Hydrocracking of Fischer-Tropsch Products. Optimization of Diesel and Naphtha Cuts

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Hydrocracking of Fischer-Tropsch synthesis products consisting of a mixture of C_4–C_{30} paraffins and olefins over a platinum/amorphous silica–alumina catalyst was analyzed and optimized. A mathematical model of a batch reactor used for hydrocarbon hydrocracking was developed and the process was studied from a modeling point of view based on the kinetics of a bifunctional catalyst. The influence of temperature on the product yield distribution was evaluated. Time and temperature optimization were performed to obtain the best operating conditions to increase the fractions of naphtha and diesel that can be produced by Fischer-Tropsch synthesis.

Key words:
Hydrocracking, Fischer-Tropsch, optimization, diesel, naphtha

Introduction

The Fischer-Tropsch synthesis (FTS) converts a mixture of CO and H_2 (syngas) into hydrocarbons and is an alternative to produce liquid fuels from natural gas. In commercial practice, the Fischer-Tropsch synthesis is suited to produce high-quality gasoline and diesel since the amount of SO_x and NO_x present in natural gas and in its derived products is low. Environmental concerns and new liquid fuel regulations to take place in Europe and in the US requires the production of less pollutant fuels with lower emissions of SO_x and NO_x. These clean fuels can be produced by Fischer-Tropsch synthesis using natural gas or biomass as feedstock.

Fischer-Tropsch products comprise of long-chain paraffins and olefins containing no sulfur, no nitrogen and only trace amounts of aromatics and heavy metals. Thus, FT products are a more environmentally friendly source for transportation fuels and lube-base oils either alone or blended with petroleum-based products.

During FT synthesis, hydrocarbons heavier than the diesel cut (waxes) are produced. Development of new catalysts with high activity and production rate yields large quantities of waxy products (hydrocarbons with more than 25 carbons).[1–4] These heavy waxy products do not have high commercial value and need selective cracking to yield hydrocarbons in the diesel and gasoline cuts.

In this work, a mathematical model of a batch reactor used for hydrocarbon hydrocracking was developed and the process was studied from a modeling point of view based on the kinetics of a bifunctional catalyst. Optimizations were carried out in the search for the best operating conditions that can convert waxy products into gasoline and diesel.

Hydrocracking

The production of paraffins of a specified carbon-number range is not possible by direct FT synthesis but may be achieved by directing the synthesis towards heavy paraffins, which can be subsequently cracked. The cracking process should predominantly fragment the hydrocarbons to a desired range of chain length and the components already in the desired range should not undergo further cracking.

Hydrocracking of Fischer-Tropsch products can be carried out over a bifunctional (acid/metal) catalyst capable to increase its reactivity with increasing carbon number of the paraffin. Hydrocracking catalysts are bifunctional catalysts characterized by the presence of acidic sites, which provide the cracking function, and of metal sites with hydrogenation–dehydrogenation function. Typical acidic supports are amorphous oxides or mixtures of oxides, zeolites and silicoalumina-phosphates. Pt, Pd or bimetallic systems (i.e. Ni/Mo, Ni/W, Co/Mo, in the sulfided form) are the most commonly used metals. Hydrocracking is generally carried out at p = 3.0 to 5.0 MPa of total pressure and at temperatures between T = 550 and 600 K.[5,6]

In recent years, hydrocracking of waxes has been studied by many researchers, especially regarding hydrocracking of FTS products,[5,7–11] but

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most researches have focused on cracking specific hydrocarbons and not hydrocarbon mixtures as the FTS product. Hydrocracking of paraffins and olefins has been studied by Sie *et al.*[5] over a bifunctional (acid/metal) catalyst and showed that the reactivity increased dramatically with increasing carbon number of the hydrocarbon chain (Fig. 1).
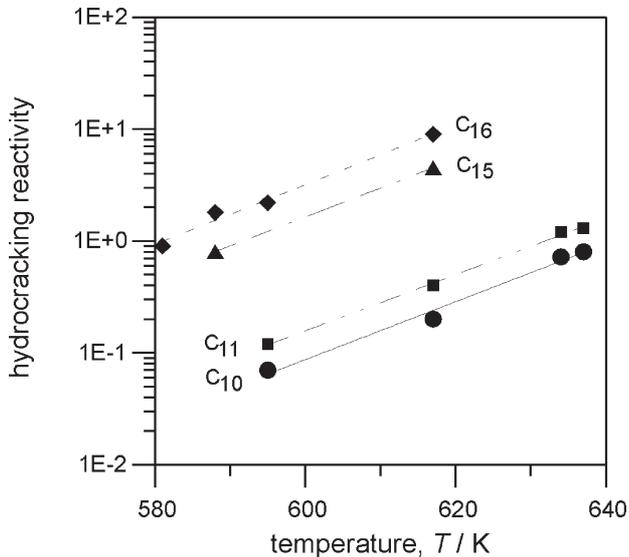
F i g . 1 – *Hydrocracking reactivity of paraffins of different chain length over a dual-functional catalyst*

