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Final Report

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1. Executive summary

The interest in liquid biofuels (vegetable oil, biodiesel, ethanol, etc) is rapidly growing, as these fuels can provide a significant contribution to greenhouse gas emission reduction. At policy level, the European Union recently issued a very important document (Directive 2003/30/EC of the European Parliament and of the Council of 08.05.2003 on the promotion of the use of biofuels or other renewable fuels for transport), which will give a considerable impulse to biofuel production and use in EU. However, liquid biofuels are mainly considered as transport fuels.

The present work examined the use of liquid biofuels for stationary decentralised energy generation, focusing on both technical and environmental aspects. Excluding very particular and niche applications (such as energy generation in remote and isolated sites), the economic balance of liquid biofuel use for stationary energy generation is not yet positive in most of the cases, but technological development could modify this situation in the medium term.

The liquid biofuels which have been considered in the present work were vegetable oil, biodiesel, ethanol and bio-crude-oil (or pyrolysis oil). The characteristics of each liquid biofuel have been given and compared to standard fossil fuels: the need for technology adaptation and modification has been identified and discussed, and critical aspects identified. The issue of material compatibility has been addressed when appropriate.

The analysis showed that pyrolysis oil could probably be applied to non-transport energy generation in the medium-short term, as similar applications are already ongoing in Nordic Countries. In particular, heat generation in medium size boilers is today technically viable and close to achieve economical sustainability, while the use of pyrolysis oil for power generation will require a longer time of development. However, the combination of feedstock price and fluctuations in taxation of fossil fuels do not make yet economically viable today the use of pyrolysis oil in medium scale heating system, even in Northern European Countries.

As regards biodiesel, it has achieved a significant market and technological maturity: its use for heat generation (mainly blended with LFO – Light Fuel Oil) is already widely implemented. Biodiesel based cogeneration (i.e. combined production of heat and power) is instead not yet common practice, mainly due to economic rather than technological constraints (technology do not differ significantly from transports).

Vegetable oil can also be used in stationary engines and heating systems, as it is well known since the Rudolph Diesel time. Especially heat generation could be efficiently done by means of non-esterified oils. Vegetable oils require technology adaptation in fuel injection/atomisation, in particular as regards their use in power generation (or transport) systems, and special care is needed when used in cold climates.

Ethanol use in stationary applications is technically possible, whether emulsified or fumigated in diesel, or blended in gasoline. With respect to stationary applications, the use of ethanol in diesel engines is in fact of particular interest, while its use in spark ignition engines seems very far from commercial interest. Recent and very innovative applications of bioethanol are instead related to direct ethanol fuel cells, which are able to convert bioethanol into electricity without a separate high temperature reforming process.

Nevertheless, until today these results are applied to very small energy system (substitution of cellular or laptop batteries).

It is finally important to remark that the impact of liquid biofuels, as documented in this study, is significant not only from the GHG emission point of view, but also with respect to other kind of "regulated" pollutants which are extremely dangerous to human health. In particular, the positive impact of biofuels on particulate emissions is a very up-to-date issue which is worth to be mentioned.

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2. Objectives of the study

The utilisation of liquid biofuels (biomass derived fuels) for the production of electricity and/or heat is object of several investigations and research activities. The more and more severe environmental issues, the objectives of GHG reduction, the necessity to find energy sources alternative to conventional fossil fuels are the driving forces of the numerous research and demonstration activities carried out in the last two decades by different organisations in Europe and world wide.

Biofuels, as alternative fuels for stationary energy generation offer several benefits:

- Sustainability
- Reduction of greenhouse gas and other pollutant emissions
- Regional development
- Social structure and agriculture
- · Security of supply

The main objective of this study is to investigate the utilisation of liquid biofuels in stationary systems, reviewing the technologies for energy conversion, pointing out critical aspects, technological barriers and R&D issues still to be developed. Finally, environmental issues, economic and market aspects are discussed.

The liquid biofuels considered in this study are:

- Bioethanol
- Bio crude oil
- Vegetable oil
- Biodiesel

3. Bioenergy in the EU

3.1. Bioenergy characterisation

Bioenergy is defined as the complex of all technological means and systems for processing and utilising biomass for energy production.

The main difference between energy generation from biomass and from other Renewable Energy Sources (RES) probably consists in the fact that in the case of bioenergy the fuel must be produced, harvested and/or collected and supplied to the generating plant while for other RES the fuel (wind, solar radiation, water) is available at no cost.

3.1.1. Biomass

Biomass is widely available and represents a local, clean and renewable resource. It does not contribute to the greenhouse effect because the carbon dioxide released during biomass combustion is approx. equal to the amount absorbed during the growing process (i.e. zero net CO₂ emissions). In industrialised countries biomass can play an important role in sustainable development because it can:

- Make valuable use of agro-industrial residues, avoiding the cost of their disposal as waste:
- Provide marginal agricultural areas with new development opportunities;
- Stimulate the development of modern technologies for conversion and utilisation;
- Guarantee local energy supply and therefore economical and political autonomy;
- Create and promote new markets for refined biomass.

A wide range of biomass materials can be considered for energy conversion, including:

- Wood in all its forms;
- Straw and sugar cane bagasse;
- Fibrous agricultural residues;
- Urban and industrial waste products (an average of 40 % of solid municipal waste is organic material);
- Dried plants and sludge from water purification or animal wastes;
- Sugar crops (sugar cane, sugar beets, sweet sorghum, etc.);
- Oil crops (sunflowers, rape seed, palm oil, etc.).

Energy crops are instead still at a rather early stage of development in comparison to conventional food crops; a major contribution will therefore be possible, only in the longer term. Nevertheless, the potential, especially of lignocellulosic biomass resources, both worldwide and in Europe is considerable and represents, in the future, a realistic and significant integration to fossil fuels. It will provide large benefits to the environment, by helping to fulfil the Kyoto targets and by improving local economies.

3.1.2. Biofuels

Besides direct biomass combustion in small systems (such as firewood), most biomass resources need to be converted into solid, gaseous or liquid fuels for their utilisation in modern and efficient utilisation systems. There are two main kinds of conversion routes:

biochemical and **thermochemical**. The first one involves processes such as anaerobic digestion or alcohol fermentation: fuel is obtained by means of chemical reactions caused by the presence of yeast, enzymes, fungus, micro-organisms. The second path, instead, involves carbonisation, gasification and pyrolysis technology: either solid, gaseous or liquid biofuels are obtained by heating and often, by the presence of a catalyst.

Biofuels can be used in heating (substituting conventional fuels), cogeneration (simultaneous production of electricity and heating) and mobility (transport) applications.

3.2. Bioenergy utilisation in EU

Data about bioenergy in Europe are given in the following paragraphs (Source: IEA STATISTICS, 2003 Edition).

Solid biomass is defined as "any plant matter used directly as fuel or converted into other forms before combustion. The term includes wood, vegetal waste (including wood waste and crops used for energy production), animal wastes, "black liquor" (by-product of the manufacture of paper) and other solid biomass. Charcoal produced is also included" [IEA, 2003].

In figure 3.1 an overview for solid biomass in the European Union is given. Production is the production of primary energy and it is calculated after removal of impurities. The transformation sector comprises the conversion of primary forms of energy to secondary forms as well as further transformation processes. Total final consumption is the sum of consumption by the different end-use sectors (industry, transport and other).

Production of primary energy by means of solid biomass (i.e. for electricity generation and for heat generation) grew from 1,406,782 TJ in 1990 to 1,746,436 TJ in 2001 in European Union countries.

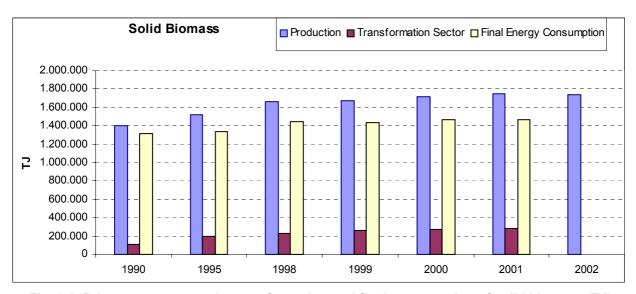


Fig. 3.1: Primary energy supply, transformation and final consumption of solid biomass (TJ)

In the second figure, **gas from biomass** data are reported. Biogas is derived principally from the anaerobic fermentation of biomass and solid wastes and combusted to produce

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heat and/or power. Included in this category are landfill gas and sludge gas (sewage gas and gas from animal slurries) and other biogas [IEA, 2003].

In figure **3.2** an overview for gas from biomass in the EU is shown. Production of primary energy by means of gas from biomass (i.e. for electricity generation and for heat generation) grew from 29,434 TJ in 1990 to 115,561 TJ in 2001 in EU countries.

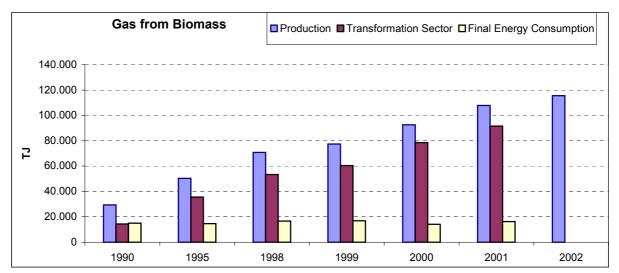


Fig. 3.2: Primary energy supply, transformation and final consumption of gas from biomass (TJ)

Finally **liquid biomass** (or liquid biofuels, bioethanol, biodiesel, biomethanol, biodimethylether and bio-oil) is given [IEA, 2003]. In figure **3.3** liquid biofuels figures in the European Union are given. Utilisation of liquid biofuels for primary energy supply (i.e. for electricity generation and for heat generation) grew from 7,000 tonnes in 1990 to 991,000 tonnes in 2001 in European Union countries.

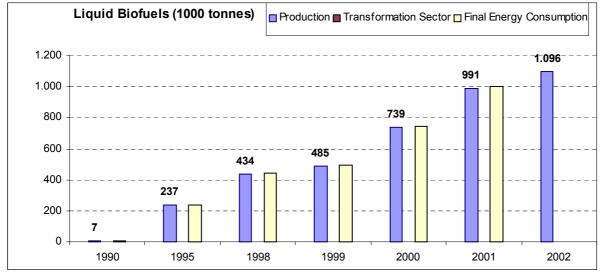


Fig. 3.3: Primary energy supply, transformation and final consumption of liquid biofuels

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4. Liquid biofuels

Liquid biofuels can be used in heating, cogeneration (simultaneous production of electric energy and heating) or in mobility (transport) applications. Among the various liquid biofuels, the most interesting ones are Bioethanol, Vegetable oil, Biodiesel, Pyrolysis oil and Biomethanol, Dimethylether (DME), Fischer-Tropsch diesel.

4.1. Overview on Liquid biofuels utilisation

At the present moment, liquid Biofuels are already playing an important role in several European countries, in most of the cases for automotive applications. The most common biofuels are ethanol and its derivate ethyl tertiary-butyl ether (ETBE), and biodiesel. Ethanol, the most world-wide used biofuel, is currently produced by fermentation of grain or sugar crops. In the future, ethanol may also be produced from lignocellulosic biomass such as woody or herbaceous crops. A wide ethanol market exists in North America, where it is typically used in low-concentration blends consisting of 5-10% ethanol in gasoline (E5-E10 blends). Blends up to 85% ethanol in gasoline (E85) are also used in dedicated vehicles or FFV (Flexible Fuel Vehicles). Ethanol is also widely used in Brazil at concentrations of about 20% in motor gasoline. Ethanol market in EU today is on as large as in US and Brazil; however it is used in limited amounts also in Europe. ETBE (produced by catalytically reacting ethanol with petroleum derivatives) can be blended at concentrations up to about 10% in motor gasoline [www.liquid-biofuel.com].

Biodiesel is produced by chemically upgrading of vegetable oils obtained through the pressing or chemical extraction from oil plants like rape, sunflower, soybean and the fruits of oil palms. By means of transesterification, the tryglycerides of the oils can be transformed into biodiesel. One ton of oil and 110 kg of methanol produce one ton of biodiesel and 110 kg of glycerine. In Austria, Sweden and Germany, pure biodiesel (B100) is used in standard vehicles. In France, commercial diesel fuel typically contains up to 5% of biodiesel (B5). Biodiesel is typically used in North America and Europe as 5-20% blends (B5 - B20) with conventional diesel fuel, and B100 is used in considerable quantities in Europe.

Vegetable oils can be also used in its untreated form or in mixtures with diesel fuel, but the market penetration of this fuel is today very small. Carbonisation processes may shorten the service life of traditional diesel engines when this fuel is used, so it is necessary to use special engines for operation with pure plant oil. In Brazil, palm oil is used for the generation of electricity with stationary diesel engines, and special engines for the operation with plant oil have been developed in Germany.

The production, upgrading and utilisation of pyrolysis oil (produced above all through the fast pyrolysis of lignocellulosic material) has also been tested in laboratories and in pilot plants in Canada, US and EU. Pyrolysis oils produced through the fast pyrolysis of biomass, potentially can replace #2 fuel oil, even if chemically are quite different. Tests of these oils are on going in heating systems, diesel engines and gas turbines.

Other biofuels like methanol, DME (di-methyl ether), and Fischer-Tropsch fuels can be produced chemically from synthesis gas (a mixture of carbon monoxide and hydrogen). Synthesis gas does not necessarily have to be produced from carbon and natural gas, but

it can also be produced from biomass. Methanol can be added to petrol and is used in the production of methyl tertiary butyl ether (MTBE). DME can be used for especially adapted diesel engines. Petrol and diesel fuel can also be produced from Fischer-Tropsch fuels. These technologies are well characterized, but the resulting fuel products are not economically competitive.

The extent to which biofuels have penetrated the fuel market varies significantly by country. The reasons for these differences are complex and include policy and market issues. Today, the prices of biofuels are higher than their petroleum equivalents. As a result, biofuels have been successfully implemented only in those countries that have recognized the value of those benefits and have made appropriate policy decisions to support biofuels.

Concerning the European Union, in 2002 biofuels production amounted to almost 1.5 million tonnes, around 75% of which was represented by biodiesel. This amount is less than 0.4% of the current market of conventional fuels. By 2005 biofuels production should rise to more than 6 million tonnes in order to meet the 2% EU target (directive 2003/30/CE): this means that at least an additional 4 million hectares of non-food and energy crops surfaces are needed in order to fulfil the first 2% biofuels target for 2005.

Biofuels are therefore going to play now an increasingly important role in the automotive sector, by replacing or integrating conventional petroleum-based transportation fuels.

4.1.1. Environmental and socio-economic benefits of biofuels

The utilisation of biofuels can significantly reduce GHG emissions in the atmosphere. In general, biofuels also help reduce the emission of other local scale pollutants when they are burned. For example, the use of oxygenated biofuels such as ethanol and ETBE in gasoline blends reduces carbon monoxide emissions, and the use of ethanol in diesel engines reduces the emission of particles; the use of biodiesel reduces the emissions of carbon monoxide, unburned hydrocarbons and soot.

Biofuels production can also generate several local, regional, and national economic benefits. The growth and conversion of biomass feedstock creates jobs for local people in rural, agriculture-based areas. Because the market for transportation fuels is large, widespread use of biofuels increases the demand for raw material and increases income for farmers. Increased demand for feedstock also helps reduce the amount of surplus crops and reduces the need for national farming subsidies. Conversion of the raw material into fuels also provides economic benefits through the construction and operation of processing facilities. These facilities provide local employment and development opportunities in the rural areas of both developed and developing countries and can help improve the financial infrastructure of these areas.

Moreover, the production of home-grown fuels decreases the dependence on crude oil and increases the security of the energy supply. The use of internally produced biofuels can also improve the self-sufficiency of countries that have net energy imports and can reduce the economic burden of importing crude oil for those nations.

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4.2. Biofuels characterisation

4.2.1. Biodiesel

Biodiesel is produced by chemical upgrading of vegetable oils (esterification process) extracted (mechanically or by means of chemical solvents) from oil-containing crops, above all rapeseed, soybean, sunflower and palm. Terms like RME and SME are often used to refer to esterified oils: RME stands for Rapeseed Methyl Ester, SME stands for Sunflower Methyl Ester. The esterification process consists in the transformation of vegetable oil molecules into molecules similar to diesel hydrocarbons, although costs of such biodiesels exceed those of fossil diesel. Usually, one ton of oil and 110 kg of methanol produce one ton of biodiesel and 110 kg of glycerine. With properties very similar to those of fossil diesel, biodiesel can be used into existing diesel vehicles and it mixes with fossil diesel in any ratio; its energy content is lower (about 8 %), but it has higher fuel density and better ignition qualities with its higher cetane number. In Austria, Sweden and Germany, pure biodiesel (B100) is utilised in unaltered vehicles; in France, commercial diesel fuel typically contains up to 5% of biodiesel (B5).

In table 4.1, some fuel characteristics are listed for RME and compared with those of other biofuels or fossil fuels.

4.2.2. Bioethanol

Bioethanol is produced from biomass sugar crops, starch or cellulosic material. The main technology for converting biomass to ethanol is fermentation followed by distillation. Ethanol is currently produced in large quantities by fermenting the sugar or starch portions of agricultural raw materials. The crops used for ethanol production vary by region, including sugar cane in Brazil, grain and corn (maize) in North America, grain and sugar beets in France, and surplus wine grapes in Spain. To reduce the cost of ethanol, research and development work is being conducted to use lower-cost lignocellulosic biomass to replace higher cost sugar and starch feedstock. Examples of lignocellulosic crops include woody material, bagasse, corn stover, or energy crops such as miscanthus, hemp, switch grass or reed canary grass. The cellulose portions of these materials are converted to fermentable sugars, which in turn are converted to ethanol. Ethanol is fully biodegradable.

Ethanol is today much used for automotive purposes, blended with petrol or sold as a special fuel for ethanol powered vehicles. In North America, for example, blends of 5 to 10% ethanol in gasoline are common. Modern vehicles use these ethanol blends with little or no modification to the engines and fuelling systems. International automobile companies like Ford also produce Flexible Fuel Vehicles for the United States, Sweden and Brazil, which can be operated with a wide range of fuels ranging from gasoline only to blends up to 85%ethanol (E85). Worldwide, tens of billions of litres of ethanol are used in motor vehicles annually.

ETBE (ethyl tertiary-butyl ether) is formed by chemically reacting ethanol with fossil raw materials. The ETBE product is blended with gasoline at concentrations of 5-10% to increase the oxygen content of petrol. The added blended fuel burns cleaner than gasoline itself and reduces the emissions of CO and unburned HC from vehicles, as well as ozone precursors. ETBE is widely used in France at present.

4.2.3. Biomethanol

Methanol (CH₃OH) is an alcohol usually made from natural gas. The first step in the production process uses steam reforming to convert the natural gas to synthesis gas and then shift this "syngas" to the required CO/H₂ ratio (CH₄ + H₂O \rightarrow CO + 3H₂ and CO + H₂O \rightarrow CO₂ + H₂). In a second step, and after removal of impurities, carbon oxides and hydrogen are catalytically reacted to methanol (CO + 2H₂ \rightarrow CH₃OH and CO₂ + 3H₂ \rightarrow CH₃OH + H₂O). Methanol production from biomass (i.e. cellulosic material, mostly wood) is technically but not yet commercially feasible. Methanol is reacted with isobutylene to form MTBE (methyl tertiary butyl ether), an anti-knock component in petrol (up to 20 %) which replaces lead-containing additives.

4.2.4. Dimethylether (DME)

DME has emerged only recently as an automotive fuel option: DME is produced by biomass gasification followed by synthesis (oxygenate synthesis). In the beginning of the 1990s, a new method for producing DME was accidentally discovered during attempts to produce synthetic petrol from synthesis gas [4]. Before that, DME had only been used in the cosmetics industry and no one ever tried to apply it as a diesel fuel. It proved to be an attractive diesel substitute due to its ability to reduce the exhaust emissions of NO_x.

4.2.5. Fischer-Tropsch diesel

The Fischer-Tropsch process was initially developed in Germany in the 1920s and produced synthetic fuels in the 1930s. Originally, fossil fuels were used as a feedstock for the process. Current developments focus on producing clean Fischer-Tropsch fuels based on biomass. Like the conversion processes for methanol and DME, the Fischer-Tropsch route also starts with gasification of the biomass, which is followed by a synthesis process.

4.2.6. Pyrolysis oil

Pyrolysis oil is produced by a thermo-chemical conversion process called pyrolysis. Pyrolysis is a process of thermal degradation in absence of oxygen, within suitable thermal reactors. Relatively low temperatures of 500-800 °C are employed, with operational pressures around atmospheric one, but also under vacuum reactors are existing. Three products are usually obtained: gas, liquid and char, the relative proportions of which depend on the pyrolysis method and reaction parameters: fast pyrolysis is used to maximise liquid product. Fast pyrolysis can give high yields of liquid (BCO or bio-oil) up 70% in weight on the feedstock: this process involves high heating rates (up to 1000 °C/s or even 10000 °C/s) combined with moderate temperature (less than 650 °C), short residence time within the reactor (some hundreds of millisecond) and rapid quenching of pyrolysis products. Any type of biomass can be used for pyrolysis processes, but lignocellulosic biomass is preferred. Before biomass is fed into the pyrolysis reactor, it has to be pre-treated (mainly drying and size reduction); typically, biomass has to be reduced to a particle size smaller than 6 mm and a moisture content below 10 weight %.

Biofuels/fossil fuels***	BIODIESEL (RME)	ETHANOL	ETBE	METHANOL	MTBE	DME	FISCHER- TROPSCH DIESEL	DIESEL	PETROL
Chemical formula	methyl ester	С2Н5ОН	C4H9- OC2H5	СНЗОН	C4H9- OCH3	СНЗОСНЗ	Paraffins	C12H26	C8H15
Molecular mass [kg/kmol]	296	46	102	32	88	46		185	111
Cetane number	54	8		5		60	74	> 45	8
Density [kg/l]*	0.88	0.8	0.74	0.79	0.74	0.67**	0.78	0.84	0.75
Lower calorific value [MJ/kg]*	37.3	26.4	36	19.8	35.2	28.4	44	42.7	41.3
Lower calorific value [MJ/I]*	32.8**	21.2	26.7	15.6	26	18.8	34.3	35.7	31
Stoichiometric ratio [kg air/kg fuel]	12.3	9		6.5		9		14.53	14.7
Oxygen content [wt-%]	10.1						0.1	0.3	
Kinematic viscosity [mm2/s]**	7.4						3.57	4	
Flash point [°C]	108						72	77	
Boiling temperature [°C]		78	72	65	55.3				110
Autoignition temperature [°C]						235		ca. 300	
Octane number (RON)		109	118	110	116				97
Octane number (MON)		92	105	92	100				86
Reid vapour pressure [kPa]*		16.5	28	31.7	57				75

Table 4.1: Properties of liquid biofuels and fossil biofuels (various sources)

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^{*} at 15°C

^{**} at 20°C

^{***} $\textit{LPG} \rightarrow \text{Lower calorific value [MJ/I]}$: 24 ; Octane number (RON) : 107

^{***} **Natural Gas** → Lower calorific value [MJ/I] : 23 ; Octane number (RON) : 120

4.3. Biodiesel and ethanol: production and market overview in EU

During the last 10 years, the European production level of **biodiesel** has been increasing by almost twelve times, from 80,000 tons in 1993 to 930,000 tons in 2001. The European production of **ethanol** as automotive fuel grew by 4.5 times from 1993, namely from 47,500 tons in 1993 to 216,000 tons (645,000 tons, considering ETBE production) in 2001. Furthermore, the European production of biofuels, in particular biodiesel and ethanol, increased remarkably, especially the past three years.

France

France already has a long history concerning biofuels and has been cultivating crops for the production of biofuels. This is not surprising, considering the agricultural heritage of the country. In 2001, the total French production of biofuels was about 590,000 tons. This amount comprises a biodiesel production of 310,000 tons and around 90,000 tons of ethanol production. Besides this, the country produces ETBE; in 2000, the production of ETBE amounted to 190,000 tons. The biodiesel produced in France mainly consists of RME and SME. Both types of biodiesel are mixed with regular diesel. SME is also used as a domestic fuel blender. Biodiesel is applied in a 30 % mixture in captive fleets. For regular diesel, there are blends with 5% of biodiesel. Different blended fuels can be found in several urban fleets: throughout the past decade, several French cities tested and used biodiesel in their public transport system.

Germany

In Germany, the production of ethanol is negligible compared to that of biodiesel. Germany is the leader on the European biodiesel market; in 2001, the production rate amounted to almost 360,000 tons. This is a substantial increase compared to the year 2000, in which 246,000 tons of biodiesel were produced.

There are about 100 refuelling stations throughout Germany where biodiesel is sold, namely oil from rapeseed, soy or other plants. No major change to the engines are necessary for the use of these fuels. Generally, RME is used in pure form in all kinds of vehicles in Germany. Germany is also one of the three countries that use 100% pure biodiesel in adapted vehicles. Germany is one of the most active countries in the European Union concerning the production and use of biofuels.

Spain

Spain mainly produces ethanol and ETBE. France and Spain are the only commercial producers of ETBE within the European Union. In 2001, the production of ethanol was almost 80,000 tons. In 2000, Spain produced about 170,000 tons of ETBE. Biodiesel production was about 80,000 tons in 2001.

Italy

The production of biofuels in Italy mainly comprises biodiesel, namely RME and SME. The production of biodiesel in 2001 is 125,000 tons. The crops used for biodiesel production are mostly traditional crops, like rape and sunflower. The crops are converted into biodiesel in eight plants. As from 1991, biodiesel has been distributed in Italy to municipalities, individual municipal transport firms and local municipal departments. SME is mainly applied as a pure fuel or as a blend with 20 % diesel fuel, in thermal uses for public and private heating. In Italy, biodiesel is also blended at 5 % in regular diesel fuel. In

2002, the Italian government set a national target of 300,000 ton of biodiesel produced per year. Bioethanol and ETBE production was about 90,000 tons in 2001.

Sweden

Sweden is one of the four European countries producing ethanol. However, differently from France and Spain, Sweden is not producing ETBE. The production of ethanol was in an experimental phase until 2001. In 2000, the production rate amounted to about 20,000 tons of ethanol. In the spring of 2001, a new distillery was opened with a capacity of 40,000 tons, thus doubling the ethanol production in Sweden in one year only, to 45,000 tons in 2001. The ethanol produced in Sweden is used in pure and blended form in automotive engines.

Greece

Greece is active in the field of pilot tests for biofuels. There has not been any commercial production of biofuels so far. Resources for these pilot tests are sunflower, maize, olive and waste oils. Moreover, sweet sorghum is used for the production of bioethanol.

