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Production of synthetic fuel hydrocarbons from biomass using the Prado-Wolan Fischer-Tropsch process

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Abstract:

The Fischer-Tropsch process was developed in Germany in the 1920's to produce automotive fuels such as gasoline using coal as a raw material. The process was used in Germany during the 1940's to produce gasoline for the war effort, since Germany had an ample supply of coal, but no petroleum. At the end of the war, the process was abandoned due to its relatively high cost and the availability of cheap petroleum.

The Fischer-Tropsch process was used again many years later in the Republic of South Africa. During the 1970's the United Nations imposed an oil embargo against South Africa because of apartheid. South Africa found itself in the same predicament as Germany 35 years earlier: no petroleum but plenty of coal. As a result, a Fischer-Tropsch plant was built in South Africa to produce gasoline and related transportation hydrocarbons such as diesel fuel and kerosene, using coal as raw material. At this time, South Africa no longer faces an oil embargo. But the original Fischer-Tropsch plant built by SASOL in 1976 is already paid for, and because of recent increases in world petroleum prices, it is actually making money. In fact, a major capacity expansion is now underway because of the current extremely high oil prices.

The Fischer-Tropsch process has been in operation at SASOL in South Africa for 30 years now and is a well established and well known process. But it is well known only to SASOL's technical staff in South Africa. SASOL has not shown any interest in licensing its technology, and until fairly recently, this process was virtually unknown in the United States.

Two local chemical engineers, Dr. John Wolan and Tino Prado, P.E, have teamed up to commercialize this technology in the United States using biomass feed such as agricultural wastes, and fast growing agricultural commodities like pine trees, miscanthus, willow, aspen, switchgrass, and energy cane. This paper will report their progress.

The problem:

Because of recent increases in energy prices in general, and petroleum prices in particular, there is a strong movement to develop alternate energy resources at lower cost. At the time this presentation was written (May 2008), petroleum was selling at \$120 a barrel. Furthermore, although the United States has not signed the Kyoto Protocol, there is nevertheless a strong trend toward “carbon neutral” energy production. This has translated into a great interest in renewable energy, particularly from biomass such as agricultural wastes, and fast growing agricultural commodities like pine trees, miscanthus, willow, aspen, and energy cane.

The interest in renewable energy has been temporarily directed to the ethanol-from-corn business. Yet, most authorities on this subject now agree that producing ethanol from corn requires more energy than the energy derived from the combustion of ethanol. Furthermore, ethanol contains less energy on a volume basis as compared to either gasoline or diesel fuels. Also, ethanol is hygroscopic which implies problems in its transportation, storage, corrosiveness and use. The only reason ethanol from corn seems so popular in the United States today is because other alternatives were not available and due to the massive subsidies offered by the federal and State governments. Essentially, the ethanol business has become a form of corporate welfare for corn farmers. To add insult to injury, the higher demand for corn has pushed the price of corn and similar agricultural commodities to very high levels, leading to hunger in many parts of the world.

Another fuel which has received a great deal of attention is biodiesel. While biodiesel is technically a superior fuel, its production is not economic either and also depends on subsidies from the government to exist. In the long run, biodiesel does not make economic sense and will eventually disappear. The demand for the production of biodiesel has also contributed to recent increases in food prices.

The attention of the market has recently focused on “cellulosic ethanol”. This implies the production of ethanol from biomass containing cellulose. The most common route to cellulosic ethanol is via biological conversion of cellulose into ethanol. While the jury is still out on the outcome of this technology, many experts have serious doubts regarding the technical and economic viability of this process. Even if cellulosic ethanol were technically and economically feasible, there still remain the basic problems of hygroscopicity, low energy content and corrosive properties which characterize the use of ethanol as an automotive fuel.

The Fischer-Tropsch process, however, can solve our fuel predicament. It is a mature process, and although originally based on coal as raw material, it can now utilize biomass as the feedstock. Several organizations in the USA and Europe are currently doing research and development in this area, but no one has yet built a full-scale commercial plant.

Prado Technology Corp. and Wolan & Associates LLC have combined their experience in the Fischer-Tropsch process to enable the recently formed joint venture to offer a technology package aimed at the eventual construction of a hydrocarbon fuels plant. A principal of Prado Technology Corp, Mr. Tino Prado, P.E., worked in the design of the original SASOL plant in South Africa in 1976. Dr. John Wolan, principal of Wolan & Associates, has done extensive research in catalyst development for optimizing the production of hydrocarbons via the Fischer-Tropsch high pressure synthesis reaction.



