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THE CHALLENGE OF DESIGNING A FISCHER-TROPSCH REACTOR

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ABSTRACT

The Fischer-Tropsch process converts synthesis gas, a mixture of carbon monoxide and hydrogen, to a spectrum of predominantly hydrocarbon products. The reaction is catalysed by cobalt, iron, nickel or ruthenium at elevated temperatures and pressures. In our studies of this system we developed a thermo-kinetic model of the reactor. One of the main challenges for the design of this type of reactor is the exothermicity of the reaction. Heat removal is critical to avoid catalyst deactivation and damage. To assess the heat removal it was therefore necessary to develop a descriptive model of the reactor.

The overall process design we are developing is based on the results of an application of our process synthesis methodologies. These methods involved initially the definition and description of the fundamental processes taking place which are reaction and heat transfer. Thus in order to achieve an optimised design we needed to consider not only the reaction rate but also the rate of heat removal. Ideally, one would prefer a highly active catalyst to increase production per unit volume. However, the advantage of a highly active catalyst is offset by the necessity to equivalently enhance the heat removal to avoid damaging or destroying the catalyst. This requires the reactor designs to accommodate a trade-off between unit volume production rate and heat removal.

This paper will address the issues involved in the thermodynamics, mass and heat transfer aspects of the Fischer-Tropsch reactor. This is further complicated by the high number of components and the multiple phases involved in the reactor. However due to the sensitivity of some information for commercial purposes in our research centre, relative values have been assigned to critical variables. This however does not compromise the quality of work.

INTRODUCTION

The Fischer-Tropsch process produces liquid fuels as a substitute to crude oil. Fischer and Tropsch discovered the conversion of synthesis gas over group (VIII) metal catalysts [1]. The synthesis gas which is a mixture of carbon monoxide and hydrogen forms a distribution of linear hydrocarbons according to the following reaction:

$$CO + 2H_2 \rightarrow -CH_2- + H_2O$$
$$\Delta H^0_{rxn} = -165 \text{ kJ/mol} \quad (1)$$

Note that the reaction is very exothermic. The reaction takes place over nickel, iron, cobalt or ruthenium catalysts. Catalysts are heat sensitive in that they are deactivated when exposed to high temperatures. The catalyst is sintered resulting in a more crystalline form and this reduces the number of pores. Generally catalyst sintering takes place around 500°C [2]. The challenge therefore in designing a Fischer-Tropsch commercial reactor is to account for the heat of reaction and the large wide range of reaction products. Heat removal is a challenge which is further evidenced by the type of reactors that have been developed.

Sie studied the history of the development of the Fischer-Tropsch synthesis process [3]. There are predominantly four types or reactors used commercially:

i) Multitubular fixed bed - consist of a number of long tubes loaded with catalyst and with internal cooling. The diameter of the tubes varies between 20 and 50 mm.
ii) Slurry bubble column - consists of catalyst particles suspended in the recycled liquid product with syngas sparged through. In slurry reactors the hydrodynamics changes with scale and a successful scale-up would require longer piloting times [4]. Also with the slurry reactor the separation of the catalyst particles from the reaction medium is difficult and costly.

However, the advantage of the slurry bed is the excellent heat transfer to the surrounding liquid medium.

iii) Circulating fluidised bed (Synthol reactor used at SASOL)

iv) Fluidised bed.

We have included this account to show that all these reactor types produce hydrocarbons economically; however the inherent heat removal capabilities of the design have led to differences in operation of the units in practice.

Another important aspect is the modelling of the reaction products. Iron catalysts generally produce lighter hydrocarbons and cobalt catalysts generally produce heavier hydrocarbons. Anderson introduced a kinetic model based on the Schulz and Flory polymerisation model [5-7]. The reaction mechanism for Fischer-Tropsch (FT) product distribution is now known as the Anderson-Schulz-Flory (ASF) mechanism as in Equation 2.

$$W_n = (1-\alpha)\alpha^{n-1} \qquad (2)$$

W_n is the weight fraction or selectivity of the hydrocarbon of chain length n and α is the chain growth probability. The -CH_2- monomer is a building block for FT products with the rate of propagation and rate of termination being the variables determining the α values. Typically industrial applications target values of α above 0.8 [8].

The aim of this paper is to highlight the challenges we have faced in developing a model for designing a multitubular fixed bed FT reactor. We have chosen the multitubular bed as our reactor because it is relatively easy to scale up which means the time it takes from conceptual design to commissioning is relatively short. The challenge of using a multitubular fixed bed becomes heat removal due to diffusion heat transfer limitations. This means taking into account the conductive transfer of heat out of the catalyst to the wall.

The first task was to examine the reaction kinetics and develop an algorithm for simulating the reactor. Heat transfer effects are analysed as a function of the reaction extents and pressure drop. The pressure drop was assumed to obey the Ergun Equation which incorporates the turbulent flow regime.

