Screening the effect of the Probability of Chain Growth on the efficiency of the Fischer-Tropsch Synthesis process design

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Introduction

Recently, there has been renewed interest in the use of Fischer-Tropsch technology for the conversion of natural gas and coal to liquid fuels. Due to this renewed interest, more FT plants are likely to be built. Existing FT plants are very capital intensive processes and so it is anticipated that future plants will be designed on the basis of the available raw materials (coal or natural gas) and the specific needs of a particular economy. For this reason, it is appropriate to make a process evaluation by looking at alternative process configurations at the early stage of design. Jess et al [1], in their paper, advocate the use of low-cost technology for countries in remote areas where the cost of natural gas is low, as the only economical solution for the conversion of natural gas to higher hydrocarbons using FT-Synthesis. This technology may not be highly efficient but it will bring benefits to the economy. This concept of a low-cost FT process is based on the use of a nitrogen-rich syngas which does not utilize a recycle loop (once-through process) to avoid any nitrogen build-up in the system.

In order to achieve a reasonable efficiency in a once through FT process of the type proposed by Jess et. al.[1] a reasonable high per pass CO conversion should be achieved. A possibility for achieving this is the use a number of reactors in series [2].

In contrast, recycle process aim at achieving higher reactor productivity by using higher syngas flow rates, due to the recycle and low single-pass CO conversion.

If a certain process configuration is chosen at the earliest stage of the process synthesis a question that is normally asked is how efficient is the chosen configuration. Sometimes alternatives are developed where more process information is available; however, developing alternatives may be laborious and "expensive" to do for alternatives that can ultimately to be discarded.

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In this study, we have shown how a process designer can use process synthesis to try and ascertain the efficiency of the design from the feed material and energy point of view. It has been shown that this can be done before laboratory data is available or indeed before a catalyst has been chosen. This furthermore can be done with relatively little effort using very simple models at the very earliest stage of the process design. We will illustrate this by considering both a recycle and once-through process.

Recently a thermodynamic technique to analyze processes has been developed [3]. This essentially looks at the Gibbs energy of the system and equates that to work. In this way one is able from very simple information to calculate a target for the process. Calculations based on this method have been employed in this paper.

Simple process design calculations have been done using the process synthesis concepts, basic thermodynamics and simple Fischer-Tropsch (FT) synthesis flowsheet models to see if the probability of chain growth or alpha value (α) has any effect on the overall carbon efficiency of the FT synthesis process.

In particular we will investigate the effect of the probability of chain growth (alpha, α) on the production of diesel fuel. This study will not rely on experimental data, but rather ask the question backwards so to speak: W*hat is the optimal alpha for an FT synthesis system producing diesel?* Once we understand what range of alpha we are targeting, we can decide on a suitable catalyst and operating conditions to achieve this alpha.

The calculations are based on the reforming of the natural gas, which we assume to be methane. We have assumed that the composition of the syngas entering the FT section is stoichiometric, which corresponds to a ratio H_2/CO of approximately 2. To illustrate the methodology, steam reforming of methane with the addition of CO_2 to obtain syngas of the required H_2 to CO ratio (reaction 1) has been used. This approach is possible with the stranded natural gas containing CO_2 or if a stream of pure CO_2 is available. The more conventional processes can be analyzed by a similar approach and produce similar results.

$$3/4CH_4 + 1/2H_2O + 1/4CO_2 \rightarrow CO + 2H_2 \quad \Delta H^o_{298}(kJ/mol) = 164.90 \qquad (1)$$

Reaction (1) is endothermic and the energy for syngas production will be derived from methane combustion shown in reaction (2) below:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H^o_{298}(kJ/mol) = -802.31 \qquad (2)$$

In this simple model, the reforming process and the energy providing steps have been decoupled. The two reactions (equations (1) and (2)) may be done in one or more pieces of equipment but the overall process needs to be at best adiabatic. All the energy and work requirements for recycling and reforming of the lighter gases in the recycle process will be similarly obtained from the combustion of methane.

The quantity of methane to be combusted to meet the energy requirements for the reaction was calculated using the following equation 3:

$$N_{CH4} = \frac{Q_{combustion}}{\Delta H_{combustion}} \tag{3}$$

Where N_{CH4} is the number of moles of methane required to be combusted to provide $Q_{combustion}$ energy. $\Delta H_{combustion}$ is the enthalpy of methane combustion (802.31 kJ/mol) as calculated in equation 2.

Carbon efficiency takes the chemical feedstocks and energy streams into account. It is thus a good measure of plant operating economics because the higher the carbon efficiency the higher the usage of feed material and energy for the production of the desired product. It is also related to the capital costs, as the lower the carbon efficiency the more material needs to be processed in order to produce the same quantity of products. Thus the process equipment will be larger with correspondingly higher capital costs. It is also a good tool for evaluating environmental impact that the process has. High carbon efficiency means that the process is environmental friendly as its emission of CO_2 into the environment is low. The design of modern chemical processes embraces the concept that decisions to protect human health and the environment can have the greatest impact and cost effectiveness when applied early to the design and development phase of a process or product.