Dr. Franz Fischer



Dr. Hans Tropsch

(1)

History of the process

In 1925, Professor Franz Fischer, founding director of the Kaiser-Wilhelm Institute of Coal Research in Mülheim an der Ruhr, Germany, and his head of department, Dr Hans Tropsch, applied for a patent describing a process to produce liquid hydrocarbons from carbon monoxide gas and hydrogen using metal catalysts. The hydrocarbons synthesized in the process are made primarily of liquid alkanes, also known as paraffins. Other by-products are olefins, alcohols, and solid paraffins (waxes).

The required gas mixture of carbon monoxide and hydrogen, referred to as synthesis gas, is created through a reaction of coke or coal with steam and oxygen, at temperatures over 900 degrees Celsius. In the past, town gas and gas for lamps were a carbon monoxide-hydrogen mixture, made by gasifying coke in gas works. In the 1970s it was replaced with imported natural gas (methane). Coal gasification and Fischer-Tropsch hydrocarbon synthesis together bring about a two-stage sequence of reactions which allows the production of liquid fuels like diesel and petrol out of the solid combustible coal.

Fischer-Tropsch Synthesis took its first serious place in industry in 1935 at Ruhrchemie in Oberhausen, now the Ruhrchemie site of the Celanese AG chemical company. By the beginning of the 1940s, some 600,000 metric tonnes of liquid hydrocarbons were produced per year in German facilities, made from coal using Fischer-Tropsch Synthesis. Licensed by Ruhrchemie, four facilities in Japan, as well as a plant in France and in Manchuria, were in service. After World War II, competition from crude oil made petrol production from coal unprofitable. The only new production facilities were in South Africa, built for political reasons starting in 1950 in Sasolburg. Currently, the three plants operated by Sasol Synfuels fulfill over 30 percent of South Africa's diesel and gasoline needs, processing 45 million metric tonnes of coal per year. (1)

The SASOL case.

SASOL is the only full-size commercial Fischer-Tropsch plant in operation and has been in continuous operation for the past thirty years. It has been a successful profit making venture, and it is currently undergoing a major capacity expansion. Because of these factors, we will examine the details of its operation, use this information as background for our discussion, and validate our prediction of the technical and economic feasibility of this technology. .

The most extensive production of synthetic liquid fuels today is accomplished via Fischer-Tropsch reactions at the South African Sasol complexes. In operation since 1955, Sasol I, produces motor fuels, liquid byproducts, and industrial gas from coal. Dry ash, oxygen-blown Lurgi gasifiers generate some 10^7 m³/day of raw synthesis gas from which about 850 t/d of liquid fuels are manufactured, equivalent to 1.25×10^6 L/d of gasoline, together with about 1.7×10^6 m³/d of 19MJ/m³ medium-CV gas. Second generation plants, Sasol II and Sasol III, each with an output of approximately 8×10^6 L/d (50 000 bbl/day) of motor fuels have been built. Sasol II, started up its initial production of motor fuels about mid-1981, with full capacity achieved by the end of 1982. Sasol III, identical to Sasol II and located adjacent to it, started up in 1985.