PROCESS SYNTHESIS

Traditionally unit operations have been optimised without regard for the whole process. The question answered is what is the best that can be achieved by a given unit operation which can either be a reactor or a distillation column given their operating conditions. At our research centre we have developed methodologies that look at the whole process simultaneously. This involves developing shortcut experimental and design methods which permit early assessment of the process without much data.

The objective of our design was to produce FT products economically and safely without destroying the catalyst. Reaction and heat transfer were identified as the fundamental processes taking place in a FT reactor system. These fundamental processes are interlinked and determine the overall behaviour of the system.

REACTION HEAT CONDUCTION

As already discussed the FT reaction heat needs to be removed from the catalyst, as it is formed. Usually a saturated liquid on the shell side is used as the cooling medium because of the large latent heat which effectively absorbs the heat. Efficient control for this process should balance heat production and removal at a reasonably low temperature gradient in order to avoid damage to the catalyst. Also higher temperatures produce more methane which is not a desired product.

The heat transfer from the catalyst in the tubes to the cooling medium in the shell side of the FT reactor is through conduction and convection. However because of the very large heat of reaction, the amount of heat removed by the gas for the small temperature rise permitted is relatively small. Thus we have simplified the heat transfer by working on the limiting case assuming that all heat generated in an element has to be removed by conduction. A one dimensional radial heat balance is carried out around a unit volume of catalyst on which reaction takes place according to Equation 3 [9].

$$\frac{\partial T^2}{\partial r^2} = -\frac{Q}{k} \qquad (3)$$

k is the thermal conductivity of the catalyst volume of radius r. Q is the rate of heat removal for a given temperature (T) change.

The rate of heat generation per unit volume is equal to the product of the reaction rate with respect to carbon monoxide consumption (R_{CO}) and the standard molar heat of reaction (ΔH^o_{rxn}). For simplicity at this stage we have assumed that R_{CO} is a constant. Furthermore the heat of conduction out of the catalyst bed is rate limiting and hence the wall temperature can be initially assumed to be at the temperature of the steam in the shell side. At steady state operation, the rate of heat removal should match this rate of heat generation. The heat generated is proportional to the extent of reaction. We can now write equations for the production rate (P) in terms of the reactor dimensions. The production rate is given in different forms in Equations 4 and 5.

$$P = nR_{CO}V_{cat} = nR_{CO}\pi r^2 L \qquad (4)$$

$$P = nG\pi r^2 \qquad (5)$$

G is the superficial mass velocity, r is the radius of the tubes, L is the tube length and n is the number of tubes.

Now that we have defined the reaction rate it is possible to calculate the rate of heat production that is matched by the rate of heat conduction. This results in Equation 3 being transformed to Equation 6 which is our new energy balance, assuming a pre-assigned value for the maximum temperature difference.

$$\frac{\partial T^2}{\partial r^2} = -\frac{\Delta H_{rxn} R_{CO}}{k} \qquad (6)$$

Equation 6 now describes the heat balance with respect to the FT process. We assume that in our heat transfer there is a maximum tolerable temperature difference (ΔT) resulting in Equation 7. This maximum is determined by the maximum temperature the catalyst can tolerate before degrading.

$$\Delta T = \frac{\Delta H_{rxn} R_{CO}}{k} r^2 \qquad (7)$$

Plotting these results in the thick and thin curves in Figure 1 define the maximum possible reaction rates for temperature differences of 20 and 10°C, respectively. The region below is achievable however the boundary sets targets for our design. Operating below the boundary would require more catalyst to achieve the same reaction rates as obtained when operating on the boundary. However this comes at the expense of more catalyst being required to achieve the same production rate.

As already mentioned when solving Equation 7 we assume a known temperature difference and the thick solid line in Figure 1 shows how tube radius varies with reaction rate to maintain this temperature difference. Relative values have been used in this calculation for illustrative purposes. To effectively remove the heat and maintain a desired temperature difference of less than 10°C is governed by the region below the thin solid line. A higher maximum temperature difference of 20°C results in a larger tube diameter for a fixed reaction rate.

