

Forestry White Paper: Forest Products Waste and the Fischer-Tropsch Process

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Abstract- This white paper was originally submitted to the Allegheny Institute of Natural History and was again submitted in revised form to the Energy Institute of the University of Pittsburgh, Bradford. It describes how the Fischer-Tropsch synthesis could be appropriate as a means of disposing of waste wood and other biomass in the Bradford area. It observes that given the goal of reducing the “carbon footprint” of waste disposal, the well-documented technologies of the 1930s would be perfectly adequate and appropriate on account of their simplicity and convenience for small scale use. The carbon economy comes from the net effect of replacing new petroleum fuel with already existing biomass which derives from atmospheric carbon dioxide.

Index Terms- Fischer-Tropsch, wood gas, waste disposal, synthetic fuel, synfuel

The Bradford area is distinguished by its wood and petroleum industries. It has a refinery and vast tracts of forest that supply local lumber mills and paper making plants. It is also home to a recycling business of interstate proportions. Recycling of waste wood materials such as chips, bark and brush has been cited as one of the needs of the Bradford region. One way of accomplishing this recycling could be the conversion of its biomass into oil that could then be refined by the refinery into valuable petroleum products. This paper discusses a technology for doing this. The essence of the idea is that wood gas like coal gas or water gas is made up largely of CO and H₂, the starting ingredients in the Fischer-Tropsch process for making gasoline.

Fischer-Tropsch has been used on an industrial scale to make diesel fuel from low-

grade coal in Africa. In other parts of the world, biomass has been used on a small scale to make diesel fuel economically. However, overall interest was low. Today in 2007, Fischer-Tropsch processes are now in vogue if not in practice. There is now a website, www.fischer-tropsch.org, simply to index the bibliography of Fischer-Tropsch. The Environmental Protection Agency and the U.S. Department of Energy issue frequent reports about it as well as fund research. A Publication called *Green Car Congress* popularizes Fischer-Tropsch (F-T) as a source of Biomass-to Liquid (BTL) technology (2007). As a technology to significantly replace natural petroleum, F-T may not yet be practicable. The technology for large-scale F-T becomes ever more expensive. However on the very small scale, as a trash disposal method that reduces the “carbon footprint”, the technology of the 1930s seems appropriate because of its simplicity and low-cost. For this purpose, efficiency would be of only secondary importance. At that time operating automobiles on wood gas was actually practiced. F-T supplied much of the gasoline needed for the WWII German war effort. The catalysts of the day were cheap and expendable. They would be so today. Consequently, unlike the case of high-efficiency catalysts proposed for large-scale F-T, catalyst poisoning need not be regarded as a serious issue.

The term Fischer-Tropsch is applied to a variety of condensation processes that synthesize petroleum substitutes. The

original term, Fischer-Tropsch Synthesis, describes a process originated by F. Fischer and H. Tropsch published in 1923. It is still the most common version of the process and is discussed in most courses in Organic Chemistry. It was an outgrowth of the illuminating gas industry. In the Fischer-Tropsch process, water gas is produced by combining hot steam with organic material. The result, primarily CO and hydrogen is then exothermically condensed with a catalyst into hydrocarbons. The chemistry is similar to alkalation in conventional petroleum refining. The reaction conditions resemble those used for hydrocracking or catalytic reforming in petroleum refining. Hence the technology is compatible with the construction of equipment available to the petroleum industry. The raw materials for F-T are CO and H₂. The source is immaterial. Wood gas could be substituted for water gas as a feedstock for the process.

Fischer-Tropsch is attractive as a means of utilizing waste wood because, unlike fermentation-type processes as would be used to form raw material for ethanol and esterified "Biodiesel" products, there is no need to separate the cellulose from the lignin. Another attractive feature is that the products of Fischer-Tropsch are alkyl rather than aryl and suited to processing in a conventional refinery. Different catalysts and conditions make the Fischer-Tropsch (F-T) product prior to fractionation resemble either gasoline or diesel oil. When iron is used as the catalyst, the product resembles gasoline. Because iron is cheap, the cost of renewing the catalyst would be much less than with other variants of the process.

