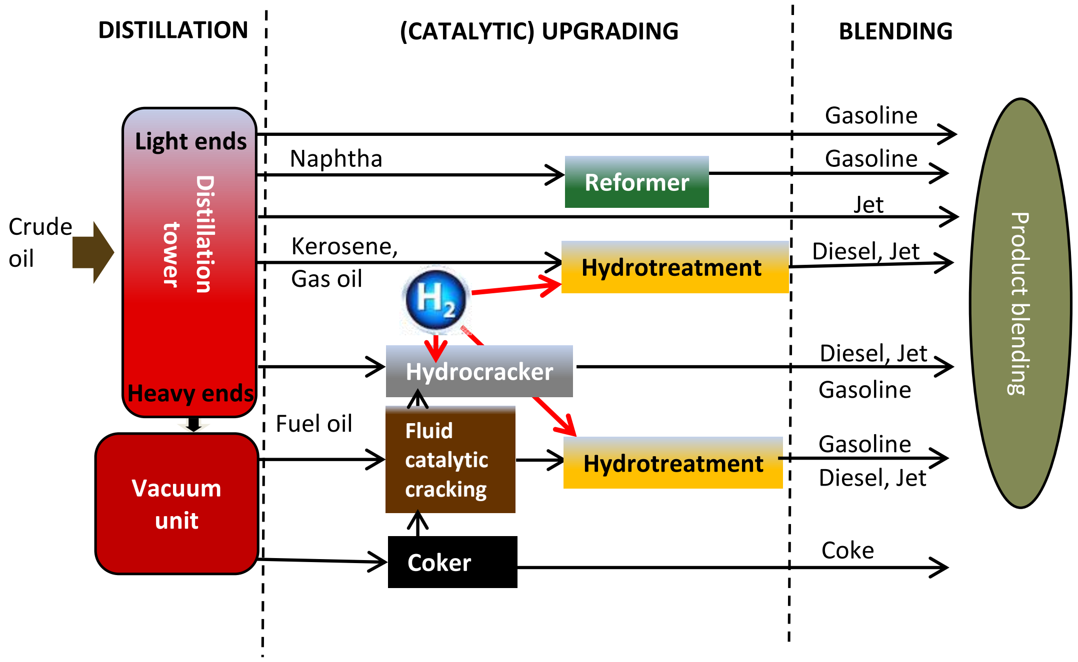


Figure 1-15: Simplified diagram of an oil refinery
(Source: adapted from US EIA, 2007)

Downstream from the distillation tower are all the upgrading units which perform the three main functions of: a) breaking apart heavy, low-valued molecules into lighter more valuable streams; b) rearranging molecules to improve performance or emission specifications (e.g. reforming gasoline cuts to boost their octane rating); and c) removing undesirable materials such as sulfur and other impurities. The upgrading units represent the biggest capital expense in a refinery. They are also costly to run as they operate at high pressures and often use catalysts and large amounts of hydrogen inputs (Figure 1-15). Hydrocrackers, hydrotreaters and FCCs are key unit operations for upgrading the increasingly marginal oil feeds. They are also important units to consider in the current study because they dictate the hydrogen demand of the refinery and are a possible "insertion point" for upgrading of drop-in biofuel intermediates to deoxygenated hydrocarbon fuel blendstocks. Blendstock is a term used to describe a fuel stock that is transported to blending terminals where they are mixed to produce finished fuels meeting specific market specifications.

1.9.3 Fluid Catalytic Cracking (FCC)

The fluid catalytic cracking (FCC) unit is predominantly a gasoline production unit and typically supplies roughly 50% of the gasoline produced in a standard refinery. FCC units crack heavy molecules to mostly gasoline and some middle and heavy distillates. They do not use hydrogen and, as a result, higher amounts of coke are formed on the surface of the catalysts. Therefore, an operating FCC always has a regenerator attached to it (Figure 1-16) where the coke on the spent catalyst is burned off and the regenerated catalyst is re-injected into the main reactor. Since biomass substrates also deposit a lot of coke on catalysts, the FCC configuration outlined in Figure 1-16 is also popular in pyrolysis-type thermochemical conversions of biomass to drop-in biofuels.

Due to the global reduction in demand for gasoline and increasing demand for diesel, the need for more FCC units, which are predominantly gasoline producing units, is declining. Even in the US, the world's biggest consumer of gasoline (both in absolute volumes and as a share of the country's total transportation fuel mix), FCC use is declining and about 20% of the FCC units in US refineries are currently idle (US EIA, 2013). It should also be noted that their decommissioning is expensive. Thus, this situation may represent an opportunity for thermochemically based drop-in biofuel processes, such as pyrolysis, to better utilize idle FCC units. However, as discussed in more detail in chapter 3, this comes with several logistic and processing challenges.

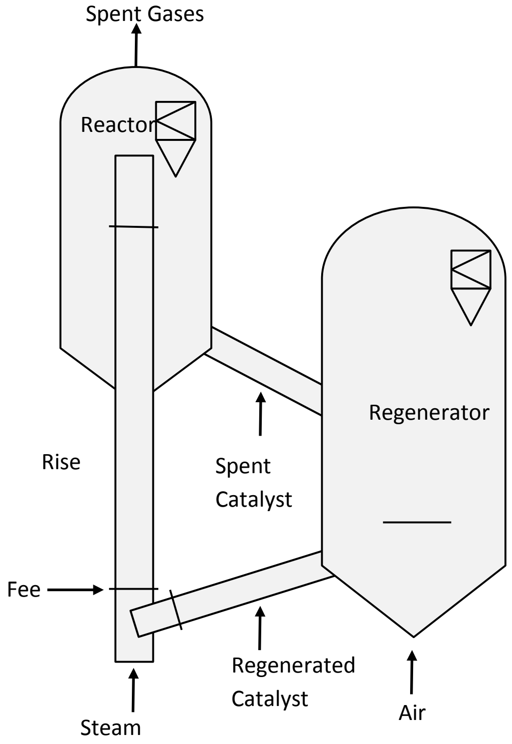


Figure 1-16: Simplified representation of a fluidized catalytic cracker
(Adapted from Corma et al., 2007)

1.9.4 Hydrotreating

Hydrotreating is a hydrogen consuming process that removes sulfur and other impurities from petroleum product streams. The process involves high temperatures and pressures as well as specialized catalysts. During hydrotreatment, the hydrogen reacts with the sulfur to form hydrogen sulfide gas which is then sent to the sour gas treatment unit of the refinery. The reactors are mostly fixed bed units and the catalysts are usually cobalt or molybdenum oxides or alumina. However, they can also contain nickel and tungsten (US EPA, 1995). Catalysts are replaced or regenerated at an offsite facility after months or years of operation. Hydrotreating facilities range in size between 50,000-150,000 bpd (barrels per day) and, depending on the quality of the feed, their hydrogen consumption can range between 7 and 285 Nm^3/barrel (bbl), pressures between 0.7 and 15.5 MPa and temperatures between 300 and 450 °C. Heavy and high sulfur feeds require the use of the top range of these conditions to be fully desulfurized (J. Speight & Özüm, 2002). Hydrotreating is also used to remove nitrogen impurities in a process known as HDN (hydrodenitrogenisation). However, HDN is typically a minor side reaction within HDS as nitrogen impurities are typically only present at low levels in petroleum liquids.

1.9.5 Hydrocracking

As the name implies, hydrocracking is a hydrogen-adding process which breaks apart low value, heavy petroleum molecules to high value light molecules. A simplified depiction of the process is shown in Figure 1-17. Hydrocracking can be viewed as a more severe form of hydrotreating. In a refinery the main function of this unit operation is to process the low quality heavy distillates obtained from the distillation tower, the FCC and coker units, and to convert them to desulfurized finished fuels (mostly for diesel and jet applications). In the emerging world of increasing fractions of heavier and more sour crude oils where low sulfur fuels are mandated and demand growth is predominantly in the diesel and jet fuel markets, hydrocracking will play an increasingly pivotal role as modern oil refineries adapt operations to meet emerging market fuel trends.

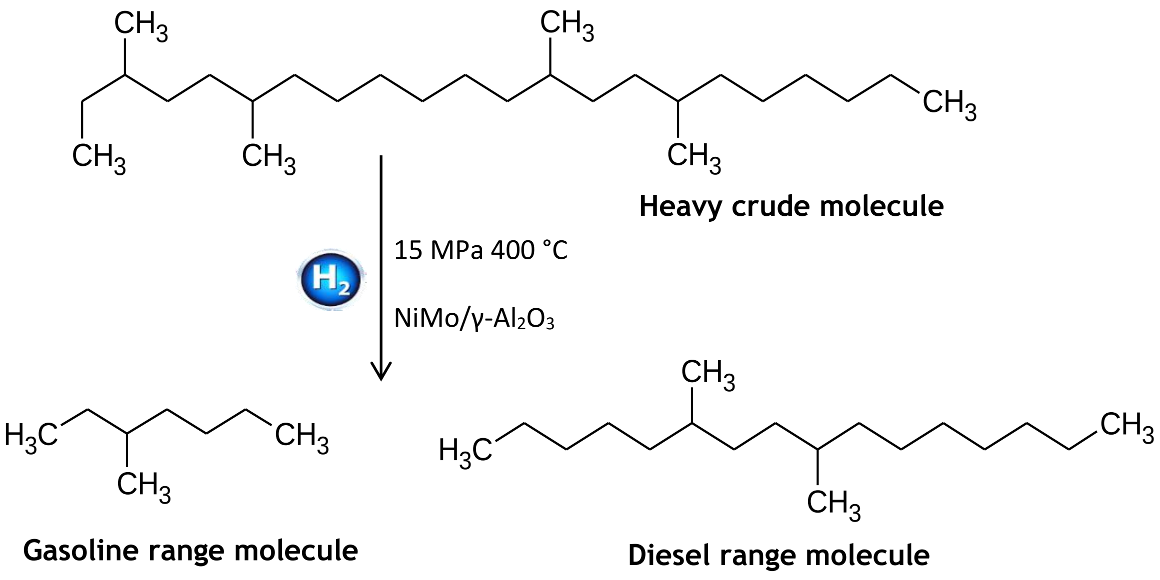


Figure 1-17: Simplified depiction of a hydrocracking reaction
(adapted from Sotelo-Boyás, Trejo-Zárraga, & Hernández-Loyo, 2012)

Hydrocrackers operate under very high pressures (1200 to 2000 psig) and most catalysts consist of a crystalline mixture of silica-alumina with small amounts of noble metals such as platinum and palladium. These catalysts are typically regenerated offsite every 2-4 years and they are sensitive to water and heteroatom impurities such as sulfur and nitrogen. Water is usually removed by passing the feed stream through silica gels or molecular sieves prior to feeding to the hydrocracker. Sulfur and other impurities are often removed by hydrotreating the feed stream prior to feeding (US EPA, 1995). An average hydrocracker has the capacity to process about 60,000 barrels of feed per day. It consumes about 57 Nm^3/bbl of hydrogen and costs over USD 400 million to build (Gary et al., 2007).

1.10 Hydrogen demand in the oil industry

As has been documented, hydrogen will be increasingly required to convert heavy and sour crude oil to high value, low sulfur finished fuels. Thus, hydrogen demand for oil processing will continue to increase and the sector will continue to be the world's biggest user of industrial grade hydrogen (Levin & Chahine, 2010; Mohamed et al., 2011). Hydrotreating capacity in the US alone is expected to double by 2030 to 27 million barrels a day, from 14 million barrels a day in 2004 (Figure 1-18). This doubling of hydrotreating capacity will be associated with an equal increase in hydrogen demand to supply US petroleum refineries.

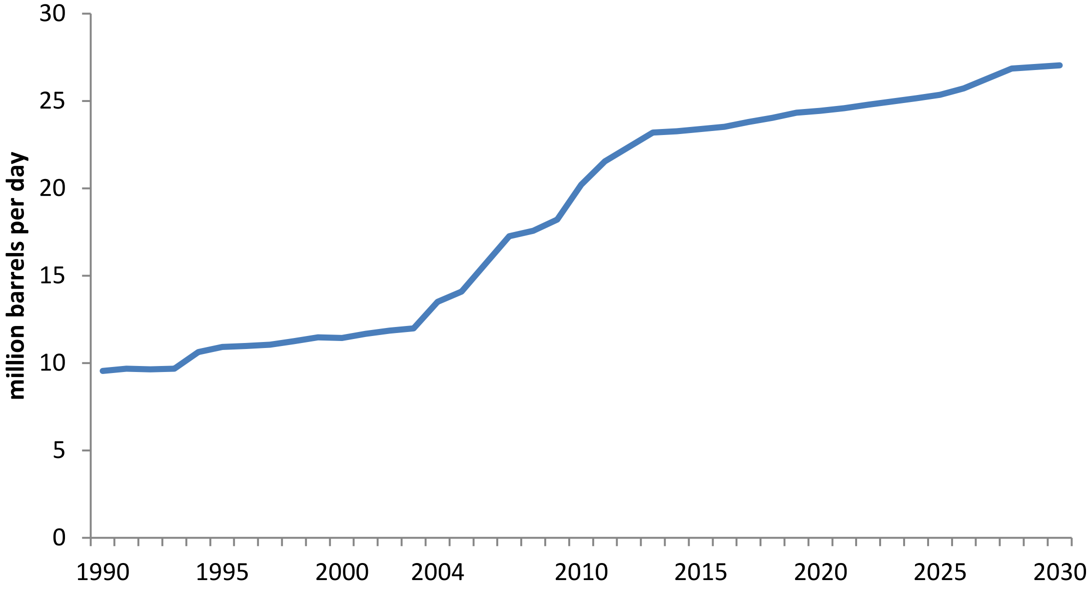


Figure 1-18: Hydrotreating capacity in the US
(Source: US EIA, 2006)

1.11 Hydrogen generation in oil refineries

Currently, most refineries produce hydrogen onsite using steam reforming of methane (SMR). The two main reactions involved in this conversion are:

$CH_4 + H_2O \rightarrow CO + 3H_2$

$CO + H_2O \rightarrow CO_2 + H_2$

In the first reaction, methane reacts with high temperature steam to form syngas (CO and H_2). In the second reaction (also called the "water-gas shift" reaction) the CO produced from the first reaction is converted to hydrogen. The methane is usually derived from natural gas, although sometimes the refinery off-gases can also be used as a source of methane and CO to feed the hydrogen-producing reactions. A typical refinery steam reformer can process about 65,000 m^3/h of natural gas and costs around USD 200 million to build (Muellerlanger et al., 2007).

As mentioned earlier, refineries that have limited access to natural gas may gasify some of the residual crude oil cuts to make hydrogen. However, this is a highly energy intensive process and the use of a petroleum feedstock to make hydrogen as opposed to natural gas is unlikely given the current trends of increasing oil prices and dropping natural gas prices. The price of natural gas has been declining for the last few years (Figure 1-19) and with the ongoing exploration and use of new technologies to help extract "unconventional" natural gas (e.g. shale gas) this low price is expected to continue for some time. Over the same time, as shown in the graph (Figure 1-19), the price of crude oil has increased, thus further increasing the cost differential between the two fuel commodities.

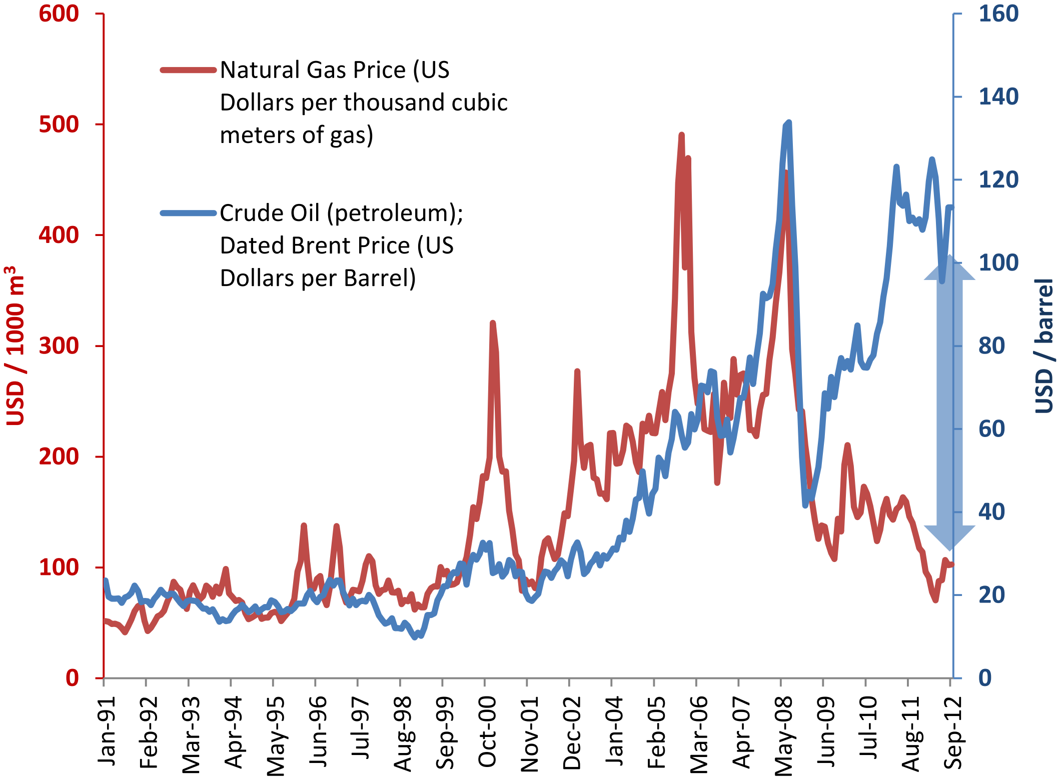


Figure 1-19: Crude/Natural gas price differentials
Source: Data from (IndexMundi, 2013)

1.12 Hydrogen use in the ammonia fertilizer industry

While oil refining utilises the largest amounts of hydrogen, the ammonia fertilizer industry is the second largest global consumer of hydrogen. Demand for fertilizer continues to increase and prices for most agricultural commodities are currently at record highs (the FAO food index has increased from 100 units in 2003 to 250 units in 2013). Diets in countries such as China and India are becoming more "westernized", resulting in an increased demand for fertilizer. Ammonia, the most widely produced fertilizer commodity in the world, is produced by chemically reducing atmospheric molecular nitrogen (N_2) to ammonia gas by reacting it with hydrogen. The hydrogen (gas) typically comes from steam reforming natural gas. Thus, natural gas is one of the most critical feedstocks for the ammonia industry. The global capacity for ammonia manufacturing was 161.3 million tonnes (on a nitrogen basis) in 2011 and it is expected to reach 182.2 by 2016 (Food and Agriculture Organization (FAO), 2012). Most of the capacity growth is expected to be in Asian countries, mainly in Southeast Asia while significant growth is also expected in Eastern Europe.

1.13 Biomass as a source of hydrogen

Although more than 90% of the world's industrial hydrogen is produced by steam methane reforming (SMR) from fossil natural gas, there are numerous technologies for producing hydrogen from renewable resources. For biomass conversion processes, the most available resource from which to derive the renewable hydrogen is the biomass itself. The most effective way of making hydrogen from biomass is to use gasification followed by steam reforming of the resulting syngas. However, this process is less than half as efficient (on an energy basis) as the conversion of natural gas to hydrogen, which approaches efficiencies of about 90%. Holladay et al. (2009) reviewed the efficiencies of technologies related to hydrogen production from both fossil and renewable biomass resources. They concluded that the efficiency of natural gas steam methane reforming is excellent. The same report described how all fossil-based technologies will continue to be more efficient than renewable hydrogen technologies for the foreseeable future. In related work, when Lau et al. (2003) performed a techno-economic analysis to compare the cost of hydrogen derived from the gasification of either bagasse, switchgrass or palm nutshell with that of natural gas (Figure 1-20) it was only competitive at a very large scale.

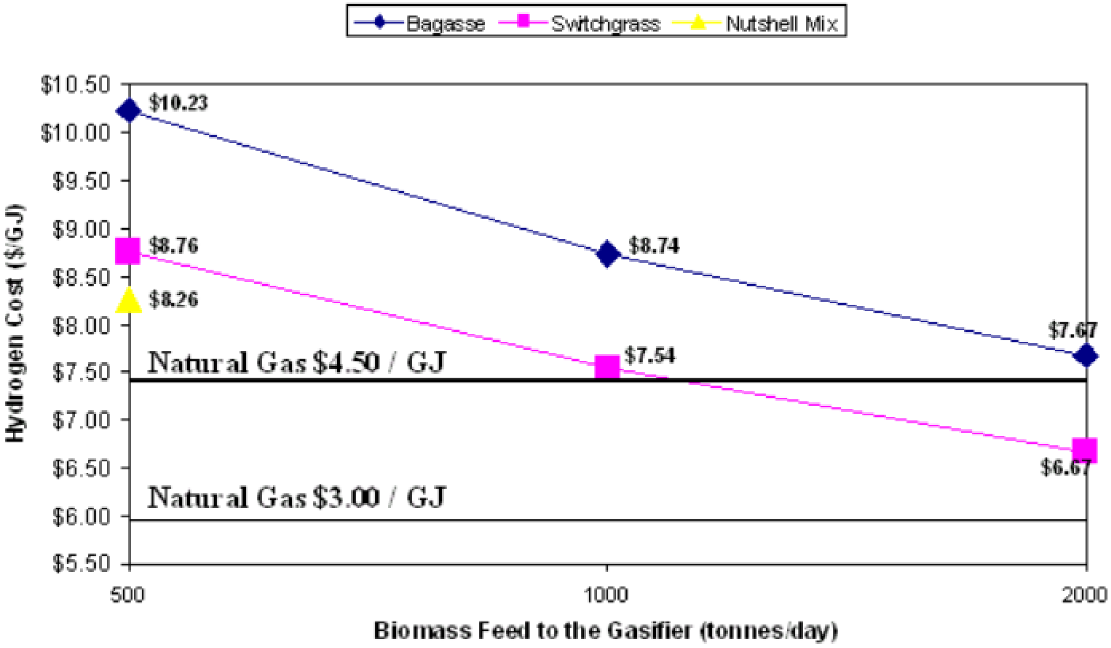


Figure 1-20: Estimated Cost Hydrogen Production from Biomass and Natural Gas Feedstocks
(Source: Lau et al., 2003)

From these estimates, it can be concluded that, at the current natural gas prices of about $4/GJ, a 1000 t/day bagasse-to-hydrogen facility would generate hydrogen that would cost almost twice as much as that derived from natural gas. This cost disparity is even more problematic when the average cost of biomass, which was $30/dry tonne (dt) for this study, is considered. Most recent techno-economic analyses estimate much higher biomass costs, in the range of $60-75/dt or higher. Most studies acknowledge that using biomass to produce hydrogen is a not an ideal option in terms of energy efficiency and associated GHG savings (Levin & Chahine, 2010).

It is apparent that a key challenge for developing drop-in biofuels will be finding cheap, sustainable sources of hydrogen. However, there is an opportunity to develop enhanced compatibility and leveraging opportunities with the current oil refinery infrastructure. It is also clear that long distance transportation such as aviation, shipping and trucking has few alternative options other than liquid biofuels. A key consideration will be the efficiency of the conversion processes used to deoxygenate biomass feedstocks. The trade-offs that will be encountered and the production and process challenges for each of the drop-in biofuel options are reviewed in the next section of the report.

CHAPTER 2: THE OLEOCHEMICAL PLATFORM

Most "drop-in" biofuel demonstrations to date have used material derived from oleochemicals. The oleochemical platform is based on lipid feedstocks such as vegetable oils or other bio-derived fats such as tallow and algal oils. These lipid based feedstocks have been the pioneers in the manufacture and demonstration of drop-in biofuels primarily because they contain low amounts of oxygen and have a high hydrogen-to-carbon (H_{eff}/C) ratio – they are already close to drop-in fuels – compared to sugar or cellulosic feedstocks. Conventional lipid based biofuel known as "biodiesel" is produced by esterification of triacyl glycerides (TAGs) to produce fatty acid methyl esters (FAME). However, biodiesel is not fully compatible with existing petroleum infrastructure. A further hydroprocessing step is required to convert lipids into deoxygenated hydrocarbon drop-in biofuels typically known as hydrotreated esters and fatty acids (HEFA). This hydrogen-requiring process represents the only route to date that has been used to deliver commercially meaningful amounts of drop-in biofuels. As noted earlier, HEFA biofuels have been the main aviation biofuel used for test flights carried out by the US Navy and many commercial airlines.

2.2 Process overview

2.2.1 Conventional oleochemical-based biofuel (esterified fatty acids)

As shown in Figure 2-1, the esterification of vegetable oils or other bio-derived fats to make biodiesel involves the reaction of a TAG lipid with methanol in presence of a base, such as NaOH, or acid, such as H_2SO_4, to form FAME and produce glycerol as a by-product. This conversion is relatively simple and, unlike HEFAs, there is no requirement for specialized catalysts or hydrogen (H_2) or for high pressures and temperatures. Rather, production of FAME can be performed at various scales ranging from small "backyard-type" units all the way to large scale biodiesel-manufacturing facilities such as the 100 million gallon per year (380 MLPY) Imperium Renewables biodiesel facility in Washington State, USA.

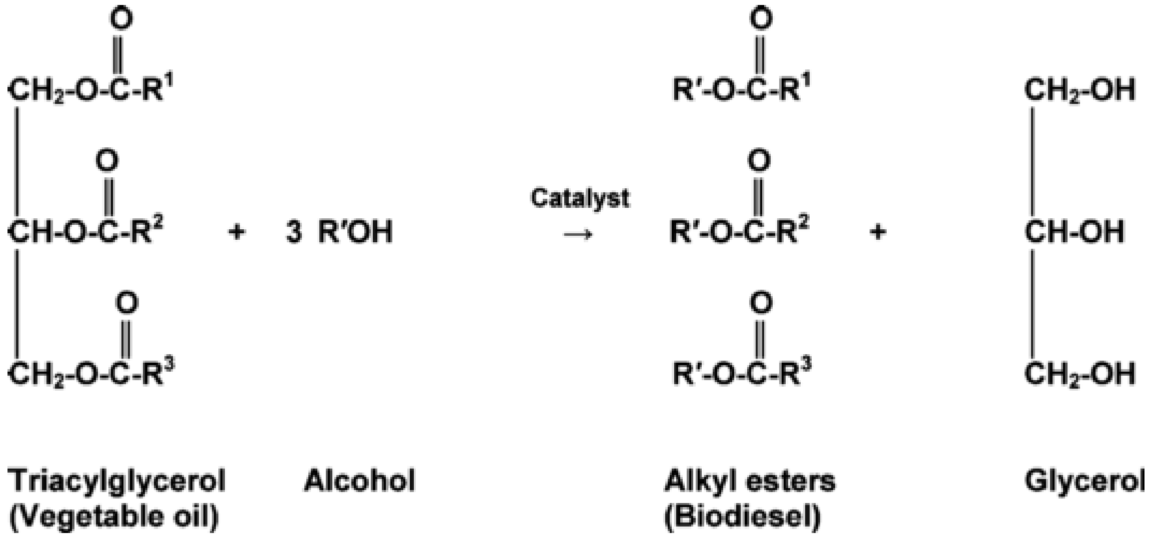


Figure 2-1: Triglyceride to Biodiesel (FAME) reaction

The major disadvantage of FAMEs when compared to HEFAs is that they are not a "drop-in" biofuel. As is shown in Figure 2-1, there is still an appreciable amount of oxygen present in the final FAME product and this imparts polar and hydrophilic chemistry that inhibits full compatibility with existing fuel infrastructure: a) it contains a lower energy content than oxygen-free hydrocarbon fuels; b) has a higher cloud point temperature which limits the applicability of the fuel in cold climates; c) reacts with water and can contaminate petroleum blends; d) reacts with metal surfaces and sticks to them and/or causes corrosion; and e) reacts with itself which reduces fuel storage life. When the properties of petroleum diesel and biodiesel are compared (Table 2-1) most of the biodiesel deficiencies are directly or indirectly related to its oxygen content, although the lower sulphur content of biodiesel is an exception and is one of the few advantages biodiesel has over petroleum-derived diesel. Aromatics are missing from all oleochemically derived biofuels (both HEFA and FAME) except tall oil.

Table 2-1: Properties of HEFA petroleum diesel and FAME biodiesel.

Properties	HEFA Renewable Diesel	Fossil Diesel EN 590 (summer grade)	FAME Biodiesel (from rape seed oil)
Density at 15 °C (kg/m3)	775 - 785	835	885
Viscosity at 40 °C (mm2/s)	2.5 - 3.5	3.5	4.5
Cetane number	80 - 99	53	51
Distillation range (°C)	180 - 320	180 - 360	350 - 370
Cloud point (°C)	−5 to −25	−5	−5
Heating value, lower (MJ/kg)	44.0	42.7	37.5
Heating value, lower (MJ/L)	34.4	35.7	33.2
Total aromatics (wt-%)	0	30	0
Polyaromatics (wt-%) (1)	0	4	0
Oxygen content (wt-%)	0	0	11
Sulfur content (mg/kg)	< 10	< 10	< 10
Lubricity HFRR at 60 °C (mm)	< 460(2)	< 460(2)	< 460
Storage stability	Good	Good	Challenging

(1) European definition including di- and tri+ -aromatics
(2) With lubricity additive
Source: (Aatola et al., 2008)

Another critical yet often overlooked challenge of biodiesel is its limited compatibility with petroleum in pipelines. Biodiesel transported through conventional petroleum pipelines can mix with the "water plugs" which are inserted into the pipeline to separate different petroleum liquids from each other when they are transported through the same pipeline at different times. Biodiesel can also stick to pipeline walls and contaminate jet fuel plugs that follow. As current jet fuel specifications are very stringent, such a contamination risk prohibits the transport of jet fuel and biodiesel in the same petroleum pipelines. Biodiesel is typically transported via road/trucks, a practice that adds to the cost and carbon footprint of the fuel. However, Kinder Morgan Energy Partners (KMEP), one of the largest pipeline companies in North America, has successfully shipped biodiesel through its Plantation pipeline network located in the southeastern United States. In this case, jet fuel contamination was prevented due to the existence of a parallel pipeline that allowed jet fuel and FAME biodiesel to remain segregated. The results of this trial were positive and, as of early 2010, KMEP allows the shipment of B2, B5, and/or B100 in over 8000 miles of pipeline (Bunting et al., 2010).

Due to these compatibility concerns, and several other issues, biodiesel is seldom used neat or as a finished fuel (100% biodiesel or B100). To try to make use of the current infrastructure and motor engine compatibility, it is typically blended with conventional diesel at ratios of 5 or 7% volume (B5 or B7). Currently biodiesel is primarily used in road transportation while its use in jet fuel blends is strictly prohibited.

2.2.2 Advanced oleochemical (hydrotreated lipids)

Hydroprocessed Esters and Fatty Acids (HEFA) is the term used to describe drop-in biofuels that are produced by hydrotreating lipids derived from vegetable, algae and animal fats. To distinguish HEFA from “biodiesel”, the terms “green diesel” or “renewable diesel” are often used. Alternative acronyms for HEFA renewable fuels include HRV (Hydrotreated Renewable Vegetable oils), HVO (Hydrotreated Vegetable Oils) and HRO (Hydrotreated Renewable Oils). Other common acronyms used to describe the type of HEFA used for jet fuels only are HRJ (Hydrotreated Renewable Jet fuel) and bio-SPK (bio-based synthetic paraffinic kerosene).

Compared to other potential biofuel feedstocks such as sugars and cellulosic biomass, fats are the simplest to convert to drop-in biofuels because, as discussed earlier, they have low oxygen content and their chemistry is closer to a hydrocarbon than saccharides or lignins (i.e., their effective hydrogen to carbon ratio is closer to 2). Despite these benefits, the conversion of fats to HEFA entails significant capital costs as well as hydrogen inputs compared to the production of biodiesel (FAME). For example, the capital expenditure for a 2000 tpd HEFA facility, as modeled by Pearlson (2011), is about USD $2.6/gal ($0.7/L) of installed capacity and the hydrogen use is 3-4% by mass of feedstock compared to USD $0.8/gal ($0.2/L) and no hydrogen inputs for FAME as modeled by Marchetti et al. (2008) for the same size facility.

<u>Process chemistry</u>

In a standalone facility, HEFA’s are typically produced in two stages (Figure 2-2) (Pearlson, 2011). During the first stage the fats are deoxygenated and their double bonds are saturated to create alkanes. The second stage involves alkane isomerisation and cracking, bringing the biofuel to a quality specification that equals or surpasses specifications for conventional petroleum fuels or fuel blendstocks.

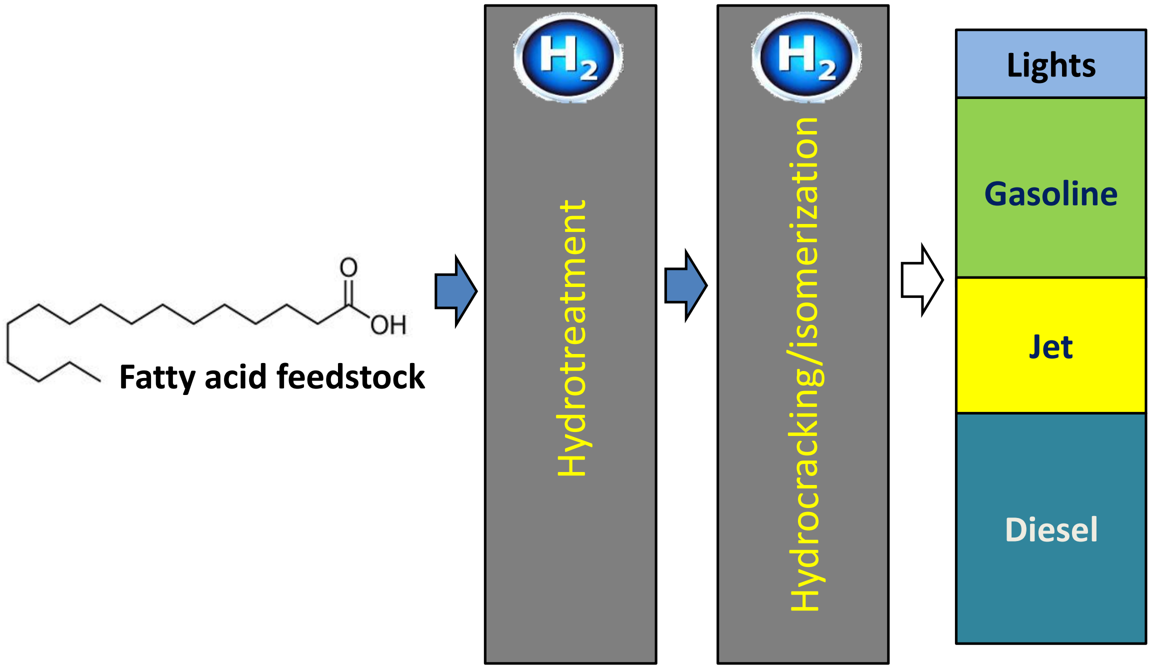


Figure 2-2: Simplified Hydroprocessed Esters and Fatty Acids (HEFA) process depicting the 2 stages of hydroprocessing

As depicted in Figure 2-3, during the first stage of HEFA production, a number of chemical reactions take place with some hydrogen initially used to saturate all of the carbon-carbon double bonds present in the triacyl glyceride (TAG). More hydrogen is added in the second reaction which removes the propane backbone of the TAG leaving 3 free fatty acids per TAG molecule. Finally the fatty acids are deoxygenated either with the addition of more hydrogen (hydrodeoxygenation, where oxygen leaves as H_2O) or with the loss of carbon (decarboxylation, where oxygen leaves as CO_2) resulting in the formation of alkyl chains. During hydrodeoxygenation (HDO) the alkyl chain length is typically preserved whereas during decarboxylation (DCO) alkyl chains are shortened due to the loss of carbon atoms as CO_2. Usually a combination of the two deoxygenation strategies is used in commercial hydrotreating facilities (Pearlson, 2011). The ratio of each deoxygenation pathway (e.g., HDO/DCO = 35/65) is of importance to the hydrotreating operations as it determines the hydrogen consumption, product yields, catalyst inhibition, gas consumption and heat balance (Egeberg et al., 2010). The tuning of the deoxygenation pathway ratio can be achieved via catalyst adjustment, depending on the strategic manufacturing priorities as well as the feedstock and hydrogen costs and the value of the fuel product or blendstock being produced. For example, the UOP-Honeywell facility opts for more decarboxylation in order to reduce capital costs while Syntroleum prioritises the preservation of longer carbon chains (higher product quality) and thus uses more hydrodeoxygenation (Pearlson, 2011).

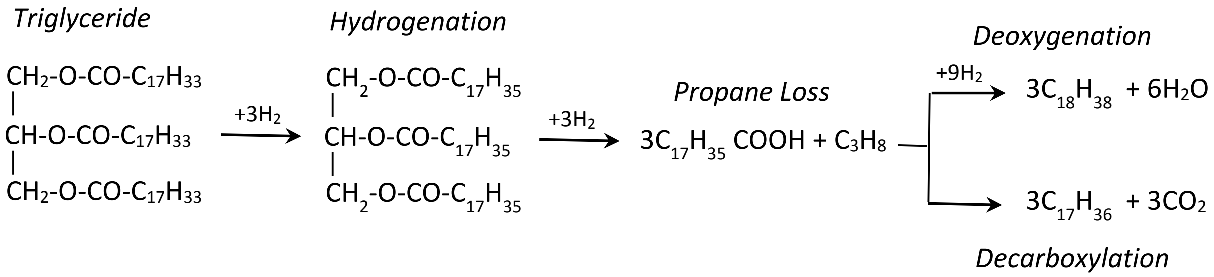


Figure 2-3: Triacyl glyceride (TAG) deoxygenation process

Source: (Pearlson, 2011)

After the first processing stage, the TAG feedstock has been converted to an oxygen-free, saturated liquid alkane intermediate. This hydrocarbon liquid can be directly blended in small quantities with petroleum diesel (Pearlson, 2011). However, it does not meet the specifications of a finished fuel due to its poor cold flow properties (propensity to freezing at lower temperatures, i.e., relatively high freeze point and high cloud point). During the second and final process stage, the unbranched long chain alkanes are cracked and isomerised in a process referred to as "dewaxing" (Pearlson, 2011). Dewaxing reduces the length and increases branching of the carbon chains, thereby reducing the freezing point of the resulting finished fuel (Conventional oil refining and the chemistry of cracking and isomerisation are reviewed in Chapter 1). The mass yield of HEFA liquids from lipid raw material is typically around 80% but varies according to the feedstock and processing conditions used (Pearlson, 2011; Sotelo-Boyás et al., 2012). The remaining 20% of material is generally composed of light gases such as propane, methane and oxygenated gases such as CO_2 and CO. Other than CO_2, these gases are usually combusted to provide power for the process. Typical HEFA liquids comprise 3 different fractions corresponding to jet, diesel and gasoline (or naphtha) blendstocks (Figure 2-2). The distribution of these three liquid product fractions can be controlled by changing the reaction conditions and catalysts. However, diesel generally predominates with only a small portion of the liquids in the jet range (Bezergianni et al., 2009; Pearlson, 2011). For example, it has been reported that in a UOP-like (decarboxylation-based) HEFA process, ca.

65 wt% of the incoming vegetable oil gets converted to diesel-range molecules and only ca. 13 wt% to jet-range; increasing this the jet yield to 50 wt% requires 30% more hydrogen and reduces the overall liquid fuel yield of the process from 80 wt% to about 70 wt% (Pearlson, 2011). The extra processing required to maximize jet fuel production imposes extra economic and logistic challenges and, contrary to common perception, jet fuel does not always command a higher price than diesel. In fact, at the time of writing jet fuel prices are around USD $3 per gallon while diesel prices are at around USD $3.20 per gallon ($0.85/L) (IndexMundi, 2013). In the absence of a price premium for jet fuels compared to diesel fuels, jet fuel would be sold as diesel since jet fuel can be fed to diesel engines (a standard practice of the US Navy to simplify logistics) but not the other way around. It would be difficult to justify the extra cost of maximizing HEFA jet yields and the cost of separating jet from diesel fractions unless there is significant price premium for HEFA jet fuel compared to HEFA diesel. As is discussed in section 2.4.2, it has been estimated that this premium would need to be USD 2-3 $ /gal ($0.53 – $0.79/L).

2.3 Potential for integration with oil refineries

It has been suggested that hydroprocessed Esters and Fatty Acids (HEFA) platforms can achieve capital savings by leveraging petroleum refineries by co-processing fats at the same time as petroleum intermediates in existing hydroprocessing facilities (ConocoPhillips, 2010; Egeberg et al., 2010). This co-processing strategy is intended to take advantage of existing petroleum refining infrastructure and fuel off-take networks while also utilizing lower cost hydrogen typically available in oil refineries. As described earlier, in a standalone facility HEFA is usually produced in two separate stages. In an oil refinery, this process could be performed in a single combined hydroprocessing stage.

2.3.1 Challenges of hydroprocessing renewable oils in conventional refineries

Hydroprocessing units (hydrocrackers and hydrotreaters) are central components of a typical oil refinery and the overall economics of operating a refinery is influenced by the performance of these units. As described below, introducing oxygen-containing renewable oils to hydroprocessing units presents a number of challenges that must be carefully addressed to ensure continued smooth refinery operation and profitability.

Renewable oils such as vegetable oils and animal fats are naturally unstable and corrosive due to their oxygen content and, consequently, problems can be encountered transporting these oils through metal pipelines within a refinery. Vegetable oils and other natural oils, especially those with a high free fatty acid content such as tall oil, can cause severe corrosion of pipes and other metal equipment upstream of the hydrocracking reactor (Egeberg et al., 2010). These oils must be handled in a similar way to highly acidic (high-TAN) fossil crudes.

The reactions involved in hydrotreating organic fats and fatty acids are distinct to the usual reactions taking place in a refinery hydrotreater. Refinery hydrotreaters are designed to remove sulfur from petroleum fuels. This process is known as hydrodesulfurization (HDS) and, as discussed earlier, is used to reduce the sulfur content of finished fuels in order to meet increasingly stringent fuel specifications such as required for Ultra Low Sulfur Diesel (ULSD, <10 ppm S). Sulfur emission regulations are tightening around the world and, consequently, hydrogen consumption in oil refineries is projected to double over the next decade. While renewable oils typically do not contain much sulfur and thus do not require hydrodesulfurization, hydrotreatment in the form of hydrodeoxygenation (HDO) is still needed to remove oxygen. Unfortunately, hydrodeoxygenation of renewable oils requires more hydrogen gas inputs than do hydrodesulfurization of crude oils. For 100% renewable feed, a hydrogen consumption of 300-400 Nm^3/m^3 is not unusual (Egeberg et al., 2010); compare this with about 34 Nm^3/m^3 for the hydrotreating of 1% sulfur petroleum (Stratiev et al., 2009). The presence of oxygen in the feed also increases reactivity and results in the formation of byproducts such as propane, water, carbon monoxide and methane (Egeberg et al., 2010). These gases must be removed by increasing the gas purge rate in the system. If not removed, these gases will cause numerous problems such as: a) altering the hydrogen partial pressure or reducing catalyst activity: b) CO and CO_2 competing with S- and N- species for hydrotreating catalyst sites; and c) liquid water and CO_2 reacting to form corrosive carbonic acid in the effluent train of the reactor. The formation of these carbonaceous byproduct gases diverts carbon from the final fuel and thus reduces process yields compared to fossil diesel hydrotreating (Egeberg et al., 2010). Methane in particular is a highly undesirable byproduct because it not only diverts one mole of carbon from the fuel, it also diverts four moles of elemental hydrogen (two moles of molecular hydrogen, H_2) from the reaction mass thus unproductively increasing hydrogen consumption in the process. These challenges have been documented by ConocoPhillips in trials performed in refineries in Texas, USA and in Ireland (ConocoPhillips, 2010).

Due to all of the above challenges, renewable oils have not yet been processed in a neat (100%) form in conventional refineries. The few trials of co-processing vegetable oils with petroleum liquids that have been carried out in commercial refineries have used low percentages of renewable oils and have only been partially successful. Poor desulfurization, hydrogen starvation and pressure drop build-up are among the issues that have been encountered using reactor setups and catalysts not specifically designed for renewable oil feeds. As an example, Haldor Topsoe, a major refinery catalyst producer, reported an industrial trial of co-processing a few percent vegetable oil in a ULSD hydrotreating facility (Egeberg et al., 2010). A few days after the renewable oil feed was introduced to the ULSD hydrotreater, the pressure drop-in the reactor increased such that the refinery had difficulty continuing operation. In related work, Haldor Topsoe showed that the CO byproduct from co-processing this biofeed reduced hydrodesulfurizing (HDS) and hydrodenitrogenising (HDN) activities of conventional CoMo-type catalysts. As NiMo catalysts did not seem to be affected by blend levels up to 15% biofeed, these type catalysts are currently favoured when designing hydrotreatment catalysts for renewable oil co-processing (Egeberg et al., 2010).

Another technical challenge for designing effective catalysts for biofeed processing is that the catalyst needs to have some dewaxing activity to enable normal paraffinic molecules to be cracked and isomerized to lighter molecules thereby improving the cold flow properties of the final fuel or blendstock product. The dewaxing requirements for catalysts processing biofeed are higher than those processing petroleum feed. The long and largely unbranched acyl chains in vegetable oils yield paraffinic chains of similar length and level of isomerisation (branching). In contrast, petroleum-derived feeds to hydrotreaters, such as light gas oil, are typically already more isomerized and cracked (partly due to the distillation and cracking processes they have been through prior to arriving at the hydrotreating unit). Dewaxing is only essential if the feed has a high content of renewable oil as at low concentrations the cold flow issues are not as prominent and they can be alleviated by blending light fractions and cloud point-depressing additives.

This complex challenge of designing catalyst beds that can help perform all the aforementioned selective reactions is currently being tackled by companies such as Haldor Topsoe, UOP Honeywell and other catalyst innovation companies. The goal is to improve oil refining catalysts and process designs for the purpose of improving the ability to process biofeeds in hydrotreating reactors.

Box 2-1: SunPine: Deriving diesel from tall oil: A renewable fuel from the forest

In 2009, Preem AB, a Swedish oil refining company, partnered with Sunpine AB, a producer of tall oil from Kraft paper mills, to produce green diesel (www.preem.se). Tall oils are a byproduct of pulp mills and they are mainly derived from the resins and extractives present in softwood feedstocks such as pine, spruce and birch. Due to being primarily comprised of large amounts of resin acids and free fatty acids they are very acidic. To improve transport logistics tall oils are typically processed to FAMEs prior to shipping from the pulp mill. The resulting tall oil FAME liquids are known by the abbreviation RTD (raw tall diesel). Under this collaboration, the Preem AB oil refinery in Gothenburgh, Sweden developed and demonstrated the ability to hydrotreat up to 30% RTD blends with 70% mineral oil, which is a record high biofeed fraction for co-processing in a conventional refinery (Egeberg et al., 2010). Haldor Topsoe provided the catalyst beds and process design. It should be noted that hydrotreating FAMEs (such as RTD) is distinct from hydrotreating vegetable oil TAGs with the major difference being that a high yield of byproduct methane is obtained processing FAMEs as opposed to propane processing TAGs.

It is important to note that, as well as addressing the technical challenges of co-processing oleochemical based biofuels in conventional oil refineries, regulatory hurdles must also be resolved. For example, the current US Renewable Fuel Standard (RFS) mandates definition of “biomass-based diesel” does not allow any renewable fuel derived from biomass to be co-processed with petroleum feedstocks. This co-processing exclusion mostly affects those biofuel intermediates which have the greatest opportunity for refinery leveraging such as vegetable oils. (Other technologies such as pyrolysis are less affected as, unlike oleochemical fuels, they also qualify under the other, mandated “advanced biofuels” categories, of the RFS). It has been suggested that, for co-processed vegetable oils in particular, this RFS limitation translates to a competitive disadvantage of up to $2/gal ($7.6/L) compared to conventional FAME (Weyen, 2012).

2.4 Commercialization aspects

2.4.1 Feedstock sensitivity

The chain length of the fatty acids in the TAG feedstock determines the products of a HEFA facility. Most of the feedstocks available today are derived from vegetable oils. These typically contain long fatty acid chains corresponding to the carbon chain length of diesel i.e. C_{16}-C_{22}. These molecules can be cracked to shorter chains to fit the "lighter" jet fuel and gasoline range. However, the cracking step is not sufficiently selective and creates by-products and reduces the overall fuel yield. For example, when a long alkyl chain is cracked, only some of the chains are of the desirable length while a number of undesirable short chains are also produced. These "too-short-waste" chains form a light naphtha-like byproduct and the overall fuel yield is reduced. Although the oils from camelina, palm kernels and most cyanophyta contain TAGs with shorter chain fatty acids (which are in the jet fuel range) (Bauen, Howes, Bertuccioli, & Chudziak, 2009; Pearlson, 2011) these feedstock's are currently only available in relatively small volumes. Camelina and cyanophyta oils are only produced in small volumes while, in year 2011/12, only about 6 million metric tonnes of palm kernel oil (not to be confused with palm oil) are produced annually of the global 160 million metric tonnes of vegetable oils production (USDA, 2013).

2.4.2 Feedstock procurement

While there are fewer technological barriers that have to be resolved to achieve techno-economically effective processing of lipids to finished drop-in fuels, lipid feedstocks themselves are likely to be difficult to source cheaply and sustainably in the volumes required for significant production of biofuels. The most widespread source of lipids for biofuel production are vegetable oils such as rapeseed and palm oils which are currently used extensively in the food market. Thus there is competition with regard to price and access to prime agricultural land for these feedstocks. Moreover, the price of these feedstocks can be and often is higher than the price finished diesel fuel commands. Commodity prices for food-grade vegetable oils are generally higher than diesel prices. For example, on January 15, 2013, rapeseed oil (also known as canola oil), a popular food-oil as well as a common feedstock for biodiesel production, had an average commodity price of $4.21 USD/gal ($1.11/L) while diesel fuel for the same month had a price of $3.22 USD/gal ($0.85/L) (IndexMundi, 2013). Oleochemical feedstock prices also appear to be linked to petroleum prices as depicted in Figure 2-4, which shows this for palm oil, one of the lower cost HEFA feedstocks. The combined production potential of HEFA is estimated to currently be in the low hundreds of thousands of barrels per day and there are significant constraints on increasing near-to-midterm production capacity, especially since these facilities would be competing for the same feedstock as existing biodiesel producers (Hileman et al., 2009). Global production of vegetable oils is currently about 3 million barrels per day. A thirty-fold (30x) increase in vegetable oil production would be required to satisfy the current 44 million barrels per day of global transportation fuel demand (IEA, 2012b)

The likely ongoing high cost of feedstock is a major impediment to successfully implementing and expanding oleochemical platforms. For example, a recent report by MIT's research program "PARTNER" assessed the cost to US commercial aviation of meeting the US Federal Aviation Administration's (FAA) aviation biofuel goal to use 1 billion gallons (3.8 billion L) of renewable jet fuel per year from 2018 onwards (Hileman et al., 2009). This analysis only considered the production and distribution costs of HEFA derived biojet fuel ("biojet"). One of the conclusions is that biojet will require a premium (implying the need for a subsidy) of $2.69 USD/gal ($0.71/L) compared to petroleum-derived jet fuels. It was suggested that this premium would have to be voluntarily paid by the aviation (and military) sector if they wanted to reach their FAA goal. It should be noted that this premium would not drop significantly by including aviation fuels in the RFS mandate. The only scenario where the premium is reduced significantly, down to $0.35 USD/gal ($0.09/L), is the case where fallow rotation land (land planted with oilseeds in between corn and oil seed crop cycles) is sufficiently available to produce all the vegetable oil feedstock needed to meet the FAA's goal. This is unlikely due to the generally low productivity of fallow land and the relatively low yield of possible new oilseed crops such as camelina.

