

## Are Fischer–Tropsch waxes good feedstocks for fluid catalytic cracking units?

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### Abstract

The potential of a highly paraffinic Fischer–Tropsch synthesis (FTS) wax as a feedstock for Fluid Catalytic Cracking (FCC) has been evaluated. A once-through microriser reactor was used to mimic realistic FCC conditions. FTS waxes are indeed attractive feedstocks for FCC. As a result of its high paraffinicity an interesting spectrum of products can be obtained by tuning process conditions and catalyst formulations. A high gasoline fraction (70 wt%) with an apparent high-quality motor octane number can be obtained. Also a relatively good diesel is expected. Due to the absence of sulfur and nitrogen in the feed extremely clean transportation fuels can be obtained that are additionally low on aromatics. The combination of an equilibrium catalyst with a steam-deactivated ZSM-5 additive yields high amounts of propene (16 wt%), isobutene (7 wt%) and *n*-C<sub>4</sub>-olefins (8 wt%).

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### 1. Introduction

There is a trend in both environmental legislation and strategies of oil companies to alter the processing of conventional feedstocks into more sustainable renewable (and preferably cleaner) feedstocks. Synthetic fuels produced by the Fischer–Tropsch Synthesis (FTS) process are highly paraffinic and are, as a consequence, very well suited for the diesel market. The contents of sulfur, nitrogen and aromatic species are exceptionally low and, hence, expensive purification operations are redundant. Inherent to modern Fischer–Tropsch Synthesis processes is the production of large amounts of long-chain paraffins that do not possess the correct boiling point for transport fuel applications. Processing these waxes in a hydrocracking unit is in that case the currently applied option. Although it yields an appealing product spectrum for the production of diesel, for gasoline this is a less attractive option as a result of the

relative low motor octane number due to its relatively low extent of branching and high level of saturation with H<sub>2</sub>. In general, the produced gases (C<sub>1</sub>–C<sub>4</sub>) are saturated and are also less valuable than their unsaturated conjugates. In addition, the high-pressure operation and the high hydrogen consumption of hydrocracking units are economically less attractive.

Processing Fischer–Tropsch waxes in a Fluid Catalytic Cracking (FCC) unit may be an interesting option. Currently, the FCC process is a key operation in the production of gasoline and LCO (an important diesel blending component) from heavy oil fractions. Essentially, the conventional operation of an FCC unit does not give the right products in terms of sulfur-content (for gasoline and diesel applications) and cetane number (for diesel applications). As a consequence, operation of the FCC process with conventional fossil feedstocks might not be attractive any more in the future from an environmental and economical viewpoint. Therefore, the FCC process may be adapted (revamped) to process other feedstocks and to produce another product spectrum. Here lies a real challenge for the

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FCC process. Is an FCC unit capable of processing other (more modern) feedstocks? In view of the large recent investments, it was decided to assess the potential of converting a Fischer–Tropsch wax under realistic FCC conditions into attractive products.

## 2. Experimental

The cracking experiments are performed in a laboratory-scale once-through microriser reactor that simulates ideally Fluid Catalytic Cracking conditions. A schematic overview of this device is shown in Fig. 1. The reactor that operates in the isothermal plug-flow regime consists of mountable loops with an internal diameter of 4.55 mm and the reactor length can be varied from 0.2 to 33.2 m (=50 ms–8 s).

The Fischer–Tropsch wax is obtained in two fractions from the pilot plant of a refiner. The “Fischer–Tropsch Light Fraction” (FT-LF,  $\sim C_5$ – $C_{30}$ ) is in the liquid state at standard temperature and pressure, whereas the “Fischer–Tropsch Heavy Fraction” (FT-HF,  $\sim C_{13}$ – $C_{50}$ ) is a solid under these conditions. Due to the high viscosity of the FT-HF at 100 °C (maximum temperature of the syringe pump) it is not possible to process this feed as a pure substance in the microriser reactor. Therefore, a blend has been made with 60 wt% ‘conventional’ Hydrowax and 40 wt% FT-HF. The cracking performance of the FT-HF is inferred by linear deduction of the performance of the pure Hydrowax at the same experimental conditions. It has been verified that no synergetic effects exist between the Hydrowax and FT-HF.

