

Development and Testing of a New Macro Kinetic Expression for the Iron-Based Low-Temperature Fischer–Tropsch Reaction

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Based on the common belief that water inhibits the intrinsic Fischer–Tropsch (FT) reaction rate in the iron-FT synthesis, water is included in almost all iron-FT kinetic expressions. A new rate expression is now proposed where vacant sites, CO, and water are all included in the denominator. This model was evaluated with data from various historical experimental studies. In all cases it was found that the effect of water is not statistically significant and should therefore be omitted from the model. The new model describes the historical data more accurately than some other popular rate equations. To validate these conclusions, new experimental data were measured in a well-mixed slurry reactor in the absence of mass transfer limitations. The experimental methodology employed ensured that the iron-FT catalyst did not suffer measurable deactivation. It was confirmed that there is no basis for including water in the denominator of the new rate equation and that it is more accurate than the rival models considered.

1. Introduction

From the review by Van der Laan et al.¹ it is clear that there is little consensus in the literature on the form of the rate expression for the iron-catalyzed Fischer–Tropsch (FT) reaction. However, there seems to be a general belief that water (and possibly also CO₂) negatively influences the intrinsic FT reaction rate. As a result, the various rate equations that have been proposed essentially all assume rate inhibition by water or CO₂. Often these alleged inhibition effects have been specified (not tested) during the derivation of the rate equations by failing to account for the possibility of vacant sites on the catalyst surface.^{2–4} In such cases, it can thus be argued that the denominator terms of the rate expressions have been prematurely simplified based on assumption rather than by testing the model against experimental data. In this paper, a new macro kinetic expression is proposed for the FT reaction in the iron-based low-temperature Fischer–Tropsch (LTFT) synthesis. It is reported how this expression was developed from existing kinetic data and validated with a new experimental study.

2. Developing a Rate Equation for the Iron-FT Reaction

In this study, it is assumed that FT and water gas shift (WGS) are two distinct reactions that can be described with separate kinetic models, as has generally been the approach in macro kinetic studies on the iron-FT synthesis.¹

2.1. Reaction Order of Hydrogen. The reaction term (numerator) of a Langmuir–Hinshelwood–Hougen–Watson (LHHW) type rate equation represents the rate-determining step of the set of elementary reactions that constitute the overall reaction scheme. Since the rate-determining step of the FT reaction is normally assumed to be the hydrogenation of a carbon-containing species, the numerator is expected to include the partial pressures of hydrogen and CO. Most of the popular iron-FT rate equations assume first-order dependency of the reaction term on the partial pressure of CO, but there

is disagreement about the reaction order of hydrogen. Two of the well-known kinetic expressions, namely the Anderson–Dry expression⁴ and the Ledakowicz–Nettelhoff expression³ (eqs 1 and 2, respectively), assume a reaction order of one for hydrogen. On the other hand, Huff et al.² incorporated hydrogen in the inhibition term of eq 1 to formulate the Satterfield–Huff rate expression (eq 3), which implies that the reaction order of hydrogen becomes increasingly larger than one, eventually approaching a value of two, as the syngas conversion increases.

$$r_{\text{FT}} = A \frac{P_{\text{H}_2} P_{\text{CO}}}{P_{\text{CO}} + b P_{\text{H}_2\text{O}}} \quad (1)$$

$$r_{\text{FT}} = A \frac{P_{\text{H}_2} P_{\text{CO}}}{P_{\text{CO}} + c P_{\text{CO}_2}} \quad (2)$$

$$r_{\text{FT}} = A \frac{P_{\text{H}_2} P_{\text{CO}}}{P_{\text{CO}} + b(P_{\text{H}_2\text{O}}/P_{\text{H}_2})} \quad (3)$$

Van Berge⁵ considered the above three equations as the main rival kinetic models for the iron-FT reaction and realized that they can all be regarded as members of the same family represented by the following generalized expression:

$$r_{\text{FT}} = A \frac{P_{\text{CO}} P_{\text{H}_2}^\alpha}{P_{\text{CO}} P_{\text{H}_2}^\beta + b P_{\text{H}_2\text{O}} + c P_{\text{CO}_2}} \quad (4)$$

where $\beta = \text{maximum}\{\alpha - 1, 0\}$.

An experimental investigation was then performed on a precipitated iron catalyst in a well-mixed micro slurry reactor (CSTR) to establish whether one of the three original equations could be regarded as the most appropriate form of the generalized expression, or whether another form of eq 4 was more suitable for describing the iron-FT reaction rate. To this end, a statistical design procedure was applied to suggest experimental conditions where the predicted reaction rates of the rival models (eqs 1–4) differed most. This approach eliminated all three of

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the original special cases as appropriate kinetic models and therefore showed that another form of the generalized expression was required. After further systematic parameter optimization, it was concluded that eq 4 could be simplified to the following form with a high degree of confidence:

$$r_{\text{FT}} = A \frac{P_{\text{H}_2}^{0.5} P_{\text{CO}}}{P_{\text{CO}} + b P_{\text{H}_2\text{O}}} \quad (5)$$

Evidently the principal difference between eq 5 and the other special cases is the reaction order of hydrogen. It therefore appears that, to distinguish the general expression from the three original special cases, the statistical design procedure deliberately selected conditions which indicated that the reaction order of hydrogen is much lower than the values suggested by eqs 1–3. Moreover, it was shown quite clearly that the kinetic data could not be described very well with a rate equation that assumed a reaction order of one or higher for hydrogen. Due to the thorough experimental and statistical procedures followed by Van Berge,⁵ the reaction term (numerator) of his proposed rate expression (eq 5) will be retained for the purpose of developing a new kinetic model.

2.2. The Inhibition Term. There is general consensus in the literature that CO must first adsorb onto the catalyst surface before it can be hydrogenated. If the reaction order of hydrogen is 0.5, it implies that hydrogen is first dissociated before taking part in the FT reaction. Since hydrogen dissociation under FT synthesis conditions can presumably only occur on the catalyst surface, this means that hydrogen also reacts from the adsorbed state, and not directly from the gas phase as assumed by Dry⁴ for the derivation of eq 1. Furthermore, from chemisorption studies⁶ (albeit at 20 °C), it seems fair to assume that hydrogen and carbon monoxide compete for adsorption onto the same types of sites. Under these assumptions, the FT reaction proceeds over two adjacent catalytic sites, which implies that the inhibition term (denominator) of the rate equation must be squared.

There seems to be convincing evidence in the literature that CO₂ does not have a notable influence on the iron-FT reaction rate;^{7,8} consequently, CO₂ was not included in the new kinetic model. There further seems to be a belief that the catalyst surface is essentially completely covered with adsorbed CO and water.^{1,4} However, we have critically reviewed the experimental results in this regard and found that there is no conclusive evidence for the notion that water competes with CO for adsorption onto the iron-FT catalyst. For example, the water co-feeding studies of Satterfield et al.⁹ were performed without adjusting the reactor pressure, with the result that the additional water diluted the reaction medium. The co-fed water also increased the WGS reaction rate. The net result was a significant lowering in the CO partial pressure upon water co-feeding, so that the observed lowering in the FT reaction rate cannot unambiguously be ascribed to the additional water. In view of the foregoing, it was decided to include a constant term (representing vacant sites on the catalyst surface) in addition to CO and H₂O in the denominator of the new rate equation. If data analysis then revealed one of the terms in the denominator to be statistically insignificant, it could always be discarded at a later stage.

2.3. Final Form of the New Iron-FT Rate Equation. Combining the reaction and inhibition terms suggested above yields the following LHHW-type kinetic expression for the iron-FT reaction:

$$r_{\text{FT}} = A \frac{P_{\text{H}_2}^{0.5} P_{\text{CO}}}{(1 + k_{\text{CO}} P_{\text{CO}} + k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}})^2} \quad (6)$$

This rate equation is in fact not new, as Van der Laan¹⁰ has already shown that it is consistent with an FT mechanism where hydrogen first dissociates on the surface of the catalyst and then reacts with adsorbed CO. Davis^{11–13} has reviewed the results from mechanistic studies and concluded that, in light of current data, the FT reaction over iron-based catalysts most likely proceeds via an oxygen-containing intermediate, i.e., that hydrogen reacts with undissociated CO.