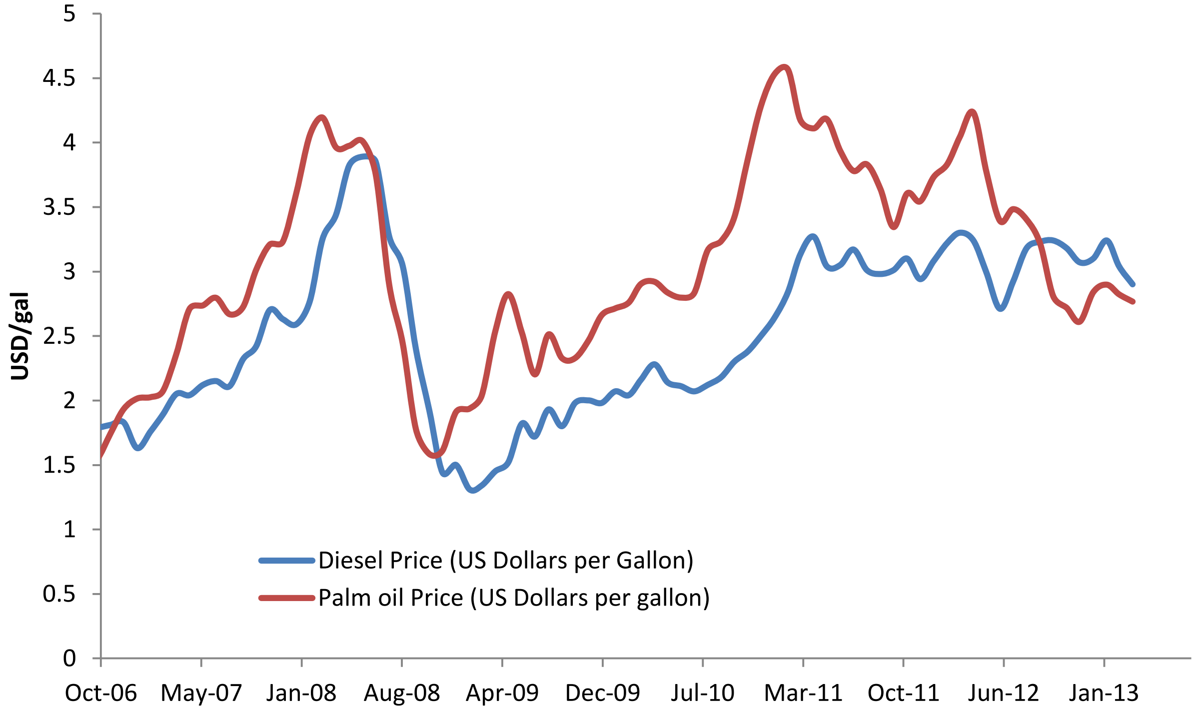


Figure 2-4: Commodity prices of Diesel and Palm Oil

Source: (IndexMundi, 2013)

However, various government and industry funded R&D programs are currently trying to improve the productivity of oilseed crops that are suitable for biofuel and for biojet applications in particular. One of the overall goals is to develop oilseed crops that compete less with food markets by producing non-edible oils with lipid fatty acid composition favourable for biofuels and growing these crops on "marginal land". The USDAs "Farm to Fly" program is a good example of this type of strategy (USDA, 2012). Alternative oleochemical feedstock sources which do not use arable land include algae (autotrophic), tall oils (a pulp mill residue as seen in Box 2-1), and waste oils and fats.

Algae have also been suggested as an alternative, non-land-use-intensive source of lipids. These micro-organisms are able to capture CO_2 and sunlight and produce lipids without utilizing productive arable land. However, major issues such as yields, maintenance of favourable growth conditions in large scale ponds and extraction of lipids in a usable form have, so far, limited commercialization. The potential of algae biofuels is more extensively reviewed in a previous IEA Bioenergy Task 39 report (Darzins et al., 2010).

As well as autotrophic algae, which use CO_2 as their carbon source, heterotrophic algae using sugar as their carbon source have been used to produce TAGs and fatty acids for drop-in biofuel production. While autotrophic algae require optimal exposure to sunlight, heterotrophic algae do not and thereby avoid some of the operational challenges of operating raceway ponds or photobioreactors. However, using heterotrophic algae requires securing a cheap and sustainable source of sugar feedstock and proving that this mode of algal production can be scaled up economically enough to enable profitable biofuel applications.

Waste oils (e.g., tall oils) and used cooking oils (UCO) have been used as feedstocks for drop-in biofuels. One benefit with these types of feedstocks is that, compared to purpose grown oils, the carbon footprint of used oils has already been absorbed by the life cycle of another product or service. However, UCOs are typically only available in small quantities and at dispersed locations (e.g., restaurants) so their collection and quality control is challenging. Although industrial waste oils such as tall oils are more centrally accumulated and there are facilities using these oils commercially today such as the Sunpine facility in Sweden (see Table 2-2) there are again limited volumes of this material available globally.

2.4.3 Commercial facilities

As mentioned earlier, oleochemical derived fuels are the only drop-in biofuels that are being produced at relatively large commercial scale today. However, as shown in Table 2-2, they account for less than one hundred thousand barrels of fuel per day. Neste Oil, a Finnish petroleum refining company, is currently the world's largest producer of drop-in biofuels and operates 3 HEFA facilities (Finland, Rotterdam, Singapore) with an annual total capacity of 630 million gallons (2.4 billion L) of palm oil-derived diesel, which is marketed as "NexBtL" (Neste Oil, 2013a). In Q1 of 2013, the company's renewable fuel division recorded an operating profit of 26 million euros (Neste Oil, 2013b). Other commercial HEFA manufacturers include three facilities in southeastern USA. One is the joint venture between Syntroleum and Tyson foods, which licensed their "Biosynfining" technology to a Dynamic Fuels commercial plant in Louisiana that currently produces 75 million gallons (284 million L) per year of green diesel (renewable diesel). Another, Honeywell-UOP, which licensed their technology to the Diamond Green Diesel facility in Kentucky (a joint venture between Darling International Inc. and Valero Corporation) for a 136 million gallon (515 million L) facility in Norco, Louisiana. The third is Emerald biofuels, which announced in May 2012 that it will build an 85 million gallon (322 million L) per year capacity plant at the Dow Chemical site in Plaquemine, Louisiana. In the EU, the ConocoPhillips Whitegate refinery in Cork, Ireland produces 1000 barrels per day of HEFA by co-processing soy oils with petroleum.

Table 2-2: Current world annual production capacity of HEFA drop-in biofuels

Company	Feedstock	million gallons/yr	million L/yr	barrels per day	Source
Neste Oil	Palm oil	626	**2,371***	45201	(Neste Oil, 2013a)
Diamond Green Diesel	Tallow	**136**	515	**10000**	(Diamond Green Diesel, 2013)
Emerald Biofuels	Tallow	**85**	322	6133	(Emerald Biofuels, 2013)
Dynamic fuels	Tallow	**75**	284	5411	(Dynamic Fuels, 2013)
Conoco Phillips Whitegate Refinery	Soy oil	13.9	52	**1000**	(Conocophillips, 2013)
Sun Pine	Tall oil	26	**100**	1906	(Chemrec, 2009)
World Total		963	3644	69651	

Bold figures are from source and all other figures calculated (bbl/day calculations based on 330 day/year operations)
*Neste Oil source listed 1,980,000 metric tonnes of diesel which were converted to 2,371 m L using diesel density of 0.832 kg/L

Other European projects have been announced by ENI and Galp Energia, which both intend to produce green diesel (Maniatis et al., 2011), although neither project has as yet started construction. As mentioned earlier, pulp and paper companies such as Sunpine and UPM Kymene produce HEFA using their tall oil (2% of wood feedstock) as feedstock. While the 100,000 t/year, 150 million euros UPM Lappeenranta facility (Kaukas mill) in Finland is under construction, Sunpine's facility in Piteå, Sweden has been operating since 2007.

2.4.4 Fuel Quality

The process of hydrotreating vegetable oils can result in the production of high quality HEFA fuels that exceed the specifications of petroleum based transportation fuels (Table 2-3). As an example, HEFA derived diesel and jet fuel have essentially no sulfur content whereas their petroleum counterparts can contain up to 3000 ppm of sulfur. Other improved characteristics of HEFA fuels include higher energy density, lower aromatics content and for diesel HEFAs higher cetane number (Table 2-3).

Table 2-3: Selected properties and specifications of fossil and renewable HEFA diesel and jet fuels.

Property		**Diesel**		**Jet**	
		Fossil	[1]HEFA	Fossil	[2]HEFA
Oxygen content	wt %	0	0	0	0
Specific gravity	kg/L	0.84	0.78	0.75-0.84	0.73-0.77
Cetane		40-52	70-90	-	-
Sulphur	ppm	<10	<2	<3000	<15
Specific energy	MJ/kg	43	44	>42.8	44.1 (typical)
Aromatics	Vol %	<12	0	<25	<0.5

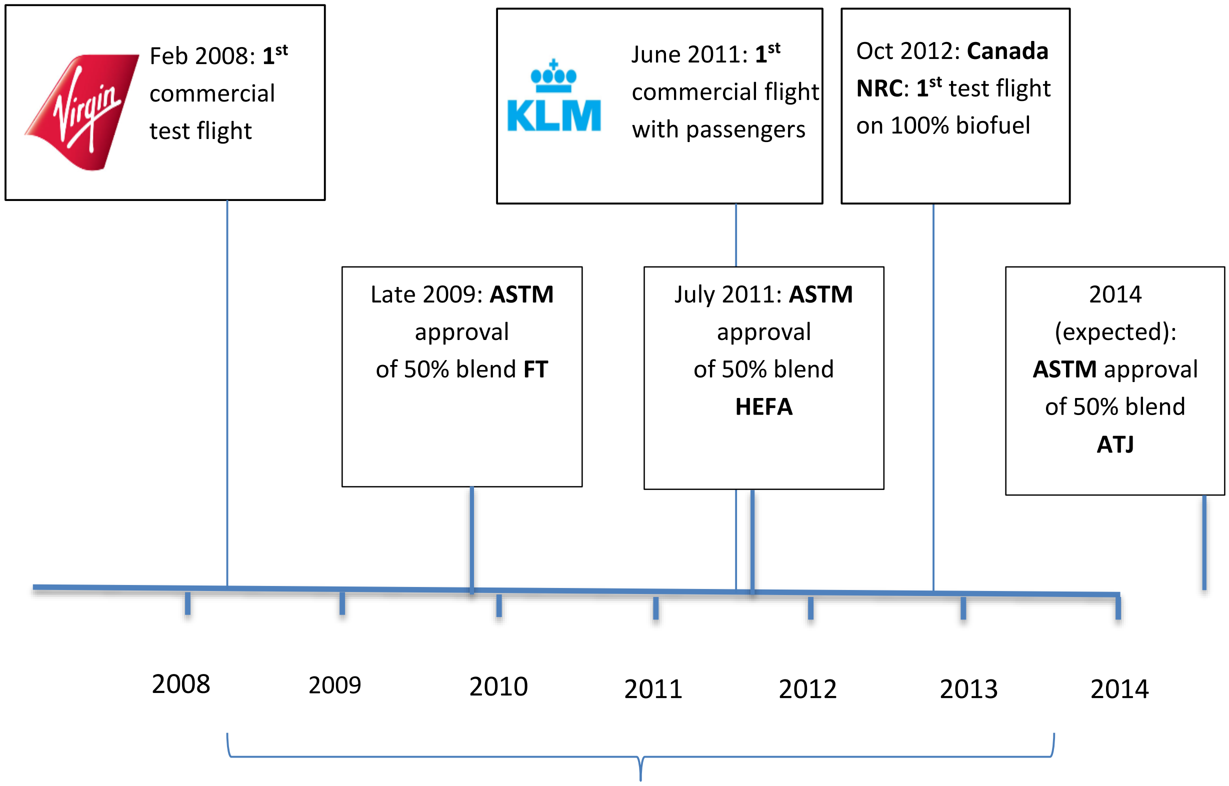
[1]Properties of renewable diesel from UOP Green Diesel. [2]ASTM D7566 Annex 1 used for hydroprocessed renewable oil specification. Source: (Pearlson, 2011)

The absence of aromatics in renewable HEFAs is generally viewed as an advantage from an air pollution standpoint since phenolic compounds are associated with emissions of polyaromatic hydrocarbon (PAH) pollutants (European Commission, 2001). While aromatics are generally undesirable in petroleum fuels, a minimum amount is actually necessary to meet transportation fuel specifications. Aromatics are energy dense molecules and are responsible for the necessary swelling of seal elastomers in an engine's fuel system. The absence of aromatics in HEFA means that these "drop-in" biofuels will be blendstocks that need to be blended with petroleum jet fuel. This is part of the reason why the ASTM standards have only approved 50% blends of HEFA biofuels for jet use (Bauen et al., 2009; Hileman et al., 2009).

2.4.5 Test flights and certification

As mentioned earlier, the aviation industry is uniquely dependent on drop-in biofuels as the only real alternative to current petroleum-derived jet fuels. Conventional biofuels such as ethanol and biodiesel are not suitable for jet engines. The unique dependence of aviation on drop-in biofuels is one of the primary drivers for ongoing commercialisation efforts. To date, the vast majority of all biofuel test flights have been based on oloechemically derived HEFAs. As shown in Figure 2-5, Virgin Atlantic conducted one of the earliest biofuel test flights in 2008, and a number of other commercial airlines and the US Navy have successfully demonstrated biofuels for aviation applications since then. These efforts contributed to ASTM's final approval of 50% HEFA blends in aviation fuels in July 2011. Note that 100% HEFA has not yet been tested commercially and the only flight that has been performed on pure biojet was an experimental flight by the Canadian National Research Council in October 2012. This flight was also one of the world's first to use biojet made from hydrotreated oils derived from an Ethiopian mustard variety as commercialized by the Canadian company Agrisoma (www.agrisoma.com).

As illustrated in Figure 2-5, a gasification-derived Fischer-Tropsch (FT) biojet fuel was approved 2 years prior to 50% HEFA without any prior test flights or these gasification-derived biofuels being commercially available. The main reason behind this rapid approval was because of prior certification of coal derived FT jet fuels. Sasol's semisynthetic jet fuel blends (containing 50% coal-derived FT-Jet and 50% petroleum-derived jet) were approved by ASTM for use in aircrafts in 2009, after a 7 year certification process. The certification of biomass FT-based jet fuels was justified on the grounds of the chemical equivalence between purified biomass syngas and coal syngas. Given their chemical equivalence, the functional equivalence was assumed by the ASTM and consequently no further testing was requested. In contrast, HEFA fuels have no chemical equivalence to any prior certified transportation fuel and hence their approval by ASTM took more time and testing in order to provide all the assurances of functional equivalence. Jet fuels have one of the most stringent ASTM specifications. While the alcohol-to-jet (ATJ) technologies will be discussed in Chapter 5, it should be noted that, as shown in Figure 2-5, ASTM certification for ATJ aviation fuels is expected to be approved in early 2014.



Various test flights by: Air NZ, Lufthansa, Continental, Japan Airlines, US Navy, US Air Force, TAM, Honeywell, Air China, Alaska, Etihad, JAL, TAM, Interjet and others (see: http://legacy.icao.int/icao/en/env2010/ClimateChange/GFAAF/Summary.htm)

Figure 2-5: Timeline of biofuel test flights and ASTM certification approvals
Source:(Alexander, 2012; ATAG, 2011; IATA, 2013; NRC Canada, 2012; SAFUG, 2014)

While ASTM certification is already in place for HEFA jet fuels, the cost and sustainability (i.e., availability) of the feedstock remain major challenges constraining extensive HEFA commercialization.

2.4.6 Sustainability certification of HEFA

Sustainability certification of oleochemical routes to drop-in biofuels is an ongoing concern, predominantly affecting the HEFA drop-in biofuel platform's feedstock sourcing. If the possible emissions due to any land-use change are ignored, the life-cycle GHG emissions of HEFA are estimated to be around half those of petroleum jet fuels (Hileman et al., 2009). However, sourcing vegetable oil feedstock for HEFA facilities will likely mean growing oilseed crops on land that will displace natural habitats or that could otherwise be used for food production. This production system has been subject to public criticism on the grounds of land use change. Examples include public concern regarding Neste

Oil's (Finland) aspirations for palm plantations in Malaysia and the *Friends of The Earth* report entitled, "Take-off in the Wrong Direction" which focused on detrimental land use change in Java, Indonesia, due to palm oil demand for jet fuel flights in Europe (FOE, 2012). While land use changes are difficult to quantify (Finkbeiner, 2013), various certification schemes such as the "Roundtable on Sustainable Biofuels" are currently considering the inclusion of indirect land use change (ILUC) in their set of standards (RSB, 2012). The company SkyNRG (a KLM – NSGSA collaboration) recently earned RSB certification for its entire supply chain and is currently the only fuel operator in the world that can deliver certified renewable jet fuel at any airport.

In summary, the oleochemical platform is well positioned to be the "first generation" approach to drop-in biofuel production due to the low oxygen content and high H/C ratio of oleochemical feedstocks. This platform for drop-in biofuels is already producing HEFAs at commercial scale with a total global capacity of about 70,000 barrels per day. Although this represents a small fraction of total global transportation fuel demand (44,000,000 barrels per day, 5,000,000 of which are jet fuels, IEA (2012)), it is the only commercially available drop-in biofuel that has been produced at significant volumes to date. The main challenges to further development of this platform mainly relate to feedstock availability, cost and sustainability. Lipid feedstocks are relatively scarce and expensive and they come with potential sustainability challenges such as land use change and competition with food markets. Prices for lipid feedstock have historically tracked with petroleum prices and they have also been priced higher than diesel fuel for long periods of time. It is clear that if HEFAs continue to be the only commercially available "biojet" fuel option, fulfilling aviation biofuel targets will likely result in higher operating expense for airlines. For example, in order to meet the US FAA target of 1 billion gallons (3.8 billion L) by 2018, it has been estimated that US aviation stakeholders would have to pay a premium of about $2.7 USD/gal ($0.71/L) for HEFA derived jet fuel. However, the advantages of using biofuels in aviation are well established and, if the sustainability concerns can be resolved, this close relationship between HEFA derived drop-in biofuels and aviation is likely to continue to grow.

CHAPTER 3: THE THERMOCHEMICAL PLATFORM

Thermochemical processes use high temperatures and catalysts to convert biomass to liquid biofuels and chemicals as well as heat and power (Brown, 2011). Unlike oleochemical technologies, which often use lipid feedstocks, these processes typically use lignocellulosic biomass as the feedstock. The biomass is reacted at high temperatures (> 500 °C) to form carbonaceous gases and liquids as well as char solids. The two main thermochemical routes are gasification and pyrolysis. The gasification process, as the name implies, converts biomass mainly to a gaseous intermediate, known as syngas. The pyrolysis process, on the other hand, maximizes the production of pyrolysis liquids, also known as pyrolysis oils or bio-oils. The gaseous and liquid intermediates of these thermochemical processes are mostly comprised of oxygenated species and thus need to be further processed to produce drop-in blendstocks. Using the Fischer-Tropsch catalytic process, syngas can be catalytically condensed to form liquid hydrocarbon mixtures known as FT liquids that, in turn, can be upgraded to fuels for gasoline, diesel and jet engines. Similarly, pyrolysis oils can be upgraded to liquid transportation fuels after further processing using catalysts and hydrogen. The main objective of catalytic upgrading is to remove the oxygen from both the syngas and bio-oil derived intermediates in order to produce petroleum-like hydrocarbon fuels. This deoxygenation process requires a chemical reducing power which is typically supplied by hydrogen derived from natural gas. As mentioned previously, the biomass itself can be used as a source of renewable hydrogen but this will result in a significant drop-in overall process yields. Bio-oil upgrading processes are usually conducted in relatively complex facilities that require both high hydrogen inputs and capital costs (Bridgwater, 2012). In most thermochemical processes there is a trade-off between capital costs, product yield and the extent of hydrogen requirements.

Co-locating thermochemical processes at refineries can be used to leverage oil refinery assets, reduce capital costs and ensure a relatively low cost source of hydrogen. Pyrolysis platforms appear particularly well suited to exploit co-location and synergy with existing refineries as pyrolysis oils can be processed using similar equipment to that currently used to upgrade crude oil. However, in practice, pyrolysis liquids contain relatively high levels of water and oxygenated species and thus are chemically quite distinct from crude oil and poorly suited to being “dropped into” existing petroleum processing units. However, it is likely that downstream refinery units such as FCCs and hydrocrackers could be configured to process thermochemical biofuel intermediates such as FT liquids and hydrotreated bio-oils to drop-in fuel blendstocks.

3.1 Overview of thermochemical processes

The most basic and widely applied thermochemical process is direct combustion of lignocellulosic biomass to produce heat and electric power. Combustion, a process recognised since the dawn of humanity, accounts for the vast majority of bioenergy applications in the world today. From relatively primitive open cooking fires and charcoal production through high efficiency industrial boilers and district heating systems, biomass combustion represented more than half of global renewable energy production in 2010 (IEA, 2012b).

From a technology standpoint, the combustion process is relatively simple and well understood (R. C. Brown, 2011). It entails the rapid reaction of biomass fuel with excess oxygen to generate thermal energy as well as highly oxidized flue gases, mainly CO_2 and H_2O. The chemical energy in the biomass is converted to thermal energy and, under optimized conditions, the exothermic reaction almost completely oxidizes the biomass. The temperatures of the generated flames can exceed 1650 °C (R. C. Brown, 2011).

Direct combustion of biomass can be used to indirectly power electrified transportation fleets. From purely a GHG emission savings perspective, biomass-powered electric vehicles can be superior to biofuel-powered internal combustion engine vehicles (Campbell et al., 2009). However, as has been discussed elsewhere, electric vehicles are relatively expensive, still require improved battery technologies and are mostly limited to light duty and short haul transportation applications (IEA, 2012).

Whereas combustion requires molecular oxygen (O_2) to be highly effective, charcoal production involves the “burning” of biomass in the presence of limited oxygen. Charcoal production can be considered the predecessor of pyrolysis and gasification processes. In its primitive form, charcoal making is conducted in clay-covered wood piles with a flue opening in the middle. A wood fire is started at the bottom of the flue and it slowly smolders the covered wood over a couple of days. Although modern industry uses more advanced charcoal production processes, this ancient technique is still widely practiced in less industrialized global communities, typically yielding about 60% by volume (25% by mass) of charcoal from the original biomass. Along with solid charcoal, this process produces liquid tar as well as flue gases.

Transportation applications of small biomass gasifiers for vehicles were developed during WWII due to reduced availability of petroleum in portions of the world, such as Scandinavia. Since the 1970s oil crises, gasification of biomass has received considerable research attention as potential sources of renewable liquid and gaseous fuels with subsequent development of fast pyrolysis for liquid fuel production since the 1980s. Unlike in traditional pyrolysis process for charcoal making, where the target product is the solid char, in the new fast pyrolysis the target product is liquid (bio-oil) and in gasification it is synthesis gases (syngas). By adjusting the processing conditions, pyrolysis can maximize the proportion of liquid products and gasification can maximize the proportion of gases. As shown in Figure 3-1, pyrolysis is conducted at intermediate temperatures of about 500 °C, in the absence of oxygen, and it produces a mixture of gases, char and liquids (water and water soluble and water insoluble organics). However, in fast pyrolysis, the residence time is reduced to a couple of seconds or less and the proportion of liquid yields can reach as high as about 75% by mass. In gasification, the biomass is reacted under pressures of 1-40 bar and at temperatures exceeding 800 °C and in the presence of regulated amounts of oxygen. Under these conditions the production of gases is favoured and can reach up to 85% by mass of the total products (Bridgwater, 2012).

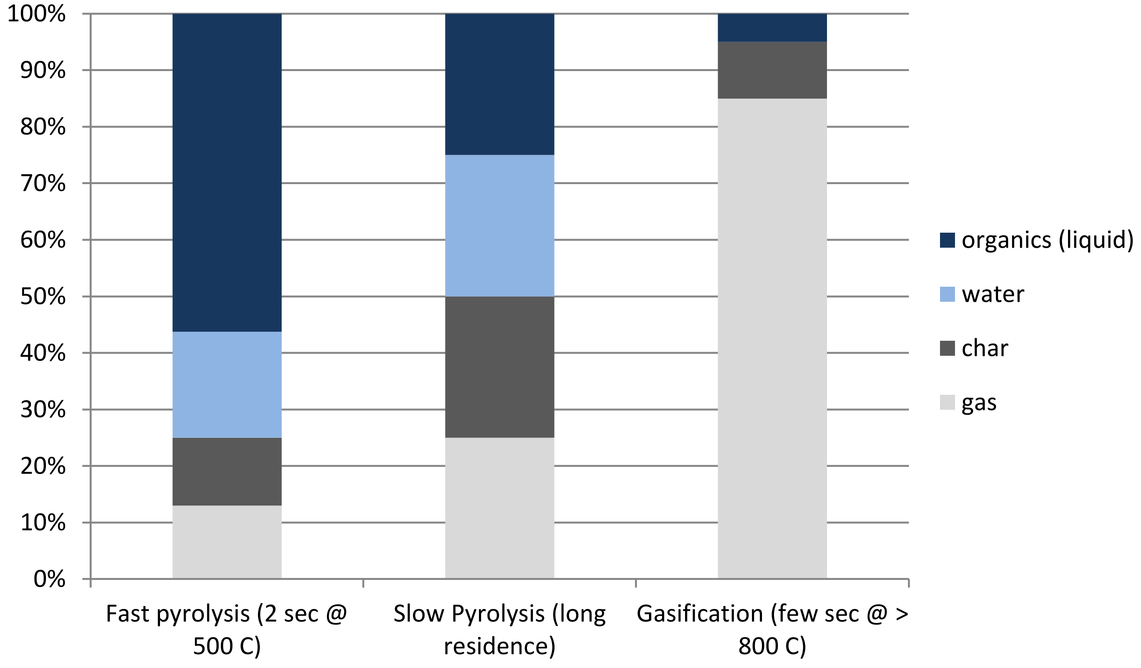


Figure 3-1: Product spectrum from thermochemical conversion of biomass
Source: Bridgwater 2012

Both syngas and bio-oil are fluid biomass intermediates that can be used as combustion fuels for stationary power applications such as burners, boilers, furnaces and industrial kilns. However, for drop-in biofuel applications, these intermediates need to be catalytically upgraded to oxygen-free hydrocarbons as shown in Figure 3-2. This upgrading takes various forms such as Fischer-Tropsch (FT) condensation to produce paraffins and 2-stage hydrotreatment to produce hydrotreated pyrolysis oils (HPO). To maximize yields, both upgrading technologies use specialized catalysts and hydrogen inputs. The resulting FT liquids and HPOs are both hydrocarbon mixtures that need to be subsequently distilled and hydrocracked in order to produce a mixture of gasoline, jet and diesel range hydrocarbons. In a similar fashion to the hydrocracking of vegetable oils (Chapter 2) and, depending on how the hydrocracking process is conducted, the proportion of gasoline, diesel and jet fractions can be adjusted.

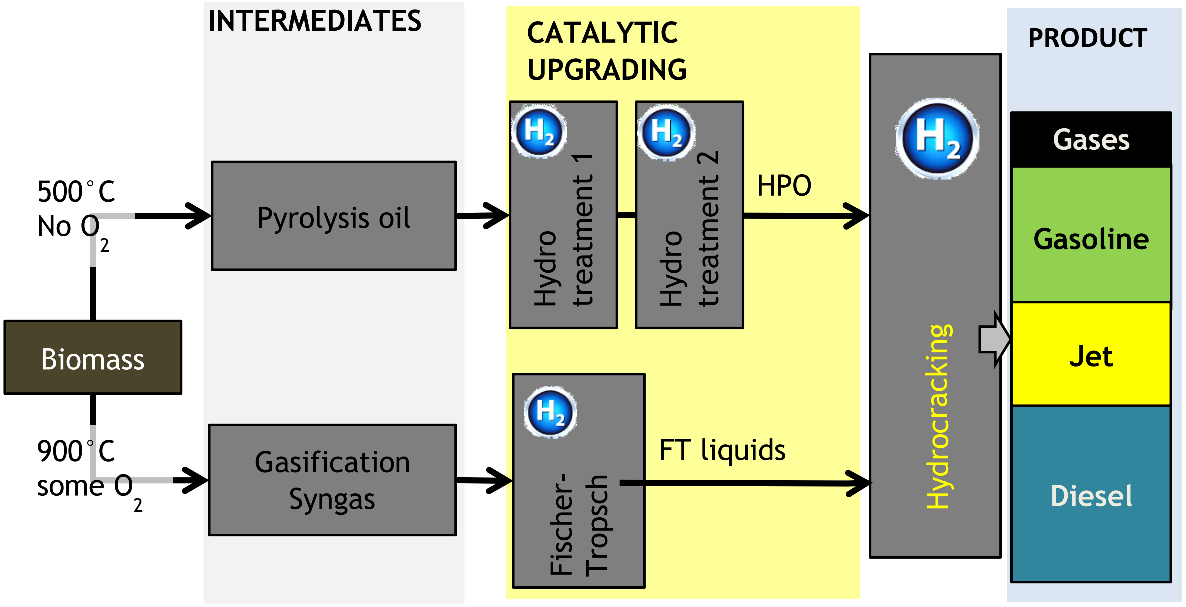


Figure 3-2: Simplified representation of major thermochemical drop-in biofuel process routes

Although pyrolysis and gasification have many fundamental characteristics in common, the two processes differ markedly in the details of their associated biomass intermediates upgrading technologies, drop-in fuel yields, capital costs and hydrogen (H_2) requirements.

3.2 Fast Pyrolysis

As noted earlier, fast pyrolysis is the thermal processing of solid biomass in the absence of added oxygen to produce bio-oil, which can be considered as an intermediate towards the production of drop-in biofuels. The production and properties of bio-oil and the technologies that can upgrade this biomass derived liquid to transport fuels as well as some techno-economic aspects of fast pyrolysis biofuels are discussed in the next section.

3.2.1 Bio-oil production

Fast pyrolysis is a thermal decomposition process which requires rapid heating of biomass to about 500 °C and a subsequent rapid cooling of the resulting vapours to room temperature. Upon cooling, these vapours condense to form the liquid bio-oil product. It has been demonstrated that rapid heating and cooling is crucial to maximizing bio-oil liquid yields at the expense of char and gas production (Bridgwater, 2012). Slow heating favours the production of solids such as charcoal while a long residence time in the high temperature zone of the reactor results in further cracking of vapours which consequently favours the production of permanent gases. A long residence time can also promote the polymerization of vapour molecules and the formation of solids. To maximize bio-oil yields (to about 75% of starting biomass by mass) rapid heating to the target temperature must be achieved throughout each biomass particle (i.e., within about one second). These high heat transfer rates (up to 1000 °C/s) ensure maximum devolatilization (vaporization) of the biomass solids and, so far, have only been achieved by a select number of reactor designs (Bridgwater, 2012).

One reactor type which is well suited for fast pyrolysis is the Bubbling Fluidized Bed (BFB) reactor. This reactor uses a hot sand fluidized bed to achieve high rates of heat transfer to biomass particles. The reactor beds are fluidized using a compressed carrier gas which is fed through the bottom of the reactor at sufficiently high rates to “fluidize” the loose solids contents of the reactor (sand and biomass) while transferring the gas-entrained char upwards. These types of BFB reactors have been used by the petroleum industry for the gasification of coke since the 1950s. They are robust systems that achieve high heat transfer rates and uniform bed temperatures (Ringer et al., 2006) which are both highly desirable attributes for fast pyrolysis reactions.

As depicted in the simplified schematic of a typical BFB fast pyrolysis process (Figure 3-3) the biomass is first dried and ground to a particle size of about 3 mm to facilitate rapid particle heat up and devolatilization. These particles enter the fluidized bed pyrolysis reactor where they are rapidly heated to a temperature of about 500 °C. After about a 2 second residence time, the generated vapours are vented to a cyclone where they are separated from the entrained solid char particles. The recovered char can be sold as a value-added product (soil amendments and activated carbon, e.g., as described in Dynamotive's business model) or used as fuel for the furnaces that generate and compress the hot recycle gas that feeds the main pyrolyser reactor. The clean vapours are then swiftly transferred to a quench cooler where they are condensed to form the bio-oil. The uncondensed fraction of the vapours along with the permanent gases is then transferred to a second condensation train such as a coalescing filter, scrubber or electrostatic precipitator (e.g. Nexterra) where additional bio-oil is recovered. The remaining flue gas is fed to the furnace that generates hot gas for the main reactor. Fast pyrolysis oils contain up to 75% of the mass and 65% of the energy that was contained in the original biomass feedstock (Bridgwater, 2012). These types of BFB reactors have been used by the Canadian company Dynamotive at a semi-commercial scale (see Table 3-1) as well as at a smaller, demonstration scale such as the 200 kg/hr unit of Union Fenosa in Spain. Both the Dynamotive and the Union Fenosa facilities are based on a design developed at the University of Waterloo and commercialized through its Canadian spin-off company RTI (Resource Transformations International) (Bridgwater, 2012; Czernik & Bridgwater, 2004).

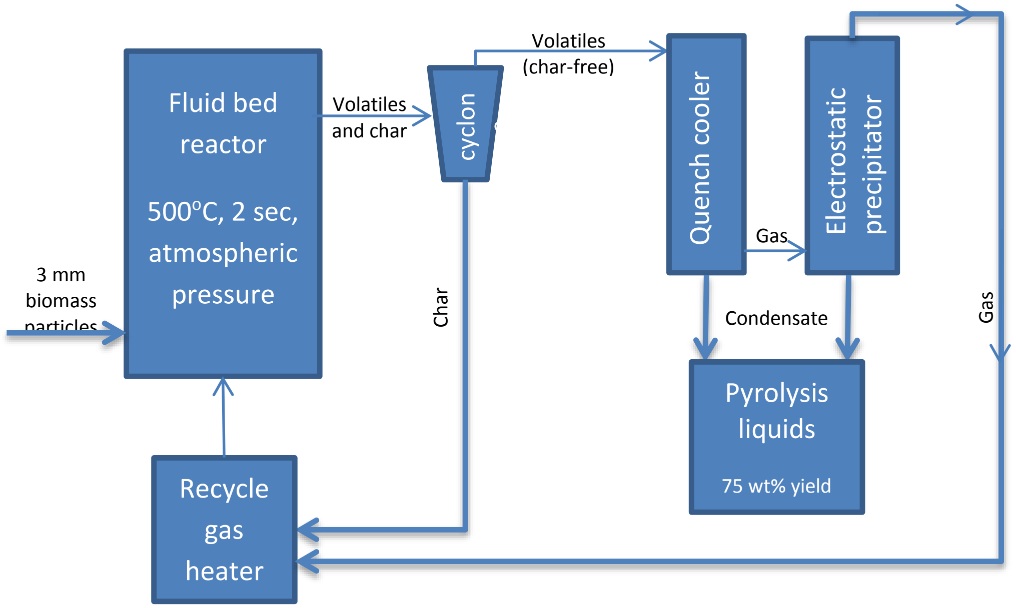


Figure 3-3: Simplified schematic of bubbling fluidized bed (BFB) fast pyrolysis
Source: adapted from Bridgwater, 2012

A more complex version of the bubbling fluidized bubbling bed (BFB) reactor is the circulating fluidized bed (CFB) reactor. This reactor configuration has been used by the petroleum industry for many decades and it has a long history of industrial operations especially in the fluidized catalytic cracking (FCC) units described earlier. This type of system (Figure 3-4) is similar to the BFB process except the compressed recycle gas is fed at much higher velocities, such that the entire loose contents of the reactor (vapors, gases, char as well as the fluidized bed's sand particles) are carried into the downstream cyclone. The char and sand are then recovered from the cyclone and they are then fed together to a combustor, where the char is burned off to heat up the sand. The cleaned hot sand (at about 800 °C) is then fed back to the main reactor entrained in the compressed carrier gas and the process cycle is repeated. This system is more expensive to install and operate than the BFB process but it comes with the advantages of constantly regenerating clean sand bed particles and achieving higher throughputs. CFB requires careful sizing of the biomass particles since the rapid gas flow only permits a very short residence time in the hot zone of the pyrolysis reactor. The CFB pyrolysis is the configuration of choice for the Canadian pyrolysis company "Ensyn" and it is marketed under the name RTP (Rapid Thermal Processing). Other developers of the CFB configuration include CRES (catalytic pyrolysis, Greece) and Ensyn for ENEL (Italy) (Ringer et al., 2006) and VTT-led consortium in Finland (Metso, UPM, Fortum).

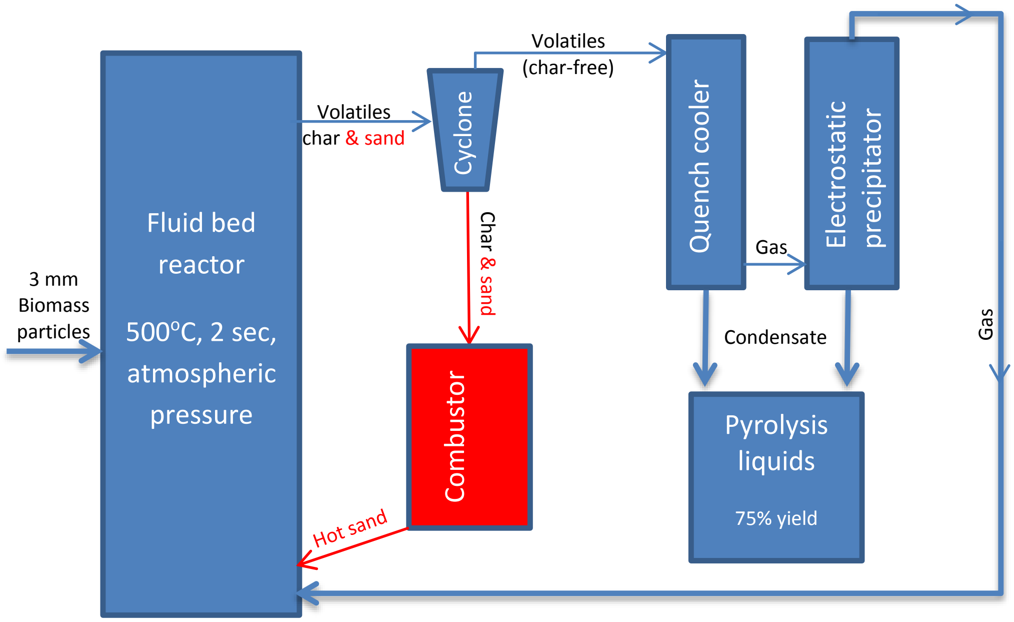


Figure 3-4: Simplified schematic of circulated fluid bed (CFB) fast pyrolysis
Source: adapted from Bridgwater, 2012

The main drawbacks of fluidized bed reactors is that they rely on a compressed carrier gas which often carries char contaminants to the bio-oil product and compressing this gas also requires high capital and operating costs. The carrier gas, used in order to mix and circulate the sand bed, carries char particles of such small submicron size that even the solids separation cyclone cannot capture them. Thus, these tiny particles remain entrained in the vapour that enters the quench cooler and they end up in the bio-oil product (Bridgwater, 2012). This can be a problem as char particles can catalyze tar and coke formation and they can plug reactor pipes and filters upon subsequent bio-oil upgrading. It should also be noted that the compressors used to deliver high speed carrier gases are capital-intensive and they are not well suited for small scale applications (Wright et al., 2010).

Alternative reactors that do not use a carrier gas have recently been developed. These reactors use centrifugal forces and mechanical motion to achieve the high rates of heat transfer needed to rapidly volatilize the biomass particles. These types of pyrolysis reactors include ablative and rotating cone designs based on the principle of sliding biomass particles against a hot surface, thus “melting” the fibre in a similar way to a block of butter melts when pressed against a hot surface. Ablative pyrolysis reactors do not use a fluidized bed or sand particles while rotating cone reactors use sand particles contacting biomass particles but without using fluidization by a carrier gas (Bridgwater, 2012; Venderbosch & Prins, 2011). The concept of ablative pyrolysis was first proposed by the CNRS laboratories in Nancy, France. Subsequent ablative reactor designs have been developed by NREL in the USA (vortex reactor) and by Aston University in the UK (plate reactor) (Bridgwater, 2012). The company Pytec has a demonstration plant for ablative pyrolysis in Germany. The rotating cones reactor concept was initially developed by the Dutch Company BTG (a University of Twente spin-off) which currently operates a 5 tpd demonstration facility in the Netherlands. BTG had designed and built a 48 tpd facility which was operated in Malaysia several years ago (see Table 3-1 below). However, these reactors use complex engineering structures to mobilize the biomass particles and achieve high heat transfer rates. Unlike BFB reactors which have a long operating history in oil refineries, these mechanical systems are less proven and their ability to be scaled up may be challenging.

Another carrier-gas-free pyrolysis reactor is the “auger” or “screw” reactor which has been used for more than 50 years in coal degassing and heavy oil coking applications(Meier et al., 2013). Due to the relatively poor heat transfer through the auger shell, this technology is not well suited for fast pyrolysis as it is only able to heat up the biomass relatively slowly. Auger reactors also produce lower amounts of bio-oil as their slower heating and longer residence time characteristics favour greater solids formation (a more “charcoal-like” process). However, it has been shown that the low grade liquid and the char can be recombined after recovery to produce pyrolysis “slurries” which can serve as an improved feed for gasification. The energy density of the slurry can be in the range of 18-25 GJ/m^3, and is typically higher than char-free bio-oils (ca. 21 GJ/m^3) or raw biomass (Dahmen et al., 2012). An example of such a system is the Bioliq™ process from KIT in Germany which proposes to use auger derived slurries to feed central large scale gasification facilities (Meier et al., 2013).

Although several groups around the world are pursuing biomass pyrolysis, the current production capacity for fast pyrolysis oils is quite low. Bio-oil facilities that have been or will be operated at the semi-commercial scale (> 50 tpd) are listed in Table 3-1 together with their characteristics and reactor type. Most pyrolysis facilities to date are based on CFB and BFB reactor designs which, as mentioned earlier, are relatively robust, scalable and result in relatively high yields of bio-oil.

The newly built KiOR facility in Mississippi, which is designed to operate at 500 tpd, is the first truly commercial pyrolysis facility. This facility is distinct from other pyrolysis oil facilities as it uses catalysts that are integrated in the CFB system (instead of sand) in order to partly deoxygenate the bio-oil prior to upgrading to diesel and gasoline, a process commonly referred to as catalytic pyrolysis (see Section 3.3.3). This design allows integration of part of the upgrading deoxygenation into the bio-oil-making step and is discussed in more detail in the next section which describes upgrading technologies.

A recent trend of some pyrolysis technology providers is to focus on small scale (1 -5 tpd) and mobile pyrolizers. These units are described as mobile densification facilities that produce liquid bio-oils or bioslurries which are intended to be subsequently transported and processed or upgraded at large, centrally located facilities. These plants can also be co-located with oil refineries to take advantage of co-processing opportunities. Companies that lead this trend for mobile pyrolizer systems development include Canada’s ABRI-Tech, California’s Cool Planet and ROI in Alabama (Meier et al., 2013).

Table 3-1: Commercial and pre-commercial (≥ 50 tpd) bio-oil facilities by 2014

Company	Location	Completion	Capacity (ODT)	Application	Reactor type
Fortum, Finland	Joensuu CHP plant	Commissioned in Nov. 2013 (EURO 20 m own funds and 8 m from Finnish govmnt)	100 tpd	CHP fuel	CFB integrated with CHP system (Metso design)
Ensyn, Canada	Renfrew, Ontario	Commissioned in 2007	100 tpd	R&D resins, chemicals and CHP fuel	CFB (Ensyn design)
Dynamotive, Canada	Guelph, Ontario	Not operating	200 tpd	R&D, chemicals and CHP fuel	BFB (Dynamotive design)
Red Arrow, USA	Rhinelander,Wisconsin, USA	Commercial	2 x 50 tpd	Food flavouring/browning products and CHP fuel	CFB (Ensyn design)
Pyrogrot, Sweden	Billerud's pulp mill in Skarblacka	Announced end of 2012 (EURO 31 m from NER300 = EU-ETS revenue) – expected in 2015	720 tpd	CHP fuel	Not announced
Green Fuel Nordic Oy, Finland	Unspecified	Q1 2014	3 x 400 tpd	CHP fuel	CFB (Ensyn design)
BTG-BtL Malaysia (Netherlands)	Palm oil processing facility (EFB feedstock)	Not operating	48 tpd	Cofiring with waste	Rotating Cone (BTG design)
KiOR, USA	Columbia, Mississippi, USA	Commissioned early 2013	500 tpd	Drop-in diesel and gasoline	Catalytic CFB

Sources: (Bayar, 2013; BTG, 2012; Dynamotive, 2009; Ensyn, 2013a; Fortum, 2013b; Green Fuel Nordic, 2013; KiOR, 2013; Landalv, 2013; Oasmaa & Czernik, 1999; Starck, 2012)

3.2.2 Bio-oil composition

Like crude oil, pyrolysis bio-oil is a dark brown and free flowing liquid fuel (Figure 3-5), composed of more than 300 different carbon molecules. However, chemically, pyrolysis oils are very different as they contain about 40% oxygen compared to the typical maximum amount of 2% oxygen found in crude oil (Speight, 2006). As discussed earlier, the oxygen content of biomass results in biofuels with undesirably high reactivity (low chemical stability) and low energy density. For example, compared to crude oil, bio-oil has less than 50% of this fossil fuels energy density (16-19MJ/kg vs 40 MJ/kg).

Figure 3-5: Pyrolysis oil sample

Source: (Empyro, 2013)

Bio-oil has a smoky odour and its chemical composition is derived from the decomposition (depolymerisation and fragmentation reactions) of the main biomass components of lignin, cellulose and hemicellulose (Oasmaa & Czernik, 1999). From a compositional perspective, bio-oil resembles woody biomass much more than it resembles crude oil (Table 3-2) and thus, in some ways, it can be thought of as “liquid wood”. In fact, “liquid wood” together with “bio-oil” are among the many alternative names that have been used in the literature to describe pyrolysis oils (Oasmaa & Czernik, 1999). Due to this elemental resemblance to wood, bio-oil has the same effective H/C ratio of about 0.2 and would be placed at the same “step” as lignocellulosic biomass on the H/C “staircase” described earlier. This, as will be detailed later, has implications for the hydrogen and processing needs of bio-oils when converting them to drop-in biofuels.

When various properties of heavy fuel oil (HFO) and bio-oil are compared (Table 3-2), the differences in the oxygen content, energy density, amount of dissolved water (up to 30%), and the poor distillation performance (1 vs 50% residue) are quite striking.

Table 3-2: Typical properties of wood pyrolysis bio-oil and of heavy fuel oil (HFO)

Physical property	Bio-oil	Heavy fuel oil
Water content, wt %	15-30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Elemental composition, wt. %		
C	54—58	85
H	5.5—7.0	11
O	35—40	1
N	0—0.2	0.3
Ash	0—0.2	0.1
HHV, MJ/kg	16-19	40
Viscosity (at 50°C) cP	40—100	180
Solids, wt %	0.2—1	1
Distillation residue, wt. %	up to 50	1

Source: (NSF, 2011; Oasmaa & Czernik, 1999)

Water is a major component of bio-oils and its content varies depending on the initial moisture content of the biomass and the pyrolysis conditions used. Severe pyrolysis conditions (high temperature and residence time) remove more water but also promote vapor polymerizations and thus increase the viscosity and solids content of the resulting bio-oil (Oasmaa & Czernik, 1999). Water is derived from both the original water in the feedstock and from the water formed during the dehydration reactions occurring during pyrolysis. An excessive amount of water in bio-oils is undesirable because it acts as a heat sink during combustion and it can also promote destabilization and phase separation of the fuel during storage. In order to minimize bio-oil's water content, the moisture content of the biomass feedstock is best kept below about 10 wt%. However, a certain amount of water is needed as it helps reduce the viscosity of bio-oils. For example VTT has studied the influence of the water content on various softwood bio-oils and found that, when the water content drops below 25%, the viscosity increases dramatically and an unacceptable degree of bio-oil destabilization also occurs (Lehto et al., 2013).

As well as water, the other major chemical components of bio-oil include hydroxyaldehydes, hydroxyketones, sugars, carboxylic acids, and phenolics (Bridgwater, 2012). As was the case with water, the amount of these compounds in the bio-oil depends on the composition of the original biomass as well as the pyrolysis conditions used. Some of these components, such as the sugars, are hydrophilic but others such as the phenolics are more hydrophobic. Thus, most bio-oils can be considered to be micro-emulsions. The continuous phase of the emulsion is the aqueous solution containing the polysaccharide decomposition products and the discontinuous phase is the pyrolytic lignin (the emulsion is mainly stabilized by weak hydrogen bonds). The breakdown of this emulsion results in the formation of two phases, a lighter, more aqueous phase and a heavier, less aqueous (Bridgewater, 2012).

The "aging" of pyrolysis oils is measured as increased viscosity over time and it occurs through reactions between the oxygenated carbon molecules in the bio-oil emulsion. Polymerization reactions between double bonded components as well as esterification and etherification reactions between hydroxyl and carbonyl groups produce high molecular weight, water-insoluble components such as gums. These reactions lead to increased viscosity and, ultimately, to a phase separation of the bio-oil into an upper aqueous phase (containing a higher proportion of acids and sugars) and a lower tar phase (containing less water and a higher proportion of water insoluble solids and lignins)(Lehto et al., 2013).

The main factors that accelerate these undesirable "aging" reactions are:

- **Time**: most bio-oils destabilize/phase-separate after storage for about 6 months or more) at room temperature.
- **Temperature**: very important!: For example the viscosity of a hardwood bio-oil doubled after a year at room temperature, after a week at 60 °C and after a day at 80 °C.
- **Alkali char**: catalyzes polymerizations thereby increasing bio-oil viscosity

(Oasmaa & Czernik, 1999)

The stability of bio-oils can be improved by removing char particles using hot filtrations (Sitzmann, 2009) or by adding solvents (Lehto et al., 2013) to improve the stability of the emulsion. For example, methanol blending is a relatively inexpensive upgrading method that has been shown to greatly improve the stability of bio-oils when used as burner fuels (Diebold, 2000). In earlier work, Diebold & Czernik (1997) showed that a 10% methanol blending reduced the bio-oil aging rate 20-fold. These and other stabilization techniques have been discussed earlier (Diebold, 2000; Oasmaa & Czernik, 1999) but nearly all of the options are costly and/or lead to bio-oil yield loss.