Three different catalyst formulations are evaluated: a commercial equilibrium catalysts “Ecat”, an undiluted

laboratory steam-deactivated ZSM-5 additive “ZSM5” and a catalyst blend of 80 wt% of the Ecat and 20 wt% of the ZSM5 additive obtained by physical mixing and denoted as “Ecat/ZSM5”. Experiments have been performed at a constant catalyst-to-oil ratio (CTO) of four. Different residence times (from 50 ms to 4 s) and different temperatures (500, 525, 585 and 625 °C) have been evaluated. Detailed information on the microriser operation, feeds and catalyst formulations can be found elsewhere [1].

## 3. Results

In Fig. 2, the simulated distillation graphs of the Fischer–Tropsch Light Fraction feed and catalytic cracking product at 525 °C and 21.2 m ( $\sim 4$  s) are shown. The FT-LF feed is well defined with *n*-paraffins lying in the gasoline ( $C_5$ : 215 °C), Light Cycle Oil (LCO, 215–325 °C) and Heavy Cycle Oil (HCO, >325 °C) boiling ranges. Circa 10 wt% of the feed consists of *n*-olefins that are observed just in advance of the *n*-paraffin peaks. Upon cracking these *n*-olefins have already been converted at 50 ms of contact time. The *n*-paraffins from the HCO fraction are fully converted. As opposed to ‘conventional’ feedstocks that contain a fair amount of aromatic species, the molecules from the ‘paraffinic’ LCO fraction display a high cracking activity. Even the upper gasoline-range molecules are cracked.

The ability of LCO and gasoline to crack is further demonstrated in Fig. 3 for the cracking of the FT-HF at 525 °C and CTO 4 (coke not shown). In Fig. 4(a and b), the detailed distribution in the  $C_5$ – $C_{11}$  fraction and gas fraction ( $H_2$ ,  $C_1$ – $C_4$ ) are given. The figures demonstrate that the