Ireland (EIRE)

Biodiesel production was about 5,000 tons in 2001.

Luxembourg

RME is applied in about 40 buses in the city of Luxembourg.

Portugal

In Portugal, SME is used in captive fleets, blended in mixtures of 30% and 5% with diesel. SME. The most used oil crop in terms of cultivation area in Portugal is sunflower oil.

United Kingdom

In the United Kingdom, domestic biodiesel is currently produced from waste oils. Furthermore, several pilot projects using ethanol and methanol were to be introduced during the course of 2001, as a result of national legislation.

5. Bioethanol

Bioethanol (CH₃CH₂OH or C₂H₅OH) is a liquid biofuel which characteristics, compared to those typical of diesel and gasoline fuels, are given in the next table.

	Gasoline	Ethanol	Diesel
LHV (MJ/kg)	43.7	26.9	42.9
Viscosity (cSt)	-	ı	2.5
Density (kg/m³) @ 15 °C	700 ; 780	790	830; 880 (854 at 25 °C)
Cetane number	-	below 8	> 45
Octane number (MON)	79 ; 98	106	-
Stoichiometric ratio	15.1	9	14.5
Boiling temperature (°C)	99.2	78.3	140
Vaporisation heat (kJ/kg)	300	842	-
Auto-ignition temperature °C	371	390	315
Flammability limits °C	(-40)-(-80)	13-42	64-150
Flammability limits % vol	1.4-7.6	3.3-19.0	0.6-5.6

(various sources)

Ethanol volatility is lower than conventional liquid fuels: problems are therefore possible at cold-start. Moreover ethanol is a corrosive fuel which poses some constrains on materials. Experience in using bioethanol in spark ignition four stroke engines is considerable. Ethanol has a high octane number (between 95 and 105). The European standard for the unleaded gasoline is 95. The higher octane number allows for bioethanol combustion without detonation in engines having high-pressure ratio, thus increasing engine efficiency. Using pure ethanol in volumetric engine means that power can be increased up to 5-10% and efficiency up to 30%.

Above a certain amount of blended ethanol in gasoline, spark ignition engines have to be adapted: low ethanol blending (10 %) are usually referred to as E10 (California Air Resource Board, 1998; 22 % in Brasil: Gregg D.J., 1998), while higher blending (typically 85 %, or even higher) need engine modifications. Special engines are also available on the market and installed in the so called Flexible Fuel Vehicles (FFV): FFVs are vehicles able to accept a wide range of blended fuel, from pure gasoline to approx 85% ethanol in gasoline (National Ethanol Vehicle Coalition and SEKAB web site).

Ethanol can also be used to produce ETBE (C_4H_9 - OC_2H_5), an oxygenated additive for gasoline.

Ethanol can also be blended with diesel oil. The use of bioethanol as blending agent for diesel oil is a very interesting issue not only for transport application (especially taking into account the required very low sulphur content of future diesel oils) but also for stationary power production. Nevertheless, as discussed later, transport and storage of blended diesel-ethanol emulsions are very important issues which need ad hoc norms and measures.

In general, limited use is reported on ethanol in diesel engines, either as blended or fumigated fuel, while this sector is of great strategic interest: up to 15 % blending is today considered for wide applications.

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In addition, very few examples of almost neat ethanol use in diesel engines exist (SEKAB web site): the main example of it has been developed in Sweden by Sekab: a special mixture of ethanol-diesel oil has been developed for the use in large urban buses.

As regards gas turbines, the (higher than gasoline) octane number has no impact the engine performance, as these energy generation systems are based on steady combustion.

Ethanol is largely used as transportation fuel: about 60 % of ethanol (in its hydrated form, e.g. 93% v/v ethanol and 7% v/v water) has a market as petrol substitute (Van Thuijl *et al*, 2003), while the remaining 40 % (anhydrous, i.e. 99.999 % v/v) is used as blended fuel in gasoline.

Today, bioethanol is mainly produced from agricultural crops by the well known process of fermentation followed by distillation. Typical feedstock's are sugar beet and sugar cane, but several others sugar-containing crops are possible (molasses, sweet sorghum, etc) or starch crops as potatoes.

Recently, a significant research effort is focused on achieving technically and economically convenient processes for ethanol production from lignocellulosic material.

Bioethanol as fuel must be denaturated in order to be used, and it is usually done by adding a certain amount (around 5 %) of gasoline. In US the ASTM D4806-9 norm gives the following specifications for bioethanol fuel.

Ethanol, vol.%	92.1
Water, vol.%	1.0 max
Methanol, mg/L	0.5 max
Acetic Acid, % w/w	0.007
Chlorine, mg/L	40 max
Copper, mg/L	0.1 max
Denaturant, vol.%	1.96-4.76

ASTM D4806-9 norm for bioethanol as fuel

Concluding, today ethanol is widely used as oxygenated blending agent for gasoline, or as neat fuel in modified spark ignition engines (E85) for transports. The use of ethanol as fuel for stationary energy generation, which is the goal of this study, is limited to very few and rare applications, nevertheless it is an interesting fuel for engines and gas turbines. Although the lower calorific value, the combustion of ethanol gives some important environmental advantages, such as the absence of ash formation and very low smoke, which could make it attractive even for stationary power production. Ethanol burns with a bluish flame of low brightness, and has a wide flammability range. Moreover, the lower flame temperature guarantees NO_x emission limitation.

A well known problem is instead given by storage, which is not possible with standard materials due to corrosion: precautions must therefore be taken with this respect. Blended biofuels, such as bioethanol with diesel or gasoline fuels, are also sensitive to this issue and the way they are stored, handled and distributed has to carefully considered.

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5.1. Energy conversion technologies for stationary systems

OTTO ENGINES

As already mentioned above, until today, the use of bioethanol has been most concentrated on transport, and the spark ignition engine (Otto cycle) has been the most used engine in combination with ethanol. The fuel is used either as neat fuel or as blended fuel at different ratios.

Ethanol use for stationary energy generation in spark ignition engines is very limited, mainly due the fact that gasoline engines are not very used in this sector for economic, lifetime, reliability reasons.

DIESEL ENGINES

The use of ethanol in Diesel engines is a rather new and a very interesting approach. In fact, most of the heavy engines as well as the agricultural machineries are based on the Diesel cycle. Therefore, bioethanol could find a commercial market in the same geographical areas were it is produced: the use of bioethanol in diesel engines would also facilitate the penetration of the stationary (decentralised) energy generation sector [Lu Nan et al., 1994]. In general, the most common approach to the use of ethanol in diesel engines is to maintain a certain share of fossil fuels (co-combustion) to facilitate fuel ignition: however, among the alcohols, methanol is also used as neat fuel for Diesel engines (DME).

A number of alternatives are possible to feed the diesel engine with ethanol. The most important are the following:

- Ethanol-Diesel blending (e-diesel)
- Fumigation
- Dual Injection
- Ethanol-Diesel emulsions (e-diesel)

Ethanol can be emulsified with diesel oil, and then this emulsion can be fed into the combustion chamber of a diesel engine: in order to do this, an additive (surfactant) is necessary. Ethanol-diesel emulsions can contain more than 15% v/v ethanol. The main advantage offered by this approach is related to the minimization of technology adaptation, while limitations exist, in particular due to the increased fuel cost.

Fumigation

Fumigation consists in adding a carburettor to the inlet manifold, which allows for bioethanol vaporization in the inlet air stream to the engine. Bioethanol can be added up to 50 %: the diesel pump operates at reduced flow, and the diesel fuel also acts as pilot fuel which ignite the air-ethanol mixture. Care has to be taken at low loads, when vaporised bioethanol can generate misfire, while at high loads pre-ignition of the mixture is possible (in both cases the quantity of bioethanol has to be reduced).

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Dual Injection

The Dual Injection system is based on the addition of a complete (second) injection system in parallel to the existing one fed with diesel: a small amount of diesel oil acts as pilot fuel, while a larger amount of bioethanol is injected (which is the main fuel). Therefore, a new complete injection system (i.e. injector and fuel pump, control, ethanol tank) has to be installed, and the associated technological aspects and cost have to be take into serious account. From the performances point of view, however, this approach allows good thermal efficiencies as well as lower NOx emissions, while CO and HC emissions are approximately the same. Bioethanol also needs additive (usually nitride glycol) to allows for a proper lubrication of the mechanical moving parts.

Other options

Glow-plugs can also be used in combination with fuels such as bioethanol: however, the temperature of the glow-plug has to be adjusted to meet the load demand, and the Specific Fuel Consumption is higher than that of diesel.

Finally, it is also possible to convert the Diesel engines into a spark ignition engine by adding a spark plug and reducing the compression ratio (from approx. 16:1 to 10.5:1). The original injection system can be maintained and modified, or eliminated and substituted by a carburettor, a spark plug and a distributor. However, the thermal efficiency is lower than that of the Diesel cycle.

The present work focuses on ethanol-diesel emulsions and fumigation, as these two options seem the most interesting ones for bioethanol-based stationary energy generation.

GAS TURBINES

Gas turbines, if properly designed and adapted, are able to operate efficiently with a wide range of gaseous and liquid fuels. If gas turbines are to be used as aircraft engines, the main problems are related to low operating temperatures and pressures (some fuels become solid at low temperature, while others quickly evaporate at low pressure).

Kerosene and its derivatives are the typical liquid fuels for gas turbine. Kerosene fuels consist of refined hydrocarbons obtained from the distillation of oil or mixtures of oil one with specific additives. Compared to gasoline, kerosene has a higher boiling point and relative density, a better lubrication behaviour and a lower vapour pressure, which reduces the losses for evaporation at the high altitudes. Kerosene fuels include the normal aviation fuel, Jet A, the JP5 to high flash point and the 1-D diesel.

In a gas turbine combustion chamber the fuel must be injected, vaporized and mixed with air before the combustion. The efficiency of the combustion depends on all these processes, which depends in wide measure from the physical characteristics of the fuel [Batchelor S., 1996].

The main physical characteristics of ethanol versus kerosene (Aviation Turbine) are given in the next table.

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Characteristics	Kerosene (Avtur)	Ethanol
Chemical formula	C ₁₂ H ₂₆	C ₂ H ₅ OH
Relative Density at 15.5°C	0.80	0.794
Lower specific energy (MJ/kg)	42.8	26.8
Molecular mass	170.3	46.068
Boiling point, (K)	423	351
Freezing point, (K)	223	156
Stoichiometric F/A ratio, mass (AFR)	0.0676 (14.8)	0.111 (9.0)
Surface tension N/m	0.02767	0.0223
Viscosity at 293K, m ² /s	1.65x10 ⁻⁶	1.51x10 ⁻⁶

A list of the most important chemical and physical characteristic of a fuel, which have to be carefully taken into account when considering its possible use in gas turbines, is following.

Relative Density

The relative density of a fuel is function of the average boiling point and the chemical composition. This value gives indication on the C/H ratio, the calorific value and about the tendency to soot formation.

Boiling point

Fuel oils are mixtures of a large number of components, each having a different boiling point. Therefore, it is more correct to indicate a range of boiling point rather than a single value. The boiling range is an important parameter because it determines the physical and combustion behaviour of the fuel, which is improved increasing this range.

Freezing point

This parameter is of particular importance for aeronautical gas turbines. While local temperatures at flight altitude can reach temperatures as low as 193 K (turbojets operate more efficiently at high flight altitude), usually fuel temperature does not reach these extreme values. However, in long-distance flights, values of 230 K for the fuel temperature have been recorded. In that case, possible problems are related to the fuel feeding (due to the fuel viscosity), and possible precipitation of solid hydrocarbons and ice formation (which can block the fuel filters). The temperature at which the fuel begins to form solid particles is said freezing point. In case of land applications, including stationary decentralised energy systems, the problems given by the fuel freezing point are reduced.

Surface Tension

The surface tension has an important impact on fuel atomization as well as on fuel combustion process in terms of efficiency and pollutant emissions: CO, unburned hydrocarbon and soot.

Viscosity

Viscosity is a physical property that depends mainly on the chemical composition of the hydrocarbons contained in the fuel. Fuel viscosity has an impact on energy demand for fuel pumping, atomization and spray formation and fuel vaporization. The higher the fuel

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viscosity, the lower the quality of the vaporization. Modern injectors are able to perform a satisfactory vaporization for viscosity values up to approximately 15 x 10-6 m²/s.

Vapour pressure

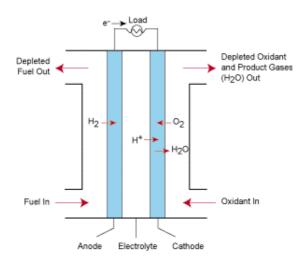
The liquid vapor pressure is the pressure exerted by the vapor on its surface at a given temperature. High vapor pressure are favourable for an efficient combustion, since it allows for fast vaporization of the fuel in the combustion primary zone. On the other side, low vapour pressure gives advantages in terms of reduction of the pressure in not ventilated tanks, lower evaporative losses (especially at high altitudes) and reduced fire risk. The vapor pressure strongly depends on temperature, and increases very rapidly at higher temperatures.

HYDROGEN PRODUCTION AND FUEL CELLS

Fuel Cells are energy conversion devices able to generate electric energy at very high efficiency. Several different types of Fuel Cells are available. The most important are:

- PEM-FC (Polymer Electrolyte Membrane FC)
- PAFC (Phosphoric Acid FC)
- MCFC (Molten Carbonate)
- SOFC (Solid Oxide)

The operation of a Fuel Cell is described in the following figure.



The electrochemical conversion process is always associated with heat production (at different temperatures depending on the type of Fuel Cell): therefore, it is necessary to remove heat in order to maintain the reaction (i.e. the FC in operation).

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Fuel Cell				Operating	Electrical
Technology	Electrolyte	Anode	Cathode	Temperature	Efficiency
PEM	lon-exchange membrane, hydrated organic polymer	Platinum	Platinum	175°F	30%–35%
PAFC	Phosphoric acid	Platinum	Platinum	392°F	35%
MCFC	Molten Li/Na/K carbonate	Nickel	Nickel oxide	1200°F	45%–55%
SOFC	Yttria-doped zirconia	Nickel	Sr-doped lanthanum manganite	1800°F	45%–47%

Main features of different types of Fuel Cells (Schmidt, Gunderson, 2000)

Gas Species	PEMFC	PAFC	MCFC	SOFC
H ₂	Fuel	Fuel	Fuel	Fuel
CO	Poison	Poison	Fuel	Fuel
	(>10ppm)	(>0.5%)		
CH₄	Diluent	Diluent	Diluent	Fuel
CO ₂ and H ₂ 0	Diluent	Diluent	Diluent	Diluent
S as (H ₂ S and	No studies to	Poison	Poison	Poison
COS)	date	(>50 ppm)	(>0.5 ppm)	(>1.0 ppm)

Tolerance of different types of Fuel Cells to fuel/contaminants (Schmidt, Gunderson, 2000)

Fuel Cells have been tested not only with pure hydrogen but also with other fuels, such as methanol. Nevertheless, the use of bioethanol, a renewable fuel which is also less dangerous than methanol in case of spills, is of great interest and under investigation. In addition, bioethanol can be reformed into hydrogen. More details on that are given in the next chapter.

5.2. Critical aspects of technologies: lessons learnt, R&D and environmental issues

OTTO ENGINES

involved in the bioethanol market.

A significant effort has been carried out since several decades to use ethanol in spark ignition (Otto) engines: this work was concentrated on engines for transport applications. Today, the use of bioethanol in otto engines for stationary power generation seems of no real commercial interest. This fact was also confirmed by direct contacts with actors

Being the present work focused on stationary application, we will therefore not report here about research work carried out on spark ignition engines for transports. However, among the most recent and new results, research on H_2 -enriched bioethanol in spark ignition engines is worth to be mentioned, even if aimed at transports (Al-Baghadi, 2003).

Generally, it has already been proven that a small amount of hydrogen can be mixed with gasoline and air (H₂ is injected just after the throttle valve of the carburettor), so to achieve a 6 times higher burning velocity: the effect is such that ultra lean combustion is possible, and therefore low flame temperature and lower heat transfer to the walls can be achieved, which means higher engine efficiency and reduced CO and NOx emissions. The same approach can be adopted with ethanol instead of gasoline as base fuel: tests (Al-Baghadi, 2003) were carried out using 2, 4, 6, 8, 10, 12 % w/w hydrogen blending in ethanol. The

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advantage of using only small amounts of hydrogen are mainly related to the problems of hydrogen storage on board. The main benefit of using hydrogen-supplemented biofuel was a reduction in specific fuel consumption (which decreases as the percentage of blended hydrogen is increased) and pollutant emission. However, the increase in compression ratio causes NOx emission increase: nevertheless, low amount hydrogen supplemented bioethanol (0-3.5 %) still shows lower NOx emissions than those of standard gasoline in spark ignition engines. In all cases, the adoption of hydrogen enriched biofuel made the engine power greater than that developed with pure gasoline.

DIESEL ENGINES

Ethanol-Diesel blending

As previously mentioned, ethanol can be mixed with diesel oil by using a proper additive. The use of bioethanol blended fuels reduces particulate emissions, but also generates some risks with respect to fuel handling and storage, which have to be carried out as for gasoline. Diesel engines, that are widely used not only for road transport but also for decentralised energy production and in agricultural machines, present significant emissions in terms of smoke, particulates and NO_x. The problem of meeting more and more stringent regulations, especially on particulate emissions, is today a major technical challenge, and new injection systems have recently appeared on the market (the "second generation" common rail systems). However, the use of oxygenated fuels, such as bioethanol, in diesel engines represents another possible and very interesting option to face the same problem, in particular towards the existing fleet of diesel engines. The same solution could therefore be used for diesel-based stationary energy generation.

By adding bioethanol in diesel oil, the ignition delay is increased, the cetane number is decreased, the viscosity as well as the fuel heating value are changed. Ethanol can be emulsified at different levels to diesel (Mc Cormick *et al*, 2001; Satgé de Caro, 2001):

- Emulsions in the range of 5-20 % v/v of ethanol are technically possible (by adding a limited amount of organic polyfunctional additives) and economically interesting.
- 2. 20-40 % v/v emulsions are possible, but the amount of additive needed per litre is considerable. The additive is needed to stabilise the emulsions and achieve a proper cetane number. In general, the interest in this approach is rather limited.
- 3. The use of almost 100 % (95 %) ethanol in diesel is also technically possible. However, costs are quite relevant.

Emulsifiers (surfactants, additives) are needed also for very low percentages (5 % v/v) of ethanol in diesel, in order to have a stable emulsion and also (a very important feature) to make the emulsion tolerant towards water and increase material compatibility.

10-20% emulsions have been widely tested in US by Archer Daniel Midland (AMD), which is one of the greatest ethanol US producer. Tests on buses have been carried out in Chicago. The fuel was composed by:

- 80% diesel oil
- 15% ethanol
- 5% additives (by Pure Emulsifier)

Additives (i) increase fuel cetane number, (ii) improve lubrication properties and (iii) stabilise the emulsion, even in presence of significant amount of water and various climatic conditions. A wide number of emulsifiers are known, a list of them is given as follows:

Suppliers/producers of emulsifiers, and suggested level of blending (% v/v)

Supplier	Suggested Ethanol levels	Emulsifier levels
	% v/v	% v/v
AAE technologies, Inc./Octel Starreon, LLC	7.7 or 10	0.5 (a)
Akzo-Nobel	10 – 15	1 - 4
Betz-Dearbon, Inc.	5, 10 or 15	0.25, 0.35-0.75, o 1
Pure Energy Corporation	5 – 15	1 - 5
Biodiesel	10	10

Source: Mc Cormick et al. 2001, NREL

(a) AAE05/Octimax 4930

In France (Satgé de Caro *et al*, 2001), two non-ionic surfactants have been identified and tested in engines:

- A1: 1-octylamino-3-octyloxy-2-propanol
- A2: N-(2-nitrato-3-octyloxy propyl), N-octyl nitramine

Possible combinations of these two additives have also been considered. These additives have been used in formulating 10-20 % emulsions (additives at approximately 2 %) which have been used to test fuel properties.

Emulsions have been produced using hydrate ethanol (i.e. 96 % v/v ethanol): the most stable emulsions were produced by adding 2 % A1 additive: also 1% A1 + 1% A2 mixtures were tested. As regards the calorific values, these are shown in the next table.

Diesel and ethanol-diesel emulsion calorific values

	Heating value
	(MJ/kg)
Diesel	42.35
Diesel +10% ethanol +1%A1+1%A2	40.98
Diesel +15% ethanol +1%A1+1%A2	40.75
Diesel +20% ethanol +1%A1+1%A2	39.59

Source: Sattgé de Caro et al, 2001

Viscosity do not represent a major problem in case of 10-20 % v/v ethanol in diesel, since it does not rise above the limit of 2 cSt @ 40 °C. The use of additive is recommended in order to improve fuel lubrication properties: however, above 40 °C the viscosity increase due to the additives is greater.

Viscosity at 40°C

Dynamic viscosity at
40°C (mPa s)
2.3
1.8
1.9

Source: Sattgé de Caro et al, 2001

As regards the cetane number, it shows a linear dependence on the ethanol content in the mixture: it decreases as ethanol percentage is increased. The use of additives maintains the cetane number above 45, which is needed by diesel engines to achieve good ignition, as indicated in the next table.

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Cetane number CN		
	CN	
Commercial diesel	49	
Diesel fuel blended with:		
15% ethanol	41	
15% ethanol + 2% A2	49.5	
15% ethanol + 1% A1 + 1% A2	47.5	
10% ethanol	43.5	
10% ethanol + 1% A1 + 1% A2	48	
20% ethanol + 1% A1 + 1% A2	45	

The behaviour of the diesel-ethanol emulsions (with additives) at low temperature is better than that typical of commercial diesel fuels. The use of additives is needed in order to

prevent possible separation problems at low temperatures.

Cloud Filter Plugging Point (CEPP)

Cloud Filter Flugging Fourt (CFFF)		
	CFPP(°C)	
Diesel	-14	
15% ethanol + 2% A2	-19	
15% ethanol + 1%A1 + 1%A2	-18	

Source: Sattgé de Caro et al, 2001

Source: Sattgé de Caro et al. 2001

The tested emulsions do not generate corrosions (steel, copper) in standard engines, even in case hydrated ethanol is used. However, it is always recommended to protect metallic parts from traces of water in the fuel: this goal is achieved by using the additive. Finally, the lower ignition temperature of ethanol does not affect engine performances, even at cold start.

Compared to diesel, safety of diesel-ethanol mixtures handling and storage is an important issue. In fact, the flammability limit of e-diesel (ethanol-diesel blend) is very close to pure ethanol, which is ~ 50 °C lower than pure diesel and ~ 30 °C lower than pure gasoline. Therefore, specific measures, norms and standards for ethanol-diesel blends have to be developed and applied in transportation and storage, while pure gasoline and diesel are safer (lower risk of fire and explosion).

Tests in DI (Direct Injection) - IDI (InDirect Injection) engines

Most of the R&D work has been carried out on transportation engines. In this respect, the following considerations can be done (Satgé de Caro *et al*, 2001):

- DI engines are more sensitive to fuel cetane number than IDI engines
- Ethanol reduces smokes and particulates. Low blends (< 15 %) of ethanol in DI reduce pollutants in the exhaust gas more than in IDI engines

Low blends (10 %) of ethanol in DI injection engines (Hatz 1D80, 667 cm³, air cooled, 3000 RPM, 10 kW) caused 5 % reduction in engine power, but only 3 % increase in fuel consumption. NOx emissions did not change significantly compared to diesel fuel, CO decreased up to 20 %, and a slight increase in HC emissions was recorded.

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Higher blends (20 %) of ethanol tested in IDI engines (Renault F8Q 706, 1870 cm³, water cooled, 4500 RPM, 50 kW) gave 11 % power reduction and 7 % consumption increase. While CO and HC slightly increased, NOx were always lower than pure diesel fuel. In addition, while ethanol reduces smoke and particulate emissions, the additives increase these emissions again: however, a 35 % reduction with respect to diesel fuel only can be achieved with ethanol-diesel-additive mixtures. The diesel-ethanol blended fuel makes the engine run in a more irregular way, and injection timing has to be modified: the additives improve ignition delay and reduce irregularities.

Neat ethanol in diesel engines

The main example of almost neat ethanol use in diesel has been developed in Sweden by Sekab: a special mixture of ethanol-diesel oil has been developed for the use in large urban buses (ETAMAX-D), which is based on 95 % w/w ethanol. However, limitations still exists with respect to the type of engines suitable for this fuel.

Specifications for ETAMAX-D are given in the table below (SEKAB Web Site).

SALES SP	ECIFIK	ATION
ETHANOL	FUEL,	ETAMAX D

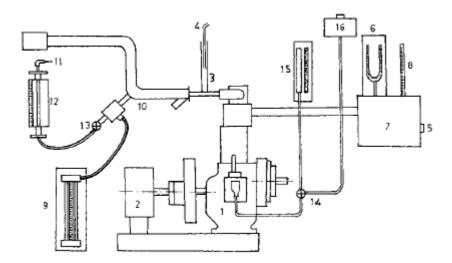
			Method of analysis
Appearance		clear, without particles	ASTM D 2090
рН		min 5,2 max 9,0	AMSE 1131
Water	% by weight	max 6,20	SS-ISO 760
Density (D 20/4)	g/ml	0,820-0,840	SS-ISO 758
Fuel composition			
Ethanol 95%	% by weight	90,2	
Ignition improver	% by weight	7,0	
MTBE	% by weight	2,3	
Isobutanol	% by weight	0,5	
Corrosive inhibitor	ppm	90	
Colour (red)			

The environmental benefits associated with the use of neat bioethanol in diesel engines are considerable: these analysis are always related to transports (CADDET). NOx are reduced at 56 % of those typical of EURO 2 diesel engines, CO to 3.2-1 % of Euro 2 standard as well as HC (8-13 % of Euro 2 standard). Compared to EURO 5, that will come into force in 2008, the ETAMAX-D CO emission is 0.1 g/kWh compared to 1.5-4 g/kWh (Eur.Stationary Cycle and Eur.Transient Cycle respectively), HC emission is also 0.1 g/kWh (versus 0.46-0.55 g/kWh), NOx emission is 3.9 g/kWh (versus 2 g/kWh) and finally particulate emission is 0.04 g/kWh (compared to 0.02-0.03 g/kWh). ETAMAX-D would therefore be rather close to meet the most stringent future emission regulation for diesel in transports, even if not yet sufficient (CTI, 2002).