Due to the substantial amounts of non-volatile materials such as sugars and oligomeric phenolics, etc., found in bio-oils, they exhibit a considerably inferior distillation performance compared to petroleum heavy fuel oil (Table 3-2). The slow heating of the oils during distillation accelerates the polymerization reactions resulting in the formation of heavy and non-volatile compounds. Heavy Fuel Oil typically leaves 1% residue after vacuum distillation whereas a bio-oil leaves up to 50% of the starting material as distillation residue (Table 3-2). This poor distillation performance has implications not only for further processing of bio-oils (e.g. to drop-in fuels) but also in their use as CHP fuels.

3.2.3 Bio-oil uses

As mentioned earlier, bio-oils have great potential as fuels for burner/boilers and burner/furnaces for stationary heat and power generation. In general, liquid fuels are easy to store, transport and combust and they can also be pumped and fed into a burner through a spraying atomizer, thus improving heat transfer through the fuel droplet and maximizing combustion efficiency (Lehto et al., 2013).

However, as discussed earlier, bio-oils contain large amounts of water and oxygenated compounds as well as char particles. They also have drawbacks as combustion fuels such as low energy density, ignition difficulties, high viscosity and instability as well as low pH and high particulate. Although bio-oils generally produce less NOx and SOx than do fossil fuels (coal and oil), they typically emit more particulate emissions due to the char content of the bio-oil (Lehto et al., 2013),.

Various trials have burned bio-oil in heat and power facilities (Bridgwater, 2012; Czernik & Bridgwater, 2004; Venderbosch & Prins, 2011) demonstrating the need for modified bio-oil storage and feeding systems. The only commercial facility that regularly uses bio-oils as a burner fuel is the Red Arrow facility in Wisconsin which uses its own bio-oils to generate heat (5 MW_{th}) for its food flavoring production process. Fortum's plant (Finland) is currently (October 2013) in start-up and is targeted at bio-oil production for use in district heating (Fortum, 2013a).

One potential use of bio-oils is to co-fire them with conventional fuels such as coal, as was demonstrated when Red Arrow's pyrolysis oils were co-fired in the coal power station at Manitowoc Public Utilities in Wisconsin (USA) (Venderbosch & Prins, 2011).

As large scale internal combustion diesel engines and gas turbines are more efficient in generating electricity than are boilers that feed steam turbines it would likely be beneficial if bio-oils could be used in these engines in the same way as HFO is used. However, the corrosiveness and char content of bio-oils currently limits their use in these facilities. Possible solutions to these drawbacks include the incorporation of a low pressure fuel supply system that preheats and filters the bio-oil, a nozzle design that allows larger fuel flows and dual fuel operation, the redesign of the hot section and the use of stainless steel parts and compatible polymeric materials. It has been noted that these modifications will likely be costly and that there is still no guarantee that the engine will operate trouble-free when using a bio-oil fuel (Lehto et al., 2013; Venderbosch & Prins, 2011).

Bio-oil can also be used as a fuel for gasification facilities. As gasification is more sensitive to scale than is pyrolysis, bio-oil production could be used as a method of densification to allow the transport of biomass over longer distances while providing the gasification facility with a better suited feedstock as opposed to a solid fuel. The advantage of using a liquid as opposed to solid feedstock in gasification is the same as in combustion, namely the faster heat transfer through the fuel (R. Swanson et al., 2010). This concept of using pyrolysis oils or slurries as a gasification fuel in order to improve access to remote biomass stocks will be reviewed in more detail in the gasification section.

3.2.4 Bio-oil standards

As mentioned earlier, the composition of bio-oils can vary significantly, depending on composition of the feedstock as well as the pyrolysis conditions used. This influences the use of bio-oils and, in particular, their upgrading to transportation fuels. For example, feedstocks with high extractives such as resinous pine wood, produce bio-oils with a frothy top layer representing up to 10% of the product's mass. Similarly, feedstocks with a high alkali content such as grasses will likely produce bio-oils containing alkali-rich char. Grasses are also less attractive pyrolysis feedstocks as they also have a low lignin and high alkali ash content, both of which lead to lower bio-oil yields (about 60% compared to 75% for wood (Bridgwater, 2012)). These examples contrast with the common perception that thermochemical biofuel processes are "feedstock agnostic". In practice, feedstock variation is among one of the major factors that contribute to the heterogeneity of bio-oils and their storage stability characteristics.

To overcome the commercialization hurdles resulting from the heterogeneity of bio-oils, a set of standards has recently been approved by ASTM. The ASTM D7544 fast pyrolysis oil burner fuel standard was approved in 2010 for Grade G and in 2012 for Grade D bio-oils. The only difference between grades D and G is the pyrolysis solids and inorganics (ash) content (Table 3-3). These standards qualify pyrolysis oils as burner fuels and they provide benchmark-type minimum requirements upon which applications and trading of bio-oils can be based.

Table 3-3: ASTM standards for pyrolysis oils

Property	Grade G	Grade D
Gross heat of combustion, MJ/kg, min	15	15
Pour point, °C, max	-9	-9
pH	Report	Report
Density at 20°C, kg/dm3	1.1-1.3	1.1-1.3
Kinematic viscosity at 40°C, mm^2/s, max	125	125
Water content, % mass, max	30	30
Pyrolysis solids content, % mass, max	2.5	0.25
Ash content, % mass, max	0.25	0.15
Sulfur content, % mass, max	0.05	0.05
Flash point, °C, min	45	45

Source: (Nummisalo, 2012)

Further standardization efforts have been announced recently by the EU CEN. Working Group 41 (Pyrolysis oils) of CEN's Technical Committee on: "Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin" will, in January 2014, start developing pyrolysis oil standards for:

a) A European Standard for a quality specification for pyrolysis oil replacing heavy fuel oil in boilers.

b) A European Standard for a quality specification for pyrolysis oil replacing light fuel oil in boilers.

c) A Technical Specification for a quality specification for pyrolysis oil replacing fuel oils in stationary internal combustion engines.

d) A Technical Specification for a quality specification for pyrolysis oil suitable for gasification feedstock for production of syngas and synthetic biofuels.

e) A Technical Specification for a quality specification for pyrolysis oil suitable for mineral oil refinery co-processing.

The first 3 (a-c) documents above are to be given precedence and be developed as soon as possible. The last two (d & e) are to be given lower priority and developed at a later stage or as market developments dictate (CEN, 2014; Maniatis, 2013).

3.2.5 Cost of Bio-oil

The cost of bio-oil is difficult to determine as no commercial production or trading of this product currently occurs. Various techno-economic analyses have estimated the cost of bio-oil production with the most recent and relevant analyses carried out by NREL (Ringer et al. 2006 and Wright et al. 2010), KIT (Karlsruhe Institute of Technology, (Henrich et al., 2009)) and by Aston University (Bridgwater 2012). According to Bridgwater (2012), the cost of bio-oil for a facility ($180 million in capital) processing 2000 tpd of wood ($83/odt) would be around $180/t. Assuming 18 GJ/t of bio-oil, this figure translates to a bio-oil cost of around $10/GJ. Similar figures were estimated by Wright et al. (2010) at $10/GJ for bio-oil from a 2000 tpd facility and an $83/t corn stover feedstock cost and by Henrich et al. (2009), $9/GJ for bioslurry (bio-oil + char) from a 200 tpd facility and an $82/t wheat straw feedstock cost. Although various parameters and assumptions often differ between techno-economic studies there seems to be general agreement that bio-oil, produced at full scale facilities (2000 tpd), would cost around $10/GJ. This is two times the assumed cost (energy basis) of the raw biomass ($82-83/odt or ca. $5/GJ) and less than half the cost of HFO which at the time of writing was selling at about 25 USD/GJ (1000 USD/tonne). Although these estimates are subject to uncertainties and sensitivities, they indicate that there is currently about 50% cost margin that can be used to upgrade bio-oils to match HFO quality. A similar percent cost margin between bio-oil and HFO was estimated by Ringer et al. (2006) who also showed that the greatest sensitivities of the pyrolysis process were the facility size and the bio-oil yield. Increasing the facility size from 500 tpd to 2000 tpd dropped the USD 7.62/GJ selling price down to USD 5.65/GJ while increasing the bio-oil yield from 60 to 70% dropped this price further down to USD 4.84/GJ.

Although pyrolysis has great potential as a low cost liquid fuel, it also has some disadvantages when compared to even low grade liquid petroleum fuels such as HFO. Most of these challenges are, mainly (directly or indirectly), related to a single overriding factor which is the relatively high oxygen content of bio-oils. In “petroleum-like” drop-in biofuels the oxygen has to be removed and this is the primary objective of technologies that try to upgrade bio-oils to transport fuels. Technology providers such as UOP have claimed that, depending on the upgrading efficiency of pyrolysis oils and the price trends of petroleum, bio-oil could become competitive in the near future. A 2005 UOP study suggested that gasoline from bio-oil would be economically attractive if bio-oil is available at $18 per barrel ($0.11 per liter) and crude oil sells for more than $50 per barrel ($0.31 per liter) (T. Marker, 2005). This suggests that bio-oil would have to be produced at 63% the cost of petroleum crude on an equivalent energy basis (per GJ). This reinforces the previous point that bio-oil needs to be at least half the cost (per GJ) of crude oil in order for the pyrolysis platform to be economically competitive.

3.2.6 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is another thermochemical process which produces a bio-oil. However, it is distinct from pyrolysis as it converts biomass to low oxygen bio-oil (5-20% Oxygen) and, unlike pyrolysis and gasification, it can utilize wet biomass. The HTL process uses high pressures (e.g. 50 - 250 bar or more) and moderate temperatures (around 250-550 °C) as well as catalysts for 20-60 min to liquefy and deoxygenate biomass (Akhtar & Amin, 2011; Elliott, 2007; Goudrian & Peferoen, 1990).

The HTL technology is not new and has been extensively studied. As early as the 1920s, Berl proposed the concept of using hot water and alkali catalysts to produce oil out of biomass (Berl, 1944). This was the foundation of later HTL technologies that attracted research interest especially during the 1970s oil embargo. It was around that time that a high-pressure (hydrothermal) liquefaction process was developed at the Pittsburgh Energy Research Center (PERC) and demonstrated (at the 100kg/h scale) at the Albany Biomass Liquefaction Experimental Facility at Albany, Oregon, US (Elliot, 2007). At the same time Shell Oil developed the HTU™ process in the Netherlands. The HTU™ process applied pressures in the range 150-180 bar and temperatures in the range 300 to 350°C (Goudrian & Peferoen, 1990; Nielsen et al., 2012). As an example, eucalyptus chips treated with HTU at 180 C and 180 bar for 6 min yielded 48.6 wt% DAF (dry and ash free basis) bio-oil, 32.8% gas and 18.6% aqueous phase. The oil contained 10% oxygen (Goudrian & Peferoen, 1990). HTL oils can be very viscous while melting points of about 80 °C have been reported (Elliott, 2007).

Due to low oil prices and other events, Shell's HTU™ process was not commercialized. However, technology companies such as **Licella**/Ignite Energy Resources (Australia), **Altaca** Energy (Turkey), and **Steeper Energy** (Denmark, Canada) continue to explore HTL.

3.3 Upgrading Pyrolysis oils to motor fuels

As discussed previously, bio-oils can be used in various stationary heat and power applications or they can be upgraded to drop-in biofuels such as diesel, gasoline and jet fuel grade hydrocarbons. However, although the relatively high oxygen content of bio-oils can be tolerated for direct combustion in stationary power applications, it is a significant problem for automobile engines and jet engines in particular. Upgrading of bio-oils to transport fuels involves extensive deoxygenation with the major challenge being to deoxygenate the bio-oil while maintaining high conversion yields and high hydrogen to carbon ratios in the finished fuel. Various upgrading techniques have been proposed over the last few decades with the top two contenders being hydrotreating and zeolite cracking (Solantausta, 2011). Both processes are catalytic and selectively promote hydrogenation reactions. Hydrotreating uses large amounts of hydrogen to remove water from bio-oils in the form of H_2O molecules. In contrast, zeolite cracking uses no hydrogen but instead rejects oxygen in the form of CO_2, thus lowering the biofuel yield. Both technologies try to elevate the effective H/C ratio of bio-oils from about 0.2 to about 2 in order to fit the functional properties of hydrocarbon motor fuels (see chapter 1). Virtually all of the current bio-oil upgrading processes originated in the petroleum industry and use specialized catalysts to improve reaction selectivity. As capital costs for upgrading bio-oils are high it would be synergistically beneficial if existing oil refinery equipment could be used to process these biomass derived liquids. The processes used to upgrade bio-oils resemble those used to upgrade vegetable oils to drop-in biofuels (as discussed in Chapter 2), although pyrolysis liquids are significantly more challenging a feedstock to upgrade than are vegetable oils (VOs).

3.3.1 Hydrotreating

Hydrotreatment is a hydrogen-intensive process for deoxygenating and upgrading bio-oils to petroleum-like transport fuels. Earlier (in Chapter 2), it was emphasized that a lot more hydrogen is required to hydrotreat vegetable oils (VOs) than petroleum. Even more hydrogen is required to hydrotreat bio-oils because they contain about 40-50 wt% oxygen compared to the 10% typically found in vegetable oils. As shown earlier on the H/C staircase diagram, the VOs have an H/C_{eff} ratio of about 1.8 while the bio-oil is around 0.2 (the same as wood). Thus bio-oils require more hydrogen and processing effort to become functionally equivalent to petroleum diesel. Similarly to hydrotreating VO's, the targeted chemical reaction in bio-oil hydrotreating is the rejection of oxygen in the form of H_2O. This hydrodeoxygenation (HDO) reaction of bio-oil is conceptually represented as:

$C_1H_{1.33}O_{0.43} + 0.77H_2 \rightarrow CH_2 + 0.43H_2O$ (Bridgwater, 2012)

As described in the equation, the process uses about 1.5 (0.77 x 2) hydrogen atoms for every carbon atom produced in the final fuel. As the carbon conversion is 100% (as every carbon in the bio-oil is converted to a hydrocarbon) the resulting hydrocarbons should be of high quality since their H/C ratio is equal to 2. However, in practice, hydrotreatment is not highly selective and the HDO reaction described above does not take place in isolation but rather in association with other reactions which divert carbon and/or hydrogen from the targeted liquid fuel product. These reactions include polymerization and condensation to form tars and coke, gasification to form methane or CO_x and reactions that form low H/C hydrocarbons such as aromatics and olefins (Bridgwater, 2012). Thus, the low selectivity for hydrodeoxygenation and hydrogenation reactions often leads to low fuel yields and high hydrogen requirements.

In most of the hydrotreating processes modelled so far the biomass to fuel yield is around 25% mass (55% energy) when hydrogen is provided externally and 15% (33%) when hydrogen is produced by gasifying the biomass (Brown, 2011; Bridgwater, 2012; Dynamotive, 2013). . However, as will be described briefly, these relatively poor carbon yields and hydrogen use efficiencies can be improved through the development of more selective catalysts and optimized processes.

In Section 1.10, it was shown that, in the US, a doubling of refinery hydrotreating capacity would be needed in order to meet the requirements for processing crude oils of deteriorating quality. A similar doubling or even tripling of today's US refinery hydrogen generation capacity would be needed if the US refineries were to provide the hydrogen amounts needed to meet the US RFS cellulosic advanced biofuels mandate exclusively with pyrolysis-derived diesel. The US RFS has mandated 15 billion gallons per year of cellulosic advanced biofuels by 2022 (includes pyrolysis diesel). If this entire mandate was to be met by biomass pyrolysis-derived fuels, around 250 facilities producing 60 million gallons per year (MGPY) of diesel/gasoline blendstocks would be required. According to the latest techno-economic analysis by Jones at al. (2013) on biomass fast pyrolysis to automotive fuels, each of the 60 MGPY pyrolysis drop-in biofuel facilities would require a hydrogen generation capacity of 44 million standard cubic feet (SCF) per day. Assuming this hydrogen requirement would come from existing US refineries, a capacity of 11 billion SCF would be required by 2022. Current US refinery hydrogen generating capacity is only ca. 3 billion SCF per day (US EIA, 2013b).

As described earlier, owing to the highly heterogeneous, oxygenated and reactive nature of bio-oils, their hydrotreatment is a lot more complex than that of petroleum. In oil refineries, hydrotreatment is mainly used to remove sulfur from petroleum feeds in a process known as hydrodesulfurization (HDS). The process conditions include temperatures that range between 300 and 600 °C, hydrogen pressures of 35 to 170 bar and liquid hourly space velocities (LHSV) of 0.2 to 10 per hour. The catalysts used in petroleum HDS are typically sulfided Co-Mo and Ni-Mo supported on porous alumina or aluminosilicate matrices. Unfortunately, as described below, these conditions are not suitable for processing bio-oils for a number of reasons:

- Sulfided Co-Mo and Ni-Mo catalysts, when in contact with bio-oils, are rapidly stripped of their sulfur and require constant resulfurization (addition of H_2S) to prevent catalyst deactivation (Huber, 2007). This deprives bio-oils of their low sulfur content advantage (Wang et al., 2013)
- Alumina supports create an acidic environment and they are not stable in the presence of water (irreversible dealumination) (Mortensen et al., 2011)
- Bio-oils are unstable at high temperatures as they can rapidly become viscous and eventually phase separate.
- Bio-oils tend to form coke residues, particularly in acidic environments and at high temperature and pressure. Coke is undesirable as it deactivates the catalysts by depositing on their active sites and it can severely plug reactor components (Wang et al., 2013).
- The water in bio-oil inhibits hydrotreating by modifying and deactivating the catalysts and by adsorbing onto active sites (Furimsky & Massoth, 1999). Aside from the water content of bio-oils (up to 30%), more water is produced upon hydrotreatment.

These and other limitations have motivated the search for hydrotreating processes and catalysts that are better suited to the highly oxygenated and heterogeneous nature of bio-oils. Early research focused on adjusting process conditions and working with model bio-oil mixtures while using the same sulfided catalysts that oil refineries use for desulfurization (Corma et al., 2007). Although these alumina supported Co-Mo and Ni-Mo catalysts have various problems in processing bio-oils, they improve hydrotreating selectivity and they are widely available at relatively low cost.

As mentioned previously, bio-oils are thermally unstable and they have to first be pretreated at lower temperatures in order to form a stable oil intermediate that can then be further hydrotreated at high temperatures. Although single stage hydrotreating of bio-oil at high temperatures has been attempted, it resulted in a heavy, tar like product (de Miguel Mercader et al., 2010; Jones et al., 2009) due to the polymerization, charring and eventually coking reactions which, at high temperatures, take place faster than the desired hydrotreating reactions. However, to achieve effective hydrotreatment high temperatures and hydrogen pressures at extended reaction times (up to 4 hours) (Elliott, 2007) are often required. To fulfill these disparate condition requirements for stabilization and complete hydrotreatment of bio-oils, a two-stage bio-oil upgrading approach is commonly used (Elliott, 2007; Jones et al. 2009). The first, mild, catalysed hydrotreatment stabilizes the bio-oil and a second, higher severity hydrotreatment stage, deoxygenates the fuel to transport-grade liquids. The first hydrotreatment typically forms at least two phases, one hydrophobic and one hydrophilic and effectively separates out a large proportion of the water within the bio-oil. The resulting hydrophobic liquid is more stable and amenable to further catalytic upgrading.

When earlier workers (Centeno et al., 1995; Ferrari et al., 2001) investigated the fundamentals of bio-oil hydrotreatment using traditional sulfide molybdenum catalysts on model bio-oil compounds such as ketones, esters and phenolics (while alcohols and carboxylic acids where formed in the process), they concluded that ketones react first at lower temperatures (> 200 °C) to form alkenes while carboxylic and phenolic groups are converted at higher temperatures (> 300 °C). This early work lead to a proposed reactivity scale for the major components of bio-oils; the scale is plotted in Figure 3-6. The olefins and other double bond species are the most reactive and can be hydrogenated to more stable components such as alcohols and alkanes at temperatures around 250 °C and below. Alcohols are dehydrated to olefins at temperatures closer to 300 °C while carboxylic groups are more recalcitrant than alcohols and aromatics are the most recalcitrant and will only react at temperatures in the vicinity of 400 °C. This reactivity scale is a very useful rule of thumb in the absence of precise reaction kinetics.

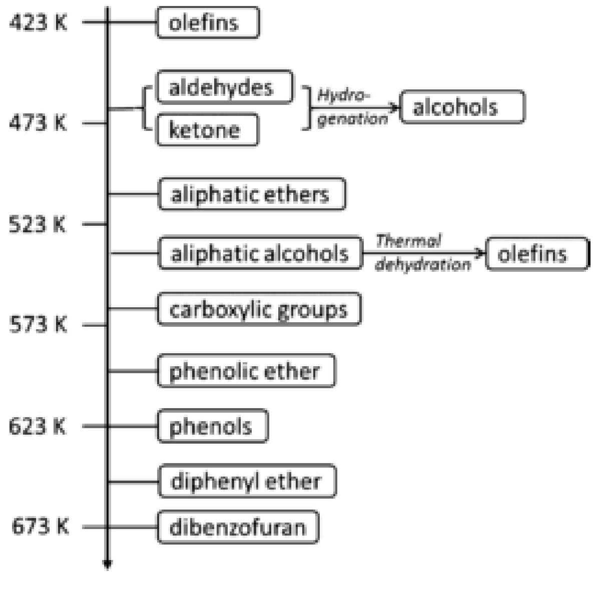


Figure 3-6: Reactivity scale of oxygenated compounds under hydrotreatment conditions.
Source: copied from Wang et al., 2013, based on work from Delmon and co-workers (Centeno et al., 1995; Ferrari et al., 2001) as adapted and plotted by Elliott, 2007.

As noted earlier, coking is a major problem during hydrotreatment as it can lead to catalyst deactivation and reactor plugging. In general, the parameters that promote coking are high temperatures, low hydrogen pressures, high acidity, and the presence of low H/C components such as phenolics, alkenes and highly oxygenated carbon molecules (Huber, 2007; Mortensen, 2011). Double bond molecules such as olefins, ketones and aldehydes are particularly prone to polymerization and coking. Fortuitously, these species can be hydrogenated relatively easily during the first, low severity, hydrotreatment stage. This improves the thermal stability of the resulting bio-oil before the second hydrotreatment step. Refinery HDS catalysts promote the formation of coke by creating an acidic environment and promoting the formation of aromatics. Aromatics are desirable up to certain concentrations since they form part of transport fuel blends, particularly gasoline (40% aromatics) (Bauen, 2009). However, aromatics are a low H/C ratio species and can act as precursors for coking reactions upon upgrading. The hydrogenation of aromatic rings is the most challenging as it requires high temperatures and hydrogen pressures (around 4.0 to 8.0 MPa of H_2) as well as highly active catalysts such as precious metals (Wang et al., 2013). Another way in which hydrogen can reduce coke formation is by converting catalyst-absorbed reactive species, such as alkenes, to stable molecules such as alkanes. In general the presence of hydrogen appears to play a pivotal role in minimizing the formation of coke.

While this more fundamental work has built an invaluable body of knowledge around the hydrotreatment and coking mechanisms of bio-oils, these studies have been mainly based on “model” as opposed to “real” bio-oils (Butler et al., 2011). In contrast, Elliott and co-workers (Elliott, 2007) used sulfide Co-Mo and Ni-Mo catalysts on real bio-oil substrates and developed a two stage process that brings the oxygen content of the bio-oil down to < 1 wt%. The first stage of the process is conducted at 270 °C and 136 bar and the second at 400 °C and 136 bar. Consistent with the known challenges of these catalysts, the authors reported catalyst deactivation and formation of gums as major drawbacks of the process.

More recent research has focused on developing catalysts that may circumvent the challenges encountered with traditional HDS catalysts such as CoMo and NiMo supported on alumina materials. Precious metals such as Ruthenium, Palladium and Platinum have been assessed as bio-oil hydrotreatment catalysts (Bridgwater, 2012). These metals performed better than CoMo and NiMo catalysts in terms of both hydrocarbon yields and H/C ratio of final product (Lin et al., 2011; Wang et al., 2013; J. Wildschut et al., 2009). They are also more stable, less acidic and do not promote coking particularly when supported on non-acidic carbon. The company, UOP, has been a leader in using precious metal catalysts for hydrotreatment of petroleum. Together with PNNL they have assessed the potential of non-sulfided metal catalysts such as Ruthenium on bio-oils. Ruthenium seems to be the lowest cost and most promising of the precious metal catalysts assessed so far (J. Wildschut et al., 2009; J. Wildschut, Melian-Cabrera et al., 2010; J. Wildschut, Iqbal et al., 2010). When Lin et al. (2011) assessed various precious metal catalysts using the model compound guaiacol, they reported that the Rh-based catalyst showed the best HDO activity and a preference to saturate benzene rings. Although Ruthenium is less expensive than Palladium and Platinum (similar price to Gold!) on June 28, 2013 the spot price for Ru was about USD $3 million/t which is more than a 100 times the same day price of Cobalt (ca. USD $30,000 USD/t), Nickel (ca. USD $10,000/t) or Molybdenum (ca. USD $20,000/t) (IndexMundi, 2013; InvestmentMine, 2013). Although precious metal catalysts are more favoured for bio-oil hydroprocessing, as they are more active in comparison to NiMo and CoMo based catalysts, their cost is so prohibitive that their use in industrial applications may be very limited.

The ability to recycle and the stability of Ru/C catalysts has been challenged by Wildschut (2009). When he conducted three successive hydrotreatment reactions (200 bar, 350 ^{o}C and 4.3 h each) where the catalyst was reused after repeated acetone washes, he found that the activity of the catalyst deteriorated even after the first repeat. After 2 repeats the oil yields dropped significantly (55 to 30%-wt.), whereas the amount of gas phase (5 to 11%-wt.) and solids (3 to 20%-wt.) increased, all indicating significant catalyst deactivation. This deactivation mostly affected the ability of the process to hydrogenate while it did not affect much of its ability to deoxygenate. The deactivation was attributed to sintering and coke formation on the surface of the catalyst. It would therefore be desirable if the catalysts could have been regenerated with a more effective technique than acetone washing.

The prohibitive price of precious metals means that novel catalysts have to be designed which will achieve high hydrotreating activity at lower cost. Although phosphide catalysts have been suggested as alternatives to sulfide catalysts they face similar issues. Once in contact with water they form phosphates which can deactivate the active sites on the catalyst (Wang et al. 2013).

Other than deoxygenation, the hydrogen treatment of bio-oils has many favourable side effects such as decreasing its water content, increasing its energy density (from 18 MJ/kg in crude bio-oil to 40 MJ/kg in hydrotreated bio-oil), decreasing its bulk density (from >1 in bio-oils to <0.8 in deoxygenated bio-oils), decreasing the coking propensity, and decreasing its viscosity (from > 100cps in raw bio-oil to <5 cps in bio-oil that contains <5% oxygen) (Elliott, 2007). All of these advantages result in higher yields and the higher H/C_{eff} ratio of the final transport fuel product. These benefits are generally absent in any bio-oil upgrading technologies that do not entail any hydrogen inputs.

3.3.2 Zeolite cracking

Zeolite cracking is a process used in the Fluid Catalytic Crackers (FCCs) of oil refineries and it has potential in bio-oil upgrading as a non-hydrogen consuming, non-pressurized alternative to hydrotreatment. The main deoxygenation mechanism of zeolite catalytic cracking is the rejection of oxygen in the form of coke and CO_2. The conceptual reaction of this mechanism is summarised below:

$$C_1H_{1.33}O_{0.43} + 0.26O_2 \rightarrow 0.65CH_{1.2} + 0.34CO_2 + 0.27\ H_2O$$

When this formula is compared with the earlier equivalent formula for hydrotreating it is apparent that, in the absence of hydrogen, as occurs in zeolite cracking, bio-oil upgrading is poor. The theoretical carbon yields for zeolite cracking are low (65% compared to 100% in hydrotreatment) and the hydrocarbons produced have a low H/C ratio (1.2 compared to 2 for hydrotreatment). This low H/C ratio indicates that the bio-oil is rich in aromatics and olefins and that the resulting fuel will have a low heating value, typically about 20-25% lower than crude oil (Balat et al., 2009; Mortensen et al., 2011). Similar to what occurs in hydrotreatment, the cracking reaction takes place alongside other undesirable reactions such as polymerization and coking which results in the diversion of some of the carbon from the targeted liquid biofuel. Thus, even in the presence of catalysts, cracking typically results in bio-oil-to-fuel yields in the range of 14-23 wt% of bio-oil (Balat et al., 2009), which is much lower than the theoretical 45 wt% yield which can be calculated from the equation above. This is largely because 26-39 wt% of the starting bio-oil goes towards the formation of solid tar and cokes (Balat et al., 2009).

Zeolites such as ZSM-5 and HZSM-5 are made of a highly porous aluminosilicate matrix and, as a result, they are typically not stable in the presence of bio-oils at high temperatures and pressures. Zeolite catalysts such as ZSM-5 have a strong acidity, high activities and shape selectivities which work well for upgrading petroleum feeds. However, for bio-oils, zeolite cracking poses severe catalyst coking and deactivation issues.

On the more positive side zeolite cracking requires no hydrogen gas and can operate at atmospheric pressures. This means that FCC-type systems can be used for bio-oil processing where the heavily coked catalyst can be rapidly regenerated in the FCC combustor. These systems have great potential to utilise the coke formed on catalysts as a fuel for heat and power generation. However, these systems often convert more biomass carbon to thermal energy than to liquid fuel products. Operating costs of FCCs are higher than regular fixed bed reactors because the faster recycling of carrier gas needed to regenerate the rapidly coked catalyst is highly energy intensive.

Other workers have recently (Vispute et al., 2010) proposed an approach that involves a mild hydrotreating step prior to zeolite cracking. The advantage of this approach is that it converts the most reactive oxygenated compounds, the carbonyls, to more thermally stable alcohols. In zeolite cracking carbonyl functionalities go directly to coke formation whereas alcohols contribute to the formation of valuable molecules such as olefins and aromatics. The introduction of a mild hydrotreatment step prior to zeolite cracking appears to result in bio-oil conversion yields (aromatics) as much as three times higher than direct zeolite cracking. This is particularly desirable for BTX (benzene, toluene, xylene) production which is the target of the Huber group’s spin off company AnelloTech (*vide supra*). However, the alkane yields are low and, while this technology may be relevant to making aromatic fractions for gasoline, it is not directly applicable to the production of the longer chain hydrocarbons that are needed for the production of diesel and jet fuels.

Cracking of bio-oils has also been attempted using platinum catalysts. Fisk et al. (2009) achieved a low oxygen bio-oil (2.8%) which was predominantly composed of aromatic and very few non aromatic oxygenates. The oil yields of the process were rather low (10-20% wt of bio-oil was converted to stable oil) when compared to hydrotreatment upgrading (ca. 40%) (Butler et al., 2011; Fisk et al., 2009).

3.3.3 Catalytic pyrolysis

Catalytic pyrolysis is a process that combines pyrolysis with zeolite cracking in a single step (Butler et al., 2011). Due to the challenges of catalyst coking, the preferred reactors for these systems are again the FCC-type reactors. The main goal is to use the catalysts inside the pyrolysis reactor to increase the reaction selectivity towards deoxygenation, thus producing a less oxygenated bio-oil. As occurs in zeolite cracking, the oxygen is primarily removed by decarboxylation, but at the expense of bio-oil yield and diminished bio-oil properties. Compared to non-catalyzed pyrolysis, catalytic pyrolysis typically yields a more viscous bio-oil that represents only 30-40% of the starting biomass (60-75% for non-catalyzed pyrolysis). A recent DOE funded project at RTI International showed that catalytic pyrolysis (vapor phase upgrading) yields dropped to as low as 6-13% compared to 48% in uncatalyzed pyrolysis (DOE, 2011).

Again the loss in bio-oil yield is compensated by an increase in power generation through combusting the excess coke and gas that is formed at the expense of liquid yields.

Despite the technical difficulties and low liquid yields of catalytic pyrolysis, the process is commercially attractive as it holds promise for capital cost savings and the production of bio-oils that are more deoxygenated and chemically stable as well as generating large amounts of renewable power. As described below, catalytic pyrolysis forms a key part of the processes proposed by several of the leading biofuel companies:

- Annellotech, a spin-off company from Professor George Huber's group at the University of Massachusetts, is licensing a fluidized bed catalytic pyrolysis platform which produces a bio-oil rich in benzene rings (hence "Anello" Tech which in Latin means "ring"). The aromatic character of this biomass derived liquid means it is good feedstock for the subsequent production of BTX (Benzene, Toluene, Xylenes). The company is primarily focussed on these value-add chemicals (Anellotech, 2013).
- The Gas Technology Institute in Chicago, USA, has recently developed a catalytic pyrolysis known as catalytic hydropyrolysis (or integrated hydropyrolysis and hydroconversion) and marketed as "IH^2". In this process biomass is converted in a fluidized bed of catalyst under hydrogen pressure of 20–35 bar and temperatures of 350–480°C and in the presence of catalysts (T. L. Marker et al., 2012). Although this process produces bio-oils with a low oxygen content (e.g. <3 wt%, T. L. Marker et al., 2012) in a single reaction step, scaling up and high hydrogen consumption remain as potential challenges of hydropyrolysis.
- KiOR uses catalytic pyrolysis (FCC-type reactor and proprietary catalysts) followed by hydrotreatment to produce transport fuels. As mentioned earlier, KiOR has recently built the world's first commercial pyrolysis drop-in biofuel plant and the company has also claimed that the catalytic pyrolysis bio-oil can be directly inserted into a petroleum refinery for further processing. KiOR's proprietary biomass fluid catalytic cracking (BFCC) process should work in both standalone pyrolysis facilities and in refinery co-processing. Although little is publically known about the technical details of the BFCC process it has been reported that clay materials and pre-impregnation of biomass with nanocatalysts are involved (Bridgwater, 2012).

3.4 Refinery integration of pyrolysis platforms

As mentioned earlier, the majority of the processes and catalysts used to upgrade pyrolysis oils originate in the oil refining industry. It has also been suggested that pyrolysis oils or their derivatives could be "dropped into" existing refineries for final processing (Corma et al., 2007; Solantausta., 2011). The main benefit of this approach is capital cost savings by utilizing facilities and off-take infrastructure that has already been built. For example, the USDA "Regional Roadmap to Meeting the Biofuels goals of the Renewable Fuels Standard" (2010) concluded that 527 new biorefineries would be needed to meet the requirements of the RFS 2, at a cost of about 168 billion USD (Weyen, 2012). A big part of this capital cost could be avoided if biomass intermediates could be upgraded to biofuels using existing oil refinery equipment. It should be noted that, in the US, refinery utilization is expected to decrease as the US EIA predicts a reduction in refinery throughput over the next decade (EIA, 2009). Another important trend that is projected for the next three decades is that refineries in the US and around the world will be producing less gasoline and more diesel and jet fuels (more middle distillates). This shift translates to refineries directing petroleum feed away from FCC units and towards hydrocracking units. According to the US EIA 2013 Annual Energy Outlook (EIA, 2013), the already decreased utilization of FCCs (83% in use in 2011) in US refineries is expected to decline further and approach 62% in 2040. In contrast the US hydrocracking capacity is expected to increase from 1.8 million bpd in 2012 to 3 million bpd in 2040.

It has been suggested that oil refiners could either dedicate whole process units such as hydrotreaters exclusively to bio-oil processing or they could co-process bio-oils together with petroleum feeds (Corma et al, 2007, Egeberg et al., 2010). Dedicating whole refinery units to upgrading bio-oil derivatives would save capital costs and avoid complications of co-processing. However, candidate refinery units for biomass liquids processing such as hydrotreating and hydrocracking facilities are very large scale and as noted earlier, they typically process around 100,000 barrels of fuel per day (see Chapter 1 for details on these refinery processes). Commercial pyrolysis facilities are usually envisioned to be about 30 times smaller at around 3,000 barrels per day, at a scale large enough to benefit from economies of scale while small enough to avoid transporting bulky and wet biomass over prohibitively long distances (Stephen et al., 2010). Thus sourcing, transporting and utilising the biomass feedstock needed to occupy a whole refinery unit will be challenging. Thus, co-processing is a more likely integration pathway than dedicating entire refinery units to biomass feeds. Co-processing also has the advantage that small amounts of biomass derived liquids can be blended with petroleum feeds in order to mitigate the problems that come with neat pyrolysis oil processing.

As mentioned earlier, neat pyrolysis oils cannot be readily co-processed with petroleum feeds as they typically contain up to 30% water and 40% oxygen and are thus not miscible with the apolar petroleum liquids (Venderbosch & Prins, 2011). As the oxygen content of bio-oils also increases coking and deactivation of zeolite and HDO catalysts they cannot be readily inserted in oil refineries before at least partial deoxygenation (hydrotreated). However, it will be important to deoxygenate only enough to meet the minimum requirements of the refinery since deoxygenation gets disproportionately costlier when approaching oxygen-free bio-oils (Elliott, 2007; Ringer et al., 2006).

Once the oxygen content of the bio-oil has been reduced by hydrotreatment, it becomes a liquid hydrocarbon intermediate (such as hydrodeoxygenated oil, (HDO)) that can potentially be inserted into an oil refinery. As HDO bio-oils, even when partially deoxygenated, are unstable at 400 °C or 500 °C (temperatures that are often used in petroleum distillation) they cannot be directly inserted with crude oil at an early process stage of the refinery. Thus bio-oil insertion is likely to occur at the refinery's hydroprocessing (hydrotreatment and hydrocracking) or fluid catalytic cracking reactors. As described earlier, these two processes are similar to the processes used for hydroprocessing and zeolite cracking of neat pyrolysis oils in stand-alone setups. A simplified schematic showing HDO bio-oil insertion points (red arrows) within a typical refinery is outlined in Figure 3-7.

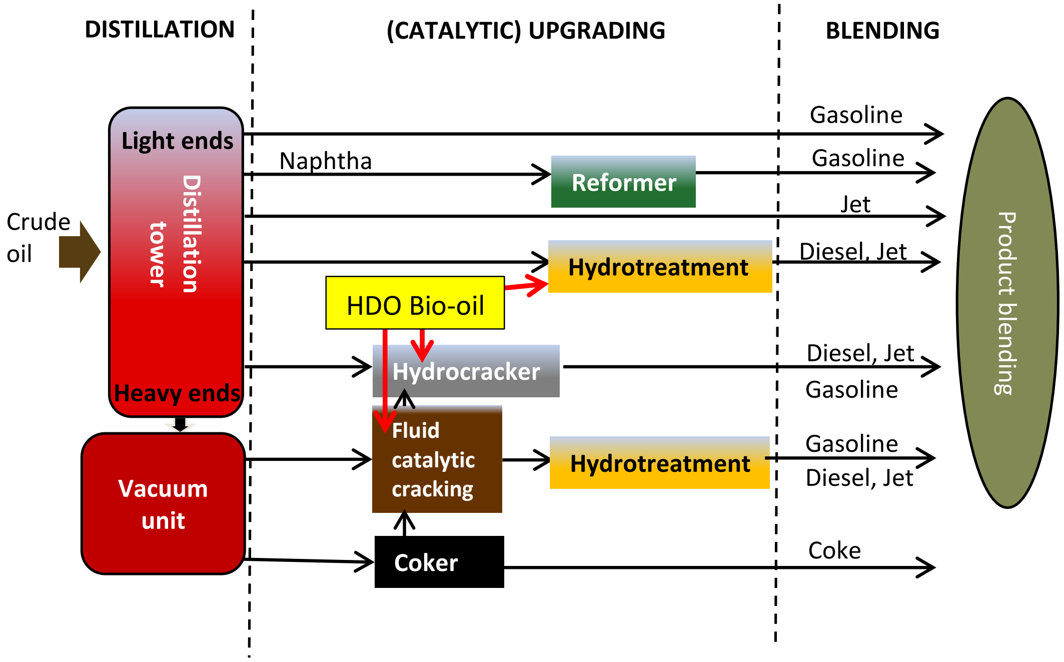


Figure 3-7: Refinery insertion points (red arrows) for HDO Bio-oils

Source: adapted from (US EIA, 2007)

It is important to clarify that the use of the term hydrodeoxygenated oil (HDO) is not well defined as it simply refers to a bio-oil that has been stabilized through hydrotreatment. However, the degree of hydrotreatment can vary markedly and it largely depends on the co-processing insertion point and the blending ratio. The FCC insertion point can take more oxygen while hydrocrackers are far more sensitive to oxygen as they operate under very high temperatures and pressures. These two HDO-petroleum co-processing strategies are discussed in detail below.

3.4.1 Fluid Catalytic Cracking (FCC) co-processing

Fluid catalytic cracking (FCC) of bio-oil mixtures with petroleum feeds resembles the earlier described zeolite cracking process. It requires no hydrogen and it is more tolerant than hydroprocessing to higher oxygen content biomass liquids (Solantausta, 2011). Unlike hydroprocessing reactors, FCCs operate at atmospheric pressure and they can efficiently regenerate the coke deposited on the catalysts by circulating them through their fluidized bed combustor loop. As described earlier, the combustion of this excess coke generates heat and thus benefits the energy balance of the refinery process. Various groups have carried out FCC-type trials of co-processing bio-oil (or bio-oil model mixtures) in blends with petroleum vacuum gas oil (VGO) (Bezergianni et al., 2009; Huber & Corma, 2007; Lappas et al., 2009). This work showed that, when partly deoxygenated pyrolysis oils were blended with VGOs, lower H/C ratio products were produced as compared to VGO processed alone. It was apparent that heavier (coke and tar) and lighter (gasoline and gases) fractions were produced at the expense of middle distillates while the gasoline produced was generally poorer in saturates and richer in aromatics.

Encouraging results were obtained after the FCC co-processing of HDO bio-oils with heavy petroleum fractions. Fogassy et al. (2010), successfully mixed 20% of an HDO (which contained 20% oxygen) with petroleum VGO and then co-processed the mixture in an FCC arrangement. Although the gasoline yields were comparable to those obtained with pure VGO FCC processing, overall the H/C ratio of the product was low and the amount of coke, aromatics and olefins produced were significantly higher. Even more encouraging results were obtained by de Miguel Mercader et al. (2010) who successfully co-processed an HDO (28% oxygen) with a Long Residue heavy petroleum feed supplied by Shell Inc. The product distribution was similar to the Long Residue processed alone with a less-than-expected increase in coke and dry gas production compared to the base feed. However, the H/C of the final product was significantly lower. These workers concluded that the effective H/C ratio of the HDO/petroleum blend is a good indicator of the quality of the resulting FCC product (de Miguel Mercader et al. 2010). Both of these recent studies (de Miguel Mercader et al. 2010, Fogassy et al. 2010) reported a synergistic beneficial effect of blending HDOs with petroleum feeds since a more than proportional decrease in coking propensity of HDOs was observed when they were blended as compared to when they were processed pure. The synergistic effects were mostly attributed to the transfer of hydrogen from the petroleum to the biomass feed during co-processing. It was apparent that this process hydrogenated coke-inducing oxygenated compounds at the expense of the overall H/C ratio of the blend. When industrial trials were subsequently performed to test if these highly oxygenated pyrolysis HDOs could be co-processed at a large scale, the 20% HDO blending proved to be challenging while, although the 5% HDO blend were found to be technically feasible, increased coking was observed (Solantausta, 2011).

3.4.2 Co-hydrotreating

Co-hydrotreating of HDOs is another co-processing strategy that could be used to insert HDO bio-oils into oil refineries. Although there is limited experimental data on co-feeding of real bio-oils with petroleum feeds in hydrotreating units studies when using model compounds, the co-hydrotreating of HDO bio-oils resulted in similar problems to those observed when co-hydrotreating vegetable oils. These included, competition with hydrodesulfurization, increased coking and catalyst deactivation as well as increased hydrogen demand and potential irregular hydrogen pressure drops inside the reactor (Butler et al. 2011). Other work also reported (Bui et al. 2009) that, when gas oil was co-hydrotreated with guaiacol over a CoMo catalyst, the gas oil did not get fully hydrotreated until the guaiacol was completely hydrodeoxygenated. This indicated that the deoxygenation reactions were prioritized at the expense of desulfurization reactions which are a highly undesirable outcome from a refiner's perspective. In today's oil industry where sulfur regulations are becoming increasingly rigorous, a compromised or slow desulfurization unit is problematic. As mentioned earlier, hydrotreatment units are rather sensitive to oxygen and unlikely to process bio-oils with an oxygen content that exceeds about 5% at blending ratios of less than 10%. These limitations could be overcome if improved catalysts such as the recently developed NiCu catalyst and other non-disclosed catalysts patented recently by participants of the BIOCOUP project in Europe (Solantausta, 2011) can be commercialised.

As also mentioned earlier, hydrocracking is a more severe form of hydrotreatment and it aims at cracking the heavy portions of bioderived hydrocarbons. This process follows hydrotreating in an oil refinery and it is even less tolerant to oxygen than hydrotreatment (due to higher pressures and temperatures). Hydrocracking units can be leveraged by biomass derived HDO oils that have been extensively deoxygenated (<2%) and some recent techno-economic studies describe design cases where highly hydroprocessed HDOs (Jones et al., 2009) are finished in the hydrocracker unit of an oil refinery in order to save capital equipment costs.

Much of the recent advances in better understanding the co-processing of HDOs with bio-oils in oil refineries have been a result of the work carried out under the European 6th Framework program BIOCOUP. This 5 year program ended in 2011 and a summary of important conclusions is listed below (Solantausta, 2011):

- Despite their low oxygen content, bio-oils catalytically upgraded without hydrogen (Decarboxylated oils or DCOs) or upgraded without catalyst or hydrogen (High pressure thermal treatment oils HPTTs) could not be co-processed while HDO bio-oils could.
- Despite their relatively high remaining oxygen content (between ~10 and 30 wt.%) and low hydrogen use (only ~100-300 NL/kg), all HDO oils could be co-processed with good results in a laboratory scale fluidised bed reactor (SP3 project). Considering that deoxygenation was initially thought to be the main goal of upgrading this was a surprising result.
- Important criteria to allow successful co-processing of the HDO oil were, low coking tendency (measured as MCRT), a high H/C and H/C_{eff} ratios and a not-too-high molecular weight of the HDO oil.
- Although some of bio-oil stabilization was accompanied by a limited deoxygenation, substantial deoxygenation in itself (requiring ~ 800 NL hydrogen/kg pyrolysis oil) was not needed.

Based on these conclusions the BIOCOUP project suggested an integrated strategy of bio-oil co-processing using the FCC as the refinery insertion point. The strategy entails using the refinery's FCC to introduce partially hydrotreated HDOs (about 20% oxygen remaining after using about 200 L of H_2 per L of oil upgraded) and prioritizing emissions and cost savings. Reduced hydrogen usage is achieved by prioritizing the hydrotreatment of the most unstable (rather than all) bio-oil components. Capital cost savings would then be achieved by using the existing FCC infrastructure early in the process flow. Although the yields might be lower, the LCA and techno-economic analyses demonstrated that the FCC based BIOCOUP approach compared favourably with other, alternative approaches in terms of both GHG emissions and economic returns. Specifically it was demonstrated that, using the BIOCOUP strategy on \$7/GJ wood, an \$18/GJ diesel could be produced (\$25/GJ is the equivalent for the August 2013 diesel spot price) (IndexMundi, 2013; Solantausta, 2011).

It is apparent that both FCCs and hydroprocessing refinery units can accept bio-oils that have been partially deoxygenated (HDOs). However, the two facilities differ in their relative suitability for biofeed insertion (Table 3-4). It has been shown that FCCs can handle lower grade (up to 20% oxygen) HDOs without the need for hydrogen and this results in low conversion yields, large amounts of waste energy production and lower value end products (low H/C ratio) which will contribute mostly to marine and bunker fuel blendstocks. In this regard FCC can be viewed as the "workhorse" of bio-oil co-processing. Alternatively, hydroprocessing could be considered the refinery's "boutique" upgrading unit as it requires more deoxygenated bio-oil co-feed (max of 3-5%) and it is designed to produce higher grade diesel and jet fuels.

Table 3-4: Comparison of FCC and hydroprocessing as refinery co-processing platforms for bio-oils

	FCC (Fluid Catalytic Cracking)	**Hydroprocessing (hydrotreating followed by hydrocracking)**
Tolerable oxygen content in bio-oil feed	Up to 20% (<5% blend)	No more than 3-5%
Pre-refinery hydrotreatment	Single stage/mild	Two-stage/severe
Hydrogen use (NL / L of bio-oil)	ca. 300	>800
Yields	Low (10-15% in standalone)	High (25% in standalone)
Downstream contamination risk with oxygenates	High	Low
Opportunity for power generation through coke combustion	High	Low
Chemistry of product	Favors aromatics (low H/C_{eff} ratio)	Favors short paraffins (high H/C_{eff} ratio)
Fuel pool (most contribution)	Gasoline and Marine fuels	Middle distillates: Diesel and Jet fuels

Source: (adapted from Solantausta, 2011)

3.5 Techno-economics and sensitivities of upgrading bio-oils

Although the technology for upgrading pyrolysis oils to biofuels is still evolving, some estimates of the overall costs involved are provided in four recent techno-economic analyses (Jones et al., 2009; Wright et al., 2010, Brown et al., 2012, Jones et al. 2013). While direct comparisons between techno-economic analyses are often problematic, these four studies have some common assumptions such as 2000 tpd processing capacity and a 10% ROI (cost year base is 2007 for the first 2 studies and 2011 for the two more recent studies, but this difference is not expected to significantly affect the gross comparisons as the Chemical Engineering Plant Cost Index for equipment increased by 13.6% between December 2007 and April 2011 (Brown et al, 2012)). The 2009 study by the US DoE Pacific Northwest National Laboratory (PNNL) (Jones et al., 2009) was based on poplar bio-oil upgraded with a 2-stage hydrotreatment system using a conventional CoMo HDS catalyst. This study, which could be considered the most detailed publically available to date, estimated a pyrolysis diesel minimum fuel selling price (PFSP) of \$2.04/gal (\$0.54/L) with this price dropping to \$1.74/gal (\$0.46/L) when hydrogen is imported to the facility rather than produced on site from biomass. Importing hydrogen (made from natural gas) was considered more favoured in the near term since the conversion of biomass to hydrogen is currently inefficient and costly. There are also considerable capital cost savings achieved when hydrogen is imported as opposed to making it from biomass as the \$303 million total project investment (TPI) drops to \$188 m when hydrogen is imported from an external source. The TPI breakdown described in

Table 3-5 shows how, out of the total \$303 million cost of the plant, only \$92 million is the cost of the fast pyrolysis process components while the remaining costs are mostly related to the hydroprocessing infrastructure. Thus very substantial capital costs could be saved if the upgrading operations could make use of the hydroprocessing and hydrogen generation facilities in an existing oil refinery. The PNNL study takes a somewhat conservative (and appropriate) approach and uses the refinery only as a source of low cost hydrogen and to perform the final hydrocracking of the heavier portions of the highly deoxygenated (2% O_2) HDO. This approach results in a capital savings of \$115 m.

Some of the assumptions used in the 2009 PNNL study are worthy of discussion, such as feedstock costs of \$51/t for a 2000 tpd facility. More recent studies have suggested that costs of around \$80/t are more likely considering the logistic challenges and the competing end uses for the biomass. The PNNL sensitivity analysis indicated that an \$80/t feedstock cost would add about \$0.20/gal (\$0.05/L) to the MFSP. Possibly the biggest concern regarding the PNNL analysis is the assumption that the hydrotreating catalyst will last at least 1 year. This is about the average life expectancy of catalysts used in refineries that hydrodesulfurize traditional petroleum cuts. As described earlier, catalysts that process bio-oils have so far proven to have much shorter life expectancies due to extensive coking. To date, no study has demonstrated more than 200 h (8 ½ days) of continuous catalyst operation when hydroprocessing bio-oils (de Miguel Mercader et al., 2011). The sensitivity analysis of the PNNL study indicated that halving the catalyst lifespan to 6 months added \$0.15/gal (\$0.04/L) to the base MFSP (minimum fuel selling price). However, a catalyst lifespan in line with current technology would be about 20 times shorter (8 ½ days vs 6 months).