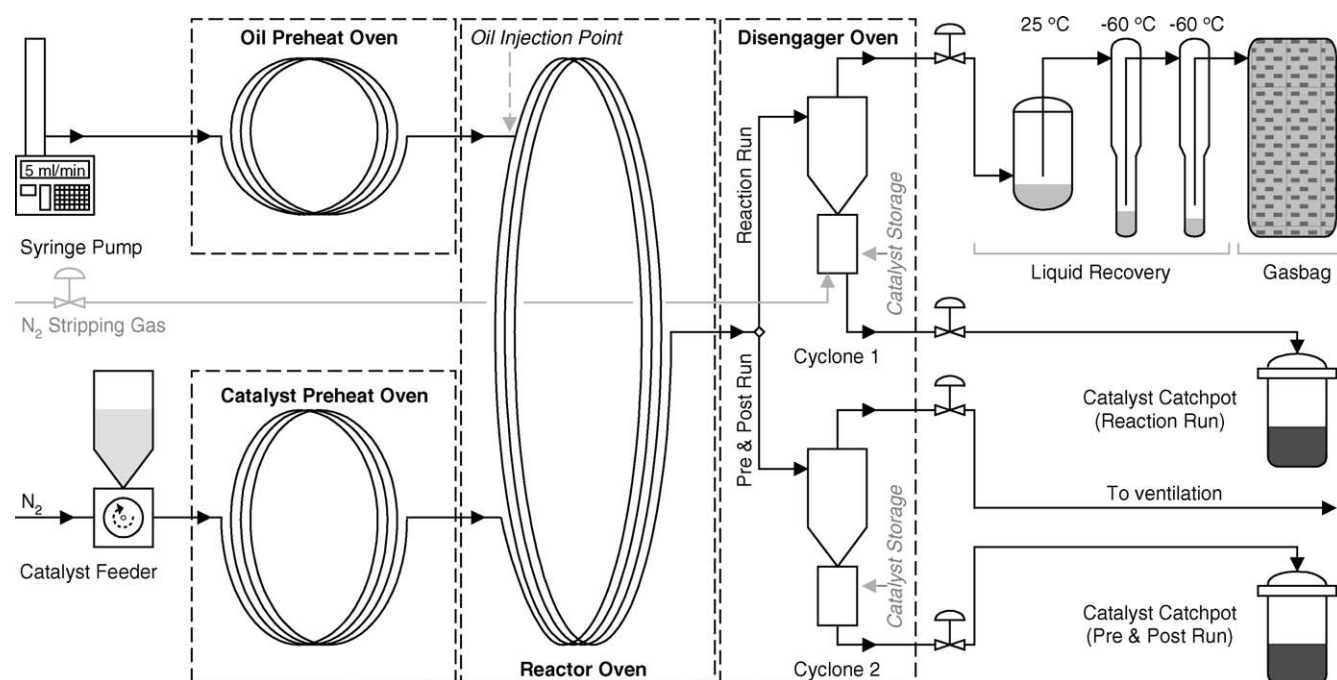


Fig. 1. Schematic overview of the once-through microriser reactor.

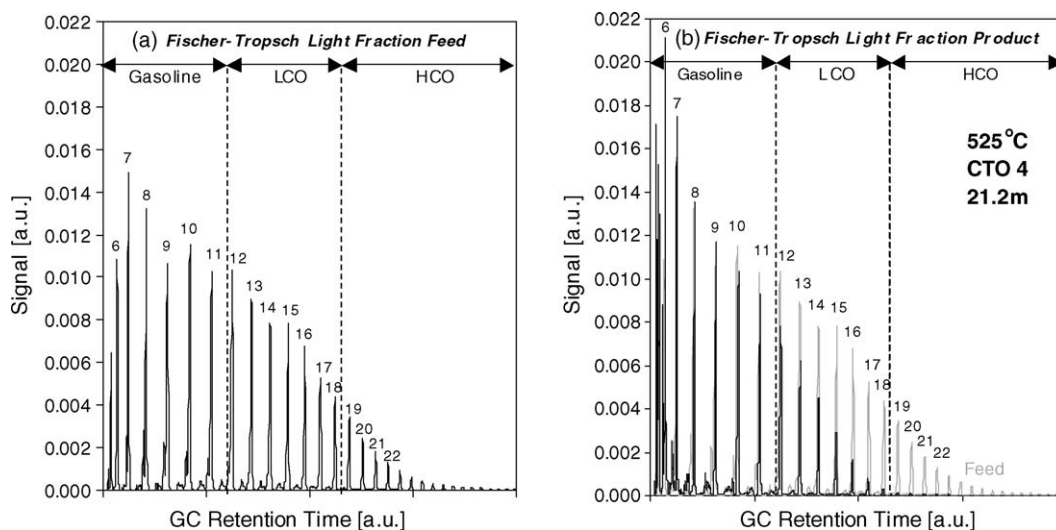


Fig. 2. (a) Fischer–Tropsch Light Fraction feed and (b) catalytic cracking product (Ecat/525 °C/CTO 4/21.2 m).

