Effects of Slurry Composition on the
Reaction Rate of the Fischer-Tropsch Synthesis

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Abstract

The reaction rates for the Fischer-Tropsch (F-T) synthesis and associated water-gas shift reaction are dependent on the concentrations of the primary reactants: H_2, CO, CO_2, and H_2O. When the synthesis is carried-out in a three-phase system, it is the solubilities of these reactants in the liquid hydrocarbon product which are important. The product, which is a molten wax at reaction conditions, has a high molecular weight and is predominantly paraffinic. Correlations for predicting the Henry's constants for H_2, CO, CO_2, and H_2O in high molecular-weight (C_{16}-C_{44}), pure n-paraffin solvents were developed from literature solubility data. The correlations are functions of temperature, and the effect of pressure is included by means of a Poynting correction. It is demonstrated that the correlations developed for pure n-paraffin solvents can be used to predict Henry's constants in mixed solvents by employing an ideal mixing rule, which is consistent with using the molar-average carbon number for the mixture in the n-paraffin correlation. The correlations satisfactorily predict the solubility of the above gases in liquid mixtures derived from the F-T synthesis. The effect of accurately accounting for changes in liquid composition on solubility is demonstrated using two examples: the determination of concentration-explicit kinetic rate constants for the F-T synthesis and the design of a F-T bubble-column slurry reactor.

Introduction

The solubility of gases in n-paraffin solvents is important in a number of processes in the petrochemical and petroleum refining industries. The designs of many industrial separation and conversion processes depend on having accurate solubility prediction methods. In particular, the kinetics of the Fischer-Tropsch (F-T) synthesis and the associated water-gas shift reaction are dependent on the concentrations of the primary reactants: H_2, CO, CO_2, and H_2O. When the F-T synthesis is conducted in a three-phase slurry reactor, synthesis gas (CO and H_2) is bubbled through a suspension of fine particles. The reaction occurs on the surface of the particles, resulting in the production of pure hydrocarbons along with a small amount of oxygenated compounds. The product distribution is primarily homologous series of n-paraffins, n-olefins (1-alkenes), and n-alcohols (1-alkanols), and can be approximated by the Anderson-Schulz-Flory (ASF) molecular weight distribution. At reaction conditions, the F-T products distribute between the vapor and liquid phases within the reactor. The lighter components are carried overhead with the unreacted synthesis gas, and the heavier components form the molten-wax phase within which the catalyst is suspended. Reactor performance is strongly dependent on the composition of the wax phase, which is predominantly paraffinic, and affects both synthesis chemistry (Satterfield and Stenger [1,2]) and hydrodynamics (Quicker and Deckwer [3]). Vapor-liquid equilibria place constraints on the composition of the two phases. Methods to predict the bulk properties of the wax phase and the phase separation have been developed (Marano and Holder [4,5]).

Previous models for the F-T slurry reactor system almost completely ignore the phase-composition problem (e.g., Fox and Tam [6], and Prakash and Bendale [7]; for an excellent review of earlier models, see Saxena et al. [8]). Only the solubility of H_2, and in a few instances the other synthesis gas components, are considered in these formulations. The solubilities of the synthesis gas components and the properties of the molten-wax phase are not allowed to vary with synthesis conditions. Correlations have been proposed for predicting the temperature dependence of Henry's constants for various solutes in F-T solvents. However, none of these correlations are functions in any way of the composition of the F-T liquid mixture. For example, Deckwer et al. [9], and Kuo [10] present correlations based on the data of Peter and Weinert [11] for a paraffin wax with an average carbon number of 24.6, and Prakash and Bendale [7] present correlations based on the data of Chao

and Lin [12] for Arge wax with an average carbon number of 36.4. For H_2, these correlations predict Henry's constants which are 34% different at 253°C [13]. It is clear therefore that composition of the mixture must be taken into account when predicting solubility in F-T liquid mixtures. Solubilities of the synthesis gas components in F-T liquids have been the subject of a number of recent experimental investigations [12,14]. There have also been numerous investigations using pure n-paraffin solvents (see [15] for complete references).