The 2009 PNNL study was recently (November 2013) updated and some of the main cost estimates and assumptions are listed in Table 3.5. The new analysis (Jones et al., 2013) was based on a similar process sequence and conversion yields reported in 2009 and the hydrotreating catalyst lifetimes are again assumed to be 1 year. The 2013 study makes a clear statement that it is not based on available technology but on technology that is expected to be available by the year 2017 (Jones et al., 2013). This new study shows significantly higher capital and operating costs for producing diesel and gasoline via fast pyrolysis of biomass. As shown in Table 3.5, the $700 million TPI and $3.39/gal ($0.90/L) MFSP reported in 2013 compares to a $303 million and $2.04/gal ($0.54/L) MFSP reported in 2009 (own hydrogen scenario) for same size (2000 tpd) facilities. Among the various differences in assumptions and other contributing factors, some of the outstanding parameters that have contributed to the high cost of the 2013 estimate include:

- Updated, increased equipment and processing costs based on more recent estimates (e.g. information from the relatively recent Ensyn/UOP joint venture)
- Higher feedstock costs ($88 per metric tonne vs $51 in 2009)
- Extra processing steps such as the 3-stage pyrolysis oil hydrotreatment/stabilization process.
- Higher Hydrogen consumption to hydrotreat raw pyrolysis oil to a stable hydrocarbon oil of <2 wt% Oxygen (5 wt% Hydrogen on dry pyrolysis oil for 2009 vs 5.8 wt% for 2013)
- Much higher indirect costs (engineering, risk, contingency etc.) which represent ca. 100% of total installed capital (TIC) costs (vs.ca. 50% in the 2009 study)

Two other recent studies (T. R. Brown et al., 2012; Wright et al., 2010) have also assessed the potential cost of producing pyrolysis biofuels for transportation. The 2010 study, which assumed imported hydrogen, estimated a similar cost of $2.11/gal (0.56/L) to upgrade the pyrolysis oil, similar to the 2009 PNNL study (after normalizing for the higher feedstock cost assumption). The assumptions in the 2010 study were updated, based on the world’s first commercial pyrolysis facility completed by KiOR, to reflect some of the characteristics of this new facility. Although the details of the KiOR process are still not fully disclosed, the authors based their analysis on the preliminary information outlined in KiOR’s initial public offering document which contained information on the expected capital and operating costs of the facility. One figure that had changed significantly was the capital cost which had more than doubled (from \$200 m to \$429 m) once the 2012 KiOR details were entered into the 2010 model. A major contributor to this difference was the power generation equipment cost which, as shown in

Table 3-5, was about 5 times that of the 2010 value (34 vs 141). This implies that KiOR places considerable emphasis on maximizing power generation for the process itself as well as for export to the grid. The reasons behind this strategy are likely related to US RFS2 compliance and the GHG emission savings achieved with increasing amounts of renewable power generated on site at the biofuel facility. The sale of power to the grid should contribute about \$12 m annually to the financial returns of the facility. This revenue explains why, compared to the 2010 analysis, the MFSP in the 2012 study is only about 20% higher (2.57 vs 2.11 USD/gal) when the capital cost is 115% higher. Other contributors to the 2012 study's high capital costs are primarily due to equipment cost inflation, a costlier hydroprocessing facility (with more emphasis on H_2 recycling) and the purchase of refiners to make actual diesel and gasoline rather than a mixture of liquid hydrocarbons.

In terms of sensitivity analysis, all four studies agree that the MFSP (Minimum Fuel Selling Price) is very sensitive to both pyrolysis yields and hydroprocessing yields. These sensitivities are indirectly related to the cost of feedstock (good yield may be irrelevant if cost of feedstock is too high) and the hydrotreatment catalyst and hydrogen cost (which largely determine the yield of the hydroprocessing facility). For example, in the 2012 ISU study, dropping the bio-oil yield (Table 3-5) from 63% to 39% increased the MFSP from \$2.57/gal (\$0.68/L) to \$3.32/gal (\$0.88/L).

Table 3-5: Recent techno-economic studies on pyrolysis-derived biofuels

	2009 PNNL (own hydrogen)	2009 PNNL	2010 ISU study	2012 ISU study (KiOR based)	2013 PNNL (based on expected technology by 2017)
Cost year basis	2007	2007	2007	2011	2011
Facility fuel output, MGPY	43	76	58.2	57.4	60.5
(MLPY)	(163)	(288)	(220)	(217)	(230)
Biomass to Bio-oil yield (mass)	65%	65%	62%	63%	64%
Biomass to HDO yield (mass)	44%	44%	41%	42%	44%
Biomass to drop-in biofuel yield (mass)	29%	29%	25%	26%	28%
Total Project Investment (million \$)	303	188	200	429	700
TPI Hydroprocessing (million \$)	110*	n/av	27	90	230*

ISBN: 978-1-910154-07-6 (electronic version)

TPI Fast pyrolysis (million $)	92	n/av	ca.30	ca. 20	279
TPI Hydrogen generation (million $)	86	n/ap	n/ap	n/ap	119
TPI Power generation (million $)	n/ap	n/ap	34	141	n/ap
Hydrogen cost ($/kg)	n/ap	2.2	1.3	1.3	n/ap
Electricity price ($/kWh)	0.064	0.064	0.054	0.054	0.069
Feedstock cost ($/MT dry basis)	51	51	83	83	88
Transportation fuel MFSP, $/gal	2.04	1.74	2.11	2.57	3.39
($/L)	(0.54)	(0.46)	(0.56)	(0.68)	(0.90)

(Jones et al. 2013.,T. R. Brown et al., 2012; Jones et al., 2009; Wright et al., 2010)

*contains product separation and finishing equipment

As for capital costs, hydroprocessing and power generation equipment are the highest expenses and they must be weighed against the potential benefits of integrating the facility with a refinery and selling electricity to the grid. The 2010 ISU study also contrasted the capital cost of a first of kind with an n^{th} plant facility. A pioneer plant would cost $911 million ($585 million for purchased Hydrogen) compared to a mature plant of $287 m ($200 m for purchased hydrogen scenario). This highlighted the high equipment risk involved in pioneer pyrolysis facilities, especially those that will produce hydrogen on site.

The three earlier techno-economic studies (Jones et al. 2009, Wright et al. 2010, Brown et al. 2012) generally agree on various points including that the cost of producing pyrolysis diesel would be in the vicinity of $2.5/gal ($0.66/L) which is equivalent to about $19/GJ. This value is similar to the one calculated by the BIOCOUP group described earlier ($18/GJ) and indicates that upgrading to drop-in biofuels adds about $10/GJ to the $10/GJ base cost of making bio-oil. However, it must be noted that the recent and most updated study by Jones et al. (2013) shows a significantly higher cost of producing drop-in biofuels from a fast pyrolysis platform with the capital cost as TPI reaching $700 million and the production costs as MFSP climbing to $3.39/gal ($0.90/L) or ca. $26/GJ. Again, these are rough comparisons and are only meant to give a “high level” sense of the currently estimated costs of pyrolysis derived drop-in biofuels. However, they can prove to be useful in helping identify the challenges and opportunities for cost reduction and eventual commercialization of the pyrolysis drop-in platform.

3.6 Pyrolysis biofuel commercialization

Although there are several groups in the process of commercialising pyrolysis derived biofuels, by way of examples, the three pyrolysis biofuels commercialization efforts of Envergent, Dynamotive and KiOR are described below. Each of these companies is pursuing a different technology with Envergent using a circulating fluidized bed (CFB), Dynamotive a Bubbling Fluidized Bed (BFB) and KiOR using catalytic pyrolysis (CP):

Dynamotive has been developing its Bubbling Fluidized Bed pyrolysis technology for several years. The company has constructed 4 installations to date with the West Lorne (2006, 130 tpd, no longer active) and Guelph facilities (2008, 200 tpd no longer active) being the largest (Bradley, 2009). Dynamotive has also been developing its so called BINGO approach, a proprietary 2-stage bio-oil hydrotreating technology which produces: 1) a liquid intermediate that is blendable with petroleum feed after the first stage, and 2) a finished transport fuel blend stock after the second stage. The yields claimed at bench scale are 25 wt% biomass to transport fuel stock (or 300 L/odt) with less than 0.01% oxygen and an even product distribution (20% heavy VGO, 30% Gasoil, 30% Jet and 20% lights) (Dynamotive, 2009). The company has not disclosed the type of catalysts it is using. In 2011, Dynamotive signed an agreement with French innovation center IFPEN and Canadian technology provider Axens to upscale and commercialize the BINGO process. Dynamotive has emphasised the value of its agrichar and biogas co-products (Dynamotive, 2009).

Envergent is a joint venture between UOP Inc and Ensyn. Ensyn is contributing its 25 years of experience in producing bio-oils (circulating fluidized bed CFB reactor development) while UOP is contributing its expertise in developing hydrotreatment catalysts and reactors for the oil industry. Envergent is building a demonstration facility at the Tesoro refinery in Kapolei, Hawaii with the help of DOE’s US$25 m. The facility will process Ensyn RTP bio-oils and is expected to start operating in 2014. The plant aims to produce 4 barrels per day of gasoline diesel and jet fuel. This project is part of a larger vision to install 4 RTP bio-oil facilities and one central upgrading facility which will use UOP hydrotreating technology. Nine more new plants are being planned in Malaysia in order to use palm oil residues which according to recent estimates amount to about 150 million dry tonnes annually across the country (Aziz & Dato’ Leon, 2012). In October 2012, Ensyn forged a strategic alliance with the

Brazilian Pulp & Paper company Fibria Celulose S.A. (NYSE: FBR). The alliance includes a joint venture between the two companies as well as US$ 20 million equity investment in Ensyn Corporation by Fibria (Ensyn, 2013b).

KiOR is one of the Khosla Ventures-backed biofuel start-ups. In April 2011, the company filed for a $100 m initial public offering (IPO) with Credit Suisse, UBS and Goldman Sachs as underwriters (KiOR, 2013; Lane, 2013). The plant (capital cost of $190 million) could be considered the world's first, commercially operational, biomass derived, drop-in biofuel facility. The Columbus based facility has the capacity to process 500 ton per day (tpd) of wood (primarily yellow pine from the local wood basket) into 49.2 MLPY (13 MGPY) of liquid biofuels. A second, larger (3x) facility is being built in Natchez, which is projected to cost about $350m by the time it is complete. The company goal is to build a total of 5 commercial facilities at a total of $1 billion in investments. KiOR has indicated that they will commit $500 million while the state of Mississippi will commit $75m in interest-free loans (KiOR, 2013; Lane, 2013). KiOR's technology (as has been discussed previously) consists of catalytic pyrolysis in a Circulating Fluid Bed configuration followed by hydrotreatment to upgrade to transport fuel blendstock. The techno-economic analysis and the fact that the KiOR facility has been built in close proximity to a natural gas pipeline, imply that the strategy might be to use imported hydrogen and all extant biomass for power generation. Prioritizing power generation will likely provide the facility with high returns from electricity sales and high GHG emission saving per volume of biofuel produced (T. R. Brown et al., 2012; KiOR, 2013; Lane, 2013). The company claims that its drop-in biofuel results in a reduction of 80% GHG emissions when compared to petroleum fuels (KiOR, 2013). Recently (March 17, 2014), KiOR announced a net loss of USD $347.5 million for 2013 as well as bringing the Columbus facility to an idle state. The company also expressed concerns about whether it would be able to attract further investor funding and avoid bankruptcy. As KiOR was considered a leader in the commercialization of drop-in biofuels, this development is a concern for the drop-in biofuel sector. Major technical problems were listed as the main reasons for the company not being able to meet performance milestones (Lane, 2014).

There are a number of other pyrolysis diesel commercialization efforts underway in the USA (such as Anellotech, GTI's new IH_2 technology) and Europe (KIT and BTG). However, most of these facilities are at the less-than 25 tpd scale (Meier et al., 2013).

In summary, the production of bio-oil intermediates via pyrolysis is relatively inexpensive and it can be decoupled from the subsequent upgrading steps thus facilitating feedstock delivery logistics (e.g. bio-oil is more energy dense and should be cheaper to transport than the original biomass feedstock). However, the resulting bio-oil is physicochemically disparate from petroleum liquids and thus the greatest costs and technological challenges of this platform are in upgrading the bio-oil to petroleum-equivalent transport fuels. Upgrading costs are estimated to account for about two-thirds of the capital expenses and about half the operating expenses. Hydroprocessing has many advantages as an upgrading technology, not least among which is that it can efficiently elevate the H/C ratio of the bio-oil prior to final conversion to transport fuels. Oil refinery FCC and hydrotreating units can be leveraged by bio-oil upgrading processes, although the insertion of insufficiently deoxygenated bio-oils poses numerous technical challenges (coking, catalyst deactivation, corrosion) and will cause a reduction in the H/C ratio of the refinery's products. However, the significant capital cost savings as well as some synergistic benefits (coking and viscosity reduction) warrant the continued interest in co-processing partially upgraded bio-oils with petroleum feeds inside oil refineries. Recent work in the pyrolysis area has suggested that the greatest benefits in upgrading bio-oils are not necessarily in maximizing oxygen removal but rather in first removing the most unstable oxygenated compounds by way of a mild hydrotreatment step. The technical area that could have the biggest impact on facilitating improved bio-oil upgrading, as implied by the assumptions in the various techno-economic models, is increasing the selectivity and lifespan of the hydrotreating catalysts that are used.

3.7 Gasification

Gasification, as the name suggests, is the conversion of solid biomass to a gas, with small amounts of liquids and char also co-produced. The process is typically conducted under conditions of high temperature and pressure using air, oxygen or steam as a gasifying agent to convert biomass to a low to medium energy gas known as producer gas or "syngas". Unlike raw biomass, syngas is relatively homogeneous and it is comprised of mostly hydrogen and carbon monoxide as well as small amounts of CO_2, H_2O and CH_4. When air is used as a gasifying agent, 50 wt% of the gas is nitrogen and thus air gasification is only appropriate for energy applications while oxygen and steam gasification are appropriate for the production of synthesis gas. The exact composition of the gas will vary depending on the composition of the feedstock but mostly on the gasification process conditions that are used. Although syngas can be used for the same applications as natural gas, it is a more oxygenated gaseous fuel with less than half the energy density of natural gas (natural gas contains about 36 MJ/Nm^3 whereas biomass syngas contains only about 4-18 MJ/Nm^3 (4 MJ/Nm^3 for air blown and 18 MJ/Nm^3 for steam blown gasification (Bain, 1992)). The quality of a syngas for synthesis applications is often measured by its H_2/CO ratio. A higher ratio typically indicates a greater energy density and therefore better potential for upgrading to drop-in biofuels. In contrast to combustion, which results in the conversion of biomass to thermal energy and fully oxidised gases (CO_2 and H_2O), gasification takes place under conditions where oxygen is limited. Therefore, some of the biomass energy is retained in the partially oxidized gaseous product.

Gasification is not a new process as it has been used since the early years of industrialization. Between the 1940s and 1970s, in most European countries and the US, "town gas" produced by the gasification of coal was used to fuel street lamps and cooking stoves. During the Second World War, in Germany coal syngas was catalytically condensed to liquid transportation fuels (widely known as the Fischer-Tropsch process). As mentioned previously, the South African company Sasol uses a variation of this technology to produce about 160,000 barrels per day of coal-derived diesel fuels and chemicals.

3.7.1 Gasification process

The gasification of biomass can generally be viewed as proceeding in four main sequential steps:

1. Drying: moisture is removed from the biomass particles
2. Devolatilization: as the dry particle is heated, it devolatilizes and the resulting volatiles exit the particle and come into contact with oxygen and other gases in the reactor.
    a. This devolatilization step is also known as the "pyrolysis" step (Bain and Broer, 2011)
3. Combustion: After contacting oxygen (O_2 or steam), the volatilized carbon is converted to carbon oxide gases (CO and CO_2). An exothermic reaction occurs which, if sufficient oxygen is present, provides enough heat for the last reduction step.
4. Reduction: This step converts the carbon and carbon oxides to the main components of syngas, i.e. H_2 and CO. Four main reactions take place during this step:
    - ○ Water Gas $C + H_2O \rightarrow CO + H_2$

- Boudouard $C + CO_2 \rightarrow 2CO$
- Water-Gas-Shift $CO + H_2O \rightarrow CO_2 + H_2$
- Methanation $CO + 3H_2 \rightarrow CH_4 + H_2O$

The chemical composition of the produced syngas depends on the relative prevalence of the reactions taking place at the reduction step of gasification. For example when adding steam to the reactor, the water-gas-shift (WGS) reaction is favoured and more hydrogen is generated which boosts the H_2/CO ratio of the resulting syngas. Alternatively, when hydrogen is fed to the reactor, the methanation reaction is favoured and the generated syngas is rich in CH_4 (useful for the production of synthetic natural gas) (Bain & Broer, 2011).

3.7.2 Gasifier types

As was described previously for pyrolysis, gasification relies on reactor configurations that maximize heat transfer through the biomass particles. Although the reactors used for gasification are similar to the ones used for pyrolysis, they typically operate at higher temperatures (800 – 1000 °C) and pressures from 1 to 50 bar). The three types of reactors that are best suited for biomass gasification are: fixed bed, fluidized bed and entrained flow (Swanson et al., 2010). While gasification reactors can be both top- and bottom-fed, the following discussion will assume top-fed reactors in order to describe and compare them on a consistent basis. The fixed bed reactor is the simplest and most established design and it tends to be found in older, smaller scale systems. In these reactors the biomass is fed from the top of the reactor to form a bed close to the bottom of the reactor. To enhance the biomass particles gasification, air (or pure oxygen) is blown through the biomass bed. This creates distinct temperature zones within the reactor with the lower temperature zones closer to the top of the reactor where the biomass is dried and devolatilized soon after it enters the reactor. The bottom of the reactor, where the air is blown, is the hottest section of the reactor and this is where the biomass gets partially oxidized (combustion) before the resulting gases undergo reduction. The gasifying biomass bed sits on top of a moving grate which removes the residual ash and char solids out the bottom of the reactor vessel. The final gas mixture is usually recovered out of the side of the reactor. There are two types of fixed bed reactors and, depending on whether the gases are blowing countercurrent or concurrent to the biomass feed, they are called updraft or downdraft fixed bed reactors (see Figure 3-8). Fixed bed reactors are typically quite simple to build and operate. However, their use is limited by poor heat and mass transfers, mainly due to the formation of preferential channel flows within the fixed biomass bed (R. Swanson et al., 2010).

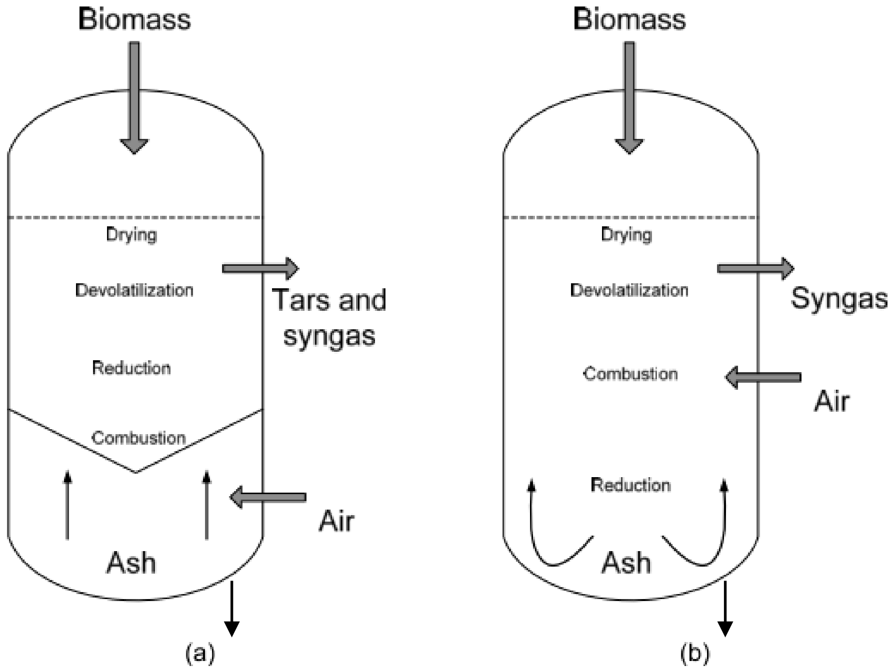


Figure 3-8: Schematic of updraft (a) and downdraft (b) fixed bed gasifiers

Source: (Swanson et al. 2010)

By increasing the volumetric gas flow of the air blown through the fixed bed, turbulence agitates the particles of the bed (thus ‘fluidizing’ the bed) and the reactor becomes a fluidized bed gasifier. In fluidized bed gasifiers the bed particles are composed of gasifying biomass as well as of very hot and small inert particles which greatly improve the heat transfer throughout the gasifying biomass particles. There are two types of fluidized bed reactors, the Bubbling Fluidized Bed (BFB) and the Circulating Fluidized Bed (CFB) reactors. These types of reactors have been described earlier in the pyrolysis section. The difference is that, for effective gasification, the operating temperatures are much higher than are used for pyrolysis since the objective is to maximize production of permanent gases as opposed to condensable vapors. As is the case with pyrolysis, there are cyclones at the exit of the reactors in order to capture fine char particles that are entrained in the produced gases. Compared to fixed beds, fluidized beds generally have higher carbon conversion efficiencies and they tend to be more easily scaled-up (Bain & Broer, 2011; R. Swanson et al., 2010).

An entrained flow reactor is another type of gasifier where biomass is fed in the form of very fine particles (or atomized pyrolysis liquids) which are entrained into a high-velocity stream of air or oxygen (Bain & Broer, 2011). These streams are fed from the top of the hot reactor where the temperatures are high enough (about 1300 °C) that the entrained biomass particles are gasified before they reach the bottom of the reactor. This temperature is also high enough to melt most of the ash components of the biomass which form a liquid slag that flows down the inside walls of the reactor. This effectively protects the metallurgy from corrosive gases. The liquid slag flows to the bottom of the reactor where it is collected. Limestone is often added as a fluxing material to help form the liquid slug although, for alkali ash-containing herbaceous biomass, this may not be necessary (Bain & Broer, 2011; R. Swanson et al., 2010). Entrained flow (EF) gasifiers have been developed for use with coal by companies such as Shell, Texaco, Conoco Philips (Bain & Broer, 2011) and, so far, they have had limited application to biomass. One of the reasons is that feed preparation costs are much higher for biomass than they are for coal and their use also involves extensive drying and size reduction (<1mm) (R. Swanson et al., 2010). Drying is important as water can act as a heat sink and compromise control over temperature levels in the reactor. Size reduction is also important, particularly when no bed is formed and the residence time is as short as the time it takes for a particle to fall the length of the reaction zone. An alternative strategy to preprocessing biomass is the approach taken by companies such as Germany's KIT ("bioliq" technology). They propose feeding EF gasifiers with pyrolysis slurries as opposed to comminuted biomass. The company claims that this approach results in an improved feed for entrained flow gasifiers and also offers the option to decouple the conversion of biomass to bioslurries from the central gasification plant in terms of space, time and synchronization. This concept is briefly described in the pyrolysis section and it is schematically represented in Figure 3-9.

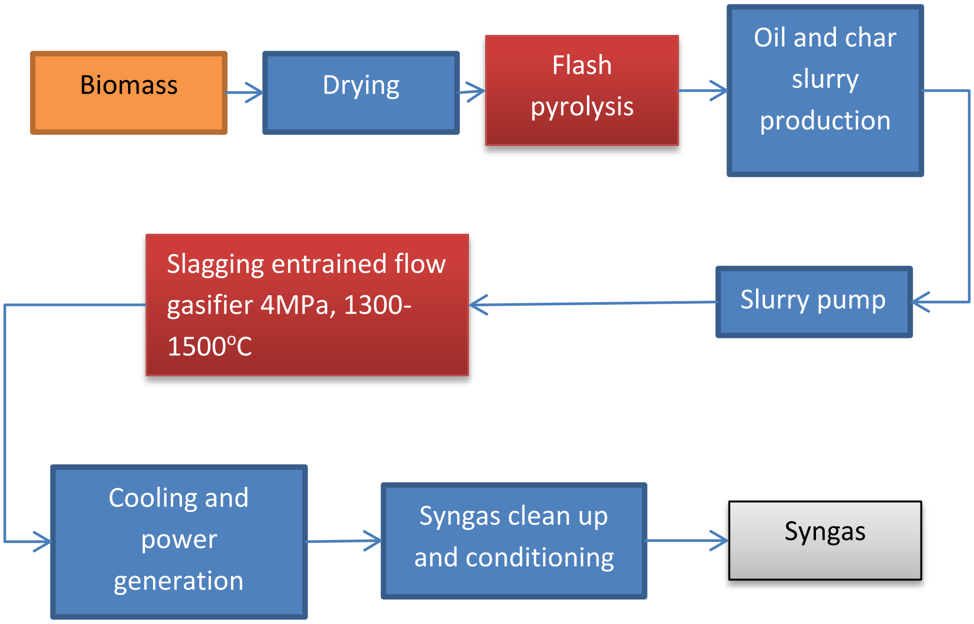


Figure 3-9: Schematic of a biomass pretreatment via fast pyrolysis followed by an entrained-flow gasifier
Source: (A. van der Drift et al., 2004)

3.7.3 Syngas cleanup

The "clean up" of syngas is an evolving area of gasification (Dayton et al., 2011). Raw biomass syngas (also termed "biosyncrude") is recovered along with numerous impurities such as small char particles, tar vapors as well as volatile nitrogen and sulfur compounds. Char is entrained in the syngas and it is comprised of non-volatilized biomass as well as ash. The tar component is formed during the polymerization of biomass vapors and it can stick to reactor walls and catalysts causing clogging and deactivation. (As described previously; coke formation during pyrolysis oil production). Sulfur and nitrogen gases are derived directly from the biomass feed and those components are deleterious to downstream processes as they cause NOx SOx emissions upon combustion and they can also "poison" the Fischer-Tropsch catalysts (Dayton et al., 2011).

When the syngas is simply burned, these impurities are of lesser concern. However, when the syngas is used for more "sophisticated" applications such as internal combustion (IC) engines, gas turbines and Fischer-Tropsch (FT) synthesis, exhaustive cleanup is required. For internal combustion (IC) engines to operate effectively, particulates, tars and acids must all be at concentrations below 50 mg/Nm^3. For FT synthesis the particulate matter must be less than 0.03 mg/Nm^3. Unfortunately, for most raw syngases the contaminant concentrations typically exceed these limits by some orders of magnitude (see Table 3-6). This is especially true for fluidized bed gasifiers which, when compared to entrained flow gasifiers, operate at lower temperatures and circulate the gas through beds that are rich in fine char solids. As summarised in Table 3-6, a Circulated Fluid Bed (CFB)-derived syngas typically contains about 10,000 mg/Nm^3 of either char or tar particles, Bubbling Fluidised Bed (BFB) up to 43,000 mg/Nm^3 and downdraft fixed beds as much as 30,000 mg/Nm^3.

Table 3-6: Char and Tar content of biomass syngas from different reactors

Reactor type	Tar content (mg/Nm^3)	Char content (mg/Nm^3)
Updraft	50,000	nd
Downdraft	1,000	9,300 – 30,000
BFB	10,000	1,040 – 43,610
CFB	10,000	1,700-13,100
Specification for IC engines	<50	<50
Specification for FT synthesis	<0.02	< 0.02

Source: Data from (Bain & Broer, 2011; Carpenter et al., 2010; A. Van Der Drift et al., 2001; Meehan, 2009; Milne et al., 1998; Wander et al., 2004)

There are various ways to reduce the accumulation of these contaminants during gasification but they all require trade-offs. For example, at high gasification temperatures (e.g. >1200 °C) the formation of char and tar is reduced and the production of permanent gases is favoured. However, high temperature gasifiers are costly to build and operate. Similarly the introduction of steam has been shown to reduce the buildup of tar by reforming it to H_2 and CO. However, steam can act as a heat sink and it can significantly compromise the heat balance and overall efficiency of the gasification plant. Higher air to fuel ratios cause more oxidative conditions and they are beneficial in reducing the char and tar content of syngas but these conditions favour more full oxidation of gases to CO_2, thus recovering less combustible gases such as CO. Pure oxygen can be used instead of air in order to improve the specificity of the gasification reaction while also reducing the nitrogen contaminants coming from atmospheric air. However, the isolation and purification of oxygen weighs significantly on the economics of the facility (Bain & Broer, 2011; Muellerlanger et al., 2007; R. Swanson et al., 2010). Clearly, a compromise has to be found between these trade-offs in order to strike the optimal quality syngas for each given application.

The ash content, another significant contamination in syngas, is largely dependent on the amount of inorganics in the initial biomass. As noted earlier, herbaceous and agricultural biomass tends to be higher in inorganics than wood derived biomass. Alkaline components of ash such as calcium and potassium are particularly undesirable since they are known to lower the overall melting point of biomass, thus promoting slagging at lower temperatures (Hayes, 2013; R. Swanson et al., 2010).

Even if the process is optimised to minimize syngas impurities by adjusting gasification conditions, some cleanup is always needed. Syngas cleanup is one of the most expensive steps of a gasification biofuel platform. This typically involves various sequential steps that follow the gasification reactor including gas cyclone removal of most of the particulate matter above 10 µm and further removal of the smaller particles by more costly methods such as wet scrubbers or electrostatic precipitators (ESPs) (Dayton et al., 2011).

Tars are particularly problematic for Fischer-Tropsch (FT) fuel synthesis as they can irreversibly deactivate the catalysts downstream. One of the reasons for the recent Range Fuels biofuel facility closure was that the gasification operations resulted in too much of a tar build up (Hayes, 2013; Lane, 2012)). Tars are typically removed by one of the two main strategies of wet scrubbing at low temperatures or cracking at high temperatures. Wet scrubbing involves significant cooling of the gas as well as the generation of wastewater streams that are contaminated with potentially toxic tar components which must be treated prior to disposal. As hot gas cleaning occurs at temperatures higher than the gasification temperatures (e.g. 1200 °C) the added energy requirements, including the need to extensively cool the gas down prior to FT processing, can compromise a facility's economic viability (G. S. Speight & Ancheyta, 2007). Another cleanup option that has attracted research attention lately is the catalytic conversion of the tars in the gasifier outlet via steam reforming (Bain et al., 2014). The primary objective of tar control strategies is to either eliminate tars or to at least bring their dew point below the operating temperatures of the ensuing processes such that tar deposition is minimized. For more detail on the various syngas cleanup and conditioning technologies proposed, the reader is referred to a recent comprehensive review by Dayton et al. (2011).

Gasification yields tend to be lower than desired as much of the original carbon is oxidized to generate heat. Only about half of the carbon is converted to usable CO while the other half is oxidized to CO_2 (Hayes, 2013). However, it has been recently demonstrated by researchers at the Universities of Massachusetts and Minnesota that the addition of methane to the gasification reaction can substantially enhance gasification yields. This is thought to be a result of methane having a higher H/C ratio of 4, thus, the hydrogen from the methane reacts with the CO_2 to form H_2O and CO (Hayes, 2013).

3.7.4 Syngas uses

The uses of syngas are similar to those of bio-oil in that they are mostly used for power and heat. The technological challenges in the utilization of syngas can be ranked as; burners < gas internal combustion (IC) engines < synthesis to biofuels and chemicals. Burners are robust but do not provide as much energy efficiency as IC engines. Synthesis has, by far, the lowest energy efficiency but it yields high value-added biofuels and chemicals. A popular power generation configuration for gasification facilities is the integrated gasification combined cycle (IGCC). This configuration is designed for maximizing power generation and it utilizes a high-efficiency gas turbine to burn the clean gas while the exhaust heat in the flue gases is recovered through a steam turbine that contributes additional power generation (Craig & Mann, 1996).

For those IGCC engines which combine heat and power recovery, power efficiencies of 35-40% have been reported and it has been suggested that efficiencies of 50% can be achieved (Craig & Mann, 1996). Although there are numerous commercial facilities generating heat and/or power from biomass gasification most of these facilities are smaller scale, in the range of 2 to 50 MW. According to the US National Energy Technology Laboratory (NETL) world gasification database, a total of 9 biomass gasification plants were operational in 2010, generating a total of 373 MW_{th} (NETL, 2013). This does not include the contributions of more recent biomass gasification plants or co-gasification facilities.

3.8 Syngas catalytic condensation for synthesis

As mentioned above, a higher-value application than just burning the syngas is to “condense” the gas to hydrocarbon liquids that can then be used for the synthesis of biofuels and chemicals (Dayton et al., 2011). This condensation has to be selective and produce the targeted hydrocarbons, thus, specialized catalysts must be employed. The types of fuels and chemicals that syngas can be condensed to are summarised in Figure 3-10. These catalytic condensation reactions convert the syngas molecules (H_2 and CO) into larger molecules to produce energy dense liquids described in figure 4-3. The choice of targeted chemicals and the efficiency of each of the conversions depend on the choice of catalyst, condensation conditions used and the H to CO ratio. More important than all of the above aspects is the level of contaminants in syngas which must be very low and preferably less than about 10 mg/Nm^3. Sulfur in particular is "poisonous" to FT catalysts and must be at concentrations that do not exceed 2 mg/Nm^3 (Dayton et al., 2011). The syngas catalytic condensation pathways that are most relevant to drop-in transport biofuels are the methanol to gasoline (MTG) and Fischer-Tropsch (FT) processes.

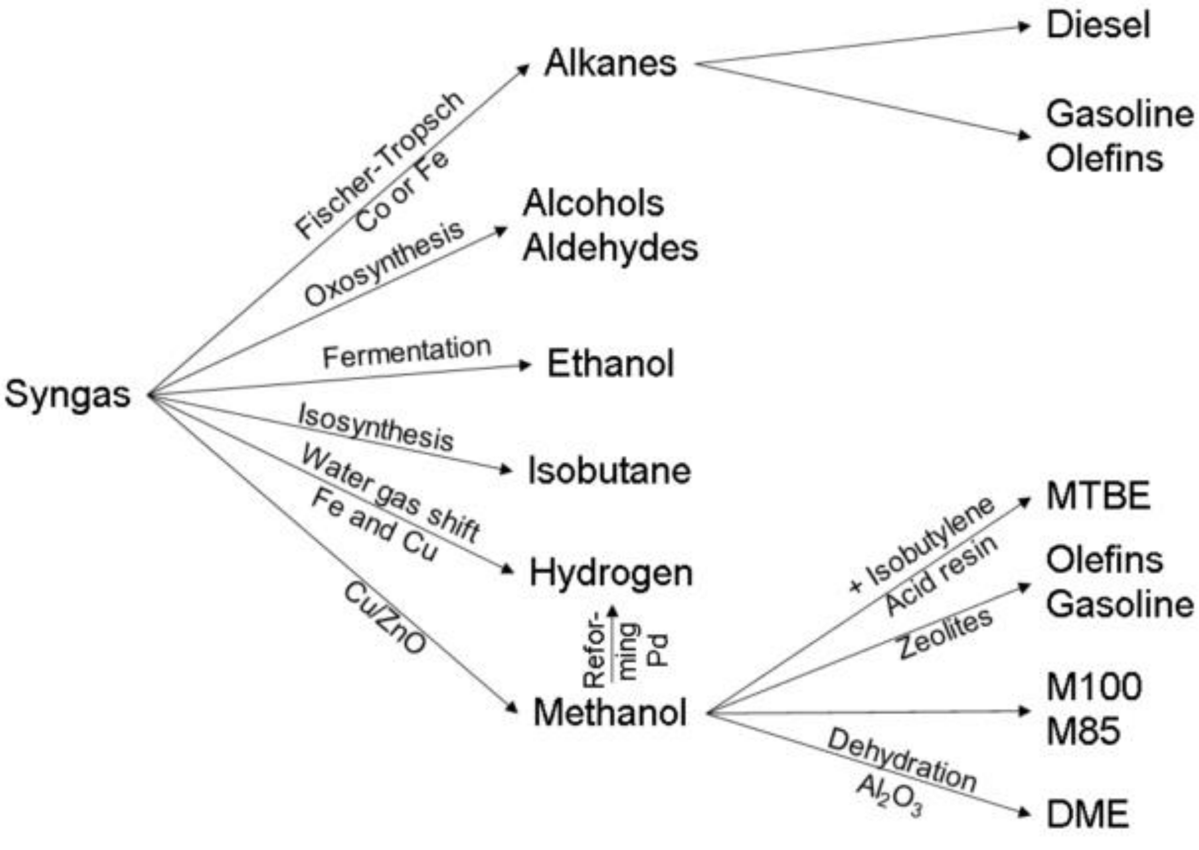


Figure 3-10: Main Syngas Conversion Pathways
Source: (Huber et al., 2006)

3.8.1 Methanol to Gasoline process

The first step in this process involves the exothermic conversion of the syngas to methanol, which is a commercial technology. As long as the syngas is pure and it contains the required ratio of hydrogen to carbon monoxide, the conversion takes place in the presence of relatively inexpensive $Cu/ZnO/Al_2O_3$

catalysts at temperatures that range between 220-275 °C and pressures of 50-100 bar. Under these conditions the catalyst can last as long as 2-5 years (Swanson et al., 2010). Although the *per pass* conversion efficiency is typically about 25%, Wender (1996) has shown that up to 99% conversion can be achieved with gas recycle. The core reaction of this conversion is the reaction of one molecule of CO with two molecules of H_2 to form one molecule of methanol.

$CO + 2H_2 \rightarrow CH_3OH$

Methanol is a liquid fuel but not a drop-in transportation fuel. However, it can be turned into a drop-in gasoline equivalent using the methanol-to-gasoline process (MTG). This process was first developed and patented by Mobil Oil Corporation (now Exxon Mobil) in the 1970s. The process entails two steps. In the first step, methanol is dehydrated over an alumina catalyst at 300 °C and 27 bar, to form a mixture of dimethyl-ether (DME), methanol and water. In the second stage, this mixture reacts over a zeolite catalyst (359°C and 20 bar) and is further dehydrated to gasoline range hydrocarbons (44 wt%) and water (56 wt%) (Phillips et al., 2011; R. Swanson et al., 2010).

The efficiency of the process can be improved by stopping the reaction after the first stage since DME can be used as a truck fuel (high cetane number). Dimethyl-ether is a gas at room temperature so it would have to be compressed before it is fed to an automobile engine (Phillips et al., 2011; R. Swanson et al., 2010).

In the 1980's, Mobil used the MTG process to run a commercial plant in New Zealand of about 14,500 barrels per day of gasoline that was marketed as "M-gasoline". The facility involved multiple reactors in order to dissipate the heat that was generated from the highly exothermic reactions. Multiple reactors also allowed for more regular cleanup of the catalyst beds. The facility was wound down in 1997 because of variable crude oil and natural gas prices and because of ownership issues of the facility.

3.8.2 Fischer-Tropsch process

In 1923 Franz Fischer and Hans Tropsch identified catalysts that can condense carbonaceous gases to alcohols. The process was patented and named "synthol". The main motivation for this research was the scarcity of petroleum fuel in post-world war one Germany. The process was further developed to produce non-oxygenated liquid hydrocarbons as feedstocks for fuels and chemicals using improved catalyst formulations. This process became known as Fischer-Tropsch Synthesis (FTS). The process has undergone continued investigation and optimisation and it has since been adapted for a diversity of feedstocks including biomass. More than 4000 publications have been dedicated to the FTS process and there is a specialized website www.fischer-tropsch.org which focuses on the history, research and industry developments around this pivotal industrial technology. Fischer-Tropsch Synthesis can use syngas derived from any source including biomass, coal or natural gas and it can produce precursors for a wide range of drop-in chemicals and fuels (see Figure 3-10). As long as the syngas is treated and conditioned properly and there is a good H_2/CO ratio, functional and chemical equivalence can be achieved between the syngas derived from these disparate feedstocks. Although with a biomass feedstock it is more difficult to achieve the same level of syngas purity as with natural gas, a near chemical equivalence can be reached. Thus it is possible to scale-up biomass based FT processes by leveraging the know-how and facilities of existing natural gas and coal gasification FTS plants. The FTS reaction takes place over specialized catalysts and, as is the case with the previously described MTG process, FT is essentially a dehydration reaction that it is highly exothermic (R. Swanson et al., 2010). The basic reaction is represented in the equation below:

$CO + 2.1\ H_2 \rightarrow -(CH_2)- + H_2O$ (delta Hr (227 °C) - 165 kJ/mol

The catalyst surface acts as an “anchor” upon which the carbon monoxide and hydrogen adsorb (see Figure 3-11 below). The chain growth begins once the carbon monoxide has been broken down, enabling the coupling of carbon and hydrogen and the separation of oxygen (which leaves as a water molecule - dehydration). Chain growth continues by adding further CO and H_2 until the newly formed hydrocarbon molecule is desorbed from the catalyst surface.

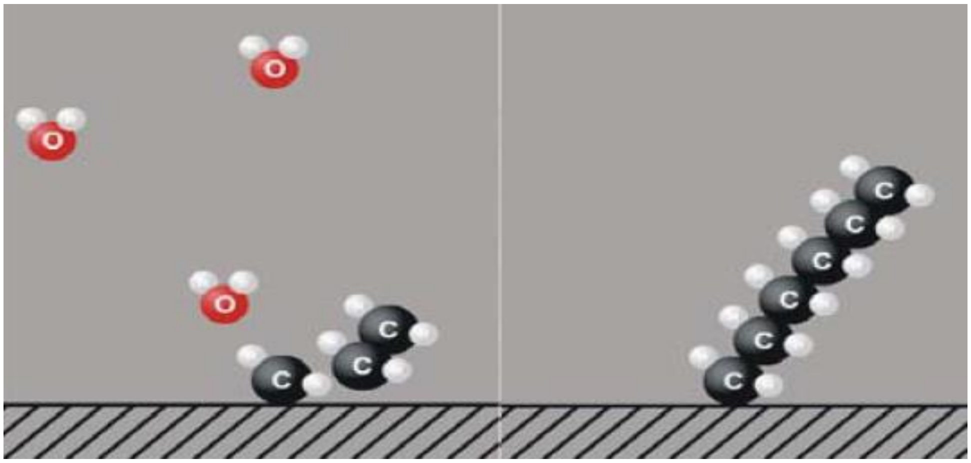


Figure 3-11: Simplified representation of Fischer-Tropsch chain growth on a catalyst surface
Source: (Blades et al., 2005)

The pressures used during the FT process range from 10-to-40 bar and the nature of the hydrocarbons produced is influenced by the temperatures and catalysts used. Higher temperatures (300 – 350 °C) and iron catalysts produce gasoline, while lower temperatures (200 -240 °C) and cobalt catalysts produce diesel and waxes. The distribution of heavier and lighter hydrocarbons can be estimated by employing the Anderson-Schulz-Flory probability model in which longer chain hydrocarbons form as the temperature decreases. The ratio of H_2 to CO also influences the product distribution with high ratios favouring the formation of lighter hydrocarbons. Iron catalysts favour the Water Gas Shift (WGS) reaction such that the H_2/CO ratio is increasing. With cobalt catalysts, WGS is not favoured and it has to be performed separately in order to achieve the desired high H_2/CO ratio (E4tech, 2009). In contrast to pyrolysis, the composition of the FT liquid product can usually be predicted from the composition of the syngas and the reaction conditions used (Dayton et al., 2011). By contrast, as discussed earlier in the pyrolysis section, the reaction kinetics involved in upgrading pyrolysis oils cannot be readily modelled, primarily because the composition of the bio-oil itself is very complex and hard to determine analytically. As the liquid hydrocarbons produced from FTS are very low in aromatics and transport fuel blends usually require some amount of aromatic content, they typically have to be blended with aromatic petroleum cuts (Bauen et al., 2009).

The choice of catalyst used is important in FTS. As was reported earlier for bio-oil upgrading, the group VIII transition metal oxides are regarded as good CO hydrogenation catalysts, based on the three main performance characteristics of lifetime, activity and selectivity. Lifetime largely depends on the quality of the syngas. Prime quality natural gas-derived syngas catalysts have been reported to last up to 3-5 years. The most active metal catalysts for FTS, ranked in order of activity, are Ru>Fe>Ni>Co. Ruthenium catalysts are the most active, (as it was for pyrolysis oil upgrading) but they are considerably more expensive than the iron catalysts (IndexMundi, 2013) and (as noted earlier) about 100 times more expensive than Nickel and Cobalt. Nickel is a methanation catalyst and does not have the broad applicability in FTS that other FT catalysts have. Iron has WGS activity but it is an acidic catalyst and it promotes carbon deposition and coking resulting in lower yields and reduced catalyst lifetimes as seen in the pyrolysis oil upgrading section. Cobalt is more alkaline and although about 200 times more expensive it produces higher yields and provides for longer catalyst lifetimes. However, it has low WGS activity and needs a separate WGS step to boost the H/C ratio of the feed to >2. Finally, as well as being highly active, a catalyst must also be selective in promoting the reactions that are most desirable. For example, Iron/manganese/potassium catalysts have shown selectivity for C_2-C_4 olefins as high as 90% (Bain & Broer, 2011).

It is also recognised that temperature control is crucial for effective Fischer-Tropsch synthesis (FTS). The FTS reaction is so exothermic that the heat generated can irreversibly deactivate the catalyst if it is not dissipated. Another reason why FTS temperatures must be kept under tight control is that, as the temperature approaches 400 °C, the methanation reaction is favoured. However, this is only desirable when the target of the conversion is to make synthetic natural gas (SNG). Therefore FT synthesis reactor design must be such that the heat from the reactors can be readily dissipated. Various reactor designs such as tubular and slurry-based have been developed for this purpose (R. Swanson et al., 2010).

Overall, the FTS-from-biomass process involves four major steps (Figure 3-12). These steps are; a) syngas production, b) syngas cleanup, c) FT synthesis and, d) product upgrading. As is apparent from the schematic in Figure 3-12, each one of these steps is performed at different temperature and pressure conditions. From an energy balance and economic viability perspective, the high pressure and temperature fluctuations throughout the process are of some concern. The high pressure consumes energy and it also results in greater capital expenditures as the gas compressors needed to feed the pressurized reactor vessels are among the most costly pieces of equipment in a gasification plant (see subsequent techno-economic section). Similarly, heating and cooling cycles incur undesirable energy "losses". If the syngas is cleaned of tars through thermal cracking at >1300 °C, it then has to be cooled down to about 300 °C and pressurized to >30 bar before it enters the FT synthesis reactors. If, on the other hand, the tars are removed by way of quenching, they have to be cooled down before they enter the wet scrubbers and again heated and pressurized before they enter the FT synthesis reactors. All of these heat-cool and compression operations are costly and they add significantly to the capital cost of biomass to liquids facilities. There is ongoing research and development to improve gasification platforms so as to minimize these costly fluctuations in temperature and pressure.

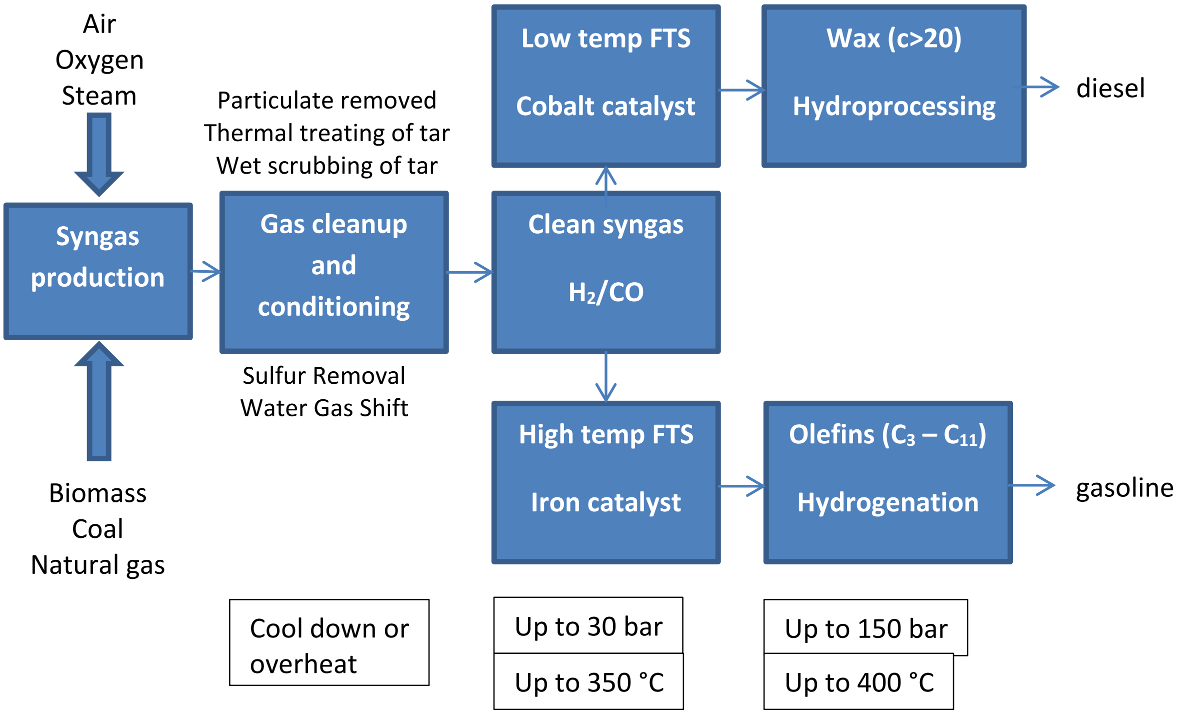


Figure 3-12: Simplified schematic of the overall biomass gasification to FT diesel and gasoline process

Source: Adapted from (Bain & Broer, 2011)

The final stage of the FTS process (Figure 3-12) is the hydroprocessing of the resulting hydrocarbon FT liquids. This step can be viewed as equivalent to the previously described processing of highly deoxygenated HDO bio-oil. These FT liquids are essentially oxygen-free and they can be easily upgraded (hydroprocessed) inside an existing petroleum refinery. For example, the Karlsruhe Institute of Technology (KIT) has proposed the co-location of its bioliq® process (a "hub and spoke" pyrolysis-then-gasification approach) with an oil refinery (Dahmen et al., 2012). The core gasification-FT facility would be located next to a petroleum refinery where the last hydroprocessing step would be performed without the need to build separate hydroprocessing reactors.

The Fischer-Tropsch process is currently being operated at an industrial scale by two main fossil fuel companies in South Africa (Sasol) and in Malaysia and Qatar (Shell). The world's first commercial-scale gas-to-liquid (GTL) plant based on FT synthesis was completed in 1993 by Shell in Bintulu, Malaysia and continues producing about 15,000 barrels per day (bpd). The previously discussed Sasol plant produces

160,000 barrels of FT-diesel per day from coal syngas to provide 41% of South Africa's transport fuel requirements. Sasol has also converted one of its coal-to-liquid (CTL) facilities to accept natural gas from Mozambique. In December 2006, Sasol started up its 34,000 bpd Oryx gas-to-liquid (GTL) facility in Qatar and today this facility produces more than its design capacity. Sasol is using the experience gained from building and operating this facility to expand operations in other countries which are endowed with significant natural gas reserves such as Nigeria, Uzbekistan, the USA and Canada (Sasol, 2013).