Van Steen et al.¹⁴ argued that the LHHW approach of a single rate-determining step (usually assumed to be the formation of the monomer), with all other elementary reactions close to equilibrium, is not valid for the FT synthesis. The objection centered on the fact that, if all other elementary reactions were in equilibrium, the thermodynamically predicted product spectrum of essentially only methane would be obtained. It is well-known that the actual methane selectivity of the FT synthesis is much lower than that expected from thermodynamics. Therefore, the LHHW method was discarded in favor of another approach that is based on the irreversibility of the FT reaction, which yielded the following kinetic equation:

$$r_{\text{FT}} = A \frac{P_{\text{H}_2}^{3/2} P_{\text{CO}} / P_{\text{H}_2\text{O}}}{(1 + k P_{\text{H}_2} P_{\text{CO}} / P_{\text{H}_2\text{O}})^2} \quad (7)$$

However, it can be argued that this objection is not quite valid. The derivation of a LHHW-type kinetic expression for the FT reaction merely requires the assumption that the monomer is quickly removed by a subsequent reaction step after its formation. Whether this step is controlled by thermodynamics (which may predominantly result in the formation of methane) or by kinetics (which may favor hydrocarbon chain growth) is of no consequence to the overall rate of CO hydrogenation, as long as the monomer is removed fast enough not to influence the overall reaction rate. In fact, by implication Van Steen et al.¹⁴ made a similar assumption in the derivation of their own rate equation, since they only included vacant sites and surface carbon in their site balance equation. The surface concentrations of the other intermediate species (CH_x or C_yH_x) can only be negligible if polymerization and subsequent desorption to final products are sufficiently fast reactions relative to the formation of surface carbon. If not, there would be a buildup of C₁ and higher intermediates on the catalyst surface, which would have to be included in the denominator of the kinetic expression. Nevertheless, as shown in the Appendix, the new iron-FT rate expression can be derived by following an approach analogous to that of Van Steen et al.¹⁴

3. Evaluation of the New Iron-FT Rate Equation with Existing Kinetic Data

In the historical studies that will subsequently be considered, kinetic models were fitted to the data by minimizing the sum of the squares of the differences and the *R*²-value was reported as a measure of the goodness of fit. Therefore, this convention will also be followed here for the reinterpretation of the existing data. For studies where the standard deviation of each measurement is available, “chi-square” (χ²) fitting can also be performed as suggested by Press et al.¹⁵ In the latter method, the weight (importance) assigned to each observation is related to the accuracy of that specific measurement.

Table 1. Comparison of Iron-FT Rate Equations with Data Measured by Van Berge⁵ at 250 °C in a Well-Mixed Slurry Reactor with a Ruhrchemie-Type Precipitated Iron Catalyst^a

kinetic equation	parameter values	R^2	χ^2
Satterfield–Huff (eq 3)	$b = 9.2$ [bar]	−0.95	15005
Ledakowicz–Nettelhoff (eq 2)	$c = 0.4$	−0.62	9361
Van Steen (eq 7)	$k = 0.02$ [bar ^{−1}]	0.27	5690
Anderson–Dry (eq 1)	$b = 3.9$	0.41	5138
Van Berge (eq 5)	$b = 1.6$	0.76	4451
new model (eq 6)	$k_{\text{CO}} = 0.10$ [bar ^{−1}], $k_{\text{H}_2\text{O}} = 0.10$ [bar ^{−1}]	0.85	3818
new model ^b (eq 6)	$k_{\text{CO}} = 0.09$ [bar ^{−1}], $k_{\text{H}_2\text{O}} = 0^b$	0.82	3280

^a Model fitting by minimizing the “sum of the squares of the differences”.^b Coefficient of water in the denominator specified as zero.

3.1. The Kinetic Study by Van Berge. Van Berge⁵ performed a kinetic study on a precipitated iron catalyst in a well-mixed slurry reactor at a temperature of 250 °C. As explained previously, a statistical design procedure was applied which showed that eq 5 was the preferred form of a family of rate expressions that can in general be represented by eq 4. The kinetic data, summarized in the Supporting Information, were now used to compare the new iron-FT rate expression (eq 6) to some other popular kinetic equations. The model parameters were optimized to minimize the sum of the squares of the differences, and the results are presented in Table 1. Two of the equations had negative regression coefficients, indicating that they describe the data substantially worse than the assumption of a constant reaction rate. This is probably a result of the experimental design procedure that was applied, which deliberately aimed at eliminating nonapplicable kinetic models. The Van Steen and Anderson–Dry equations also fit the data quite poorly. Of the old rate equations, the one by Van Berge describes the data by far the best, which is in line with his conclusions.⁵ The new expression, with quite a high regression coefficient, is a notable improvement on the Van Berge equation. Even though the coefficients of CO and water in the denominator term of the new equation assumed similar optimized values, this falsely creates the impression that water has an important influence on the reaction rate. In the last row of Table 1, it is shown that the omission of water from the inhibition term has a small influence on the R^2 -value. It can therefore be argued that the coefficient of water in the new equation is not significantly different from zero, so that there is no basis for including water in the kinetic model. Since the standard deviations of the reaction rates reported by Van Berge⁵ were available, the value of χ^2 could be calculated for every model fit and is reported in the last column of Table 1. These values confirm that the new kinetic model is better able to describe the FT reaction rate than the other equations considered here. Furthermore, by omitting water from the inhibition term of the new kinetic expression, the χ^2 -value of the model fit actually decreased (i.e., the weighted error was lower), even though the sum of the squares of the differences (“unweighted” error) increased slightly. This means that the inclusion of water in the new expression merely improved the prediction of the “inaccurate” rate measurements, but that the measurements with a high degree of accuracy were in fact described worse. This suggests that the water term merely served to predict the erroneous variations in the data, and corroborates the previous conclusion that there is no basis for including water in the inhibition term of the new equation.

The kinetic models were also fitted to the data by minimizing the χ^2 -value. Only selected results are presented in Table 2, because the other equations again fitted the data poorly. These

Table 2. Comparison of Iron-FT Rate Equations with Data Measured by Van Berge⁵ at 250 °C in a Well-Mixed Slurry Reactor with a Ruhrchemie-Type Precipitated Iron Catalyst^a

kinetic equation	parameter values	χ^2
Van Berge (eq 5)	$b = 0.98$	2918
new model (eq 6)	$k_{\text{CO}} = 0.11$ [bar ^{−1}], $k_{\text{H}_2\text{O}} = 0$ [bar ^{−1}]	2599

^a Model fitting by minimizing χ^2 .**Table 3. Comparison of Iron-FT Rate Equations with Data Measured by Ledakowicz et al.³ at 220–260 °C in a Stirred Slurry-Phase Reactor with a Potassium-Promoted Precipitated Iron Catalyst**

kinetic equation	Parameter values	R^2
Ledakowicz–Nettelhoff (eq 2)	$c = 0.24$	0.99
new model (eq 8)	$k_{\text{CO}} = 0.12$ [bar ^{−1}]	0.99

results confirm all the previous findings. For the new rate equation, the optimized adsorption coefficient of water assumed a value of zero (under the physical constraint that this parameter cannot be negative), suggesting that FT site occupation by water is negligible. Furthermore, the new kinetic model is able to describe the data better than the best of the existing rate expressions without increasing the number of model parameters, as is evident from the lower χ^2 -value. It therefore seems as if the following equation is an appropriate macro kinetic expression for the iron-FT reaction:

$$r_{\text{FT}} = A \frac{P_{\text{H}_2}^{0.5} P_{\text{CO}}}{(1 + k_{\text{CO}} P_{\text{CO}})^2} \quad (8)$$

3.2. The Ledakowicz–Nettelhoff Study. Ledakowicz et al.³ reported an FT kinetic study on a potassium-promoted precipitated iron catalyst, performed in a stirred autoclave slurry-phase reactor. The catalyst had such a high WGS activity under these conditions that the water concentration inside the reactor was negligible. It was expected that the measured FT reaction rate would be directly proportional to the hydrogen partial pressure, since both the Anderson–Dry and Satterfield–Huff rate expressions (eqs 1 and 3, respectively) approach simple first-order kinetics in hydrogen at low water partial pressures. Notwithstanding, a deviation from first-order kinetics was observed. Consequently, rate inhibition due to competitive adsorption between CO and CO₂ was assumed and the Ledakowicz–Nettelhoff kinetic expression for the iron-catalyzed FT reaction (eq 2) was proposed.