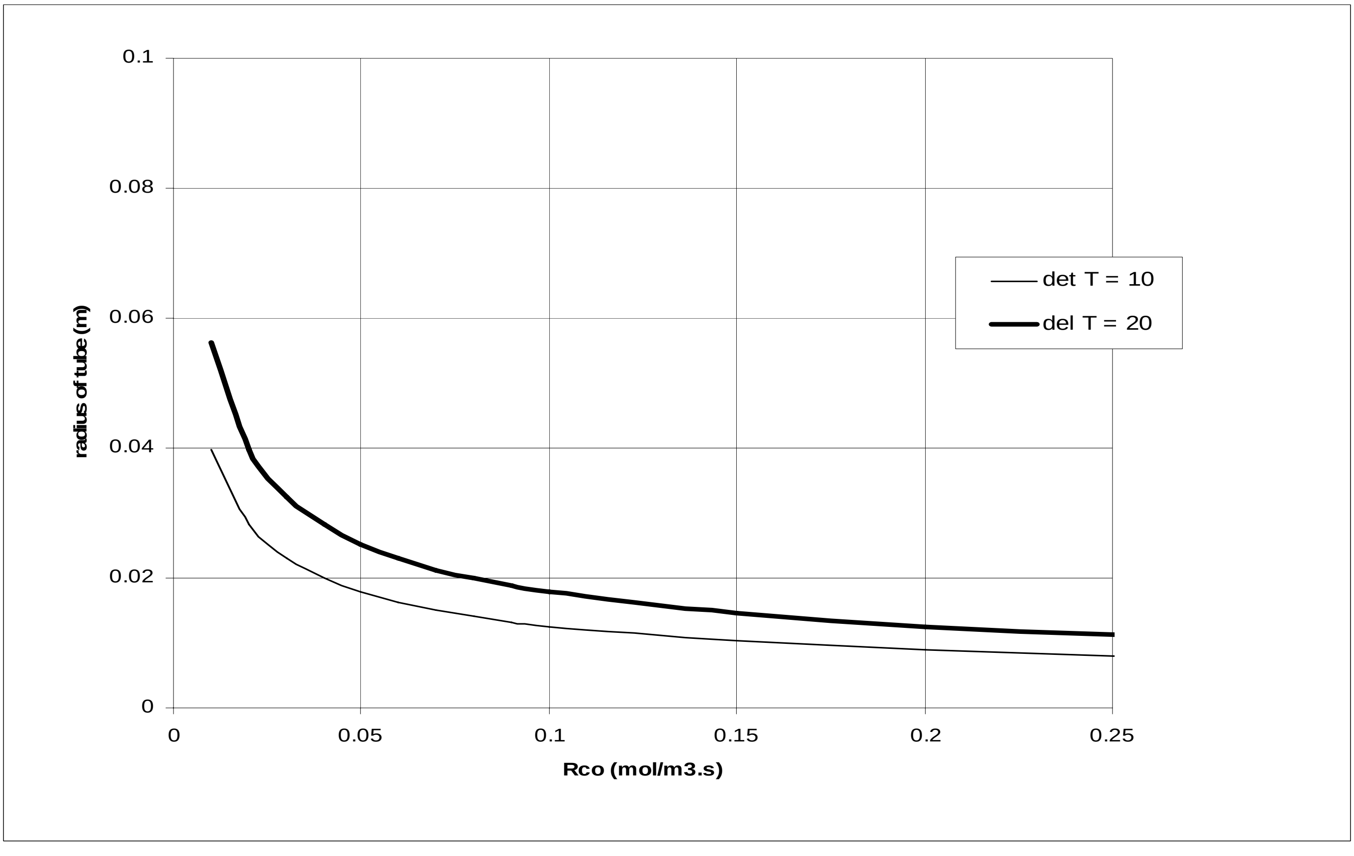

Figure 1: The boundary of reaction rates as a function of tube radius for two temperature differences.

INTEGRATING HEAT AND PRESSURE EFFECTS

A multi-tubular fixed bed reactor consists of long tubes and this result in pressure drop. There is a maximum pressure drop one can tolerate through the tubes otherwise pumping costs get very high or we can crush the catalyst. We use the Ergun equation, Equation 8, to account for the pressure drop.

Looking at the system of Equations 3-7, the variables that characterise our system are easily identified as;

i) Tube radius (*r*),
ii) Number of Tubes (*n*),
iii) Reaction rate (R_{CO}),
iv) Thermal conductivity (*k*), and
v) Superficial mass velocity (*G*).

Using the Ergun equation, for turbulent flow and substituting for some of the variables we consider important, we get Equation 9.

$$\Delta P_r = -\frac{1.75G^2}{\rho d_p}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)L \qquad (8)$$

$$r = -\left[\frac{1.75P^3 M^2{}_r(1-\varepsilon)}{\rho d_p n^3 \pi^3 R_{co} \varepsilon^3 \Delta P_r}\right]^{1/6} \qquad (9)$$

Suppose we now set a limit on the value of the pressure drop in the system that we can tolerate, we can plot contours on the same axis as Figure 1 for various values of the number of tubes. Where the contours of the lines from the heat transfer and pressure drop intersect are possible designs for those values of the variables read off the graph and the values making up the contours. Thus Figure 2 constitutes a set of deigns for various possibilities. Notice also hidden in these designs are the length of the tubes and these values need to be taken into account in making final decisions of the size of the reactor and the catalyst operating conditions.