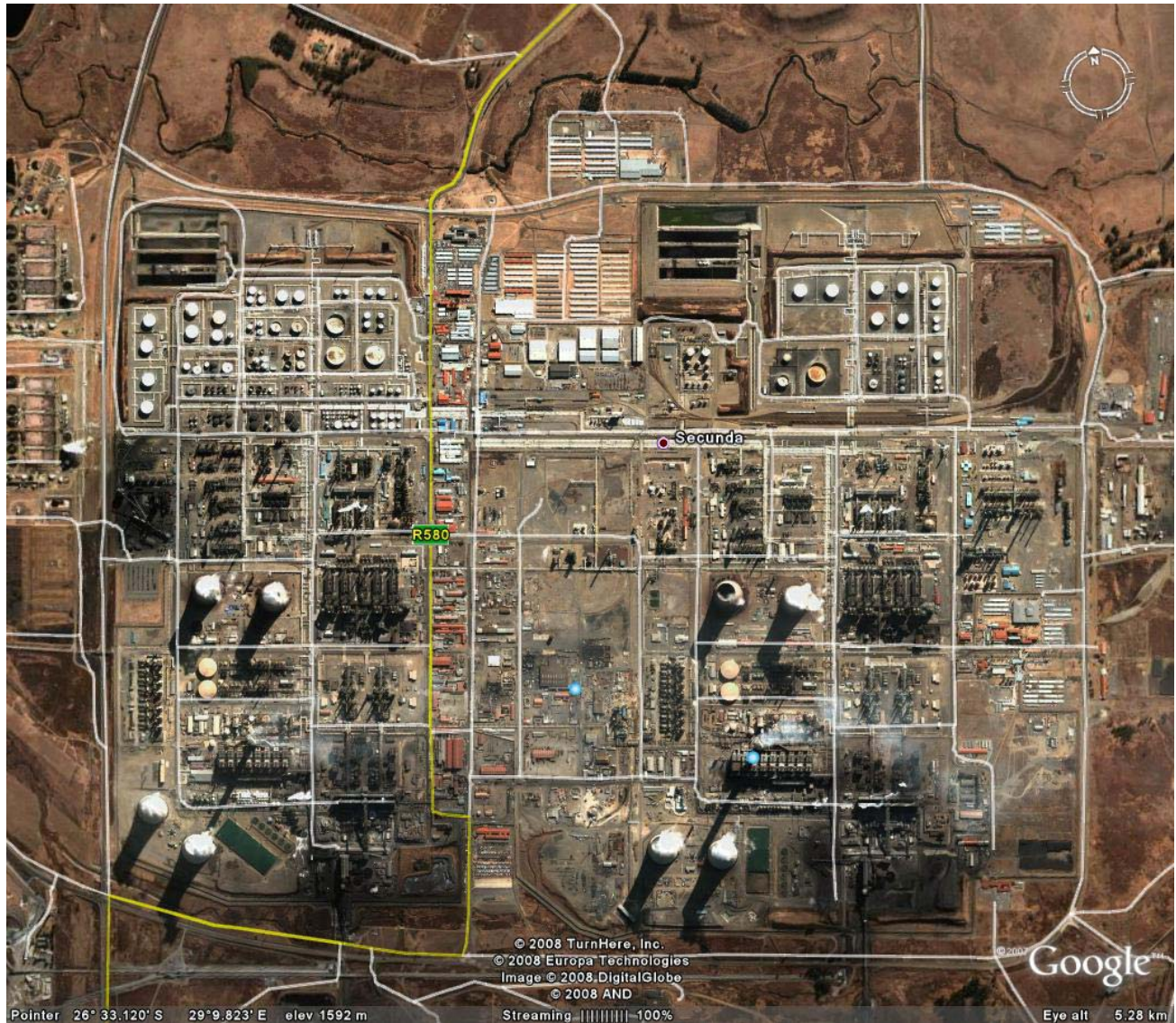
At Sasol I there are 13 Lurgi gasifiers each about 4 m in diameter and operating at a pressure of 2.9 Mpa and producing a total of about 10^7 m³/day of syn gas. This gas is quenched and scrubbed for removal of particulate matter, tar, and ammonia, following which hydrogen sulfide and carbon dioxide are removed by the Lurgi Rectisol system. At Sasol I two kinds of Fischer-Tropsch synthesizers operate in parallel: the Arge system, which employs a pelletized iron catalyst in a fixed bed tubular reactor, and the Synthol system, which uses a promoted iron catalyst powder in a circulating entrained flow design. The fluid bed system operates at higher temperatures, has a greater output per reactor volume, and is useful for the production of lighter hydrocarbons. The fixed bed system is suitable for the production of higher molecular length hydrocarbons such as diesel fuel.

The Sasol II plant has a design output of about 60 kg/s of 48MJ/kg fuel, principally gasoline. This is equivalent to 2.5×10^8 MJ/d. The plant has 36 Lurgi gasifiers and incorporates many improvements gained from Sasol I. It differs mainly in that only the Synthol circulating fluid bed reactor is incorporated, for the main purpose of producing gasoline. The plant contains 7 Synthol reactors, each with a design capacity of about 3.5 times those of Sasol I or about 1.1×10^6 L/d capacity compared with 0.3×10^6 L/d. Other differences is that all of the methane and lighter gaseous hydrocarbons are steam reformed to synthesis gas. Overall thermal efficiency is considerably reduced the, but gas is not used in South Africa, and a distribution system is not in place to pipeline it. In the United States, on the other hand, both methane and gasoline are useful products, so their coproduction would be desirable.

As stated earlier the SASOL II plant has seven Synthol reactors. Fresh feed syngas mixed with 2 to 3 volumes of recycle gas enters at 160 to 200°C and about 2.2 MPa. The gas entrains the catalyst which is added through slide valves at 340 to 350°C. The suspension enters the fluidized bed reaction section where the Fischer-Tropsch and the gas shift reactions proceed at a temperature of from 315 to 330°C. Heat released by the exothermic reactions is removed by circulating coolant within tubes inside the reactor. In Sasol I, cooling oil is circulated and subsequently used to raise steam. In Sasol II, water is the coolant, and high pressure steam is generated directly. Some of the steam is used to preheat the gas fed to the reactor. The mixture of product, reactants, and catalyst enters the catalyst hopper where the decreased gas velocity causes most of the catalyst to settle out. The gas then passes through two banks of internal cyclones in series which separate out the remaining catalyst from the off gas. The off gas is scrubbed with cooled recycle oil to condense out the heavier hydrocarbon products. The vapors are then further cooled and washed with water in a tower where the light oil and aqueous chemicals are condensed and separated from the remaining light gas. Some of the gas is recycled, and at Sasol II the remaining "tail gas" goes to a gas reforming unit for conversion back to carbon monoxide and hydrogen. Alternatively, this tail gas could be converted to SNG or used directly. (2)

The SASOL II project engineering was done by Badger Engineers in Cambridge, Massachusetts, and one of the authors of this paper, Tino Prado, was a member of the project design team in 1975.