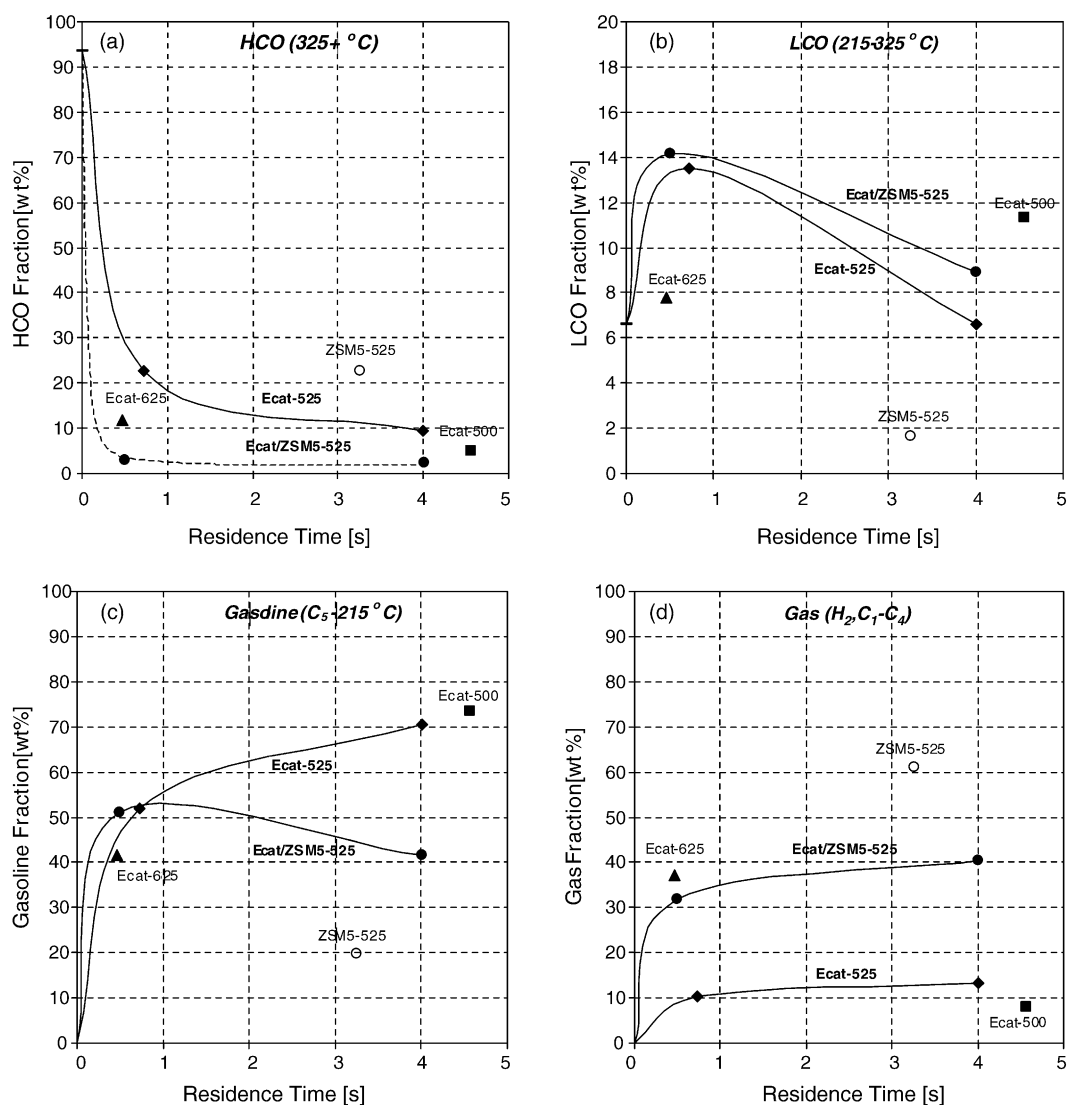


Fig. 3. Cracking of the Fischer–Tropsch Heavy Fraction at CTO 4. (a) HCO, (b) LCO, (c) gasoline, and (d) gas (H<sub>2</sub>, C<sub>1</sub>–C<sub>4</sub>). (■) Ecat-500 °C, (◆) Ecat-525 °C, (▲) Ecat-625 °C, (●) Ecat/ZSM5-525 °C, and (○) ZSM5-525 °C.