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Tests in stationary engines

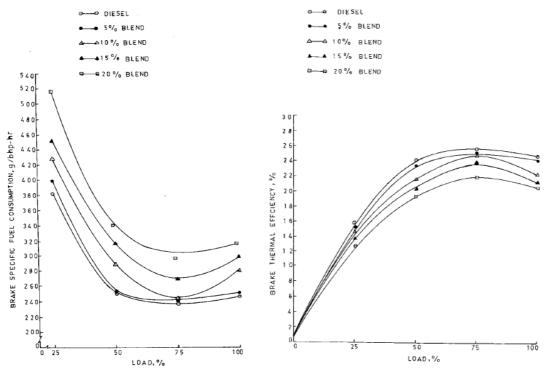
As already mentioned, few works deal with the use of bioethanol in diesel engines for stationary power production. Ajav *et al*, 1999 proved that small size (7.4 kW, water cooled) high speed (1500 rpm) stationary engines can be run on ethanol-diesel blends (no additive). 5 %, 10 %, 15 % and 20 % ethanol in diesel was tested. No significant reduction in power was reported, while slightly higher fuel consumption (due to fuel density and calorific value) and therefore slightly higher brake specific fuel consumption were observed. Lubricating oil temperature was instead lower than that of pure diesel oil. Exhaust emissions were improved (up to 62 % reduction in CO emissions and 24 % in NOx emissions for the 20 % ethanol blending).



Schematic diagram of the experimental set-up for using diesel and ethanol-diesel blends.1

¹ 1. Engine; 2. Dynamometer; 3. Exhaust gas temp. Probe; 4. Thermocouple; 5. Orifice; 6. U-tube manometer; 7. Surge tank; 8. Mercury thermometer; 9. Water manometer; 10. Exhaust extension; 11. Gas sampling point; 12. Gas flow meter; 13. Valve (one-way); 14. Valve (two-way); 15. Fuel measuring device; 16. Fuel tank.

(from Ajav et al, 1999)



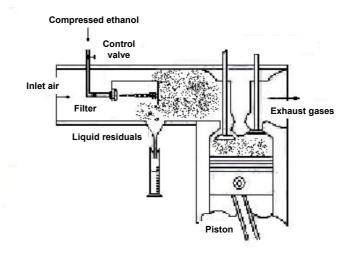
(from Ajav et al, 1999)

Ethanol fumigation

Ethanol can be fumigated in the inlet flow of air by adding a carburettor or an injector. The main advantages given by fumigations are the following:

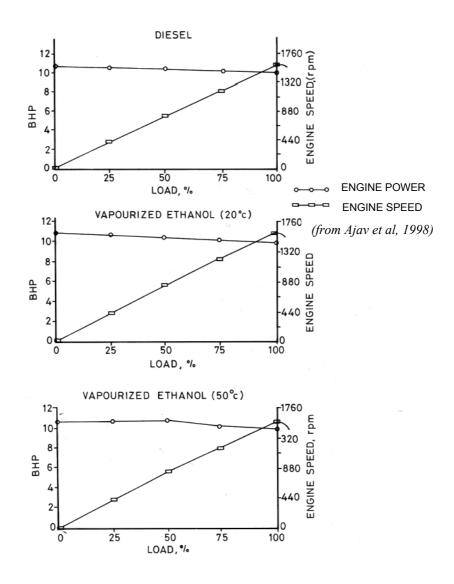
- Very limited modifications to the engine are needed
- Ethanol flow is kept separated from the diesel fuel. Therefore, the engine is still able to run on diesel oil only
- A significant amount of energy (up to 60 %) can be produced by fumigated ethanol

A sketch of the ethanol fumigation is shown in the figure.



When fumigation is done by means of a carburettor, a relatively simple and inexpensive modification to the engine, it is necessary to preheat the inlet flow of air to provide the energy necessary for ethanol vaporization.

Ajav *et al*, 1998, carried out a comprehensive experimental work on a 7.4 kW – 1500 rpm stationary engine. 25 % to 100 % load was tested, using both heated and unheated ethanol. Brake horsepower (BHP) is reported in the next figure. It is interesting to observe that 50 °C preheated air ethanol mixture shows a decrease in brake horsepower (BHP) at high load. This is due to the reduced density of charge, which cause poor combustion. At full load, BHP was 10.71 with pure diesel, 10.80 with ethanol 20 °C and 10.57 with ethanol 50 °C. So, maximum BHP was at ethanol 20 °C.



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As regards brake specific fuel consumption (BSFC), the pattern of pure diesel is significantly different from ethanol vapourized in diesel. In fact, at low loads BSFC is higher for fumigated ethanol mixture, while the situation is the opposite at loads higher than 75 %. It is important to remark that:

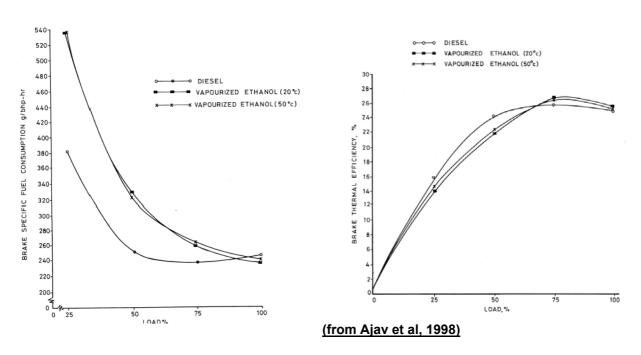
- the diesel replacement at low loads was higher (33.6 % w/w) than that at high loads (15 % w/w)
- The use of fumigated bioethanol as a diesel substitute for stationary diesel generators allows to achieve better BSFC if the systems works close to nominal conditions

As regards brake thermal efficiency (BTE), the maximum value is found at 75 % load conditions: unheated fumigated bioethanol showed 27 % (BTE), compared to 25.7 % and 26.7 % of diesel and preheated ethanol respectively. Therefore, BTE is higher for unheated bioethanol. However, at partial loads (below 75 %), diesel fuel behaves better.

Both exhaust gas temperature and lubricating oil temperature decrease in case of fumigated ethanol.

CO emissions were lowest using diesel only, while increased with both unheated and preheated bioethanol. With preheated bioethanol, a 60 % increase in CO emissions was registered.

NOx emissions, instead, remained more or less unchanged (minimal variations: 0.4 increase for unheated and 0.7 % decrease for preheated bioethanol).



Other similar works are available in literature (such as Noguchi *et al*, 1996; Lu Nan *et al*, 1994; Kowalewicz *et L*, 2003; ETC), but these are almost always focused on transportation engines. In order to control engine knocking it was found necessary to modify and control diesel injection timing.

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MATERIAL COMPATIBILITY

It is well know that care has to be taken on engine (and storage tank) material compatibility when ethanol is used as fuel. Tanks, pumps, sealants, filters, etc materials have to be selected according to their characteristics. Specifications are already available. A list of material is given in the next table.

Compatibility of Commonly Used Materials With Ethanol and Ethanol Blends

Recommended Not Recommended

Metals

Aluminum Zinc-galvanized (ethanol only)

Carbon steel Stainless Steel Bronze

Elastomers

Buna-N (hoses & gaskets) (note 1)

Fluorel (note 1)

Buna-N (seals only) (Note 1)

Neoprene (seals only)

Fluorei (note 1) Neoprene (seais Fluorosilicone (note 2) Urethane rubber

Neoprene (hoses & gaskets)

Polysulfide rubber

Natural rubber (ethanol only)

Viton (note 1)

Polymers
Acetal Polyurethane (note 2)

Nylon Alcohol-based pipe dope (recently applied)

(note 2) Polypropylene Teflon (note 1)

Fiberglass reinforced plastic (note 2)

NOTES

1. Registered trademark

2. The manufacturer of the specific material should be consulted.

Source: Renewable Fuel Association, 2002

Long-term tests (2000 hours) have also been recently conducted on non-automotive engines to verify material compatibility with 10 and 20 % ethanol in gasoline (Orbital, 2003). Metal, brass and polymeric materials were investigated. Corrosion of several metallic parts normally exposed to fuel was reported: a particular attention has to be given to those parts where the oxides could dislodge and become trapped between moving parts, thus accelerating component wear-out. All brass components showed to be tarnished, indicating that oxidation was occurring: this can affect fuel metering and control in carburettors. Finally, some polymeric components (as fuel line connectors, delivery hoses, bulbs, etc) were also significantly affected by the contact with ethanol: this cannot be accepted, as it could cause fuel leackage.

A number of guidebooks and information documents are available as regards handling, storing and dispensing ethanol fuels (Renewable Fuel Association, 2002; Center for Transportation Research, 2000).

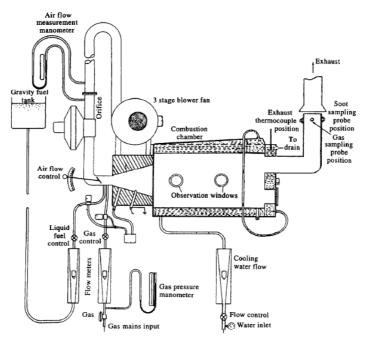
GAS TURBINES

Fuel combustion

The most important combustion characteristics :are

- flame temperature
- chemical reaction rate
- burning range
- soot and smoke formation.

These issues require a detailed investigation before feeding a gas turbine with the bioethanol. In fact, one of the most important differences between spark / compressed ignition engines and gas turbines is given by the fact that combustion is occurring in steady conditions. Therefore, in order to compare these properties for kerosene and ethanol fuels, experimental work has to be carried in a combustion test rig, as shown in the figure below. Tests concentrated on kerosene, diesel oil and mixtures of diesel-ethanol at 5, 10 and 20% v/v [Asfar et al, 1998].



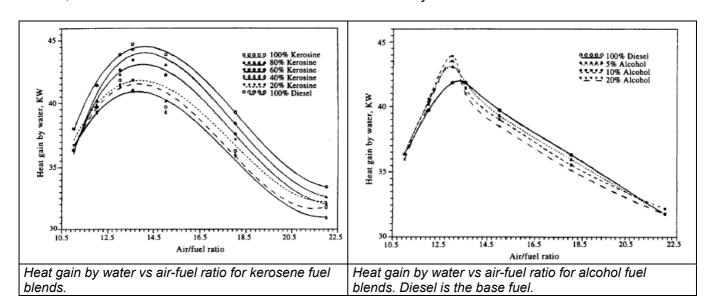
Sketch of the combustion test rig (Asfar et al, 1998)

The following issues have been investigated for each fuel blending:

- Thermal balance analysis
- Heat transfer and combustion efficiency (evaluated by measuring the heat absorption by cooling water for different air/fuel ratio)
- Exhaust gas temperature and smoke concentration

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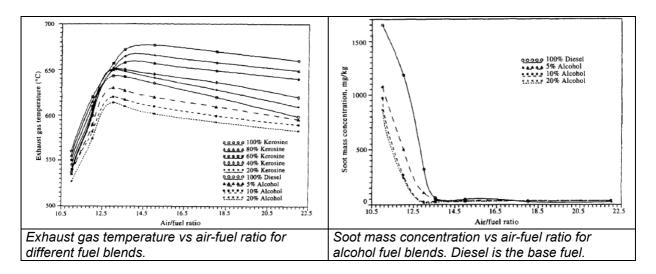
The amount of heat absorbed by the water (heat gain) at various air/fuel ratios is given in the next figures for kerosene, diesel oil and their mixtures (left) and diesel-ethanol mixtures (right). For all the examined cases the absorbed heat is low for rich mixtures, due to incomplete combustion. The maximum value of the heat gain is approximately found at the stoichiometric value of the A/F ratio: it then decreases for lean mixtures (due to excess air), as well as for rich mixtures (due to incomplete combustion). The heat absorbed from the water is maximum for pure kerosene thanks to its higher heat of combustion. If kerosene is blended with diesel oil, the heat of combustion decreases as the share of diesel oil is increased. The figure at right shows instead the heat gain for diesel oil-ethanol in mixture. When diesel oil is mixed with ethanol, the calorific value, the unburned fuel and the tendency to produce smoke and soot are all decreasing. Considering 20% of ethanol in diesel, smoke emissions and unburned fuel are both very low.



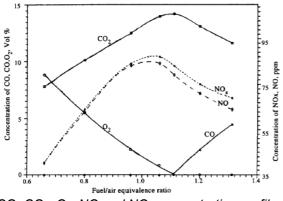
Exhaust gas temperatures versus air/fuel ratio are shown in the next figure (left) for different fuels. In each cases the temperature profile shows the same trend, with a maximum corresponding to the stoichiometric equivalence ratio (i.e. 1). The exhaust gas temperature is a measure of the flame temperature. The kerosene fuel has the maximum flame temperature, if the diesel oil is blended with ethanol, both the flame and exhaust gas temperature are decreasing. The exhaust gas temperature is maximum for slightly rich air/fuel mixtures.

Smoke emissions (soot) for different air/fuel ratio is shown in figure at right. Emissions are higher in case of rich mixtures, but they rapidly decrease at the stoichiometric combustion A/F ratio. Diesel oil has the greater tendency to form particulates and smoke (due to the low H/C ratio). As alcohol fuels have higher H/C ratio, the effect of ethanol blending in diesel oil is a reduction in exhaust smoke emissions, which increases as the amount of blended ethanol is increased.

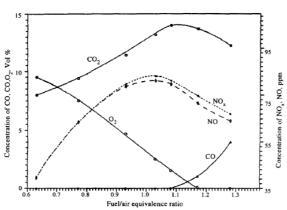
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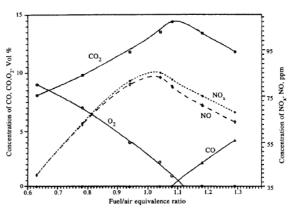
CO and NO_x emissions are shown in the following figures. In particular, as the amount of blended ethanol is increased, a reduction of both CO and NO_x emissions is observed. The O_2 concentration in exhaust gas is lower because of the lower A/F ratio. Summarizing, mixing high H/C ratio conventional fuel (as diesel oil) with ethanol improves the combustion efficiency increased and reduces pollutant emissions (NO_x , CO, smoke).



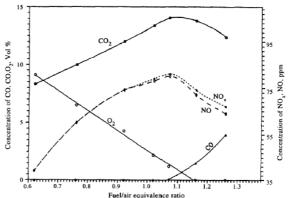
CO, CO₂, O₂, NO and NO_x concentration profiles, vs equivalence ratio for diesel fuel.



CO, CO₂, O₂, NO and NO_x concentration profiles, vs equivalence ratio for 3% ethanol-7% isobutanol-90% diesel fuel blending.



CO, CO₂, O₂, NO and NO_x concentration profiles, vs equivalence ratio for 1.3% ethanol-3.7% isobutanol-95% diesel fuel blending.



CO, CO₂, O₂, NO and NO_x concentration profiles, vs equivalence ratio for 7% ethanol-13% isobutanol-80% diesel fuel blending.

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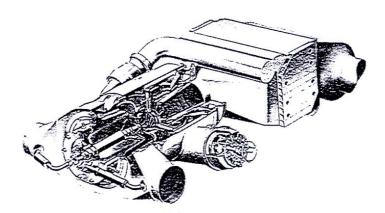
Use of bioethanol in gas turbine

Ethanol as fuel for gas turbine was seriously considered by Volvo in the 90's (Johansson, 1997). The LPP (Lean Premixed Prevaporised) combustor of the VT100 microturbine was tested with ethanol. Volvo developed two experimental vehicles, respectively named ECT (Environmental Concept Truck) and ECB (Environmental Concept Bus): both these vehicles were equipped with an hybrid engine coupling a gas turbine with an electric generator. The main goal of the experimental campaign was to assess the feasibility of ethanol as fuel for hybrid vehicles in transports: however, the results of this work are also applicable to stationary energy production, and therefore are here reported.

The VT100 turbogenerator is composed by a single-stage centrifugal compressor, a single -stage centripetal turbine, and an electric generator on the same shaft of the turbine. The turbogenerator characteristics are shown in the next table.

Output	110 kW
Pressure ratio	4.8 : 1
Overall efficiency	32% (recuperated) in upper power
	range
NO _x emission	1.0 g/kWhe
CO emission	1.5 g/kWhe
HC emission	0.05 g/kWhe
PM emission	0.05 g/kWhe

VT100 engine performance data.



VT100 Turbogenerator.

Combustor Design - In order to achieve low NOx emissions, flame temperature must be kept below the stoichiometric value: however, the flame temperature has also to be high enough to allow for complete fuel combustion.

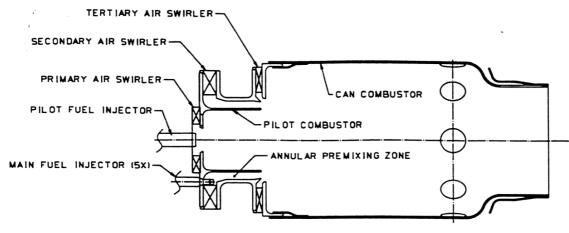
In a LPP combustor, a low flame temperature is achieved by using a lean fuel/air mixture (without liquid fuel droplets) to the combustor. In order to do this, the liquid fuel has to be first vaporised and then premixed with the air before entering the primary combustion zone. This fuel process preparation phase (premixing – prevaporising) needs a certain residence time in order to be fully completed.

On the other hand, residence time should be minimized in order to reduce risks of flash-back in the premixing duct. The LPP combustor is constituted by three radial swirler, five

atomizers airblast, an annular premixing zone, an inner zone for the pilot flame and a main central combustor. The combustor design values are summarized in the next table, and a short description of these components is following.

Inlet pressure (Pin)	4.8 bar
Inlet air temperature (Tin)	890 K
Air mass flow	0.8 kg/s
Combustor residence time (hot)	8 ms
Combustor pressure drop	4.0 %

Combustor design condition.



VT100 Dry low-NOx combustor

<u>Main Combustor</u> - The main combustor is cooled by air jets from the outside of the liner in order to avoid the quenching of the hot gases close to the walls, producing excessive CO and UHC (Unburned HydroCarbon) emissions. The stability of the combustion process is obtained by severe swirling of flows and changes of section between annular premixing duct and the main combustor.

<u>Central Pilot Combustor</u> - The pilot flame is mainly used for ignition, starting and idle. At high loads the pilot flame uses only a small share of the fuel flow: the aim is to maintain the flame stability while having only very limited NO_x production. The flame in the pilot combustor is stabilised by the recirculating the flow in the primary swirler. The walls are cooled by the air from the annular premixing duct.

<u>Pilot Fuel Injector</u> - The pilot injector is an air assisted pressure swirl atomizer. Compressed air is directly taken from the compressor outlet (at higher pressure and lower temperature with respect to the air supplying the combustor). Fresh air increase the quality of the spray reducing the risk of ethanol over heating through the injector.

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<u>Secondary Air Swirler</u> - It is a radial swirler composed by 15 radial vanes, which gives a strongly swirled flow (greater than that generated by the tertiary swirler), thus stabilizing fuel combustion in the main combustion zone.

<u>Main Fuel Injectors</u> - The five main injector are airblast type, displaced with constant pitch in circumferential direction. As for the pilot injector, air is taken directly from the compressor outlet.

<u>Annular Premixing Zone</u> - In order to limit NOx emissions while firing liquid fuel, fuel has to be prevaporized and premixed with air before entering the main combustion chamber. A certain residence time is needed to complete properly the three phases of vaporization, preheating and mixing. Nevertheless, vaporization time should be minimized in order to avoid the pre-ignition of the fuel. Moreover, vaporization and mixing must be accomplished in a quite homogenous flow in order to avoid wakes in the mixing device that can produce flash-back and pre-ignition in the premixing zone. The strongly swirled flow inside the annular duct applies high shear stresses on the fuel droplets, thus contributing to a fast vaporization but also giving possible non-homogeneities in the flow. The length of the annular zone need a residence time of 1.2 ms for completing the vaporization and premixing processes. This residence time has to be compared with the auto-ignition time.

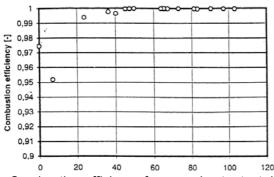
<u>Tertiary Air Swirler</u> - This swirler is composed by 15 radial vanes, counter-rotating with respect to the secondary swirler to increase the mixing process.

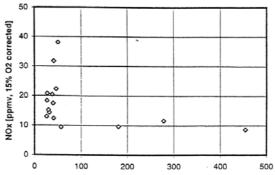
EXPERIMENTAL ACTIVITY - COMBUSTOR TEST RIG

Before testing the whole engine, a detailed experimental campaign has been carried out to test the combustion chamber in a combustor test rig. The goal was to evaluate the ignition characteristics, the flame stability, the pollutant emissions, and to verify that metal temperatures are below limit values (which is needed to achieve satisfactory engine reliability). Tests were performed under pressure conditions and at an air inlet temperature of 700 K. Air pressure and temperature, and the pressure drop through the combustor were monitored, while exhaust gases were analysed.

The figure at left shows combustion efficiency in the range of minimum and maximum power: this value is higher than 99.6 % between 30 % and 100% of the thermal load. At idle conditions, instead, when only the pilot flame is in operation, the efficiency decreases at 95%. Therefore, it can be concluded that high combustion efficiency values are recorded above 25-30 % of the thermal load.

 NO_x , CO and UHC emissions are also reported. The chart showing NO_x emissions versus CO emission at different thermal loads provides some useful information on the premixing zone performances. In this case, it can be concluded that the efficiency is sufficiently good, as 10 ppm of NO_x and 50 ppm of CO are registered for the best test conditions.

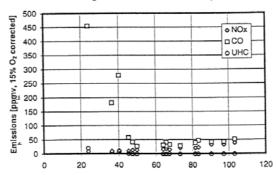




Combustion efficiency from combustor test rig.

CO versus NOx emissions from combustor test rig.

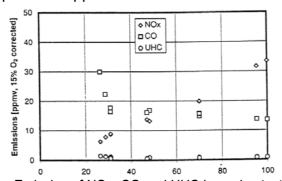
 NO_x emission are approximately 40 ppm @ $15\%O_2$ in the whole working range. CO and UHC emissions are lower than 50 ppm @ $15\%O_2$ and 5 ppm respectively until 50% of the load. Moreover, CO and UHC emissions are lower when testing the complete engine and not the combustor only, thanks to the higher air inlet temperature.



Emission of NOx, CO and UHC from combustor test rig

EXPERIMENTAL ACTIVITY - ENGINE TEST

The next figure shows the NO_x , CO and UHC emissions @ 15% O_2 as a function of the engine power output. NO_x emission are below 35 ppm in the whole working range. CO and UHC are lower than 20 ppm and 2 ppm for thermal loads above 50%.



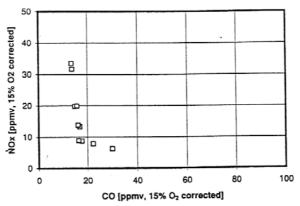
Emission of NOx, CO and UHC in engine test

As expected, comparing this graph with the previous one (combustor test rig), it can be seen that CO and UHC emissions measured on the whole working range stay below than the values recorded during in combustor test rig at the same loads. This reduction

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depends on the higher temperature as well as on the "post-combustion" effect during turbine expansion.

NO_x emissions versus CO emission is also given.



NOx/CO trade-off characteristics in engine test.

Next tables give engine cycle and emission value as "g per kWh" of electric power measured during engine test.

Engine cycle definition.

Output power (%)	100	75	60	30
Time (%)	25	50	15	10

Emission weighting from engine test

	Measured emission	Target emission
NO _x (g/kWhe)	0.90	1.0
CO (g/kWhe)	0.40	1.5
UHC(g/kWhe)	0.033	0.05

USE OF ALCOHOLS IN THERMAL POWER PLANTS

Thermal power plants using pulverized coal or heavy oil as fuel need light oils during the start-up phase in order to warm up the furnace. The time needed to carry our this warm-up phase is considerable, in case of large thermal power stations, since very precise conditions have to be established to achieve stable fuel combustion. In fact, if the temperature of the wall is too low, the heat absorbed by the walls of the combustion chamber cool down the flame: due to the low temperature, combustion is incomplete, flue gas contain unburned fuel and the system efficiency is decreased.

Prieto Fernandez *et al* (1999) observed that the addition of alcohol (either ethanol or methanol) improve the combustion during this initial phase, thanks to the oxygen contained in the fuel and the low boiling temperature of alcohols (compared to light oils). The low fuel viscosity also give a further positive contribution, as it makes fuel atomization easier. The lower ignition temperature of alcohols, compared to hydrocarbon fuels used in large thermal power station, reduced the time needed to complete flame stabilization. Emissions are also improved during this phase, as both methanol and ethanol produces lower pollutant emission. The only negative aspect of alcohol in large furnaces is instead the fact that the radiation heat to the furnace walls is lower than heavy oil, due to the low flame temperature.

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Summarising, from the pollutant emission point of view, the use of bioethanol in gas turbines gives some advantages, not only in terms of CO₂ but also in terms of other pollutants typical of the combustion processes.

The pollutant emissions produced by a gas turbine fired by ethanol are lower than using a conventional fuel because of the lower flame temperature typical of bioethanol. In addition, using hydrate ethanol (94-95% v/v concentration), the water in the fuel reduces NO_x emissions similarly to what is usually done in industrial gas turbines by water injection (a widely used technique). CO emission are very low as indicated in literature.

HYDROGEN PRODUCTION FROM ETHANOL AND FUEL CELLS

Hydrogen production from ethanol

As regards hydrogen generation from ethanol, catalytic reforming [Kaddouri *et al*, 2002; Marino *et al*, 2000; Rampe *et al*, 2000] is currently under investigation at research level. Bio oils and pyrolysis oils have also been tested on various catalysts [Marquevich *et al*, 2000].

By means of the steam reforming process, alcohols – treated with steam - are converted into a gas composed by H_2 , CO, CO_2 , CH_4 and H_2O [Amphlett *et al*, 1998].

Research work is focused on the selection of catalysts, and the identification of optimal operating conditions (temperature, velocity of ethanol, steam conditions, pressure): the goal is to achieve a higher selectivity to hydrogen as well as reducing energy demand of the process.

Ethanol reforming is followed by a shift conversion reaction, which is basically similar to the one used in biomass gasification. In particular, Kaddouri *et al*, 2000, on the basis of experimental results achieved on Co/Al₂O₃-IMP e Co/Si₂-IMP catalysts, propose the following set of reactions:

- <u>First phase</u>: bioethanol dehydrogenation into acetaldehyde and hydrogen
 C₂H₅OH → CH₃CHO + H₂
- Second phase: acetaldehyde decomposition into carbon monoxide and methane:
 CH₃CHO → CO + CH₄
- <u>Third phase</u>: reaction of carbon monoxide (i) with water (*shift reaction*) into CO₂ and water, or (ii) with hydrogen into methane and water (*methanation*, which is the inverse reaction of Steam Methane Reforming SMR)

$$\begin{array}{ll} \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 & \textit{(shift)} \\ \text{CO} + 3 \text{ H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O} & \textit{(methanation)} \end{array}$$

Depending on which type of catalysts is used, either the shift or the methanation reaction can prevail. Using Co/Al_2O_3 -IMP as catalyst, shift reaction was observed to prevail, while the same has not been observed with Co/SiO_2 -IMP catalyst.