The solubility of a solute in a solvent can be expressed in a number of different ways. Henry's law is a particularly useful means of expressing this information for sparingly soluble-gases up to moderate pressures. However, even here many different Henry's constants are presented in the literature in a variety of units. Henry's law in a number of forms has been used to predict the solubility of F-T reactants and product gases in three-phase reactors (e.g., Prakash [16], and Stern et al. [17]). To clarify the notation and units used here in, the following expression for equilibrium of a solute gas in a pure liquid solvent will be employed:

$$f_{i,V}\, p_i = H_i x_i \tag{1}$$

with:

$$\ln H_i = \ln H_i^\infty + \overline{V}_i^\infty \left(P - P_{j,sat} \right) \big/ RT \tag{2}$$

where in (1): $f_{i,V}$, is the vapor-phase fugacity coefficient, p_i is the partial pressure (i.e. $y_i P$), H_i is the effective Henry's constant, and x_i is the liquid-phase mole fraction of solute component i; and in (2): H_i^∞ is Henry's constant for solute i at infinite dilution, $\overline{V}_i^\infty$ is the partial molar volume at infinite dilution, P is the system pressure, $P_{j,sat}$ is the vapor pressure of saturated pure j at temperature T, and R is the ideal-gas constant. The pressure-dependent term in (2) (also known as the Krichevsky-Kasarnovsky equation) is often referred to as the Poynting factor. It represents a correction to the liquid-phase fugacity due to pressure effects. In the above formulation, it has been implicitly assumed that $\overline{V}_i$ is only a weak function of pressure and can be replaced with the partial molar volume at infinite dilution. This is often the case at low to moderate pressures (less than 50 bar). Gasem and Robinson [18] have indicated care should be taken in attributing physical significance to infinite-dilution properties determined by fitting solubility data to (2). In particular, partial molar volumes reported vary considerably between investigators (as discussed later), and from values obtained from volumetric measurements or predictions made from equations of state. Fortunately, large errors in $\overline{V}_i^\infty$ lead to only small errors in predicted fugacities at low to moderate pressures (Lyckman et al. [19]).

For the gases: H_2, CO, CO_2, and H_2O, at F-T synthesis conditions (200-330°C, 10-25 bar), the vapor-phase fugacity coefficient may be approximated as unity. Therefore, for use with kinetic rate expressions (as discussed below), where it is preferable to express liquid concentration, c, on a moles per unit volume basis, the partial pressure of the solute gases may be written as:

$$p_i = H_i\, c_i \big/ c_L \tag{3}$$

where i refers to a component and L the solvent. The units for expressing Henry's constants in the above equations are units of pressure. Unfortunately, these are not the only units used in the literature. Depending of the units chosen to express solute concentration, Henry's constants may be reported in units of: {pres.}{wt.-solvent}/{moles-solute}, {pres.}{vol.-solvent}/{moles-solute}, or {vol.-solvent}/{vol. solute}. All data used for the correlations reported here were converted to pressure units of bar as needed. In addition, many of the Henry's constants reported in the literature for F-T derived liquid solvents represent neither H_i or H_i^∞; but rather, an average value over the pressure range used to measure the solubility data. For sparingly-soluble gases, a plot of vapor-phase fugacity (often approximated as either the total or partial pressure) vs. solute concentration yields an approximately straight-line through the origin. However, the slope of this line, which will be referred to as $\overline{H}_i$, can vary considerably from either H_i or H_i^∞. In order to evaluate this data, it was assumed that $\overline{H}_i$ is equivalent to H_i evaluated at the average fugacity (average pressure) of the data used to construct the straight line through the origin. This is roughly what one would expect from a linear curve-fit of the data.

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Property Correlations for H_i^∞ and $\overline{V}_i^\infty$

An extensive literature search was conducted in order to identify data for developing Henry's constant correlations. The results of this survey are summarized elsewhere [15]. In edition to the synthesis gas components, light-hydrocarbon components up to $C_{10}H_{12}$ produced by the synthesis and N_2 where included in this survey and resulting correlations. The data were reported in a variety of different forms (see above), it was often necessary either to adjust or calculate the infinite-dilution Henry's constants and partial molar volumes. The adjustments most often took the form of applying a correction for nonideal gas behavior in the vapor phase. It was also necessary in some instances to calculate infinite-dilution Henry's constants from reported gas chromatograph retention volumes. When measurements were made at elevated pressures and partial molar volumes were not reported, (2) was used to determine values for $\overline{V}_i^\infty$. A number of data identified in the literature search were found to be of questionable accuracy and were omitted from further analysis. These data appeared inconsistent when compared to data from adjacent solvent carbon numbers or at similar temperatures. The solvents spanned n-C_{16} to n-C_{36} and in some cases n-C_{44}. The correlations were developed for the temperature range from 0 to 300°C; however, data were not available for all solutes up to 300°C. Very limited data were available for partial molar volumes at infinite dilution. Correlations for $\overline{V}_i^\infty$ were only developed for H_2, CO, CO_2, CH_4, C_2H_4, and C_2H_6.

