Increasing the selectivity of the Fischer Tropsch process by periodic operation

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The Fischer Tropsch synthesis converts synthesis gas to hydrocarbons. An inherent limitation of the reaction mechanism is the very wide product distribution. In this work the possibilities for narrowing this distribution by periodic operation are examined using a model based approach. The basic idea is to switch periodically between two feed streams with different feed compositions. It was found that the diesel fraction could be increased with 20%. Future research will have to verify this experimentally. Also some of the implications of this periodic operation on the rest of the process are presented.

1 Introduction

The Fischer Tropsch synthesis is a process to convert synthesis gas to hydrocarbons that can for instance be used as transportation fuels. The process is heterogeneously catalyzed and can be carried out in a variety of reactors including trickle bed reactors, slurry reactors and fluidized bed reactors. A drawback of this process is the very wide product distribution, ranging from methane till heavy waxes. The reason for this can be found in the reaction mechanism. The ratio between the termination reaction rate and the propagation reaction rate is chain length independent, giving rise to the Anderson-Schulz-Flory distribution (Dry, 1996):

$$M_n = \alpha^{n-1}(1 - \alpha) \tag{1}$$

Where M_n is the molar fraction in the product with a chain length of n , n is the chain length and α is the chain growth probability that is independent of the chain length.

The value of α can be influenced by the choice of catalyst, the reactor temperature and pressure and the hydrogen carbon monoxide ratio of the synthesis gas.

As a consequence the maximum achievable diesel weight fraction is 39%, corresponding with an α of 0.87. In the recently build Shell Middle Distillate Synthesis (SMDS) process in Bintulu Malaysia the diesel fraction is increased by first producing predominantly

heavy products that are subsequently hydrocracked into the desired product spectrum (Sie, 1998). Figure 1 gives a schematic overview of the resulting process. In this work the possibilities for increasing the selectivity by dynamic operation are investigated using a model based approach. The basic idea is to periodically switch between a feed with a low hydrogen/carbon monoxide ratio and a feed with a high hydrogen/carbon monoxide ratio. During the low ratio period predominantly chain growth takes place, while the high ratio is in favor of chain termination. The aim is to maximize the selectivity towards

Figure 1: Simplified flowscheme of the SMDS process.

diesel (C10 - C20). In the next section the basics of dynamic operation is given. Then the modeling assumptions are discussed, followed by the implementation. Then the results are presented, including a discussion of the process implications for dynamic operation. Finally some conclusions are presented.

2 Periodic operation

Most continuous chemical processes are designed to operate under steady-state conditions. However transient conditions can sometimes provide benefits. By periodic operation the time averaged yield or selectivity sometimes can be increased to values that are not achievable in the steady-state. This is called resonance. Stankiewicz and Kuczynski (1995) give an overview of processes that can benefit from periodic operation.

In the literature some indications can be found that periodic operation has an influence on the product distribution of the Fischer Tropsch process, but no work in the field of optimizing the diesel fraction, or model based studies for this process were found. Adesina et al. (1995) presents an overview of the experimental work on periodic operation of Fischer Tropsch synthesis.

Van Neer (1999) has investigated the requirements for resonance in catalytic processes. Two phenomena for catalytic processes that are sufficient to obtain such resonance phenomena are presented:

- The sorption behaviour of the forced component must be at least as fast as the sorption of the other component involved.
- The surface of the catalyst has to be almost totally occupied at steady-state in the considered concentration range.

The essence of these conditions is that strong non-linearities need to be present to obtain resonance. Since the two conditions mentioned above are satisfied in the Fischer Tropsch synthesis process it is expected that a higher selectivity can be obtained by dynamic operation.

3 Modeling assumptions

Kinetic model In the literature there is no general consensus about the reaction mechanism. The mechanism we used in this work is shown schematically in figure 2. It is mainly based on the work of Dry (1996) and Van der Laan (1999). Hydrogen and carbon monoxide adsorb dissociatively on the catalyst surface. The oxygen reacts in two steps to water. The adsorbed Carbon reacts with the adsorbed hydrogen to the carbide intermediate that serves as building block. Chain growth occurs due to the reaction of the adsorbed chain with the adsorbed carbide building block. Termination occurs either to paraffins or olefins.

Figure 2: Reaction mechanism.

Kinetic parameters For the kinetic model presented above, two types of parameters are required: rate constants and surface coverage fractions of the various components. In the literature no complete set of parameters for this model can be found. Therefore the estimation of parameters for this model is a combination of various literature sources. A detailed description of all parameters with their numerical value is presented in De Deugd et al. (2001). The only reaction modeled far from equilibrium is the dissociative adsorption of hydrogen.

