Determination of Feasible and Stable Regions of Reaction Extent in Fischer Tropsch Synthesis

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Fischer Tropsch Synthesis (FTS) is an important chemical process whereby carbon monoxide and hydrogen are reacted over a supported metal catalyst to produce hydrocarbons and water. One of the side reactions in FTS with iron catalysts is the water gas shift reaction (WGS) which is an equilibrium limited reaction in which water and carbon monoxide react to form carbon dioxide and hydrogen. In this paper we will develop a graphical method to examine how these two reactions interact with each other and how this influences the overall process.

We express the mole balance, corresponding to these reactions in terms of reaction extents. The extent relating to a given reaction indicates the number of moles produced or consumed for any participating species in the reaction. In this way a maximum possible reaction extent can be determined for the production of hydrocarbons.

The mole balance will be determined for reacting species as well as products. The Fischer Tropsch reaction is assigned extent 1 (E1) and the Water Gas Shift reaction is assigned extent 2 (E2).

Fisher Tropsch Synthesis: $CO + H_2 \rightarrow [CH_2] + H_2O$ *E1*
Water Gas Shift: $CO + H_2O \rightarrow CO_2 + H_2$ *E2*

The purpose of expressing the mole balance in terms of extents is to determine a Region of Possible Reaction Extents. This is achieved by firstly imposing the constraint that the number of final resulting moles (moles of each species in the exit stream) must always be positive. The numbers of final moles are then in turn set equal to zero. The mole balances are arranged so that E2 is the subject of the formula. Thus a line can be shown, on a plot of E2 verses E1, for each species which indicates where the number of moles of that species is zero. It is then possible to determine on which side of the line the numbers of moles are positive. Using this property a region can be found in which all the moles are positive. The benefit of using a simple method as described above is that the only information required in determining the Region of Feasible Reaction Extents is the initial number of moles of all species.

It was found, as shown in Figure 1, that one of the vertices of this Region of Possible Extents represents the maximum production of hydrocarbons, that is maximum E1.

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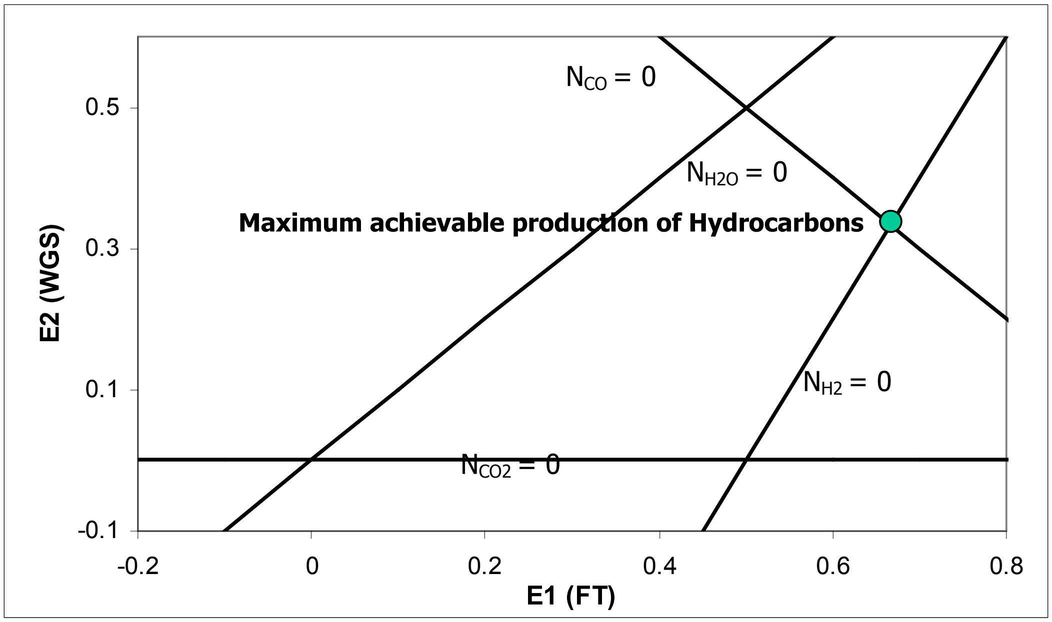

Figure 1: Region of Possible Reaction Extents

The number of feed moles for each species was then varied to produce the various regions resulting from the different feed ratios. The affect of doing this is to change the positions (not the slopes) of the straight lines that define the boundaries of the feasible region. As the region is convex and is bounded by straight lines small changes in the non-active feeds will not affect the answers.

The results show that the amounts of water and carbon dioxide in the feed had no effect on the maximum extent of hydrocarbon production. Therefore only the relative amounts of carbon monoxide and hydrogen have an effect on this maximum point. This is counter-intuitive as it has been thought that adding H_20 and/or CO_2 to the reactor feed may change the amount of hydrocarbons produced.