According to IEA [Milne et al, 2002], a large number of studies have been done on methanol, but long term demonstration is still a weak point. Nevertheless, in the short term

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it seems that methanol will most likely be the main alcohol fuel used as hydrogen source in combination with Fuel Cell.

On the other hand, research work on bioethanol as hydrogen source is growing: activities are concentrated on the selection and verification of catalysts and the identification of their best operational conditions.

Ethanol Fuel Cell

In US, Epyx Corporation (a subsidiary of Arthur D.Little) of Cambridge, Massachusetts, has been deeply involved in fuel cell research. Epyx has announced the development of a multi-fuel processor able to convert both renewable fuels (such as ethanol) and hydrocarbon fuels (as gasoline) into hydrogen, that will be then used to feed a Fuel Cell (source: U.S. Department of Energy, Oakridge National Laboratory, Epyx Corporation, Fuel Cells 2000, Renewable Fuels Association, U.S. Department of Agriculture).

An interesting fact is that hydrated ethanol is compatible with fuel cells: therefore, low cost ethanol can be adopted instead of high grade (and costly) anhydrous ethanol.

Caterpillar, Nuvera Fuel Cells and Williams Bio-Energy (an ethanol producer) have been awarded in 2001 of a 2.5 MUS\$ to develop the first commercial ethanol powered stationary fuel cell (Source: Renewable Fuels Association web site). The system (14 kW, continuous power) aimed at powering the Williams Visitors Centre in Pekin, Illinois. The target system efficiency is > 25 % (inverter > 93 %, Reformer > 80 % and Fuel Stack > 50 %). The goal was to achieve 4000 h durability testing completed.

In EU, the project "BIO H2 – Producing Clean Hydrogen from Bioethanol" has to be mentioned (Contract ERK6-CT-1999-00012). The goal of the project is to develop a complete bio-ethanol reformer system for the production of hydrogen. Hydrogen is produced by catalytic steam reforming. A complete bench-scale 5 kW fuel cell system will be implemented in this 36 months research project. The coordinator of this FP5 project is CRF (Centro Ricerche Fiat, I). Volkswagen is also developing and testing an ethanol fuel cell for transports applications (CAPRI project, JOE3950039), in which ABB, ECN and Johnson Mattey are partners.

Other research activities are on going also in Europe on direct ethanol fuel cell, mainly focusing the attention of substituting batteries of cellular phones, laptop and similar electronic devices. Significant results have recently been recently obtained in Italy on a special non-noble catalysts and low temperature fuel cells.

Medis Technology in US has developed a liquid ethanol micro fuel cell which aims at substituting batteries for communications. Medis micro fuel cell can deliver up to 5,000 mA/h using 16 cc of ethanol or methanol. The "Power Pack" has a size of 80 x 55 x 30 mm and a weight of 120 gr (200 gr when fuelled): the cell adopt a liquid electrolyte, while the use of noble metal has been reduced (platinum is not used at the cathode).

However, it has to be remarked that the fuel to be used in the energy conversion device is not simply ethanol, but a (patented by Medis) mixture containing sodium borohydride and other additives.

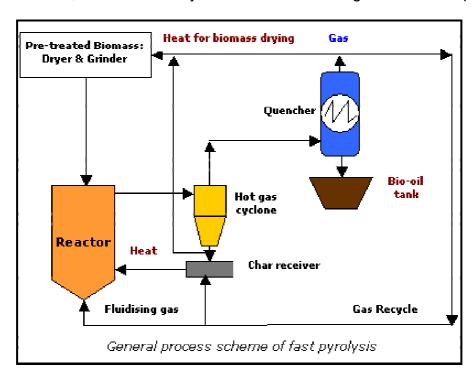
5.3. Economics and market perspectives

This is probably the most critical aspect, with respect to the use of bioethanol for stationary applications. At the present moment, only research work has been found in this area, and no commercial application was identified. Bioethanol market actors, which have been contacted, didn't show real interest in this sector (stationary power generation), due to the higher market value of ethanol as transport fuel compared to the low prices of fossil fuels for stationary energy generation. In fact, current prices of ethanol (0.4-0.55 for low grade hydrated ethanol in Southern EU) do not make yet economically viable the use of bioethanol for applications other than transports.

6. Pyrolysis oil

Amongst biomass conversion technologies, a very promising route is the production of biomass-derived oil through pyrolysis (in particular fast pyrolysis), thanks to its economic viability and simple integration into conventional energy systems: this liquid biofuel is called bio crude oil (BCO), pyrolysis oil (PO) or simply bio-oil. Pyrolysis is attractive because converting in one step solid biomass and wastes into liquid products presents advantages in transport (energy density is increased about four-fold in comparison to the feedstock), storage, handling, retrofitting, combustion, flexibility in supply and marketing.

Pyrolysis is a process of thermal degradation in absence of oxygen, within suitable thermal reactors. Relatively low temperatures of 500-800 °C are employed, the operational pressure is usually the atmospheric one, but also vacuum reactors are existing. Three products are usually obtained: gas, liquid and char, the relative proportions of which depend on the pyrolysis method and reaction parameters. Flash or fast pyrolysis maximises either gas or liquid products according to the process temperature. Fast pyrolysis gives higher yields in terms of liquid product (BCO or bio-oil) up 70% in weight on the feedstock: this process involves high heating rates (up to 1000 °C/s or even 10000 °C/s) combined with moderate temperature (less than 650 °C), short residence time within the reactor (some hundreds of millisecond) and rapid quenching of pyrolysis products. Currently, several pyrolysis plants - at laboratory scale or pilot plants - have been developed world wide, characterised by different reactor configuration and capacity.



Pyrolysis liquid typically is dark brown, the colour shading depending on the method of fast pyrolysis and initial feedstock. The fuel contains several hundred different chemicals in widely ranging proportions, from low molecular weight and volatile formaldehyde and acetic acid to complex high molecular weight phenols and anhydrosugars. PO density is

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much higher than fossil fuels (approx. 1.2 kg/dm³), thus counterbalancing in part the low energy content, due to the high oxygen content. Moreover, the polar nature of pyrolysis oil makes not possible its mixing with hydrocarbons.

The physical-chemical properties of pyrolysis oil are variable, depending on feedstock type and characteristics, the technology of the production facility and its process parameters (heating ratio, temperature, etc.). Here below typical values of PO are given, based on Bridgwater (2000):

Fuel property	Unit	Pyrolysis oil	Diesel oil	HFO
Density @ 15°C	kg/dm ³	1.22	0.85	0.96
Molecular weight	kg/mol		170-200	
Kinematic viscosity @ 50°C	cStoke	13	2.5	351
Lower heating value	MJ/kg	17.5	42.9	40.7
Flash point	°C	66	70	100
Pour point	°C	-27	-20	21
Ash	%wt	0.13	< 0.01	0.03
Water content	%wt	20.5	0.1	0.1
Elemental analysis				
Carbon	%	48.5	86.3	86.1
Hydrogen	%	6.4	12.8	11.8
Oxygen	%	42.5	0.9	0
Sulphur	%	0	0.15-0.30	2.1

Table 6.1 - Fuel properties of BCO, diesel oil and HFO

6.1. Energy conversion technologies for stationary systems

Pyrolysis oil has the potential to be burnt directly in thermal power plants, in modified Diesel engines or gas turbines; potential PO application can be summarised as follows:

- Utilisation of PO for heat production in large thermal plant (over 1 MW_{th}), replacing heavy fuel oil (HFO)
- Utilisation of PO for heat production in medium and small boilers (from 1 to less 0.1 MW_{th}), replacing light fuel oil (LFO)
- Utilisation of PO for electricity production (also combined to heat) in diesel engines, replacing light fuel oil (LFO) or in gas turbines
- Utilisation of PO for reburning in power plants, the main benefit being the reduction of NO_x and SO_x

Campaigns have been carried out and are currently on going to test pyrolysis oil in heating systems, diesel engines and gas turbines, in facilities in Europe, USA and Canada. These campaigns pointed out that, up to now, the utilisation of PO for energy production is still at

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demonstration phase; most of the experiences are not sufficiently developed and long-term duration tests are still needed. Moreover, special care has to be taken in PO storage and handling, due to the aggressive nature of PO with regard to materials conventionally used. Finally, it should be remarked that the utilisation of PO as transport fuel, other than the technical problems, is hampered also by the high costs of production and upgrading.

Heating systems

Pyrolysis oil has been tested as heating oil by several organisations in Europe, USA and Canada; even though some difficulties in comparison to conventional fuels exist, e.g. low energy content, high water content, acidity, PO utilisation in substitution of LFO in a longer term is one of the most promising routes, thanks to the current high cost of conventional LFO (examples in some countries).

Then, while the replacement of HFO with PO does not seem a realistic target at short term for economic reasons, the combustion of PO in small (less than 100 kW_{th}) and medium (less than 1000 kW_{th}) boilers is considered to be economically viable. From a technical point of view, the goal of most of the past and current research work is on one side to adapt the existing heating systems to PO (retrofitting of special burners on existing boilers), thus avoiding expensive upgrading of the oil, and, on the other side, to improve the pyrolysis process to achieve a production of higher quality and more stable BCOs.

Campaigns aimed at testing PO in heating systems have been carried out by Canmet in Canada, Fortum and VTT in Finland (Gust, 1997 – Gust, 1999 – Sipilä, 1999 – COMBIO, 2003), Red Arrow in the USA (Shaddix, 1997), Birka Energy in Sweden (Lindman, 1999) and Oilon in Finland (Oasmaa, 2001).

The main problems relates to PO high viscosity, high water content and elevated ignition temperature, thus causing blocking and clogging of the nozzles due to PO polymerisation, as well crust formation on some components of the burner. In order to avoid these phenomena, Canmet adapted the burner by means of in-line preheating of pyrolysis oil, while Fortum experimented the addition of alcohol through an auxiliary dual fuel system; in any case preheating with conventional fuels before switching to PO and a more complex start-up sequence is required as PO is not miscible with fuel oil or diesel. It was moreover found out that, once burning, emissions are quite acceptable (Gust, 1997). Another major issue is the adoption of acid resistant materials for components like valves and nozzles.

Diesel Engines

The production of electricity by using PO is a main issue, on which many organisations are working; extended engine tests have been performed by Ormrod diesel (Leech, 1997), who have achieved many hours running experience on a modified 250 kW_{el} dual fuel diesel engine, CNR Istituto Motori (Bertoli, 2001); Kansas University and MIT (Shihadeh, 1998); BTG (NL) and VTT and Wärtsilä Diesels (Solantausta 1993 and 1995 – Jay, 1995); moreover, Pasquali Macchine Agricole and Kassel University (Baglioni, 2001) on small scale diesel engines fuelled with bioemulsions.

Until now, the direct application of PO in diesel engines has still to be demonstrated by endurance tests: a common outcome of the performed campaigns is that pyrolysis oil is chemically aggressive towards steel. In fact, one of the main issue is the acidity of the oil, which causes corrosion of the engine; problems of polymerisation and corrosion and/or erosion of the injection system components indicate that long-term operational experience

is still required to identify the basic phenomena, select optimum materials and establish most favourable operating conditions and finally obtain sufficient data for warranties of performance.

In the above-mentioned experiences, a common conclusion is that the utilisation of PO in diesel engines (but in gas turbines also) is possible only if the energy conversion system is significantly modified. However, another option is the direct injection of PO/diesel oil emulsions in diesel engines with no major modification, thus making easier the market penetration of fast pyrolysis liquids as a diesel oil substitute. In this direction, some recent experiences (Baglioni, 2000; Chiaramonti, 2002; Ikura, 2002; Bertoli, 2000) report about the development of emulsions between conventional diesel oil and fast pyrolysis oil and experimental tests on diesel engines fuelled by these emulsions. The performed tests proved that it is possible to operate a diesel engine by BCO/ Diesel emulsions, but also in this case the technical problems related to the aggressive nature of PO requires further development in order to prove the long term behaviour of the engines.

Gas turbines

Concerning the utilisation of pyrolysis oil in gas turbines, research activity on this issue already started some 20 years ago: these first tests reported several problems including entrained char in the bio-oil which blocked the fuel injection systems and generating erosion; ash fouling downstream of the gas turbine, corrosion to turbine components and increased smoke emissions (Kasper, 1983). More recently, Orenda Aerospace in Canada reported promising results of filtered pyrolysis oil in a combustor of a 2.5 MW_{el} gas turbine (Andrews, 1995, 1996 and 1997). Bridgwater reports that the turbine has been run successfully for several hours on 100% pyrolysis liquids and about flame tunnel tests aimed at examining the long-term resistance of turbine parts to corrosive attack from alkali metals in the ashes of pyrolysis liquids (Bridgwater, 1997). In Europe Lopez (Lopez, 2000), performed preliminary tests on combustion of wood derived fast pyrolysis oils and their mixtures with ethanol in a gas turbine combustor, highlighting the fact that the high viscosity of fast pyrolysis oil creates problems at injection, and that a potential solution could be a mixture with ethanol. Also ENEL (CRT laboratories, Pisa) in Italy studied the effect of PO combustion in small gas turbines.

Summarising, also in the case of gas turbines, further analysis and experience seem necessary for a wider understanding of the basic phenomena and technical aspects, and long term operational experience is still needed.

Another interesting approach is the utilisation of vacuum Pyrolysis oil is the Integrated Pyrocycling combined cycle (IPCC) by Pyrovac (Canada). The combustion of pyrolysis products through an Integrated Combined Cycle can result in 18-30% increase of electricity output per ton of biomass compared to direct biomass combustion; in this way the advantage of decoupling fuel production from its utilisation is lost. The increase in efficiency is achieved by the conversion of biomass into oils, gases and charcoal using the Pyrocycling technology and by using them in a combined cycle fuelled with bio-oils: PO is combusted in a gas turbine; the gas turbine cycle is combined with a steam generator (HRSG) using the exhaust gases of the gas turbine to produce steam driving a steam turbine. Also the combustion of the wood charcoal is carried out in a steam boiler. Combined cycle is theoretically more efficient than the direct combustion of wood in a

conventional power plant with a Rankine cycle. The gas turbine is supplied by Orenda Aerospace (Boucher, 2000).

Material compatibility

As already observed, PO oil is very acid (pH 2.5-3), then storage and handling need to be carried out using acid resistant materials. Since pyrolysis oil degrades when stored at temperatures higher than 50 °C, heat and contact with light and oxygen must be avoided. Because pyrolysis oil diesel is not mixable with fossil diesel, the existing diesel infrastructure cannot be used for gradually introducing this biofuel.

Another problem related to utilisation in stationary energy systems is PO stability; in fact, one key characteristics of PO is its tendency to "age" due to slow polymerisation or condensation type reactions with the polyphenols. This causes an increase in viscosity and this effect is accelerated by higher temperatures, exposure to oxygen and exposure to ultra-violet light. At temperatures above 100 °C the effect results in phase separation.

6.2. Critical aspects of technologies: lessons learnt, R&D and environmental issues

The above mentioned projects identified a series of problems related to PO handling, storage and utilisation, thus underlining that improvement in the utilisation of PO for energy generation is still needed. The main critical factors limiting the utilisation of PO in boilers, diesel engines and gas turbines are PO stability, solid content, acidity, low heating value, high water content and viscosity.

6.2.1. Pyrolysis oil as heating fuel

The utilisation of PO in substitution of HFO, even if less problematic from the technical point of view than substituting LFO, is not likely in a short/medium term period because not economically convenient; therefore, most of the current projects are related to testing the utilisation of PO in small and medium systems for heat production replacing LFO, a rather high cost fuel for the final consumers.

A strong effort in this direction has been made in the Nordic countries, such as Finland and Sweden, where good market opportunities for PO as heating fuel exist. Fortum Oy (former Neste Oy), in collaboration with VTT and local manufacturers, started in 90s a series of projects aimed at demonstrating the utilisation of PO as heating fuel.

The basic idea behind this work was to adapt and modify existing and commercially available technologies, with the goal to minimise the requirements for the upgrading process. Nevertheless, a minimum PO quality is essential to have a good combustion; some PO properties like viscosity and solids content should be reduced through an efficient production process, while other fuel properties like acidity, poor lubricity, ignition temperature can be handled with combustion system modifications (Gust, 1997).

In any case, a good combustion of pyrolysis oil is definitely correlated to fuel stability and reactivity, depending on the type of production process and feedstock, that can cause serious problems in storage, handling and utilisation. From this point of view, a low quality PO can cause problems like phase separation, polymerisation, high temperature coking, coating of the components' surface.

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The technical goal (Gust S., 1997: Combustion of pyrolysis liquids) was the utilisation as wide as possible of commercial components for the heating system, e.g. a conventional pressure atomisation equipment used for traditional LFO. In order to take into account the peculiarities of PO and its different behaviour from conventional LFO, a variety of refractory lined combustion chambers was tested; a preheater was used in order o adjust the fuel temperature at 60-90 °C; a variety of commercial nozzles were tested. Valves, nozzles and pressure regulators were replaced using materials resistant to the aggressive nature of PO; finally the original pump was placed by a progressive cavity pump. The viscosity of the fuel was reduced by adding some alcohol.

A specific tests procedure was implemented:

- warm up of the combustion chamber with mineral oil through nozzle 1;
- preheater to raise PO temperature to 60-90 °C;
- switch on PO in nozzle 2 and switch off nozzle 1;
- adjust air for oxygen level in flue gas to 6-9%;
- on shut down, flushing of alcohol in order to avoid blocking.

The main results of the tests are reported in the table below: both particulate and NOx (NOx due to nitrogen content in PO and particulate from ash and solids in the fuel) emissions are higher than LFO; in any case, it can be concluded that PO can be combusted through a traditional atomisation equipment with a reduction of noxious emissions to acceptable levels, but the quality of the oil is a basic aspect to avoid problems in storage, handling and utilisation.

	medium light	Flash pyrolysis	Wood	heavy fuel oil
	fuel oil	liquid	chips	
Water content wt%	0.02	1825	1520	0.5
Heating value MJ/kg	42.4	1715	1612	41
MJ/l	36.9	2118	86	39.4
Viscosity cSt 30 °C	9	900150		600
50 ℃	4	15020	1	180
80 °C	2	_ 246	[50
Flash point °C	90	60100		80 -
Solids	-	0.7 0.01		<0.05
Ash wt%	<0.010	0.10.01	24	0.03
Sulfur wt%	0.15	0	0	1
Nitrogen wt%	0	0.030.1	0.10.2	0.3
Sauter diameter um	30-40	60-40		50-70
	10 bar,	20 bar,	`	30 bar,
	20 C	85 C		130 C
Typical emissions	-	!		
CO (ppm)	15-30	30-50	500-6000	5-30
NOx (ppm)	80-120	120-150	80-160	200-400
particulates(Bach.)	0.2 - 1	2.5-5	+tars, PAH	1-4
mg/Nm3			<u></u>	50-150
Pour point C	15	-27		0

Table 6.1 – PO properties and emissions [Gust, S., 1997: Combustion of pyrolysis liquids]

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More recently, Fortum and Vapo Oy in Finland (Nieminen J.-P, 2003) tested the utilisation of pyrolysis oil (ForesteraTM) in an existing light fuel boiler. Previous experiences demonstrated that combustion takes advantages from low solids content (micro char, ash, and sand), so it was reduced to less than 0.05 wt%.

The tests have been performed in collaboration with Oilon Oy (the biggest manufacturer of boilers in Finland), which prepared the prototype burner and fuel handling system. More than 8,000 litres of PO have been combusted in this boiler, with more than 1,500 heating cycles. Both the burner and the fuel handling system behaved in a proper way during the heating cycles; the measured emissions were very low, approaching the emissions of conventional LFO.

The main result of these first tests is that the combustion of PO is strongly related to the quality of PO, above all its solids content, and that PO can be combusted in existing LFO boilers with low emissions. In any case, further development is still needed for commercial use

In Sipila *et al.*, 1996, a campaign performed by Neste Oy aimed at investigating PO utilisation in boilers from 200 to 1,500 kW_{th}, where typically LFO is used, is reported. The tests on the 200 kWth boiler were performed by fitting a refractory section to assist PO ignition; the tests were performed on bio-oils from VTT, Union Fenosa and Ensyn, with promising achievements in terms of performance and emission reduction. An interesting table with problems and practical solutions is given below:

Problem	Possible solution
Difficult to ignite	Co-fire with fuel oil, heat up boiler with fuel oil, ignition enhancers
High viscosity	Preheat, add low viscosity component
Low energy content	Use larger storage thanks, refill more often
Poor stability when exposed to air or high temperatures	Avoid exposure to air, rinse out hot nozzles with alcohol, add stabilisers
Low pH, corrosive and poor lubricity	Choose proper materials, stainless steel, plastics and corrosion inhibitors
Higher emissions than LFO	Adjust air/furl ratios; add combustion improvers

Pyrolysis oil applications in boilers (Sipila et al, 1996)

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6.2.1.1 Pyrolysis oil as heating fuel: tests at Oilon Oy

The combustion properties of various pyrolysis oils were studied at Oilon (Lahti, Finland) within a project carried out by VTT together Vapo Oy, Fortum Oil & Gas and Oilon Oy. (Oasmaa *et al.*, 2001); Oilon Oy is the biggest burner manufacturer in Finland.

The combustion tests were carried out employing a cylindrical, water-cooled test furnace of 8 MW nominal capacity; a n umber of changes were made in the furnace to run with PO. The burner was equipped with the dual fuel lance, enabling the utilisation of two different liquid fuels; heavy fuel oil was used as support and start-up fuel. The combustion tests were divided in two main phases:

- 1. testing and optimisation of the combustion conditions with one PO
- 2. combustion tests with typical pyrolysis oils

The POs used for the combustion tests were produced from various hardwoods and softwoods using either bubbling fluidised bed or circulating fluidised beds.

The first phase was realised using PO from hardwood produced through a circulating fluidised bed reactor; the oil was inhomogeneous due to the long storage time outdoors, therefore it was necessary to add methanol (20% vol.) to make it more homogeneous and to reduce the viscosity of PO (from about 200 to 35 cSt @ 50 C°). Several adjustments to the feeding and boiler were tested: a special type of front head was employed inside the boiler in order to prevent heat losses; an extra cylinder inside the furnace allowed a more "dense" flame, higher temperature and hence faster volatilisation; the burner head was changed from a diverging type to converging one, thus allowing a narrower and more intense flame. During this phase, combustion conditions were optimised and basic regulations of the combustion systems were adjusted by burning the test oil. In general the test oils burned relatively well and the emissions were fairly good; no significant problem appeared in the combustion, the flame being usually unbroken and stable.

The combustion tests (phase 2) usually proceeded relatively well; the combustion of the "best" oils have been continued a long time without any change or problem in combustion or fouling; from the tests it is clear that the chemical composition of PO affects significantly the atomisation behaviour of the oil. The main results of the combustion tests can be summarised as follows:

- 1. PO can be burned relatively well in conventional furnaces and boilers; boilers and oil burners may require small modifications or additions;
- 2. support fuel is required at the start of the combustion and preferably in the combustion of low quality PO to maintain good and stable combustion;
- 3. emissions from combustion are in general between those from light fuel oil and the lightest heavy oil, but the particle content is higher. There are no SOx emissions. The NOx emissions level was rather high for the test oil (due to higher water content and the rapid combustion of added ethanol), while particles emissions were small. The behaviour during the combustion tests with typical POs (that is with no addition of methanol) was different: the NOx emissions were lower than that of tests oils, but the particles emissions were clearly higher;

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4. quality specifications for PO are necessary, especially inn terms of content and solids water; viscosity is an important parameter to achieve good atomisation. The PO quality moreover has a strong impact on emissions; e.g. high solids content in PO can cause high particulate emissions;

the pipeline clearly corroded during the tests: acidity of PO (pH 2-3) and the combined effect of acids and high water content when raising the temperature set special requirements for materials. Acid-proof steel, certain special steels, brass and plastics stand well pyrolysis oils.

6.2.2. Diesel engines

The utilisation of pyrolysis oil in diesel engines for power production is far from being used commercially. More problems are encountered in comparison to those reported for heating systems, since the engine sets even more severe requirements for the fuel than boiler applications, as the injection pressure is higher. The critical aspects are mainly three: PO ash content, PO high viscosity and low pH. The most significant activity in this field has been performed by Ormrod Diesels (UK) and Wärtsilä Diesels (Finland), which studied PO injection for diesel engines in long term tests; however, also other research organisations are working with lab and smaller capacity tests devices.

Up to now, performed tests have been relatively short in time, thus further development and long term experience is needed to demonstrate PO utilisation in power engine generators. Most of the performed activities found out that the wear of the injection system is the most critical aspect when PO is used as fuel in diesel engines. The utilisation of materials resistant to the aggressive nature of pyrolysis oil (above all the injection nozzles, but also valves, pumps, etc.) is a mandatory prerequisite to achieve long term and efficient operation conditions of the engine; after, further development is required to reduce the emissions and fuel consumption and to achieve good engine performances.

VTT initiated some experiments on diesel engines in 1993 (Sipila *et al.*, 1996), with a Valmet 64 kW engine equipped with pilot injection. The diesel tests indicated that PO (from Ensyn) was difficult to ignite, so pilot injection is necessary, but once ignited it burns quickly (same conclusions in Leech, 1997).

Wärtsilä Diesels initiated in 1993 an experimentation on V32 line of engines (power output form 1.445 to 6.515 MWel); the fuel versatility of this engine makes it well-suited for alternative fuels, so it was tested with Ensyn PO. Ahnger and Graham (1996) report that single-cylinder tests on V32 engine were successful with respect to efficiency, emissions and the speed of biofuel combustion, as reported also by Gros, 1995 and Jay et al., 1995. Jay et al. reports a thermal efficiency comparable to the reference diesel fuel operation. NOx and CO emissions were lower than normal diesel operation although total HC emissions were slightly higher. Moreover, engine inspection revealed no detrimental damage. The tests pointed out that the engine required pilot fuel for ignition at continuous level of 3-5%, while operating primarily on liquid biofuel; but, once ignited, the biofuel burns very quickly and efficiently. The Wärtsilä tests demonstrated that basically the engine was suitable for operation on PO, but work is needed to achieve a reliable commercial injection system.