Process Description

The Fischer-Tropsch reaction itself involves primarily carbon monoxide and hydrogen as its feedstock. These are usually obtained through the partial combustion of an

organic material. This step is termed gasification. This gasification process needs to be tailored to the material at hand. Once that is accomplished, the Fischer-Tropsch process itself does not care where the hydrogen and carbon monoxide came from. Since the starting organic material has traditionally been coal, I will describe a model process for coal discussed by Nowacki (1979) for the purposes of calculating Fischer-Tropsch economics. The pressures and temperatures used are much higher than needed or than would be appropriate for F-T as a small scale waste disposal process.

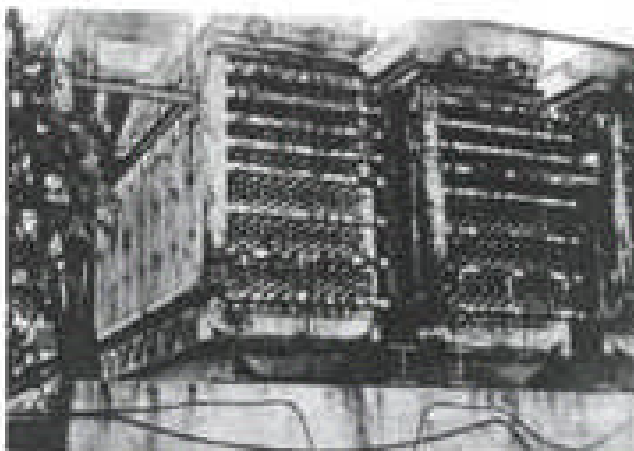
In the process considered by Nowacki, the gasification of coal was accomplished using a "bi-gas" system of two stages. In the first stage coal was heated to 3000 °F and steam was admitted at 1300 psig. The second stage of the reaction took place separately at 1700 °F. The products of gasification were gas and char. The gas was then scrubbed to remove acid gasses (carbon dioxide and sulfur products).

The next step was to correct the ratio of hydrogen to carbon monoxide. Water was reacted with the gas in a shift converter. The final feedstock to the Fischer-Tropsch reactor was 30.9 mol % CO and 56.5 mol % hydrogen. A methane reformer was used following the shift converter to further reduce the amount of CO and provide the 1300 °F steam needed in the first step. Ahead of the inlet to the Fischer-Tropsch reactor were guard reactors that used zinc oxide at 571 °F to remove sulfur to protect the catalyst. The spent zinc oxide was periodically replaced. The Fischer-Tropsch (F-T) reactor itself was a fixed bed reactor operating at 556 °F and 407 psig. The catalyst used was iron, the original F-T catalyst. The product of the F-T reactor was fractionated into a variety cuts which were then further processed. One of these products was light diesel fuel. Using the market price

of this as an index, it is possible to characterize Nowacki's financial cost accounting in a few words: At the 1970 price level, the process would break even if the price of light diesel was greater than \$5.50 / bbl. Since a barrel (oil) is 42 gallons, this is a remarkably low price, less than 14¢ per gallon, by today's standards. Nowacki's model process required paying for the coal (at the price level of the time). It also was typical and traditional in that it primarily aimed to produce high-octane gasoline. Newer catalysts and types of reactors have

increased reaction rates and average chain length.

There are various types of F-T reactors. The fixed bed reactor using iron as a catalyst may not be the most economical to operate in today's fuel market although it is probably well-suited to waste disposal applications because of its simplicity and that fact that it needs no power to operate. This type of reactor was used by Fischer and Tropsch and was the basis for German synfuel production in WWII.



Fischer-Tropsch Unit at Leipzig Gas Works
Reported by W.A. Home and J.P. Jones on behalf of U.S. Technical
Industrial Intelligence Committee, COG Item No. 30, File No. J11V140
July 22, 1948

Fixed bed reactors using iron as the catalyst at the Leipzig Gas Works during WWII.