According to Sie *et al.*[5] the more internally located C-C bonds have higher scission reactivity and terminal or near-terminal C-C bonds show relatively little tendency to break (Fig. 2). This preference to break at more centrally situated C-C bonds contributes to a strong dependence of the reactivity of hydrocarbon molecules on chain length.
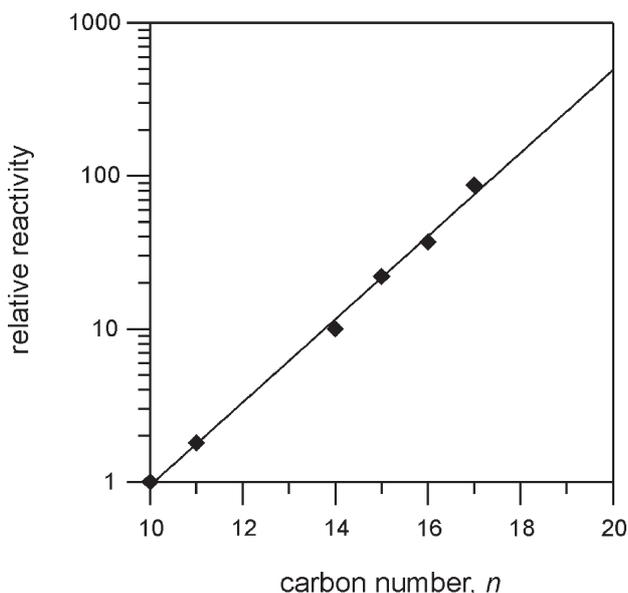
F i g . 2 – *Relative reactivity for cracking of hydrocarbons as function of carbon number*

Mathematical modeling

The mathematical model developed herein considers a batch reactor operating under isothermal conditions and assumes negligible mass and heat transfer resistances between the catalyst and the liquid. The feedstock for the hydrocracking reaction consists of heavy paraffins, olefins and hydrogen.

Olefins exhibit much higher reactivity compared to n-paraffins and react almost instantaneously with hydrogen. The model assumes that all the olefin fed into the reactor was converted instantaneously into paraffin at the beginning of the reaction, according to:[6]

$$[O_n] + [H_2] \rightarrow [P_n] \tag{1}$$

Cracking of n-paraffins occurs according to the following reaction:[5]

$$[P_n] + [H_2] \rightarrow [P_s] + [P_r] \tag{2}$$
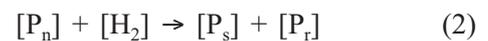
where $n = r + s$

It is generally assumed that cracking generates two hydrocarbons with the same number of carbon atoms[5,6,12] and as such, it is considered that when n is an even number, $s = r = n/2$ and when n is an odd number, $s = r + 1 = (n/2 + 0.5)$.

The mass balance for the reacting species is given by the equation:

$$\frac{d[P_n]}{dt} = \rho_{cat} \cdot \begin{pmatrix} k_{2i-1} \cdot [P_{2i-1}] + 2 \cdot k_{2i} \cdot [P_{2i}] + \\ + k_{2i+1} \cdot [P_{2i+1}] - k_i \cdot [P_i] \end{pmatrix} \cdot [H_2] \cdot V_R \tag{3}$$

The rate constant used in the simulations are dependent on the number of carbons in the chain and on temperature as shown in eq. (4).

$$k_i = 0.001819 \cdot \exp(1.8765 + 0.6255 \cdot i) \cdot$$
$$\cdot \exp\left(40.48 - \frac{25819.68}{T}\right) \tag{4}$$

Due to the assumption of isothermal conditions in the reactor, which can be considered based on academic reports,[6] only the mass balances for each hydrocarbon species were considered in this work. All heat produced by the reaction is assumed to be removed by the cooling jacket of the reactor.

To solve the mathematical model, the equations were numerically integrated using a fifth order Runge-Kutta method. The operating conditions used in the simulations are presented in Table 1.

T a b l e 1 – *Operating conditions and reactor parameters*

temperature, T/K	550 – 650
total pressure, p/bar	50.0
H_2 to paraffin ratio, Γ	0.10
catalyst density, ρ/kg m^{-3}	1987

The initial conditions (product concentrations) for the numerical integration assume that all olefin feedstock was converted into paraffin by instantaneous hydrogenation and the amount of paraffin and hydrogen at the beginning of the reaction were given by:

$$[P_n] = [P_n]^F + [O_n]^F \tag{5}$$

$$[H_2] = [H_2]^F - \Sigma [O_i]^F \quad i = 2 \text{ to } 30 \tag{6}$$

where superscript F represents the concentrations of the species before entering the reactor.