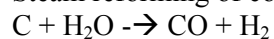
Aerial view of the SASOL II plant in Sasolburg, Republic of South Africa:



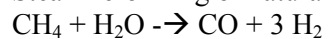
(3)

Chemical reactions:

Steam reforming of coal:



Steam reforming of natural gas (methane):



View of the SASOL II refinery in Sasolburg, Republic of South Africa



(3)

Current developments.

Two years ago, the U.S. Department of Energy published a technical paper claiming that the Fischer-Tropsch process was not economically viable because petroleum would have to sell for at least \$60/barrel, an unthinkable number at that time. Well, today (May 2008), oil is being sold for 125/barrel, well beyond the minimum figure imagined by the US DOE!

Because of the current interest in renewable fuels and the predicted future increases in fuel prices, the co-authors of this paper, Dr. John Wolan and Tino Prado, P.E. have joined forces to assemble a technology package to convert syngas into mixed hydrocarbons. The syngas would be produced by the Pearson Reformer, supplied by Pearson Technologies Inc. of Baton Rouge, Louisiana.

The Pearson reformer is different from other reformers in that it is of the “indirect” type, meaning that the syngas and the flue gases are kept separate. Therefore, there will be no contamination with nitrogen and CO_2 , a major problem with the traditional direct gasifiers.

The Prado-Wolan Fischer-Tropsch (F-T) reactor system features a bed of granular catalyst through which the syngas is circulated. The heat produced by the exothermic reaction is removed by boiling water. The steam generated is used for heating various operations in the plant. Mixed hydrocarbons leaving the F-T reactor are sent to a condenser where all hydrocarbons over the C_4 range are condensed. The light hydrocarbons (C_1 –

C₃) and the unreacted syngas can be either be sent to a secondary reformer for the production of additional syngas, or can be combusted as “parasitic” load in the reformer, which is an endothermic reaction.

At the end of the Fischer-Tropsch synthesis system, there is the possibility of providing a refinery for the separation of the various components produced by the F-T reactor. However, a complete oil refinery is a capital intensive proposition, and there is a question if economies of scale would justify this option. So, one of the options available for the operator of a small plant is to sell the mixed hydrocarbons to the nearest oil refinery as a premium crude oil, with a zero sulfur content. Another option is to build a refinery at a central location to process the output of several F-T plants. The problem faced by F-T plants using biomass as feedstock is that transportation costs and biomass availability will limit the size of a typical F-T plant. Therefore, if biomass is used as feedstock, an economic analysis will be needed to determine the optimum strategy regarding the tail end of the plant.

On the other hand, it is possible to use low quality coal or coal fines as feed for this type of plant. In fact, this is what is done at SASOL in South Africa. This option would allow a very large plant, eliminating the economies of scale problems. The downside of using coal as feedstock is that coal would produce a large CO₂ footprint, thus negating the environmental virtues of this process. However, in view of the increasing demand for liquid automotive fuels in the United States, and in spite of the politically incorrect concept of using coal, it is the opinion of the authors of this paper that coal may well be an important feedstock for the plants we are promoting.

A third alternative exists, however. It consists of using natural gas as feedstock. Natural gas is produced in numerous oil producing operations throughout the world and is known by the name of stranded gas. Many petroleum producing operations are located in remote regions and off-shore platforms where natural gas is a useless by-product and is typically flared. The use of natural gas does generate CO₂, however, this CO₂ is produced anyway by the flaring of the natural gas, so its use as feedstock would be neutral. Prado Technology Corp. has one current project and several pending projects involving the use of stranded natural gas from off-shore producers.

What the future holds

The Prado-Wolan organization is not the only one currently involved in developing and promoting Fischer-Tropsch technology. In fact, several medium and large-size companies in Europe and the USA are also involved in this business. However, the Prado-Wolan organization is the only one specifically geared to small biomass projects which the “big boys” have neglected. We believe that the market for this process is sufficiently large to allow the presence of several organizations offering their services to different markets. At this time, Prado & Wolan is proceeding with pilot plant operations which will provide the next level of scale up and demonstration of the process. We expect an exciting future.

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