The data presented by Ledakowicz et al.³ were now also used to validate the new FT rate equation. As the water partial pressure was negligible for all the points, it was not sensible to consider kinetic models that assume an influence of water on the reaction rate. Consequently, only the Ledakowicz–Nettelhoff expression and the new model in the form of eq 8 were considered. Only three to four data points were measured at each of the four reaction temperatures. The reaction rate constants of the two involved equations were optimized for each temperature, but due to the limited amount of data, the respective adsorption coefficients were assumed to be constant (independent of temperature). The results of the re-analysis, presented in Table 3, indicate that both models described the data near perfectly. The excellent fit of these equations is probably on account of the small amount of data with a limited variation in the process conditions and is therefore in itself not much proof of the validity of either. However, this data set is of major significance, since the water concentration inside the reactor was negligible. Although not shown here, it was verified that the reaction rate was described significantly worse by a first-

Table 4. Comparison of Iron-FT Rate Equations with Data Measured by Zimmerman et al.¹⁶ at 250 °C with an "In-House" Prepared Precipitated Iron Catalyst (Promoted with Potassium)

kinetic equation	parameter values	R^2
Anderson–Dry (eq 1)	$b = 5.0$	0.90
new model (eq 8)	$k_{\text{CO}} = 0.08 [\text{bar}^{-1}]$	0.96
new model (eq 6)	$k_{\text{CO}} = 0.07 [\text{bar}^{-1}]$, $k_{\text{H}_2\text{O}} = 0.05 [\text{bar}^{-1}]$	0.97

Table 5. Comparison of Iron-FT Rate Equations with Data from Run 9 Reported by Huff^{17a}

reaction temp (°C)	Satterfield–Huff (eq 3)	new model (eq 6)
232	$b = 21.4 [\text{bar}]$; $R^2 = 0.85$	$k_{\text{CO}} = 0.33 [\text{bar}^{-1}]$, $k_{\text{H}_2\text{O}} = 0 [\text{bar}^{-1}]$; $R^2 = 0.83$
248	$b = 9.0 [\text{bar}]$; $R^2 = 0.71$	$k_{\text{CO}} = 0.51 [\text{bar}^{-1}]$, $k_{\text{H}_2\text{O}} = 0 [\text{bar}^{-1}]$; $R^2 = 0.82$
263	$b = 5.5 [\text{bar}]$; $R^2 = 0.65$	$k_{\text{CO}} = 0.58 [\text{bar}^{-1}]$, $k_{\text{H}_2\text{O}} = 0 [\text{bar}^{-1}]$; $R^2 = 0.81$

^a Measurements performed in a mechanically stirred slurry reactor with a fused iron catalyst.

order rate equation in hydrogen. The fact that an inhibiting effect on the kinetics was observed even in the absence of water suggests that the premise of rate inhibition by water only is not correct. Based on CO₂ co-feeding studies,^{7,8} it was also concluded previously that CO₂ could not be responsible for this retarding effect, eliminating the Ledakowicz–Nettelhoff expression as well. Instead, it appears more and more that the presence of vacant sites on the catalyst surface has a significant influence on the iron-FT reaction rate. Moreover, the value obtained for the CO coefficient is very similar to that obtained previously.

3.3. The Zimmerman Study. Zimmerman et al.¹⁶ performed an FT kinetic study in a stirred-tank slurry reactor. For their "in-house"-prepared precipitated iron catalyst, seven data points were obtained at a reaction temperature of 250 °C. It was reported that the Anderson–Dry expression (eq 1) could describe these data better than the Satterfield–Huff expression (eq 3). In the current study, these data were therefore used to compare the predictive capability of the new kinetic model (eq 8) with that of the Anderson–Dry equation, and the results are presented in Table 4. Both equations described the reaction rate well. Nevertheless, the new expression was somewhat better, and the value obtained for the CO coefficient is reasonably well in line with the values reported earlier. It should also be noted that the inclusion of a water term in the denominator of the new rate expression merely improved the data fit marginally (as indicated in the last row of Table 4), so that once again there is not much basis for including water in this kinetic model.

3.4. The Kinetic Study by Huff. Huff et al.² performed a kinetic study on a potassium-promoted fused magnetite catalyst in a well-mixed slurry reactor. The experiments were performed at three different temperatures, namely 232, 248, and 263 °C. It was shown graphically that the linearized form of the Satterfield–Huff expression (eq 3) correlated reasonably well with the kinetic data, and it was concluded that this model was an adequate description of the iron-FT reaction rate. The new iron-FT rate expression (eq 6) was now compared to the Satterfield–Huff equation by means of nonlinear regression of data reported by Huff¹⁷ (Table 5). For all three reaction temperatures, the coefficient of water in the new equation assumed a value of zero under the physical constraint that this parameter cannot be negative. Furthermore, the regression coefficients of the new kinetic expression were comparable to or higher than those of the Satterfield–Huff equation. It should be noted that the coefficient of CO in the new model increases with temperature, which is opposite to what one would expect from an adsorption coefficient. However,

considering the derivation presented in the Appendix, this model parameter is not necessarily a real adsorption coefficient, since it may consist of the actual adsorption coefficient as well as the rate constants of certain elementary reaction steps. Depending on the relative activation energies of the involved elementary reaction steps, the value of the observed CO coefficient can either increase or decrease with temperature. A further notable observation is that the coefficient obtained for CO is much higher than that of the other studies considered here. The only obvious difference between the Satterfield–Huff study and the other studies is that the former utilized a fused iron catalyst, whereas the others made use of precipitated (mostly Ruhrchemie-type) iron catalysts.

3.5. The Study by Van Steen. Van Steen et al.¹⁴ proposed an FT rate equation that was intended to be valid for both iron- and cobalt-based FT catalysts (eq 7 of this publication). Using data obtained with various iron-FT catalysts, eq 7 was compared with the Satterfield–Huff model (eq 3). To this end, the two equations were linearized to assume the following forms:

Van Steen (linearized):

$$\left[\frac{P_{\text{H}_2}^{3/2} P_{\text{CO}}}{P_{\text{H}_2\text{O}} r_{\text{FT}}} \right]^{1/2} = \frac{1}{A^{1/2}} + \frac{k}{A^{1/2}} \frac{P_{\text{H}_2} P_{\text{CO}}}{P_{\text{H}_2\text{O}}} \quad (9)$$

$$\text{Satterfield–Huff (linearized): } \frac{P_{\text{H}_2}}{r_{\text{FT}}} = \frac{1}{A} + \frac{b}{A} \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} P_{\text{CO}}} \quad (10)$$

The regression coefficients (R^2 -values) of the linearized Van Steen equation were reported to be between 0.94 and 0.97 for the various catalysts, while that of the linearized Satterfield–Huff model were much lower at around 0.1–0.5. Van Steen et al.¹⁴ therefore concluded that the Satterfield–Huff equation described the kinetic data quite poorly, while the Van Steen equation could predict the FT reaction rate very accurately. It was, however, later acknowledged that eq 7 cannot describe the FT reaction rate under all synthesis conditions, since a zero reaction rate is predicted in the absence of water.¹⁸ An alteration in the scheme of elementary reaction steps was proposed to explain why the FT reaction could still proceed in the presence of pure syngas, but such schemes of possible reaction pathways can become so complex and numerous that one can probably provide an explanation for any deviation observed from the measured reaction rate. The zero reaction rate predicted when no water is present will probably remain a point of concern over the Van Steen kinetic model.

The iron-FT data used in the foregoing historical study were obtained¹⁹ and now re-analyzed as part of the current investigation. First, the Satterfield–Huff model (eq 3) was linearized in an alternative way to more closely resemble the linearized form of the Van Steen model:

Satterfield–Huff (alternative linearization):

$$\frac{P_{\text{H}_2}^2 P_{\text{CO}}}{P_{\text{H}_2\text{O}} r_{\text{FT}}} = \frac{b}{A} + \frac{1}{A} \frac{P_{\text{H}_2} P_{\text{CO}}}{P_{\text{H}_2\text{O}}} \quad (11)$$

The foregoing three linearized models were then fitted to the iron-FT kinetic data, and the regression coefficients obtained are presented in Table 6. As reported by Van Steen et al.,¹⁴ eq 9 has very high R^2 -values, while eq 10 correlates very poorly with the data. However, contrary to expectation, the R^2 -values obtained for eq 11 are quite high and comparable to those of the linearized Van Steen expression. It is insightful to note that,

Table 6. Regression Coefficients (R^2 -Values) Obtained by Fitting Various Linearized Kinetic Models to the Iron-FT Data Reported by Van Steen^{19a}

catalyst	Van Steen, linearized (eq 9)	Satterfield–Huff, linearized (eq 10)	Satterfield–Huff, alternative linearization (eq 11)
Fe	0.94	0.10	0.89
FeMn	0.97	0.50	0.99

^a Data measured in a stirred slurry reactor with an iron catalyst at 225 °C and an iron–manganese catalyst at 275 °C.