No attempt was made to develop correlations for H_i valid for all n-paraffins and n-olefins solvents from C_3 to polyethylene, but rather one valid for the limited range applicable to F-T liquid mixtures. This approach was necessitated by the scarcity of reliable Henry's constant data for the solutes of interest in n-paraffin solvents over a wide range of carbon numbers and temperatures. It was also not necessary to consider paraffin solvents with carbon numbers less than about sixteen. The molten-wax product from the F-T synthesis is predominantly paraffinic and has an average carbon number ranging from about 28 to 60. The correlating functions used for $\ln H_i^\infty$ and $\overline{V}_i^\infty$ as a function of carbon number n are:

$$\ln H_i^\infty = H_{i,o} - n\Delta H_i \qquad (4)$$

$$\overline{V}_i^\infty = V_{i,o} + n\Delta V_i \qquad (5)$$

where $H_{i,o}$, $V_{i,o}$, ΔH_i, and ΔV_i are determined from data regressions. The basis for these relationships is presented in [15]. It was observed from the solubility data that ΔH_i and ΔV_i were nearly independent of temperature (with the exception of water). Therefore, all temperature dependence was attributed to $H_{i,o}$ and $V_{i,o}$. These temperature dependencies should be similar to those for pure component vapor pressure and molar volume, respectively. Therefore, based on earlier work [20], the following forms were used:

$$H_{i,o} = A + B/T + C\ln T + DT^2 + E/T^2 \qquad (6)$$

$$V_{i,o} = A + BT \qquad (7)$$

Data for partial molar volume are so limited, only a linear dependence on temperature could be assumed. The values for $P_{j,sat}$ and c_L ($= 1/V_L$) required in (2) and (3), respectively, can be estimated using asymptotic behavior correlations available to predict properties of n-paraffins and n-olefins from C_3 to polyethylene [20].

The optimized parameters obtained for (4) through (7) are reported for H_2, CO, CO_2 and H_2O in Tables 1 and 2. These tables also includes descriptions of the data used and report values for the errors associated with each correlation. For H_2, CO, and CO_2 the percent absolute average deviations (%AADs) for H_i^∞ are all less than 1. The value for water is about 1.5. This is a result of using a constant value for ΔH_i. The correlation for water is based on data for only two n-paraffin solvents from a single investigation; therefore, including a temperature dependence in ΔH_i did not seem justified. Over the range of carbon numbers considered, the assumption $\ln H_i^\infty$ is linear with n, holds extremely well for most solutes. However, as was discussed earlier, the correlations presented here were not developed in order to extrapolate to the extremely high carbon numbers (>10,000) exhibited by polyethylenes. Instead, they are to be used over the very modest range of carbon numbers (~28-60) associated with F-T waxes. Comparisons with data reported in the literature [21] indicate the present correlations under-predict Henry's constants of low-density polyethylenes. It is therefore recommended the correlations not be extrapolated very far beyond the carbon numbers indicated in Table 1. Fortunately, only modest extrapolation is necessary for some of the F-T solvents considered here.

Very few experimental studies have been carried out at elevated pressures in order to determine $\bar{V}_i^\infty$ by means of (2). Correlation parameters based on this limited data are given in Table 2. The %AAD for these correlations are 2.7 for H_2, 5.7 for CO, and 7.7 for CO_2, and in no instances were there more than 18 data points available from which to develop the correlations. In many instances, it was necessary to omit data points in order to develop a correlation consistent with data from various investigators. Since no data was discovered for water, it is recommended that $\bar{V}_i^\infty$ be approximated with either the molar volume of pure water at 1 atm or the saturation pressure. Fortunately, H_i is not very sensitive in the pressure range of interest, to the value used for $\bar{V}_i^\infty$, which enters the calculation through the Poynting correction.

