

FISCHER-TROPSCH PRODUCTS FROM COMPACT REACTOR AND HIGH-TEMPERATURE IRON CATALYST

Albin Czernichowski and Mieczyslaw Czernichowski

ECP – GlidArc Technologies, 45240 La Ferté St Aubin, France

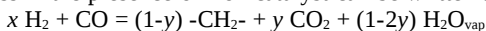
Introduction

GlidArc plasma technologies have been designed and developed by ECP for many years to convert waste carbonaceous liquids, vapors or gases into clean synthesis gas (syngas). For example, the waste glycerol stream from Biodiesel industry can be made valuable by syngas generation¹. Other wastes like bone oil, tallow, lard or other animal fats, used vegetable oils, waste alcohols, wood oil, etc. have also been successfully processed into clean syngas during preliminary tests. A simple gasification or pyrolysis of waste carbonaceous matter can be used for the separation of inert solids, and very dirty "producer gas" can then be selectively converted and reformed into clean syngas using GlidArc Technology².

Consequently such clean synthesis gas generation opens a paradigm to the synthesis of extra-clean transportation fuels at a scale adapted to local resources via Fischer-Tropsch (FT) process. The main advantage of such biobased FT fuels is that they constitute "drop-in replacements" for fossil Diesel oil, gasoline or kerosene, hence no modifications are needed in engines, vehicles and distribution systems. The biofuels can also be used as additives to various types of engine fuels to improve certain fuel properties, i.e. cleanliness and cetane number. Another important advantage is their much lower toxicity for man and the environment compared to conventional fuels.

Process Chemistry, Energetics, and Reactor

These points were described in our previous contribution³. The FT process in the presence of Iron catalyst can be written as:



(1)

where $y = (2-x)/3$.

The FT synthesis is quite exothermic. An average standard enthalpy of reaction (1) for $x = 1$ and $\text{C}_{10}\text{H}_{20}$ to $\text{C}_{16}\text{H}_{32}$ range is equal to -110 ± 2 kJ per mol of converted CO. Therefore any FT reactor has to be intensively cooled. Since 1930's classical tubular fixed bed structures are put inside huge pressurized steel vessels cooled by steam. For Co-catalyst working at 250°C the steam pressure is up to 40 bars while for our Fe-catalysts working at 350°C the corresponding pressure would be 160 bars. ECP has proposed therefore another way of the process cooling by inserting the FT reactor tubes inside well conducting metal plates that are in a good thermal contact with other metallic plates devoted for intensive heat removal⁴. Figure 1 presents a principle of our reactor.

A FT catalyst fills separate tubes inside a metallic "Reactive" plate (R). A coolant crosses a similar plate called "Cooling" (C). Any number of R and C plates can be assembled in a sandwich.

¹ A. Czernichowski, M. Czernichowski, J.P. Sessa, Waste glycerol conversion into syngas, *235th National Meeting of ACS, New Orleans, LA, 2008*, 2 pp preprint.

² A. Czernichowski, P. Czernichowski, Plasma-assisted selective partial oxidation of tars and other pollutants in producer gases, *this Meeting*, 2 pp preprint.

³ A. Czernichowski, M. Czernichowski, P. Czernichowski, J. Hardvigsen, Compact reactor and process for syngas to wax conversion using high-temperature Iron catalyst, *235th National Meeting of ACS, New Orleans, LA, 2008*, 2 pp preprint.

⁴ M. Czernichowski, A. Czernichowski, *French Patent No. 2824755, 2001*.

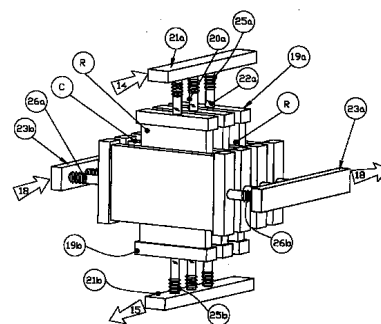


Figure 1. Principle of multiple-plate sandwich FT reactor.