The equilibrium curve corresponding to the Water Gas Shift reaction was calculated using simple thermodynamics. The equilibrium constant was expressed in terms of the reaction extents and the curve could thus be imposed onto the region of reaction extents. Equilibrium curves at various temperatures were plotted on the extent axes and this is shown in Figure 2. It was found that regardless of reaction temperature or initial number of moles of each species these equilibrium curves always pass through the vertices of the extent region which correspond to the minimum and maximum reaction extents for the FTS and WGS reactions.

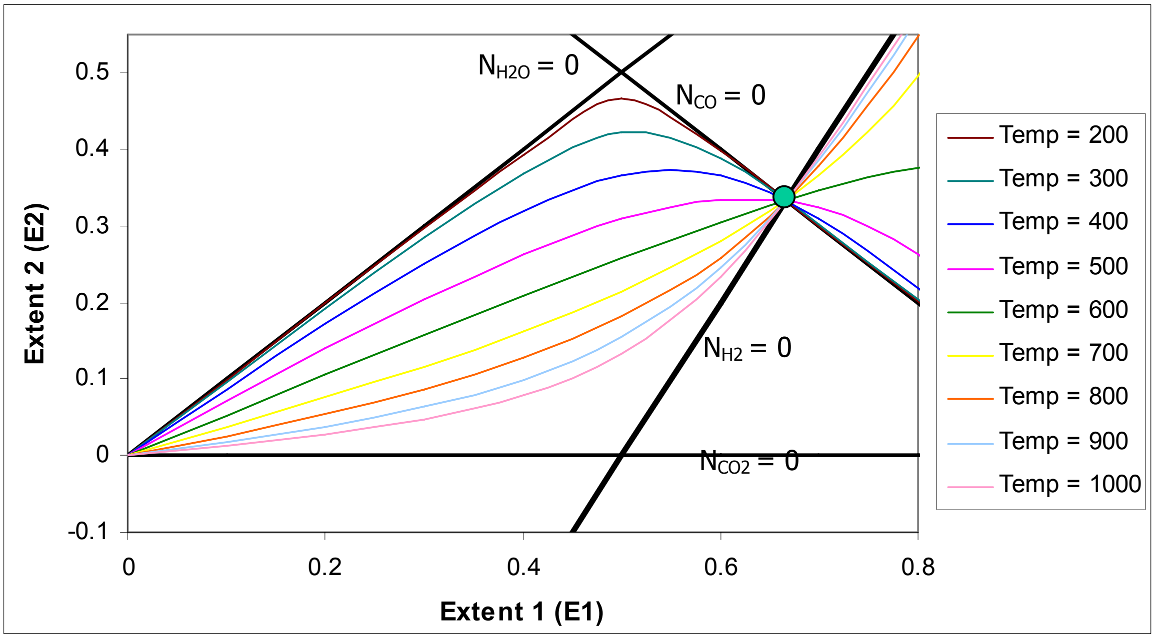

Figure 2: WGS Equilibrium Curves at Various Temperatures

The reason for this is that the equilibrium curves must pass through positive molar regions. The consequence of this property is that the WGS reaction can be used in order to achieve the maximum production of hydrocarbons, which is higher than if the FTS reaction is used in isolation.

As an addendum to the above research the regions, in terms of extents, of catalyst stability were investigated. The two catalysts which were studied were cobalt and iron, where iron is water gas shift active. The effect of secondary reactions on the catalyst stability was determined by expressing the equilibrium constant of these reactions in terms of E1 and E2. This was achieved by saying that the number of moles of products and reactants in these secondary reactions are so small we can assume that the number of moles from the FTS and WGS reactions remain unchanged by the secondary reactions. The equilibrium curves were then plotted on the extent axes with the Region of Possible Reaction Extents. This allowed an idea of the regions of catalyst stability to be obtained. These regions were reproduced at different temperatures to show temperature effects on catalyst stability. In Figure 3 and 4it can be clearly seen from these regions that there are certain restrictions imposed by catalyst activity in obtaining the maximum production of hydrocarbons.