Results and discussion

Several simulations were carried out to understand the effect of temperature and time on the product distribution of the hydrocarbon mixture, especially in a range of transportation fuels. The simulation study assumed that the rate laws for the hydrocracking reaction were valid for the entire range of process parameters as observed experimentally by Sie *et al.*[5]

The feedstock used in the simulations consisted of a typical FTS product produced in a slurry reactor. The FTS product distribution of the feedstock is shown in Fig. 3 and consists of a mixture of mainly
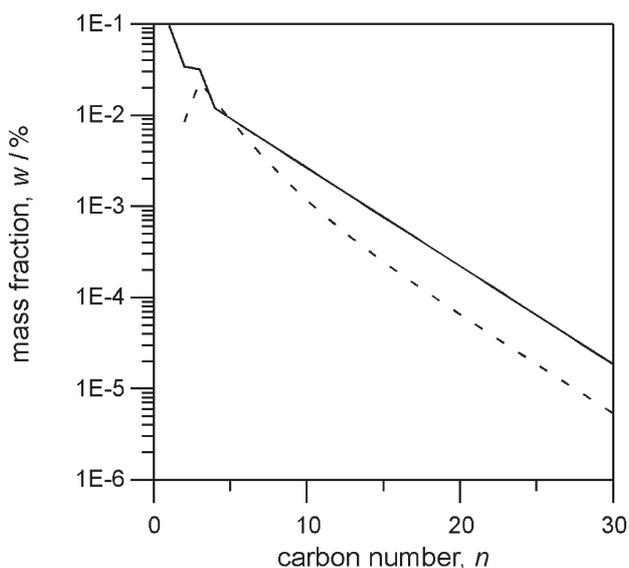
F i g . 3 – *Carbon number distribution of the FTS product used as feedstock. Full line represents total hydrocarbons and dashed lines represent olefin and paraffin fractions*

α-olefins and n-paraffins that has been previously optimized to direct production towards heavy paraffins.[13]

As expected, an increase in temperature increased the formation of lighter products narrowing the hydrocarbon product distribution. High temperatures (over $T = 600$ K) produced a great amount of hydrocarbons in the light gas and gasoline cuts, and only trace amounts of heavy paraffins remained. Low temperatures ($T = 550$ K) favored a mild hydrocracking and only hydrocarbons with long chains cracked, yielding higher amounts of diesel. At mild temperatures ($T = 580$ K) the hydrocarbons in the diesel cut began to crack, yielding naphtha but without presenting further cracking to produce light gases (Fig. 4).
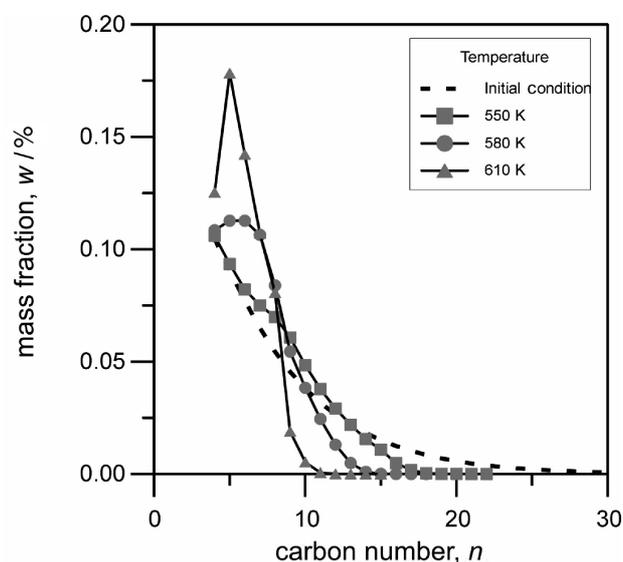
F i g . 4 – *Product distribution as a function of hydrocracking temperature (Processing time: 15 min). Dashed line represents the initial product distribution*

Optimization of the hydrocracking process was conducted in search for the operating conditions (temperature and processing time) that resulted in the highest production of naphtha and diesel. A program in FORTRAN was developed to maximize the production of these cuts, using the method of quasi-Newton and finite-difference gradient. The optimization problem solved was described as:

Find: T, t

Maximize: Product mass fraction (g product cut / g total hydrocarbon)

$$\max \{\Phi = \Sigma w_i\}$$

where the product is naphtha or diesel

within the range of operating conditions:

$$550 \text{ K} < T < 630 \text{ K}$$

Table 2 presents the best operating conditions obtained to hydrocrack FTS product into naphtha and diesel cuts. Figs. 5 and 6 show the hydrocarbon product distribution obtained at the optimized process conditions.