Results

The results presented here are based on calculations of carbon efficiency at various alpha values for one-through and recycle processes.

The results in figure 1 show that at intermediate alpha values, there is a big advantage in operating a process with a recycle stream as the recycled and reformed gases improve overall carbon efficiency through the utilization of the lighter gases which are flared in the once-through process.

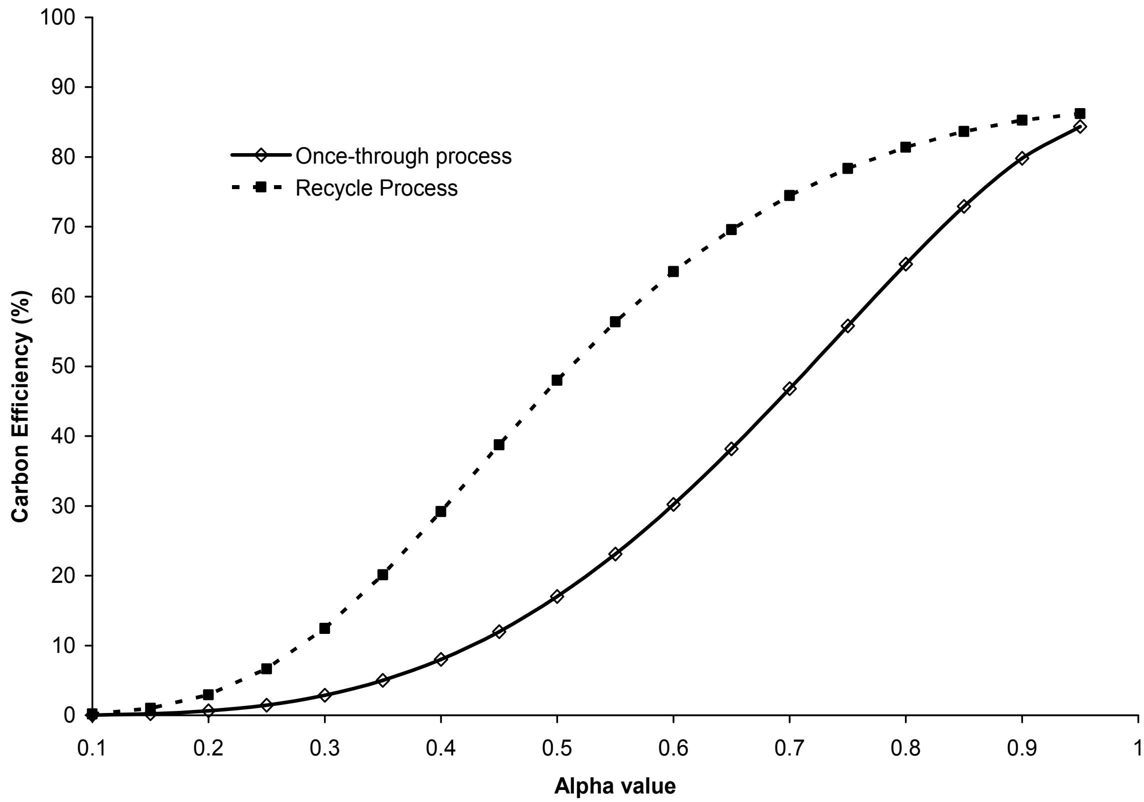

Figure 1. Comparison of carbon efficiencies at different alpha values in once-through and recycle processes at 100% conversion without wax hydrocracking.

These results also show that the maximum carbon efficiency for both processes is the same at 85% because at the highest alpha value of 1, there are no lighter gases produced. It is thus possible to achieve the same carbon efficiency by using either of the two processes; however, carbon efficiency values achieved in the process with a recycle stream at lower alpha values will only be achievable at higher alpha values in a once-through process. Between alpha values of 0.35 and 0.85, there is a big difference in the value of carbon efficiency obtained in the two processes at the same alpha values. However, at α =0.95 -1, it is apparent that it does not matter what process configuration is used to achieve this value of alpha because very close values of carbon efficiency can be achieved either way.

The process of wax hydrocracking to maximize diesel production was incorporated in the analysis and results presented in figure 2.