The world's largest GtL facility was built by Shell in collaboration with Qatar Petroleum. It has a capacity of 140,000 bpd and it has been fully operational since 2012. Construction of this facility began in 2007 with an original timescale of 2 years and a budget of $5b. Five years later the facility was finally completed but at a final cost of about $19 b (Platts, 2013). There were several difficulties encountered with the conversion of natural gas to liquid hydrocarbons and some problem areas have yet to be fully resolved. Thus, it is likely that a biomass FT gasification process will encounter similar or even more challenging problems. It has been suggested that when a biomass-to-liquids process is compared to a GtL plant the main challenges will be: processing a more heterogeneous biomass feedstock, producing a lower quality syngas and the smaller scale and feedstock availability risks (Hileman et al., 2009).

3.9 Syngas upgrading techno-economic considerations

The cost of gasification-derived biofuels can be estimated quite accurately since the processes are based on established industrial processes in the coal gasification industry. A recent techno-economic study by ISU/ConocoPhillips/NREL (Swanson et al., 2010) has estimated the cost of gasoline produced from FT conversion of biomass syngas. The study assumed a corn stover cost of $83/odt, a 2000 tpd facility and a 10% ROI and compared two scenarios of: a) low temperature using a fluidised bed gasifier at 870 °C, and b) high temperature using an entrained flow gasifier at 1300 °C. Both scenarios were followed by Fischer-Tropsch synthesis and hydroprocessing of the resulting FT liquids. Some of the results for both the high temperature (FTHT) and the low temperature (HTLT) scenarios are summarised in Swanson et al., (2010). Although the FTHT scenario had 20% higher capital costs, its minimum fuel selling price (MFSP) was about 10% lower. This was achieved because of the much higher conversion efficiency of the high temperature approach. The highest sensitivities of the FTHT scenario are mainly the capital costs, feedstock costs and compressor capacity. A 30% increase in capital costs resulted in an 18% increase in MFSP. An increase in the feedstock cost from 75 to $100/odt, resulted in a MFSP of 10%

increase. An increase in the compressor install factor from 1.2 to 3 further increased the MFSP by 17% (Swanson et al., 2010).

Table 3-7: Techno-economic studies on gasification-derived biofuels
(plant size: 2000 tpd of dry basis biomass, cost basis year: 2007)

	2010 NREL (FTHT)	**2010 NREL (FTLT)**
Facility fuel output (MGPY)	39.8	32.3
(MLPY)	(150)	(122)
Fuel yield (gasoline gallon Equivalents/metric tonne)	61	47.2
(gasoline L Equivalents/metric tonne)	(231)	(179)
Total Project Investment (TPI, million $)	606	498
(equipment only, million $)	(309)	(254)
TPI for Gasifier (million $)	68	28
TPI for Syngas cleanup & conditioning	34	29
TPI fuel synthesis	49	59
TPI Hydroprocessing	33	30
TPI Power generation	46	39
Transportation fuel MFSP (Minimum Fuel Selling Price ($/gal)	4.27	4.83
($/L)	(1.13)	(1.28)
($/GJ)	(31.4)	(35.5)
MFSP Feedstock	28.9%	32.9%
MFSP Capital Depreciation	14.8%	13.9%
Feedstock cost ($/MT)	**75**	**75**

Source: (Swanson et al., 2010)

Overall, the estimated MFSP and capital costs for both low and high temperature scenarios are high and they range between $4.3 and $4.8/gal ($1.1-1.3/L or $31-36/GJ), and between $500 and $600 (TPI) million respectively. These costs represent mature facilities while pioneer facilities were estimated to have about twice the TPI capital cost ($1400 million for the high temperature scenario and 830 million for the low temperature scenario). These costs are double the values estimated for pyrolysis, as discussed earlier. However, a direct comparison is difficult to make, both because of the known disparities in assumptions and costing of these types of analyses and also because of technological maturity differences. Despite its high apparent cost, the gasification platform can be viewed as being more technologically mature than pyrolysis (especially when compared to the low maturity of pyrolysis oil upgrading technologies) and it has also leveraged know-how from industrial coal gasification. For example, the assumed catalyst lifespan in gasification is about 3 years, and it is more likely to be reached than the 1 year catalyst lifespan projected for pyrolysis oil upgrading as discussed in Section 3.5.

When the sensitivities of the pyrolysis and gasification analyses are compared, the biggest sensitivities for pyrolysis relate to yields, catalysts and hydrogen costs while for gasification they are the capital expenditure and the feedstock costs. Compared to pyrolysis, gasification is a high capital expense platform due to the higher operating temperatures that are needed, the complexity of the process, the multiple process steps and the requirement for various heat-cool and compression cycles. As gas compressors are very energy and capital-intensive the compressors accounted for about 18% of total equipment costs. The compressor capacity of a gasification facility is directly related to the process efficiency, thus the lower the *per pass* yield of a process, the more a compressor has to work to recycle the gas stream enough times until it has reacted fully.

When comparing gasification to pyrolysis facilities, hydroprocessing equipment (mainly used for cracking the heavy ends of FT liquids) usually represents a lower proportion of overall capital costs (see Table 3-7). The insertion of hydrogen into a gasification process contrasts with what was discussed earlier for pyrolysis. In gasification, unlike pyrolysis, there is usually minimal to no external hydrogen supply (except for some cases like the gasification platform of Sundrop Biofuels which uses natural gas-derived hydrogen inputs) and the biomass syngas itself is the source of the energy and hydrogen needed to reduce and deoxygenate carbohydrates to drop-in biofuel hydrocarbons.

Another recent NREL techno-economic study by Phillips et al. (2011) looked at a gasification biofuel platform based on the methanol-to-gasoline (MTG) process as opposed to the Fischer-Tropsch process. This study assumed a 2000 tpd facility with 10% ROI and a feedstock cost of around $56/odt (as compared to $83/odt in the FT studies). The results of the MTG study show that both the capital ($ 1.95/gal or 0.52/L) and operating costs ($199 m) were low compared to those calculated by Swanson et al. (2010) for the FT process. Although these two studies should not be directly compared, these low cost estimations for the MTG design case warrants further investigation as to whether the MTG approach is indeed a lower cost conversion process than Fischer-Tropsch for biomass-to-gasoline gasification platforms. The main sensitivities of the MTG design were the same as those for the FT designs with capital cost showing the greatest sensitivity.

As the capital cost showed the greatest sensitivity for the gasification platform, it is not surprising that large scale facilities are projected to reduce the high MFSP of gasification biofuels. It has been suggested that a 500 MW_{th}, facility, or one with 2000 tpd of feed or producing 95 MLPY (25 MGPY) of biofuel, is the minimum scale at which a biomass FT facility can be viable (Hayes, 2013; Chemrec, 2012; NNFCC, 2009). This would not be considered to be a large facility when compared to the currently operating fossil FT facilities of Sasol and Shell. (Table 3-8 provides a direct comparison of the scale of these facilities).

Table 3-8: Scale of selected GtL and BtL facilities

Technology	Facility	Scale MLPY(MGPY)
Biomass (Corn Stover) gasification (2000 tpd)	ISU/COP/NREL techno-economic analysis	133 (35)
Coal gasification	Sasol, Secunda, South Africa	6,250 (1,650)
GTL (gas to liquids)	Pearl GTL, Shell, Natural gas, Qatar	15,900 (4,200)

Source: Company websites and (R. M. Swanson et al., 2010)

What has been modelled to represent a full scale, biomass-to-biofuel facility is at least 50 times smaller than the current commercial Sasol CtL (coal to liquid) main gasification facility and even smaller than Shell's Pearl GtL (gas-to-liquids) facility. As noted, the scale of a biomass facility will likely be limited by its access to feedstock and thus a larger scale facility will be challenged to reach the scale of the fossil based facilities which utilise denser and more transportable feedstocks.

Although gasification is generally viewed as a process requiring large scale facilities to be more economically attractive, some technology providers have recently advocated the construction of smaller plants. For example, the company Velocys has built small scale gas conversion facilities to liquefy the flair gas from ocean oil rigs. Leveraging on this experience, the company is now trying to commercialize a biosyngas-FT liquids platform based on a microchannel reactor design which can be applied to small scale biomass gasification platforms (around 300-500 tpd). Velocys is also providing the upgrading technology for *Solena Fuels*, a FT-biofuel company (Velocys, 2014).

3.10 Progress in the commercialization of biomass gasification and fuel synthesis

Currently there are various commercial-scale gasification facilities that are either operational, under construction or in the planning stages. While most of these facilities have been built for heat and power generation, there are several that hope to also manufacture liquid biofuels. There have been and will continue to be, valuable lessons learned from the more established, commercial heat and power-generating gasification facilities. Some of these facilities are reviewed below and are listed according to gasifier type and technology provider.

3.10.1 Fixed Bed gasifiers

As discussed earlier, fixed bed gasifiers are mostly suitable for small scale applications and are not ideally suited for drop-in biofuel synthesis. Updraft gasifiers are less favoured for drop-in biofuel synthesis as they typically produce a tar-rich syngas (see Table 3-6). However, there are various technology developers that are trying to commercialize updraft gasifiers at scales of 2-40 MW_{th} for heat and power applications. An example of such a facility is the newly completed (2012) ***Nexterra Inc.*** 2 MW_e updraft gasifier located on the Vancouver campus of the University of British Columbia (www.nexterra.com). These types of gasifiers are best suited for local small scale CHP applications. Although many useful lessons can be learned from these facilities, their commercial applications are not reviewed in detail.

3.10.2 Bubbling Fluidized Bed facilities

CARBONA

The *Carbona* company (a subsidiary of the Andritz Group), is currently trying to commercialize the RENUGAS technology which was originally developed by the Gas Technology Institute (GTI) in Chicago, US. The technology involves directly heated, pressurized, steam and oxygen-blown BFB gasification coupled with syngas-fed IC gas engines for CHP generation (E4tech, 2009). Carbona's technology has been tested in the Tampere, Finland pilot facility (72 odt/day) since 1993 (E4tech, 2009). A larger 150 odt/day (5.4 MW_{e}, 11.5 MW_{th}) Carbona gasifier (partly funded by the US DOE) has been in stable operation at the

Skive (a local district heating provider) facility in Denmark since 2012 (Hansen, 2013). The Skive facility uses three GE Jenbacher (Austria) gas IC engines and it has also recently tested the production of liquid fuels using the Haldor Topsoe's *Tigas* process (a variation of the methane-to-gasoline process) (Hansen, 2013).

Enerkem is a Canadian company that uses its own gasification technology to produce methanol and ethanol through catalytic condensation of biomass (or municipal solid waste, MSW) derived syngas. The Enerkem platform involves a fluidized bubbling bed gasifier followed by cyclone filtration and wet scrubbing of the syngas. The clean syngas is then catalytically converted to mixed alcohols. A 5 MLPY (1.3 MGPY) demonstration facility has been operating at Westbury, Quebec since 2009, gasifying old electricity poles to make syngas (since 2009), methanol (since 2011) and ethanol (since 2012). A second 38 MLPY (10 MGPY) facility has been constructed in Edmonton, Alberta and will use a MSW feedstock (2014). A third 38 MLPY (10 MGPY) facility is at the licensing stage at Pontotoc, Mississippi, USA. A fourth 38 MLPY (10 MGPY) facility at Varrennes, Quebec is at the planning stages and it will be a joint venture between Enerkem and Canadian corn ethanol company *Green Field Ethanol Inc.* (Enerkem, 2013)

Carbona's RENUGAS technology is the gasification technology of choice for the proposed UPM (Finnish **UPM-Kymmene** Oy) Stracel biofuel facility in France. The Gas Technology Institute in Chicago is testing the gasification platform for UPM at its 5 MW_{th} pilot plant. UPM has recently received 170 million Euro from the EU's NER300 program and they expect to begin construction of the 300 MW_{th} facility in 2014 (Landalv, 2013).

3.10.3 Circulating Fluidized Bed facilities

Foster Wheeler (FW) is among the oldest gasification technology providers. The main technology is a relatively simple atmospheric circulated fluid bed (CFB) gasifier which was developed in the 1980s. The first three biomass gasifiers were built in the early 1980s for the European pulp and paper industry in order to replace oil –fired lime kilns. These facilities are still operating and they include a 15 MW_{th} gasifier in Portugal (Portucel's Rodao), a 20 MW_{th} in Sweden (Norrsundet) and a 28 MW_{th} in Finland (Schauman mill's Pietarsaari). More recently the Foster Wheeler CFB technology has or will be used in four additional facilities:

- In 1993, at a 14 MW_{th} IGCC demonstration facility in Varnamo which belongs to Sweden's utility company ***E.ON Sverige*** (previously *Sydkraft*). Although this plant has been mothballed since 2011, in 2013 the company applied for 450 million Euro form the EU's NER300 program to help build a 200 MW_{th} facility named *"Bio2G"*.
- In 1998, at a 48 MW_{th} facility in Kymijärvi which belongs to Finland's utility company ***Lahden Lämpövoima.***
- In 2001, at a 32 MW_{th} facility in Varkaus which belongs to Finland's coreboard company ***Corenso***. The facility currently produces heat for the lime kiln of the pulp mill and it also produces small amounts of Fischer-Tropsch waxes.
- In 2007, Foster Wheeler was the gasification technology provider for the commercial FT diesel facility from the joint biofuel venture between Neste Oil and Stora Enso (***NSE biofuels Oy***). However, plans to build this facility were shelved in August 2012, after the company failed to obtain the requested 500m Euro of NER300 funding.

(EBTP, 2013; Foster Wheeler, 2013)

Thyssen Krupp Uhde is a global engineering company that has long engaged in developing gasification technologies for various feedstocks including biomass. Among Uhde's gasification platforms the most relevant to biomass are the HTW^{TM} (High temperature Winkler) and PRENFLO^{TM} (entrained flow) reactors. The HTW process is a CFB design which was developed in the early 1970s by Rheinbraun (now RWE) and it is the pressurized version of an even older CFB technology which was developed by the German, Fritz Winkler (hence the name) in the 1920s. The technology has been incorporated into various pilot plants at operating pressures that ranged 1.5-27 bar, temperatures between 700-950 °C and carbon conversion efficiencies (gasification step only) that reached 95%. Uhde has recently purchased the HTW technology from RWE and applied it to various projects. These projects are at the design and development stages in various locations around the world including Japan, Sweden, India and Australia (E4tech, 2009; Radtke, 2011).

Uhde's HTW technology was selected by the Colorado-based company *Sundrop fuel*s. Sundrop's overall technology platform is a methanol to gasoline (MTG) process which will use natural gas as well as solar heating inputs. Sundrop is a good example of a process that utilizes natural gas to produce hydrogen-replete biomass syngas. The hydrogen-rich CH_4 in the natural gas is essentially utilized to replenish the hydrogen deficient biomass feedstock and to increase yields. Solar power is used as a way to increase the renewable energy credit of the facility. A 3500 barrel/day facility in Alexandria Louisiana USA is planned to begin operations in 2014 (Sundrop Fuels, 2013).

Uhde's HTW has also been the technology of choice for the Swedish gasification company Varmlandsmetanol AB. This well-funded project (recently approved for an additional 11 million Swedish kroners) hopes to produce 15 MW_{th} and 100 kton/y methanol (total of 111 MW_{th} equivalent) with operations scheduled to begin in Q4 2015 (Värmlandsmetanol, 2012)..

Another Uhde gasification technology relevant to biomass is the entrained flow gasification platform called PRENFLO^{TM}. This platform, originally developed for coal gasification, is well suited for a torrefied biomass feed and it is at the heart of a fairly recently announced (2010), 113 million Euro *BioTfuel* project. The BioTfuel consortium aims at producing FT drop-in biofuels derived from the gasification of torrefied wood biomass using two planned facilities in France (Dunkerque and Compiegne locations) by the year 2016 (Radtke, 2011).

3.10.4 Dual Fluid Bed facilities

The Dutch ***ECN*** research institute is commercializing a dual-bed CFB steam gasifier and air blown BFB char combustor (similar concept to Repotec although reported to be more compact and indirectly heated) technology which is marketed under the acronym MILENA (ECN, 2008). ECN has also developed an oil-based tar removal technology which is marketed by the company Royal Dahlman with the acronym OLGA. The

MILENA and OLGA technologies will be assessed at a 12 MW facility in Alkmaar (The Netherlands) which is currently under construction and expected to begin operations in 2014 (B. van der Drift, 2013).

Repotec has collaborated with the pulp and paper technology provider Metso to provide the gasification technology for the new ***GoBiGas*** facility in Goteborg Sweden. Phase 1 of this ground-breaking facility will produce 32 MW_{th}, in addition to 20 MW methane. The high purity methane will be produced using Haldor Topsoe technology and it will be fed into a specialized grid catering to a local fleet of 40,000 gas-powered automobiles. The plant is almost complete and is expected to start operations by Q4 2013. The facility has also received EU NER300 funding support (Gunnarsson, 2013).

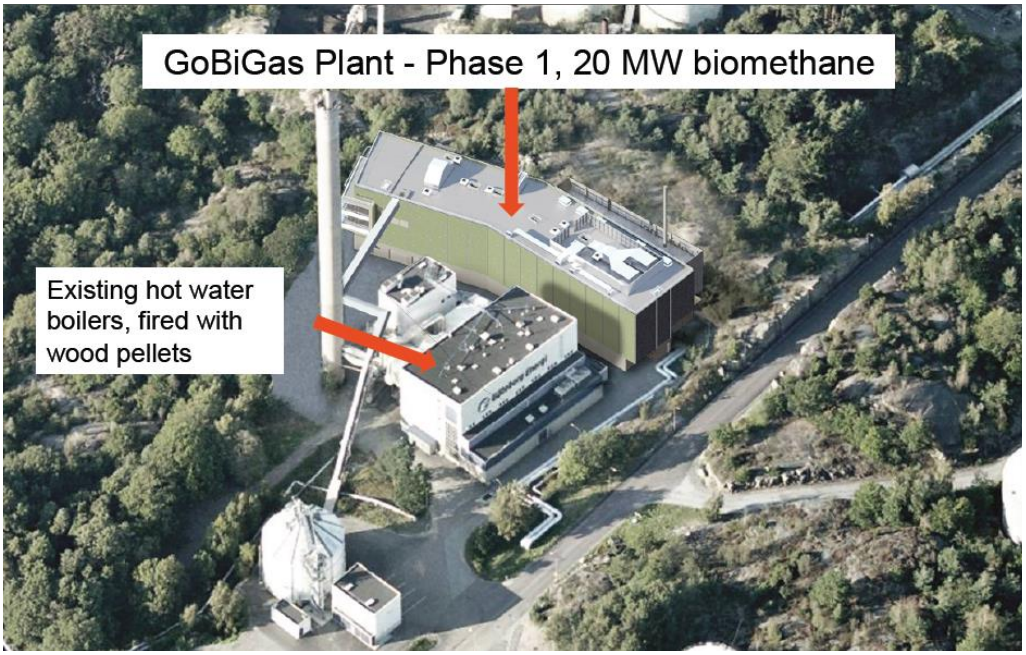


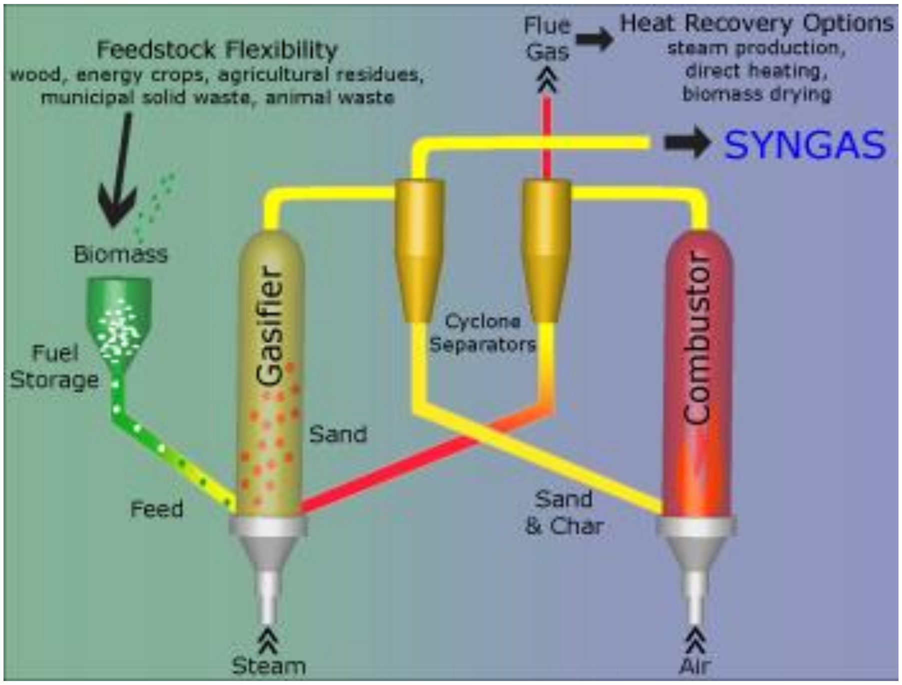
Figure 3-13: The Goteborg biomass gasification to methane facility
Source: (Gunnarsson, 2013)

Repotec / TUV (Vienna University of Technology)

The Austrian company ***Repotec*** is a technology provider and its integrated technology platform includes two interconnected fluid bed reactors. The first is a steam blown gasifier and the second a combustor which burns the resulting coke byproduct (Repotec, 2013). The syngas is fed to a gas IC engine and the flue gas heats an Organic

Rankine Cycle (ORC) turbine that generates additional power. The system is designed for maximum power generation and it has been operating at the Guessing facility in Austria since 2002 (8 MW_{th}, 2 MW_{el}). Another plant, which is under commissioning at the time of writing for Senden, Germany (14 MW_{th}, 5 MW_{el}) will provide power for 21,000 inhabitants (Repotec, 2013).

Rentech (www.rentech.com) has purchased the rights to the dual fluid bed gasification process known as "Silvagas". The process was first developed at Battelle's Columbus Laboratories in the US (thus also known as the "Battelle Process") and the rights were sold in 1992 to FERCO Enterprises and in 2001 to Biomass Gas & Electric. This dual fluid bed technology (shown in the schematic below) is comprised of two fluid bed reactors one of which is the gasifier (which is steam assisted and operates in the absence of oxygen) and the other the combustor (which operates in conditions of excess oxygen). The gasifier sends sand and char particles to the combustor which are entrained in the flowing gas (particles are separated from product syngas with the use of a cyclone). The combustor then burns the char and returns clean hot sand to the gasifier (isolated from the flue gas with the use of another cyclone).



The advantage of this configuration is that the gasification can take place in the absence of oxygen inputs, thus minimizing oxidation reactions on the biomass feed. The oxidation step discussed in Section

3.7.1 is necessary to produce the heat to drive the final syngas producing reactions. However, in the Silvagas process this heat is indirectly supplied by the combustor reactor which heats the fluidized sand by combusting the char residues coming from the gasifier (E4tech, 2009). Rentech added syngas clean-up and Fischer-Tropsch fuel synthesis components to the technology and recently entered the drop-in biofuels commercialization arena. However, in early 2013, Rentech’s plans for a commercial drop-in biofuel facility in Natchez, MS, USA were shelved and its R&D facilities in Colorado were also closed. Other opportunities with more near term returns were the company’s reason for these developments (Lane, 2013b).

3.10.5 Entrained Flow Gasification facilities

Choren, a German company established in the early 1990’s, developed the *Carbo-V* process, which is an entrained flow biomass gasification technology comprising three process steps (see Figure 4-6). The first step involves slow pyrolysis of the raw biomass at 400-500 °C, producing mainly gases and char. The gases are fed into a second high temperature (1200-1500 °C) chamber where the tars are cracked or converted to permanent carbonaceous gases. The char from the first step is fed together with the cracked gases from the second chamber into the third entrained flow reactor which operates at 700-900 °C. The main advantage of this multistage approach is that the final EF gasifier operates with an optimized and pulverized solid feed entrained in a tar-free carbonaceous gas. The process has been reported to perform well with thermal efficiencies of 91% and cold gas efficiencies of 81%. In 1998 Choren built a 1 MW$_{th}$ pilot plant in Germany, Freiberg which was operated for thousands of hours, including the production of liquid fuels using Shell’s gas-to-liquids process. Scale-up from 1 to 45 MW$_{th}$ was begun in 2003 but it was never completed. Reported reasons included the long time it took to troubleshoot the scale-up of each process step and the resulting loss of investors’ patience. These developments culminated in Choren filing for bankruptcy in 2011 and selling the Carbo-V process to Linde engineering in 2012 (E4tech, 2009; Linde Engineering, 2012).

Choren’s Carbo-V is also the gasification technology of choice for the biofuel facility proposed by Finnish company **Forest-BtL Oy,** a subsidiary of Vapo Group. The 480

MW$_{th}$ facility has just received 170 million Euro worth of NER300 funding and is due begin operations in 2016-2017 (Landalv, 2013).

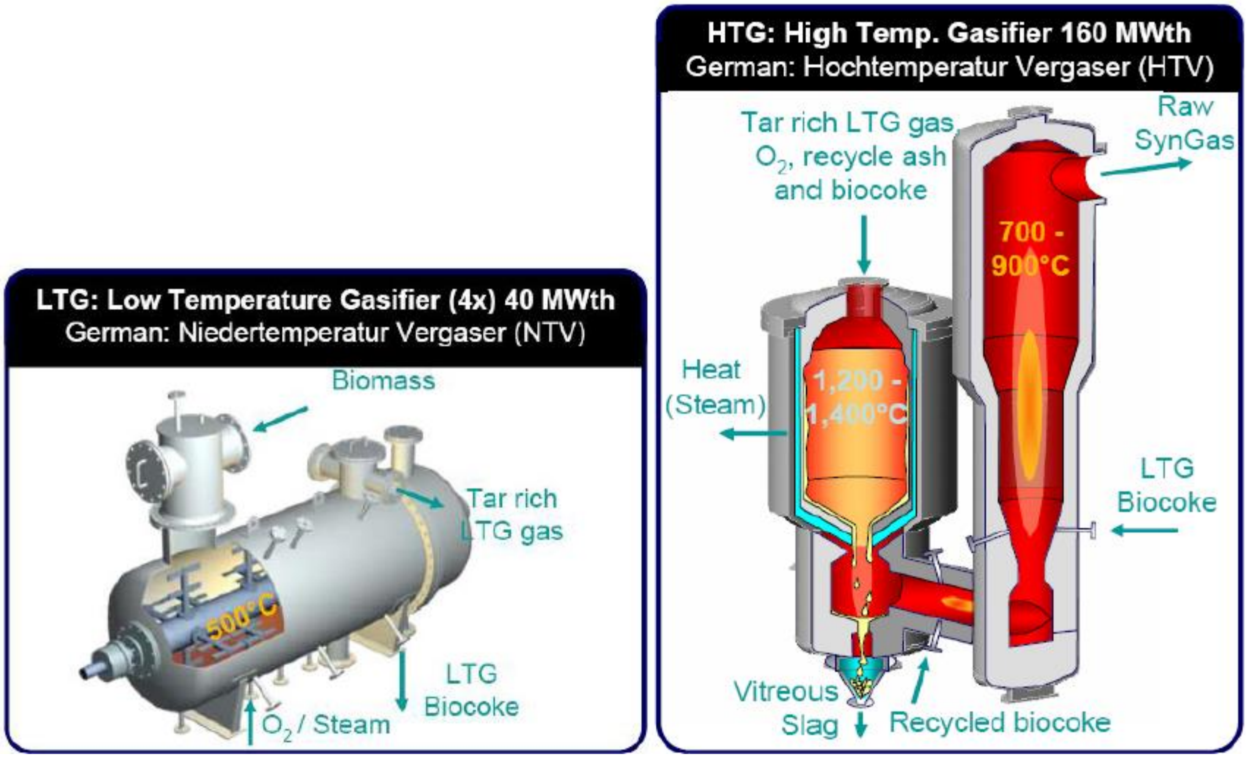


Figure 3-14: The Choren gasification/FT process
Source: (E4tech, 2009)

Range fuels, a Khoshla Ventures company, is another entrained flow gasification technology which has also encountered scale up challenges culminating in the closure of the company in late 2011. The process, originally named the "Klepper Pyrolytic Steam Reforming Gasifier", after the surname of its US inventor Robert Klepper, was marketed under the name "K2". Two separate reactors were used, the "devolatilization" reactor (low temperature gasification) and the reforming reactor (gasification). In the first reactor the biomass was heated to 230 °C where the most reactive proportion of the biomass (possibly most of the hemicellulose) was removed (devolatilized) in the form of flue gases. The feed temperature continued to rise until it was entrained with an 815 °C steam stream and fed into the main gasifier. The reported thermal efficiency of the process was around 75%. Unique features that contributed to Range Fuels' efficiency and compact design included the recycling of the steam and part of the syngas to be used as carrier gases in the next gasification cycle and the incorporation of the cyclone filters and water condensers inside the main reactor. In 2009 Range Fuels began building a 150 MLPY (40 MGPY) facility at its Soperton site in Georgia, US. However, it encountered severe tar accumulation and scale up challenges. The size of the facility was subsequently revised down to a 75 MLPY (20 MGPY) facility and then to a 15 MLPY (4 MGPY) methanol plant instead of the promised ethanol facility. The project received more than $160 million in investor funding, plus $162.25 million in government commitments. Aside from this loan guarantee the government provided an additional $76 million DOE grant in 2007 and a $6.25 million state grant. In total, the DOE released $43.6 million of the project funds before suspending payments and terminating the agreement with Range in August 2011. In an attempt to salvage part of the invested funds, Range's assets were transferred by its investor group to LanzaTech (a syngas fermentation company that is discussed later) at the end of 2011 (Lane, 2011b).

The KIT bioliq® process was developed in a project carried out at the Karlsruhe Institute of Technology and supported by a collaboration between Lurgi AG and Future Energy GmbH. Lurgi is now part or the Air Liquide Group (since 2007) and Future Energy part of the Siemens Power Generation Group (since 2006). The KIT bioliq® process has been discussed in the pyrolysis section of the report. The main principle is producing energy dense biomass slurries in separate auger-pyrolizers and then feeding these "bioliq SynCrude" slurries into a central entrained flow gasification facility. The resulting syngas is purified using Lurgi's Rectisol and Purasol processes. Testing has been carried out since 2006 using a 2MW$_{th}$ bio-slurry pilot plant. In 2007 a second phase was approved and funded in order to build a 5MW$_{th}$ facility that included an 85 bar gasifier. The second phase completion was announced in February 2013 with successful operation and the ability to produce very high quality, almost "tar-free", biomass syngas (KIT, 2013).

Chemrec, a Sweden-based gasification company, has specialized in technology development for black liquor gasification (see box 3-1 below). A 3 MW$_{th}$ pilot plant has been installed next to the Smurfit Kappa pulp mill in Pitea, Sweden since 2005. This pioneer facility has collaborated with Haldor Topsoe to convert its syngas to Dimethyl Ether (DME). They reached 4 t/day of DME production in H1 2013. Volvo has tested the DME in truck engines with encouraging results. The Chemrec facility is now part of the EU's 28 million Euro 7th framework programme BIODME project which includes various high profile collaborators such as Haldor Topsoe, Total, Preem AB and Volvo (BioDME, 2013). The company, COWI (which is the commercialization agent for the Chemrec technology as it has evolved at the Pitea pulp mill) has carried out a feasibility study to produce 55 000 tons of methanol for New Page in Michigan, USA. The plant will use 30% of the black liquor flow from the pulp mill (COWI, 2013). COWI has also performed a feasability study and cost estimate for a full scale biofuel production plant, including a black liquor gasification unit, to be located at Domsjö Fabriker, Sweden. Although neither methanol nor DME can be considered drop-in biofuels, they are direct precursors to gasoline and their conversion to drop-in fuels is technologically mature and proven in the chemicals industry. Lulea University of technology's holdings company has recently (February 2013) acquired Chemrec and its Pitea pilot plant. LTU Green Fuels will be the name of the new company (RISI, 2013).

Box 3-1: Black liquor gasification: Improving thermal efficiency and value streams for pulp mills

Kraft mills produce a highly carbonaceous pulping process effluent known as "black liquor". This liquid stream contains process chemicals as well as half of the carbon that was present in the starting biomass, mainly in the form of lignin (lignin gives the liquid its dark brown colour hence the name "black") (IEA Bioenergy, 2007). In Kraft mills, black liquors are concentrated and combusted in large recovery kilns where the inorganic chemicals are recycled and the heat and power generated are used to feed the pulping process. Due to recent sustainability and bio-economy trends, pulp mills have been considering replacing their recovery kilns with entrained flow gasifiers in order to improve their energy efficiency and provide them with the flexibility of utilizing their syngas to diversify their product range into liquid fuels and chemicals (via for example Fischer-Tropsch synthesis). Over the last couple of years Canada and the US have used subsidies (e.g. Black liquor subsidy) to encourage their pulp and paper mills to enhance the utilization of their black liquors and improve their business competitiveness. Although various pilot plants have been installed in pulp mills in Sweden and the USA, mostly using Chemrec technology (the largest being the 50 t/day black liquor gasification demonstration facility at Weyerhauser's New Bern pulp mill in N. Carolina, USA, (Babu, 2005)), there appear to be no commercial sized black liquor gasifiers operating at this time. Part of the reason is that only large scale facilities that accumulate black liquor equivalent to more than 1000 t of dry solids daily are practically able to consider the conversion to gasification (IEA Bioenergy, 2007).

3.10.5.1 Biomass Co-gasification with coal

Entrained flow gasifiers are widely used for coal gasification and thus have been used in many biomass co-gasification applications. Co-gasification allows for mitigating some of the biomass gasification issues. Examples of currently operating co-gasification plants include the:

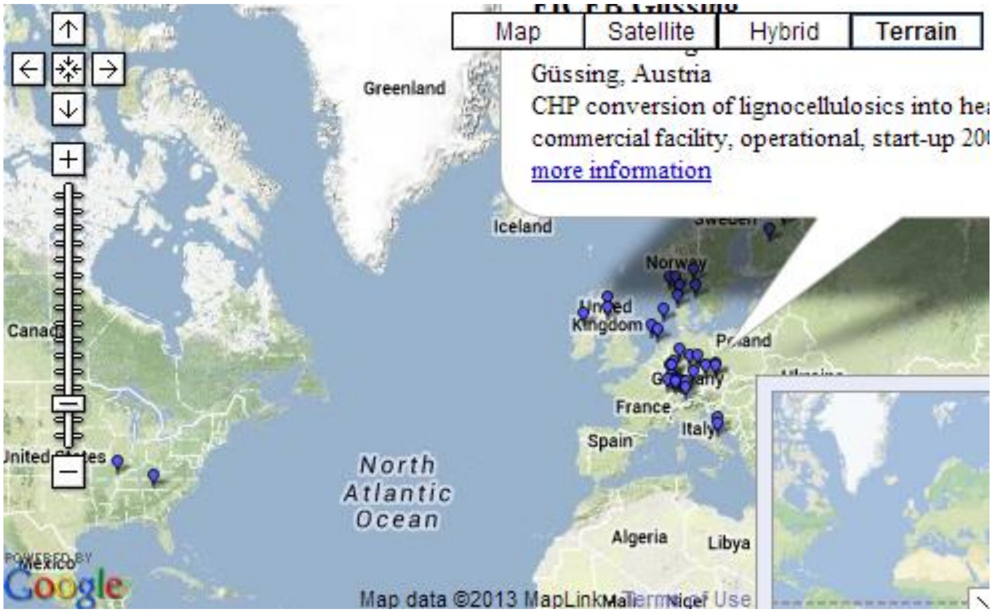
- 230 MW_e and 170 MW_{th}, The Vaasa, Finland, facility, cofires up to 40% forest residue in an existing pulverized coal utility boiler. The facility has been in successful operation since December 2012 (Simet, 2013).
- 50 MW_e & 90 $MW_{th,}$ Lahti Energia (MSW feedstock) facility in Finland, Metso technology (Breitholtz, 2013; Simet, 2013)
- 140 MW_{th} Vasikuodon Voima facility in Finland, Metso gasification technology (Breitholtz, 2013)
- 80 MW_e Essent's Amer Power Plant in the Netherlands (Essent, 2013)

3.10.6 Plasma gasifiers

Although plasma gasifiers have a similar structure to entrained flow reactors they operate using plasma torches at extremely high temperatures of 1500 °C – 5000 °C (atmospheric pressure). Although they are supposedly costly to operate, they are able to produce a very high quality syngas which needs little further cleanup (E4tech, 2009). In this process, the biomass is converted to syngas and the inorganic ash is vitrified to inert slag. Although this technology is being developed by various start-up companies including California-based ***Solena*** and US-based ***InEnTech*** the technology is still at the development stage. InEnTech has been selected as a gasification technology provider for the California-based ***Fulcrum bioenergy*** (E4tech, 2009)***.***

3.10.7 The IEA Bioenergy Task 33 gasification facilities database

For an extensive list of global demonstration and commercial gasification facilities, the reader is referred to IEA Bioenergy's Task 33 (Gasification) online database. This online tool (see Figure 3-15) features an interactive world map with the gasification facilities at demonstration or operation stage. According to this interactive map, most of the biomass gasification activities are concentrated in Germany, Austria and the Scandinavian countries.



Güssing, Austria
CHP conversion of lignocellulosics into he
commercial facility, operational, start-up 20
more information

Figure 3-15: The IEA Bioenergy Task 33 gasification facility database

Biomass gasification has developed substantially over the last couple of decades as indicated by the more than 500 MW of operating biomass gasification CHP facilities around the world. The biogas-to-distillates end of the process will also benefit from industrial "know-how" based on the operation of Sasol coal-to-liquids facilities. However, the upgrading of syngas to transport fuels remains a significant challenge primarily due to high capital costs. These costs are due to the high temperature and high complexity of the gasification platforms which typically include various heat-cool and compression cycles. To try to mediate these high capital costs, it has been suggested that a minimum scale of 2000 tpd size facility will be needed. However, this can be considered to be relatively small scale when compared to current, commercial fossil based FT-distillates facilities which are at least 50 times larger. It can be anticipated that FT synthesis facilities which gasify biomass will be equally, if not more, challenging to operate at scale than are their fossil counterparts (CtL and GtL). However, a major advantage of gasification is that the perceived technology risk will likely be lower than that of the other biofuel platforms because, from a chemical standpoint, syngas is sufficiently similar to commercially upgraded fossil syngas. This perception might be challenged, though, as biomass syngas is generally of inferior quality to coal-derived syngas and especially natural-gas-derived syngas. For example, the tar content in biomass syngas (gasification and tar conversion technology dependent, up to thousands of ppm) can be much higher than in coal-derived syngas and orders of magnitude higher than can be accommodated in FT synthesis (about 5 ppm) to biofuels. Tar accumulation, capital costs and scale up challenges have been suggested to be the main reasons behind the recent failure of the three commercial size start-up, biomass-to-distillates gasification facilities of NSE biofuels, Range Fuels and Choren (Lane, 2011b; Rapier, 2011; Lane, 2012; Hayes, 2013; EBTP, 2013). Techno-economic studies have shown that the manufactured selling price (MFSP) of gasification biofuels can be between \$31-\$36/GJ while the capital costs (TPI) required to build a pioneer commercial facility can be in the vicinity of \$1 billion for a drop-in gasification plant processing 2000 tpd of biomass (dry basis). However, there is still significant potential for gasification technologies as new systems and technologies are developed. From a systems point of view, the "hub and spoke" model of biomass logistics may provide an opportunity for a gasification facility to be built at a very large scale where pyrolysis will provide the densified biomass feed and oil refineries will be used for the last upgrading steps of the FTS process. From a technology point of view, researchers and companies, (such as Velocys which claim efficient FTS of biomass at small scale (<500 tpd)) continue to make significant progress in all aspects of the process. For example, cleaning technology (e.g. KIT claiming production of "tar free" syngas from entrained flow gasifiers) and an increased interest in dimethyl-ether as an alternative fuel to diesel (e.g. the "BioDME" project in Europe) have already made an impact on the technical end economic feasibility of this approach to drop-in biofuel production (E4tech, 2009; Rapier, 2011; Linde Engineering, 2012).

CHAPTER 4: THE BIOCHEMICAL PLATFORM

Biomass conversion through biological means, such as by enzymatic hydrolysis followed by biological sugar conversion, has been termed the “biochemical” approach to producing drop-in biofuels. In the same way that glucose is fermented to ethanol for conventional (sometimes termed first generation) biofuel production, these “advanced” biocatalytic processes convert sugars to less oxygenated, more energy-dense molecules such as longer chain alcohols (butanol, butanediol) and higher molecular weight compounds such as isoprenoids and fatty acids. As shown in Figure 4-1, there are numerous biological pathways, feedstocks, and microorganisms that have been proposed for the production of drop-in biofuels and their intermediates. Microorganisms such as cyanobacteria and algae can directly capture CO_2 from the atmosphere and convert it to ethanol or lipids. Alternatively, bacteria, yeasts and heterotrophic algae can utilise sugars derived from sugar cane, sugar beet, starch and other energy storage polysaccharides, or from the hydrolysis of the cellulose and hemicellulose carbohydrates in cellulosic biomass. Other bacteria can utilise hydrogen and carbon monoxide in syngas. Although the intermediates produced can be used for diesel or gasoline production, generally more oxygenated higher alcohols are better suited for gasoline production and higher molecular weight, longer chain more saturated lipids and isoprenoids are better suited for energy dense diesel and jet fuel fuels. Cyanobacteria, yeasts and bacteria can be selected or engineered to produce either higher alcohols or isoprenoids and lipids and the metabolic pathways from one organism can be heterologously expressed in another. However, after biological production, regardless of which biosynthesis route is used, some form of hydroprocessing of the produced intermediate is typically required before blending with conventional petroleum fuels. As described earlier, the more oxygenated and unsaturated the intermediate, the more hydrogen is required for it to be upgraded to a fungible drop-in functional equivalent to diesel, jet or gasoline blendstock.

From a commercialization point of view, one of the most attractive characteristics of these technologies is the potential to “piggy-back” onto existing ethanol facilities by switching the microorganism being used in the microbe-to-ethanol process to obtain a “microbe-to-drop-in fuel or fuel intermediate” process. However, high process efficiencies must also be achieved and the industrial robustness of the process at commercial scale must be proven. These and other aspects of the various emerging biological pathways to drop-in biofuels are still evolving.

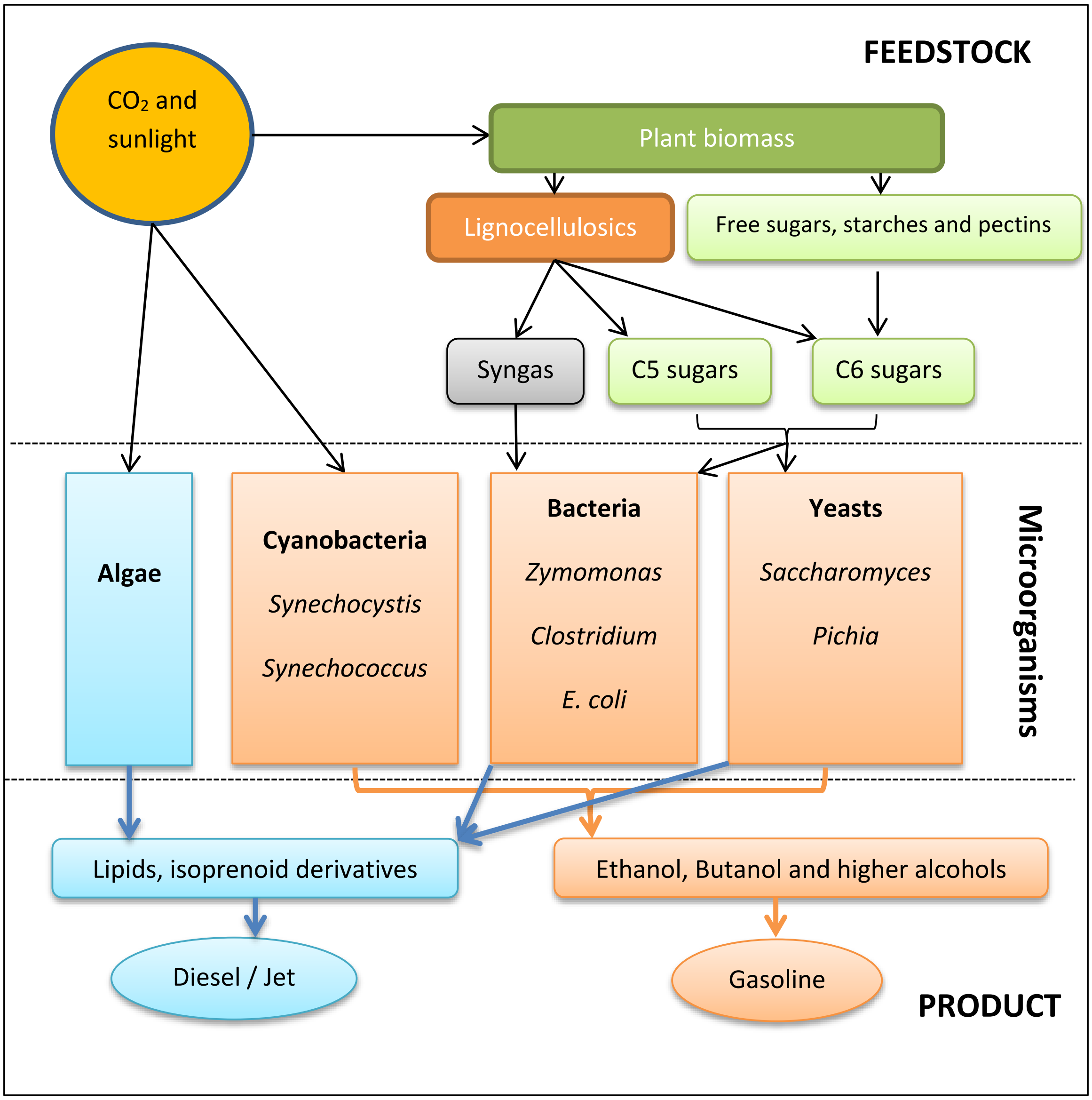


Figure 4-1: Schematic overview of the microorganism-to-drop-in-intermediate or biofuel derived for various renewable feedstocks
Source: adapted from (Weber et al., 2010)

4.1 Ethanol

Ethanol, the world's most widely used biofuel, is currently biochemically produced from sugars or starch by varieties of the yeast *Saccharomyces cerevisiae*. Although ethanol is not a drop-in biofuel it is the benchmark process against which alternative biological conversion pathways should be compared. A typical bioethanol process entails three steps:

- Either direct utilization of the sugar or the hydrolysis of sucrose or starch (or cellulose and hemicellulose in the case of non-food lignocellulosic feedstocks) to monosaccharides such as glucose.
- The metabolic conversion (anaerobic fermentation) of glucose (or other monosaccharides) to ethanol.
- The recovery and concentration of ethanol from the fermentation broth (beer).

The "ethanologenic" microbe itself typically contains the invertase enzyme needed to break disaccharide sucrose (derived from cane or sugar beet) down to its hexose monomers (fructose and glucose). For starch hydrolysis, externally sourced "amylase" enzymes are usually used and this is the dominant route practiced in the US corn ethanol industry (which, as discussed in Chapter 1, is currently the world's largest ethanol production model; sucrose from sugarcane to produce ethanol is the second largest). A more complex process is required to hydrolyse lignocellulosic carbohydrates to fermentable hexose and pentose monosaccharides. There are many approaches, but all are technically and economically challenging, especially as in many lignocellulosic feedstocks as much as 30 wt% of total sugars are pentoses (primarily xylose) that are not readily converted to ethanol by wildtype microorganisms. A detailed description of a typical "cellulosic ethanol" process that involves pretreatment, enzymatic hydrolysis, fermentation, product recovery and residual solids utilization, etc., is beyond the scope of this report and the reader is referred to other publications that more extensively review options and progress in cellulosic ethanol development (Humbird et al., 2011; Saddler et al., 2012).

The main metabolic pathway used by yeasts in ethanol fermentation is the Embden–Meyerhof–Parnas or EMP pathway. The pathway involves an initial glycolysis step, where one molecule of glucose is metabolized, and two molecules of pyruvate are produced. Each pyruvate is then metabolized to one molecule of ethanol (Bai et al., 2008). The overall glucose-to-ethanol reaction is stoichiometrically represented by the equation below:

$$C_6H_{12}O_6 + 2ADP + 2\ P_i \rightarrow 2C_2H_5OH + 2\ CO_2 + 2\ H_2O + 2\ ATP$$

This equation shows that four of the six carbons in the hexose sugar feedstock end up in the ethanol product and two are oxidized to CO_2 (on a mass basis, 49% is converted to ethanol and 51% to CO_2). The carbon oxidation to CO_2 displaces carbon from ethanol production but gives rise to usable energy in the form of two ATP molecules while it also generates the reducing power necessary for the chemical reduction (“deoxygenation”) of the sugar to the ethanol molecule. The stoichiometric conversion yield in the above equation is theoretical, meaning lower conversion yields are achieved in practice. This is because some of the carbon is used as structural material for actively growing microbial cells and the metabolic efficiency of this conversion may be compromised by various mechanisms such as feedback inhibition, toxic chemicals, biological contaminants, osmotic pressure stress or inadequate nutrition (Sanchez and Cardona, 2008). Yeasts are the “workhorse” microorganism used in the current ethanol industry, as they have a long history of use and routinely achieve more than 90% of the above theoretical conversion in non-sterile industrial settings (Ingledew, 2008). Traditionally, alcohol plants produce a “beer” of 5% – 10% v/v ethanol/water concentration. However, more recent plants are able to produce beer of up to 20% volume ethanol (by carefully monitoring conditions and dosing yeast nutrients) (Ingledew, 2008; Walker & Brew, 2011). This performance is unmatched by other fermentative microorganisms and it is attributed to a number of unique characteristics exhibited by *Saccharomyces cerevisiae’s* ability to convert glucose.

- These yeasts have evolved to produce large amounts of ethanol and to tolerate high concentrations of ethanol. In fact, 20 vol% ethanol concentrations have been reported in industrial settings without the occurrence of significant feedback inhibition.
- These yeasts are relatively resistant to toxic inhibitors such as organic acids, aldehydes, inorganic salts, etc.
- Their cell growth consumes little carbon and it is directly associated with vigorous ethanol production. This contrasts with many fermentative microorganisms which only produce alcohols under stress and as secondary metabolites.
- They ferment sugars at low pH values, which minimizes contamination.
- They are relatively fast growing microorganisms which adapt readily to changing fermentation conditions.

- They are highly selective in producing ethanol and CO_2 and only minute amounts of carbon are diverted to other fermentation metabolites such as organic acids, esters and aldehydes

(Ingledew, 2008; Walker & Brew, 2011)

Alternative microorganisms are also being evaluated and developed for ethanol production such as *Zymomonas mobilis,* which is a rapidly fermenting ethanologenic bacterium, and thermophilic bacteria that can operate at the higher temperatures typically used for enzymatic hydrolysis of cellulose.