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Leech (1997) reports about an experience of Ormrod Diesels (UK) on a dual fuel engine fuelled with pyrolysis oil. A 250 kW_{el} medium speed diesel engine was modified to operate in dual fuel mode: the main fuel (95% by energy) was PO, the pilot fuel diesel oil to provide a source of ignition. Nearly 200 hours of operation were achieved running on one cylinder, much of which by using pure PO untreated and unfiltered, the longest run being nine hours continuous operation at full load. Several changes to the fuel feeding system were made to improve operability and reliability.

The most important issue from this experience is that during all the tests a pilot fuel (5% by energy) was injected into the used cylinder; this proved essential because when, during one test, the pilot fuel was notably reduced, the engine started to run incorrectly, with evidence of un-burnt fuel and a strong increase of the emissions; when the pilot was shut off, the engine seized, thus showing that PO does not ignite at the normal compression temperature of a diesel engine.

In any case, this experience resulted in promising results: a stationary diesel engine can be relatively easily modified to run on 95% PO with no deterioration in output or rating; further work is needed to monitor emissions and performance and to demonstrate long-term run.

Concerning the utilisation of emulsions, an experimental campaign was implemented in Italy, Germany and UK to test the behaviour of PO/diesel oil emulsions combusted in small and medium scale diesel engines in the frame of a EC funded project. The main results of this campaign are as follows (Baglioni, 2001 – Chiaramonti, 2002):

- The emulsion proved to perform well in both small scale engine during the first minutes
 of the tests: then, the engine performances degraded very quickly due to bad injection
 (enlargement of injector holes, damages to the needle, sticking of the needle, deposits).
- A first improvement was obtained by adding a dedicated cooling system to the injector.
 This action was successful in the case of the tests in Italy but similar results were not reported in Germany on different engines.
- The injector degradation as been deeply investigated in Italy and Germany. Tests aimed at identifying the reasons for the injector degradation, both cool and electrically heated tests, were performed. It was concluded that the injectors holes and the injector needle are degraded by a combined corrosive-erosive effect. In fact, the injector material resulted sensitive also to pure PO, even if in longer terms. The use of emulsions, due to a combination of corrosive attack with cavitation/fluid dynamic phenomena that remove the light deposit at low PO content emulsions, increase the velocity of degradation of the injector (hours or even less).
- Similar effects on the injectors were reported in UK on the large engine (250 kW).
- Final tests (25 %wt PO in Diesel emulsion) performed in Germany with stainless steel nozzle showed the solution of the injector problems. The test length was 5 hours continuous operation: then the engine was switched off due to damages to the injector needle, made of standard material (no stainless steel needle).
- The 75 %wt PO in Diesel emulsion caused greater problems, maybe due to the high viscosity of the fluid. It would be possible that the engine needs more significant modification: a deep analysis on engine is recommended for that purpose.

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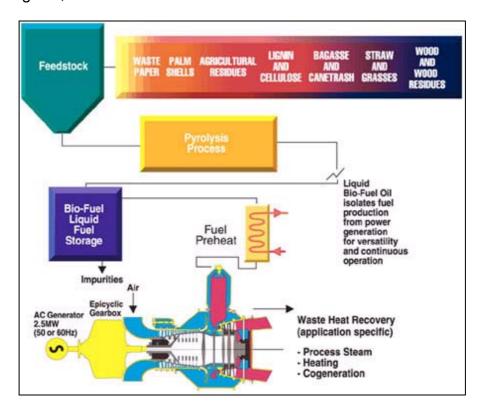
6.2.3. Gas turbines

Most of the activities in this field have been implemented by Orenda, in Canada. Orenda Aerospace Corporation initiated in nineties an extended work on the utilisation of PO for power generation in gas turbines; the promising results encouraged Orenda to schedule in 2003 the execution of long-duration turbine tests with three various pyrolysis liquids from large producers. On this purpose, Orenda set up preliminary specifications, through which they evaluate the suitability of pyrolysis liquid for the gas-turbine.

In the past year, Orenda studied and developed process parameters in the fuel production and implementation of engine and auxiliary system design modifications for the utilisation of PO for gas turbine applications. The main modifications were:

- <u>Fuel Nozzle and Combustion Liner</u>: design modification to accommodate biofuel high viscosity and low heating value
- Hot Section Component Upgrades: development of protective coatings to allow hot section components to survive the aggressive biofuel combustion environment
- <u>Fuel Post-Processing</u>: development of techniques to optimise biofuel for use as a gas turbine fuel
- <u>Fuel System</u>: dual fuel system designed to start on diesel fuel and transition to biofuel: system components and materials optimisation to handle high viscosity fuel; preheating system to improve fuel flow and atomisation characteristics

The biofuel is being developed for application to power the GT2500 2.85 MW industrial package. The following is a schematic diagram of the application process of this fuel to gas turbine engines;



The characteristics of the turbine (<u>www.orenda.com</u>) are:

Compressor

- 9 Axial Flow Stages (Variable Inlet Guide Vanes) plus one Centrifugal Stage
- Compression Ratio 12:1

Combustor

- Two Tubular Radial Flame Tubes (each with an Igniter)
- Natural Gas or Distillate Fuel

Turbine

Three Axial Stages

Rotor

- Speed: 14,000 RPM
- Tilt Pad Thrust & Journal Bearings at the front and Radial Roller Bearing at the rear
- Integral Epicyclic Speed Reduction Gearbox

Data at rated power and ISO 2314 conditions

- Mass Flow 15 kg/s (33 lbs/sec)
- Exhaust Temperature 435 °C (815 °F)
- Output Power: 2.85 MW at Shaft Flange
- Efficiency: 28.5%

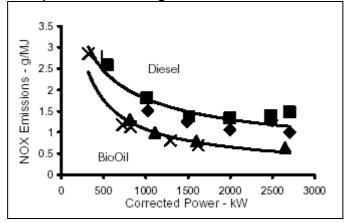


The GT2000 gas turbine

In "Fast Pyrolysis Of Biomass For Green Power Generation" (Thamburaj, 2002) it is reported about the experience made by Orenda in this field: briefly, over 13,000 litres have already been combusted by Orenda in gas turbine engine tests and another 8,000 litres in rig testing. These activities pointed out the suitability of PO being utilised for gas turbine applications. This work was important because it made possible the identification of the necessary development required for achieving commercial operation with the majority of turbo machines already used with of heavy fuels.

These tests not only revealed the feasibility of operation but also demonstrated that similar performance could be achieved for PO and diesel. Although CO and particulate emissions were higher than diesel, testing revealed that NOx emissions were about half that from diesel fuel and the SO_2 emissions levels were almost undetectable by the instrumentation.

The author report that the considered turbine offers significant technical advantages in comparison to other engines. Unlike aero-derivative engines, it has been designed as an industrial engine with durability being one of the main design criteria (and not weight). Moreover, "in addition to the ruggedness, the distinct "silo" type combustion system allows for easy access and modifications to the entire combustion system, which is one of the critical systems for the adaptation of the engine to PO".



Pyrolysis Oil NOx Emission Reduction

In addition to engine design, further important modifications are necessary to compensate PO properties: in fact, PO has an energy density about half of diesel fuel. Therefore, to meet the same energy input requirement, the flow rate must be approx. double. This requires design changes to the fuel system to be able to control higher flow rates and also modify the fuel nozzle to accommodate this larger flow. This lower energy density also can affect combustion since physically there must be twice as much fuel in the combustion chamber as with diesel. This, however, is another advantage of using an industrial engine. since industrial gas turbines combustion chambers are designed with a significantly longer residence time (and therefore a larger volume) for a given power output. Moreover, higher fuel viscosity reduces the efficiency of atomisation which is a critical aspect to complete combustion. Large droplets require long residence time to burn. Proper atomisation is addressed in three ways. Firstly, the fuel system is designed to deliver a high-pressure flow since atomisation is improved with larger pressure drops across the fuel nozzle. Secondly, the fuel is pre-heated to reduce the viscosity to acceptable levels. Thirdly and most important, the fuel nozzle has been redesigned to improve spray characteristics. These design improvements are important for complete combustion and effectively reducing CO emissions. Due to its relatively low pH, material selection is also critical for all components interested by PO: some standard fuel system materials cannot be used; typically, 300 series stainless steels are acceptable materials as well as high-density polyethylene (HDPE) or fluorinated HDPE for polymers. Although looked at as a contaminant for diesel fuel, the water content in PO has some advantages. Firstly, it is helpful in reducing the viscosity, since it is a relatively low viscosity fluid. It is also a factor lowering thermal NOx emissions. The solids content is a combination of ash and char fines which have carried-over to the liquid part of the PO. The effect of these solids is to cause sticking of close tolerance surfaces and secondly, they can result in particulate emissions because of the long residence time required to fully combust. It is important that the solids level in the PO is controlled to be less than 0.1 wt%. The ash content in the fuel represents the material that cannot be combusted. Depending on the elements in the ash, it can result as a deposit on the hot gas path components that will reduce the turbine efficiency. This operational problem is well known when using low grade fuel oils, which also have a high ash content. The solution is a turbine wash system. This typically consists of two separate systems in which an abrasive medium is injected during operation to physically 'scrub' off the deposits. This allows turbine cleaning without any downtime. The second system is an offline process which injects a cleaning fluid and allows a soak period to loosen the deposits which are then removed when the engine is started.

The alkali elements present in the ash can result in hot corrosion of the hot gas path components with sodium and potassium being the most critical elements in PO. These elements form low melting temperature compounds, which, as a liquid, will stick to the hot gas path components and then react and corrode the component. This effect can be mitigated through the use of fuel additives. As with the turbine wash systems, this technology was developed for the use of heavy fuel oils in gas turbines and has been in use for decades. The concept is to inject specific elements, which preferentially react with the alkali metals such that they do not liquefy. This reduces the tendency to stick to a surface and also reduces or completely eliminates its rate of attack. In combination with the additives, hot section coatings are being developed specifically for the type of attack that may be associated with PO. Due to the poor ignition characteristics of PO, one other key design issue is the development of a PO specific ignition system or process. To overcome this, the OGT2500 system starts on diesel fuel flowing through the primary channel in the fuel nozzle. Following a warm-up period, PO is fed into the secondary channel at an increasing rate while the diesel fuel flow is reduced until 100% PO flow is achieved. Polymerisation is another key issue with PO. This is the growing of molecular chains, which can result in an increase in fuel viscosity. This process is highly dependent on time and temperature. For example, the equivalent change in properties can be achieved in 6 months at room temperature, compared to eight hours at 90 °C. Therefore, as part of the fuel and combustion system design, maximum temperatures and fuel recirculating are carefully controlled to ensure polymerization is maintained at a rate without consequences for engine operation.

Research work and an extended test campaign demonstrated both the feasibility and the significant benefits in utilising PO in a gas turbine. Tests programme are on going to achieve performance and durability levels required for commercial operation. This means achieving high efficiencies, maintaining high availability, typical time between overhauls and capital cost comparable with current gas turbine power generating packages. Key to this work is the use of a variety of POs to ensure turbine suitability for a range of fuel characteristics as wide as possible. This will maximise the applicability of the PO gas turbine system to a variety of bioenergy applications. Technically, this work is proceeding accordingly to two distinct routes:

 <u>Performance</u>: Optimisation of the combustion system; determination of the improved engine and emission characteristics; development and test a turbine wash system based on current systems; <u>Durability</u>: Design and test fuel system equipment and components for long term operation with PO; development of hot section coatings specific to the PO combustion environment; development of a fuel treatment system to upgrade fuel quality through filtering, additives injection and alkali removal.

6.2.4. Conclusions

All the experiences here reported pointed out some common problems related to the utilisation of PO in diesel engines, gas turbines or heating systems. These problems are all related to specific characteristic properties of PO: some of them can be addressed by means of proper modifications of the technology, other need a further improvement at the biofuel production stage (for instance the stability of the fuel).

When replacing fossil fuels with PO, **solids content** must be low, since solids can cause blocking in the nozzles and increase in the emissions of particulate matter. Especially in the case of the substitution of LFO, more efforts should be done in order to have pyrolysis oils with a very low content of solid matter. Another drawback is the **low pH** (typically 2.6-3). This can cause erosion, and combined with solids, also erosion; the solution to this problem is the adoption or appropriate materials and, in parallel, the production of liquids with a higher pH, thus facilitating the utilisation of PO both for power and heat production. The last problem to be addressed is the **high viscosity** (related also to water content) of pyrolysis oils; this aspect require the utilisation of appropriate devices for PO pumping and make difficult the atomisation of the fuel in the injections system, thus contributing to a low efficiency combustion, decrease of performance and increase of the emissions. Upgrading of PO in this sense is still an important issue.

Heating systems. Due to the high costs of LFO, the utilisation of PO as heating fuel in small and medium boilers seems a economically viable solution; the replacement of HFO, even if simpler from a technical point of view, is hampered by the very low costs of this fuel. The accomplished experiences pointed out that an auxiliary dual fuel system should be used, due to the high water content and ignition temperature. The main problems encountered are related to the atomisation system, namely blocking of the nozzles and formation of deposits in the burner. The realised experienced showed that the solution could be the adoption of a burner equipped with fuel pre-heater and dual nozzle burner; in this way most of the problems can be overcome, with the condition the nozzles, valves and pressure regulators are made of acid resistant materials and viscosity is reduced to 10-15 cSt at the atomisation temperature. A major issue is in any case to use good quality pyrolysis oil.

Tests in **Diesel engines** performed by Wärtsilä Diesels and Ormord Diesels demonstrated that PO was difficult to ignite, so pilot injection is necessary, but once ignited it burns very quickly. Up to now, performed tests have been relatively short, thus further development and long term experience is needed to demonstrate PO utilisation in diesel engines and to achieve a reliable commercial injection system. Most of the performed activities found out that the wear of the injection system is the most critical aspect when PO is used as fuel in diesel engines. The utilisation of materials resistant to the aggressive nature of pyrolysis oil is necessary to have long term and efficient operation conditions of the engine; after, further development is required to reduce the emissions and the fuel consumptions and to have a good engine performance.

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Concerning PO applications for **gas turbines**, research work and an extended test campaign performed mainly in Canada by Orenda demonstrated both the technical feasibility and significant benefits in utilising PO for the operation of a gas turbine. Tests programme are on going to achieve performance and durability levels required for commercial operation.

Concerning the environmental issues, being pyrolysis oil utilisation in a less advanced stage, compared to other biofuels, the discussion on environmental issues is more difficult, due to the lack of long-term tests and of sufficient measures. This issue is for sure one of the aspects related to PO utilisation still requiring more research work.

6.3. Economics and market perspectives

The large scale utilisation of PO for heat and electricity generation is strongly linked to the present situation of the market of conventional fossil fuels. As already observed, the utilisation of PO in small scale heating systems could be an interesting option also from an economic point of view, given the rather high costs of light fuel oil (often due to high taxation). So, in case proper tax exemption measures in favour of PO are taken, PO itself can be considered competitive for this kind of applications. However, economic changes in local conditions can actually prevent the commercial utilisation of these products.

An example of this situation is given by the recent announcement from Fortum and Vapo (Finland), concerning the conclusion – with good results - of the field tests with ForesteraTM biofuel but also the postponing of the commercialisation (ref. 41, www.fortum.com)

In fact, "the ForesteraTM field tests were successful and the fuel quality was improved. The emissions were reduced to those of an oil boiler in good conditions. However, economic changes in the Swedish fuel market are presently preventing the commercial launch of the product. These are an increase in price of wood waste due to strong, local demand and changes in fuel taxation in Sweden, which will take place at the beginning of next year". The conclusion is that, in order to commercialise the ForesteraTM biofuel, external economic conditions should come back to more favourable levels.

Concerning the production costs of PO, it is difficult to provide precise values, given the relatively early stage of the production technology; from different sources, a range between 5 and 15 Euro/GJ can be estimated, depending on the size of the pyrolysis plant and the feedstock cost (lower values are related to large capacity plants and assume improvements from learning effect and economy of scale).

Finally, the market applications: while Bridgwater (Bridgwater, 2002) reports that fast pyrolysis coupled to diesel engine system has great potential to generate electricity at a profit in the long term, with lower cost than any other biomass to electricity system at small scale, other sources (Nieminen, 2003 & COMBIO, 2003) report that the utilisation of PO in substitution of LFO in small scale heating system is potentially the most promising market, at least in an initial stage.

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7. Vegetable oil

Vegetable oils are derived from oil crops like rapeseed, sunflower, soybean and palm. They are extracted from oil seeds mechanically and/or by means of solvents. High viscosity, poor thermal and hydrolitic stability, low cetane number are typical properties of vegetable oils like, which make difficult their utilisation in energy conversion systems; then, for the utilisation of plant oils in non-modified diesel engines, it is necessary to "upgrade" the oil so that its characteristics meet the requirements of available diesel engines: this can be achieved through the esterification process, in which molecular structure of the vegetable oil (triglycerides) is converted into methyl esters that are similar in size to diesel oil components. The obtained product is called Biodiesel, more suitable to be used in non modified diesel engines or heating systems.

However, in comparison to biodiesel, vegetable oils offer advantages in terms of lower production costs and better energy balance (i.e. lower energy needs for fuel production); for this reason, examples exist of utilisation of non-esterified vegetable oil in diesel engines, gas turbines or heating systems. On the other side, the utilisation of vegetable oil in the automotive sector is not considered as a realistic option, due to technical (need for modified engines) and commercial issues (fuel distribution system). Nevertheless, some engine developers (for instance Elsbett) offer special engines running on vegetable oil that can be used in conventional vehicles.

In Europe, on the other hand, the utilisation of vegetable oils (and the corresponding blends) for stationary applications (production of electricity and/or heat) seems a feasible option, from both the technical and the economical point of view.

Fuel properties

In the following, the main properties of vegetable oils (raw materials rape, sunflower and palm fruits) are given; as shown in the table, some properties, such as viscosity @ 20 °C can considerably vary depending on the specific oil crop.

Fuel property	Unit	Rape seed oil	Sunflower oil	Palm oil	Diesel oil n. 2
Density @ 15°C	kg/dm ³	0.92	0.92	0.91	0.84
Kinematic viscosity @ 20°C	cStoke	77.8	65.8	88.8	4-5
Lower heating value	MJ/kg	37.3	37.0	36.5	42.7
Lower heating value	MJ/litre	34.3	34.1	33.2	35.7
Stoichiometric air/fuel ratio	kg _{air} /kg _{fuel}				14.5
Flash point	°C			> 344	77
Cetane number		44-51	33	42	> 45
Conradson Carbon residue	% wt	0.25	0.42		0.15
Sulphur content	% wt	0.0001	0.01		0.29
Oxygen content	% wt				0-0.6

Table 7.1 – Fuel properties vegetable oil and comparison with diesel oil

Vegetable oils may be used as fuels in two different ways:

- by adapting the energy system (using natural vegetable oil just as it is or in blends)
- by adapting the fuel (transesterification into vegetable oil methyl ester, i.e. biodiesel); this issue will be discussed in next chapter.

The properties of vegetable oils differ considerably from those of standardised diesel fuel, especially viscosity, flash point, combustion characteristics etc. The combustion of vegetable oils results in deposits which makes difficult the utilisation in conventional diesel engines, above all in direct injection engines; only special types of engines for automotive purposes are currently used with vegetable oils as fuel. Also, during wintertime vegetable oil engines can only be used to a limited extent. For these reasons, the utilisation of vegetable oils as automotive fuel is currently limited to a niche and small market.

Nevertheless, vegetable oils could be used in thermal and power plants for heat and electricity production (this could be a strategic aspect in the developing countries, where the development of the bioenergy chain offers several socio-economic benefits). it should be highlighted that for these applications the most important barriers are non technical, but mainly related to the market and production costs.

7.1. Energy conversion technologies for stationary systems

7.1.1. Diesel engines

The use of vegetable oils in internal combustion engines is not new; Rudolph Diesel himself already in 1912 wrote about the role that vegetable oils could have in replacing fossil fuels; moreover, during an exhibition in Paris in early 1900, he fuelled one of his engines with peanut oil. In the last years, several experiences aimed at testing the utilisation of vegetable oils in DI and IDI diesel engines, both for energy production and automotive purposes.

Several sources report that vegetable oils cannot fuel DI diesel engines, because engine coking occur after some hours of operation (this happens after a longer period even if vegetable oil is blended with diesel oil); on the other hand, the utilisation in modified diesel engines with indirect injection, in form of semi refined vegetable oil or blended with diesel oil seems possible, as well as in special plant oil engines.

Several researchers remarked the fact that 100% vegetable oils cannot be used safely in a DI diesel engines for a long period; for instance in Bandel *et al.*, 1994, is reported that "vegetable oils without further processing cannot be used at all as fuel in DI diesel engines and only with difficulty in the pre-chamber engines, since their use in the engine always lead to problems, particularly carbon deposits".

Other than high fuel viscosity, problems related to vegetable oils in diesel engines are the poor thermal and hydrolytic stability and, in some cases, the low cetane number, resulting in worse combustion characteristics and less favourable ignition qualities (Van Thuijl *et al.*, 2003).

Various experiences on vegetable oils are reported in literature, such as the swirl chamber Elsbett engine: this engine is able to run directly with vegetable oils, on the basis of the principle of the "duothermic combustion system", with a special combustion chamber that works with the principle of turbulence.

The ELSBETT duothermic combustion system is based on the principle that the air circulates inside the combustion chamber and arranges itself into different layers according to differences in heat and density, thus forming a central hot air combustion area and an external surrounding layer of cooler excess air. The combustion chamber must be spherical and located in the piston itself. The shape and size of the inlet ducts are such that the inlet air moves in a circular motion. The fuel is injected tangentially and directed towards the inside of the combustion area, thus causing it to blend perfectly with the air. It does not reach the wall of the combustion chamber and, therefore, the formation of unwanted deposits is avoided. The external layer of cooler, excess air acts as a thermal and acoustic insulator and prevents the fuel from making contact with the chamber walls. The reduced size of the surface of the combustion chamber wall minimises heat flow and the loss of energy (www.elsbett.com).

"Deutz" also developed an IDI engine allowing the utilisation of purified vegetable oils; its consumption is approx. 6% higher than other diesel engines, but it is has proved to be a robust a reliable engine. Other sources report that the fuel consumption of IDI engines with swirl chamber is 10-20% higher than convention diesel oil used in DI engines (EC DG XII, 1994).

The most critical parameter of vegetable oil in diesel engines is probably the high viscosity: vegetable oils are generally ten times more viscous than conventional diesel oil or derived methyl ester, thus causing, in standard diesel engines, problems in the injection system and in combustion chamber impeding the engine running in short or long term use (EC DG XII, 1994).

When using pure plant oils in DI diesel engines, coke deposits at the injector and in the combustion chamber walls, as well as in components like pistons, valves, etc. occur. These problems of build-up of deposits are due mainly to the high fuel viscosity and carbon residue of vegetable oils. Higher viscosity, in fact, means, that the fuel flow and the spray pattern from conventional injector nozzles are significantly altered with respect to standard behaviour, thus greatly affecting the whole combustion process. The deposits at the injector holes can partially block the injection itself; moreover, a reduction of the fuel flow in the injection duct can take place, thus reducing nozzle cooling and lubrication. These facts eventually lead to engine power and efficiency reduction, increase of pollutant emissions as smoke and misfiring in multi-cylinders engines; moreover, further problems can occur in the cylinders, leading to piston ring stickiness and worse lubrication, and finally to engine breakdown.

7.1.2. Boilers

The utilisation of vegetable oil as fuel for heating systems (either for industrial or civil applications) is rather promising for the following main reasons:

 depending on the country, the costs of the conventional heating fuels can be rather high for customers (especially for small and medium users), thus creating more market opportunities for biofuels;

- in some cases when used for heating purposes, vegetable oils do not need complex or costly upgrading process, thus allowing lower costs in comparison to other applications;
- the modification of burners and the related maintenance needs are less demanding than in case of power generation systems, like engines and gas turbines, thus making easier the utilisation of vegetable oil as heating fuel.

Tests were performed on a small scale boiler with rapeseed oil, as reported by Marquez and Riva (Marquez et al., 1998). This work demonstrated that is relatively easy to burn vegetable oil in medium scale industrial boilers, while the utilisation in small scale domestic appliances presented various problems.

Some boilers manufacturers commercialise burners that can be fuelled with vegetable oil: MAN Brennerbau (Germany) sell 15-60 kW burners (Marquez et al., 1998) designed for rapeseed oil, in the form of mixtures with conventional fuel, vegetable oil being 40%. Dunphy Burners in UK (www.dunphy.co.uk), produce special burners that can burn also vegetable oil.

7.1.3. CHP units and Gas turbines

Large stationary conventional engines are suitable to run on low grade fuel oils, including thick crude oil. Fuel heating and filtration are utilised, while the used injectors are designed to spray these thick oils efficiently. The slow speed and size of these engines gives more time for a complete combustion of the fuel. A diesel engine equipped to burn such fuels can burn also vegetable oils; but, the very low costs of low grades fuel oils, limit the utilisation of vegetable oils in large scale applications; nevertheless, the utilisation of vegetable oil in small scale CHP units can be considered an application close to market penetration; there are many examples, above all in Germany and Austria, of CHP plants fuelled by vegetable oil operated with no major problems; in addition, most of the manufactures come from Germany and Austria.

In Austria for instance, (Rathbauer, 2002) in February 2002 a total of 18 CHP plants were operated with vegetable oil and 13 systems to be operated with plant oil were being built. The plants are made by Austrian and German manufacturers, the output ranging between 4 and 80 kWel. It is also reported that, due to market and economic conditions (favourable feed-in tariff, low rapeseed oil price) the demand for such plants is rising.

A research work (Thuneke *et al.*, 2003), supported by the Bavarian State Office for Environmental protection, was aimed at assessing general feasibility, emissions an long term behaviour of a 8 kW_{el} CHP unit fuelled with rape seed oil. During the investigation period of almost two years, exhaust gas emissions, fuel consumption, exhaust gas pressure and temperature, were recorded.

Marquez and Riva report about an experience (Marquez et al., 1998) aimed at assessing the technical feasibility of the utilisation of vegetable oil in gas turbines:; the main achievement of this experience is that, in general, purified vegetable oils are suitable to be used with no particular operational problems in gas turbines, and without particular modifications to the energy systems and its operation and maintenance procedure. The main problems are actually are market penetration and warranty issues (Riva G., 2003).