Table 7. Regression Coefficients (R^2 -Values) Obtained from Nonlinear Regression of Kinetic Models to the Iron-FT Data Reported by Van Steen^{19a}

catalyst	Van Steen (eq 7)	Satterfield–Huff (eq 3)
Fe	0.26	−0.30
FeMn	−0.63	−0.39

^a Data measured in a stirred slurry reactor with an iron catalyst at 225 °C and an iron–manganese catalyst at 275 °C.

by merely changing the method of linearization, the Satterfield–Huff model could be converted from a linear equation with almost no correlation with the data to a linear equation that describes the data as well as the linearized Van Steen model. This vividly illustrates the mathematical artifacts that can be created by linearization of rate expressions. In view of this, the Van Steen and Satterfield–Huff equations were fitted to the same two sets of data by means of nonlinear regression and the R^2 -values are reported in Table 7. The regression coefficients assumed either negative or very small positive values, indicating that neither equation can describe the reaction rate well. As graphical confirmation of the foregoing, the correlation between the Van Steen model and the data obtained with the pure iron catalyst is presented in linear and nonlinear forms (Figures 1 and 2, respectively). Despite the apparent correlation between the data and the linearized model (Figure 1), the parity plot of the nonlinear model (Figure 2) verifies that there is actually little agreement between the model and the data. This was indeed also the case when the other kinetic models mentioned in this paper were considered.

3.6. Iron Catalyst Optimized for the Production of Olefins.

An experimental study has been performed at Sasol on a precipitated iron-based catalyst optimized for olefin production. In addition to the normal promoters of the Ruhrchemie-type catalysts, this catalyst contained metals such as zinc and manganese. The study was performed in a micro slurry reactor, and most of the measurements were made at 240 °C. The data are summarized in the Supporting Information. Note that there is a fair amount of repetition in the data, as the original aim of the experimental study was wider than merely to investigate the shape of the kinetic model. Various rate expressions were fitted to this set of data, and the results are presented in Table 8. The R^2 -values for all the equations are reasonably high. Possibly the variation in the data was not extensive enough to allow for clear discrimination between the various kinetic models considered. Nevertheless, the results are broadly in line with those found previously. During model optimization, the water coefficient in the new kinetic equation assumed a value of zero, while the CO coefficient was similar to the values obtained previously (around 0.1). Furthermore, the new kinetic model was somewhat better than all the other rate equations. It is also interesting to note that, for eqs 1, 2, 3, and 5, the coefficients of water and carbon dioxide were either zero or negligibly low.

4. Validation of the New Kinetic Model

The foregoing reinterpretation of existing data showed that the new kinetic expression is more generally valid than any of the other equations considered here. Nevertheless, the proposed model is somewhat controversial, as it does not account for any effect of water on the reaction rate. Therefore, an experimental study was performed to discriminate unambiguously between the new kinetic equation and those rate expressions that incorporate water in the inhibition term. Since the study of Van Berge⁵ was very effective to eliminate a number of other rate expressions, eqs 5 and 8 are regarded as the main rival models; consequently, the current experimental design procedure will specifically aim to discriminate between these two expressions.

4.1. Experimental Design. In principle, the operating points of the kinetic study can be selected by means of a statistical design procedure which ensures that a wide range of random process conditions are covered. This will typically require a substantial number of measurements and still does not guarantee that the data obtained will allow for clear model discrimination. It is also trivial to prescribe specific conditions inside the reactor where the rival rate expressions predict different reaction rates, but it can be quite difficult in practice to bring about a specific set of reagent partial pressures at the outlet of a CSTR type of reactor. It was therefore decided to rather develop a methodology of varying the system inputs which would ensure that operating conditions are covered where the rival kinetic models differ significantly.

Since the aim of the study is to perform kinetic measurements under conditions where eqs 5 and 8 predict significantly different reaction rates, a range of conditions must be identified where the ratio of the two equations varies substantially. Since the reaction terms of the two expressions are the same, this essentially means that the experimental approach must ensure a large variation in the ratio of their inhibition terms (defined here as R_{inh}):

$$R_{\text{inh}} = \frac{P_{\text{CO}} + k_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}}}{(1 + k_{\text{CO}}P_{\text{CO}})^2} \quad (12)$$

It thus follows that only the partial pressures of CO and H₂O are important. For the purpose of the current comparison, the hydrogen partial pressure is irrelevant, since the two expressions have exactly the same dependency on hydrogen. The values of the water and CO coefficients in the denominators of eqs 5 and 8, respectively, varied slightly according to the method of data analysis. Selecting the values obtained via “least squares” fitting, the ratio of the inhibition terms is expressed in eq 13. A three-dimensional plot of R_{inh} as a function of P_{CO} and $P_{\text{H}_2\text{O}}$ is presented in Figure 3.

$$R_{\text{inh}} = \frac{P_{\text{CO}} + 1.6P_{\text{H}_2\text{O}}}{(1 + 0.09P_{\text{CO}})^2} \quad (13)$$

FT kinetic studies are often performed at constant total pressure and with a feed gas consisting only of hydrogen and carbon monoxide. Different conditions inside the reactor are then obtained by varying the space velocity (i.e., conversion) and the H₂/CO ratio of the feed. Since 1 mol of water is produced for every mole of CO consumed by the FT reaction, there is always a risk that FT kinetic data may contain an inverse relationship between the partial pressures of CO and H₂O (as illustrated in Figure 4). Considering Figure 3, it is clear that this type of interrelationship runs more or less along a contour

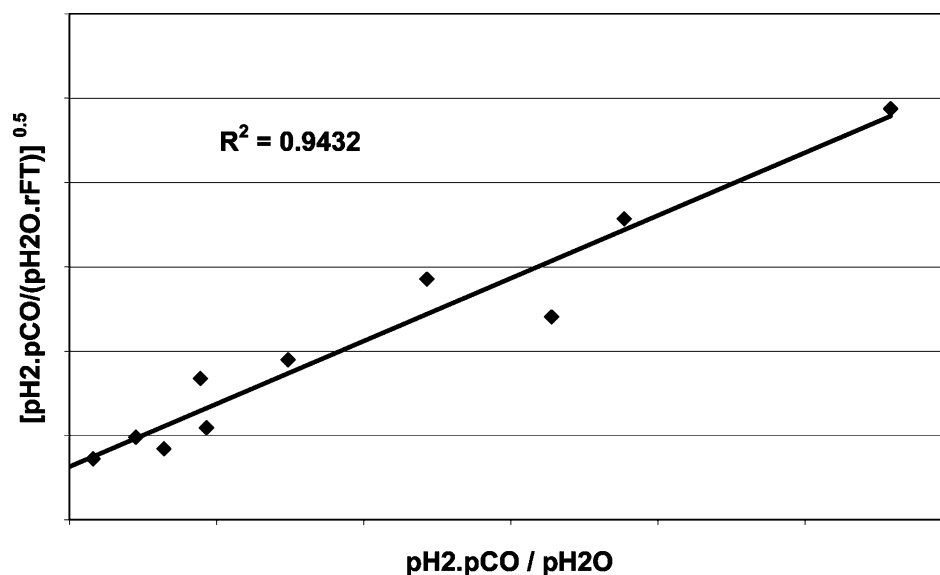


Figure 1. Correlation between the linearized Van Steen kinetic model and the kinetic data for the pure iron catalyst. Data measured by Van Steen¹⁹ at 225 °C in a stirred slurry reactor.

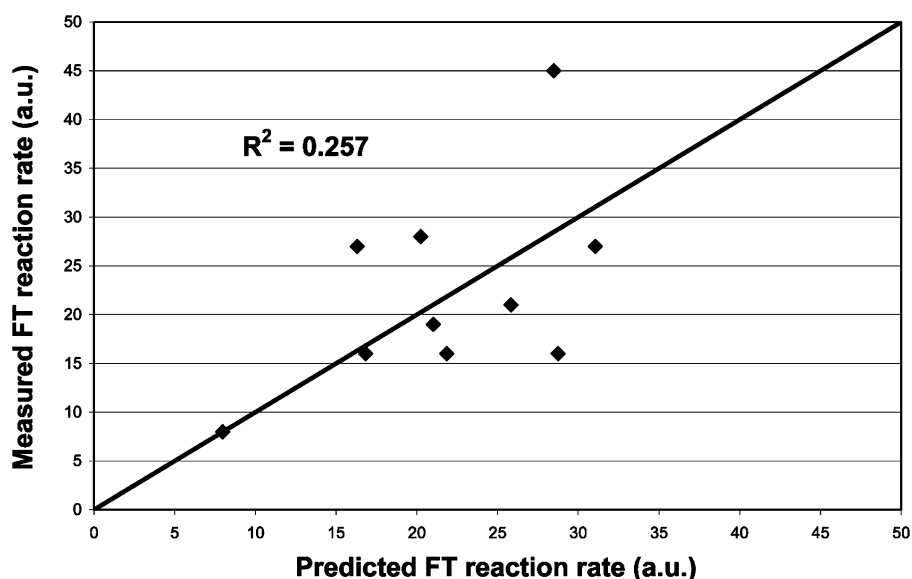


Figure 2. Parity plot of nonlinearized Van Steen kinetic model for data obtained with the pure iron catalyst. Data measured by Van Steen¹⁹ at 225 °C in a stirred slurry reactor.