Zymomonas mobilis is a highly productive and selective ethanologen bacterium that has been studied since the 1970s. This bacterium is used to ferment sugar-rich plant saps such as obtained from agave cacti to produce the traditional pulque drink of Mexico (Swings and Deley, 1977). It is an anaerobic, gram negative bacterium. Instead of the EMP pathway used in yeast, it uses the Entner-Doudoroff pathway, producing only one ATP (instead of two in the EMP pathway) per molecule of glucose metabolised. The lower ATP production means that less ATP is accumulated intracellularly and less carbon is funneled into growth of cell mass, leaving more available for ethanol production. It also means that *Z. mobilis* strains must achieve higher specific rates of glucose utilization than yeast. *Z. mobilis* tolerates up to 120 g/L of ethanol and its specific productivity is 2.5-5 times higher than traditional baker's yeast (*S. cerevisiae*) and is able to produce ethanol at yields approaching 97% of theoretical (Bai et al., 2008). While *Z. mobilis* ferments glucose efficiently, fructose and sucrose and mixtures of biomass sugars are more challenging feedstocks. Genetically engineered *Z. mobilis* strains have been developed that are able to ferment pentoses as well as hexoses. An engineered *Z. mobilis* strain is currently being assessed at DuPont Cellulosic Ethanol's (DCE) 250 KGY cellulosic ethanol facility in Vonore, Tennessee (USA). A possible limitation on the commercial use of *Z. mobilis* for fermentation of corn starch is that the process residual Distillers Dry Grains and Solubles (DDGS) would need to be proven to be acceptable for animal feed. Sales of DDGS present an important co-product revenue stream and can account for up to 20% of a corn ethanol mill's total revenue (Bai et al., 2008, Walker & Brew, 2011).

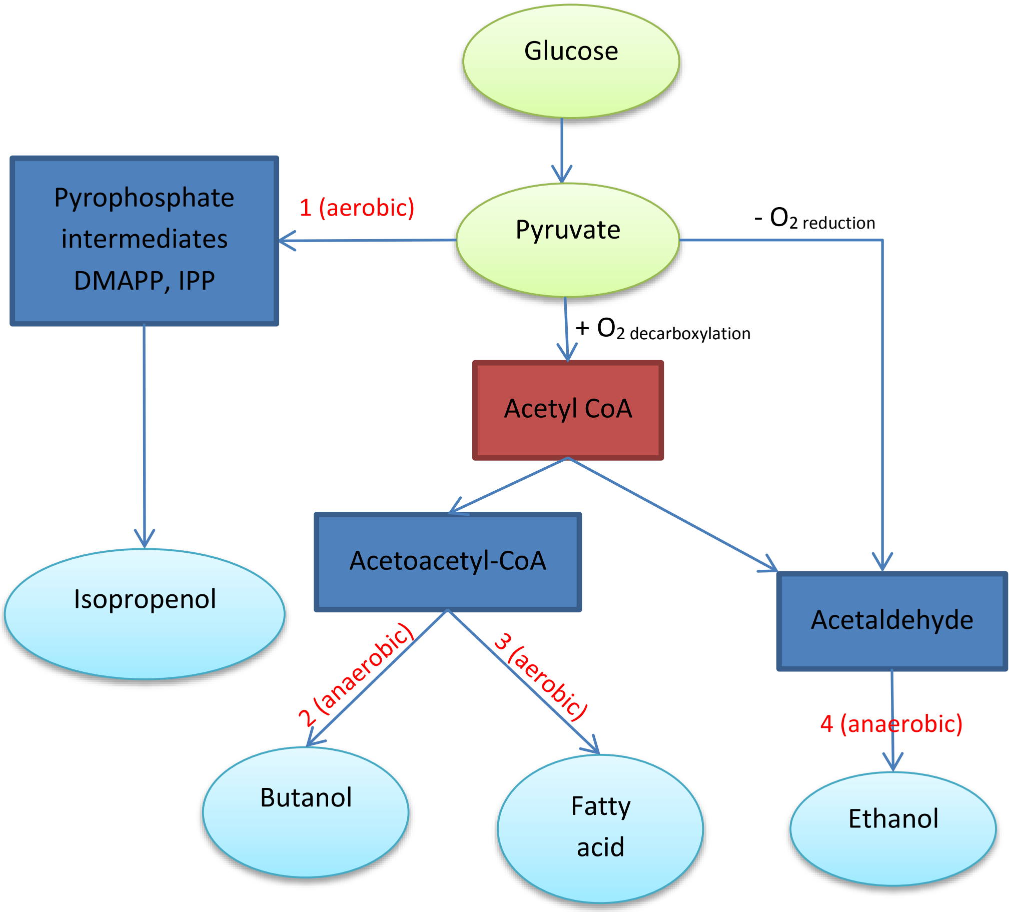
Thermophilic bacteria such as *Thermoanaerobacterium saccharolyticum* are able to tolerate higher temperatures than 30-35°C which is the optimum temperature range for most mesophilic yeast. An ablity to operate at higher temperatures can have numerous process advantages, especially for enzyme based cellulosic ethanol production. In particular, enzymatic hydrolysis of cellulose is typically performed by cellulolytic enzymes that exhibit temperature optima of 45-50 °C or even higher. The discrepancy in temperature optima between the sequential steps of enzymatic hydrolysis and fermentation creates a need to cool the process medium prior to fermentation. In contrast, thermophilic ethanologens are able to operate at the same temperature as the hydrolytic enzymes, circumventing the need for cooling. Lower feedback inhibition on the enzymes is an additional advantage of this simultaneous saccharification and fermentation approach (SSF) as glucose is simultaneously produced and converted in the same process step. However, to date, the performance of thermophilic bacteria that have been investigated for this application is below that of *S. cerevisiae* and *Z. mobilis,* and their ethanol tolerance is also significantly lower (*cf* 2%-5% vol for thermophilic bacteria vs up to 20% vol or higher for industrial strains of *S.cerevisiae*) (Weber et al., 2010).

Ethanol has a high vapour pressure and can readily be recovered and concentrated by distillation of the aqueous fermentation beer. However, ethanol forms an azeotrope with water such that distilled ethanol still contains 3 wt% or more water. This remaining water can be removed (if it needs to be) through molecular sieves or other dehydration technologies (e.g., pervaporation or ternary distillation), which are widely practiced at industrial scales. Ethanol recovery and purification are relatively well understood processes compared to recovery of other potential biofuels such as butanol and higher molecular weight compounds which have lower vapour pressures and are produced at lower maximum titers.

Despite ethanol's established industrial processes and biofuel markets, the ethanol molecule is too oxygenated to be a drop-in biofuel. So called "advanced biological conversion" pathways can produce less oxygenated (more reduced, higher H_{eff}/C) molecules such as higher alcohols (e.g., butanol), fatty acids (e.g., palmitic acid) and bio- hydrocarbons (e.g., farnesene). Although these latter molecules are better suited as intermediates for drop-in biofuel production, their production will still require the resolution of significant operational and scale up challenges compared to sugar, starch or cellulosic ethanol production processes.

4.2 Biological conversion to drop-in biofuels

As described earlier, there are four main metabolic pathways that have been proposed for the conversion of glucose to the chemically reduced molecules that could constitute drop-in biofuels. The four pathways are shown in Figure 4-2 and they all begin with the oxidation of glucose to two pyruvate molecules (glycolysis). From there the pathways differ as the pyruvate is converted to various intermediates such as Acetyl CoA or acetaldehyde. The pathways that lead to butanol and alcohol are anaerobic whereas the pathways that lead to more saturated longer chain molecules such as isoprenoids or fatty acids are aerobic (Jin et al., 2011). Each pathway plays a different role in the production of drop-in biofuels in terms of productivity and suitability for drop-in biofuel production.



1. Isoprenoid pathway (aerobic)
2. ABE pathway (anaerobic)
3. Fatty acid pathway (aerobic)
4. Ethanol pathway (anaerobic)

Figure 4-2: Simplified schematic of major metabolic pathways relevant to drop-in biofuel production

4.2.1 The butanol pathway

Although butanol is not directly a drop-in fuel, it is considered to be a more favorable drop-in biofuel intermediate than ethanol because it is less oxygenated (lower O/C ration and higher C_{eff}/H). Butanol is a four carbon primary alcohol with a volumetric energy content of 28 MJ/L which is higher than ethanol's 19 MJ/L and closer to gasoline's 36 MJ/L (Pfromm et al., 2010). Other favourable characteristics of butanol when compared to ethanol are its lower volatility and less hydroscopic and corrosive properties. The octane number of normal butanol (n-butanol) is about 87 while branched chain butanols (isobutanol) have an even higher octane number (Nexant, 2012). Although the butanol molecule is not a true drop-in fuel component, it can be directly blended with gasoline at high volumetric ratios (Jin et al., 2011).

Butanol (n-butanol) is a commodity chemical with a current 3 Mt/year global market valued at USD $7.5 b/year based on a spot price of USD $2500/t) (Indexmundi, 2013). It is used in diverse applications such as coatings, plasticizers and solvents and is currently produced from petroleum using the oxo-synthesis (hydroformylation) process (Machado, 2010). The raw material, propylene, reacts with carbon monoxide and hydrogen over catalysts (Co, Ru and Rh) to yield aldehyde mixtures. These aldehydes are then hydrogenated (catalytically) to produce the final product which is a mixture of butanol isomers. The BASF and Dow Chemical companies are currently the world's leading butanol manufacturers and jointly account for about 35% of global production (Machado, 2010).

From 1914 up until WWII, butanol was primarily produced via fermentation using the bacterium *Clostridum acetobutylicum* (Qureshi & Blaschek, 1999). This microorganism is able to convert a wide range of sugars (including pentoses) to acetone, butanol and ethanol (known as the "ABE" fermentation process) at typical ratios of about 3:6:1 by weight. Initially coatings and paints were the main uses of these solvents, although during WWII butanol was also used as a fuel for British Royal Air Force planes and acetone was used to manufacture cordite, a smokeless type of gunpowder (Machado, 2010). With the development of cheap petroleum in the 1950s, most of the world's biological route butanol (ABE) fermentation facilities closed (other than some facilities in Russia and South Africa which continued to operate up to the 1980s) in favour of manufacturing butanol from petroleum using the chemical process (Lee et al., 2008).

The fermentation of sugars to n-butanol has been advocated as a potential platform to produce drop-in biofuel intermediates. The equation below describes the theoretical stoichiometric conversion of glucose to butanol via the ABE pathway.

$C_6H_{12}O_6 + 2ADP + 2\ P_i \rightarrow C_4H_9OH + 2\ CO_2 + H_2O + 2\ ATP + CoA$

Although the theoretical carbon conversion is the same as for the EMP pathway used by yeasts (2/3 of the sugar carbon ends up in the alcohol product), *Clostridium sp.* have, so far, been challenged to reach this theoretical yield in industrial practice. Although the theoretical butanol yield is 41% by mass, a mass yield of only about 15% is typically achieved (Jang et al., 2012; Lee et al., 2008). *Clostridium* species also tend to be slower-growing and, while they can exhibit a wide sugar substrate range, they are susceptible to solvent toxicity by butanol (product feedback inhibition). Solvent toxicity is arguably the biggest challenge of the ABE metabolic pathway and industrial bio-based butanol production process as cellular inhibition becomes severe at butanol concentrations higher than 10-20 g/L (Jin et al., 2011). This is primarily a result of the hydrophobic nature of the butanol, which enables it to penetrate into the lipid bilayer of cell membranes and disrupt cellular function. It is also hydrophilic enough to remain in aqueous solution up to concentrations of 70-80 g/L, although at concentrations above this it phase separates and creates a butanol-rich upper “oil-like” layer in aqueous systems (Jin et al., 2011). Genetic engineering efforts have already achieved a more-than-doubling of butanol titers, from 8 g/L in early wild type strains to about 20 g/L (2% w/v) in improved stains (Peralta-Yahya & Keasling, 2010; Weber et al., 2010). However, this is still a low titer and almost an order of magnitude lower than what can be achieved in the ethanol industry today (16% w/v or 20% vol) (Walker & Brew, 2011).

The lipophilic nature of butanol makes it much more toxic to microbial systems than ethanol. As it accumulates intracellularly, it disrupts phospholipid components of the cell membrane causing an imbalance in cellular metabolism by disturbing the selective flow of metabolites, nutrients and toxics in and out of the cell (Jin et al., 2011). Other challenges to using *Clostridium* sp. in industrial settings are their relatively slow growing nature and susceptibility to bacteriophage attack and cell degeneration, as well as a requirement to maintain strictly anaerobic conditions (Weber et al., 2010).

To try to circumvent these drawbacks, some technology developers have heterologously expressed the ABE pathway in industrially robust yeasts (Jin et al., 2011; Peralta-Yahya & Keasling, 2010). Although these genetically modified microorganisms are expected to be more amenable to large scale industrial processing conditions, the solvent toxicity issues of ABE pathway products will continue to be a challenge to achieving robust production performance. While n-butanol is the isomer that is naturally made by the ABE pathway, some companies such as Gevo and Butamax have engineered pathways in yeast cells to produce isobutanol. This isomer has proven to be easier to produce in yeast and it is also more valuable as a biofuel feedstock as a result of having a branched carbon chain. Although little is known about the scale up performance of these isobutanol producing pathways, Gevo has obtained a fivefold higher productivity than they obtained for n-butanol (Nexant, 2012).

Another strategy to overcome solvent toxicity of butanol (or ABE pathway products) is to design production systems that enable continuous product removal. *In situ* removal strategies include liquid-liquid extractions using co-solvents, gas stripping and the use of membrane based separations. Ezeji and co-workers are working on reactor designs that are able to perform continuous butanol product removal (Ezeji et al., 2010). Ranjan and Moholkar (2012) recently reviewed solvent extraction strategies and concluded that the most promising technologies are gas stripping and pervaporation. However, both processes have certain drawbacks. In particular, the butanol recovered by gas stripping contains relatively high levels of water and further azeotropic distillation is required to recover butanol of sufficient purity (Liu et al., 2004) while pervaporation requires specialized membranes that are, to date, easily fouled by fermentation broth components(Lee et al., 2008). Although novel techniques such as a hybrid vapor stripping/vapor permeation process have been proposed (Vane et al., 2013), such techniques can consume more energy than contained in the butanol molecule itself. As the efficiency of these recovery techniques is highly sensitive to the butanol titer (concentration), improvements in process titers will enhance both butanol fermentation performance and product recovery efficiency.

4.2.2 The fatty acid pathway

Fatty acids are precursors to some of the best known storage lipids, namely triacyl glycerides (TAGs). TAGs are formed by three long alkyl chains (C12 to C22) connected to a glycerol head via ester bonds (see Figure 2-1). As discussed in Chapter 2, TAGs are found in the vegetable oils of oilseed plants (such as palm, jatropha, rapeseed/canola and soy) and can be used to produce diesel and jet fuel blendstocks. Many diverse microbes including green algae, bacteria and fungi can also produce high levels of TAGs through specialized metabolic pathways (Peralta-Yahya & Keasling, 2010). As shown in the simplified pathway for palmitate fatty acid production (Figure 4-3), fatty acid biosynthesis involves chain lengthening thiol-esters produced by low molecular weight acyl carrier proteins (ACP) (Jovanovic Tews et al. 2010). Up to the formation of butyryl-ACP, this pathway resembles the butanol production pathway. In order to elongate the 4-carbon butyryl chain to a 16-carbon palmitate chain, 6 elongation cycles are required (Jovanovic Tews et al. 2010). With each elongation cycle, two carbon units are sequentially condensed onto the growing fatty acyl chain. Each elongation cycle expends the reducing power of two NAPDH molecules. Replenishing this reducing power typically requires a portion of feedstock carbon to be oxidized to CO_2 and H_2O via aerobic respiration (Jovanovic Tews et al. 2010). The NADPH generation process takes place within the pentose phosphate pathway (PPP), as shown in Figure 4-3. The reducing power of NADPH essentially provides a means of hydrogen insertion. In fact, inserting molecular hydrogen via alternative means has been shown to increase yields (and decrease the need for carbon-consuming NADPH generation) in metabolic processes involving chemical reduction of carbohydrates (Yerushalmi et al., 1985). The longer and more saturated the fatty acid chain, the more

ISBN: 978-1-910154-07-6 (electronic version)

elongation cycles and greater reducing power required. This reducing power has to come from either alternative hydrogen inputs or from oxidation of feedstock carbon which sacrifices yield.

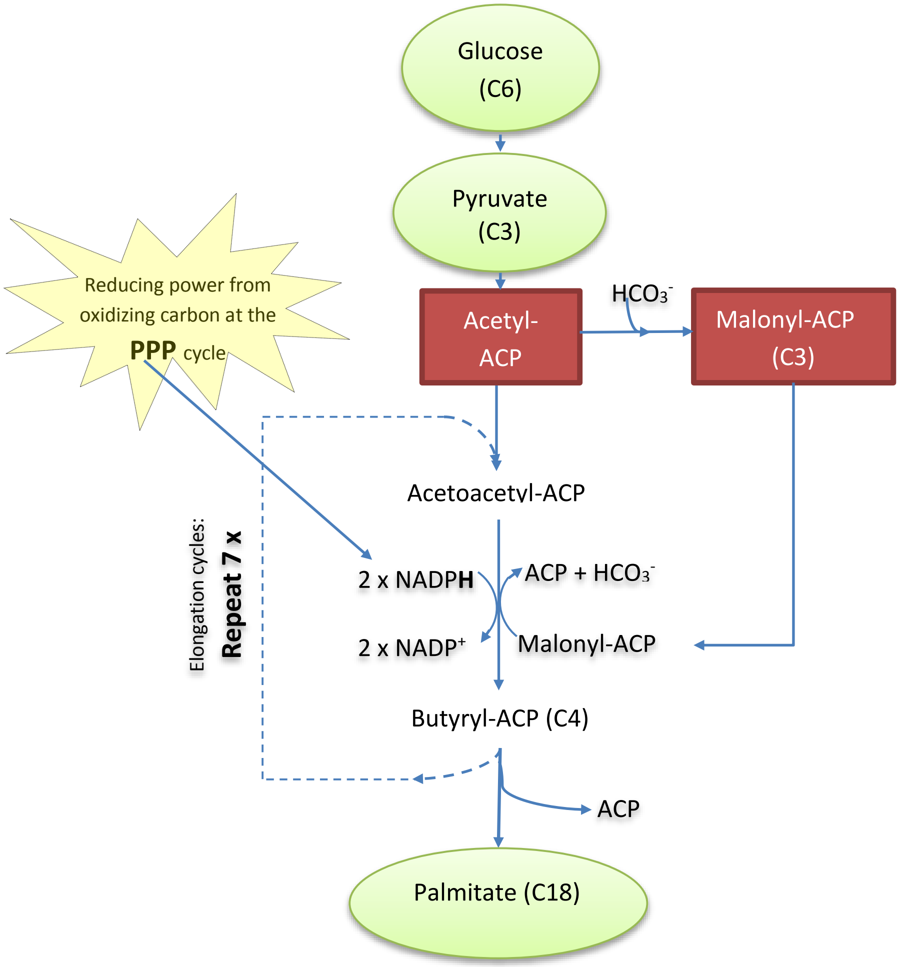


Figure 4-3: Biosynthesis of fatty acid, palmitate
Source: adapted from Jovanovic-Tews et al. (2010)

Cyanobacteria (also known as microalgae) can also be used to accumulate high levels of TAGs via the fatty acid pathway. Autotrophic cyanobacteria use photosynthesis to convert atmospheric CO_2 to glyceraldehyde-3-phosphate, which in turn forms pyruvate through the same glycolytic process used to metabolize glucose in heterotrophic microbes. Thus, these photosynthetic microbes are able to utilise the most oxidized form of carbon (CO_2) and convert it to highly-reduced energy-dense triacyl glyceride molecules. As cyanobacteria do not require soil or arable land to grow, it has been suggested that, on a per unit land basis, they are potentially higher yielding than any terrestrial oilseed crop. However, there are several technical challenges to achieving large scale economical cultivation and harvest of algae, as reviewed in a recent Task 39 report (Darzins et. al, 2010). Despite these challenges, considerable interest remains in advancing algal-based route as indicated by recent funding awards such as:

- The European Commission's 7th framework programme which supported 3 algae contracts for a total of €19.2 million under the "Algae Cluster" initiative. "Biofat" was supported with €7.1 million, "ALL GAS" with €7.1 million and "Intesusal" with €5 million;
- The US DOE's $50 million USD award to the US's National Alliance for Advanced Biofuels and Bioproducts (NAABB); and
- The $600 million USD research alliance between ExxonMobil and Craig Venter's Synthetic Genomics company to develop high performing algae for biofuels production.

4.2.3 The isoprenoid pathway

Isoprenoids are members of the lipid class of molecules and they can also be used as intermediates for diesel and jet blendstock biofuel production. As their carbon chains are more branched than fatty acids they exhibit lower viscosities, lower boiling points and higher octane numbers and are thus better suited for conversion to transport fuels than straight chain paraffinic molecules (e.g., dodecane) (Renninger et al. 2010). The main metabolite produced from the isoprenoid pathway is isopentenyl diphosphate (IPP) (Figure 4-4) and its isomer, dimethyl allyl diphosphate (DMAPP). These 5-carbon intermediates are biologically condensed by phosphatase enzymes to form longer chain and branched alcohols or alkenes such as the 15-carbon alkene farnesene (Jovanovic Tews, 2010). Most efforts to date on exploiting the isoprenoid pathway have focussed on optimizing production of the 15-carbon amorphadiene, a key precursor to the synthesis of various pharmaceuticals (Peralta-Yahya & Keasling, 2010). The biggest challenge in these processes is maximizing yield of C_5 IPP and DMAPP precursors. In nature, only trace amounts of these compounds are made by prokaryotes such as *E. coli* via pyruvate using the deoxy-xylulose (DXP) pathway. This pathway is the only one in Figure 4-2 that does not involve the formation of Acetyl-CoA. However, Martin et al. (2003) have increased yields of IPP and DMAPP through formation of Acetyl-CoA by heterologously expressing the mevalonate pathway of *Saccharomyces cerevisiae* in *E. coli*. Expressing this pathway in the yeast cell itself has been suggested as an even better strategy as it would leverage the yeast's capability as an industrially robust microbe and also exploit the yeast's eukaryotic ability to more highly overexpress terpene (10-carbon isoprenoid-derived alkenes) synthases which are usually of plant origin (e.g., *Artemisia annua*) and thus more difficult to express at high activities in prokaryotes. The pioneering work of Ro et al. (2006) showed that overproduction of IPP and DMAPP is possible in yeast and these researchers have engineered yeast cells to produce 115 mg/L of artemisinic acid, a closer intermediate to the antimalarial drug artemisinin than amorphadiene. One of the highest profile companies operating in this area is Amyris, which has leveraged its original research which was focussed on developing artemisinin as an antimalarial drug. Amyris is now using further derivatives of its modified microorganisms to produce farnesene, a diesel fuel precursor.

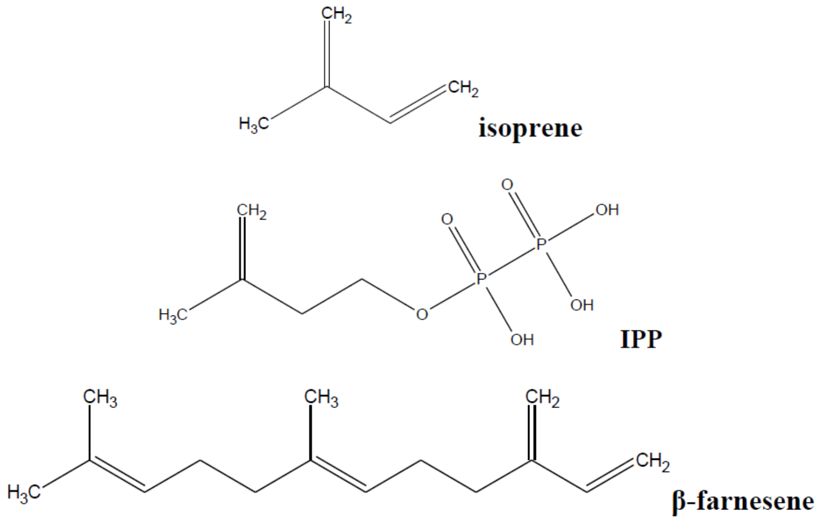


Figure 4-4: example isoprenoids

Other pathways such as the ketoacid pathway are also able to produce longer chain carbohydrates (Jovanovic-Tews et al., 2010). They are not reviewed here, however, because at present they are primarily applied to produce pharmaceutical and other specialty molecules, not biofuels.

4.3 Feasibility considerations

The promise of advanced biological pathways and processes for converting carbohydrate feedstocks to biofuels or drop-in biofuels intermediates is that they can be "bolted on" to existing sugar or corn starch mills. The economic viability of such processes is primarily influenced by biological conversion performance, efficiency and the amount of process inputs (e.g., nutrients, process energy and equipment) required to produce and recover the target product molecules from aqueous production broth. As sourcing sugar feedstocks as carbon sources for such processes is relatively costly, to achieve good process economy the biofuel (or biofuel intermediate) production and recovery process steps must be highly efficient and robust to achieve the type of performance demonstrated by the "gold standard" of established ethanol fermentation processes. The efficiency of biological conversion processes is typically characterized using the five measures described below:

- **Yield** (mass of product per unit mass of feedstock)**:** The proportion of carbon source feedstock (e.g., sugars or biomass) converted into the desired product as opposed to less desirable products such as cell mass, CO_2, or non-target compounds. The minimum product yield required to achieve cost competitive production is a strong function of feedstock cost.
- **Titer:** The concentration (g/L) of product in the production medium at the completion of the biological production process. The final product titer is strongly associated with process capital and operating costs since lower titers typically mean more production vessels (or volume) are required to produce a given quantity of product and greater amounts of process energy are required to recover a given amount of product.
- **Productivity:** The volumetric production rate (g/L/h) at which product is formed. Productivity strongly influences capital expenditure since slower production rates mean a greater residence time (e.g., more fermenter vessels) is required to achieve a given production target (e.g., t/d). For example, doubling volumetric productivity results in a 50% reduction in capital costs per unit of product.
- **Recovery:** It is insufficient to simply generate a desired product, as it must also be recovered at high yields and in usable form. The percent product recovery indicates how much of the generated product is economically recoverable, especially for products that are accumulated intracellularly. This is often well below 100%. For example, most fatty acids are generated intracellularly and their recovery requires cells to be permeabilised or lysed, making high levels of product recovery more techno-economically challenging.
- **Robustness:** The biological production microorganism must be able to be used at an industrial scale where there is less ability to precisely maintain targeted operating conditions (e.g., pH, temperature, concentration of dissolved gases, etc.). Yeasts, especially *S. cerevisiae* strains that

convert sugar feedstocks (hexoses in particular), are well recognized for their unrivalled industrial robustness. This is why many companies pursuing commercialization of biological drop-in biofuels technologies are proposing to heterologously express desirable metabolic pathways found in less industrially-proven microbes such as *Clostridia* and *E. coli* bacteria into yeasts.

The volumetric productivity metric combines biological process production time and final product titer. The volumetric productivity, expressed as mass of product per liter of reactor capacity per unit time (g/L/h), represents an overall average productivity for the biological process and provides one good indicator of its relative capital intensity. Higher volumetric productivity indicates that less reactor volume is needed to produce the same amount of targeted product. A higher product titer generally means a less costly product recovery system. The titer and volumetric productivity of selected biological processes relevant for drop-in biofuel production are summarized in Table 4-1, with the corresponding values for conventional ethanol fermentation processes.

Another important process metric is product yield. As noted earlier, ethanol processes are relatively efficient in channeling a significant proportion of substrate carbon to product, routinely achieving 90–95% of theoretical yield in converting 45 – 48% of feed sugar on a mass basis to ethanol. Lower theoretical and mass yields can be expected for biological conversion processes that produce more reduced molecules with higher H_{eff}/C ratios, as proportionally more oxygen, which represents approximately 46% of carbohydrate mass, must be removed. As a result, theoretical butanol mass yields from carbohydrates via the ABE pathway are 41% compared to 51% for ethanol. In reality, primarily due to product feedback inhibition, butanol mass yields from carbohydrates are in practice typically only 10-15%, about 33% of theoretical (Ranjan & Moholkar, 2012). Similarly, theoretical mass yields of the highly reduced molecule farnesene from glucose are estimated to be only 25 – 29% (Rude & Schirmer, 2009). To date, achieved yields have been about 50-67% of this theoretical value, with Amyris reporting 17 wt% farnesene yields from glucose (Pray, 2010) and the National Advanced Biofuels Consortium (NABC) analysis of Amyris' process reporting a 13% mass yield (Foust, 2011).

One notable feature of the Amyris process is that, according to the NABC, the carbon efficiency of the process is in the order of 60% with the remaining 40% available for energy production (O'Connor, 2013). While this results in low farnesene yields it can translate into a GHG credit that can be used as a positive attribute for marketing the technology. Essentially this 40% carbon is in the form of non-farnesene carbohydrates that end up in the anaerobic digester of the facility. Thus, for every unit of farnesene

Table 4-1: Biological process performance metrics for selected biofuel production microorganisms

Product (Fuel)	Production Microbe	Fermentation time	Titer (g/L)	Volumetric Productivity (g/L/h)	Theoretical Yield (g/g glucose)*	Major start-up companies	Major technological challnge	Reference
Ethanol	*Saccharomyces sp.*	6-12h	47 – 55 (6-11% v/v)[1]	2.00-3.00	0.51	commercial	Cost of sugar or starch **feedstock**	(Bai et al., 2008; Khosla, 2011)
Butanol	*Clostridium sp.*	48-96h	8 -17	0.08-0.46	0.41	Butamax, Cobalt, Gevo, Green biologics, etc.	End product **inhibition - low titers**	(Jang et al., 2012)
Butanol	*Clostridium sp.*	72h	20	0.34	0.41	Idem	Idem	(Qureshi & Blaschek, 1999)
Farnesene	Amyris *Saccharomyces sp.*	150h	104	0.70	0.25-0.29	Amyris	**Yield, productivity**	(Pray, 2010; Rude & Schirmer, 2009)
Ethanol	*Syngas fermentation Clostridium ljungdahlii*	n/a	11-48	n/a	n/d	LanzaTech, INEOS Bio, Coskata	**Gas-liquid mass transfer**/low water solubility of H_2, CO	(Munasinghe & Khanal, 2010)
Fatty acids	*Dunaliella Salina*	n/a	2-6	0.3 $g/m^2/h$	0.29	Solazyme	Yield, recovery	(Darzins et al., 2010)

[1] more than 12% w/v in US conventional corn-to-ethanol mills

(diesel) energy, one unit of methane energy is produced. This methane is combusted to generate heat and power (about 87 kWh of power per tonne of sugar according to O'Connor (2013)). As half the recoverable energy (excluding carbon in CO_2) from the sugar is stored in the diesel product and the other half is utilized for combustion this results in a significant GHG savings credit to the overall process. Amyris claims that the life cycle of their *Biofene* fuel emits 80% less GHG than petroleum diesel (Amyris, 2013b)

A significant degree of technological uncertainty and risk remains in biological processes for producing drop-in biofuel-relevant molecules, especially when genetic engineering of the production microorganisms is involved. The lipids and solvent-type product molecules used as precursors for drop-in blendstocks are usually secondary metabolites which are not directly associated with cellular energy metabolism but more with cell growth, maintenance and survival. They are typically produced in only small amounts in excess of what is required for cell growth unless the microorganism is stressed. Another challenge is that, when larger amounts of these types of products are produced, it is usually at the expense of cell growth. For example, algae produce higher yields of lipids when they are nitrogen starved and are thus limited in carrying out the protein synthesis needed for growth (Darzins et al. 2010). From a microbe survival standpoint, saturated compounds like lipids are accumulated in non-growing cells as a means of storing energy to protect the organism against potential future energy limitations (Darzins et al., 2010; Jovanovic Tews et al., 2010). There is also usually a lag in the time between the initiation of the biological process and the onset of accumulation of secondary metabolites like lipids. In contrast, ethanol production by yeast (or bacteria) occurs by a central metabolic pathway linked to primary energy metabolism (Bai et al., 2008). As such, fermentative ethanol production is directly associated with cell growth and there is no time lag in ethanol production after the process is initiated.

The industrial robustness of microbial production strains and the ease of scale up of biological production processes will also have a significant influence on how quickly advanced biological processes for drop-in-relevant products can be successfully commercialized. The industrial challenges differ signficantly for aerobic (isoprenoid and fatty acid) and anaerobic processes (n-butanol and isobutanol). Although biobutanols can be produced in strictly anaerobic processes for which considerable industrial experience has been developed over the past decades, butanol production processes so far continue to exhibit relatively slow growth rates and low product titers, which makes them more susceptible to contamination by competing microbes (as well as bacteriophages if bacterial production hosts are used).

A recent techno-economic assessment comparing butanol and ethanol production found that, on an energy basis (lower heating value, LHV), butanol had 50% of the yield and 25% of the productivity of ethanol, with the lower yield translating into higher feedstock costs per unit of fuel energy produced while the lower productivity translated into higher capital costs (Pfromm et al., 2010). No minimum fuel selling price (MFSP) was reported in this study but other work using the US DOE standard large scale process model basis (2000 tpd feedstock input, 10% return on investment) and a feedstock price of US $65/t, projected the MFSP of butanol to be US $5-6/gal ($1.3-1.6/L) (Jovanovic-Tews *et al*., 2010), which is slightly higher than the commodity chemical price for butanol (ca. USD $5.00/gal or $1.32/L, (Informa Economics, 2013)) and significantly higher than the energy equivalent gasoline price (US $2.25/gal or $0.60/L, based on USD $2.9/gal & 36 MJ/L gasoline and 28 MJ/L butanol).

The two aerobic processes discussed in this chapter, isoprenoid and fatty acid (lipid) synthesis, have not yet been demonstrated to be industrially robust at large scale (> 500,000 L) thus their technology risk and contingency allowances remain higher than currently projected for butanol (Amyris, 2013; LS9, 2013; Gevo, 2013). Another issue is that in order to produce the reducing power required to drive biosynthesis a significant proportion of feed carbon source must be oxidized to CO_2 a reaction which is also exothermic. The exothermic nature of aerobic submerged biological production processes, as well as the need to constantly supply molecular oxygen (O_2) at sufficient levels to maintain aerobic conditions, pose significant challenges to achieving economical scale up. Table 4-1 compares scale up issues encountered in aerobic biological production and anaerobic fermentation processes.

Table 4-2:Scale up issues for anaerobic vs aerobic fermentation

	Anaerobic	Aerobic
Heat generation	235 KJ/mole	2840 KJ/mole
Ability to dissipate heat externally	Yes	No
Compressed air inputs	Yes	No
Largest reactor size	3,700,000 L	1,430,000 L
Average reactor size	2,800,000 L	380,000 L
Risk of ceasing digestion due to high pressure	Lower	Higher

Source: (Hannon et al., 2007)

The challenging task of assessing the feasibility of biological (and thermochemical) drop-in biofuel processes is being tackled by the US DOE-funded National Advanced Biofuels Consortium (NABC) (box 4-1). Notably, the NABC has selected Amyris's aerobic isoprenoid metabolism-based farnesene production process as one of its two most promising technologies for scaling up commercial production of drop-in biofuel precursors.

Box 4-1: NABC: The US DOE grand challenge for drop-in biofuel technologies

The National Advanced Biofuels Consortium (NABC) is a partnership of 17 industry, national laboratory, and university members to develop technologies to convert lignocellulosic biomass feedstocks to biofuels that are compatible with the existing US transportation infrastructure. With $35 million of American Recovery and Reinvestment Act funding from the U.S. Department of Energy and $14.5 million of partner funds, the National Advanced Biofuels Consortium program started in 2011 and is due for completion by the end of 2013. In stage I (early 2011), NABC examined six process routes spanning biochemical, thermochemical and hybrid approaches to assess their potential to meet project objectives. In Stage II, the Amyris biochemical and Virent hybrid (catalytic sugar processing technology, discussed in Chapter 5) process routes were selected for further research and development. Two thermochemical routes – hydropyrolysis and hydrothermal liquefaction – were refocused to address key process issues. The consortium continues to develop and assess the feasibility of these downselected processes (NABC, 2013).

Another aspect of industrial scale up is the opportunity to leverage existing oil refinery infrastructure. In the case of biological production processes, the only step that can readily be performed at a petroleum refinery is the final hydrotreatment step, if needed, as well as perhaps final blending to create a fungible blendstock. As long as the oxygen content of biologically produced intermediates can be brought to roughly the same level as vegetable oils or fatty acids (~ 10 wt%), they can be treated in a similar way as oleochemical feedstocks, as discussed in Chapter 2.

In addition to hydrotreatment, molecular hydrogen (H_2) can also be used to boost reducing processes in metabolic pathways and thereby improve yields. The more external hydrogen that can be used as a source of “reducing” energy in biological production processes, the more carbon can be preserved in the final fuel product. The higher the energy content and the lower the oxygen content of the product molecules, the more energy is required by the production microorganism for its biosynthesis. For every step of decarboxylation or reduction of metabolic intermediates, some fermentable carbon is consumed and oxidised to CO_2 in order to provide the necessary reducing power (in the form on NADPH or HCO_3) for the reductive biosynthesis reactions to occur. In other words, making energy-dense and low oxygen content biohydrocarbons via biological processes consumes extra carbon and thus reduces yields. As is emphasized in the next section, Chapter 5 on hybrid conversion platforms, the use of external hydrogen inputs can be employed in syngas fermentation, particularly when the syngas source is hydrogen deficient. For example, LanzaTech's biological approach is able to use CO_2, the most oxidized form of carbon, but only if significant molecular hydrogen is also provided.

4.4 Commercialization efforts

A number of companies are trying to commercialize the biochemical route to drop-in biofuels and some examples are summarized below.

4.4.1 Butanol

Butamax, a joint venture between Dupont and BP, is focused on isobutanol production by engineered microbes. It is operating in a similar technology space as Gevo (see below) and the two companies are engaged in on-going litigation over intellectual property. One of Butamax's patents is on isobutanol production in yeast (Feldman et al., 2008) and another one on increasing dihydroxyacid dihydratase (DHAD) activity (Dundon et al., 2011) to improve production of isobutanol and other metabolites in yeast. Butamax has a demonstration unit in Hull, UK. They ultimately plan to utilize the 190 MLPY (50 MGPY) High Water corn ethanol facility in Minnesota, USA for commercial production (Lane, 2011a). In November 2012, Butamax added a technology laboratory in Paulina, Brazil in order to further test its biosynthetic isobutanol production technology using sugarcane derived sucrose feedstock (Biofuels-Journal, 2010).

Gevo, based in Colorado, USA, is trying to commercialize their patented Gevo Integrated Fermentation Technology (GIFT) approach to isobutanol production. Unlike n-butanol, isobutanol is branched and more suitable for fuel blends (as discussed in section 4.2.1). The company claims it can achieve higher yields and recoveries of isobutanol compared to n-butanol. The GIFT process consists of genetically engineered yeast and continuous *in situ* recovery tailored to isobutanol extraction from fermentation broth. Although details are not publically disclosed, based on publically available presentations and patents (Evanko et al., 2012), the preferred recovery route is likely to be gas stripping because isobutanol has a boiling point of 108 °C compared to n-butanol's boiling point of 118^{o}C. This attribute in itself possibly makes the recovery less energy intensive. The exact productivity of the GIFT platform is not publically known although in consultancy reports Gevo has claimed 5 times higher productivity than reported to date for n-butanol (Nexant, 2012). Assuming that n-butanol's practical volumetric productivity is 0.3 g/L/h, the GIFT platform should achieve 1.5 g/L/h. This rate is half the current productivity of ethanol as summarized in Table 4-1. Gevo has a strategic collaboration with ICM, the engineering company that has designed 60% of the US's existing corn to ethanol mills. The first 3.8 MLPY (1 MGPY) demonstration facility was "bolted on" to a corn to ethanol facility in St Joseph, Missouri. In September 2010, Gevo acquired its first production facility in Luverne, Minnesota. In early August 2013, Gevo announced that its second, one million liter fermenter and GIFT system was brought online at its Luverne, Minnesota facility, and they also announced they would be opening a facility for catalytically upgrading isobutanol to renewable paraxylene and jet fuel in Texas in September 2013. Other strategic partnerships have been formed, including with Mustang engineering for jet fuel tests and certifications and with Cargill to develop a yeast biocatalyst for cellulosic feedstock derived isobutanol.

While Gevo and Butamax are targeting isobutanol, many other biobutanol start-ups are focused on "conventional" n-butanol produced via the traditional ABE pathway. Cobalt, Green Biologics, GranBio, Microvi, Optinol and Rhodia are all examples of companies working to commercialize n-butanol production. Several of these companies intend to retrofit existing sugar or corn mills for butanol fermentation and recovery. Most companies claim they will be able to achieve cost parity with ethanol on an energy basis.

4.4.2 Fatty acids, long chain alcohols and alkenes

Amyris is a University of California, Berkeley spin off company founded in the San Francisco Bay area in California, USA in 2003. In 2005, the company received a grant from the Bill and Melinda Gates Foundation to optimize a yeast-based isoprenoid biosynthetic platform for producing the antimalarial drug precursor artemisinic acid (Amyris, 2013). Using this same synthetic biology platform Amyris later collaborated with the French oil company Total to commercialize production of farnesene as a diesel and jet drop-in biofuel component. Farnesene, marketed by Amyris under the trade name Biofene^{TM}, is also used as a precursor for cosmetic ingredients such as squalene which is normally extracted from the fat of large sea mammals. The biofuel application of Biofene derivatives such as the alkane farnesane were tested in blends of diesel for automobiles and in blends of jet fuel for aircraft at the 2013 Paris Air Show (Amyris, 2013a). The blending ratio of Amyris biofuel in the petroleum jet fuel was not specified.

LS9 is another San Francisco Bay area company that has developed a proprietary synthetic biology platform based on *E. coli*, with long chain fatty alcohols currently its main product focus (LS9, 2013). By leveraging *E. coli*'s natural ability to metabolize a range of hexose and pentose sugars, the company claims they are well positioned to utilize lignocellulosic sugars and provide a "capital-light" production platform (LS9, 2013). They have partnered with Virdia, a company targeting biomass sugars production, on a $9 million US DOE grant to build a demonstration plant in Florida, USA to convert woody biomass to fuels. However, the facility will initially use glucose (starch derived sugar) as the feedstock. In 2010, LS9 purchased a demonstration facility in Florida, and has since successfully demonstrated its production technology in a 135,000 L fermenter (LS9, 2013). In the short term, LS9 is primarily focusing its technology on higher value chemicals rather than biofuels.

Solazyme is another San Francisco Bay Area company which has developed a proprietary biotechnology platform based on heterotrophic algae. Using sugar feedstock Solazyme's algae are able to make a range of biological oils (TAGs), with various products sold in cosmetics stores. Algenist^{TM}, for example, is a line of anti-aging skincare products formulated with alguronic acid sold in about 1000 stores across the US, Canada and the UK (Solazyme, 2013). The company has stated that its strategy is to first develop the skin care, cosmetics and other value-added chemicals markets and then to scale up production to supply transport fuel markets. In 2010, the company sold 80,000 L of hydrotreated algal oils to the US Navy for use in marine fuel blends. These oils cost several times more than their equivalent petroleum based counterparts, as profiled in several media outlets (Alexander, 2012; Roig, 2012). However, the company claims that their oils can be priced in the same range as heating oils which at the time of writing is about 1000 USD/t (IndexMundi, 2013; Solazyme, 2013)

4.5 The value added chemicals opportunity

Current trends in biochemically based drop-in biofuel technologies suggest that the production of higher value chemicals is a more attractive value proposition than biofuels, at least in the near term. Although biochemically based drop-in biofuels have the potential to “piggy-back” on existing sugar or starch-to-ethanol facilities, the lower volumetric productivities and yields of these still evolving industrial processes is proving challenging when trying to achieve cost competitive biofuel production. In fact, some biochemical products can be used either as biofuels or as chemical feedstocks or solvents. Thus, the biochemical based platforms have an advantage in that they can be used to also produce higher value chemicals at high selectivities (See Box 4-2 describing NatureWorks approach). As the use of these products as chemical feedstocks tends to be more profitable than as fuels, it is unlikely that most biochemical drop-in production will be used as fuels before their higher value markets as chemicals are saturated. Normal butanol, for example, commands a price of ca. USD $5.00/gal or $1.32/L, (Informa Economics, 2013) as a commodity chemical versus US $2.25/gal or $0.60/L (based on USD $2.9/gal & 36 MJ/L gasoline and 28 MJ/L butanol) as a gasoline energy equivalent. As biochemical product chain length gets longer even more valuable applications are possible. For example, as Amyris has demonstrated, longer chain lipids are likely to command higher prices in the cosmetics industry.

From an energy and hydrogen balance standpoint, biochemical platforms are more efficient at producing oxidized products than highly reduced molecules. Highly oxidized products such as lactic, acetic and adipic acids command significantly higher prices than ethanol or biodiesel and they are challenging to make by non-biochemical platforms. Such oxidized molecules can also be produced by oxidation of petroleum cuts using various processes (e.g., the oxosynthesis process for butanol). While technically feasible they are costly and entail the risk of over-oxidizing and thus “burning” up a portion of the petroleum feed and incurring associated yield losses (Gary et al., 2007; Vennestrøm et al., 2011). Since sugar molecules inherently contain high amounts of oxygen, it is more efficient to convert them to oxidized intermediates and aim for higher value chemicals markets. The H_{eff}/C ratio staircase shown in Figure 4-5 demonstrates the number of steps that have to be taken to bring sugar feedstocks to the functional equivalence of petroleum products. It is apparent that fewer steps must be ‘climbed’ (or none in the case of sugar conversion to acetic or lactic acids) along the H_{eff}/C ‘staircase’ for sugar to be converted to intermediates that, in the short term at least, can be sold as chemical precursors rather than as fuels. Synthetic biology is advancing rapidly and new tools provide ever greater flexibility as to the range of products and their tuning for desired customized chemical properties that can be achieved through biochemical platform routes. The ability to tailor complex molecules and achieve extremely high production selectivity is generally absent in thermochemical technologies.

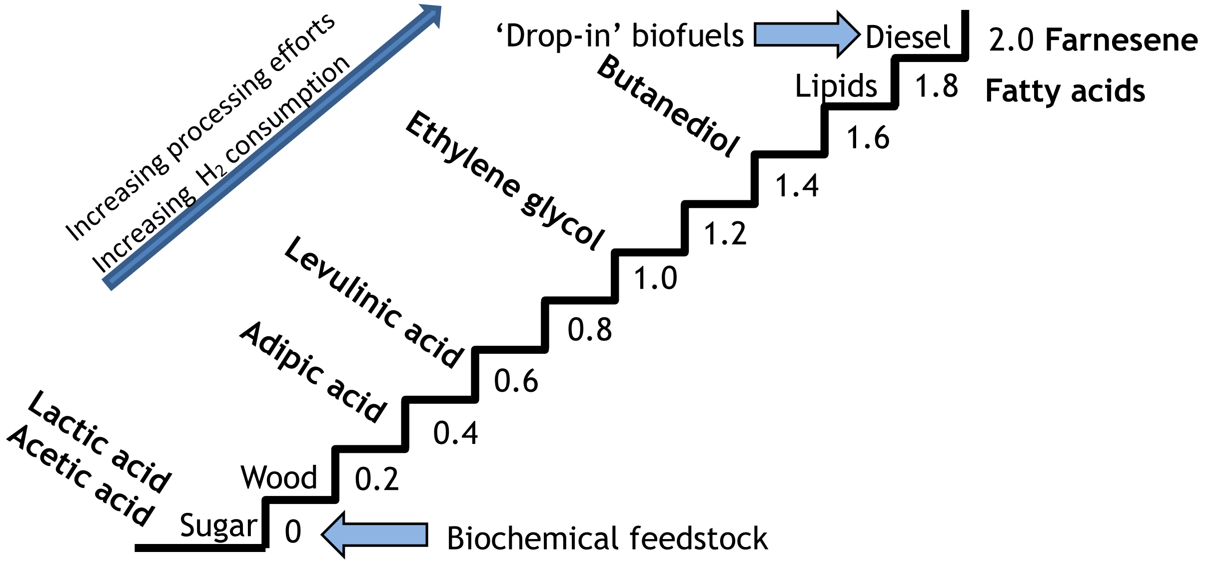


Figure 4-5: The H/C_{eff} ratio in relation to the biochemical platform and its intermediates

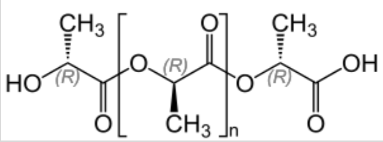
An example of a biofuel process that produces intermediates that are of potentially higher value as chemicals than fuels is the technology proposed by Zeachem. The company uses the acetogenic bacterium *Clostridium thermoaceticum* to convert sugars to acetic acid (a more oxygenated compound than ethanol, see staircase in Figure 4-5) and the acetic acid is then recovered (in the form of acetate salts) and hydrogenated to ethanol (Zeachem, 2013). Hydrogen for hydrogenation is imported, although in theory it can also be generated from biomass lignin residues. The biggest advantage of this acetogenic pathway is that all carbon is funneled to acetic acid formation and there is no carbon “waste” funneled to the formation of CO_2. Although this platform can be used to produce biofuels, the acetic acid it produces is too oxidized to be a drop-in biofuel intermediate, and the hydrogen required to convert it to ethanol may outweigh the economic and environmental benefits of avoiding CO_2 production. At the time of writing, the value of acetic acid (USD $3000/t) is higher than the net revenue that would be achieved by hydrogenating it to ethanol (USD $850/t).

Another notable example of sugar feedstocks being used to produce higher value oxygenated chemical intermediates, such as polylactic acid (PLA) for polymer applications is NatureWorks, which was originally formed as a joint venture between Cargill and Dow. Natureworks primary manufacturing facility in Blair, Nebraska has the capacity to produce 140,000 t/year of PLA from corn starch derived glucose. PLA polymers have many uses in textiles and plastics markets, including as renewable packaging materials (see Box 4-2). Sugar conversion to lactic acid by fermentation exhibits a theoretical mass yield from glucose of 1.00 and process production yields of up to 0.9 g/g are reported (Hofvendahl & Hahn-Hägerdal, 2000).

The counterargument for using biological processes to convert renewable feedstocks to higher value chemicals instead of fuels is that the markets for chemical products are quite limited compared to those for fuels. Although this is true, bio-based chemical markets are growing rapidly and expected to continue to expand for the foreseeable future, largely as a result of a sustained increase in petroleum prices and growing awareness of the benefits of being able to market renewably sourced products. Several of the advanced biological conversion companies reviewed earlier (e.g., Amyris, Gevo, LS9, Solazyme, etc.) are currently generating a significant part of their revenue from sales of biobased products rather than drop-in biofuels (Amyris, 2013a; Bomgardner, 2012; Gevo, 2013; LS9, 2013; Solazyme, 2013). Other companies have clearly stated they are primarily targeting value added oxygenated products such as dicarboxylic acids (e.g., Myriant’s succinic acid) and dialcohols (e.g., Genomatica’s butanediol or DuPont’s 1,3-Propanediol). A 2012 issue of E&EN magazine provides a world map showing the breadth of biochemically based facilities being built for the production of chemical feedstocks (Bomgardner, 2012). Most of these facilities are located in biofuel producing countries such as the US and Brazil.