This technology is ideal for small- to medium-size plants with limited local resources and land. Iron-based catalysts are ideal for low H_2/CO ratio syngas from waste biomass gasification. ECP's proprietary high-temperature catalysts used in enhanced heat-exchange configuration further contribute to size reduction of the reactor and increased productivity. The reactor can be easily assembled and disassembled at the sites where a carbonaceous feed is available. Moreover, the activation of the catalyst can be done in a separate plant, so that ready-to-use R plates can be shipped to the final user for a simple standard exchange and return of deactivated plates for regeneration; recycling is key to conservation.

Several successful tests have been performed in ECP's facility. Real syngas, for the long tests, was periodically generated from a pipe-grade natural gas using ECP's GlidArc-assisted POX reformer at close-to-atmospheric pressure. Ambient or O_2 -enriched air was used as oxidant. Resulting syngas was compressed to 150 bars and stored in several 50-L gas cylinders, and then used as a feed to supply our test FT reactors ranging from one 14-mm tube (0.2-L) to eight 20-mm tubes (two plates, 5.5-L size, see Fig. 2).

Figure 2. Two-plate, 8-tube ECP's FT test reactor of 5.5-L active catalyst volume (upper manifold).



Several Iron-based catalysts, engineered by ECP, were successfully tested under 20–25 bars. Depending on catalyst composition the system produces various synfuels. A wax-type product was derived, which could be cracked into any type of transportation fuel according to specific needs. We are producing such waxes at unusually high temperatures of 310–330°C.

High yields were observed, with single-pass CO conversion rates of 90% and high space velocities. Only a very limited amount of light hydrocarbons were generated. Figure 3 shows distillation curves of our two products.

Figure 3. Real distillation curves of ECP products (from 100-g samples).

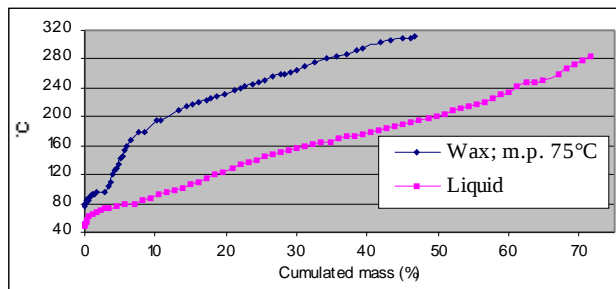


Figure 4 provides a more precise analysis of our typical wax-type product containing a large spectrum of hydrocarbons ranging from C_{18} to C_{50} molecules. Deviations of our product with respect to products synthesized using classical Iron catalysts are observed. Triple peaks of a highly specific type are evident. The strongest peak corresponds to a linear alkane (50% of mass occurrence in wax) whereas its left neighbor presents the saturated monocyclo-alkane (48%). The right peak reflects one ^{13}C natural Carbon isotope in the alkane. Although this wax has the basic characteristics of classical FT-products, it also has differentiating characteristics, which are intriguing and non-classical; this type of FT product has never been described. Further study and evaluation of this sample may provide additional direction as to the best-value applications for this type of product. Since our product does not contain any polycyclic substances, it follows that it will give very good environmental and functional performances.

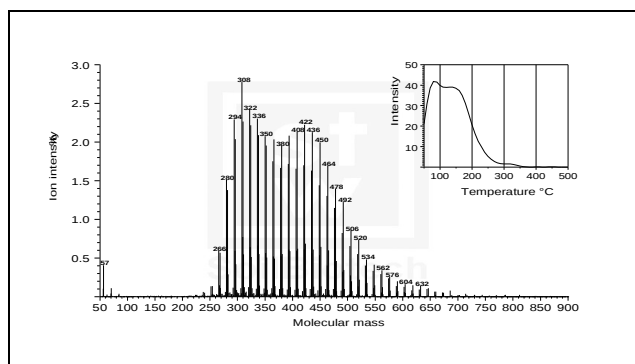


Figure 4. Py-FIMS analysis of a typical ECP wax performed by Prof. P. Leinweber and Dr. A. Schlichting in *Steinbeis-Transferzentrum Soil Biotechnology*, Rostock, Germany.