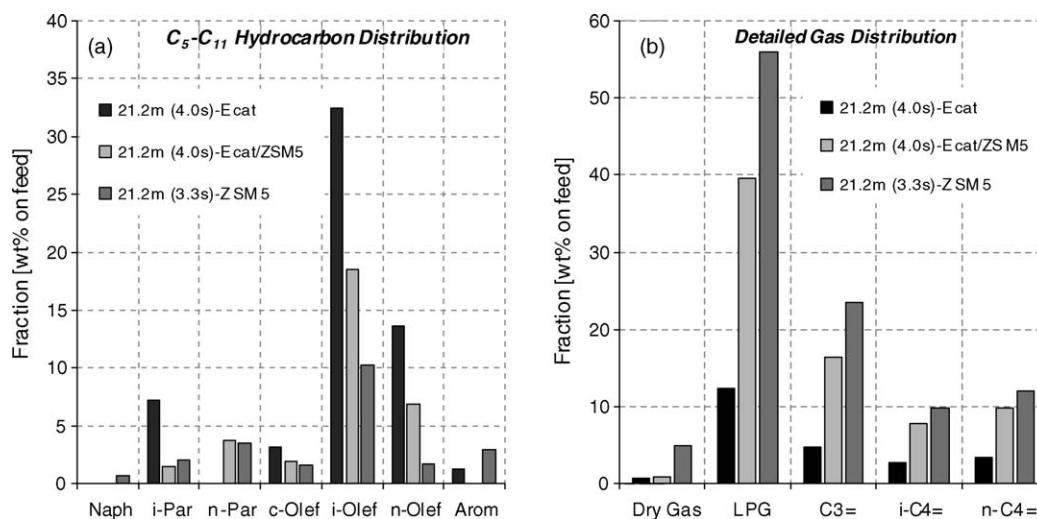


Fig. 4. Distributions in the (a) C<sub>5</sub>–C<sub>11</sub> hydrocarbon range and (b) C<sub>1</sub>–C<sub>4</sub> gas fraction.

cracking of the LCO is beneficial for the gasoline fraction, i.e. a fraction of 70 wt% can be obtained that contains high amounts of *i*-olefins and *n*-olefins. A significant amount of *i*-paraffins is formed, whereas the naphthenes and aromatics amounts remain low. The addition of the ZSM-5 additive to the Ecat enhances the conversion process. Gasoline-range molecules are cracked to gas (H<sub>2</sub>, C<sub>1</sub>–C<sub>4</sub>). As a result, a high LPG fraction is found that contains 16 wt% propene, 7 wt% isobutene and 8 wt% *n*-C<sub>4</sub>-olefins. Between the Ecat and ZSM-5 additive a synergetic effect is present, as with the undiluted ZSM5 catalyst only the conversion is remarkably reduced.

#### 4. Discussion

The high reactivity of the Fischer–Tropsch wax originates from nature of the feed. In Fig. 5, an artist's impression of the processes taking place in the conversion of a 'conventional' FCC feed and a Fischer–Tropsch wax are shown. The conventional feedstock consists of aromatic cores that are linked through (branched) paraffinic fragments. Upon cracking in the paraffinic fragments the feed molecules cleave, where the aromatics are 'uncrackable' under the conditions applied. Mono-aromatics and di-branched aromatics end up in the gasoline- and LCO fraction, respectively. Larger aromatics retain in the HCO fraction. From the small-branched LCO aromatics only the alkyl-chains will have a possibility to dealkylate from the core. This explains the low reactivity of LCO for conventional feedstocks. The properties of Fischer–Tropsch waxes are completely different. Paraffins from the LCO-range can easily crack further to gasoline and gas-range species. Applying the right process conditions enable the direction of the products spectrum towards the desired products. In other words, the cracking of paraffins obeys serial kinetics, whereas for conventional feedstocks the

relatively stable cracking intermediates (LCO and gasoline) disguise the serial kinetics network. As a result of the branching a gasoline can be obtained that is expected to possess an acceptable octane number. The degree of branching in the LCO is anticipated to be lower and is expected to possess a relatively high cetane number [1]. Due to the absence of sulfur and nitrogen in the feed extremely clean transportation fuels can be obtained that are additionally low on aromatics.