Box 4-2: NatureWorks, LLC: Biodegradable sugar-derived polymers at commercial scale

NatureWorks LLC
ingeo: ingenious materials from plants not oil



Nature Works LLC is a joint venture between Cargill and Dow, currently producing an annual total of 140,000 tonnes of polylactic acid (PLA). This polymer is produced at a dedicated facility in Blair, Nebraska, USA using corn dextrose as the feedstock. The dextrose is fermented by Lactic Acid Bacteria (LAB) and the resulting lactic acid is then polymerized to form various types of PLA polymers for use in textiles and plastics formulations. The facility converts $400-500/t dextrose to $3000-4000/t PLA (approximate global prices at the time of writing, www.alibaba.com). The company was founded in 1997 as Cargill Dow LLC with original plans to begin operations in 2001. The company was renamed NatureWorks LLC in 2003 and full operations at the Nebraska facility began in 2009. The PLA product is marketed as Ingeo^{TM} and its production is reported to result in significantly lower GHG emissions than petroleum derived equivalents (Binder & Woods, 2009). The polymer is biodegradable and degrades without generating significant amounts of methane (Kolstad et al., 2012). The 2012 London Olympics used 8,000 t of Ingeo^{TM} for food and other packaging, which after use was composted to produce soil amendments.

A number of business intelligence organizations have also published estimates of the future size and growth rate of biobased chemicals markets. For example, Nexant projects that by 2015 global biobased chemical markets will grow to 5 million metric tonnes per year (Bomgardner, 2012) while Lux Research projects that biobased materials markets will grow 17.7% per year to reach 8.1 million tonnes by 2015 (Lux Research, 2010). The UK's National Centre for Biorenewable Energy, Fuels and Materials (NNFCC) estimates that by 2020 the global market for renewable chemicals and polymers will reach 50 million metric tonnes and that oxygenated fermentation products such as alcohols and carboxylic acids will account for 17% of this market (i.e., 8.5 million metric tonnes) (Higson, 2011).

The Forest Products Association of Canada recently published its "Biopathways" strategic analysis, which assessed various scenarios for adding value to Canada's forest products industry (FPAC, 2011). A key conclusion was that value added renewable chemicals should be prioritized to help modernize the Industry, diversify its markets and improve its profits. As an example, the bio-plastics and plastic resins market is expected to grow by 23.7% a year to reach USD $3.6 billion market by 2015 (FPAC, 2011). Although these markets are still quite small compared to transport fuels markets of 2 billion tonnes and USD $3 trillion, they are sizeable compared to the current capacity of the biomass processing sector and of similar scale to the current biofuel production volume of 60 million tonnes (IEA, 2012b).

In summary, the biochemical platform, in contrast to the oleochemical and thermochemical platforms, can produce pure molecular streams of functionalized molecules which currently command higher market prices in chemical markets than as intermediates for drop-in biofuels. The primary role of the metabolic pathways involved in drop-in biofuel production is to biologically deoxygenate the sugar feedstock (low H_{eff}/C) to produce a more highly reduced or saturated products such as isoprenoids and fatty acids (high H_{eff}/C). These biological processes are in general comparatively energy- and carbon-intensive and achieve productivities about one order of magnitude lower than conventional sugar-to-ethanol fermentation processes. Despite this situation, interesting possibilities exist to increase rates and yields of biochemical based processes by inserting externally supplied hydrogen or otherwise supply the needed reducing power. The addition of external hydrogen could be used to minimize the need for microbes to generate their own reducing power by oxidizing a portion of the sugar, starch or cellulose carbon feedstock. However, hydrogen inputs are costly and unlikely to be used in biochemical platforms to produce commodity drop-in intermediates.

With fewer processing steps and less hydrogen consumption and higher feedstock conversion yields, biochemical platform technologies can be used to produce oxygenated and low H_{eff}/C products that will likely generate higher revenues as higher value chemicals than as biofuels. Market saturation issues for renewable chemical products should not be too much of a concern in the near term due to projected strong growth in bio-based material markets.

CHAPTER 5: HYBRID PLATFORMS

Although the majority of drop-in biofuel technologies are captured under one of the previously described oleochemical, thermochemical or biochemical platforms, some technologies combine approaches from two or more platforms and are thus referred to as "hybrid" routes to drop-in biofuels. The main examples include:

- Biological conversion (fermentation) of biomass gasification-derived syngas to alcohols. Companies that have investigated or are developing this approach include Coskata, LanzaTech and INEOS Bio.
- The thermochemical catalytic conversion of biochemical platform-produced sugars and perhaps other solubilized carbon species to hydrocarbon biofuels. The company Virent Energy Systems ("Virent") is the primary current developer trying to commercialize this approach.
- The thermochemical catalytic conversion of biochemical platform produced alcohols (e.g., ethanol or butanol) to hydrocarbon biofuels. Companies pursuing this approach include BIOGY, Cobalt and Gevo.

Each of these hybrid technologies offer advantages as well as present new challenges compared to thermochemical or biochemical platform routes discussed in chapters 3 and 4, respectively. For example, traditional sugar fermentation is able to ferment only the saccharide portion of biomass whereas syngas can be produced from the entire biomass carbon (i.e., including lignins, extractives and other non-sugar carbon-containing compounds) such that there is potential to convert more of the feedstock to fuel product(s) via syngas fermentation. Similarly, catalytic conversion of sugars and other organic carbon compounds offers the potential to convert sugars and perhaps more than just sugars to a broader range of higher energy products than available via traditional biological conversion technologies. The third approach, alcohol-to-drop-in, involves the catalytic conversion of higher H_{eff}/C alcohols rather than lower H_{eff}/C sugars (for which $H_{eff}/C = 0$) but is otherwise conceptually similar to catalytic upgrading of sugars. These three hybrid routes to drop-in biofuels or fuel blendstocks are discussed further in the following sections.

5.1 Syngas fermentation

As described in Chapter 3, the conversion of syngas to liquid biofuels can be achieved thermo-catalytically. However, some fermentative microorganisms can also utilise syngas as their carbon and energy source while producing potential drop-in biofuel intermediates as a major product. Some autotrophic microorganisms can use single carbon compounds such as CO and CO_2 as sources of carbon and energy-rich compounds such as CO and H_2 as sources of energy. In the same way thermochemical syngas upgrading involves the use of catalysts, microorganisms that convert syngas to biofuels such as ethanol require metals such as cobalt and nickel (in relatively trace amounts) to catalyze essential metabolic enzyme activities (Hayes, 2013). A range of microorganisms can ferment syngas to intermediates such as ethanol, butanol and acetic acid, including acetogenic bacteria such as *Clostridium ljungdahlii* and *Clostridium carboxidivorans* (Munasinghe & Khanal, 2010). These microorganisms use the *Wood-Ljungdahl* pathway to reduce CO to Acetyl-CoA, from which ethanol and butanol are produced via the pathways described in Chapter 4. The reducing power required for the first reaction comes from the H_2 in the syngas or from the oxidation of CO to CO_2 via a carbon monoxide dehydrogenase enzyme (Daniell et al., 2012; Weber et al., 2010). Here again, as seen in thermochemical deoxygenation routes discussed in Chapter 3, there is a trade-off between carbon efficiency and hydrogen consumption. From an evolutionary perspective these metabolic pathways are found in some of the most primitive microorganisms on earth. Approximately 4 billion years ago, well before oxygen became abundant in the atmosphere, these types of microorganisms survived by metabolising CO and H_2 gases (Daniell et al., 2012).

Syngas fermentation is claimed to have several advantages compared to its “parent” processes, i.e., sugar fermentation and thermocatalytic syngas conversion (Daniell et al., 2012; Munasinghe & Khanal, 2010). For example, compared to sugar fermentation, this approach is able to utilise lignin in addition to carbohydrate fractions of biomass. In comparison to thermocatalytic syngas conversion it has also been claimed to be economical at a smaller scale, because of lower capital costs, while proving to be less sensitive to impurities (Daniell et al., 2012). However, the volumetric productivity of this hybrid approach is still quite low, as summarized in Table 4-1, which shows current volumetric productivities are around 0.3 g/L/h, similar to the biochemical production of butanol and farnesene. The primary limiting step for syngas fermentation is the low solubility of CO and H_2 gases in aqueous solutions as these gases must first be absorbed into the aqueous fermentation broth to be microbially assimilated

(Bradwell et al., 1999). As the gas-liquid mass transfer and solubility of both molecular hydrogen and carbon monoxide in water are quite low compared to more conventional sugar substrates (where gas-liquid mass transfer isn't needed), syngas fermentation rates are typically constrained by physical mass transfer limitations rather than being limited by metabolic capacities. From an energy balance perspective, syngas also has to be cooled down from a production temperature of ca. 700 °C or higher to ca. 50 °C or less before it can be fermented. This significant cooling requirement is of concern because, as discussed in Chapter 3, large temperature fluctuations in gasification systems result in significant engineering challenges and generally have an adverse effect on process energy efficiency.

The gas-liquid mass transfer challenge of syngas fermentation platforms has been a long-standing focus of engineering research and various reactor designs have been assessed to try to improve the contact surface area between gases and liquids and achieve increased dissolution and diffusion rates. Designs include continuous stirred tank, microbubble dispersion stirred tank, bubble or gas lift columns, hollow fiber and other membrane-based systems, trickle bed and monolithic biofilm reactors. A detailed description of possible reactor designs and their operation and relative efficiencies is provided by Munasinghe & Khanal (2010).

Several companies and research institutions are trying to develop and commercialize drop-in biofuels based on variations of the syngas fermentation technology platform. Some of the leading companies and their recent activities to commercialize this hybrid route are briefly described below:

INEOS Bio is a fully owned subsidiary of the oil and chemicals company INEOS. Their technology builds on the pioneering development of syngas fermentation technology carried out by James Gaddy and colleagues at the University of Arkansas and then Bioengineering Resources beginning in the 1980s (Bryan, 2011; INEOS, 2013). INEOS Bio's technology is based on a patented process using proprietary microorganisms to convert biomass derived syngas to ethanol and other bio chemicals. INEOS Bio recently completed a 30 MLPY (8 MGPY) syngas to ethanol facility in Vero Beach, Florida, USA. This facility, named the Indian River Bioenergy Center, started producing and commercially selling ethanol in August 2013. The plant, which cost $130 million to construct (backed by $75 million in US DOE loan guarantees), uses as feedstock municipal solid waste (MSW) from the Vero Beach municipality. Besides producing ethanol, the facility is designed to coproduce 6 MW (gross) of power. Facilities capable of using MSW feedstock can have a significant competitive economic advantage because they essentially operate as a waste management facility and receive a tipping fee for taking in feedstock and thus are producing products from a negative cost feedstock. The 6 MW power generation component is important to the economics of the Indian River facility as their power can be sold at a relative premium compared to many other jurisdictions in the USA (INEOS, 2013).

Founded in New Zealand in 2005, and headquartered in Chicago, Illinois, LanzaTech has developed a gas-substrate fermentation process to produce ethanol and other and chemicals from carbonaceous CO-rich gases. LanzaTech operates research laboratories in the USA, China and New Zealand, and currently operates two sub-commercial scale facilities (Lanzatech, 2013). Their pilot facility, located at the BlueScope Steel mill in New Zealand and linked directly to the mill's off-gas exhaust, has been operating since 2008 and has an ethanol production capacity of 15,000 gal/year (56,800 L/year). In November 2012, LanzaTech completed the first phase of a multi-phase project with Baosteel, China's largest steel producer. This demonstration facility has an ethanol production capacity of 100,000 gal /year (380,000 L/year) and will convert CO-rich waste gas from Baosteel's production facility using LanzaTech's gas fermentation technology. The demonstration facility is intended to be a precursor of a 190 MLPY (50 MGPY) commercial facility to be built in 2014. In 2012, construction of a second demonstration facility was initiated near Beijing in partnership with Capital Steel, China's fourth largest steel producer. LanzaTech also plans to operate a commercial facility in Soperton, Georgia, USA to be named the Freedom Pines Biorefinery based on its January 2012 acquisition of the former Range Fuels biomass gasification facility (described in Chapter 3). The company has a number of high profile partners including Siemens, Petronas and Baosteel on the production side and Virgin Atlantic and Boeing on the product off-take side. For its aviation fuel projects, LanzaTech has partnered with Swedish Biofuels AB which specializes in alcohol-to-jet catalytic conversion technology. All of the plants, other than the Soperton facility, will use CO-rich waste gases from either the steel or oil refining industries as their carbon source feedstock (LanzaTech, 2013).

LanzaTech recently announced a new process pathway to convert CO_2 to ethanol using its proprietary microorganisms (LanzaTech, 2013). Although this process has received a considerable amount of press attention as a potential carbon capture solution, significant amounts of hydrogen will be required to convert this fully oxidized form of carbon to a chemically reduced alcohol product.

Syngas fermentation companies have shown ethanol can be commercially produced from CO and H_2-rich gases (syngas) or CO-rich gases via fermentation. Although ethanol is itself not a drop-in biofuel, at the right price point it can be an attractive intermediate for drop-in fuel production. Moreover, the prospect holds that similar fermentative pathways as used in gas-based ethanol production can be used to produce even more reduced products, for example alcohols such as butanol, which are better suited than ethanol as drop-in biofuel intermediates.

5.2 The Zeachem process

Zeachem's process is based on using an acetogenic bacterium isolated from the digestive system of termites to convert sugars to acetic acid at near 100% carbon efficiency. Unlike sugar fermentation to ethanol, in which one molecule of CO_2 is lost for every molecule of ethanol formed, no CO_2 is produced in Zeachem's sugar to acetic acid fermentation process. The acetic acid produced is subsequently reduced to ethanol through the addition of hydrogen. Zeachem claims higher ethanol production yields are possible using this "indirect ethanol" approach than in conventional "direct" sugar to ethanol fermentations (Zeachem, 2013). However, the need to produce hydrogen, nominally by gasification of biomass or lignin residues, introduces additional capital costs and operational complexities. The Zeachem process represents a hybrid platform that uses fermentation to produce an acetic acid intermediate and gasification to generate hydrogen to chemically reduce acetic acid to ethanol or other chemicals or biofuel intermediates. The company currently operates a 3.8 MLPY (1 MGPY) ethanol demonstration facility in Boardman, Oregon, USA and sees potential to expand on its technology platform to produce more highly reduced C3 and C4 products that could be used as drop-in biofuel intermediates (Zeachem, 2013).

5.3 Aqueous phase reforming and the Virent process

The technology for catalytically converting sugars or polyol feedstocks to monooxygenates, also known as aqueous phase reforming (or APR), is being developed by the company Virent Energy Systems (Virent), which intends to use it to produce drop-in fuels and value-added renewable hydrocarbon chemicals (Blommel & Cortright, 2008). This technology is classified as a hybrid platform because it converts sugars, nominally a biochemical platform feedstock, to drop-in biofuels using a thermochemical catalytic process. Variations of APR also have been used to produce hydrogen from the aqueous residues of pyrolysis oil separation and upgrading processes (Bridgwater, 2012). The APR technology builds on the pioneering work of researchers at the University of Wisconsin who showed that highly reduced carbon molecules could be produced when sugars (or other polyols) in aqueous solution were mixed with molecular hydrogen and passed over ZSM-5 catalysts (Cortright et al., 2002; Huber et al., 2004; Huber & Dumesic, 2006). This initial work ultimately lead to the creation of Virent and the development of its patented BioForming^{TM} process, which comprises a combination of the original APR process combined with upgrading technologies used in oil refineries, as further refined by Virent. In overview, this process employs heterogeneous catalysts operating at moderate temperatures (175 to 300 °C) and pressures (10 to 90 bar) and reduces the oxygen content of the (plant biomass derived) sugar or polyol feedstock through the three main steps described below (Blommel & Cortright, 2008; Hayes, 2013; Huber & Dumesic, 2006):

a) Acid-catalyzed dehydration of sugars;
b) Aldol condensation of dehydrated carbohydrates over solid base catalysts to form large organic molecules;
c) Dehydration/dehydrogenation of the large organic molecules to alkanes using bifunctional catalysts (this step represents a variation of conventional catalytic processing as found in petroleum refineries)

A schematic representation of the process is shown in Figure 5-1.

The Virent process yields a product exhibiting similar properties to petroleum reformate, although the exact mixture composition depends on the nature of the catalysts and reaction conditions used. Acidic catalysts such aluminosilicates (e.g., ZSM-5) favour the production of shorter molecules of more phenolic nature (more suitable for gasoline blends) while base catalysts favour chain elongation through aldol condensation and thus form longer chain liquid products (more suitable for diesel blends) (Blommel & Cortright, 2008). Noble metal catalysts such as Pt and Rh favour reforming of carbohydrates to hydrogen and CO_2 (Bauldreay et al., 2010). The reformate can then be upgraded to a drop-in biofuel using conventional refinery processes. The process consumes 12 wt% (of dry feedstock) hydrogen, some of which is produced via the APR process itself, as shown in Figure 5-1. Virent claims that >90% of the lower heating value (LHV) in the sugar and the hydrogen inputs is recovered in deoxygenated hydrocarbon products. Note, however, that there is so far limited public information on technical or economic details of Virent's process.

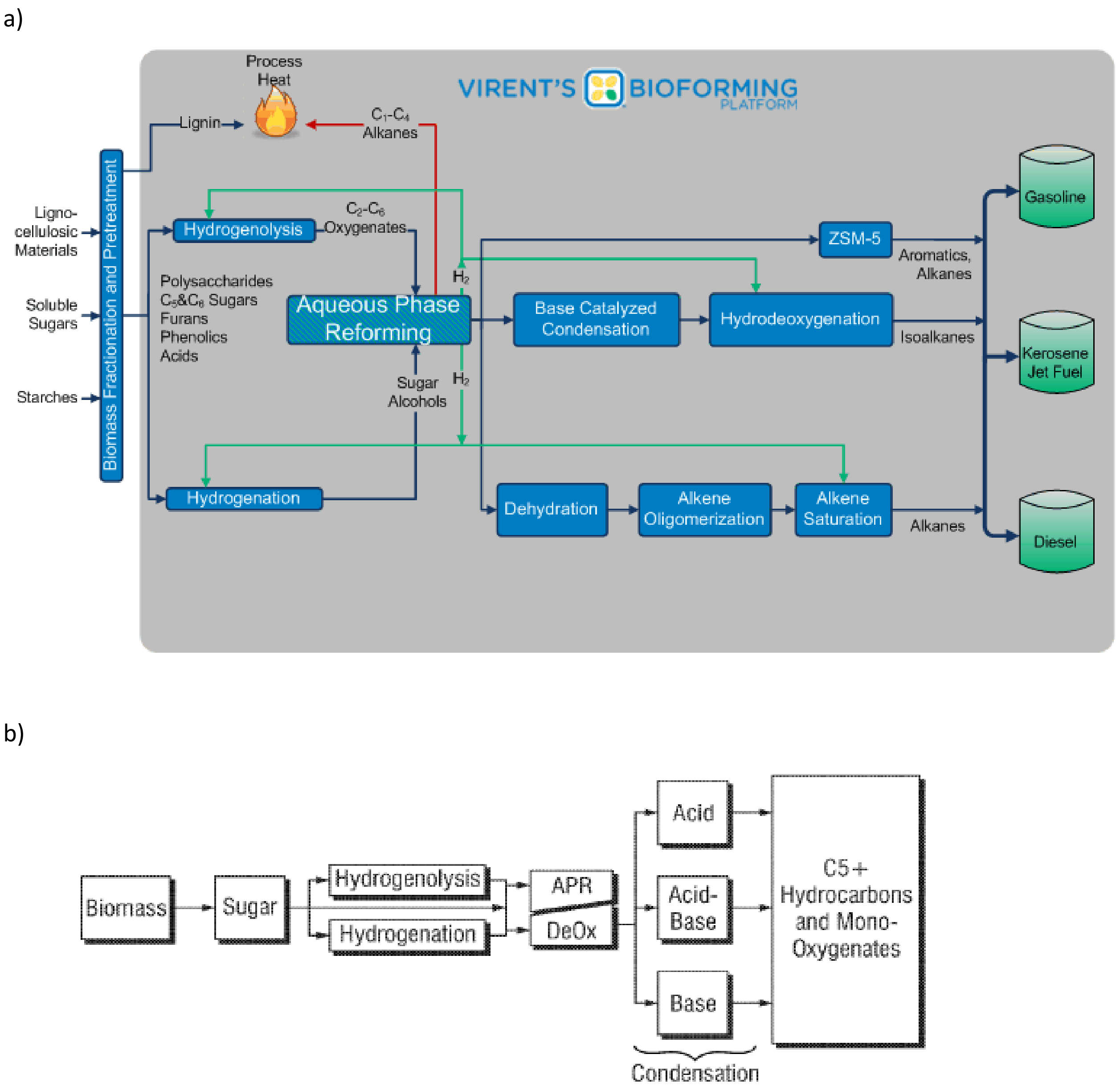


Figure 5-1: The Virent process. (a) Entire process. (b) simplified representation emphasizing key steps.
Source: (Bauldreay et al., 2010; Blommel & Cortright, 2008)

Compared to fermentation, the APR approach is attractive because it has the potential to be used to produce highly reduced (high H_{eff}/C) hydrocarbons from a diversity of water soluble organic carbon compounds including both C5 and C6 carbohydrates and at much faster reaction rates than are possible using biochemical routes (e.g., residence times of minutes vs hours or days). However, the APR reactions are less selective than fermentation processes and produce a complex mixture of organic molecules. Although the APR process uses non-exotic process components and catalysts, it faces similar catalyst coking and deactivation challenges to those previously discussed in chapter 2 for pyrolysis oil upgrading. This is because during catalytic upgrading of water soluble saccharides and bio-oil fractions, catalyst coking and deactivation have been shown to increase with decreasing feedstock H_{eff}/C ratio; feedstocks with an H_{eff}/C effective ratio less than 0.15 have been shown to cause large amounts of coke formation (more than 12 wt%) from homogeneous decomposition reactions Zhang et al. (2011). Given that sugars have an H_{eff}/C effective ratio of 0, demonstrating the ability to avoid coking problems through effective catalyst regeneration schemes will be key to commercializing aqueous phase reforming technology.

Headquartered in Madison, Wisconsin, USA, Virent was founded in 2002 with a goal of producing fuels and chemicals from renewable sugars and other water soluble organic carbon compounds. Virent has a 10,000 GPY pilot facility in Madison, built in collaboration with Shell, one of Virent`s major investors. Other investors include Cargill and Honda. Other funding sources include the US DOE, USDA and the US Dept. of Commerce (Virent, 2013). The Virent process was selected (alongside the Amyris process) by the US DOE NABC program (see Chapter 4) as a promising advanced biofuel platform to further develop for scale up to commercial production. In collaboration with Coca-Cola, Virent is also trying to commercialize a proprietary process to convert sugars to paraxylene (branded BioFormPX) (Virent, 2013).

5.4 The alcohol to jet process (ATJ)

As the name suggests, the alcohol-to-jet (ATJ) process converts ethanol or other alcohols such as butanol to hydrocarbon mixtures which can be used as drop-in biofuels intermediates or blendstocks. In the US, the ATJ process is receiving increasing attention both as a potential solution to the ethanol blendwall as well as to possible production of ethanol beyond RFS mandated volumes.

The ATJ process is relatively simple, resembling the methanol to gasoline process discussed previously in the syngas upgrading section of Chapter 3. The main processes, which have all been performed in the chemical and fuel industries for decades, involve dehydration, oligomerization and hydrogenation. Although the technology risk is low and the ethanol feedstock costs can be estimated, it will likely be economically challenging as it is an energy intensive process involving highly exothermic reactions. Experience based on established methanol-to-gasoline processes (Shell's MTG, see Chapter 3) have shown that alcohol to hydrocarbon reactions are difficult to scale up due to the requirement for multiple reactors and extensive heat exchanger installations (Allen et al., 1986). However, the exothermic heat of reaction for ethanol-to-gasoline conversion is smaller than that of methanol to gasoline. At an average value of 450 Btu per pound of hydrocarbons produced from pure ethanol, the amount of heat to be dissipated will be about 3.7 times smaller than that from methanol (Allen et al., 1986). However, another challenge, as discussed for the oleochemical platform, is the final drop-in product might command a lower price than the feedstock alcohol.

The use of externally supplied hydrogen can be used to help increase the product yield although this increases operating costs. Some proposed processes do not use hydrogen but generally result in lower yields. The Oak Ridge National Laboratory (ORNL) in the US has recently developed a process that operates without hydrogen inputs and at moderate reaction conditions (atmospheric pressure and 310 °C) to convert hydrous ethanol to hydrocarbons at yields reported to be over 50 wt% (Narula et al., 2012). Preliminary techno-economic analysis of this process by NREL indicates that a minimum fuel selling price (MFSP) of $3-4 per gasoline gallon ($0.8-1/L) can be achieved (Narula, Davison, & Keller, 2012; Davison, pers. comm. 2013). This work is still at a relatively early stage and other than this preliminary techno-economic analysis little public information is available on the performance and economic attributes of ATJ biofuel processes. However, NREL and MIT are in the process of conducting separate techno-economic analyses of ATJ technologies that are expected to be published soon (Pearlson, pers. comm., 2013).

As discussed in Chapter 2, ASTM approval for ATJ renewable jet fuel is expected sometime in early 2014 and this should further facilitate the commercialization of ATJ technologies. In anticipation of this approval, large airline companies and the US Dept. of Defense have offered support to companies which produce jet fuels from alcohols. Virgin Atlantic is supporting Lanzatech and Swedish Biofuels AB in their goal of converting Lanzatech's bioethanol to jet fuels (Lanzatech, 2013). Qatar Airways has invested in the California-based alcohol-to-jet company BYOGY (Byogy, 2013). The biobutanol company Gevo is also focusing on converting some of its alcohol product to jet fuel blendstocks (Gevo, 2013). In July 2012, the

US Air Force flew a test flight powered with a 50/50 blend of Gevo's ATJ blendstock and petroleum JP-8 (Gevo, 2013).

The three hybrid biofuel platforms described in this section have a potential role in drop-in biofuel production. They also demonstrate that opportunities exist to create effective synergies between thermo-catalytic and bio-catalytic processes. The performance of these hybrid platform processes again demonstrate the repeating theme of this report that significant trade-offs exist between drop-in intermediate or product yields and process inputs. As with the thermochemical and biochemical platform processes, there is a need to either sacrifice yield on feedstock or consume substantial amounts of hydrogen to produce highly reduced carbon molecules that are well suited for drop-in biofuel production from biomass derived feedstocks whether these be sugars, synthesis gases or alcohols. However, direct comparisons of these processes' potential economic feasibilities are not currently possible due to a lack of detailed public domain information on their techno-economic performance. It is apparent that each hybrid platform has unique advantages such as fuller utilization of feedstock carbon in syngas fermentations, shorter reaction times in sugar catalytic upgrading or lower technical risk in alcohol-to-jet technologies. However, as discussed above, each approach also has significant challenges to overcome before they can be economically scaled up for drop-in biofuel applications. Encouragingly, INEOS Bio's and LanzaTech's syngas fermentation technologies are currently operating at relatively large demonstration scales and appear to be making good progress in their respective commercialization strategies. While the other hybrid routes are also progressing, they are still mostly at the R&D and pilot stages and the timing of larger scale demonstrations for drop-in biofuels applications remains unclear.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

This report defines drop-in biofuels as “liquid bio-hydrocarbons that are functionally equivalent to petroleum fuels and are fully compatible with existing petroleum infrastructure”. Although conventional biofuels such as ethanol and biodiesel have been produced and utilized at significant scales for many years, they are not fully compatible with existing combustion engines or the overall liquid transportation fuel refining and distribution network. Tremendous entrepreneurial activity to develop and commercialize drop-in biofuels from aquatic and terrestrial feedstocks has taken place over the past several years. However, despite these efforts, drop-in biofuels represent only a small percentage (around 2%) of global biofuel markets. The predominant drop-in fuels produced today are being made using oleochemical platform routes to convert relatively highly reduced renewable feedstocks such as palm oil, crops such as rape seed (Canola), used cooking oils, tallow, etc., to fully saturated products. Much more highly oxygenated feedstocks – lignocellulosic biomass, sugars and ethanol – are being assessed for thermochemical, biochemical and hybrid platform routes to drop-in biofuels. Most thermochemical based processes intend to use some form of biomass feedstock and current production technologies are mainly proven at pilot or demonstration scales. However, some larger scale thermochemical based processes exist, such as KiOR’s 49 MLPY (13 MGPY) fast pyrolysis facility in Mississippi, USA, (although success is now looking more problematic due to KiOR’s recently announced $350 million net loss for 2013). Sugars (also from starch or biomass) are the primary feedstock for most biochemical based approaches to making drop-in biofuels. The higher energy products ($H_{eff}/C \geq 1$) typically produced by this route can be readily upgraded to drop-in biofuels, although they are also well suited for applications in the rapidly growing bio-based chemicals market. Regardless of the production platform, the major interconnected parameters that are influencing the rate of commercialization of drop-in biofuels are capital and operating expenditures, process yields and productivities, and feedstock sourcing. As described in greater detail in the main chapters of this report, each platform approach has a different degree of sensitivity to each of these parameters.

Oleochemical platform processes exhibit high yields, require relatively low capital and hydrogen inputs (due to the use of relatively high H_{eff}/C feedstocks compared to lignocellulosic or sugar feedstocks) and are currently at a relatively high level of technological maturity. This is reflected by oleochemical based drop-in biofuels already being produced at large scale and approved for use by ASTM since July 2011. However, sourcing large quantities of feedstock (lipids) at a low enough cost to result in profitable drop-in biofuel production remains challenging and is a major constraint limiting the expansion of this platform.

Thermochemical platform pyrolysis based processes require significant hydrogen inputs and specialized heterogeneous hydroprocessing catalysts that have not, as yet, been proven at scale. Although pyrolysis oils should be relatively inexpensive to make (about USD $10/GJ based on a USD $83/t feedstock, according to Bridgwater, 2012; Wright et al. 2010 and Henrich et al., 2009), they contain up to 40 wt% oxygen and are thus costly to hydroprocess and upgrade to highly saturated drop-in biofuel products. Upgrading of pyrolysis oils to transportation fuel blendstocks has been estimated to account for about two thirds of capital costs and one third of operating expenses (Jones et al., 2009). Given current technology status and market trends, it is unlikely in the near to midterm that hydrogen required for upgrading will be generated from biomass feedstocks at the expense of fuel yields and more likely it will be sourced from fossil natural gas. It has been estimated that hydrogen generation capacity in US refineries would have to be tripled to meet the US RFS targets of 15 billion advanced biofuels by 2022 with biomass pyrolysis fuels. Due to the heterogeneous nature of bio-oils it has been suggested that a two-stage hydrotreatment would be a more cost effective approach to bio-oil upgrading (Elliot, 2007; Jones et al., 2009). The first step would stabilize the bio-oil by selectively hydrotreating its most reactive (unstable) organic species and, after stabilization a second step would be used to complete hydrotreatment. This two-step approach lends itself to a spoke and hub model where the first stabilization step is performed at many smaller scale facilities located near feedstock supplies and the second final upgrading step is performed at a few larger centralized facilities – perhaps petroleum refineries – where greater economies of scale are possible and existing capital assets, if available, can be used. Once hydrogen sourcing and catalyst issues are resolved, the pyrolysis platform holds great potential since it can effectively utilize a range of biomass feedstocks and has relatively low capital costs (compared to gasification), particularly if it can be developed to leverage the substantial existing petroleum refining infrastructure.

Most proposed pyrolysis technologies that have been commercially pursued use reactor designs not dissimilar to fluidized catalytic crackers (FCCs) located at modern oil refineries. Both the FCCs and hydroprocessing units within an oil refinery could potentially be used to upgrade bio-oils or bio-oil-petroleum blends. Currently, a considerable amount of the FCC capacity in the US is not fully utilised, creating an opportunity to leverage these "stranded" assets. However, using these FCC facilities will be challenging as conventional FCC processing takes place in the absence of hydrogen. The processing of lower H_{eff}/C pyrolytic oils is likely to exacerbate yield losses and coking in FCC units. Current petroleum catalysts are incompatible with highly oxygenated biomass derived compounds and biomass feedstocks increase the risk of contaminating downstream refinery units with oxygenated and inorganic species (originating from biofeeds). There is also a large disparity in scale between pyrolysis and refinery FCCs. Encouragingly, despite these challenges, partially upgraded (20% oxygen) pyrolysis oils have been successfully inserted into an FCC, demonstrating the potential viability of this type of approach and resulting in significant techno-economic benefits (Solantausta, 2011). These include better use of existing refining equipment, easier access to hydrogen as well as the ability to use any excess coke and gas formed as combustion fuels for the process. With current technology, pyrolysis oil hydroprocessing in oil refineries requires the bio-oil oxygen content to be lower than about 5 wt%. Alternatively, blending higher oxygen content bio-oils with petroleum liquids is another way of maintaining oxygenated species at acceptable levels for processing in oil refinery catalytic reactors (Huber et al., 2007; Bunting et al., 2009; Jones et al., 2009).

The greatest challenge for gasification based production routes to drop-in biofuels is the likelihood that high capital expenditures will be required to meet the capital equipment economies of scale needed to achieve cost competitive economics. A related challenge is the logistics and costs of sourcing sufficient amounts of biomass feedstock required to operate a large facility. The capital and operating expenses of gasification platform processes are estimated by techno-economic analyses to be about double those for pyrolysis (Anex et al., 2010), however the technology risk for gasification is thought to be significantly lower than for pyrolysis since biomass gasification is already practiced commercially (about 500 MW capacity globally) and upgrading of fossil fuel based syngas to liquid fuels is practiced at scales that exceed 20 billion L/year. Large scale fossil fuels-to-liquids facilities include Sasol's coal-to-liquid facility in South Africa that has been operating since the 1980s and Shell's recently built Pearl GtL natural gas-to-liquid facility in Qatar. Although these commercial plants have demonstrated the industrial robustness of FT catalysts, they are each about 100 times larger than current "large scale" biofuel facilities. Moreover, the processing of more highly oxygenated biomass derived syngas is expected to result in considerably more challenges than coal or natural gas feedstocks. Biomass syngas has a lower energy density (volumetrically up to 4 times lower), a lower H_2/CO ratio, and orders of magnitude higher concentrations of problematic contaminants such as tars (if not sufficiently mitigated in the conversion process) than fossil fuel derived syngas. To deal with these shortcomings, biomass syngas is often extensively cleaned and hydrogen is added, either by oxidizing carbon monoxide (via the water-gas shift reaction) or by inserting externally supplied hydrogen (e.g., as practiced by Sundrop Biofuels). These processes add to the cost of gasification-derived biofuels. The syngas can be upgraded to liquid fuels via several routes such as mixed alcohol synthesis and then catalytic upgrading to drop-in biofuels (e.g., the MTG or ATJ processes), DME synthesis and then further upgrading to drop-in biofuels, or direct production to drop-in biofuels via FT synthesis. The efficiency of these processes can be roughly ranked as alcohols > DME > MTG > FT, and this trend generally follows the oxygen content and H_{eff}/C ratios of the products generated by these thermochemical syngas upgrading processes. The use of biomass pellets or pyrolysis oils might help gasification platforms deal with some feedstock logistic challenges encountered at a large scale. Alternatively, companies such as Velocys claim that small scale gasification systems can be built and operated commercially, however their economic feasibility has yet to be proven.

It has been suggested that one of the advantages of biochemical platform technologies for producing drop-in biofuel intermediates is the potential for new processes to be “bolted on” to existing sugar and starch mills to leverage existing biorefining assets and thereby reduce capital and operating costs (Amyris, 2013a; Gevo, 2013). The metabolic pathways used to convert oxygen-rich sugar feedstocks ($H_{eff}/C = 0$) to highly reduced products such as fatty acids and isoprenoids ($H_{eff}/C = 1.8 – 2$) for drop-in biofuel production are, however, energy- and carbon-intensive compared to conventional sugar fermentation. For example, fatty acid biosynthesis requires a significant portion of the feedstock carbon to be consumed to produce the energy required to drive fatty acid elongation. Each elongation cycle requires one reducing NADPH molecule to drive biosynthesis, such that one molecule of a C16 fatty acid (i.e., palmitic acid) requires 7 repetition cycles and thus 7 NADPH molecules, which are usually generated by oxidizing feedstock carbon at the expense of product yield. Even operating aerobically, reported biological routes to convert sugars to drop-in intermediates have so far only achieved volumetric productivities that are an order of magnitude lower than anaerobic sugar-to-ethanol fermentations (Table 4-2). However, with fewer processing steps and lower NADPH requirements (or hydrogen consumption), biochemical platform routes are already well suited to make oxygenated products such as carboxylic acids, alcohols and polyols that can generate high revenues in the rapidly growing bio-based chemicals markets. Less oxygenated microbial metabolites with potential to be drop-in biofuel intermediates such as Amyris’s farnesene and Gevo or Butamax’s butanol are already being sold in the value added chemicals and cosmetics markets. Thus, market competition for biochemical drop-in products is expected to remain significant and grow in the near to mid-term as markets for biobased chemicals continue to expand. Estimates are that these markets will reach 10-50 million tonnes per year by 2020, equal to the current market size for biofuels (Lux Research, 2010; Higson, 2011; Bomgardner, 2012).

Several hybrid platforms for drop-in biofuel are also under active commercial development, including catalytic aqueous phase reforming (APR) (e.g., Virent), alcohol-to-jet (ATJ) (e.g., Cobalt, Gevo), acid-to-alcohol (e.g., Zeachem) and syngas fermentation (e.g., INEOS Bio, LanzaTech). Based on the limited information in the public domain, each of these approaches appears to have distinct advantages but also significant challenges. For example, the APR process can produce drop-in fuel blendstocks but relies on new catalysts that have not, as yet, been proven at industrial scale or over prolonged operations with highly oxidized (hydrogen-deficient) renewable feeds. Similarly, syngas fermentation offers the potential to convert higher proportions of feedstock carbon to product but the limited solubility of the CO gas in the aqueous solutions makes scale up difficult, and the need to cool syngas from over 700 °C to below 50 °C for fermentation hinders process thermal efficiency. However, two hybrid platform companies focused on syngas fermentation technology -- INEOS Bio and LanzaTech – have built and are operating large demonstration scale or small commercial scale facilities. Although ATJ and acid-to-alcohol technologies are technically proven, the would-be drop-in intermediates or their feedstocks, such as ethanol, acetic acid, ethyl acetate, etc., are typically more valuable (on an energy basis) as chemicals than as jet or alcohol fuel products. However, jet fuels from alcohols are expected to acquire ASTM certification in early 2014, which raises the possibility that ATJ drop-in jet fuel could become commercially attractive in countries such as Brazil and the US where ethanol is available at relatively low cost.

Hydroprocessing in one form or another is a final processing step shared by almost all drop-in biofuel platforms. This is the step where FT liquids, hydrotreated pyrolysis oils, HEFA lipid feedstocks and partially oxygenated or unsaturated biochemical platform drop-in intermediates are upgraded to gasoline, diesel or jet fuel blendstocks. Therefore, a large as yet mostly unrealized opportunity exists to better leverage existing oil refinery infrastructure by employing hydroprocessing units to upgrade drop-in biofuel intermediates. However, recent trials where vegetable oils were co-processed with petroleum in hydrocrackers showed that current catalysts have limited ability to effectively process feeds containing moderate levels of oxygenated species. This relatively simple vegetable oil insertion into an oil refinery's hydrocracker is, so far, the only reported industrial scale example of biofeed processing in a petroleum refinery.

Due to the increased processing and resource requirements (e.g., hydrogen and catalysts) needed to make drop-in biofuels as compared to conventional biofuels, large scale production of cost-competitive drop-in biofuels is not expected to occur in the near to midterm. Rather, dedicated policies to promote development and commercialization of these fuels will be needed before they become significant contributors to global biofuels production. Currently, no policies (e.g., tax breaks, subsidies etc.) differentiate new, more fungible and infrastructure ready drop-in type biofuels from less infrastructure compatible oxygenated biofuels. While some mandates distinguish between conventional and advanced biofuels in terms of their greenhouse gas emissions reduction potential (e.g., the US RFS), there are currently no such incentives for drop-in biofuels. While oleochemical platforms are commercial today, their future growth is constrained by the cost and availability of feedstocks. Although thermochemical based processes have considerable potential ongoing R&D is needed to resolve scale and catalyst issues. In the short term, biochemical platform routes to drop-in fuels face stiff market competition from biobased chemicals markets and as a result will likely focus on the production of higher value chemicals while building the experience and capacity needed to be able to scale up drop-in biofuel production when the demands for chemicals plateau. Several hybrid routes to jet fuel from alcohols are progressing to support specific market opportunities but here again cost competitiveness remains a challenge. Thus, while tremendous technical progress has been made in developing and improving the various routes to drop-in fuels, supportive policies directed specifically towards the further development of drop-in biofuels are likely to be needed to ensure their future commercial success.

References

Aatola, H., Larmi, M., Sarjovaara, T., & Mikkonen, S. (2008). *Hydrotreated Vegetable Oil (HVO) as a Renewable Diesel Fuel: Trade-off between NOx, Particulate Emission, and Fuel Consumption of a Heavy Duty Engine. SAE Technical Paper 2008-01-2500*. *SAE Technical Papers* (p. 12). doi:10.4271/2008-01-2500

Akhtar, J., & Amin, N. A. S. (2011). A review on process conditions for optimum bio-oil yield in hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews*, *15*(3), 1615–1624. doi:10.1016/j.rser.2010.11.054

Alberta Government. (2007, June 20). Facts and Statistics. *Alberta Energy*. Retrieved June 10, 2013, from http://www.energy.alberta.ca/oilsands/791.asp

Alexander, D. (2012, July). U.S. Air Force tests biofuel at $59 per gallon. *Reuters News*. Retrieved from http://www.reuters.com/article/2012/07/15/us-usa-military-biofuels-idUSBRE86E01N20120715

Amyris. (2013a). Amyris - official website. *various sections*. Retrieved August 23, 2013, from www.amyris.com

Amyris. (2013b). Amyris - Products - Diesel. *Press releases*. Retrieved August 28, 2013, from http://www.amyris.com/Content/Detail.aspx?ReleaseID=166&NewsAreaID=21&ClientID=1

Anellotech. (2013). Anellotech, Inc. Retrieved August 07, 2013, from http://www.anellotech.com/

ATAG. (2011). *Where are we with biofuels - Presentation* (p. 19). Montreal, Quebec, Canada. Retrieved from http://www.icao.int/Meetings/EnvironmentalWorkshops/Documents/2011-SUSTAF/18_Steele.pdf

ATAG. (2012). *Powering the future of flight, March 2012* (p. 20). Retrieved from http://www.atag.org/component/downloads/downloads/152.html

Aziz, N. A., & Dato’ Leon, K. M. (2012). Malaysia’s biomass potential. *Biomass SP, BE Sustainable*, (April), 35–39. Retrieved from http://issuu.com/besustainablemagazine/docs/besustainablemagazine-issue_0

Babu, S. (2005). Biomass gasification for hydrogen production–process description and research needs. In *Technology Report from IEA Bioenergy Task 33 for ExCo56* (p. 11). Retrieved from http://www.ieabioenergy.com/wp-content/uploads/2013/10/IEA-Bioenergy-Update-35-Task-33-Technology-Report.pdf

Bai, F. W., Anderson, W. a, & Moo-Young, M. (2008). Ethanol fermentation technologies from sugar and starch feedstocks. *Biotechnology Advances*, *26*(1), 89–105. doi:10.1016/j.biotechadv.2007.09.002

Bain, R. L. (1992). *Material and Energy Balances for Methanol from Biomass Using Biomass Gasifiers* (p. 136). Golden, CO, USA. Retrieved from http://www.nrel.gov/docs/legosti/old/17098.pdf

Bain, R. L., & Broer, K. (2011). Gasification. In R. C. Brown (Ed.), *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power* (1st ed., pp. 47–77). Chichester UK: Wiley-VCH.

Balat, M., Balat, M., Kırtay, E., & Balat, H. (2009). Main routes for the thermo-conversion of biomass into fuels and chemicals. Part 1: Pyrolysis systems. *Energy Conversion and Management*, *50*(12), 3147–3157. doi:10.1016/j.enconman.2009.08.014

Bauen, A., Howes, J., Bertuccioli, L., & Chudziak, C. (2009). *Review of the Potential for Biofuels in Aviation*. *E4Tech*. Retrieved from http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Review+of+the+potential+for+biofuels+in+aviation#0

Bauldreay, J. M., Blommel, P. G., Cortright, R. D., & Price, R. J. (2010). LIQUID FUEL COMPOSITIONS. Retrieved from http://www.patentlens.net/patentlens/patents.html?patnums=US_2010_0218417_A1&language=en&query=(US_2010_0218417_A1 in publication_number)&stemming=true&returnTo=structured.html?query=US+2010/0218417+A1

Bayar, T. (2013, March). Sweden's Bioenergy Success Story. *Renewable Energy World*. Retrieved from http://www.renewableenergyworld.com/rea/news/article/2013/03/swedens-bioenergy-success-story

Bezergianni, S., Kalogianni, A., & Vasalos, I. a. (2009). Hydrocracking of vacuum gas oil-vegetable oil mixtures for biofuels production. *Bioresource Technology*, *100*(12), 3036–42. doi:10.1016/j.biortech.2009.01.018

Binder, M., & Woods, L. (2009). *Final Report Comparative Life Cycle Assessment Ingeo TM biopolymer , PET , and PP by* (p. 61). Boston, MA, USA.

BioDME. (2013). BioDME. *Press releases*. Retrieved August 28, 2013, from http://www.biodme.eu/

Biofuels-Journal. (2010). Butamax Opens Biobutanol Technology Laboratory in Brazil. *Advanced Biofuels*. Retrieved from Butamax Opens Biobutanol Technology Laboratory in Brazil

Blades, T., Rudloff, M., & Schulze, O. (2005). Sustainable SunFuel from CHOREN ' s Carbo-V ® Process. In *ISAF XV, San Diego, September 2005* (pp. 1–6). San Diego CA. Retrieved from http://www.eri.ucr.edu/ISAFXVCD/ISAFXVAF/SSFCCVP.pdf

Blommel, P. G., & Cortright, R. D. (2008). *Production of Conventional Liquid Fuels from Sugars*.

Bomgardner, M. M. (2012, September). Biobased summer. *C&EN*, 10–13.

Bradley, D. (2009). *2nd Generation Biofuels and Trade An exploratory study* (pp. 1–55). Retrieved from http://www.bioenergytrade.org/downloads/2ndgenerationbiofuelsfinaldec142009.pdf

Bridgwater, A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and Bioenergy*, *38*, 68–94. doi:10.1016/j.biombioe.2011.01.048

Brown, R. C. (2011). *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power*. (R. C. Brown, Ed.) (1st ed., p. 330). Hoboken, NJ, USA: Wiley-VCH. Retrieved from http://onlinelibrary.wiley.com/book/10.1002/9781119990840

Brown, T. R., Tilakaratne, R., Brown, R. C., & Hu, G. (2012). Techno-economic analysis of biomass to transportation fuels and electricity via fast pyrolysis and hydroprocessing. *Fuel*. doi:10.1016/j.fuel.2012.11.029

Bryan, P. (2011). Turning Waste Into Fuel: How the INEOS Biorefinery Is Changing the Clean Energy Game. *News from Biomass Program, Office of Energy Efficiency & Renewable Energy*. Retrieved from http://energy.gov/articles/turning-waste-fuel-how-ineos-biorefinery-changing-clean-energy-game

BTG. (2012). Biomass Technology Group - official website. *Technologies/Fast pyrolysis*. Retrieved August 07, 2013, from http://www.btgworld.com/en/rtd/technologies/fast-pyrolysis

Bui, V. N., Toussaint, G., Laurenti, D., Mirodatos, C., & Geantet, C. (2009). Co-processing of pyrolisis bio oils and gas oil for new generation of bio-fuels: Hydrodeoxygenation of guaïacol and SRGO mixed feed. *Catalysis Today*, *143*(1-2), 172–178. doi:10.1016/j.cattod.2008.11.024

Bunting, B., Bunce, M., Brone, T., & Storey, J. (2010). *Fungible and compatible biofuels: literature search , summary , and recommendations* (p. 112). Oak Ridge, TN, USA. Retrieved from https://www.bioenergykdf.net/sites/default/files/Bruce_Bunting/20110512135206-0.pdf

Butler, E., Devlin, G., Meier, D., & McDonnell, K. (2011). A review of recent laboratory research and commercial developments in fast pyrolysis and upgrading. *Renewable and Sustainable Energy Reviews*, *15*(8), 4171–4186. doi:10.1016/j.rser.2011.07.035

Byogy. (2013). Byogy - official website. *various sections*. Retrieved August 28, 2013, from www.byogy.com

Campbell, J. E., Lobell, D. B., & Field, C. B. (2009). Greater transportation energy and GHG offsets from bioelectricity than ethanol. *Science (New York, N.Y.)*, *324*(5930), 1055–7. doi:10.1126/science.1168885

Carpenter, D. L., Bain, R. L., Davis, R. E., Dutta, A., Feik, C. J., Gaston, K. R., … Nimlos, M. R. (2010). Pilot-Scale Gasification of Corn Stover, Switchgrass, Wheat Straw, and Wood: 1. Parametric Study and Comparison with Literature. *Industrial & Engineering Chemistry Research*, *49*(4), 1859–1871. doi:10.1021/ie900595m

CEN. (2014). European Committee for Standardization, technical committee on gaseous and liquid fuels, lubricants and related products of petroleum, syntehtic and biological origin, list of working groups. *official website*. Retrieved from http://www.cen.eu/cen/Sectors/TechnicalCommitteesWorkshops/CENTechnicalCommittees/Pages/TCStruc.aspx?param=6003&title=Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin.

Centeno, A., Laurent, A., & Delmon, B. (1995). Influence of the Support of CoMo Sulfide Catalysts and of the Addition of Potassium and Platinum on the Catalytic Performances for the Hydrodeoxygenation of Carbonyl, Carboxyl, and Guaiacol-Type Molecules. *Journal of Catalysis*, *154*(2), 288–298. doi:10.1006/jcat.1995.1170

Chemrec. (2009). A brand new renewable engine fuel from the forest. *Chemrec News*. Retrieved August 30, 2013, from http://www.chemrec.se/SunPine_producing_tall_oil_diesel.aspx

Connor, D. O. (2013). *Advanced Biofuels – GHG Emissions and Energy Balances*. vancouver. Retrieved from http://task39.org/files/2013/05/Energy-and-GHG-Emissions-IEA-Bioenergy-T39-Report-May-2013-rev.pdf

ConocoPhillips. (2010). Renewable Fuels: A Refiner's Perspective. Retrieved May 21, 2013, from http://www.topsoe.com/research/Topsoe_Catalysis_Forum.aspx~/media/PDF files/Topsoe_Catalysis_Forum/2010/tushar.ashx

Conocophillips. (2013). ConocoPhillips - official website. *company reports - the whitegate story*. Retrieved August 27, 2013, from http://www.conocophillips.com/EN/about/company_reports/spirit_mag/Pages/whitegate_story.aspx

Corma, A., Huber, G., Sauvanaud, L., & Oconnor, P. (2007). Processing biomass-derived oxygenates in the oil refinery: Catalytic cracking (FCC) reaction pathways and role of catalyst. *Journal of Catalysis*, *247*(2), 307–327. doi:10.1016/j.jcat.2007.01.023

Cortright, R., Davda, R., & Dumesic, J. (2002). Hydrogen from catalytic reforming of biomass-derived hydrocarbons in liquid water. *Nature*, *418*(August), 54–57. Retrieved from http://www.nature.com/nature/journal/v418/n6901/abs/nature01009.html

COWI. (2013). *Black Liquor to Methanol or DME Technical information - Black Liquor to Methanol or DME*. Retrieved from http://www.cowi.se/menu/projekt/Industri-och-Energi/Documents/Black Liquor to Methanol or DME Chemrec.pdf

Craig, K. R., & Mann, M. K. (1996). *Cost and Performance Analysis of Biomass-Based Integrated Gasification Combined-Cycle (BIGCC) Power Systems* (p. 70). Golden, CO, USA. Retrieved from http://www.nrel.gov/docs/legosti/fy97/21657.pdf

Czernik, S., & Bridgwater, A. (2004). Overview of applications of biomass fast pyrolysis oil. *Energy & Fuels*, (12), 590–598. Retrieved from http://pubs.acs.org/doi/abs/10.1021/ef034067u

Dahmen, N., Henrich, E., Dinjus, E., & Weirich, F. (2012). The bioliq® bioslurry gasification process for the production of biosynfuels, organic chemicals, and energy. *Energy, Sustainability and Society*, *2*(1), 3. doi:10.1186/2192-0567-2-3

Daniell, J., Köpke, M., & Simpson, S. (2012). *Commercial Biomass Syngas Fermentation*. *Energies* (Vol. 5, pp. 5372–5417). doi:10.3390/en5125372

Darzins, A., Pienkos, P., & Edye, L. (2010). Current Status and Potential for Algal Biofuels Production, (August).