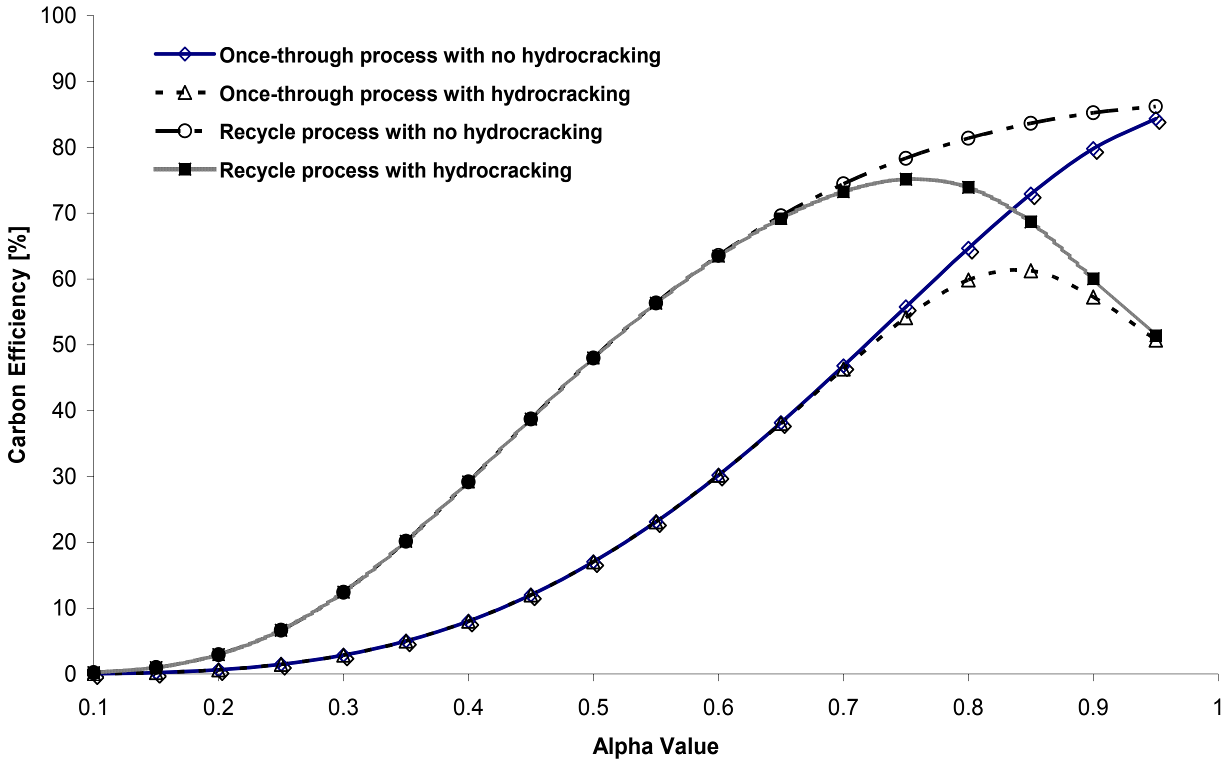

Figure 2. Carbon efficiency as a function of alpha value in a once-through and recycle process.

In the once-through process hydrocracking of waxes into diesel drops the maximum carbon efficiency to 60% and this correspond to an optimal alpha of 0.82. In the recycle process the maximum carbon efficiency drops to 75% which occurs at an optimal alpha of around 0.75. This loss in carbon efficiency is purely due the increased requirement of natural gas (methane) for H_2 production and compression to process the heavier hydrocarbons to liquid fuels. The more waxes are formed, the more H_2 is needed to hydrocrack them. Since H_2 is produced from CH_4, there will be an increase in C feedstock to the reactor for H_2 production.

Conclusion

Using the results from this study and what is already known about Fischer-Tropsch Synthesis product distribution, we can conclude that:

- By using the probability of chain growth (α) as a variable and the resultant carbon efficiency, we have established a basis for comparing the two operations. This has been achieved by using process synthesis and simple process models without any experimental data or detailed and complicated modeling.
- By using carbon efficiency as the measure of plant operating economics, this analysis has enabled us to deal with the issue of designing an environmentally friendly process that is at the same time economically feasible, at least, from the material and energy utilization point of view, at an early stage of process design.
- Designing an FT process with recycling and reforming of the lighter gases, is very beneficial especially if the reaction products are described by low to middle values of alpha because higher values of carbon efficiency are obtained and the amount of overall CO conversion is enhanced.
- In both the once-through process and the recycle process, the trend should be to reduce the formation of lighter gases by increasing the alpha value because carbon efficiency increases with the increase in alpha values.
- However, if the aim is to maximize diesel production by hydrocracking the waxes, then an optimal alpha value should be sought in order to reduce the cost of hydrocracking very heavy waxes. Compared with the processes without hydrocracking, the incorporation of wax hydrocracking in the two processes drops carbon efficiency for alpha values beyond 0.7, thereby making it uneconomical to produce very long chain hydrocarbons.

References

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