Table 8. Testing Various Iron-FT Rate Equations with the Data Obtained with a Catalyst Optimized for Olefin Production^a

kinetic equation	parameter values	R^2
Van Berge (eq 5)	$b = 0$	0.75
Van Steen (eq 7)	$k = 0.02 \text{ [bar}^{-1}\text{]}$	0.77
Satterfield–Huff (eq 3)	$b = 0 \text{ [bar]}$	0.81
Ledakowicz–Nettelhoff (eq 2)	$c = 0$	0.81
Anderson–Dry (eq 1)	$b = 0.2$	0.82
new model (eq 6)	$k_{\text{CO}} = 0.12 \text{ [bar}^{-1}\text{]},$ $k_{\text{H}_2\text{O}} = 0 \text{ [bar}^{-1}\text{]}$	0.85

^a Measurements performed at 240 °C in a well-mixed slurry reactor.

(band of constant values) of R_{inh} . Even if the newly proposed expression (eq 8) were a more appropriate kinetic model than the traditional equations, it is not surprising that the Anderson–Dry type inhibition term was historically believed to be the correct denominator of the rate equation. Even for the kinetic study of Van Berge⁵ where the reagent partial pressures were varied independently, the value of R_{inh} did not change extensively enough to make a final conclusion regarding the form of

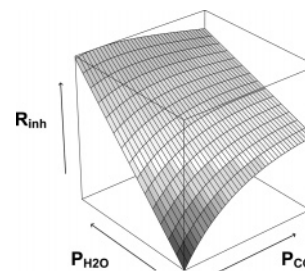


Figure 3. Ratio of the inhibition terms of the two rival kinetic models (eqs 5 and 8) as a function of carbon monoxide and water partial pressures.

the inhibition term. For 10 of the 13 data points, the value of R_{inh} fell in the narrow band of 2.5–3.2.

For the new experimental program, it is thus clear that the partial pressures of CO and H₂O must be varied in a fairly constant ratio (as illustrated in Figure 5). This can be achieved by keeping the feed composition and conversion more or less constant, while varying the reactor pressure. By superimposing Figure 5 on Figure 3, it is clear that this approach will ensure

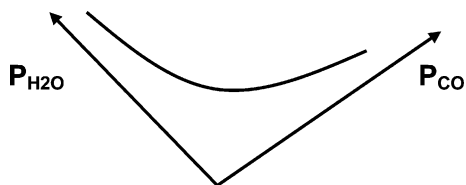


Figure 4. Inverse relationship between P_{CO} and P_{H_2O} that is often encountered in FT kinetic data.

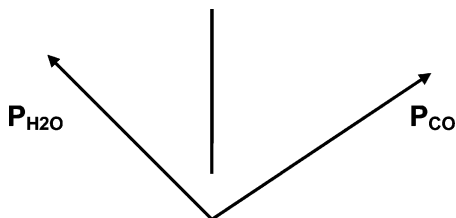
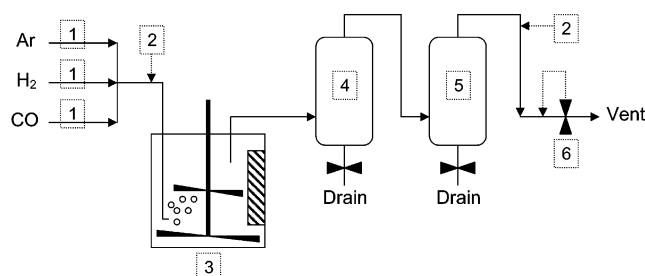


Figure 5. Relationship required between P_{CO} and P_{H_2O} to discriminate between the two candidate FT kinetic models.



1. Gas supply lines
2. Gas sample points
3. Slurry reactor with gas supply, impeller system and baffles shown
4. Hot knock-out pot
5. Cold knock-out pot
6. Back-pressure regulator

Figure 6. Schematic diagram of reactor rig layout used for kinetic validation run.

a substantial variation in R_{inh} and thereby generate data where the two rival kinetic models predict significantly different reaction rates. Very low reactor pressures are especially important, since the slope of the curved plane that represents R_{inh} is at its steepest when both P_{H_2O} and P_{CO} are low.

4.2. Experimental and Data Analysis. 4.2.1. Experimental Setup, Gas Analysis, and Data Processing. A schematic showing the layout of the reactor rig is provided in Figure 6. The FT synthesis was performed in a mechanically stirred slurry reactor with an internal volume of 600 mL. The reactor has a cylindrical shape with the impeller shaft running down the center. The shaft is fitted with two impellers, namely one at the bottom of the reactor and one about halfway up the reactor height. The reactor is also equipped with three vertical baffle plates which help to induce turbulent mixing inside the agitated reactor. Gas is supplied via a dip tube that is situated next to the inner wall of the reactor. This tube extends down to just above the bottom impeller, where the gas is released into the slurry. The exit line at the top of the reactor is equipped with a sintered metal filter so that the catalyst particles are retained inside the reactor. The position of the exit line determines the liquid level inside the reactor, as the excess liquid, together with the gaseous effluent, passes through this line to the hot knock-out pot (maintained at 200 °C). The waxy liquid that accumulates inside the hot pot is usually drained once a day. The gas flows to the cold knock-out pot (maintained at 25 °C), where water and oil are condensed. From the cold pot, the gas passes through a back-pressure regulator (responsible for maintaining

the pressure of the system) into the vent line. The tail gas sample point is situated between the cold knock-out pot and the back-pressure regulator. The total feed and the tail gas are analyzed with an online gas chromatograph (Gow-Mac Series 600) equipped with a thermal conductivity detector (TCD).

The catalyst used in this study was a Ruhrchemie-type spray-dried, precipitated iron catalyst as described in detail elsewhere.²⁰ Calcined catalyst (20 g) was loaded together with 350 g of FT wax into the reactor. The following gases, with minimum purities indicated, were fed from cylinders: hydrogen (99.999%), CO (99.9%), and Ar (99.999%). The feed gas composition and the temperature were kept constant during activation and synthesis. The feed consisted of the following gases with the approximate volume percentages given in parentheses: hydrogen (50%), carbon monoxide (32%), and argon (18%). The feed flow rates of the three gases were controlled with Brooks mass flow controllers. Catalyst activation was performed for 16 h at 240 °C and 20 bar (gauge) with syngas of the same feed composition as used during synthesis, but at a very high space velocity (similar to the procedure followed elsewhere²¹). After activation, the total feed flow rate was lowered to a predetermined value, while the temperature and pressure were kept at 240 °C and 20 bar (gauge), respectively. This represented the baseline operating condition, which was maintained until it was certain that the catalyst achieved stable performance before the kinetic measurements commenced. The stabilized syngas conversion at the reference conditions was about 45%.

Argon served as an internal standard for the purpose of data processing. Being an inert, it passes through the reactor unconverted, which means that the argon inlet and outlet flow rates are known from the calibration curve of the Brooks mass flow controller. Combining this flow rate with the GC-TCD analyses, the inlet and outlet flow rates of the other permanent gases (hydrogen, CO, and CO₂) could be determined. Since water was not measured, its production rate was calculated from an oxygen balance under the assumption that the contribution from oxygenates in the product spectrum was negligible. The Fischer–Tropsch reaction rate was defined as the amount of CO converted to hydrocarbons per unit time per unit amount of catalyst, i.e., independent of the water gas shift rate. It was calculated as the total rate of CO consumption minus the rate of CO₂ production.

In FT kinetic measurements, significant errors are often unavoidable, but at the very least cognizance should be taken of these. For example, if the error in the CO and CO₂ flow rates were assumed to be a mere 1% for the current set of experimental data, the accumulated error in the calculated FT reaction rate could be up to 6%. Furthermore, even though the catalyst is known to have a fairly low oxygenate selectivity under the reference conditions of the kinetic experiments, the omission of the oxygenate contribution from the oxygen balance could have resulted in an overestimation of between 4% and 7% in the water production rate, depending on the CO₂ selectivity of the involved data point. Clearly errors in the primary data that appear insignificant can be accumulated and amplified via the data processing procedure to assume notably large values in the final results. The experimental design of FT kinetic experiments is therefore of the utmost importance to ensure that conditions are covered where rival kinetic models differ so extensively that model discrimination can be clear and unambiguous, despite the involved experimental errors.