Slurry reactors for F-T appeared in the 1930s although the first patent for one was issued in 1928. In slurry reactors the gas to be reacted is forced through an agitated slurry consisting of an oil containing a suspended catalyst, usually cobalt in a particle size of 2.5 to 254 microns. Iron can also be used although cobalt gives higher reaction rates. Iron was used in Germany during WWII. Iron produces high-octane number components while cobalt produces

high-cetane number components. Cobalt catalysts in a slurry reactor have produced reaction rates as high as 3 kg product per kg catalyst per hour at 225 °C. This is about seven times the rate for iron (Sapienza et al, 1981). Fluidized bed reactors have also been used. Various tar crackers have been developed to allow total conversion of the initial coal feedstock. Total conversion may not be worthwhile for waste disposal.

Fischer-Tropsch Using Wood

The gasification of wood has a long history. Wood gas was one of the first “syngases”. As with coal, wood is reacted with steam. This takes place at temperatures above 700 °F. The gasification may take place in two stages. In the first stage, pyrolysis, aromatic hydrocarbons are released along with a variety of other compounds. The char from the first stage is then reacted with steam to produce syngas. The gas produced by the two stage process is essentially free of tar. Gasification of wood chips using a fluidized bed is commercially operational in Güssing Burgenland, Austria. The raw wood gas contains typically 18-27% CO and 14-21% hydrogen. It is 42-51% nitrogen. The high nitrogen content differs from coal-produced syngas.

The production of useful wood gas need not be highly complicated as is illustrated by two examples of wood powered vehicles below.



In the Depression Era of the 1930s, wood powered automobiles were produced and in use. These operated conventional engines off of wood gas produced under the hood.



A home-brew farm vehicle that runs on wood appears to have been made by attaching an antique wood gas converter onto a small truck. Wood undergoes partial combustion in the large cylinder at the left.

In March 2003 ECN Biomass in the Netherlands (Boerrigter, 2004) reported a successful test of a system designed to efficiently convert biomass including wood chips. The nitrogen was allowed to pass through the F-T reactor and appears to have merely acted as a diluent. The biomass was reacted with a mixture of steam and oxygen. Another test configuration used a low temperature gasifier and a tar cracker. It gave comparable results although the first system was reported as preferable in some ways. A feature of both configurations was a water scrubber to remove ammonia and HCl. A highly desirable feature of the products was their low sulfur content.

Wood and forest waste are currently used for heating homes in the Bradford area. A recent development in the area of wood heaters is the gasifier type which converts the wood into wood gas and then burns the wood gas to heat water for radiators. Since this type of heater produces wood gas, conceptually it could produce synfuel were some or all of the wood gas directed into an F-T reactor. The best scenario is one where the reactor operates at atmospheric pressure. Atmospheric pressure reactors were used by the Germans, for example the ones at

Leipzig shown above. Those reactors operated at 390°F, a good oven temperature. Since the reactions is exothermic, the heat from the reactor is available for use.

Conclusion

The Fischer-Tropsch process seems suited to the job of recycling Bradford's forest products waste. As described, diesel fuel and other valued hydrocarbon products can be produced by refining F-T oil produced from wood chips and other biomass. Once the material is collected and dried, the production sequence involves three steps: gasification, Fischer-Tropsch synthesis followed by conventional petroleum refining. The F-T process is exothermic and can be used to power other processes as well. The F-T oil produced in the second step could be sold to a local refinery and blended with other feedstocks.

Research is needed to identify the most economical process configuration to meet Bradford's local needs. While the exact configuration of the F-T reactor depends on the choice of the ultimate products to be sold, the configuration of the gasifier depends on the material being gasified. While it is possible to make gasifiers that work with "biomass" generally, not all waste wood has the same proportions of sulfur, water and nitrogen for instance. Optimization of the gasifier for locally produced wood chips could possibly eliminate the cost of unnecessary scrubbers or other pre-treatments. This would increase the economic vitality of the F-T recycling endeavor.

More advanced research could address issues of improving overall efficiency through incomplete gasification of wood. Supplementing conventional F-T with ring-breaking of aryl creosote products and aldol-type condensations fuel at least one's imagination.

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