7.2. Critical aspects of technologies: lessons learnt, R&D and environmental issues

7.2.1. Diesel engines

There are many variations on diesel engine design. Some engines are more suited to vegetable oil fuel use; in http://vegburner.co.uk an overview on the utilisation of vegetable oils in diesel engines is reported; in the following the most interesting results are given:

Direct Injection (DI)

When using fuel oil with viscosity greater than that for which the engine was designed, the injector is not able produce a suitable fine spray and the fuel oil will not burn efficiently leaving carbon/oil deposits. For this reason great care has to be taken to make sure that only sufficiently heated oil is burnt in this type of engine. Hemmerlein et al. tested three unmodified DI engines with rapeseed oil, one 2.6 litre air cooled and two larger engines, 6.6 litre and 12 litre, turbo charged and intercooled with liquid cooling. All three engines failed durability tests due to problems caused by carbon build up. Karaosmanoglu et al. tested a one litre single cylinder DI engine running sunflower oil. The engine successfully completed long term engine testing when started and shut down for 5 minutes with diesel fuel. The engine was run at a constant low speed under partial load.

Indirect Injection (IDI)

The fuel is injected and atomised in a separate combustion chamber when it enters the cylinder where combustion is completed. The atomisation processes in IDI units make them less prone to problems from using thicker fuel oil. Hemmerlin et al. tested three unmodified IDI engines running on rapeseed oil. A small 1.6 litre swirl chamber engine failed durability testing due to carbon build up within the engine. Two larger IDI engines, a 6.2 litre prechamber engine and a 5.7 litre swirl chamber engine completed the durability testing. Fuls et al. found that an unmodified IDI engine in a tractor successfully completed extended service tests using sunflower oil as a fuel. Togashi et al. found that a small Yanmar IDI engine could be reliably operated on refined or de-acified rapeseed oil. Mercedes prechamber engines have been operated on refined, food grade rape oil for extended periods without problems.

Injector Pump

Most injector pumps have a transfer pump to feed the fuel into the injector pump from the fuel tank, others are supplied by a separate lift pump, many have both. There are two basic designs of injector pump:

In-Line Pump - An in-line pump has a small plunger to supply fuel to each cylinder of the engine. This plunger pushes the fuel oil up the high pressure fuel lines to the injector. These pumps have proved to be very reliable when fuelled with vegetable oil. For instance Mercedes IDI engines with in-line pumps have been run on vegetable oil for extended periods without conversion.

Rotary Pumps - These pumps use a single pumping mechanism which pumps through a rotating valve into all cylinders. They look similar to a petrol engines distributor. On a four cylinder engine the pump mechanism is working four times as hard as it is in-line equivalents. Due to the high stress, these pumps should be run only with fuels having similar viscosity to diesel fuel in order to maintain operational life.

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Injector pumps can be modified to allow them to function more reliably with vegetable oil. Injectors with a pre injection have been found to be superior when fuelled with vegetable oil as the bulk of fuel is injected into a burning fuel/air mixture, providing superior combustion (extracted from http://vegburner.co.uk).

Bouché (Bouché *et al.*, 1998) report that engines compatible with vegetable oils are either IDI engines, which have the disadvantage of higher fuel consumption compared to DI engines, and specially designed DI multi fuel engines. A special engine designed by the German company "AMS Antriebs- und Maschinentechnik Schönebeck GmbH", operated reliably during a 600 h durability run with neat rapeseed oil, with less exhaust gas emissions compared to diesel fuel operation of the engine. This reflects the importance of the optimisation of a CI engine to the different fuel characteristics of vegetable oils.

De Almeida (de Almeida *et al.*, 2002) analysed the use of pure palm in stationary diesel engines for energy supply; in the installation of the engine, the following issues should be taken into account:

- 1. Vegetable oils present higher values of viscosity than diesel oil at the same temperature with consequent poor atomisation in the injections.
- 2. It is necessary to use lubricant oil with higher detergency due to the alteration of its required physical specifications and contamination after about 100 hours of engine operation.
- 3. Vegetable oils present lower heating value
- 4. The filtering (3 mm mash) of the oil is necessary.
- 5. Injectors should be cleaned and tested after 150 h of operation.
- 6. The constituents of the palm oil react with copper piping existing in the engines when their temperature is above 50 °C.
- 7. Diesel should be used to start and warm up the engine.

Experiment and tests were conducted on a naturally aspirated MWM 229 direct injection four-stroke 70 kW diesel generator; a naturally aspirated engine is more sensitive to fuel quality due to the longer ignition delays and lower performance of the injection equipment typical of this engine design, but it represents a large population of engines used for electric generation in the Amazon Region, for this reason it was selected.

The high viscosity value presented by palm oil and its characteristics to react with certain metals are considered in order to specify the fuel system. The fuel system was designed based on two different tanks: a conventional tank for the diesel oil (used for switching on and off the engine) and a stainless steel palm oil tank. The same material is used for the piping connecting the tank to the engine. The engine was started with diesel oil until it warmed up. Then the fuel was switched to pure palm oil. After running with palm oil, the fuel was always switched back to diesel and the engine was run until all the palm oil had been purged from the fuel line, injection pump and injector in order to prevent deposits in the combustion chamber due to the temperature decrease. Because of its higher viscosity, palm oil was heated before the fuel pump and before the injectors to promote smooth flow and to avoid fuel filter clogging. During the first 50 hours of diesel-generator test, the palm oil admission temperature was 50 °C. At this temperature, some deposits in the combustion chamber and injector cooking were observed. In order to avoid deposit formation due to incomplete combustion, the palm oil admission temperature was increased to 100 °C until the end of the test. At this temperature, the oil presented better

combustion and less deposits in the following 300 hours of engine test. Two filters were installed: one at the exit of the tank and the other one at the fuel pump. These filters had to be changed every 100 hours of operation, because they were clogged.

The following pictures describes graphically the results of the experimental tests: exhaust gas temperature versus operation hours and load, specific fuel consumption:

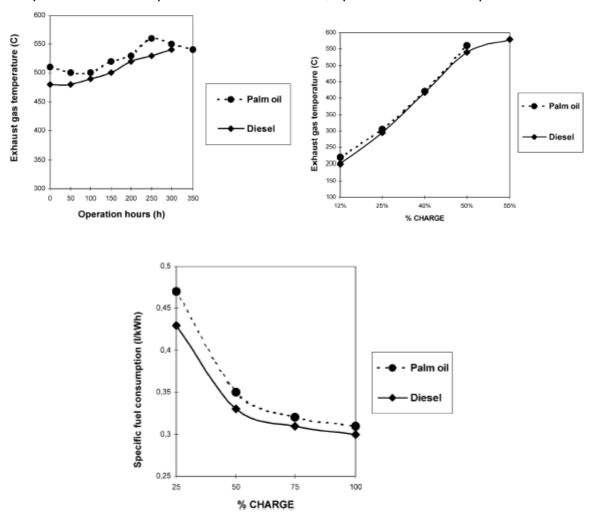


Fig. 7.1 - Performance of a DI diesel generator running on vegetable oil (de Almeida, 2002)

Specific fuel consumption of palm oil is slightly higher than diesel (almost 10% higher at low loads). The lower mass based heating values of vegetable oils required larger mass fuel flows to maintain constant energy input to the engine. Also at given injection pump settings, higher densities of vegetable oils caused mass fuel flow to increase.

Exhaust gas emissions after 350 hours of operation with palm oil and diesel oil were analysed (see following pictures). The lower CO emissions were obtained with diesel. The maximum increase of CO emissions reaches 100% related to diesel fuel (75% of charge). Due to the high viscosity, the air–fuel mixing process is affected by the difficulty in atomisation of the palm oil. The resulting locally fuel rich mixtures cause more CO to be produced during the combustion, due to the lack of oxygen. The emissions of CO increase with the increase of load. The higher the load, the richer fuel mixture is burned, and thus, more carbon monoxide is produced.

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Carbon monoxide and unburned hydrocarbon emissions are products of incomplete combustion. The lower cetane number of palm oil results in lower tendency to form ignitable mixture, and thus, higher CO and HC. The most significant factor that causes NOx formation is high combustion temperatures. The NOx emissions increase with the increase of charge, due to the increase of combustion temperatures. The NOx emissions are lower with engine operation with palm oil. Other researchers also observed a decrease in NOx emissions when operating with pure vegetable oil.

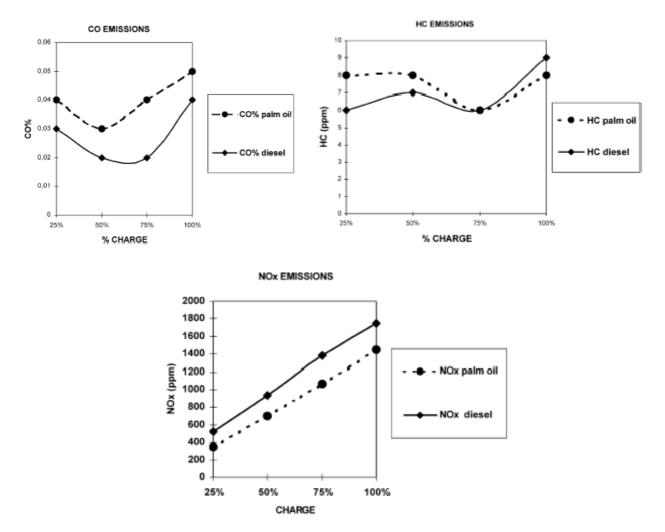


Fig. 7.2 - Emissions of a DI diesel generator running on vegetable oil (de Almeida, 2002)

The work proved that a diesel-generator set can be adapted to run with palm oil. Increasing the palm oil temperature the performance of the diesel generator increases. The deposits on the cylinder head presented high levels when the engine operated with palm oil heated at 50 °C and acceptable levels when heated at 100 °C (almost similar to the operation with diesel oil).

However, other engine modifications are required to improve lubricating oil degradation, performance, emissions and reach a more efficient combustion. On the technical side, the work pointed out the following recommendations:

increase fuel injection pressure;

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- install a turbo-charger in diesel engine in order to increase the temperature and pressure inside the cylinders;
- use special lubricants with convenient additives;
- adapt the injections system to the particular use.

7.2.2. Boilers

In a research work performed in Spain (San José Alonso *et al.*, 2002), the utilisation of sunflower vegetable oil blended with diesel oil for heating purposes is assessed; the trials have been performed by using a commercial diesel burner and a cast-iron boiler with a nominal capacity of 23,000 kcal/h. The tests have been performed on different fuels, using sunflower oil achieved by means of mechanical "expellers"; in general, these oils contain a significant amount of impurities, consequently post-treatment, e.g. filtering and purification, is necessary. The high viscosity of the oil makes difficult the utilisation in pure form in heating systems; one possible way to use vegetable oil in conventional boilers, avoiding expensive processes like esterification, is its utilisation in mixtures with traditional diesel oils. The reported activity then focuses on the combustion of mixtures sunflower oil/diesel oil in different percentages by volume: 10% (10 is the percentage of refined vegetable oil in diesel oil), 20%, 30% and 40%; the main results of this work were:

- the tested energy system does not require major changes to obtain an adequate combustion; it is only necessary to regulate the pressure and air-flow using a conventional diesel burner;
- the equipment can work without interruption using mixtures with different concentration;
- the measurements resulted, in comparison to pure diesel oil, in a notable reduction of CO emissions, corresponding to the vegetable oil content, and in a small increase of the NOx emissions.

A research promoted by the Home-grown Cereals Authority in United Kingdom (Marquez I. Riva G., 1998), aimed at assessing the technical viability of the utilisation of raw rapeseed oil in industrial and civil boilers. Concerning the utilisation in industrial boilers, a Nu-Way burner (capacity ranging between 147 and 542 kW) mounted on a cylindrical water cooled combustion chamber, diameter 0.5 metres and length 4 metres, was tested running on rapeseed oil. The campaign found out the following main results:

- in order to achieve a good combustion, the geometry of the atomisation nozzles should be slightly different with respect to traditional fossil fuel (angle of 45° instead of 60°);
- the optimal fuel preheating temperature should be around 65 °C, with a atomisation pressure of 2.2 MPa;
- once the nominal conditions are reached, the combustion occurs without problems, similar to the combustion of diesel oil;
- the gas exhaust emission level are very promising; besides the ordinary reduction of carbon dioxide and sulphur oxides emissions, the smoke index is usually very low, CO and also NO_x emissions are notably lower than the emissions related to traditional diesel oil as fuel.
- when on-off cycles are performed (10 minutes on, 5 minutes off), carbon deposits derived from the vegetable oil take place in the combustion chamber; this is due to the delay of development of the flame with respect of fuel atomisation, accordingly to the high flashpoint value (around 320 °C). Such an inconvenience can be solved by using

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50/50 rapeseed oil/diesel oil mixtures or by using traditional diesel oil for the first second of operation, adopting specific dual fuel systems. Another solution could be the utilisation of vegetable oils in applications where the temperature of the walls of the combustion chamber is over 100-150 °C (for instance steam production).

Unfortunately, the campaign in UK did not give so that satisfactory results concerning the utilisation of rapeseed oil as fuel in commercial burners for domestic applications (capacity 60 kW): a good ignition of the fuel is not possible, even if mixtures between rapeseed oil and diesel oil are adopted; good results have been instead achieved by using as fuel mixtures between vegetable oil and kerosene.

7.2.3. CHP units and Gas turbines

Thuneke (Thuneke *et al.*, 2001), in "Operational Safety of CHP-Units fuelled with Vegetable Oil" report about CHP-units fuelled with vegetable oils: three CHP-units fuelled with rape seed oil were examined in practice. There were specific weak points typical of vegetable oil, which especially affect the fuel feeding and injection systems. By using a certain quality vegetable oil and considering its specific requirements on the facility components, characteristic operational failures of these CHP-units can largely be avoided.

A subsequent research work (Thuneke *et al.*, 2003), was performed in order to assess general feasibility, emissions an long term behaviour of a 8 kW_{el} CHP unit fuelled with rape seed oil. In particular, the main objective was the analysis of the soot and ash emissions of a CHP unit fired by rapeseed oil, provided with a special particulate filter system, given that on this issue little work has previously done. issue During the investigation period of almost two years, exhaust gas emissions, fuel consumption, exhaust gas pressure and temperature, were recorded, with promising and interesting results concerning the utilisation of vegetable oils in small scale CHP units.

In any case, currently there are several manufactures, above all in Austria and Germany offering CHP units that can burn vegetable oils; for instance Senertec in Germany, Zordan S.r.l. in italy (CHP based on diesel engines, from 2.2 kVA to 1,400 kVA, driven by vegetable oil such as rape seeds, soybean, sunflower seeds).

As an example, the Bavarian village of Greussenheim decided for instance to use vegetable oils for its energy consumption; since 1997, in place of individual oil-fired boilers, a district heating plant is used to serve about 30 homes in a newly developed part of Greussenheim with both heat and power from plant oil. The system is based on an adapted diesel engine, which runs on cold-pressed rapeseed oil. The heat accounts for 55%, and power for 35%, of the available energy, for a total efficiency up to 90%. Moreover, it should be noticed that the fuel used in the plant is grown in the fields surrounding Greussenheim: with 7,000 hours of operation per year, the CHP unit requires some 90,000 litres of oil, thus meaning approx. 85 hectares of rapeseed cultivation each year. The harvested rapeseed is cold-pressed in the oilseed mill and the oil can be used without further processing. The oil is non-toxic, sulphur-free, and easy both to store and transport as its flashpoint is over 200 °C. Should any accidental spillages or leakages occur, the oil biodegrades quickly without any damage to the groundwater. Moreover, any by-products, such as straw and residues, can return easily to the natural cycle. Other benefits of using fuel produced so locally are that only local transport is needed

(minimizing emissions from that source), and that the money allocated on fuel remains within the community, providing local farmers with new and secure sources of income.

As far as regards gas turbines, an interesting experience is reported by Marquez I. and Riva G., aimed at assessing technical, environmental and economic perspectives of utilisation of vegetable oils on medium scale gas turbines. In fact, since vegetable oil, among the other biofuels, seems not suitable for automotive purposes (like BCO), could be a technically feasible option for the production of electricity and/or heat.

Concerning the technological side of the project, the goal was the assessment of the feasibility of utilisation of raw vegetable oil in gas turbines; on this purpose, in collaboration with ENEL, a comparative analysis of the properties of vegetable oil and the traditional fossil fuels used in gas turbines was performed (see next table). The main issues from this analysis are the following:

- density of vegetable oil (rapeseed) is higher of 5-15%;
- viscosity of vegetable oil is greatly higher;
- flash point of rapeseed oil is considerably higher;
- nitrogen content is higher in vegetable oil;
- sulphur content is very low in vegetable oils;
- metals content considerably higher than conventional fuels.

From this analysis, it comes out that a process of filtering and purification of the oil is important to have properties closer to conventional fossil fuels; but, even with refined oils, some parameters like density and viscosity are too high than usual values; this drawbacks can be overcome by preheating the fuel, but the main problem probably remains the extremely high content of metals and ashes, as well the carbon residue value. The high carbon residue can be source of deposits in the injection nozzles, while the high content of metals can be source of high temperature corrosion and generation of deposits on the surface of the turbine blades.

In order to assess the environmental impact, i.e. the pollutant emissions, the company Nuovo Pignone in Florence performed an experimental campaign on a 4.5 MW_{el} gas turbine fuelled with refined vegetable oil and methyl ester. The turbine was adapted by increasing the fuel feeding pressure and fuel preheating up to approx. 70 °C. The most important result achieved is that the behaviour in terms of emissions is very similar when comparing rapeseed vegetable oil to methyl ester, as shown in fig. 7.3; moreover, the tests pointed out that, basically, refined oils can be used in gas turbines, with no major problem and without important modification to the energy system.

Fuel property	Unit	Rape seed oil - Raw	Rape seed oil - Refined	Traditional fossil fuel
Density @ 15°C	kg/dm ³	0.92	0.92	0.82-0.88
Kinematic viscosity @ 50°C	cStoke	23.8	27.0	2-4
Kinematic viscosity @ 100°C	cStoke	12.4	12.6	-
Higher heating value @ 15 °C	MJ/kg	39.60	39.18	44-46
Flash point	°C	255.2	167.1	55-95

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Fuel property	Unit	Rape seed oil - Raw	Rape seed oil - Refined	Traditional fossil fuel
	cor	ntinued		
Ash	% wt	0.029	0.002	0.0002-0.005
Carbon residue	% wt	0.52	0.24	0.03-0.3
Carbon content	% wt	77.69	78.21	-
Hydrogen content	% wt	11.24	11.14	12.2-13.2
Nitrogen content	% wt	0.065	0.065	0.005-0.06
Sulphur content	% wt	0.017	0.0067	0.1-0.8
Oxygen content	% wt	10.72	10.29	-
Clorures	ppm	1627	176	-
Sodium + potassium	ppm	6	3	1
Vanadium	ppm	0.17	0.07	0-0.1
Calcium	ppm	10.8	5.1	0-2
Lead	ppm	2.7	0.6	0-1

Table 7.2 – Comparative analysis of some properties of vegetable oil (raw and refined) and fuels usually employed in gas turbines

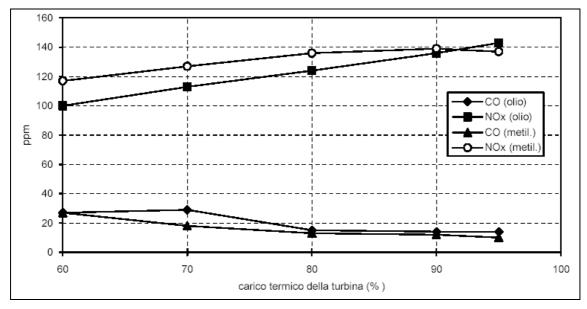


Fig. 7.3 – Emissions of the PGT5 gas turbine fuelled with refined vegetable oil and methyl ester at different thermal load (100% = 18.4 MW_{th})
[Nuovo Pignone – AEM – Istituto di Ingegneria Agraria, 1994]

7.2.4. Conclusions

The analysis pointed out that the utilisation of vegetable oil for energy purposes does not present particular technical problems if specific adaptations of the energy conversion technology are implemented; especially for medium and large heating systems it is

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possible to use oils that are similar to the dense fuels conventionally used: the barrier is mainly of economic nature. There are different companies that commercialise diesel engine based CHP systems, which are more economically convenient given the added value related to heat production. Also tests in gas turbines experienced that the operation with vegetable oils is technically feasible. Concerning diesel engines, there are also examples of vehicles fuelled by vegetable oils, specifically realised for this purpose: for instance the German Elsbett company or Autozubehör-Technik Glött GmbH, offering kits converting diesel-operating vehicles to straight vegetable oil; moreover, the work pointed out that basically IDI diesel engines are more suitable to be operated with vegetable oil than DI engines.

7.3. Economics and market perspectives

Vegetable oils are generally characterised by lower production costs, a better energy balance and a much simpler production technology compared to the corresponding methyl esters. All these aspects lead to the consideration that vegetable oil can be very attractive for developing countries market, where main objective is self energy production at low costs, maximising energy yield (the energy necessary for oil extraction is just a small fraction of oil energy content).

Nevertheless also in OECD countries vegetable oil seems to have interesting opportunities in the distributed energy generation market, e.g. small-medium size CHP plants based on marine engines or gas turbines, as well as heating systems. However, even if technology barriers have been successfully overcome, the utilisation of vegetable oil for energy production presents several economic constraints in OECD countries, mostly related to commercial issues, namely lack of distribution network, need for adaptation of the energy conversion systems, and, in most of the applications, high cost if compared with conventional fossil fuels.

8. Biodiesel

Biodiesel is produced from vegetable oils, which are derived from oil crops, e.g. rapeseed, sunflower, soybean and palm.

Vegetable oils are extracted from oil seeds mechanically or by means of a solvent; the derived oil can be used directly in engines for energy production purposes, but this requires engine modifications; this is due mainly to the very high viscosity of vegetable oils, the poor thermal and hydrolitic stability, in some cases the low cetane number. In order to use plant oils in non-modified diesel engines, the oil should be modified so that its characteristics meet the requirements of available diesel engines: this can be achieved through the esterification process, in which the large, branched molecule structure of the vegetable oil (triglycerides) are converted into smaller straight-chained molecules (methyl ester) that are similar in size to diesel oil components. The obtained product is called Biodiesel. Most of the methyl esters are produced through a catalytic transesterification process of the oil with methanol, the catalyst usually being sodium hydroxide (caustic soda) or potassium hydroxide.

Fuel properties

The transesterification process is based on a well-known technology and it is already largely applied throughout Europe and worldwide. The end product, Biodiesel, is an amber-yellow coloured liquid, with a viscosity considerably reduced in comparison with the vegetable oil (for rapeseed from 78 to 7.5 cSt), closer to the viscosity of conventional fossil diesel fuel. In table 8.1 the properties of different Biodiesels are compared to conventional diesel oil and the initial vegetable oil:

Fuel property	Unit	Diesel fuel Nr. 2	Rape seed oil	RME	Sunflower oil	SME
Density @ 15°C	kg/dm³	0.84	0.92	0.88	0.92	0.88
Molecular weight	kg/mol	170-200		296		
Kinematic viscosity @ 20°C	cStoke	4-5	77.8	7.5	65.8	
Lower heating value	MJ/kg	42.7	37.3	37.3	37.0	35.3
Lower heating value	MJ/litre	35.7	34.3	32.8	34.1	33.0
Stoichiometric air/fuel ratio	kg _{air} /kg _{fuel}	14.5		12.3		
Flash point	°C	77		91-135		110
Cetane number		>45	44-51	52-56	33	45-51
Conradson Carbon residue	% wt	0.15	0.25	0.02	0.42	0.05
Sulphur content	% wt	0.29	0.0001	0.002	0.01	0.01
Oxygen content	% wt	0–0.6		9.2-11.0		

Table 8.1 – Fuel properties of diesel oil, vegetable oils and corresponding methyl ester RME = rape methyl ester; SME = sunflower methyl ester [various sources]

As reported in the table above, the properties of Biodiesel, independently on the raw material, are very close to conventional diesel fuel, above all viscosity, cetane number, and density. Moreover, the storage capability of Biodiesel is notably higher than pure vegetable oils; the conclusion is that esterified vegetable oils are suitable for applications in conventional diesel engines in substitution of fossil fuels. The benefits related to the transesterification process of the vegetable oil can be summarised as follows:

- Esterified vegetable oil is well suited for mixture or replacement of fossil diesel fuel;
- The utilisation of esterified oils is effective in eliminating injector problems in directinjection diesel engines;
- Viscosity of Biodiesel is notably lower than the corresponding vegetable oil, similar to diesel fuel:
- Methyl esters are more stable than vegetable oil from which they are derived;
- Cetane number of Biodiesel is compared to conventional diesel fuel.

8.1. Energy conversion technologies for stationary systems

8.1.1. Introduction

Biodiesel is today effectively used in diesel engines in the transport sector, both when blended with fossil diesel fuel and in pure form. Tests undertaken by motor manufacturers in the European Union on blends with diesel oil between 2% and 30% and 100% pure diesel have resulted in guarantees for each type of use. Minor modifications (seals, piping) are required for use at 100% pure, unless specifically guaranteed by car manufacturers. The use of Biodiesel as a transport fuel does not require any changes in the distribution system, therefore avoiding expensive infrastructure changes.

Biodiesel is also used as efficient **heating oil**. Since over ten years, biodiesel is used as fuel in heating systems of different sizes, with very positive results in terms of efficiency, emissions and technological viability; in fact, since biodiesel is very similar to conventional heating fuel, it is possible to use it in traditional burners, only with minor and low-cost modifications, which make possible the use of pure biodiesel. Even, biodiesel can be considered safer than traditional diesel oil, because of its biodegradability and higher flash point. Concerning its utilisation as heating fuel, the calorific value of biodiesel is lower than diesel oil (33 compared to approx. 35 MJ/litre), because it is an oxygenated fuel, with oxygen content of approx. 11% wt. This means a higher fuel consumption, but, at the same time, a more efficient and complete combustion of the fuel, requiring a lower amount of air, then the increase of fuel consumption passing from diesel to biodiesel is usually very limited.

Concerning the utilisation of biodiesel in diesel engines for the production of electricity, not many specific experiences on this topic were found; this is not due to technical reasons - it is enough to think about the successful experiences in diesel engines for automotive purposes, subject to more severe running conditions – but to market reasons, given the high costs of biodiesel in comparison to conventional oil used for electricity production in diesel engines (usually at very low costs). In any case, it is worthwhile to mention a very visible project, that is the energy supply of the German Parliament Buildings ("Deutscher Reichstag") with a Biodiesel-fuelled CHP plant, using ca. 3.000 ton of Biodiesel per year.