Reactor model It is important that a distinction can be made between kinetic effects and reactor effects. Especially since a large variety of reactor types can be applied for this process. In order to be as generic as possible we have modeled the reactor as a ideal mixed reactor with a high space velocity. The reactor is assumed to be operating in a regime where mass transfer limitation can be neglected. Although the Fischer Tropsch process is highly exothermal, the reactor is assumed to be isothermal. It is assumed that all the heat can be transferred to a cooling medium, e.g. boiling feed water that is flowing through cooling tubes.

4 Implementation

The model was implemented in gPROMS (gPROMS user guide, 2000). The model consists of molar balances for paraffins and olefins up to C21. All heavier components are lumped into a heavy fraction. The diesel weight fraction is defined as the sum of the weight fractions of the paraffins and olefins from C10 till C20.

The periodic operation was implemented using a block profile for the feed composition. Figure 3 gives such a typical profile. This profile is described by four parameters. We have chosen to describe the profile with the cycle time, pulse time, base ratio and peak ratio. The total inlet flowrate is adapted such that the pressure in the reactor and the outlet flowrate are maintained constant.

Figure 3: Feed profile.

The time average diesel fraction is given by:

$$x_{diesel} = \frac{\int_{cycle} \phi_{m,diesel} dt}{\int_{cycle} \phi_{m,hydrocarbons} dt}, \quad (2)$$

where x_{diesel} is the weight fraction diesel, $\phi_{m,diesel}$ is the mass flow diesel and $\phi_{m,hydrocarbons}$ is the total hydrocarbon massflow.

5 Results

Steady-state analysis In the literature no consistent set of dynamic data is available to validate the dynamic model. Therefore only a steady-state validation of the model was done. Also a quantitative steady-state analysis is very hard to do since consistent data sets are lacking in the literature.

The product distribution obtained by static operation was indeed the Anderson-Schulz-Flory distribution. Also the maximum diesel yield under static operation was in accordance with the ASF distribution.

Furthermore a number of trends that are generally accepted were checked qualitatively (Van der Laan, 1999). Table 1 presents these trends.

Dynamic optimization The optimization was performed by varying the four variables that determine the block profile from figure 3 in order to maximize the objective function

Table 1: Steady state model verification

Cause	Effect
increase H ₂ /CO ratio	decrease average chain length decrease olefin content
increase pressure	increase average chain length
decrease space velocity	decrease olefin content
introduce water in feed	decrease conversion

given by equation 2. The optimum feed-profile has a cycle period of $1.0 * 10^4$ s, a pulse time of $1.1 * 10^3$ s, a base ratio of $1.0 * 10^{-3}$ (almost pure carbon monoxide) and a pulse ratio of 19. The corresponding value of the objective function is 0.47, about 20% higher than the best achievable steady state result. However the time average ratio is far from stoichiometric (0.19 instead of 2) resulting in very low carbon monoxide conversions. Adesina et al. (1996) report time scales in the range from 10^2 to 10^3 seconds instead of the 10^4 from this present work. However this is not in conflict with our findings since they focus on smaller products (till C₁₀).

Figure 4 shows the optimal product distribution that was obtained with the periodic operation, compared with the optimal distribution with static operation. This figure shows that not only the diesel fraction is increased, also the heavy fraction is increased, resulting in a decrease of the light fraction. This is also favorable from an economic point of view.

Figure 4: Optimum with static and periodic operation.

6 Process Implications

The feed profile in this study is a block profile. On a lab-scale this profile is easy to generate. However on an industrial scale the profile will probably be smoothened. This can have a negative effect on the selectivity.

Usually the feed to the Fischer Tropsch process is a mixture of hydrogen and carbon monoxide with a molar ratio of about 2. Sufficient technologies exists to produce this in

one step. For periodic operation two feed streams are required with different compositions. So additional separation might be required to make the two streams with different composition.

The reactor effluent will also have a periodic composition. This can lead to difficulties in operating the distillation section. Several parallel units that operate out of phase might solve this problem.

7 Conclusions

It was demonstrated that periodic operation of the Fischer Tropsch synthesis can produce a diesel yield that is 25% higher than the best achievable yield under steady state operation. However the model depends on number of assumptions was required in order to obtain a consistent model. The dependence of the results on the assumptions needs to be checked more rigorously. Ongoing research is aimed at the experimental validation of these results.

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