T a b l e   2 – *Processing time for batch hydrocracking of FTS products and operating temperature required to optimize the production of naphtha and diesel cuts*

Product	Time t/min	Temperature T/K
Naphtha	90.2	560
Diesel	0.5	560

When naphtha was the desired product, the hydrocracking process was very successful and a 50 % increase was observed on the mass fraction of naphtha after $t = 90.2$ min at $T = 560$ K (Fig. 5). The result is very satisfactory because the theoretical maximum increase that could be obtained was 89 % (considering that all hydrocarbons heavier than naphtha cut cracked and no hydrocarbons of the naphtha cut would undergo cracking).

To produce hydrocarbons in the diesel cut low temperatures should be employed to enhance the selectivity of the cracking reaction, since as shown in Fig. 3, high temperatures favor the production of naphtha cut. In the best condition found, the diesel cut increased by 16 % after hydrocracking (Fig. 6). This enhancement is also satisfactory, since a maximum theoretical enhancement of 26 % could be obtained.
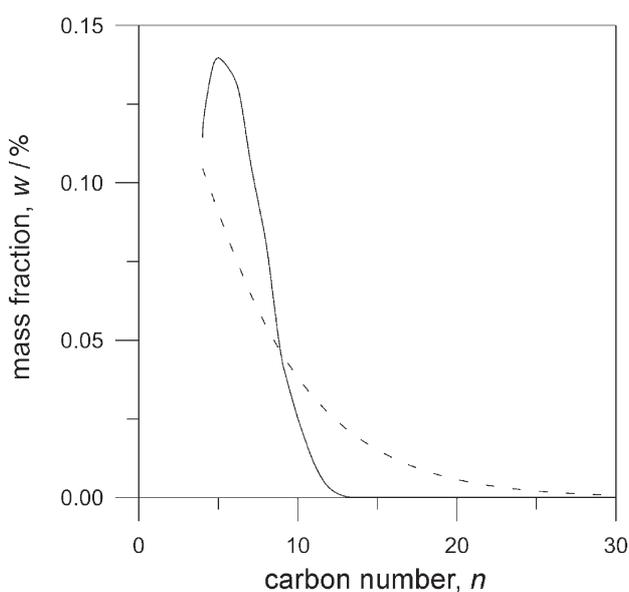
F i g . 5 – *Product distribution after hydrocracking aiming at optimization of naphtha cut. Full line represents the final product distribution. Dashed line represents the initial product distribution*
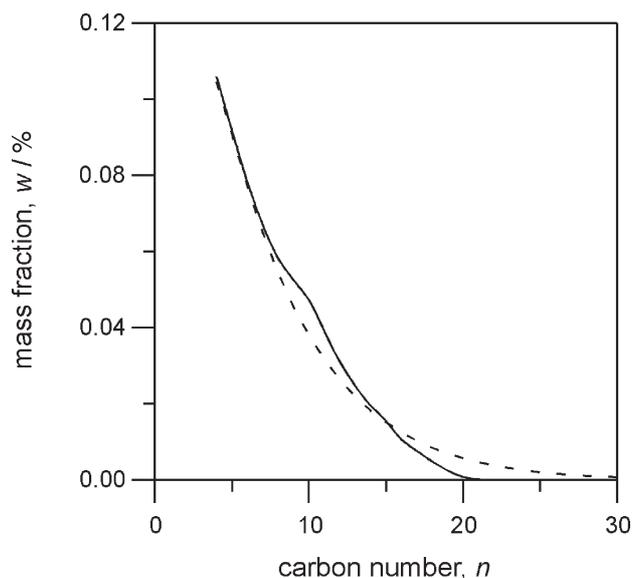
F i g . 6 – *Product distribution after hydrocracking aiming at optimization of diesel cut. Full line represents the final product distribution. Dashed line represents the initial product distribution*

Conclusions

The hydrocracking of a FTS product consisting of C_4 to C_{30} paraffins and olefins was studied by means of a mathematical model aiming process optimization.

The results have shown that the enhancement on the production of naphtha may be considered high, as well as the conversion into diesel. The amount of waxes in the final product is reduced to almost zero and the amount of light gases produced is also low, leading to a very high yield of transportation fuels.

The process showed to be an important step in the production of diesel and naphtha through the Fischer-Tropsch synthesis.

N o m e n c l a t u r e

$[H_2]$ – amount of hydrogen, mol

k_n – cracking rate coefficient for a hydrocarbon with n carbons, 1 g^{-1} mol^{-1} s^{-1}

n – number of carbons in the hydrocarbon molecule

$[O_n]$ – amount of olefin with n carbons, mol

$[P_n]$ – amount of paraffin with n carbons, mol

p – pressure, MPa

Γ – H_2/paraffin concentration ratio

t – time, s

T – thermodynamic temperature, K

V_R – reactor volume, m^3

w_n – mass fraction of a hydrocarbon with n carbons, %

ρ_b – catalyst density, g m^{-3}

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