4.2.2. Elimination of Mass Transfer Restrictions. By means of calculation, it was estimated that the effectiveness factor of

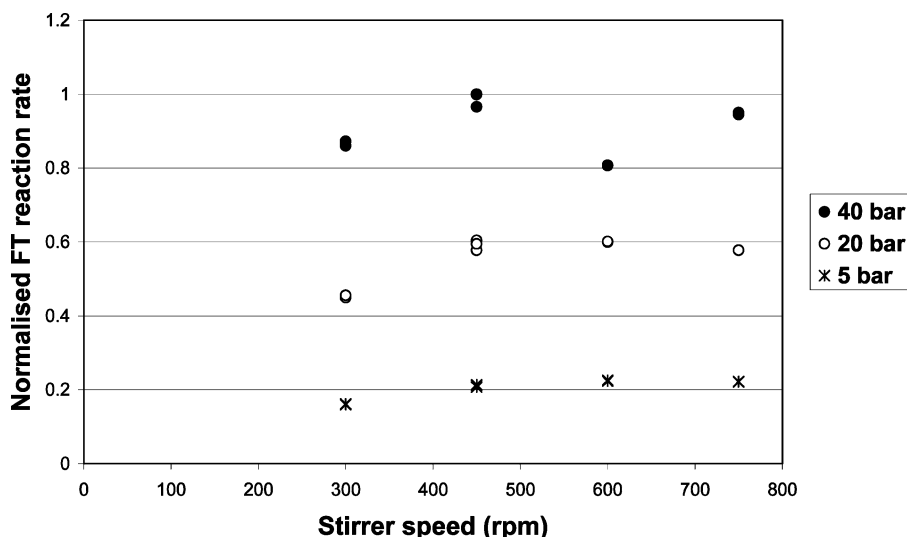


Figure 7. Effect of stirrer speed on FT reaction rate at various operating pressures. This run was performed at high space velocity (high FT reaction rates) to demonstrate that mechanical stirring was sufficiently fast during the kinetic validation run to eliminate gas–liquid and liquid–solid mass transfer limitations. The FT reaction rate was normalized to the highest rate measured during the run.

the catalyst particles was above 98% for all kinetic measurements (see the Supporting Information). The fine spray-dried catalyst particles used in this study therefore ensured that the kinetic measurements were not notably influenced by intraparticle mass transfer limitations. A run was also performed where the stirrer speed of the mechanical agitator was varied to confirm that interparticle (gas–liquid and liquid–solid) mass transfer limitations were eliminated. This run was performed at 5, 20, and 40 bar (gauge) to cover the whole pressure range of the kinetic experiments, since both the mass transfer rate and the intrinsic FT reaction kinetics are dependent on pressure. High space velocities were also employed during this run so that the resulting FT reaction rate was between 30% and 100% higher than during the actual kinetic measurements at the corresponding pressure. In other words, mass transfer restrictions were eliminated at higher chemical reaction rates than those encountered during the actual kinetic experiments. The effect of the stirrer speed on the FT reaction rate is presented in Figure 7. The data in this graph were normalized to the highest reaction rate of the run. Clearly there was no effect of the stirrer speed on the reaction rate beyond 450 rpm. Therefore, the stirrer speed of 450 rpm used during the actual kinetic measurements was sufficient to eliminate interparticle mass transfer limitations.

4.2.3. Kinetic Measurements. In our experience at Sasol, the iron-based catalyst in the LTFT synthesis can be notoriously unstable if operated over the wide range of process conditions normally required for a kinetic study. To ensure a stable intrinsic activity of the catalyst, the following methodology was employed. The reactor was essentially maintained at reference conditions, and changes to other operating points were only made for short intervals. Calculations showed that, at the involved feed flow rates, it would not take more than about 1 h for five replacements of the combined gas inventory of the reactor and the knock-out pots. Therefore, a change in operating conditions was made in the morning and three samples were taken between 2 and 6 h after such a change had been effected. Subsequently, the system was returned to the reference conditions, which were maintained until the next morning, when another kinetic measurement was made. The aim of this procedure was therefore to allow sufficient time for the reactor to attain steady state with regard to the permanent gases, but insufficient time for the catalyst to respond notably to the new conditions. The reference measurements taken regularly through-

out the run, as well as the three samples taken at the nonbaseline conditions over a period of 4 h, could confirm that the FT activity of the catalyst was indeed stable. It should be noted that two separate, duplicate runs were performed in this manner to ensure confidence in the outcome of the study. Since the results of the two runs were essentially the same, only one run will be discussed.

It can of course be argued that, for practical application of rate equations, it is only important to describe the overall steady-state kinetics of the system. A rate equation that incorporates both the intrinsic reaction kinetics and the manner in which the catalyst responds to its environment should therefore be sufficient. However, since such a rate expression would attempt to combine two fundamentally unrelated aspects as one phenomenon, it would be highly empirical. It is believed that much better understanding and predictive accuracy can be achieved by rather studying and describing these two aspects separately. Therefore, this study is only concerned with the intrinsic kinetics of the FT reaction.

4.2.4. Data Analysis. Since the operating pressure during the experimental runs varied from 5 to 40 bar and the iron-FT reaction rate is more or less proportional to the syngas partial pressure, the measured reaction rates covered a very broad range. If the kinetic models were fitted to the data by minimizing the absolute error, a higher importance would have been assigned to the rates measured at high pressure. This would have defeated the aim of the experimental design procedure, which indicated that rate measurements at very low pressures are especially important for discriminating between the two rival models. To rather assign equal weights to the rate measurements across the whole range of reactor pressures, it was thought more appropriate to minimize a relative error. Consequently, whenever rate expressions were fitted to kinetic data, the relative variance was minimized (as defined by Van der Laan¹⁰).

4.3. Results and Discussion of the Kinetic Measurements. Apart from the reference operating pressure of 20 bar (gauge), kinetic measurements were also performed at reactor pressures of 5, 10, 30, and 40 bar (gauge). As mentioned previously, three samples were taken at each of the nonreference conditions between 2 and 6 h after a change from the reference condition was made. The run history (operating pressure as a function of synthesis time) is presented in Figure 8, while the measured FT reaction rates (normalized to that of the first measurement

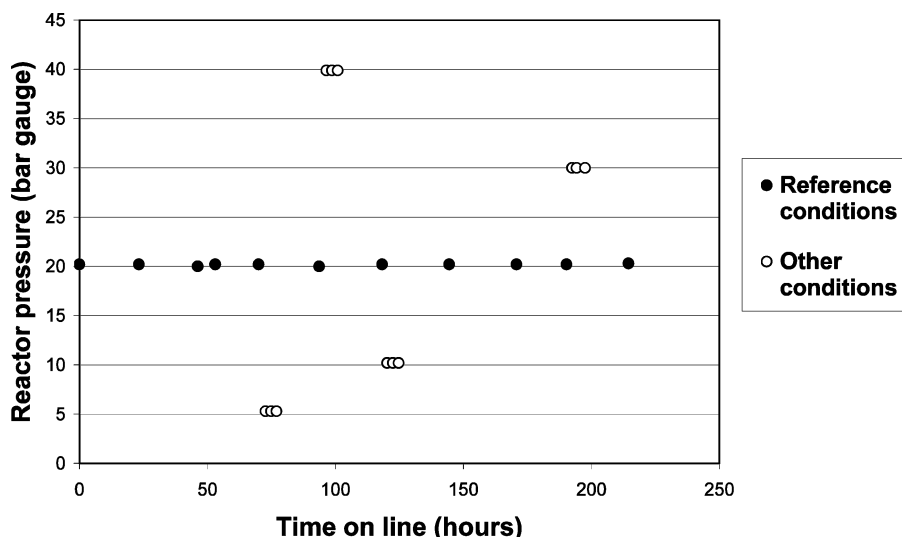


Figure 8. Reactor pressure versus time on line for the kinetic validation run performed with a precipitated (Ruhrchemie-type) iron catalyst at 240 °C in a well-mixed slurry reactor.

