

A PRELIMINARY UNIFIED APPROACH TO THE STUDY OF FISCHER-TROPSCH KINETICS

Rafael L Espinoza
Sastech (Pty) Ltd
P.O. Box 1, Sasolburg 9570
South Africa

Keywords: Fischer-Tropsch, kinetics, modelling

INTRODUCTION

The standard approach to the study of Fischer-Tropsch (FT) kinetics is mainly based on statistical techniques. The rate expression is chosen on the grounds of the "best data fitting" as measured by the correlation factor in parity plots.

For each FT metal (like Co or Fe), there are different - and sometimes conflicting - rate expressions proposed in the literature. The development of a rate expression based on well designed experimental data is a relatively simple task. Therefore we are inclined to believe that - at least most - of the proposed rate expressions are basically correct for the catalyst used to generate the experimental data.

The objective of this study was to ascertain what role the specific characteristics of the FT catalyst plays in its kinetic behaviour. Once the main parameter(s) that affect this behaviour are identified, it should be possible to propose a general rate expression. The results of such a study are presented in this paper, in which a "unified" kinetic approach was taken and a single kinetic expression is proposed for all the different FT metals.

METHODOLOGY

The necessary data were obtained in two ways:

- Simulation of the data from well known kinetic expressions, and
- Using experimental data from the literature.

Use is made of a new kinetic technique, the "Singular kinetic path"¹ (SKP), to study kinetic data available in the literature for different FT metals. In short, the SKP technique discriminates between kinetic expressions based on the relative conversion path. This technique needs little experimental data, in the form of pairs of data points obtained at different space velocities. The two space velocities are selected to be in a ratio of 1 to 4 and this ratio is kept constant through the study. Because the data are relative and normalized, the reconstruction of the conversion path can be performed using pairs of data points obtained at different temperatures, pressures, pairs of space velocities (at a constant ratio) and feed compositions.

Use is also made of a simplified general kinetic model for the generation of the conversion path, based on the pairs of datum point mentioned above. This model is a simple stochastic model in which the feed composition generates large numbers of input molecules. These molecules go through many iterations in which they are converted into products according to the path dictated by the particular rate expression used. The new numbers and species of molecules are updated between iterations. The retention time is simulated by the number of iterations, while the space velocity is simulated by the initial numbers of molecules. Other inputs are the pressure and temperature. Factors like transport phenomena, temperature profiles, etc. do not have an effect on this study due to the relative and normalized handling of the data by the SKP technique¹.

KINETIC ANALYSIS

The following kinetic expressions were used to generate the data for the construction of the SKP plot:

Case 1. "Standard" precipitated Fe catalyst, Anderson²:

$$-r_{\text{CO} + \text{H}_2} = a P_{\text{H}_2} P_{\text{CO}} / (P_{\text{CO}} + b P_{\text{H}_2\text{O}}) \quad (1)$$

Case 2. "Standard" cobalt catalyst, Satterfield³:

$$-r_{\text{CO} + \text{H}_2} = c P_{\text{CO}} P_{\text{H}_2} / (1 + d P_{\text{CO}})^2 \quad (2)$$

Case 3. High Water-Gas-Shift (WGS) Fe catalyst, Ledakowicz⁴:

$$-r_{\text{CO} + \text{H}_2} = e P_{\text{H}_2} P_{\text{CO}} / (P_{\text{CO}} + f P_{\text{CO}_2}) \quad (3)$$

Case 4. Ruthenium catalyst, Everson⁵:

$$-r_{\text{CO} + \text{H}_2} = g P_{\text{H}_2} P_{\text{CO}}^{-0.36} \quad (4)$$

Case 5. In addition, we used experimental data⁶ for a Co-Mn catalyst that exhibited a similar degree of WGS as a typical potassium promoted precipitated iron catalyst.

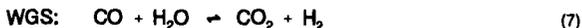
The SKP plot for these 5 cases is shown in Figure 1. In this figure, the ratio of the space velocities is an arbitrary 4 to 1. Notice that the two iron catalysts (cases 1 and 3) follow a different path. The same comment applies to the two cobalt catalysts (cases 2 and 5). The most noticeable difference between these catalysts is their WGS activity.