Such stable waxes can be easily and safely transported even to remote locations for a simple refining (e.g. distillation and hydrocracking) to become finished commercial fuel. Hydrocracking is a quite simple and inexpensive process (also in small scale). It would result in the final fuel containing approximately 25% long-chain alkylated monocyclic substances, and the remainder non-cyclic alkanes. Hydrocracking at the same time saturates a large proportion of any existing double bonds in the fuel. Long-chain alkylated monocyclic substances have a low toxicity; in fact similar substances can be found in food. The cyclic structures will have positive impact on several functional properties in an engine. An increase in molecule size will also give a corresponding increase in energy content per liter of fuel. Larger-size molecules also improve lubricity and a content of cyclic substances will improve cold flow properties.

Conclusions

Based on a series of tests it is concluded that the new type of FT reactor and ECP's proprietary Iron-based catalysts can produce up to C_{50} waxes at unusually high synthesis temperatures (310-330°C). Use of ECP's proprietary (and unconventional) catalysts during synthesis yields a final product that can be either light or heavy, according to local requirements. Single-pass conversion rates of CO, attaining 90% yields are potential at high space velocities. Additionally, due to efficient heat removal, the ECP FT reactor can be significantly reduced in size provisioning the following additional benefits:

- Easily transported, assembled/disassembled,
- Excellent accessibility for catalyst exchange,
- Uses inexpensive, environmentally friendly Iron catalyst.

Moreover, the catalyst activation can be accomplished at a separate facility so that ready-to-use R-Plates can be batch produced and inventoried to allow prompt shipment to the final user for a simple core exchange of deactivated R-Plates for regeneration (like cartridges for printers). Handling in this manner shall offer protection of ECP's intellectual property concerning catalyst formulation, preparation, reduction, and final activation. It also opens GlidArc-assisted syngas generation to small or medium-sized FT facilities in local markets and biomass resources. Operation of these 'Systems' shall not require highly trained or specialized staff, nor will a separate plant be required for spent catalyst exchange; it can be performed on-site. The time necessary to start producing syngas at optimal level is also substantially reduced to only few hours. "Ready-to-Use" R-plates shall be manufactured, inventoried, and easily shipped *via* ordinary drayage. R-Plates heavier than 300 kg are not anticipated, and one ECP R-Plate shall be up to thousand times lighter than a contemporary FT reactor.

Efficient heat removal not only allows reactor size reduction, but also provides for a FT synthesis temperature increase from 230°C up to 330°C. Such temperature increase improves process kinetics by factor of three. Alternatively, three times more product can be generated at the same temperature, or the kinetics may be maintained by reducing the catalyst activity by factor of three. Such a reduction in catalyst activity should offer greater resistance to poisoning and longer catalyst life. By increasing the temperature from the "classical" 230°C up to unconventional temperatures of 330°C, the overall efficiency of power generation (using by-product heat from syngas reactor cooling) shall also be increased by 20%. Such Combined Heat and Power (CHP) generation accomplished at smaller, local syngas production site(s) shall substantially contribute to the overall economic viability of biomass to transportation fuels conversion.

Though our waxes were made from real syngas (produced from natural gas), industrial syngas can be manufactured from almost any renewable carbonaceous matter using first a simple gasifier and then thoroughly converting the resulting dirty producer gas into very clean syngas in a second-step GlidArc-assisted unit².

Our FT fuels will be at least an order of magnitude less toxic than conventional Diesel oil, due to the extremely low content of aromatics, polyaromatics, naphthenics, and other potentially toxic substances in the fuels, free from sulfur and nitrogen, and having excellent functional properties.

Acknowledgement. Remarks of Per Hedemalm (Áibmi AB, Sweden) on Py-FIMS analysis results are highly appreciated.