Table 1: Infinite-Dilution Henry's Constant Parameters for Gases in n-Paraffins

$$\ln H_i^\yen = H_{i,o} - n\Delta H_i , \ \text{(bar)}$$

$$H_{i,o} = A + B/T + C\ln T + DT^2 + E/T^2 , \ (T \text{ in K})$$

Solute	H_2	CO	CO_2	H_2O
Solvent CNs	16,20,28,36	16,18,20,28,36	16,18,20,28,36,44	16,28
ΔT (K)	300-553	298-573	298-573	413-525
Pts	38	52	79	43
ΔH_i	0.0200959	0.0173238	0.0210941	0.0605329
A	12.9353	5.79833	6.65249	7.88232
B	22.9058	19.5937	15.2964	14.4370
C	-0.974709	0.152199	-0.0760998	-0.0648305
D	-1.20408×10^{-6}	-1.89733×10^{-6}	-2.56080×10^{-7}	0
E	2244.61	2031.63	-144960	-465952
RMSE	0.0198	0.0135	0.0100	0.0164
AD	-0.0061	-0.0050	0.0037	-0.0117
AAD	0.0423	0.0292	0.0252	0.0562
%AAD	0.6736	0.4834	0.5534	1.4152

Table 2: Partial Molar Volume Correlation Parameters for Gases in n-Paraffins

$$V_i^\yen = V_{i,o} + n\Delta V_i , \ \text{(cm}^3\text{/mole)}$$

$$V_{i,o} = A + BT , \ (T \text{ in K})$$

Solute	H_2	CO	CO_2
Solvent CNs	20,28,36	20,28,36	20,28,36,44
ΔT (K)	323-423	323-573	313-573
Pts	8	9	18
ΔV_i	0.704424	1.50538	5.50000
A	-64.9424	-18.3528	-124.328
B	0.237301	0.160773	0.250075
RMSE	1.3997	3.2455	5.7896
AD	-0.6621	1.0498	0.4818
AAD	1.4905	4.7614	10.2678
%AAD	2.6840	5.6741	7.7490

Prediction of Henry s Constants for F-T Liquid Mixtures

The F-T mixtures of interest consist primarily of long-chain n-paraffins; therefore, it is reasonable to assume that these mixtures will exhibit ideal-solution behavior. In this case, the Henry's constant for the mixture is given by:

$$\ln H_{i,mix} = \sum_j x_j \ln H_{ij} \tag{8}$$

where the summation is taken over all j components in the solvent. Since the form used for the correlations given by (4) and (5) is linear in n, it can readily be shown based on the mixing rule (8) that the Henry's constant for a solute in a mixture of n-paraffins can be calculated using (4) and (5) directly and the *number-average* carbon number of the mixed solvent. The theoretical basis for using the number average is implicit in the mixing rules employed by Sanchez and Lacombe [22] in their lattice-fluid theory for polymer solutions, and results from the assumption of identical *mer* (-CH$_2$-) interaction energies and close-packed volumes for long-chain molecules. In (2), $P_{j,sat}$ is based on the average carbon number of the solvent, and is insignificant for high molecular weight solvents.

Only limited experimental data for the solubility of H$_2$, CO, CO$_2$, and H$_2$O in F-T liquids or similar fluids are available to test the correlations and mixing rules proposed. These data are summarized elsewhere [15], and the reader is referred to a previous paper [4] for descriptions of the compositions, carbon-number distributions, and physical properties of these mixtures. Parity plots of the comparisons appear in Figures 1, 2 and 3. The various investigators reported Henry's constants in a variety of forms: H_i^∞, H_i, and $\overline{H}_i$. The correlations developed for H_i^∞ and $\overline{V}_i^\infty$ were used to estimate the Henry's constants in the forms reported. These values are the basis for the comparisons shown in the parity plots. It can be seen from the parity plots that the errors, which in some instances are quite large, are fairly evenly distributed for all the correlations. The most data and greatest number of different F-T solvents are for the H$_2$ and CO solutes. The %AADs for these solutes are 12.3 and 14.7, and the percent maximum absolute deviations (%MADs) are 59.7 and 61.3 , respectively. For CO$_2$, the %AAD and %MAD are 8.63 and 28.8, respectively. For H$_2$O, with data for only two different solvents, the %AAD and %MAD are 18.7 and 49.9, respectively. The correlations developed from pure n-paraffin solvent data do a reasonable job of predicting solubility in most F-T liquid mixtures given the possible inaccuracies of the solubility data and the average carbon numbers used.