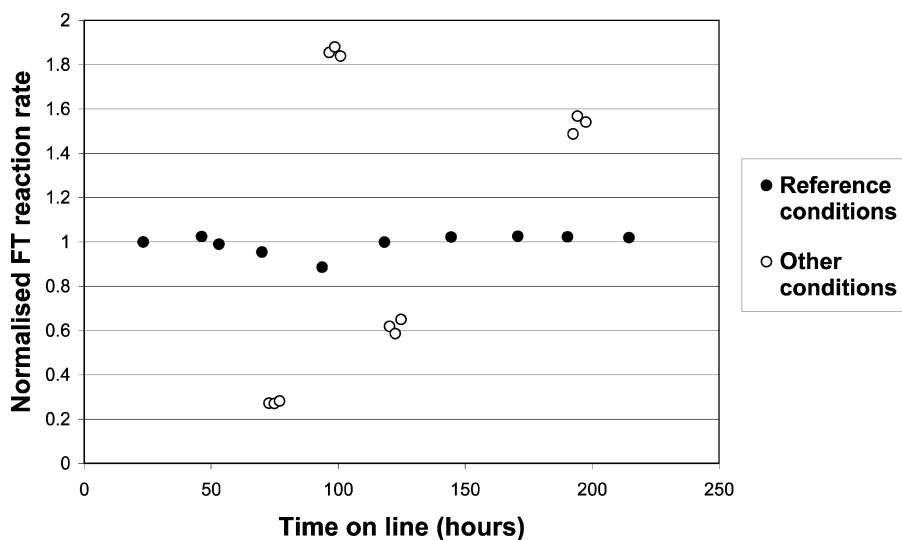


Figure 9. FT reaction rate versus time on line for the kinetic validation run. FT reaction rate normalized with respect to the first measurement taken at reference conditions. Measurements performed with a precipitated (Ruhrchemie-type) iron catalyst at 240 °C in a well-mixed slurry reactor.

at reference conditions) are presented in Figure 9. Apart from very limited scatter in the data, the reference FT reaction rate was fairly constant over the period of synthesis, indicating a stable FT activity during the intrinsic kinetic measurements. Furthermore, at each of the nonreference pressures, the three measurements taken were fairly similar to one another, indicating that the time allowed for the reactor to reach steady state was sufficient and that the catalyst did not respond significantly to the 6-h-long change in conditions. It is further clear that the changes in the FT reaction rate due to varying operating pressures were substantially larger than the scatter in the data, so that the random experimental errors are not expected to have a significant influence on the interpretation of the results.

The kinetic data from this run are presented in the Supporting Information. For data analysis purposes, only three representative reference (baseline) points were selected: one at the beginning, one in the middle, and one at the end of the run. This ensured that the reference conditions did not have more weight than any of the other conditions. The two rival FT rate expressions were fitted to the kinetic data, and the results are presented in Table 9. When the adsorption coefficients were assigned their original values ($k_{\text{H}_2\text{O}} = 1.6$ in the case of eq 5 and $k_{\text{CO}} = 0.09$ in the case of eq 8), it was found that the Van

Table 9. Testing the Two Rival Iron-FT Kinetic Models, as Well as Some Previously Discarded Models, with Data from the New Kinetic Validation Run^a

kinetic equation	optimized parameter values	S_{rel} (%)
Van Berge (eq 5)	$k_{\text{H}_2\text{O}} = 1.6^b$	51.6
new model (eq 8)	$k_{\text{CO}} = 0.09^b$ [bar ⁻¹]	8.1
Van Berge (eq 5)	$k_{\text{H}_2\text{O}} = 0$ ($k_{\text{H}_2\text{O}} = -1.3$ unconstrained)	41.2
new model (eq 8)	$k_{\text{CO}} = 0.09$ [bar ⁻¹]	8.1
Van Steen (eq 7)	$k = 0.01$ [bar ⁻¹]	22.8
Anderson–Dry (eq 1)	$k_{\text{H}_2\text{O}} = 0$	11.2
Satterfield–Huff (eq 3)	$k_{\text{H}_2\text{O}} = 0$ [bar]	11.2
Ledakowicz–Nettelhoff (eq 2)	$k_{\text{CO}_2} = 0$	11.2

^a Measurements performed with a precipitated (Ruhrchemie-type) iron catalyst at 240 °C in a well-mixed slurry reactor. ^b Specified values.

Berge equation had a very high relative variance, whereas the new kinetic model had a fairly low variance. This suggests that the Van Berge model is incapable of describing the data, but that the new model is very much in line with the measured data. The two models were also compared graphically by plotting the ratio of the measured to the predicted FT reaction rate as a function of the syngas partial pressure inside the reactor (Figure 10). Clearly the Van Berge equation has a very serious systematic deviation with variation in syngas pressure which is

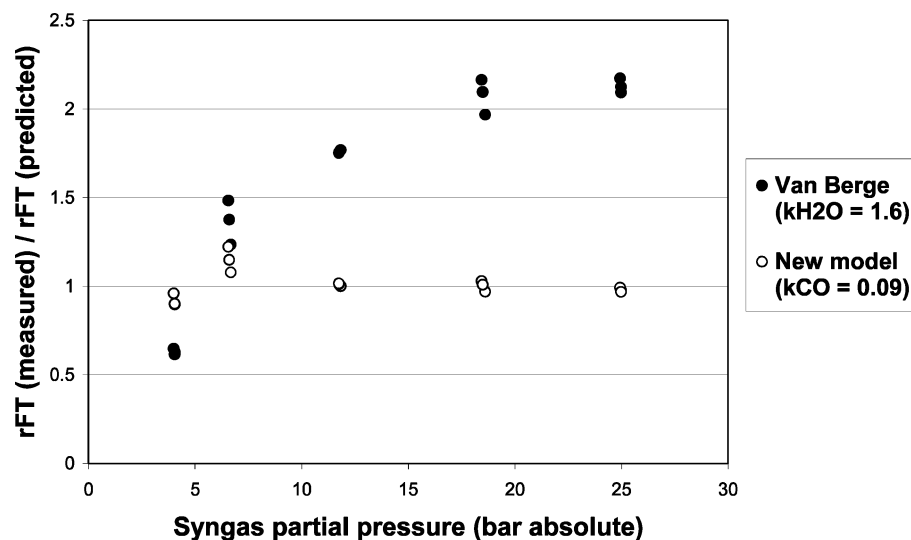


Figure 10. Accuracy of the two rival models as a function of syngas partial pressure for the kinetic validation run. Original model parameters were applied. Data measurements performed with a precipitated (Ruhrchemie-type) iron catalyst at 240 °C in a well-mixed slurry reactor.

especially evident at low pressures. The slight deviations in the new kinetic expression appear to be random scatter, and the model is generally very accurate.

The adsorption coefficients of eqs 5 and 8 were also reoptimized with the new data set to establish whether either of these expressions could benefit from improved parameter values. The results of this reoptimization are also presented in Table 9. When the water coefficient in the Van Berge expression was unconstrained during the optimization procedure, it assumed a significantly large negative value (−1.3). This physically impossible situation indicates that this rate equation does not correctly account for the effect of water on the FT reaction rate. In fact, it suggests that the inhibition term of eq 5 (and especially the notion of FT rate inhibition by water) is principally flawed. By applying the physical constraint that an adsorption coefficient must be nonnegative, the water coefficient assumed an optimized value of 0. Even though the omission of water from the denominator improved the fit of the Van Berge expression somewhat (as indicated by the slight decrease in S_{rel}), it reduced the model to a simple half-order equation in hydrogen. To the contrary, the reoptimized CO coefficient in the new FT rate expression was almost exactly the same as the original estimate, which installs further confidence in the new model. As a further test of whether water should be included in this model, a water term was added to the denominator of the new rate equation. Although not shown here, the coefficient of water assumed a value of 0. This confirms that water should not be included in the denominator of the new FT kinetic equation.

The other FT rate expressions considered in this study (eqs 1, 2, 3, and 7) were also fitted to the data of the kinetic validation run to verify that they have been rightfully discarded in the past. The results are included in Table 9. The Van Steen equation (eq 7), which did not describe any of the historical data sets adequately, here also has a rather high relative variance. For eqs 1, 2, and 3, the fairly low values of S_{rel} suggest reasonable descriptions of the FT reaction rate, but this is somewhat misleading. In each case the coefficient of the inhibiting agent (water or carbon dioxide) assumed the lowest value that is physically meaningful, namely zero. This means that all three of these expressions were reduced to a simple first-order expression in hydrogen. As the Anderson–Dry expression previously appeared to be the best of these three equations, it was selected for a case study where the influence of the water coefficient on the relative variance of the model fit was

Table 10. Effect of Water Coefficient Value in the Anderson–Dry Equation on the Ability of the Model To Fit Data from the New Kinetic Validation Run^a

specified value of k_{H_2O}	S_{rel}^b (%)
0	11.2
0.5	15.3
1.0	18.6
1.5	21.1

^a Measurements performed with a precipitated (Ruhrchemie-type) iron catalyst at 240 °C in a well-mixed slurry reactor. ^b After reoptimization of kinetic rate constant.

investigated. The value of the water coefficient was increased stepwise, and at each of these values the reaction rate constant was reoptimized. The resulting values of the relative variance are reported in Table 10. As the assumed inhibiting influence of water on the reaction rate becomes significant, the model fit clearly becomes quite poor. This is despite the fact that the water coefficient values in Table 10 are still well below the range of about 4–5 that have typically been obtained when this kinetic model was used to describe historical kinetic data measured with similar catalysts. In view of the above, it is concluded that eqs 1, 2, 3, and 7 were indeed rightfully discarded in the past.