Moreover, Biodiesel can be used as low environmental impact additive in kerosene and gas oil; its utilisation as **additive**, in fact, reduces the wear of the engine and injection system, given its relevant lubricating properties. Performed tests indicate that low sulphur diesel oils added with specific additives and the same diesel oil with the addition of biodiesel (20% vol.) have lubricating properties very similar. Also in the case of jet fuels, the addition of 1-2% of biodiesel notably reduces the wear of the injection nozzles. Therefore, biodiesel can be considered a lubricity improver, in the same way as specific chemical additives, and used in low sulphur content oils. Performed studies demonstrated that even small quantities of biodiesel could considerably improve the lubricity of a fuel with a low environmental impact.

8.2.2. State of the art

In this paragraph an overview of the current utilisation of biodiesel for stationary applications is given, with reference to specific experiences achieved in this field. The experiences strictly related to the transport sector are not considered here, unless the related issues are considered useful for the analysis of the utilisation of biodiesel in stationary applications.

Today, biodiesel is used pure as heating fuel or blended with conventional fossil fuel in automotive diesel engines: in both the cases biodiesel can be used immediately in conventional equipment, with no major modification. When used as heating oil, it is sufficient the replacement of compatible materials (pipes, seals, gaskets) and adjust the amount of combustion air. When used in diesel engines, in blendings not over 30%, no modification and no particular adjustment of the engine is requested.

Biodiesel in heating systems

Concerning heating systems, the research found out some activities in Italy (Casalini *et al.*, 1999; Carraretto *et al.*, 2001), where the utilisation of biodiesel as heating fuel is a quite common practice, in particular in public buildings. Moreover, some experiences on Biodiesel Blends for Heating Equipment performed in USA are given.

The factors encouraging biodiesel utilisation as heating oil are the following: the related environmental benefits, good performance of the burner and better characteristics of handling and storage. In comparison to natural gas, biodiesel is less clean, but the conversion from oil to natural gas is more difficult and expensive (also due to safety restrictions) and not in every area natural gas distribution is available. In the following the main results are reported concerning an interesting experience of the Municipality of Padova (Italy), which in 2000-2001 started the experimentation on a heating system of a public school fuelled by biodiesel (Carraretto et al., 2001).

Two units, each one of 512 kW_{th}, one conventional oil-fired boiler and one converted to biodiesel, constitute the entire heating plant. Previous studies and tests pointed out that the conversion from oil to biodiesel does not cause particular problems, apart from a higher fuel flow rate - at equal developed power – and the necessity to use compatible materials for pipes and seals. Therefore, the old burner has been replaced with one more suitable to biodiesel, with appropriate materials and with nozzles suitable to higher flow rates; moreover, the tank is brand new, because of the aptitude of biodiesel to solubilise the residues accumulated on the bottom of the tank (Carraretto et al., 2001).

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The main results of the experience done in winter 2000-2001 are (Carraretto et al., 2001):

- □ The heating system worked in fully automatic way; during the entire operation time, no technical problem occurred;
- □ The typical smell related to biodiesel combustion did not represent a problem;
- □ No damage to the gaskets, pipes and seals was registered;
- □ The performance of the biodiesel unit was higher than conventional oil and is almost constant in time (this is due to a minor build up in the boiler). This is confirmed also by the fact that the stack temperature was lower, thanks to the absence of SO2 in the exhaust gas;
- \square CO and CO₂ emissions were definitely between diesel oil and biodiesel; NO_x emissions were not measured, but, accordingly to other experiments, a decrease of approx. 30% is expected, thanks to oxygen content in biodiesel that makes possible a better combustion;
- □ Although the higher performance and density, the fuel consumption is higher and then the running costs.

Another research activity carried out in Italy (Casalini *et al.*, 1999), demonstrated that the utilisation of biodiesel for thermal energy production can be environmentally effective, both when used as oxygenated additive in mineral oil, and used in pure form. As already said, biodiesel is an oxygenated compound, the oxygen allowing combustion reactions more complete with the consequent reduction of pollutant emissions.

The tests have been carried out on an experimental unit formed by a combustion chamber at atmospheric pressure and the corresponding burner c/o Ansaldo Termosud (Bari): the tests have been performed by using six different fuels:

- 1. Pure mineral oil;
- 2. 5-95 %wt biodiesel/mineral oil
- 3. 10-90 %wt biodiesel/mineral oil
- 4. 25-75 %wt biodiesel/mineral oil
- 5. 50-50 %wt biodiesel/mineral oil
- 6. Pure biodiesel

For each fuel, NO_x , CO, CO_2 and O_2 emissions have been measured: the most important result of the tests are that in blendings with 5 %wt in biodiesel, NO_x emissions are reduced by 5% in comparison to pure mineral oil; this reduction increases to 14, 15 and 22% passing to fuels 3, 4 and 5. From 50 %wt of biodiesel up to pure biodiesel (fuel nr. 6), the reduction of NO_x emissions is practically constant, at some 22%. In conclusion, being the reduction of NO_x emission an important technical issue, the utilisation of biodiesel in heating systems is for sure a good method to achieve this difficult goal.

Another interesting experience concerning biodiesel as heating fuel was the evaluation of the performance of blends of biodiesel and home heating oil in space heating applications initiated by Brookhaven National Laboratory (Krishna, 2001) under the sponsorship of the Department of Energy (DoE) through the National Renewables Energy Laboratory (NREL). A number of blends of varying amounts of a biodiesel in home heating fuel were tested in both a residential heating system and a commercial size boiler. The results demonstrated that blends of biodiesel and heating oil can be used with few or no modifications to the equipment or operating practices in space heating. The results also showed that there

were environmental benefits from the biodiesel addition in terms of reductions in smoke and Nitrogen Oxides (NO_x) emissions. The latter result was particularly surprising and of course welcome, in view of the previous results in diesel engines where no changes had been seen. Nevertheless, this result is in good agreement with the studies previously reported.

In the recent document "Combustion testing of a Biodiesel fuel oil blend in residential oil burning equipment" (Batey, 2003), the main achievements on a combustion test programme on biodiesel resulting from a collaborative work between the National Oilheat Research Alliance (NORA), Massachusetts Oilheat Council (MOC), New England Fuel Institute (NEFI), Advanced Fuel Solutions, Inc., Energy Research Center, Inc., are reported. The purpose was to evaluate the combustion performance of a blend of 20% soy-based biodiesel fuel combined with 80% low sulphur (0.05%) highway diesel compared to conventional home heating oil. The main results are hereby summarised. Biodiesel fuel blends have been shown to lower air emissions in residential and small commercial oil heating equipment. Tests were conducted using a range of conventional oil powered boilers and furnaces over a range of fuel firing rates and excess combustion air settings. Key observations and findings of these combustion tests include:

- □ Nitrogen Oxide emissions are frequently reduced by about 20% by using the biodiesel/low sulphur blend.
- Combustion stability with the biodiesel blend is very good as indicated by low levels
 of carbon monoxide that are similar to the conventional fuel oil.
- Sulphur Oxide emissions are reduced by 83 percent by using the biodiesel blend.
- □ Smoke numbers are lower with the biodiesel blend than the home heating oil when the same burner air setting is used.
- □ Fuel oil and combustion odours are improved by using the biodiesel/low sulphur oil blend compared to home heating oil based on these preliminary tests.

This combustion test project demonstrated that very good combustion performance is produced by the biodiesel fuel blend in the conventional residential oil heating equipment that was tested. No significant changes in carbon monoxide levels (incomplete combustion) were observed. The reduction of pollutant emissions with the biodiesel blend is substantial, producing much lower environmental impacts. This includes reductions in sulphur oxides (83%), nitrogen oxide (20%), carbon dioxide (20%), and particulate matter. Preliminary analyses indicate that the 20% soy-based biodiesel/low sulphur diesel blend has an environmental cost that is lower than natural gas when gas leakage during transmission, storage, and distribution are included. This transforms home heating oil into a premium fuel with very favourable environmental impacts. Other benefits include improved odour characteristics, and domestic production of part of the fuel supply from soybean farms.

Biodiesel in gas turbines

An example of utilisation of biodiesel for combined heat and power production was found in (Mimura, 2003); the document reports about the adoption of micro CHP to use biodiesel from waste oil. Reformed waste edible oil is used as a fuel for a 28 kW_{el} micro gas turbine.



Effective use of waste edible oil

The properties of biodiesel and the light oil to replaced are the following:

Items/Type of Fuel	Reformed Oil (Measured)	Light Oil (Reference Value)
Specific Gravity g/cm ³	0.887	0.835
Flash Point	174	96
K.Viscosity mm ² /S	6.17	3.8
Pour Point	-7.5	-15
Cetane Value (Index)	58	57
Calorific Value kcal/kg	9,560	10,930
Sulfur Content	0.03	Less than 0.20

The following are the main characteristics of the Kanazawa Biodiesel Fuel CHP System:

- □ Turbine Unit: Capstone Model 330 Liquid Fuel Type
- Output: 28kW 480V 50 Hz

- □ Waste Heat Recovery: Hot Water Collection Boiler 197MJ/hour
- □ Transformer: Dry Type 480/210 V 50 Hz
- □ Low Noise Enclosure: 65 dB(A) at one meter from the Main Body

During the tests, an electric efficiency of the turbine of 21% was measured, being the thermal efficiency 43%, thus giving an overall efficiency of 64%.



View of the system - Project Site: A Public Hospital in Ishikawa Prefecture

Biodiesel in diesel engines

As already mentioned, the utilisation of biodiesel for the production of electricity does not seem a common practice: this is not due to technical reasons, but mainly to economic and market reasons; in any case, some results related to experiences in diesel engines (stationary and heavy duty) have been analysed and the main results are here reported.

On the basis of the research that has been carried out, the most important experiences regarding biodiesel utilisation in stationary applications are in Germany.

The realisation of an engine-based cogeneration plant in the Reichstag building in Berlin is probably one of the more visible examples in this sense; the plant runs with biodiesel and provides the entire energy supply for the historical building. The exhaust emissions from the plant's four diesel engines are kept extremely low by the use of SINOx catalysts, in addition to a soot filter and an oxidation catalyst for carbon monoxide and HC reduction. This exhaust cleaning system developed by the Siemens Power Generation Group (KWU) already has a proven service record in numerous engine-based cogeneration plants worldwide. Sources (Grimm P., 2003) report that the engine-based cogeneration plants can attain energy utilization factors of almost 90 percent, with an output of 1,600 kilowatts of electricity and 1,840 kilowatts of heat. Beside biodiesel the four engines can also alternatively be operated using commercially available diesel fuel. The exhaust heat from the engines is directly utilised for heating purposes via heating networks. The first period of operation did not reveal particular problems to the engines (four different groups), save for usual problems related to the operation and maintenance of usual diesel engines.

Also, examples of biodiesel generators in operation (both small and large scale) have been found in USA and Canada, but technical data on these experiences are not available.

In literature many experiences and research activities of tests performed on diesel engines fuelled by biodiesel are available, but these information always refer to automotive applications; in any event, some of these results can be considered valid also in the case of stationary applications.

The analysis of several sources, brought to the conclusion that the use of biodiesel in conventional compression ignition engines (DI, direct injection and IDI, Indirect Injection), either as a pure fuel or blended with diesel fuel, does not create problems during the engine operation; moreover, efficiency and engine wear are absolutely analogous to conventional diesel oil and the fuel consumption is only slightly increased. From the environmental point of view, the utilisation of biodiesel in diesel engines results in a reduction of unburned hydrocarbons, carbon monoxide, and particulate matter. Emissions of nitrogen oxides, which lead to the formation of ozone, are either slightly reduced or slightly increased depending on the duty cycle of the engine and its design. Moreover, in the automotive sector, the absence of sulphur oxides makes possible an improvement of the efficiency of the catalyst, thus resulting in a further reduction of HC emissions.

The optimum blend of biodiesel and diesel fuel, based on the trade-off of PM decrease and NOx increase, but also on economic considerations, is widely recognised as a 20/80 biodiesel/diesel fuel blend. In fact, theoretically Biodiesel can be used pure or mixed in any proportion with diesel #2 or diesel #1 (kerosene), but 20% blend of biodiesel with 80% diesel - called B20 – is preferred for a variety of reasons (NREL, 2001):

- B20 minimizes the impact of the biodiesel cost on the customer.
- □ 20% blend keeps NOx increases small (1-4%)
- □ 20% blend still gives good emission benefits by reducing soot, particulates, hydrocarbons, carbon monoxide, and carbon dioxide by more than 10% each.
- □ B20 does not create major problems with filter plugging and deposit formation that can result from the interaction between biodiesel and the accumulated sediments and sludge that form in diesel storage tanks.
- □ B20 controls the increase in cloud and pour point by a manageable level that cold flow additives can control.
- Few material compatibility problems arise with B20. Higher blend levels will cause more problems with rubber seals, gaskets, and hoses unless these have been replaced with biodiesel resistant materials.

B20 is therefore basically a compromise between cost, emissions, cold weather, material compatibility, and solvency issues. It is a good starting point for new users because B20 users rarely encounter problems. Users should be careful when moving from B20 to higher blends since the risk of encountering problems increase. Higher blends have been used over extended periods of time and some commercial fleets are using B100. Blends of 35%, 50%, and higher can provide significant emission reduction benefits for carbon monoxide, particulates, soot, and hydrocarbons. Higher blend levels of biodiesel significantly reduce polycyclic aromatic hydrocarbons and other toxic or carcinogenic compounds found in diesel exhaust. Higher blend levels also provide significant reductions in greenhouse gas emissions and increase the renewable content of the fuel.

Emission	B100*	B20**
Carbon Monoxide	-43.2%	-12.6%
Hydrocarbons	-56.3%	-11.0%
Particulates	-55.4%	-18.0%
Nitrogen oxides	+5.8%	+1.2%
Air toxics	-60% to -90%	-12% to -20%
Mutagenicity	-80% to -90%	-20%
Carbon dioxide***	-78.3%	-15.7%

^{*}Average of data from 14 EPA FTP Heavy Duty Test Cycle tests, variety of stock engines

Tailpipe Emission Changes with Biodiesel Fuels

One drawback of higher blend levels is an increase in nitrogen oxides emissions (NOx). Biodiesel with high levels of polyunsaturates produce more NOx emissions than biodiesel with high levels of saturates. Research has identified one additive that provides a certain control on NOx emissions. One percent DTBP (ditertiary butyl peroxide) by volume in B20 can make B20 NOx neutral with diesel fuel. The effect of five percent DTBP in B100 has different effects on different biodiesels. This problem may be resolved in the near future as other additives or solutions are identified. Higher blends of biodiesel are popular with users in vulnerable (e.g. natural parks, lakes, mountains, etc.) environments, because they are biodegradable and reduce the toxicity of diesel fuel. B100 is used in commercial fleets, marine vessels, and in mining equipment. Extra precautions may be required to resolve solvency concerns or to protect the customer from cold weather. Modifications may be required to replace materials with compatibility concerns.

Kalligeros *et al.* (2002) report about an "investigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine". The work focuses on exhaust emission and fuel consumption measurements from a single cylinder, stationary, diesel engine: the engine was fuelled with fuel blends containing two different types of biodiesel (sunflower oil and olive oil), at proportions up to 50%; the adopted engine is a stationary diesel powered Petter engine, model AV1-LAB with the following characteristics:

□ Engine type: single cylinder, indirect injection

□ Speed: 1500 rpm

Compression ratio: 19=1
 Total displacement: 553 cm³
 Maximum output: 3.8 kW

The engine was fuelled with pure marine diesel and mixtures containing 10%, 20%, and 50% of two types of biodiesel. The two types of biodiesel were methyl esters produced from sunflower oil and olive oil. The tests included measurements of HC, CO, NO_X and PM emission under various loads up to 3.8 kW, the load being measured by shaft output. Also the volumetric fuel consumption was measured.

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^{**}Average of data from 14 EPA FTP Heavy Duty Cycle tests, variety of stock engines

^{***}Life cycle emissions

Properties	Value			Test method
	Marine diesel	Sunflower oil methyl ester	Olive oil methyl ester	
Density at 15°C (kg l ⁻¹)	0.860	0.885	0.880	ASTM D 1298
Distillation curve (%v v-1)				ASTM D 86
Recovered at 250°C	12			
Recovered at 350°C	76			
Recovered at 370°C	86			
Sulfur (wt%)	0.22	0.0047	0.0010	ASTM D 4294
Copper strip corrosion	1A	1A	1A	ASTM D 130
Flash point (°C)	73	110	> 110	ASTM D 93
Kin. viscosity at 40°C (cSt)	3.8	4.391	4.700	ASTM D 445
Water (mg kg ⁻¹)	100	518	243	ASTM D 1744
Cetane index	46			ASTM D 4737
Cetane number		58	61	DIN 51773
Ash (wt%)	0.12	0.0007	0.0054	ASTM D 482
Conradson carbon residue (wt%)	0.2	0.98	0.22	ISO 10370
CFPP (°C)	-6	-2	-6	IP 309
Cloud point (°C)	-6	1.5	-2.0	ASTM D 2500
Pour point (°C)		-3	-3	ASTM D 97
Suspended matter (mg kg-1)	< 24			DIN 51419
Oxidation stability (g m ⁻³)	< 25	36	16	ASTM D 2274
Low heating value (kJ kg ⁻¹)	42191	38466	32781	ASTM D 2015

Marine diesel oil and SMR properties, Kalligeros et al. (2002)

In this case, NO_X emissions were reduced in all cases when the different blends of biodiesel were used. The reason for the decrease in NO_X emissions, was that the cetane number of biodiesel is higher than that for the marine diesel fuel, and this is usually associated with lower NO_X emissions.

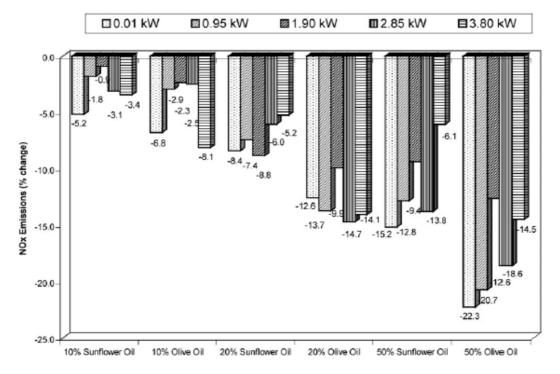


Fig. 8.1 - Percentage change of the total nitrogen oxide emissions at different loads (ppm)

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Moreover, biodiesel addition reduced particulate emissions in all cases. At maximum load the reduction was rather low, whereas the most significant reductions of emissions was recorded at 75% load. The reason for this behaviour is the different amount of sulphur between the marine diesel (0.22 wt%) and the marine biodiesel blends (0.0047 wt% for sunflower oil methyl ester and 0.0010 wt% for olive oil methyl ester). The literature verifies that PM emissions generally increase or decrease in relation to the sulphur concentration. Sulphur into the fuel, results in sulphates that are absorbed on soot particles and increase PM emissions. In addition, the increase of oxygen content in the fuel, which contributes to a complete fuel oxidation, leads to a significant decrease of PM.

Figure 8.3 illustrates that the addition of sunflower and olive oil reduced the unburned HC emissions in all cases. For minimum load and 10% biodiesel into the mixture, the reduction was practically unaffected by the addition of any biodiesel. The most beneficial reduction appeared at intermediate loads. Figure 8.4 shows the reduction in CO emissions, due to the addition of sunflower and olive oil biodiesel, respectively, while figure 8.5 shows no greater quantity of biodiesel was injected in the tests in order to supply the same engine torque.

In conclusion, the substitution of marine diesel with biodiesel from sunflower oil and olive oil leads only to positive outcomes. The two types of biodiesel performed in a similar way. They decreased particulate matter, carbon monoxide, hydrocarbon and nitrogen oxide emissions and resulted in a slight increase of the volumetric fuel consumption.

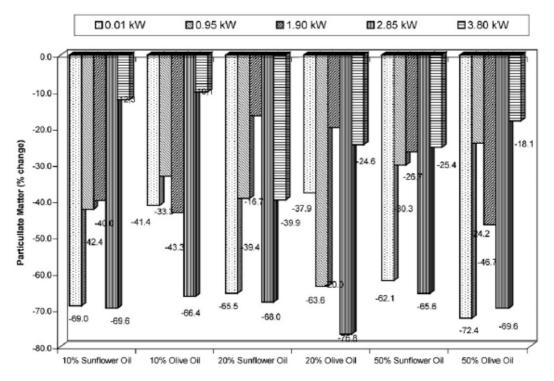


Fig. 8.2 - Percentage change of the particulate matter emissions (mg/m³)

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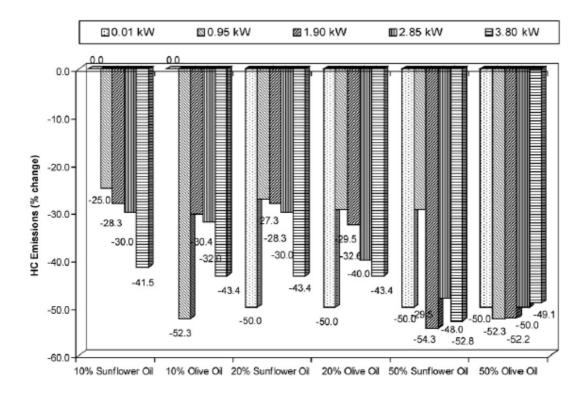


Fig. 8.3 - Percentage change of the HC emissions (ppm)

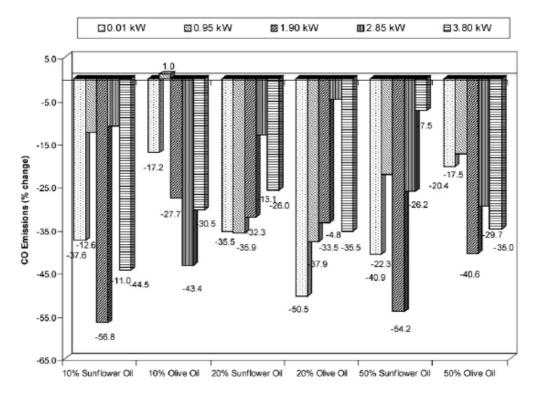


Fig. 8.4 - Percentage change of the CO emissions (vol%)

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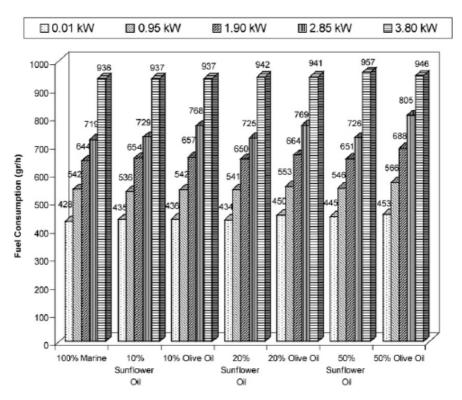


Fig. 8.5 - Fuel consumption for conventional marine diesel fuel and fuel blends with biodiesel (g/h)

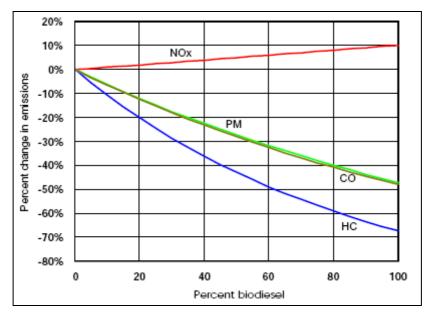
The study "A Comprehensive Analysis of Biodiesel Impacts on Exhaust Emissions" (EPA, 2002), presented a technical analysis of the effect of biodiesel on exhaust emissions from diesel-powered vehicles, on the basis of pre-existing data from various emissions test programs to investigate these effects. Hereby are presented the main results of the study.

The Environmental Protection Agency has conducted a comprehensive analysis of the emission impacts of biodiesel using publicly available data. This investigation made use of statistical regression analysis to correlate the concentration of biodiesel in conventional diesel fuel with changes in regulated and unregulated pollutants. Since the majority of available data was collected on heavy-duty highway engines, this data formed the basis of the analysis. The average effects are shown in following pictures and tables.

Al already said, one of the most common blends of biodiesel contains 20 volume percent biodiesel and 80 volume percent conventional diesel. For soybean-based biodiesel at this concentration, the estimated emission impacts are:

	Percent change in emissions
NOx	+ 2.0 %
PM	- 10.1 %
HC	- 21.1 %
CO	-11.0 %

Emission impacts of 20 vol% biodiesel for soybean-based biodiesel added to an average base fuel



Average emission impacts of biodiesel for heavy-duty highway engines (EPA, 2001)

The investigation pointed out that biodiesel impacts on emissions is variable depending on the type of biodiesel (soybean, rapeseed, or animal fats) and on the type of conventional diesel to which the biodiesel was added. With one minor exception, emission impacts of biodiesel did not appear to differ by engine model year. The highway engine-based correlations between biodiesel concentration and emissions were also compared to data collected on non-road engines. On the basis of this comparison, it is not possible to conclude that this category responds to biodiesel in the same way that heavy-duty highway engines do. Thus no prediction was made concerning the impacts of biodiesel use on emissions from diesel-powered non-road equipment.

8.2. Critical aspects of technologies: lessons learnt, R&D and environmental issues

Material Compatibility

Brass, bronze, copper, lead, tin, and zinc will oxidize diesel and biodiesel fuels and create sediments. Lead solders and zinc linings should be avoided, as should copper pipes, brass regulators, and copper fittings. The fuel or the fittings will tend to change colour and sediments may form, resulting in plugged fuel filters. Affected equipment should be replaced with stainless steel or aluminium. Acceptable storage tank materials include aluminium, steel, fluorinated polyethylene, fluorinated polypropylene, and Teflon.

The effect of B20 on vulnerable materials is diluted compared to higher blends. Some slow oxidation can occur, although it may take longer to materialize. Biodiesel can also affect some seals, gaskets, and adhesives, particularly those made before 1993 and those made from natural or nitrile rubber (NREL, 2001). It is primarily for these reasons that vehicle and storage equipment are modified. Most engines made after 1994 have been constructed with gaskets and seals that are generally biodiesel resistant.

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Earlier engine models or rebuilds may use older gasket and seal materials and present a risk of swelling, leaking, or failure. Fuel pumps may contain rubber valves that may fail.

<u>Material</u>	BXX	Effect compared to diesel fuel
Teflon	B100	Little change
Nylon 6/6	B100	Little change
Nitrile	B100	Hardness reduced 20%
	B100	Swell increased 18%
Viton A401-C	B100	Little change
Viton GFLT	B100	Little change
Fluorosilicon	B100	Little change in hardness
	B100	Swell increased 7%
Polyurethane	B100	Little change in hardness
	B100	Swell increased 6%
Polypropylene	B100	Hardness reduced 10%
	B100	Swell increased 8-15%
Polyvinyl	B100	Much Worse
	B50	Worse
	B40	Worse
	B30	Worse
	B20	Comparable
	B10	Comparable
Tygon	B100	Worse

Material Compatibility with Biodiesel Fuels (NREL, 2001)

Biodiesel handling and storage

Biodiesel storage needs the procedures usually adopted for conventional fossil fuels: dry conditions, clean place and without excessive changes of temperature. Storage facilities should be made of steel, polyethylene, and fluorine polypropylene; on the other, biodiesel should not be stored in concrete tanks because it breaks up this material.