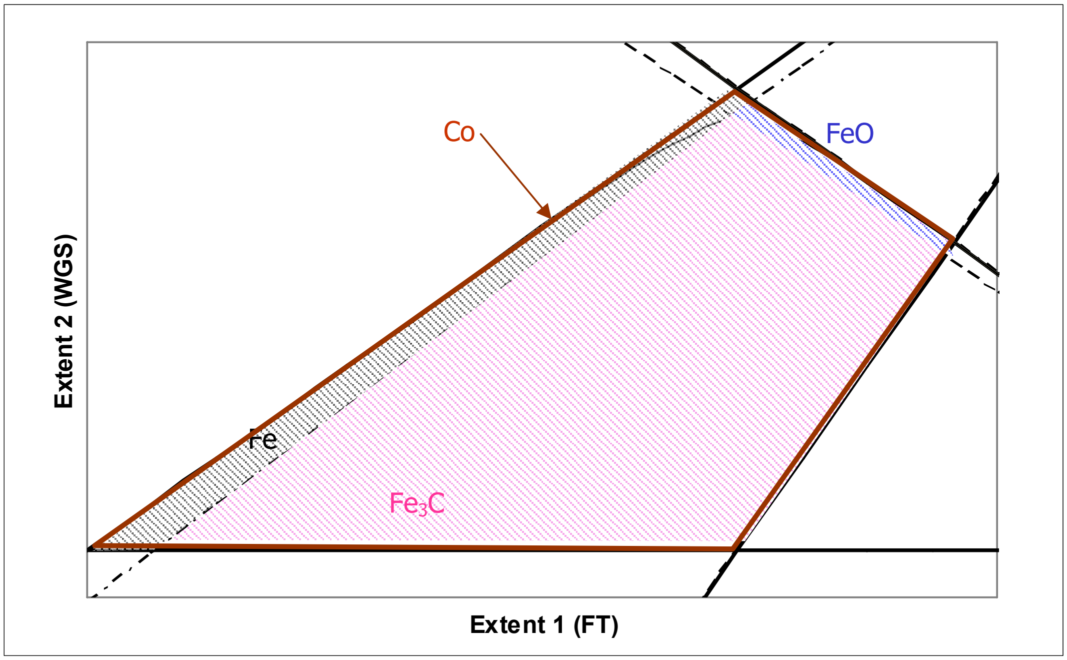

Figure 3: Region of Active Catalyst Phase (Temperature = 200°C)

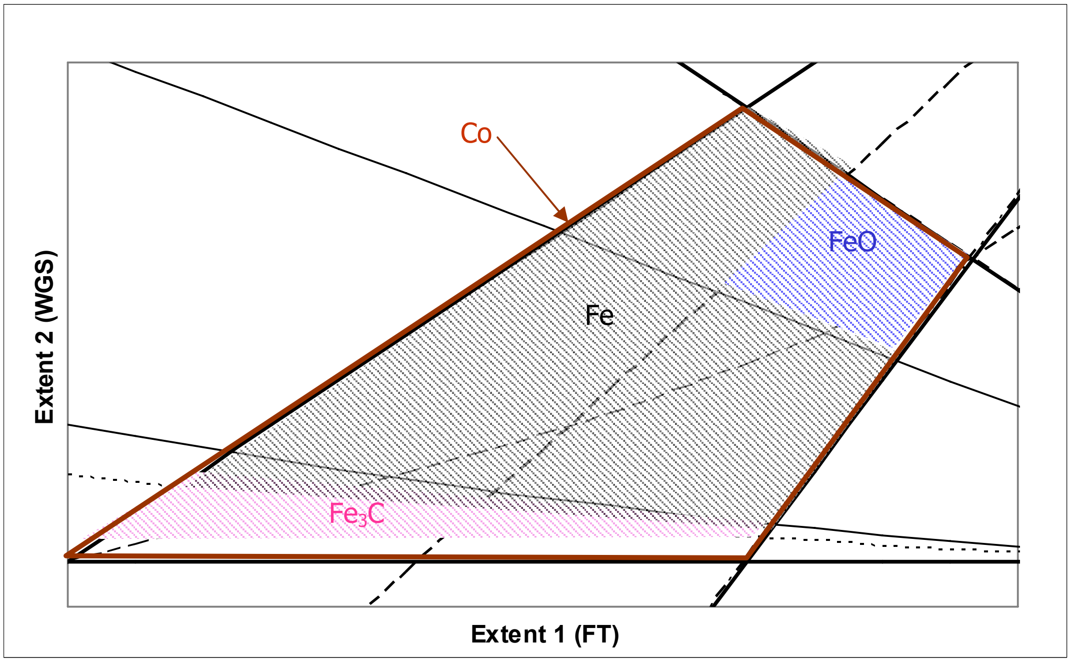

Figure 4: Region of Active Catalyst Phase (Temperature = 700°C)

By using this simple method of analyzing the mass balance as well as the thermodynamic equilibrium of the WGS and various secondary reactions the following information can be identified; the Region of Possible Reaction Extents and the point which gives the maximum production of hydrocarbons and the stable regions of active catalyst phase. This method is by no means completely precise but does give an idea of where one would like to operate the FTS reactor in order to ensure maximum reaction extent as well as ensuring that catalyst activity will be kept at a maximum