5. Findings and Conclusions

5.1. Experimental and Data Analysis Methodology. It was shown that linearization of rate equations for the purpose of kinetic analysis may introduce mathematical artifacts that can make the correlation between the model and the data appear much better than it actually is. It is thus recommended that kinetic expressions rather be fitted to data by means of nonlinear regression.

The aim of the experimental study was to validate the new FT kinetic model under conditions where the catalyst activity was constant. Since iron-based LTFT catalysts are notorious for responding to changes in operating conditions, a specific methodology was followed. The catalyst was kept at reference conditions for most of the run. Changes to other conditions were only made for fairly short periods that allowed enough time for the reactor to reach steady state with respect to the permanent gases, but insufficient time for the catalyst to respond to these changes. In doing so, a wide range of water partial pressures could be covered without affecting the activity of the catalyst.

It is believed that this approach is essential in iron-FT studies to separate chemical reaction kinetics from catalyst instability effects.

An experimental design procedure was applied with the explicit aim of discriminating between two rival kinetic models. This procedure prescribed how system inputs should be varied, rather than stipulating specific reagent partial pressures inside the well-mixed reactor. The procedure was extremely effective—despite the fairly small number of kinetic measurements, the data could discriminate beyond any doubt between the two involved rate expressions.

By varying the reactor operating pressure over a very wide range (5–40 bar) while keeping the conversion more or less constant, the water partial pressure inside the reactor could be varied from 0.4 to 3.5 bar without causing a measurable decrease in the intrinsic FT activity of the catalyst. These results can therefore be regarded as important information in the debate of whether water has an inhibition effect on the intrinsic FT reaction rate.

5.2. Iron-FT Kinetic Models. From the historical kinetic studies considered in this paper, it appears as if a given set of kinetic data could usually be described well by the rate expression that was specifically developed from that set of data. However, these traditional iron-FT rate equations seem to lack general applicability, since none were found to describe various data sets satisfactorily.

A new macro kinetic equation was proposed that included vacant sites, CO, and water in the denominator (inhibition term). The denominator was also squared, as it seems difficult to rationalize a single site mechanism as implied by some of the existing rate expressions. When the new equation was fitted to historical kinetic data, as well as the data from a new experimental study, the effect of water was always found to be statistically insignificant. At the very least, this means that the hydrocarbon formation rate in the typical temperature range of the iron-based LTFT synthesis (around 240 °C) can be described well without accounting for the influence of water. More generally speaking, it casts some doubt over the belief that water inhibits the iron-FT reaction rate at these temperatures.

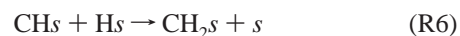
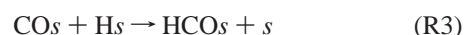
With the omission of water, the new rate equation had no more parameters than any of the other kinetic expressions it was compared to. Yet it was found that this new model could describe each set of historical data at least as well as (and often better than) the specific equation that was originally reported to be the most applicable. The new experimental study discriminated even more clearly between the new model and the rival expressions considered here. Though not shown in this paper, it should be noted that we have also tested other equations with different reaction orders for hydrogen and CO and different inhibition terms. However, we could not find another rate equation that can describe the data from all the historical studies, *as well as* the data from the new kinetic data, as accurately as the proposed model.

The new experimental data were measured under conditions where some parameters were kept more or less constant, because this experimental study was designed with the explicit aim to discriminate between two specific rate equations. It should, however, be kept in mind that the combined variation in the historical data sets was quite extensive. For example, in the study by Van Berge,⁵ the H₂/CO ratio varied from 1 to above 10, whereas the H₂/CO ratio varied from about 0.6 to 2.7 for the data reported by Zimmerman et al.¹⁶ This indeed covers an extensive range as far as FT is concerned, yet the new model fitted the data from both these studies very well.

The optimized value obtained for the CO coefficient of the new model was almost always close to 0.1, even though a variety of kinetic studies by different researchers were considered. This consistency in the value of the model parameter installs further confidence in the new kinetic expression.

Appendix

The following serves merely to illustrate that the new rate equation can be derived by assuming irreversibility of the hydrogenation steps in the FT reaction, and not to suggest the precise mechanism whereby the reaction proceeds or the specific monomer involved in the polymerization steps. Consider, for example, the following scheme of elementary reactions where it is assumed that all hydrogenation steps (reactions R3–R6) are irreversible:



If the steps in reactions R1, R2, and R7 are at equilibrium, the surface concentrations of CO, hydrogen, and water can be expressed as follows:

$$[\text{COs}] = K_1 P_{\text{CO}} [s] \quad (\text{A1})$$

$$[\text{Hs}] = K_2^{0.5} P_{\text{H}_2}^{0.5} [s] \quad (\text{A2})$$

$$[\text{H}_2\text{Os}] = K_7 P_{\text{H}_2\text{O}} [s] = k_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} [s] \quad (\text{A3})$$

In this example, the overall FT rate is taken as the formation rate of the CH₂ monomer (reaction R6):

$$r_{\text{FT}} = k_6 [\text{CHs}] [\text{Hs}] \quad (\text{A4})$$

Under the steady-state approximation, the intermediate species (HCOs, Cs, CHs) cannot accumulate on the catalyst surface, so their formation rates must equal their consumption rates; thus

$$k_3 [\text{COs}] [\text{Hs}] = k_4 [\text{COHs}] [\text{Hs}] = k_5 [\text{Cs}] [\text{Hs}] = k_6 [\text{CHs}] [\text{Hs}] \quad (\text{A5})$$

By eliminating the surface concentration of hydrogen and rearranging:

$$[\text{COs}] = \frac{k_4}{k_3} [\text{COHs}] = \frac{k_5}{k_3} [\text{Cs}] = \frac{k_6}{k_3} [\text{CHs}] \quad (\text{A6})$$

This means that the surface concentrations of these intermediates are all directly proportional to [COs], which in turn is proportional to the partial pressure of CO in the gas phase (provided that the adsorption of CO is fast enough to be at equilibrium). By combining eqs A1, A2, A4, and A6, the FT reaction rate becomes

$$r_{\text{FT}} = k' [\text{COs}] [\text{Hs}] = k P_{\text{CO}} P_{\text{H}_2}^{0.5} [s]^2 \quad (\text{A7})$$

Due to the proportionality between the CO partial pressure and the surface concentrations of various C_1 intermediate species, the site balance equation can account for these intermediates without complicating the overall rate equation. Water is also included in the site balance equation. The site balance therefore becomes²²

$$[s_o] = [s] + [COs] + [COHs] + [Cs] + [CHs] + [H_2Os] = [s](1 + k_{CO}P_{CO} + k_{H_2O}P_{H_2O}) \quad (A8)$$

$$\frac{[s]}{[s_o]} = \frac{1}{1 + k_{CO}P_{CO} + k_{H_2O}P_{H_2O}} \quad (A9)$$

Substituting the site balance equation into the FT rate equation yields the new LTFT kinetic expression (eq 6 above). It is thus evident that the third elementary reaction step in the scheme provided above is not necessarily a slow, rate-determining step (as was assumed during the LHHW derivation), but can also be viewed as the first step in a series of consecutive irreversible hydrogenation reactions. It should be noted that k_{CO} (the observed coefficient of CO) in the new kinetic model does not necessarily only account for adsorbed molecular CO. From eq A6, it follows that k_{CO} is a function of the actual CO adsorption coefficient (k_{CO}^A) and some reaction rate constants:

$$k_{CO} = k_{CO}^A \left(1 + \frac{k_3}{k_4} + \frac{k_3}{k_5} + \frac{k_3}{k_6} \right) \quad (A10)$$

From the derivation provided above, it is clearly impossible to distinguish between the surface coverage of molecularly adsorbed CO and that of the other C_1 intermediate species by merely describing the macro kinetics of the FT reaction with the new rate equation.

Supporting Information Available: Historical and newly measured iron-FT kinetic data, as well as the calculation method to estimate the effectiveness factor of the catalyst during the new experimental study. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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Received for review April 20, 2006

Revised manuscript received August 3, 2006

Accepted August 16, 2006

IE060491H