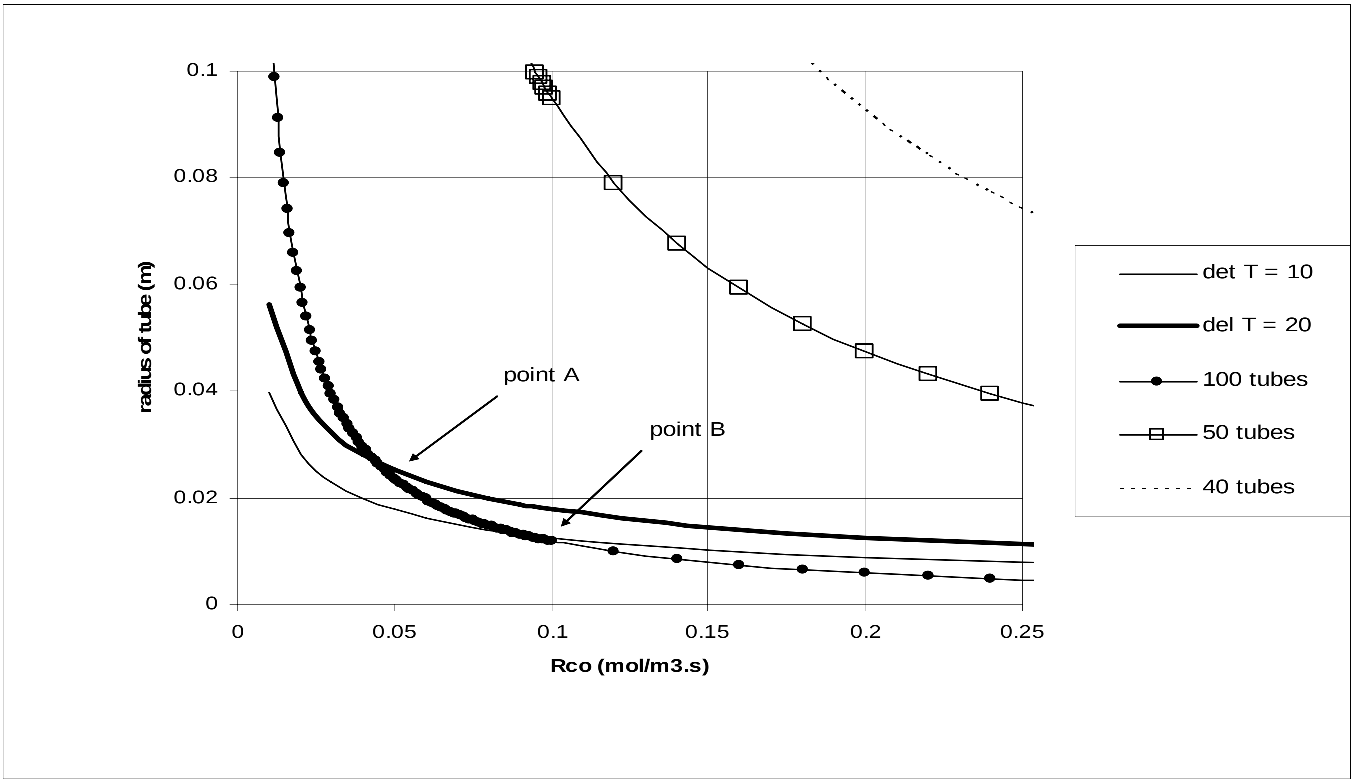

Figure 2: Setting targets in the design of the FT process.

We see that the pressure drop in the reactor is more sensitive to tube radius than the constant temperature difference curve. Hence small changes in reaction rate will cause large changes in the pressure drop. Thus the balance between achieving the production, efficient heat removal and acceptable pressure drops is quite complex.

CONCLUSSION

This work shows that when one integrates the reaction heat removal and flow characteristics, the FT reactor design yields interesting and sometimes counterintuitive results. A look the reaction alone suggests that the more active the catalyst the better. However in order to achieve efficient heat removal the tube diameter has to be made smaller and the more active the catalyst is. The pressure drop across the reactor is very strongly dependant on tube radius and **thus if a too active a catalyst is chosen, this results in very high pressure drops!** Thus the choice of catalyst and reactor operation conditions, which set the reaction rate R_{CO}, must be done in conjunction with the process design, in that pressure drop across the reactor is strongly dependant on the catalyst activity. This is very counterintuitive as one usually chooses the most active catalyst possible and then designs the reactor for this. However as we have shown this may not be feasible in an FT reactor. This strange and interesting result is because of the high heat of reaction. Thus matching the heat removal with the reaction rate, constrains the design as shown in our very simple approach.

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