Dayton, D., Turk, B., & Gupta, R. (2011). Syngas cleanup, conditioning and utilization. In R. C. Brown (Ed.), *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power* (1st ed., pp. 78–123). Chichester UK: Wiley-VCH.

De Almeida, E. F., Bomtempo, J. V., & de Souza e Silva, C. M. (2008). The performance of Brazilian biofuels: An economic, environmental and social analysis. In *OECD and International Transport Forum, Biofuels: Linking Support to Performance*. OECD Publishing. doi:10.1787/9789282101803-6-en

De Miguel Mercader, F., Groeneveld, M. J., Kersten, S. R. a., Geantet, C., Toussaint, G., Way, N. W. J., … Hogendoorn, K. J. a. (2011). Hydrodeoxygenation of pyrolysis oil fractions: process understanding and quality assessment through co-processing in refinery units. *Energy & Environmental Science*, *4*(3), 985. doi:10.1039/c0ee00523a

De Miguel Mercader, F., Groeneveld, M. J., Kersten, S. R. a., Way, N. W. J., Schaverien, C. J., & Hogendoorn, J. a. (2010). Production of advanced biofuels: Co-processing of upgraded pyrolysis oil in standard refinery units. *Applied Catalysis B: Environmental*, *96*(1-2), 57–66. doi:10.1016/j.apcatb.2010.01.033

De Miguel Mercader, F., Hogendoorn, K. J. a., Venderbosch, R., Kersten, S. R. a., & Groeneveld, M. J. (2010). Pyrolysis oil upgrading by high pressure thermal treatment. *Fuel*, *89*(10), 2829–2837.

Diamond Green Diesel. (2013). Diamond Green Diesel - official website. *Homepage*. Retrieved July 28, 2013, from http://www.diamondgreendiesel.com/Pages/default.aspx

Diebold, J., & Czernik, S. (1997). Additives to lower and stabilize the viscosity of pyrolysis oils during storage. *Energy & Fuels*, *0624*(10), 1081–1091. Retrieved from http://pubs.acs.org/doi/abs/10.1021/ef9700339

Diebold, J. P. (2000). *A Review of the Chemical and Physical Mechanisms of the Storage Stability of Fast Pyrolysis Bio-Oils* (p. 59). Golden, CO, USA. Retrieved from http://gisceu.net/PDF/U918.pdf

DOE. (2011). DOE Office of Biomass Program Review. Retrieved July 27, 2013, from http://www.obpreview2011.govtools.us/thermochem/

Drift, A. van der, Boerrigter, H., Coda, B., Cieplik, M. K., & Hemmes, K. (2004). *Entrained flow gasification of biomass: Ash behaviour, feeding issues, and system analyses* (p. 58). Retrieved from http://www.ecn.nl/docs/library/report/2004/c04039.pdf

Drift, A. Van Der, Doorn, J. Van, & Vermeulen, J. W. (2001). Ten residual biomass fuels for circulating uidized-bed gasiÿcation, *20*, 45–56.

Dundon, C. A., Aristidou, A. A., Hawkins, A., Lies, D., & Albert, L. H. (2011). Methods of increasing dihydroxy acid dehydratase activity to improve production of fuels, chemicals, and amino acids.

USA. Retrieved from http://www.patentlens.net/patentlens/patents.html?patnums=US_8017376&language=en&query=(US_8017376 in publication_number)&stemming=true&returnTo=structured.html?query=(US_8017376+in+publication_number)&stemming=true&collections=US_B,EP_B,AU_B,US_A,WO_A,AU_A&language=en&pageLength=10&fields=publication_number,title,abstract,inventor,applicant

Dynamic Fuels. (2013). Dynamic Fuels - official website. *About*. Retrieved August 28, 2013, from http://www.dynamicfuelsllc.com/about.aspx

Dynamotive. (2009). Dynamotive | Dynamotive Upgrades BioOil from Multiple Biomass Sources to a Uniform Hydrocarbon Product. Provides Update on Upgraded BioOil® Corroborating Analysis. Retrieved August 06, 2013, from http://www.dynamotive.com/2009/10/28/dynamotive-upgrades-biooil-from-multiple-biomass-sources-to-a-uniform-hydrocarbon-product-provides-update-on-upgraded-biooil-corroborating-analysis/

E4tech. (2009). *Review of Technologies for Gasification of Biomass and Wastes Final report* (p. 130). London. Retrieved from C:\Users\Sergios\Dropbox\NEW DROP IN\CH 3 THERMO\(http:\wiki.gekgasifier.com\f\Review+of+Biomass+Gasification+Technologies.NNFCC.Jun09.pdf

EBTP. (2013). Euorpean Biofuels Technology Platform - official website. *Biomass to Liquids*. Retrieved August 28, 2013, from http://www.biofuelstp.eu/btl.html

ECN. (2008). *MILENA gasification process* (p. 2). Retrieved from https://www.ecn.nl/fileadmin/ecn/units/bio/Leaflets/b-08-021_MILENA.pdf

Egeberg, R. G., Michaelsen, N. H., & Skyum, L. (2010). *Novel hydrotreating technology for production of green diesel* (p. 21). Lyngby, Denmark. Retrieved from http://www.topsoe.com/business_areas/refining/~/media/PDF files/Refining/novel_hydrotreating_technology_for_production_of_green_diesel.ashx

EIA. (2009). *Annual Energy Outlook 2009 with projections to 2030* (p. 230). Washington, DC, USA. Retrieved from http://www.eia.gov/oiaf/aeo/pdf/0383(2009).pdf

EIA. (2013). *Annual Energy Outlook 2013: Early Release Overview* (p. 16). Washington, DC, USA. Retrieved from http://www.eia.gov/forecasts/aeo/er/pdf/0383er(2013).pdf

Elliott, D. C. (2007). Historical Developments in Hydroprocessing Bio-oils. *Energy & Fuels*, *21*(3), 1792–1815. doi:10.1021/ef070044u

Emerald Biofuels. (2013). Emerald Biofuels - official website. *Projects*. Retrieved August 29, 2013, from http://www.emeraldbiofuels.com/projects.php

Empyro. (2013). Pyrolysis oil - Empyro - energy & materials from pyrolysis. Retrieved August 28, 2013, from http://empyroproject.eu/index.php?id=12&

Ensyn. (2013a). Ensyn - official website. *projects/renfrew-ontario*. Retrieved June 25, 2013, from http://www.ensyn.com/projects/renfrew-ontario/

Ensyn. (2013b). Ensyn I RTP Renewable Liquid Fuels from Residual Biomass. Retrieved August 07, 2013, from http://www.ensyn.com/

Essent. (2013). ISSUU - Natural Power: Essent's vision for a bio-based economy. *ISSUU*. Retrieved August 28, 2013, from http://issuu.com/essentnl/docs/bio-based-economy

European Commission. (2001). *Ambient air pollution by Polycyclic Aromatic Hydrocarbons (PAH).* Retrieved from https://www.google.ca/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&ved=0CDEQFjAA&url=http%3A%2F%2Fec.europa.eu%2Fenvironment%2Fair%2Fpdf%2Fpp_pah.pdf&ei=Fn3RUpPzMcb6oASKvYCoDg&usg=AFQjCNHuPetBH5hlhEYcEtGr3YFyyt9tLw&sig2=jVDOglH4ikdA_tMPBQr63Q&bvm=bv.59026428,d.cGU

Evanko, W. A., Eyal, A. M., Glassner, D. A., Miao, F., Aristidou, A. A., Evans, K., … Hawkins, A. (2012). Recovery of higher alcohols from dilute aqueous solutions. USA. Retrieved from http://gevo.com/assets/patents/US8283505.pdf

Ezeji, T., Milne, C., Price, N. D., & Blaschek, H. P. (2010). Achievements and perspectives to overcome the poor solvent resistance in acetone and butanol-producing microorganisms. *Applied Microbiology and Biotechnology*, *85*(6), 1697–712. doi:10.1007/s00253-009-2390-0

Feldman, R. M., Gunawardena, U., Urano, J., Meinhold, P., Aristidou, A. A., Dundon, C. A., & Smith, C. (2008). Yeast organism producing isobutanol at high yield. USA. Retrieved from http://www.patentlens.net/patentlens/patents.html?patnums=US_8017375&language=en&query=(US_8017375 in publication_number)&stemming=true&returnTo=structured.html?query=(8,017,375+in+publication_number)&stemming=true&collections=US_B,EP_B,AU_B,US_A,WO_A,AU_A&language=en&pageLength=10&fields=publication_number,title,abstract,inventor,applicant#tab_0

Ferrari, M., Bosmans, S., Maggi, R., Delmon, B., & Grange, P. (2001). CoMo/carbon hydrodeoxygenation catalysts: influence of the hydrogen activity of a CoMo/carbon catalyst. *Catalysis Today*, *65*(2-4), 257–264.

Finkbeiner, M. (2013). *Indirect land use change (iLUC) within life cycle assessment (LCA) – Scientific robustness and consistency with international standards* (p. 62). Retrieved from http://www.ufop.de/files/5213/6853/0753/RZ_VDB_0030_Studie_ENG_Komplett.pdf

Fisk, C. a., Morgan, T., Ji, Y., Crocker, M., Crofcheck, C., & Lewis, S. a. (2009). Bio-oil upgrading over platinum catalysts using in situ generated hydrogen. *Applied Catalysis A: General*, *358*(2), 150–156. doi:10.1016/j.apcata.2009.02.006

FOE. (2012). *Biokerosene : Take-off in the wrong direction* (p. 28). Retrieved from https://www.milieudefensie.nl/publicaties/rapporten/take-off-in-the-wrong-direction

Fogassy, G., Thegarid, N., Toussaint, G., van Veen, A. C., Schuurman, Y., & Mirodatos, C. (2010). Biomass derived feedstock co-processing with vacuum gas oil for second-generation fuel production in FCC units. *Applied Catalysis B: Environmental*, *96*(3-4), 476–485. doi:10.1016/j.apcatb.2010.03.008

Food and Agriculture Organization (FAO). (2012). *Current world fertilizer trends and outlook to 2016*. Rome. Retrieved from ftp://ftp.fao.org/ag/agp/docs/cwfto16.pdf

Forsberg, C. W. (2005). *Hydrogen Markets : Implications for Hydrogen Production Technologies* (p. 13). Oak Ridge, TN, USA. Retrieved from http://www.ornl.gov/~webworks/cppr/y2001/pres/122902.pdf

Forsberg, C. W. (2009). Meeting U.S. liquid transport fuel needs with a nuclear hydrogen biomass system. *International Journal of Hydrogen Energy*, *34*(9), 4227–4236. doi:10.1016/j.ijhydene.2008.07.110

Fortum. (2013a). Fortum to start supplying bio-oil to a local energy company. *Press releases*. Retrieved November 15, 2013, from http://www.fortum.com/en/mediaroom/pages/fortum-to-start-supplying-bio-oil-to-a-local-energy-company.aspx

Fortum. (2013b). Fortum's bio-oil plant commissioned in Joensuu - first of its kind in the world. *Press releases*. Retrieved November 30, 2013, from http://www.fortum.com/en/mediaroom/pages/fortums-bio-oil-plant-commissioned-in-joensuu-first-of-its-kind-in-the-world.aspx

Foster Wheeler. (2013). Foster Wheeler - official website. *Biomass Gasifiers & Co-firing Systems*. Retrieved August 29, 2013, from http://www.fwc.com/What-We-Do/Power/Auxiliary-Equipment/Biomass-Gasifiers.aspx

Foust, T. (2011). *National Advanced Biofuels Consortium (NABC) presentation at the 2011 DOE Biomass Program Review* (p. 52). Washington DC. Retrieved from http://www.obpreview2011.govtools.us/presenters/public/InsecureDownload.aspx?filename=NABC DOE Peer Review-Foust_FINAL-BC.pdf

FPAC. (2011). *The New Face of the Canadian Forest Industry Bio-pathways* (p. 12). Retrieved from http://www.fpac.ca/publications/BIOPATHWAYS II web.pdf

Furimsky, E., & Massoth, F. (1999). Deactivation of hydroprocessing catalysts. *Catalysis Today*, *52*. Retrieved from http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:Deactivation+of+hydroprocessing+catalysts#0

Gary, J., Handwerk, G. E., & Kaiser, M. J. (2007). *Petroleum Refining and Economics* (5th ed., p. 488). Golden, CO, USA: CRC Press.

Gerdes, K., & Skone, T. (2009). *An evaluation of the extraction, transport and refining of imported crude oils and the impact on life cycle greenhouse gas emissions* (p. 42). Morgantown, WV, USA. Retrieved from http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:An+Evaluation+of+the+Extraction+,+Transport+and+Refining+of+Imported+Crude+Oils+and+the+Impact+on+Life+Cycle+Greenhouse+Gas+Emissions#0

Gevo. (2013). Gevo - official website. *various sections*. Retrieved August 23, 2013, from www.gevo.com

Gilmore, C. K., Barrett, S. R. H., Yim, S. H. L., Murray, T., Kuhn, S. R., Tai, A. P. K., … Waitz, I. A. (2011). *Environmental Cost- Benefit Analysis of Ultra Low Sulfur Jet Fuel Environmental Cost-Benefit Analysis of Ultra Low Sulfur Jet Fuel* (p. 140). Cambridge, MA. Retrieved from http://partner.mit.edu/projects/environmental-cost-benefit-analysis-ultra-low-sulfur-jet-fuels

Goudrian, F., & Peferoen, D. G. R. (1990). Liquid fuels form biomass via a hydrothermal process. *Chemical Engineering Science*, *45*(8), 2729–2734.

Green Fuel Nordic. (2013). Green Fuel Nordic - official website. *various sections*. Retrieved August 25, 2013, from www.greenfuelnordic.fi

Gunnarsson, I. (2013). *The GoBiGas-project* (p. 20). Oslo, Norway. Retrieved from http://nobio.no/upload_dir/pics/Ingemar-Gunnarsson.pdf

Hannon, J. R., Bakker, A., Lynd, L. R., & Wyman, C. W. (2007). Comparing the Scale-Up of Anaerobic and Aerobic Processes. In *American Institute of Chemical Engineers, Salt Lake City, Utah, November 8, 2007* (p. 15). Salt Lake City, Utah, USA. Retrieved from http://www.bakker.org/cfm/publications/AIChE-2007-Hannon.pdf

Hayes, D. J. M. (2013). Second-generation biofuels: why they are taking so long. *Wiley Interdisciplinary Reviews: Energy and Environment*, *2*(3), 304–334. doi:10.1002/wene.59

Henrich, E., Dahmen, N., Dinjus, E., & Karlsruhe, F. (2009). Cost estimate for biosynfuel production via biosyncrude gasifi cation. doi:10.1002/bbb

Higson, A. (2011). Biorefining and Bio-based Products Today ’ s Presentation About the NNFCC, (February).

Hileman, J., Ortiz, D., Bartis, J., & Wong, H. (2009). *Near-term feasibility of alternative jet fuels* (p. 150). Santa Monica, CA. Retrieved from http://stuff.mit.edu:8001/afs/athena.mit.edu/dept/aeroastro/partner/reports/proj17/altfuelfeasrpt.pdf

Hofvendahl, K., & Hahn-Hägerdal, B. (2000). Factors affecting the fermentative lactic acid production from renewable resources. *Enzyme and Microbial Technology*, *26*(2-4), 87–107. Retrieved from http://www.ncbi.nlm.nih.gov/pubmed/10689064

Holladay, J. D., Hu, J., King, D. L., & Wang, Y. (2009). An overview of hydrogen production technologies. *Catalysis Today*, *139*(4), 244–260. doi:10.1016/j.cattod.2008.08.039

Huber, G. W., & Corma, A. (2007). Synergies between bio- and oil refineries for the production of fuels from biomass. *Angewandte Chemie (International Ed. in English)*, *46*(38), 7184–201. doi:10.1002/anie.200604504

Huber, G. W., Cortright, R. D., & Dumesic, J. a. (2004). Renewable alkanes by aqueous-phase reforming of biomass-derived oxygenates. *Angewandte Chemie (International Ed. in English)*, *43*(12), 1549–51. doi:10.1002/anie.200353050

Huber, G. W., & Dumesic, J. a. (2006). An overview of aqueous-phase catalytic processes for production of hydrogen and alkanes in a biorefinery. *Catalysis Today*, *111*(1-2), 119–132. doi:10.1016/j.cattod.2005.10.010

Huber, G. W., Iborra, S., & Corma, A. (2006). Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering. *Chemical Reviews*, *106*(9), 4044–4098. doi:10.1021/cr068360d

Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., … Dudgeon, D. (2011). *Process design and economics for biochemical conversion of lignocellulosic biomass to ethanol* (p. 147). Golden, CO, USA: National Renewable Energy Laboratory.

IATA. (2013). *Fact Sheet: Alternative Fuels* (p. 2). Retrieved from https://www.iata.org/pressroom/facts_figures/fact_sheets/pages/alt-fuels.aspx

IEA. (2011a). *Medium Term Oil &Gas Markets 2011* (p. 272). Paris: OECD Publishing.

IEA. (2011b). *Technology Roadmap: Biofuels for Transport* (p. 56). Paris: OECD Publishing. doi:10.1787/9789264118461-en

IEA. (2012a). *Medium-Term Oil Market Report 2012* (p. 144). Paris: OECD Publishing. doi:10.1787/9789264188471-en

IEA. (2012b). *World Energy Outlook 2012*. *International Energy Agency (IEA), Paris* (p. 690). Paris. Retrieved from http://203.117.10.102/media/news_pdfs/WEO2012 Singapore Fatih Birol.pdf

IEA Bioenergy. (2007). Black liquor gasification. In *Summary and Conclusions from the IEA Bioenergy ExCo54 Workshop* (Vol. 64, p. 12). doi:10.1002/cjce.5450640221

IMO. (2012). North American emission control area comes into effect on 1 August 2012. *International Maritime Organization Press Briefings*. Retrieved June 04, 2013, from http://www.imo.org/mediacentre/pressbriefings/pages/28-eca.aspx

IndexMundi. (2013). Commodity Prices - Price Charts, Data, and News - IndexMundi. Retrieved August 07, 2013, from http://www.indexmundi.com/commodities/

INEOS. (2013). INEOS. *official website*. Retrieved August 15, 2013, from http://energy.gov/articles/turning-waste-fuel-how-ineos-biorefinery-changing-clean-energy-game

Informa Economics. (2013). *BIO-BUTANOL: THE GAME CHANGER, An Emerging Biofuel and Biochemical. A Multi-Client Study in Partnership with Chemical Strategies Group* (p. 17). Retrieved from http://www.informaecon.com/MCSBiobutanol2013.pdf

Ingledew, W. M. (2008). Starch-Based Ethanol Production. Retrieved August 28, 2013, from http://www1.agric.gov.ab.ca/$department/deptdocs.nsf/all/crop12128

InvestmentMine. (2013). Commodity and Metal Prices, Metal Price Charts - InvestmentMine. Retrieved August 07, 2013, from http://www.infomine.com/investment/metal-prices/

Jang, Y.-S., Malaviya, A., Cho, C., Lee, J., & Lee, S. Y. (2012). Butanol production from renewable biomass by clostridia. *Bioresource Technology*, *123*, 653–63. doi:10.1016/j.biortech.2012.07.104

Jin, C., Yao, M., Liu, H., Lee, C. F., & Ji, J. (2011). Progress in the production and application of n-butanol as a biofuel. *Renewable and Sustainable Energy Reviews*, *15*(8), 4080–4106. doi:10.1016/j.rser.2011.06.001

Jones, S. B., Valkenburg, C., Walton, C. W., Elliott, D. C., Holladay, J. E., Stevens, D. J., … Czernik, S. (2009). Production of Gasoline and Diesel from Biomass via Fast Pyrolysis , Hydrotreating and Hydrocracking : A Design Case, (February).

Jovanovic Tews, I., Jones, S. B., Santosa, D. M., Dai, Z., Ramasamy, K., & Zhu, Y. (2010). *A Survey of Opportunities for Microbial Conversion of Biomass to Hydrocarbon Compatible Fuels* .

Khosla, V. (2011). What matters in Biofuels & where are we? *Green Tech Media*. Retrieved from https://www.greentechmedia.com/articles/read/guest-post-vinod-khosla-on-what-matters-in-biofuels

King, A. (2012). Ultra-low sulfur jet fuel on the radar. *RSC Chemistry World*. Retrieved June 04, 2013, from http://www.rsc.org/chemistryworld/2012/05/ultra-low-sulfur-jet-fuel-radar

KiOR. (2013). KiOR, Inc. - official website. *various sections*. Retrieved August 07, 2013, from http://www.kior.com/

KIT. (2013, February 28). bioliq® Pilot Plant: Successful Operation of High-pressure Entrained Flow Gasification. *Press releases*. Jutta Sendelbach. Retrieved August 28, 2013, from http://www.kit.edu/visit/pi_2013_12692.php

Knothe, G. (2011). A technical evaluation of biodiesel from vegetable oils vs. algae. Will algae-derived biodiesel perform? *Green Chemistry*, *13*(11), 3048. doi:10.1039/c0gc00946f

Kolstad, J. J., Vink, E. T. H., De Wilde, B., & Debeer, L. (2012). Assessment of anaerobic degradation of Ingeo^{TM} polylactides under accelerated landfill conditions. *Polymer Degradation and Stability*, *97*(7), 1131–1141. doi:10.1016/j.polymdegradstab.2012.04.003

Landalv, I. (2013). *Status report on Demonstration Plants for Advances Biofuels Production - Thermochemical Pathways*. Retrieved from http://www.biofuelstp.eu/spm5/pres/landalv.pdf

Lane, J. (2011a). Highwater Ethanol is first in Butamax Early Adopters Group, seeks biobutanol options. *Biofuels Digest*. Retrieved August 28, 2013, from http://www.biofuelsdigest.com/bdigest/2011/12/05/highwater-ethanol-is-first-in-butamax-early-adopters-group-seeks-biobutanol-options/

Lane, J. (2011b). The Range Fuels failure : Biofuels Digest. *Biofuels Digest*. Retrieved August 28, 2013, from http://www.biofuelsdigest.com/bdigest/2011/12/05/the-range-fuels-failure/

Lane, J. (2012). *Advanced Biofuels and chemicals The race for scale 2012-2025 1300 + refineries by 2025* (p. 6). Retrieved from https://www.google.ca/url?sa=t&rct=j&q=&esrc=s&source=web&cd=1&cad=rja&ved=0CC4QFjAA&url=http%3A%2F%2Fwww.ascension-publishing.com%2FBIZ%2FWBM-0312-1.pdf&ei=i3nRUpPxDMTboASztIHwBg&usg=AFQjCNH37e25uRH6h4EnfP14SAVE5JW4mg&sig2=PrvCkoDPGYnXcH3Dl9FjYw&bvm=bv.59026428,d.cGU

Lane, J. (2013). KiOR commences shipments of cellulosic gasoline : Biofuels Digest. Retrieved August 07, 2013, from http://www.biofuelsdigest.com/bdigest/2013/07/02/kior-commences-shipments-of-cellulosic-gasoline/

Lanzatech. (2013). Lanzatech - official website. *various sections*. Retrieved August 24, 2013, from www.lanzatech.com

Lau, F., Bowen, D., Zabransky, R. R., Slimane, R., & Doong, S. (2003). *Techno-economic analysis of hydrogen production by gasification of biomass*. *Department of Energy …* (p. 4). Des Plaines, IL, USA. Retrieved from http://www.eere.energy.gov/hydrogenandfuelcells/pdfs/32405b5.pdf

Lappas, a. a., Bezergianni, S., & Vasalos, I. a. (2009). Production of biofuels via co-processing in conventional refining processes. *Catalysis Today*, *145*(1-2), 55–62. doi:10.1016/j.cattod.2008.07.001

Lee, S. Y., Park, J. H., Jang, S. H., Nielsen, L. K., Kim, J., & Jung, K. S. (2008). Fermentative butanol production by Clostridia. *Biotechnology and Bioengineering*, *101*(2), 209–28. doi:10.1002/bit.22003

Lehto, J., Oasmaa, A., Solantausta, Y., Kytö, M., & Chiaramonti, D. (2013). *Fuel oil quality and combustion of fast pyrolysis bio-oils*. *vtt.fi*. Retrieved from http://www.vtt.fi/inf/pdf/technology/2013/T87.pdf

Levin, D. B., & Chahine, R. (2010). Challenges for renewable hydrogen production from biomass. *International Journal of Hydrogen Energy*, *35*(10), 4962–4969. doi:10.1016/j.ijhydene.2009.08.067

Lin, Y., Li, C., Wan, H., Lee, H., & Liu, C. (2011). Catalytic Hydrodeoxygenation of Guaiacol on Rh-Based and Sulfided CoMo and NiMo Catalysts. *Energy & Fuels*, 890–896. doi:dx.doi.org/10.1021/ef101521z

Linde Engineering. (2012). http://www.the-linde-group.com/en/news_and_media/press_releases/news_120209.html. *Press releases*. Retrieved July 16, 2013, from http://www.the-linde-group.com/en/news_and_media/press_releases/news_120209.html

Liu, J., Fan, L. T., Seib, P., Friedler, F., & Bertok, B. (2004). Downstream process synthesis for biochemical production of butanol, ethanol, and acetone from grains: generation of optimal and near-optimal flowsheets with conventional operating units. *Biotechnology Progress*, *20*(5), 1518–27. doi:10.1021/bp049845v

LS9. (2013). LS9 official website. *various sections*. Retrieved August 25, 2013, from www.ls9.com

Lux Research. (2010). *Bio-based Fuels and Materials through 2015: Growing Capacity Past a Drop in the Bucket*. Retrieved from https://portal.luxresearchinc.com/research/report_excerpt/7015#executivesummary

Mabee, W. (2007). Policy options to support biofuel production. *Biofuels*, (April), 329–357. doi:10.1007/10

Machado, C. (2010). *Technical characteristics and current status of butanol production and use as biofuel* (p. 23). Retrieved from http://www.olade.org/biocombustibles/Documents/Ponencias Chile/Sesion 5_C Machado_Enbrapa_Brasil.pdf

Maniatis, K. (2013). Personal email comminucation on 23 Decenber 2013, with K.Maniatis, European Commission, DG Energy.

Maniatis, K., Weitz, M., & Zschoke, A. (2011). *2 million tons per year : A performing biofuels supply chain for EU aviation* (pp. 1–27).

Marchetti, J.M., Miguel, V.U., & Errazu A.F. (2008) Techno-economic study of different alternatives for biodiesel production, *Fuel Processing Technology*, 89:740–748

Marker, T. (2005). *Opportunities for biorenewables in oil refineries. Final Technical Report*.

Marker, T. L., Felix, L. G., Linck, M. B., & Roberts, M. J. (2012). Integrated Hydropyrolysis and Hydroconversion (IH 2) for the Direct Production of Gasoline and Diesel Fuels or Blending Components from Biomass , Part 1 : Proof of Principle Testing, *31*(2), 191–199. doi:10.1002/ep

Meehan, P. M. (2009). *Investigations into the fate and behavior of selected inorganic compounds during biomass gasification by*. Iowa State Univeristy. Retrieved from http://lib.dr.iastate.edu/cgi/viewcontent.cgi?article=1727&context=etd

Meier, D., Beld, B. Van De, Bridgwater, A. V, Elliott, D. C., Oasmaa, A., & Preto, F. (2013). State-of-the-art of fast pyrolysis in IEA bioenergy member countries. *Renewable and Sustainable Energy Reviews*, *20*, 619–641. doi:10.1016/j.rser.2012.11.061

Milne, T., Abatzoglou, N., & Evans, R. (1998). *Biomass gasifier“ tars”: their nature, formation, and conversion* (p. 204). Golden, CO, USA. Retrieved from http://www.ps-survival.com/PS/Gasifiers/Biomass_Gasifier_Tars_Their_Nature_Formation_And_Conversion_1998.pdf

Mohamed, M. a., Soelem, R., Attar, F., & Ozalp, N. (2011). Hydrogen Production and Utilization in Petroleum Refineries: A Study of the U.S. Oil and Gas Industry. In *ASME 2011 5th International Conference on Energy Sustainability, Parts A, B, and C* (pp. 903–916). Asme. doi:10.1115/ES2011-54752

Mortensen, P. M., Grunwaldt, J.-D., Jensen, P. a., Knudsen, K. G., & Jensen, a. D. (2011). A review of catalytic upgrading of bio-oil to engine fuels. *Applied Catalysis A: General*, *407*(1-2), 1–19. doi:10.1016/j.apcata.2011.08.046

Muellerlanger, F., Tzimas, E., Kaltschmitt, M., & Peteves, S. (2007). Techno-economic assessment of hydrogen production processes for the hydrogen economy for the short and medium term. *International Journal of Hydrogen Energy*, *32*(16), 3797–3810. doi:10.1016/j.ijhydene.2007.05.027

Munasinghe, P. C., & Khanal, S. K. (2010). Biomass-derived syngas fermentation into biofuels: Opportunities and challenges. *Bioresource Technology*, *101*(13), 5013–22. doi:10.1016/j.biortech.2009.12.098

NABC. (2013). National Advanced Biofuels Consortium, USA. *official website*. Retrieved July 27, 2013, from http://www.nabcprojects.org/about.html

Narula, C. K., Davison, B. H., & Keller, M. (2012). *Catalytic conversion of bio-alcohols to hydrocarbons Inventors : Technology - Platform for converting bioalcohols to hydrocarbon blend-stocks*. ORNL. Retrieved from http://web.ornl.gov/adm/partnerships/events/SPARK_Dec12/Presentations/04_Catalytic Conversion-Bio-alcohols to Hydrocarbons-Speck.pdf

Neste Oil. (2013a). Neste Oil Production Capacity. *Renewable Fuels*. Retrieved January 06, 2014, from http://www.nesteoil.com/default.asp?path=1,41,11991,22708,22720

Neste Oil. (2013b). Neste Oil's Interim Report for January-March 2013. Retrieved May 21, 2013, from http://www.nesteoil.com/default.asp?path=1,41,540,1259,1261,20618,21191

NETL. (2013). Gasification Plant Databases. Retrieved August 28, 2013, from http://www.netl.doe.gov/technologies/coalpower/gasification/worlddatabase/

Nexant. (2012). *Bio-derived Jet Fuel Cost Benchmarking, Nexant report prepared for Gevo* (p. 35).

Nielsen, R. P., Olofsson, G., & Søgaard, E. G. (2012). CatLiq – High pressure and temperature catalytic conversion of biomass: The CatLiq technology in relation to other thermochemical conversion technologies. *Biomass and Bioenergy*, *39*, 399–402. doi:10.1016/j.biombioe.2012.01.035

NRC Canada. (2012). NRC flies the world's first civil jet powered by 100 percent biofuel. *News Releases*. Retrieved August 22, 2013, from http://www.nrc-cnrc.gc.ca/eng/news/releases/2012/biofuels.html

NSF. (2011). *Developing New Paradigms for Biofuel Separations to Enable an Alternative Fuels Future (Based on the April 4-5, 2011 Workshop at Arlington, VA)* (p. 27). Arlington, VA, USA.

Nummisalo, V. (2012, December). Standardisation of fast pyrolysis bio-oil under CEN. *IEA Bioenergy Task 34 Newsletter #32*, (December), 15–16. Retrieved from http://www.pyne.co.uk/Resources/user/PyNe Issue 32 - December 2012 - website.pdf

Oasmaa, A., & Czernik, S. (1999). Fuel Oil Quality of Biomass Pyrolysis Oils: State of the Art for the End Users. *Energy & Fuels*, *13*, 914–921.

Pearlson, M. N. (2011). *A techno-economic and environmental assessment of hydroprocessed renewable distillate fuels (Master Thesis)*. Massachusetts Institute of Technology. Retrieved from http://dspace.mit.edu/handle/1721.1/65508

Peralta-Yahya, P. P., & Keasling, J. D. (2010). Advanced biofuel production in microbes. *Biotechnology Journal*, *5*(2), 147–62. doi:10.1002/biot.200900220

Pfromm, P. H., Amanor-Boadu, V., Nelson, R., Vadlani, P., & Madl, R. (2010). Bio-butanol vs. bio-ethanol: A technical and economic assessment for corn and switchgrass fermented by yeast or Clostridium acetobutylicum. *Biomass & Bioenergy*, *34*(4), 515–524. Retrieved from http://www.sciencedirect.com/science/article/pii/S0961953409002645

Phillips, S., Tarud, J., Biddy, M., & Dutta, A. (2011). Gasoline from wood via integrated gasification, synthesis, and methanol-to-gasoline technologies, (January). Retrieved from http://www.osti.gov/greenenergy/rddetail?osti_id=1004790

Plattts. (2013). Shell mulls more efficient, but still costly GTL mega-project on US Gulf - Oil | Platts News Article & Story. Retrieved August 28, 2013, from http://www.platts.com/latest-news/oil/london/shell-mulls-more-efficient-but-still-costly-gtl-26061813

Pray, T. (2010). *Amyris presentation at the DOE Biomass R&D technical advisroy comittee: Drop-in Fuels Panel* (p. 20). Aurora, Colorado, USA. Retrieved from http://www.biomassboard.gov/pdfs/biomass_tac_todd_pray_09_29_2010.pdf

Qureshi, N., & Blaschek, H. P. (1999). Production of acetone butanol ethanol (ABE) by a hyper-producing mutant strain of Clostridium beijerinckii BA101 and recovery by pervaporation. *Biotechnology Progress*, *15*(4), 594–602. doi:10.1021/bp990080e

Ranjan, A., & Moholkar, V. S. (2012). Biobutanol : science , engineering , and economics, (December 2011), 277–323. doi:10.1002/er

Repotec. (2013). Repotec-official website. *Technology*. Retrieved July 15, 2013, from http://www.repotec.at/

Ringer, M., Putsche, V., & Scahill, J. (2006). *Large-Scale Pyrolysis Oil Production : A Technology Assessment and Economic Analysis* (p. 93). Golden, CO, USA. Retrieved from http://www.nrel.gov/docs/fy07osti/37779.pdf

RISI. (2013). Luleå University of Technology takes over Chemrec and its plant for gasification of green fuels in Piteå, Sweden. *TECH CHANNEL*. Retrieved August 28, 2013, from http://www.risiinfo.com/techchannels/powerenergy/Lulea-University-of-Technology-takes-over-Chemrec-and-its-plant-for-gasification-of-green-fuels-in-Pitea.html

Ro, D.-K., Paradise, E. M., Ouellet, M., Fisher, K. J., Newman, K. L., Ndungu, J. M., … Keasling, J. D. (2006). Production of the antimalarial drug precursor artemisinic acid in engineered yeast. *Nature*, *440*(7086), 940–3. doi:10.1038/nature04640

Roig, S. (2012, July). U.S. Navy's "Great Green Fleet" debuts in Pacific. *Reuters News*. Retrieved from http://uk.reuters.com/article/2012/07/19/uk-usa-navy-greenfleet-idUKBRE86I0C320120719

Rosillo-Calle, F., Thrän, D., Seiffert, M., & Teelucksingh, S. (2012). *The Potential Role Of Biofuels In Commercial Air Transport–Biojetfuel*. *IEA bioenergy Task 40*. Retrieved from http://scholar.google.com/scholar?hl=en&btnG=Search&q=intitle:The+Potential+and+Role+of+Biofuels+in+Commercial+Air+Transport+-+Biojetfuel#0

RSB. (2012). *Indirect Impacts of biofuel production and the RSB Standard*. Retrieved from http://bioenergywiki.net/images/e/ec/12-04-13_RSB_Indirect_Impacts.pdf

Rude, M. A., & Schirmer, A. (2009). New microbial fuels: a biotech perspective. *Current Opinion in Microbiology*, *12*(3), 274–281. Retrieved from http://dx.doi.org/10.1016/j.mib.2009.04.004

S&T2. (2013). *Crude oil production updates* (p. 80). Delta, BC, Canada. Retrieved from http://www.ghgenius.ca/reports.php

SAFN. (2011). *Sustainable Aviation Fuels Northwest, Powering the next generation of flight* (pp. 1–131). Retrieved from http://www.safnw.com/sustainable-aviations-fuels-bibliography/

SAFUG. (2014). Sustainable Aviation Fuel Users Group - official website. *Case studies*. Retrieved January 06, 2014, from http://www.safug.org/case-studies/

Sasol. (2013). Overview | Sasol. Retrieved August 28, 2013, from http://www.sasol.com/innovation/gas-liquids/overview

Sawaya Jank, M. (2011). *Biofuel Industry: A local and global view. Presentation at the BBEST conference in Campos de Jordao, Brazil on August 15th 2011*. Retrieved from http://www.bbest.org.br/2011/images/palestras/marcos_jank

Schnepf, R., & Yacobucci, B. D. (2013). *Renewable Fuel Standard (RFS): Overview and Issues* (p. 35). Washington, DC, USA. Retrieved from http://www.fas.org/sgp/crs/misc/R40155.pdf

Sims, R., Taylor, M., Saddler, J., & Mabee, W. (2008). *From 1st - to 2nd - generation biofuel technologies, An overview of current industry and RD&D activities* (p. 124). Paris. Retrieved from http://www.task39.org/LinkClick.aspx?fileticket=+KPhJZy8YAI=&tabid=4426&language=en-US

Sitzmann, J. (2009, October). *Upgrading of fast pyrolysis oils by hot filtration*. Aston University, UK. Retrieved from http://eprints.aston.ac.uk/15742/

Solantausta, Y. (2011). *BIOCOUP, Co-processing of upgraded bio-liquids in standard refinery units, Final Activity Report* (pp. 1–38). Espoo, Finland. Retrieved from http://www.biocoup.com/uploads/media/BIOCOUP_Publishable_final_activity_report_01.pdf

Solazyme. (2013). Solazyme - official website. *various sections*. Retrieved August 23, 2013, from www.solazyme.com

Sorda, G., Banse, M., & Kemfert, C. (2010). An overview of biofuel policies across the world. *Energy Policy*, *38*(11), 6977–6988. doi:10.1016/j.enpol.2010.06.066

Sotelo-Boyás, R., Trejo-Zárraga, F., & Hernández-Loyo, F. de J. (2012). Hydroconversion of Triglycerides into Green Liquid Fuels, Hydrogenation,. In I. Karamé (Ed.), *Hydrogenation*. Mexico City. doi:10.5772/48710

Speight, G. S., & Ancheyta, J. (2007). *Hydroprocessing of heavy oils and residua*. (G. S. Speight & J. Ancheyta, Eds.) (p. 345). CRC / Taylor & Francis.

Speight, J. (2006). *The Chemistry and Technology of Petroleum, Fourth Edition* (4th ed., p. 984). Boca Raton, FL, USA: CRC Press. Retrieved from http://books.google.ca/books?id=ymL2S9RWzx4C&pg=PA190&lpg=PA190&dq=oxygen+content+in+petroleum&source=bl&ots=buwkrrFYLi&sig=TZEK3JoNSmQA3HIKbAnN4QqSQUE&hl=en&sa=X&ei=sG72UqrqMeWFyQGuk4GIBA&ved=0CCkQ6AEwAA#v=onepage&q=oxygen content in petroleum&f=false

Speight, J., & Özüm, B. (2002). *Petroleum refining processes* (p. 706). New York, NY, USA: Marcel Dekker Inc. Retrieved from http://books.google.com/books?hl=en&lr=&id=4ciEKGUOyksC&oi=fnd&pg=PP1&dq=Petroleum+Refining+Processes&ots=R4w4ok15dU&sig=M0fznbD-gzmbQcj5gp3_E1ZOaE4

Starck, J. (2012, July). Green Fuel Nordic. *IEA Bioenergy Task 34 Newsletter #32*, 5–6. Retrieved from http://www.pyne.co.uk/Resources/user/PyNe July 2012 - Issue 31.pdf

Stephen, J. D., Mabee, W. E., & Saddler, J. (2010). Biomass logistics as a determinant of second-generation biofuel facility scale , location and technology. *Biofuels Bioproducts & Bioerefining*, *4*(5), 513–518. doi:10.1002/bbb

Stratiev, D., Tzingov, T., Shishkova, I., & Dermatova, P. (2009). Hydrotreating units chemical hydrogen consumption analysis: A tool for improving refinrey hydrogen management. In *44th International Petroleum Conference, Bratislava, Slovak Republic, September 21-22, 2009 HYDROTREATING* (pp. 1–14). Retrieved from http://www.vurup.sk/sites/vurup.sk/archivedsite/www.vurup.sk/conferences/44_ipc/44ipc/Sustainable Crude Oil Processing_Tudays and Future Technologies, the role of the catalysis/posters/Hydrotreating Units Chemical Hydrogen Consumption Analysis_Stratiev.pdf

Swanson, R. M., Platon, A., Satrio, J. a., & Brown, R. C. (2010). Techno-economic analysis of biomass-to-liquids production based on gasification. *Fuel*, *89*, S11–S19. doi:10.1016/j.fuel.2010.07.027

Swanson, R., Satrio, J., Brown, R., Platon, A., & Hsu, D. (2010). *Techno-economic analysis of biofuels production based on gasification*. *Contract* (p. 165). Golden, CO, USA. Retrieved from http://www.nrel.gov/docs/fy11osti/46587.pdf

Trench, C. J. (2001). *How Pipelines Make the Oil Market Work – Their Networks, Operation and Regulation* (p. 22). New York, NY, USA. Retrieved from http://www.iatp.org/documents/how-pipelines-make-the-oil-market-work-their-networks-operation-and-regulation

Tyner, W. E. (2010). Why the push for drop-in biofuels? *Biofuels*, *1*(6), 813–814.

Tyner, W. E., & Viteri, D. (2010). Policy Update: Implications of blending limits on the US ethanol and biofuels markets. *Biofuels*, *1*(2), 251–253. doi:10.4155/bfs.09.24

USDA (2010). A USDA Regional Roadmap to Meeting the Biofuels Goals of the Renewable Fuels Standard by 2022 (p. 21). Retrieved June 15, 2013 from http://www.usda.gov/documents/USDA_Biofuels_Report_6232010.pdf

USDA (2012). Agriculture and Aviation: Partners in Prosperity (p. 49). Retrieved June 17, 2013 from http://www.usda.gov/documents/usda-farm-to-fly-report-jan-2012.pdf

USDA (2013). Major Vegetable Oils: World Supply and Distribution. *Foreign Agricultural Service statistics database*. Retrieved May 20, 2013 from http://apps.fas.usda.gov/psdonline/psdReport.aspx?hidReportRetrievalName=Table+03%3a+Major+Vegetable+Oils%3a+World+Supply+and+Distribution+(Commodity+View)+++++++++++++++++++++&hidReportRetrievalID=533&hidReportRetrievalTemplateID=5

U.S. EIA. (2006). Changing Trends in the Refining Industry. *Independant statistics and analysis, U.S. Energy Information Administration*. Retrieved June 10, 2013, from http://www.eia.gov/oiaf/aeo/otheranalysis/aeo_2006analysispapers/tri.html

U.S. EIA. (2007). *Refinery outages, description and potential impact on petroleum product prices* (Vol. SR/OOG/200, pp. 1–53). Washington, DC: Energy Information Administration. US Department of Energy. Retrieved from http://www.eia.gov/oiaf/servicerpt/refinery_outages/sroog200701.pdf

U.S. EIA. (2010). International Energy Statistics. *Independant statistics and analysis, U.S. Energy Information Administration*. Retrieved June 09, 2013, from http://www.eia.gov/cfapps/ipdbproject/iedindex3.cfm?tid=5&pid=62&aid=2&cid=regions&syid=2006&eyid=2010&unit=TBPD

US EPA. (1995). *Profile of the petroleum refining industry* (p. 146). Washington, DC, USA. Retrieved from http://books.google.com/books?hl=en&lr=&id=nlxEAAAAYAAJ&oi=fnd&pg=PP10&dq=Profile+of+the+Petroleum+Refining+Industry&ots=QdIbMEq1Oi&sig=xx1Rl6TzoYYcfdRCZam-hHNmgn8

US EPA. (2013, November 15). Renewable Fuel Standard (RFS). *Fuels and Fuel Additives, U.S. Envioronmental Protection Agency*. Retrieved June 09, 2013, from http://www.epa.gov/otaq/fuels/renewablefuels/index.htm

Van der Drift, B. (2013). *Biomass gasification in the Netherlands: IEA Bioenergy Task 33 Report* (p. 33). Retrieved from http://www.ieatask33.org/app/webroot/files/file/country_reports/NL_July2013.pdf

Van Noorden, R. (2013, September). European Parliament votes to limit crop-based biofuels. *Nature News Blog*. Retrieved from European Parliament votes to limit crop-based biofuels

Vane, L. M., Alvarez, F. R., Rosenblum, L., & Govindaswamy, S. (2013). Efficient recovery and dehydration of 1-butanol, acetone/butanol/ethanol (ABE), and isobutanol from dilute aqueous solutions using hybrid vapor tripping-vapor permeation process. In *35th Symposium on Biotechnology for Fuels and Chemicals*.

Värmlandsmetanol. (2012). *World ' s first Commercial Scale Biomethanol Plant in Hagfors SWEDEN Biomass as received District heat export Methanol energy* (p. 11). Retrieved from http://www.varmlandsmetanol.se/dokument/History March 12.pdf

Venderbosch, R., & Prins, W. (2011). Fast Pyrolysis. In R. C. Brown (Ed.), *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals and Power* (1st ed., pp. 144–176). Hoboken, NJ, USA: Wiley-VCH. Retrieved from http://onlinelibrary.wiley.com/book/10.1002/9781119990840

Vennestrøm, P. N. R., Osmundsen, C. M., Christensen, C. H., & Taarning, E. (2011). Beyond petrochemicals: the renewable chemicals industry. *Angewandte Chemie (International Ed. in English)*, *50*(45), 10502–9. doi:10.1002/anie.201102117

Vermeire, M. B. (2012). *Everything You Need to Know About Marine Fuels* (p. 32). San Ramon, CA, USA. Retrieved from http://www.chevronmarineproducts.com/docs/Chevron_EverythingYouNeedToKnowAboutFuels_v3_1a_DESKTOP.pdf

Vispute, T. P., Zhang, H., Sanna, A., Xiao, R., & Huber, G. W. (2010). Renewable chemical commodity feedstocks from integrated catalytic processing of pyrolysis oils. *Science (New York, N.Y.)*, *330*(6008), 1222–7. doi:10.1126/science.1194218

Walker, G. M., & Brew, J. I. (2011). 125th Anniversary Review : Fuel Alcohol : Current Production and Future Challenges, *117*(1), 3–22.

Wander, P. R., Altafini, C. R., & Barreto, R. M. (2004). Assessment of a small sawdust gasification unit. *Biomass and Bioenergy*, *27*(5), 467–476. doi:10.1016/j.biombioe.2004.04.003

Wang, H., Male, J., & Wang, Y. (2013). Recent Advances in Hydrotreating of Pyrolysis Bio-Oil and Its Oxygen-Containing Model Compounds. *ACS Catalysis*, *3*(5), 1047–1070. doi:10.1021/cs400069z

Weber, C., Farwick, A., Benisch, F., Brat, D., Dietz, H., Subtil, T., & Boles, E. (2010). Trends and challenges in the microbial production of lignocellulosic bioalcohol fuels. *Applied Microbiology and Biotechnology*, *87*(4), 1303–15. doi:10.1007/s00253-010-2707-z

Wender, I. (1996). Reactions of synthesis gas. *Fuel Processing Technology*, *48*(I 996), 189–297. Retrieved from http://www.sciencedirect.com/science/article/pii/S037838209601048X

Weyen, R. (2012, March). A Refiner ’ s Perspective on Advanced Biofuels. *NABC Highlights*, 4. Retrieved from http://www.nabcprojects.org/pdfs/refiner_perspective_advanced_biofuels.pdf

Wildschut, B. J. (n.d.). *Pyrolysis Oil Upgrading to Transportation Fuels by Catalytic Hydrotreatment*.

Wildschut, J., Iqbal, M., Mahfud, F. H., Cabrera, I. M., Venderbosch, R. H., & Heeres, H. J. (2010). Insights in the hydrotreatment of fast pyrolysis oil using a ruthenium on carbon catalyst. *Energy & Environmental Science*, *3*, 962–970. Retrieved from http://pubs.rsc.org/en/content/articlehtml/2010/EE/B923170F

Wildschut, J., Mahfud, F. H., Venderbosch, R. H., & Heeres, H. J. (2009). Hydrotreatment of Fast Pyrolysis Oil Using Heterogeneous Noble-Metal Catalysts. *Industrial & Engineering Chemistry*, *48*(23), 10324–10334.

Wildschut, J., Melian-Cabrera, I., & Heeres, H. J. (2010). Catalyst studies on the hydrotreatment of fast pyrolysis oil. *Applied Catalysis B: Environmental*, *99*(1-2), 298–306. Retrieved from http://www.sciencedirect.com/science/article/pii/S0926337310002869

Wright, M. M., Daugaard, D. E., Satrio, J. a., Brown, R. C., & Hsu, D. D. (2010). Techno-Economic Analysis of Biomass Fast Pyrolysis to Transportation Fuels. *Fuel*, *89*(November), S2–S10. doi:10.1016/j.fuel.2010.07.029

Yerushalmi, L., Volesky, B., & Szczesny, T. (1985). Effect of increased hydrogen partial pressure on the acetone-butanol fermentation by Clostridium acetobutylicum. *Applied Microbiology and Biotechnology*, *22*(2), 103–107. doi:10.1007/BF00250028

Zhang, H., Cheng, Y.-T., Vispute, T. P., Xiao, R., & Huber, G. W. (2011). Catalytic conversion of biomass-derived feedstocks into olefins and aromatics with ZSM-5: the hydrogen to carbon effective ratio. *Energy & Environmental Science*, *4*(6), 2297. doi:10.1039/c1ee01230d