Usually, the shape selectivity of the ZSM-5 additive causes an overall reduced HCO cracking activity for 'conventional' feedstocks. The pores of the steam-deactivated ZSM-5

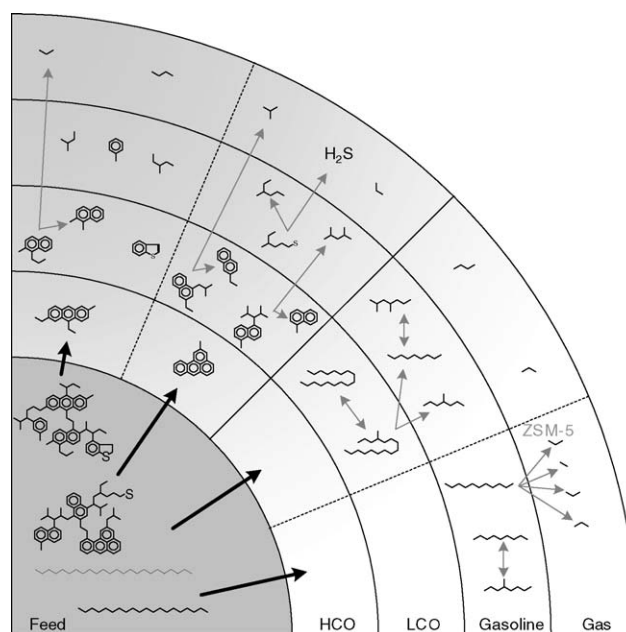


Fig. 5. Schematic representation of the  $\beta$ -scission of large aromatic and paraffinic HCO molecules. The fragments (with exception of the aromatic cores) can either be paraffins, olefins and/or carbenium ions. Serial reactions are indicated by the arrows.

catalyst are smaller than those of the faujasite Ecat zeolite, and as a consequence, larger and highly branched molecules can diffuse hardly or not into the pores of the of ZSM-5 zeolite. For this reason, the effect of ZSM-5 on the cracking of the FT-HF is much more profound than that for the conventional feeds. The pre-cracking activity of the Ecat in the Ecat/ZSM5 system cracks the large *n*-paraffins into smaller fragments that subsequently diffuse into the ZSM-5 zeolite. These linear or small-branched products undergo cracking through the  $\beta$ -scission mechanism. When the formed olefins in the ZSM-5 pores are not able to leave the channels rapidly enough they are easily activated. Gasoline-range olefins are overcracked to gas-range olefins. Due to the high partial pressure of olefins in the case of ZSM-5 this zeolite has a somewhat increased tendency to produce aromatic species. Cyclisation of olefins yields naphthenes that are precursors for the formation of aromatics.

## 5. Conclusions

The cracking of the highly paraffinic Fischer–Tropsch waxes under realistic FCC conditions has demonstrated that an interesting spectrum of products can be obtained by adapting different process parameters and catalyst formulations. The ability for LCO to crack to gasoline results in gasoline selectivities higher than those for conventional feedstocks. The amounts of aromatics and naphthenes are significantly lower than those in a gasoline derived from a conventional feedstock, but fair amounts of *i*-paraffins and *i*-olefins are formed. This indicates that the gasoline possesses an acceptable motor octane number that is low on sulfur- and nitrogen compounds. Also the diesel-range product is expected to possess good characteristics. High amounts of

light *n*-olefins and *i*-olefins are formed that can be attractive compounds for the (petro)chemical industry. ZSM-5 addition to the equilibrium catalysts enhances the production of light olefins, in particular propene (16 wt%) and butenes (15 wt%) due to the high diffusivity of the molecules involves and the shape selectivity of ZSM-5.

The cracking of the Fischer–Tropsch Synthesis waxes offers a high flexibility to the FCC process. Depending on the market demands the primary product can either be gasoline or propene/butenes. The production of high-quality LCO as a secondary product can be optimised. With respect to this it can be stated that the FCC unit, in cooperation with a hydrocracker unit, the production of low-sulfur and low-aromatic fuels and lower olefins from natural gas resources can be fruitful [2].

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