Concerning the compatibility with materials, Biodiesel can be cause of ageing and swelling phenomena of some types of elastomers and natural rubbers. Therefore when biodiesel is used, some care is necessary, by replacing adduction pipes or gaskets with components made of compatible material, mainly when the biodiesel is used pure or in blending over 30%. Biodiesel is compatible with materials like copper, carbon steel, brass, fluorine rubbers, nitrogen rubbers, and polyethylene, while it should not be used with rubbers like ethylene-acetate, ethylene-propylene, natural rubbers and styrene-butadiene. Tests performed on biodiesel-diesel oil blends pointed out that the effects on materials like polymers and elastomers are the same that in the case of pure diesel oil.

Diesel engines

The esterification of vegetable oil make possible the employment of biodiesel in conventional diesel engines, given the similarity of important properties like cetane number, viscosity, density. In any case, viscosity of biodiesel remains higher than traditional diesel oil: this can affect the atomisation of the fuel during the injection phase. Another drawback of the utilisation of biodiesel in diesel engines is the *winter performance*: at low temperatures (below 0 °C), problems occur with the supply of fuel from the tank to

the engine. This can be solved by using a higher content of methanol in the transesterification process: in this way the viscosity of biodiesel is reduced, but at the same time also the flash point is considerably decreased, thus causing safety problems. These problems therefore are usually solved by pre-heating the fuel or by adding specific flow enhancers, which allow safe operation of the engine also at low temperatures.

A negative aspect of the utilisation of biodiesel for energy purposes is that its combustions in some cases provokes a characteristic smell that can cause some inconveniences, especially if burnt in urban areas (for instance small scale heating systems).

The flash point, that is the minimum temperature to which the fuel has to be heated for the ignition of the mixture air/fuel vapour, is higher in case of biodiesel when compared to conventional diesel oil; this requires a higher temperature to be reached for biodiesel, but at the same time the safety in fuel handling is improved.

Biodiesel has been tested both neat and in different blending with diesel oil, above all for automotive applications. The most important result is that blends diesel/biodiesel up to 30% of biodiesel on a volumetric base can be used with no modification to the engine, with performances absolutely similar to conventional fossil diesel oil and with neglectable differences of the fuel consumption; moreover, the life of the engine is not affected, the wear of the engine is similar and particular procedures of maintenance are not requested.

There are also many examples of utilisation of blends, with biodiesel content greater than 30% in volume, in automotive diesel engines, in laboratory, by means of endurance trials and in public fleets; in all the cases the performance of the biodiesel/diesel oil blends resulted very similar to conventional diesel oil as such.

Some considerations that can be of interest for the utilisation of blends in diesel engines for stationary applications are:

- engine wear and performance are not affected by the adoption of biodiesel
- the fuel consumption is slightly greater (2-3%) than conventional diesel oil, given the lower LHV of biodiesel;
- concerning cold starts, biodiesel can be added with specific flow enhancers in order to guarantee the operation in a wide range of temperatures;
- the materials used for fuel handling and transportation typically are not subject to damages, above all when materials expressly compatible with biodiesel are used;
- procedures for engine maintenance have not to be modified
- in comparison to conventional fossil fuels, safety is improved; in fact, biodiesel can be stored at ambient temperature and pressure, flash point is higher, is not toxic (when pure) and is biodegradable.

Heating systems

The utilisation of biodiesel as fuel for heating systems is already practiced: biodiesel in heating systems is used pure in non modified conventional heating systems, requiring only some minor adjustment of the combustion air, of the feeding system and of the materials (pipes and gaskets).

When biodiesel is used in multi-stage burners of heating systems, it is necessary to reduce the combustion air, in some cases drastically on the primary flame. This is due to the fact that biodiesel is an oxygenated fuel, with oxygen content at some 11%. Moreover, in order to have a rapid ignition, it is necessary to increase the distance between the electrodes so that to have an electric arc as wide as possible.

The flame is an important factor to have good combustion performance; basically, the injection nozzles used for conventional diesel oil are appropriate also in the case of pure biodiesel: in any case, in order to have a good flame in the burner, it is advisable the utilisation of nozzles with an angle ranging between 30° and 80° and with a distribution of the pulverised fuel concentrated in the central or peripheral part. Moreover, some adjustments of the ratio between primary and secondary air are recommended when biodiesel is used as fuel.

Concerning the fuel feeding systems, a notable advantage is that the components used for heating oil can be used also in the case of biodiesel. The pump is the same of the conventional system, the only recommendation is to increase the operating pressure from 12 bar (usual value for heating oil) to 13-13.5 bar when biodiesel is used, in order to take into account the differences in viscosity and density. The material of some components like o-rings, seals should be verified as far as regards the compatibility of biodiesel (see paragraph on materials), by replacing these items e.g. with fluorine elastomer rubbers that are compatible with biodiesel.

Concerning other components, like pipes, filters, no particular recommendation has to be done, save for the utilisation of compatible materials.

Environmental issues

The main conclusion about biodiesel as fuel in stationary applications is that the utilisation of biodiesel in combustion engines, both pure and blended, makes possible a significant reduction of the pollutant emissions, like CO, SOx, soot, HC and, of course, CO₂ when the entire carbon cycle is considered, while NOx and particulate matter emissions behave in a different way depending on the type of engine and type of test; in any case the emissions of PM are usually lower in the case of biodiesel.

Tests performed in U.S. by the Mine Department [www.novaol.it] aimed at studying the particulate matter from diesel engines fuelled with biodiesel, pointed out that the correlated mutagenesis (that is the capability of external agents to cause mutations dangerous for the health) is 50% lower in comparison to fossil diesel oil: this behaviour is explained with the lack of aromatic compounds and polycyclic aromatic hydrocarbons. Other tests confirmed that also the emissions of blending of diesel oil with biodiesel are characterised by a lower content of dangerous polycyclic aromatic hydrocarbons like Naphthalene, Fluorene, benzopyrene. Moreover, biodiesel does not contain noxious metals like lead, cadmium, vanadium, while the content of sulphur in biodiesel is very low, thus reducing the content of sulphates in the particulate matter and the risk of acid rains.

Concerning the utilisation as heating fuel, the research and demonstration activities showed that biodiesel definitely combusts more cleanly than conventional mineral oils: all the pollutant emissions (including NO_x , in a different way from diesel engines) are lower than diesel oil, either used pure and blended.

Biodiesel improves the lubricating properties of diesel fuels with low sulphur content and it can substitute additives of fossil raw materials. Diesel engines can run with low emissions if the fuel shows an extremely low sulphur content; these fuels display very bad lubricating

properties and can thus cause damages in the injection equipment. It has been proven that a blending of 2% of biodiesel is sufficient to reach the necessary lubricating property.

In comparison to conventional fossil fuels, biodiesel is safer when handled and stored, because of its higher flash point and its high biodegradability, equal to 95% after 28 days, compared to 40% of conventional diesel oil.

Therefore, being biodiesel not toxic and rapidly degradable, the risks of handling, transporting and storing biodiesel are greatly reduced, thus biodiesel can be used for energy production in environments particularly vulnerable like mountains, natural parks, lakes and so on.

8.3. Economics and market perspectives

The production of biodiesel from vegetable oils is a well-established technology; it is applied on a large scale in several European countries. Current production costs of RME amount to approximately 0.50 €/litre (or 15 €/GJ). These costs depend on the prices of the feedstock and the size and type of the production plant. On the longer term, these costs may decrease by about 30%, assuming economies of scale. Other important factors determining the production costs of RME are the yield and value of by-products of the biodiesel production process, such as oil seed cake (a protein rich animal feed) and glycerine (used in the production of soap and as a pharmaceutical medium). Longer-term projections indicate a future decrease in RME production costs by more than 50%, down to approximately 0.20 €/litre (or around 6 €/GJ) (Van Thuijl E., 2003).

Up to now, the utilisation of biodiesel for electricity production (and/or CHP) is constrained by the very low cost of oil used in power plants based on engines: the energy production from an economic point of view is not convenient, even if from the technical point of view no particular problem is reported. Nevertheless, the impact on the environment of biodiesel fuelled power and CHP plants should be further studied, due to the difficulty to make assumptions based on data concerning the automotive sector (EPA, 2001).

One possible market could be the utilisation of biodiesel in micro CHP. In fact Micro CHP has the potential to strongly modify the electricity industry in Europe. It is a cost-effective method of generating electricity with an estimated high potential. It can be economically viable for the end-user without any form of subsidy. Moreover, there is now a substantial potential for installations in rural areas where a natural gas network is not available and opportunities for network support are considerably greater. Of greater significance, perhaps, is that these installations may also provide the earliest opportunity for the utilisation of liquid biofuels, and demonstrating the longer term role of micro CHP as a carbon-free domestic energy supply option (Harrison J., 2003).

Finally, the heating market. Biodiesel used as heating fuel is already a reality; in many European countries the price of heating oil is very high, due to high taxation. So, biodiesel could become competitive in a short term in this market (residential and commercial boilers) – in case appropriate fiscal incentives are introduced - in areas not yet covered by natural gas distribution and contributing to cover in part the energy needs of domestic and commercial buildings that represents approx. 1/3 of the primary energy consumption.

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9. Conclusions

The scope of this study was to identify and discuss the technological issues related to the use of biofuels for stationary decentralised energy generation.

The most important (i.e. diffused) biofuels have been identified (namely bioethanol, vegetable oil, biodiesel and bio-oil or pyrolysis oil) and discussed, and their use in energy conversion technologies analysed. Power generation systems have been considered (mainly engines, turbogas and fuel cells), as well as heat generation technologies, when applicable (boilers).

A main conclusion of the present work is that the use of biofuel for decentralised energy generation is not really limited by technological constraints, even if in some cases technological issues (especially those related to plant reliability and availability) are still to be properly addressed. These constraints however depend on the kind of technology considered and the (associated) level of innovation and performances targeted: steam cycles, for instance, are certainly the most reliable and well proven technological option while, on the opposite, fuel cells still need research and development work. In general, however, it can be concluded that it is technically possible today to feed biofuel to small-medium scale power and/or heat generation system with success.

The most significant barrier to the use of biofuel for stationary energy generation is instead represented by economic issues: the biofuel cost is the most critical element in a decentralised and liberalised energy market, where low fossil fuel prices do not act in favour of renewable fuels, unless externalities are not taken into account.

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ANNEX B - GLOSSARY

AUTOIGNITION TEMPERATURE: The temperature at which there is a spontaneous ignition of some or all of the fuel-air mixture in the combustion chamber of an internal combustion engine

BCO: Bio Crude Oil

BHP: Brake Horse Power. The net effective power of a prime mover, as a steam engine, water wheel, etc., in horse powers, as shown by a friction brake

BSFC: Brake Specific Fuel Consumption. This is the fuel consumption in kg/kWh

BTE: Brake Thermal Efficiency. The ratio of brake power output to power input

CETANE NUMBER: The percentage by volume of cetane (cetane number 100) in a blend with α -methylnaphthalene (cetane number 0); indicates the ability of a fuel to ignite quickly after being injected into the cylinder of an engine

CI: Compression Ignition. Ignition produced by compression of the air in a cylinder of a internal combustion engine before fuel id admitted

DI: Direct Ignition, in which the fuel is injected directly in the combustion chamber

DME: Dimethylether (CH3OCH3)

ETBE: Ethyl Tertiary Butyl Ether

FLAMMABILITY LIMITS: The stoichiometric composition limits (maximum and minimum) of a ignited oxidizer-fuel mixture that will burn indefinitely at given conditions of temperature and pressure without further ignition

FLASH POINT: The lowest temperature at which vapours from a volatile liquid will ignite momentarily upon the application of a small flame under specified conditions; test conditions can be either open- or closed-cup

GT: Gas Turbine

HHV: High Heating Value. Heat absorbed by the cooling medium in a calorimeter when products of combustion are cooled to the initial atmospheric (ambient) temperature

IDI: Indirect Ignition in which the fuel is injected and the combustion starts in precombustion chamber

LHV: Low Heating Value. The heat value of a combustion process assuming that none of the water vapour resulting from the process is condensed out, so that its latent heat is not available. Also known as lower heating value; net heating value.

MON: Motor Octane Number

PO: Pyrolysis Oil

POUR POINT: Lowest test temperature at which a liquid will flow

REID VAPOUR PRESSURE: A measure in a test bomb of the vapour pressure in pounds pressure of a sample of gasoline at 100 °F (37.8 °C)

RME: Rapeseed Methyl Ester

RON: Research Octane Number. Expression for the antiknock rating of a motor gasoline as a guide to how vehicles will operate under mild conditions associated with low engine speeds

SAUTER DIAMETER: A measure to estimate the mean size of a droplet or solid particle

SME: Sunflower Methyl Ester

SMOKE NUMBER: The dimensionless term quantifying smoke emissions. Smoke Number is calculated from the reflectance of a filter paper measured before and after the passage of a known volume of a smoke-bearing sample

STOICHIOMETRIC AIR/FUEL RATIO: The exact air/fuel ratio required to completely combust a fuel

VAPOUR PRESSURE: For a liquid or solid, the pressure of the vapour in equilibrium with the liquid or solid

VISCOSITY: Energy dissipation and generation of stresses in a fluid by the distortion of fluid elements.

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ANNEX C - ANALYSIS OF JOURNALS

Other than the sources mentioned in the bibliography, a specific research on **scientific journals** was carried out, with approximately 75 relevant scientific papers identified on several journals published by Elsevier and ASME international, the American Society of Mechanical Engineers. The list of reviewed papers is as follows:

Journal: Fuel

Volume 82, Issue 11, Pages 1297-1439 (July 2003)

Exhaust emissions from a Diesel engine fueled with transesterified waste olive oil, *Pages 1311-1315*

M. P. Dorado, E. Ballesteros, J. M. Arnal, J. Gómez and F. J. López

Volume 82, Issue 11, Pages 1297-1439 (July 2003)

The fuel properties of three-phase emulsions as an alternative fuel for diesel engines, *Pages 1367-1375*, Cherng-Yuan Lin and Kuo-Hua Wang

Volume 82, Issue 1, Pages 1-106 (January 2003)

Heat of wood pyrolysis, Pages 81-91

J. Rath, M. G. Wolfinger, G. Steiner, G. Krammer, F. Barontini and V. Cozzani

Volume 81, Issue 16, Pages 2019-2145 (1 November 2002)

Performance of a diesel generator fuelled with palm oil, Pages 2097-2102 Silvio C. A. de Almeida, Carlos Rodrigues Belchior, Marcos V. G. Nascimento, Leonardo dos S. R. Vieira and Guilherme Fleury

Volume 24, Issue 2, Pages 89-164 (1998)

Combustion of fat and vegetable oil derived fuels in diesel engines, *Pages125-164 Michael S. Graboski and Robert L. McCormick*

Journal: Applied energy

Volume 59, Issues 2-3, Pages 73-232 (February 1998)

Assessing the viability of using rape methyl ester (RME) as an alternative to mineral diesel fuel for powering road vehicles in the UK, Pages 187-214 Ann-Marie Williamson and Ossama Badr

Volume 54, Issue 4, Pages 287-391 (August 1996)

Diesel Fuel and Olive-Cake Slurry: Atomization and Combustion Performance, *Pages 315-326*, Moh'd Abu-Qudais and Gassan Okasha

Volume 54, Issue 4, Pages 287-391 (August 1996)

Performance of Rapeseed Oil Blends in a Diesel Engine, *Pages 345-354* O. M. I. Nwafor and G. Rice

Journal: Biomass and Bioenergy

Article in press

An experimental comparison of methods to use methanol and Jatropha oil in a compression ignition engine, In Press, Corrected Proof, Available online 28 February 2003

M. Senthil Kumar, A. Ramesh and B. Nagalingam

Volume 25, Issue 1, Pages 1-117 (July 2003)

Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines - Part 1 : emulsion production, Pages 85-99

D. Chiaramonti, M. Bonini, E. Fratini, G. Tondi, K. Gartner, A. V. Bridgwater, H. P. Grimm, I. Soldaini, A. Webster and P. Baglioni

Development of emulsions from biomass pyrolysis liquid and diesel and their use in engines - Part 2: tests in diesel engines, Pages 101-111

D. Chiaramonti, M. Bonini, E. Fratini, G. Tondi, K. Gartner, A. V. Bridgwater, H. P. Grimm, I. Soldaini, A. Webster and P. Baglioni

Bio-oil from pyrolysis of cashew nut shell—a near fuel, *Pages 113-117* Piyali Das and Anuradda Ganesh

Volume 24, Issue 3, Pages 163-262 (March 2003)

Emulsification of pyrolysis derived bio-oil in diesel fuel, *Pages 221-232* Michio Ikura, Maria Stanciulescu and Ed Hogan

Volume 24, Issue 2, Pages 81-161 (February 2003)

An investigation of using biodiesel/marine diesel blends on the performance of a stationary diesel engine, Pages 141-149

S. Kalligeros, F. Zannikos, S. Stournas, E. Lois, G. Anastopoulos, Ch. Teas and F. Sakellaropoulos

Volume 23, Issue 6, Pages 397-493 (December 2002)

Biodiesel from palmoil—an analysis of its properties and potential *Pages 471-479*, M. A. Kalam and H. H. Masjuki

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Volume 23, Issue 5, Pages 315-395 (November 2002)

Oil from Pistachia Palestine as a fuel

Pages 381-386, M. Al-Hasan

Volume 23, Issue 4, Pages 245-314 (October 2002)

The production and evaluation of bio-oils from the pyrolysis of sunflower-oil cake, *Pages 307-314*, Hasan Ferdi Gerçel

Volume 23, Issue 2, Pages 81-159 (August 2002)

Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification, *Pages 129-152*

Michiel J. A. Tijmensen, André P. C. Faaij, Carlo N. Hamelinck and Martijn R. M. van Hardeveld

Volume 20, Issue 4, Pages 237-325 (April 2001)

The effect of biodiesel oxidation on engine performance and emissions, *Pages 317-325*

Abdul Monyem and Jon H. Van Gerpen

Volume 20, Issue 2, Pages 71-150 (February 2001)

Characterization of the pyrolysis oil produced in the slow pyrolysis of sunflower-extracted bagasse, Pages 141-148

S. Yorgun, S. Sensöz and Ö. M. Koçkar

Volume 20, Issue 1, Pages 1-69 (January 2001)

Performance and emission characteristics of a diesel engine fueled with coconut oil-diesel fuel blend, Pages 63-69

Herchel T. C. Machacon, Seiichi Shiga, Takao Karasawa and Hisao Nakamura

Volume 19, Issue 5, Pages 281-361 (November 2000)

Bio-oils obtained by vacuum pyrolysis of softwood bark as a liquid fuel for gas turbines. Part II: Stability and ageing of bio-oil and its blends with methanol and a pyrolytic aqueous phase, *Pages 351-361*

M. E. Boucher, A. Chaala, H. Pakdel and C. Roy

Volume 19, Issue 4, Pages 209-279 (October 2000)

Influence of particle size on the pyrolysis of rapeseed (*Brassica napus* L.): fuel properties of bio-oil, *Pages 271-279*, S. §ensöz, D. Angln and S. Yorgun

Volume 19, Issue 2, Pages 63-135 (August 2000)

Preliminary test on combustion of wood derived fast pyrolysis oils in a gas turbine combustor, *Pages 119-128*, G. López Juste and J. J. Salvá Monfort

Volume 18, Issue 6, Pages 441-527 (1 June 2000)

Catalytic production of biodiesel from soy-bean oil, used frying oil and tallow, *Pages 515-527*

R. Alcantara, J. Amores, L. Canoira, E. Fidalgo, M. J. Franco and A. Navarro

Volume 18, Issue 3, Pages 175-262 (March 2000)

Some remarks on the viscosity measurement of pyrolysis liquids, *Pages 209-222*, M. Radovanovic, R. H. Venderbosch, W. Prins and W. P. M. van Swaaij

Volume 17, Issue 4, Pages 279-367 (October 1999)

Experimental study of some performance parameters of a constant speed stationary diesel engine using ethanol-diesel blends as fuel, *Pages 357-365* E. A. Ajav, Bachchan Singh and T. K. Bhattacharya

Volume 15, Issue 6, Pages 417-509 (December 1998)

Performance of a stationary diesel engine using vapourized ethanol as supplementary fuel, 493-502, E. A. Ajav, Bachchan Singh & T. K. Bhattacharya

Volume 14, Issue 2, (23 March 1998)

Carbon Cycle For Rapeseed Oil Biodiesel Fuels, *Pages 91-101,* Charles L. Peterson and Todd Hustrulid

Characterization of biomass-based flash pyrolysis oils, *Pages 103-113* Kai Sipilä, Eeva Kuoppala, Leena Fagernäs and Anja Oasmaa

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Ethyl ester of rapeseed used as a biodiesel fuel--a case study, *Pages 331-336*, Charles L. Peterson, Daryl L. Reece, Joseph C. Thompson, Sidney M. Beck and Craig Chase

Volume 9, Issues 1-5, Pages 1-439 (1995)

Feasibility of power production with pyrolysis and gasification systems, *Pages 257-269*, Y. Solantausta, A T Bridgwater and D Beckman

Journal: Bioresource Technology

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Volume 85, Issue 3, Pages 217-333 (December 2002)

Experimental evaluation of the transesterification of waste palm oil into biodiesel, *Pages 253-256*, Mohamad I. Al-Widyan and Ali O. Al-Shyoukh

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Volume 85, Issue 1, Pages 1-105 (October 2002)

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G. Antolín, F. V. Tinaut, Y. Briceño, V. Castaño, C. Pérez and A. I. Ramírez

Volume 80, Issue 1, Pages 1-91 (October 2001)

Preparation and characterization of bio-diesels from various bio-oils, *Pages 53-62*, X. Lang, A. K. Dalai, N. N. Bakhshi, M. J. Reaney and P. B. Hertz

Volume 73, Issue 1, Pages 1-93 (May 2000)

Techno-economics of rice husk pyrolysis, conversion with catalytic treatment to produce liquid fuel, *Pages 67-75*, M. N. Islam and F. N. Ani

Volume 70, Issue 1, Pages 1-115 (October 1999)

Biodiesel production: a review, Pages 1-15, Fangrui Ma and Milford A. Hanna

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Economic feasibility review for community-scale farmer cooperatives for biodiesel, *Pages 81-87*, Martin Bender

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Yeast and mould contaminants of vegetable oils, *Pages 245-249* G. C. Okpokwasili and C. N. Molokwu

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L. G. Schumacher, S. C. Borgelt, D. Fosseen, W. Goetz and W. G. Hires

Volume 56, Issue 1, Pages 1-130 (April 1996)

Macroeconomic effects of a community-based biodiesel production system, *Pages 1-6,* D. L. Van Dyne, J. A. Weber and C. H. Braschler

Diesel fuel derived from vegetable oils, VI: specifications and quality control of biodiesel, *Pages 7-11*, Martin Mittelbach

Hydroprocessed vegetable oils for diesel fuel improvement, *Pages 13-18* Mark Stumborg, Al Wong and Ed Hogan

Improved conversion of plant oils and animal fats into biodiesel and coproduct, 19-24, Praveen R. Muniyappa, Scott C. Brammer and Hossein Noureddini Emissions and engine performance from blends of soya and canola methyl esters with ARB #2 diesel in a DDC 6V92TA MUI engine, Pages 25-34

Claude Romig and Alex Spataru

Performance improvement by control of flow rates and diesel injection timing on dual-fuel engine with ethanol, *Pages 35-39*

Noboru Noguchi, Hideo Terao and Chikanori Sakata

Physical properties of low molecular weight triglycerides for the development of bio-diesel fuel models, *Pages 55-60*

John W. Goodrum and Mark A. Eiteman

Alcohol from bananas, Pages 125-130

J. Brent Hammond, Richard Egg, Drew Diggins and Charlie G. Coble

Volume 55, Issue 2, Pages 95-173 (February 1996)

Production and treatment of rapeseed oil methyl esters as alternative fuels for diesel engines, *Pages 145-150*

Ján Cvengros and Frantis ek Povaz anec

Volume 53, Issue 3, Pages 195-287 (1995)

Testing of alternative diesel fuel from tallow and soybean oil in cummins N14-410 diesel engine, *Pages 243-254*

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Volume 27, Issue 7, Pages 625-713 (July 2002)

Bio-oil production from pyrolysis and steam pyrolysis of soybean-cake: product yields and composition, *Pages 703-713*, Ayşe E. Pütün, Esin Apaydin and Ersan Pütün

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A development perspective for biomass-fuelled electricity generation technologies. Economic technology assessment in view of sustainability: Roland V. Siemons, In Press, Corrected Proof, Available online 17 May 2003

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Volume 28, Issue 9, Pages 1325-1489 (July 2003)

Combustion of jojoba methyl ester in an indirect injection diesel engine, *Pages 1401-1420*, M. Y. E. Selim, M. S. Radwan and S. M. S. Elfeky

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Volume 16, Issues 1-4, Pages 611-1283 (4 January 1999)

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Journal of Energy Resources Technology

Volume 123, Issue 1, pp. 1-103 (March 2001)

Transportation Fuel Substitutes Derived From Biomass

S. Gouli, A. Serdari, S. Stournas, and E. Lois, pages 39-43

Volume 122, Issue 4, pp. 169-248 (December 2000)

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Journal of Engineering for Gas turbines and Power

Volume 123, Issue 3, pp. 481-712 -- July 2001

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Volume 123, Issue 2, pp. 265-475 -- April 2001

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A. Serdari, K. Fragioudakis, S. Kalligeros, S. Stournas, and E. Lois, pages 624-631

Volume 122, Issue 2, pp. 185-364 -- April 2000

Preliminary Economics of Black Liquor Gasifier/Gas Turbine Cogeneration at Pulp and Paper Mills

Eric D. Larson, Stefano Consonni, and Thomas G. Kreutz, pages 255-261

Volume 121, Number 3 -- July 1999

Combined Biomass and Black Liquor Gasifier/Gas Turbine Cogeneration at Pulp and Paper Mills, E. D. Larson, T. G. Kreutz, and S. Consonni

Volume 121 - Number 1 -- January 1999

A Numerical Analysis of the Emissions Characteristics of Biodiesel Blended Fuels, C. Y. Choi and R. D. Reitz

A Small Scale Biomass Fuelled Gas Turbine Engine

J. D. Craig and C. R. Purvis