In the case of iron catalysts, the well known Anderson equation has a water partial pressure term in the denominator. That is, the accumulation of water has a negative effect on the rate of reaction. The Anderson equation is not able to reproduce Ledakowicz's data, since almost all the reaction water disappears due to the very high WGS activity of his catalyst. To solve this problem, Ledakowicz used a CO_2 term in the denominator of his kinetic expression. Notice that both the Anderson and Ledakowicz kinetic expressions can be considered particular cases of the more general rate expression:

$$-r_{\text{CO} + \text{H}_2} = h P_{\text{H}_2} P_{\text{CO}} / (P_{\text{CO}} + i P_{\text{H}_2\text{O}} + j P_{\text{CO}_2}) \quad (5)$$

Where for the "standard" iron, $j = 0$, and for the very high WGS iron, $i = 0$.

The FT and WGS equations can be represented by:



From equations (6) and (7), it is evident that the extent of the $(\text{CO} + \text{H}_2)$ conversion is proportional to the generation of $\text{CO}_2 + \text{H}_2\text{O}$. Therefore, it should be possible to use the $(\text{H}_2 + \text{CO})$ conversion (CONV) in the denominator of the rate expression, instead of the CO_2 and H_2O terms.

Such an approach was used to reproduce the SKP paths shown in Figure 1. We found that it was necessary to use the square root of the CO term in the numerator. The expression to reproduce the SKP paths is:

$$-r_{\text{CO} + \text{H}_2} = m P_{\text{H}_2} P_{\text{CO}}^{0.5} / (P_{\text{CO}} + k \text{CONV}) \quad (8)$$

In this expression, the conversion can be represented in terms of the partial pressures of the H₂, CO and the generation of H₂O and CO₂.

The k constants for the different catalysts are:

Ruthenium catalyst:	about	0.01 - 0.02
"Standard" cobalt catalyst:	about	0.01 - 0.02
"Standard" precipitated iron catalyst:		0.3 - 0.5
"High" WGS cobalt catalyst:		0.4 - 0.5
High WGS iron catalyst:		3.5

The WGS activity of typical ruthenium and cobalt catalysts is very low compared to typical precipitated iron catalysts⁷. The WGS activity of the high WGS cobalt catalyst is very similar to that of precipitated iron catalysts⁸, while the WGS activity of the high WGS iron catalyst⁹ was so high that practically all the water reacted to CO₂. It seems therefore that the k constant in equation (8) is a function of the WGS activity of the catalyst.

This observation is reinforced by the fact that two different FT catalysts that have similar WGS activity (the cobalt catalyst of case 5 and the "standard" iron catalyst of case 1) follow the same specific kinetic equation of Anderson².

Equation (8) shows that it is possible to express the interaction of the reactants or SKP path for different FT catalysts using a single equation. The next step is to consider the activation energy.

The activation energies proposed in the literature are not so different from each other, even for different FT metals. Most of the published activation energies for cobalt are between 93 - 103 kJ/mol³. For iron, the range for the published activation energies is somewhat larger⁸, mainly from 70 - 100 kJ/mol; while for ruthenium, Everson³ proposes 80 kJ/mol.

Since these activation energies overlap, as a first approximation a figure of 93 kJ/mol will be assumed for use in equation (8). The general equation would then be:

$$-r_{\text{CO} + \text{H}_2} = n \theta^{-93/RT} P_{\text{H}_2} P_{\text{CO}}^{0.5} / (P_{\text{CO}} + k \text{ CONV}) \quad (9)$$

The accuracy of the proposed general equation (9) was tested by comparing it with experimental data or kinetic rate expressions and SKP path for the 5 different catalysts described previously. The range of operating conditions used in the comparison is shown in Table 1.

The results are plotted in Figure 2 in the form of a parity plot. This figure shows that the general FT equation reproduces the experimental data or the predicted conversions using specific equations in an acceptable manner. There are some deviations which could be due to the fact that the proposed equation (9) is still not the optimal one. In addition, some deviations from proposed kinetic expressions are usually present due to experimental error.

CONCLUSIONS

It seems to be possible to model the conversion shown by different FT catalysts using a single kinetic rate expression. This expression applies to different metals and for catalysts that, despite having the same FT metal, exhibit different kinetic behaviour. This general kinetic expression is a first approximation, and it should be possible to improve it. Its objective was to ascertain the feasibility of a unified kinetic approach to FT kinetics.

The only variable in this expression is a term that is a function of the WGS activity of the specific catalyst being modelled. We can only speculate about this relationship at present. There may be an overlap for the sites responsible for the FT and the WGS reactions, which could explain the intimate relationship between the FT and WGS activities (besides the one due to the effect of FT and WGS on partial pressures) and its impact on the FT kinetic rate expression.

Should this be the case, then the path followed by the FT reaction is more dependent upon the reduced/oxidized state of the surface than on the chemical composition of the FT catalyst under consideration.

The applicability of the general kinetic rate expression means that there is still much to be done in FT catalysis, particularly in the surface field, in the understanding of the nature of the active sites for the FT and the WGS reactions, and in their interaction.

The results from this study also point out that perhaps different FT metals should not be studied in isolation and that more insight could be gained from an unified research approach.

REFERENCES

1. Espinoza, R.L., *Preprints, Int. Conf. on Catalysis & Catalytic Processing*, pp 391 -402, 1993, Cape Town, South Africa.
2. Anderson, R.B., *Catalysis, Emmet, P.H., (Ed) Vol 4, Reinhold*, 1956, New York.
3. Satterfield, C.N., Yates, I.C., *Energy & Fuels*, 1991, 5, 168 - 173.
4. Ledakowicz, S.; Nettelhoff, H.; Kokuun, R.; Deckwer, W.-D., *Ind. Eng. Chem. Process Des. Dev.*, 1985, 24, 1043 -1049.
5. Everson, R.C.; Mulder, H.; Keyser, M.J. *Proceedings of 7th Nat. Meeting of the South African Institution of Chem. Engineers*, pp 840 - 848, 1994, Esselen Park, South Africa.
6. Keyser, M., Ph.D. Thesis, Potchefstroomse University, Thesis submitted.
7. Dry, M.E., *The Fischer-Tropsch Synthesis, Catal. Science and Technology*, Anderson, J.R. and Boudart, M. (Eds), Vol 1, Springer-Verlag, 1981.
8. Huff, G.A.; Satterfield, C.N., *Ind. Eng. Chem. Process Des. Dev.*, 1984, 23, 696 -705.

TABLE 1: Range of operating conditions for the comparison of the proposed General Kinetic expression versus experimental data or specific kinetic equations for the 5 cases under study.

Catalyst	Pres. (bar)	Temp. (°C)	H ₂ /CO (in)	Mode of comparison
Case 1	20 - 35	220 - 260	1 - 3	Anderson eq.
Case 2	20 - 35	210 - 240	0.5 - 3	Satterfield eq.
Case 3	10	220 - 260	0.7 - 0.8	Exp. data
Case 4	20 - 35	210 - 240	0.5 - 2	Everson eq.
Case 5	5 - 20	220	1 - 5	Exp. data

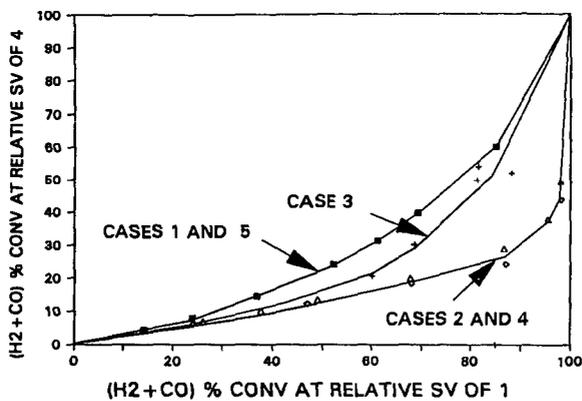


Figure 1. SKP Plot for the 5 different catalysts

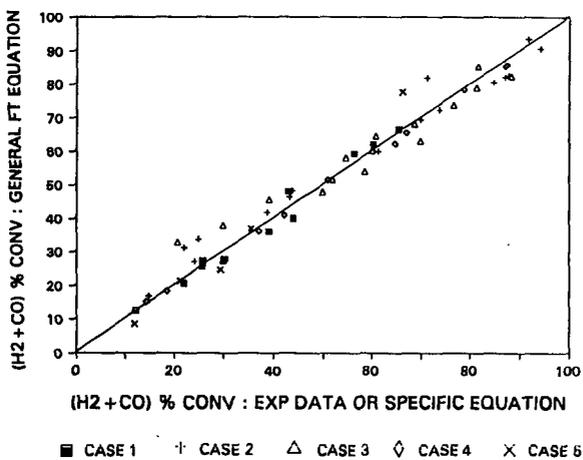


Figure 2. Parity plot between the general FT equation and specific FT equations or experimental data for the 5 cases under study