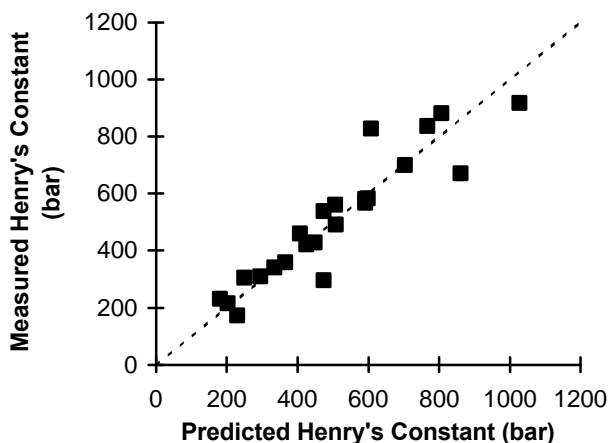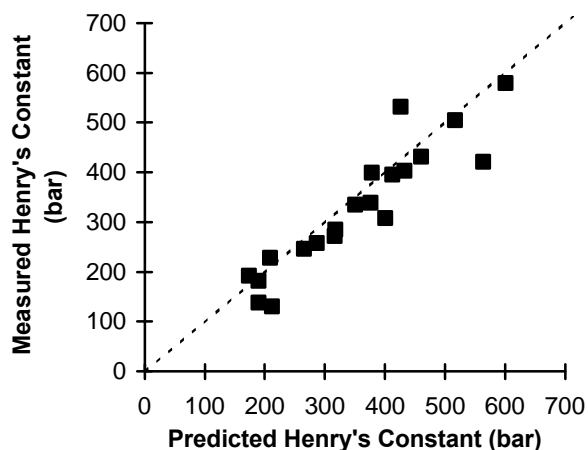**Figure 1: Parity Plot for Henry's Constants of H$_2$ in F-T Liquid Mixtures**

Figure 2: Parity Plot for Henry's Constants of CO in F-T Liquid Mixtures

Determination of Kinetic Rate Constants for the F-T Synthesis

Rate constants for slurry-phase F-T synthesis are typically determined using bench-scale stirred reactors (see [23-27]). The gas phase flow is continuous; where as, the slurry phase may be batch or flowing. Rate expressions are often expressed in terms of the partial pressures of the reactants. This can lead to difficulties when using these expressions to scale-up the synthesis to bubble column reactors. The solubility of the reactants may be different in the slurry bubble column due to different operating pressures and temperatures, mass transfer effects, or phase-contacting patterns in the column; all of which can affect the phase split between vapor and liquid F-T products, and thus the average molecular weight of the

**Figure 3: Parity Plot for Henry's Constants
of CO_2 and H_2O in F-T Liquid Mixtures**
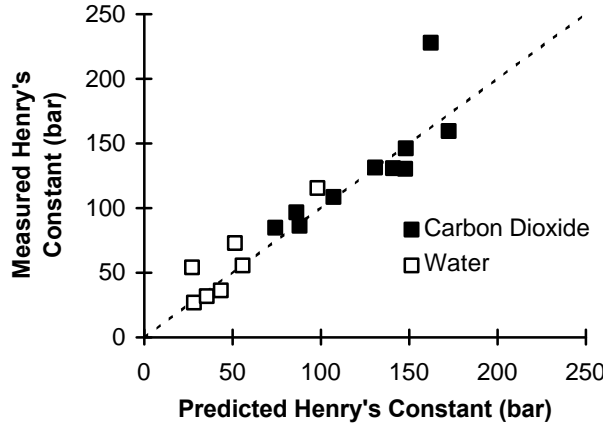
molten wax. Changes in the composition of the molten wax will also affect the determination of the rate constants from bench-scale experiments. This is especially true if the slurry phase is run in batch mode, where composition will be continuously changing from that of the starting medium to that of steady-state F-T product [28]. To illustrate this point, consider the rate expression proposed by Anderson [29]:

$$r_{FT} = \frac{k_o p_{CO} p_{H_2}}{p_{CO} + a p_{H_2O}} \tag{9}$$

For a precipitated iron catalyst, Zimmerman and Bukur [27] report the following values: k_o = 0.063 mol/g-cat h MPa, and a = 5.3, at 250°C. These were obtained in a stirred reactor with a batch slurry phase. The starting material was reported to be the commercial wax FT300 which has an average molecular weight of about 730 (CN of 52), and the end-of-run wax was assumed to have an average molecular weight of 420 (CN of 30). For scale-up, it is preferable to have the rate expression (9) in units of concentration. Substituting (3) into (9):

$$r_{FT} = \frac{k_o \left(H_{CO} H_{H_2} / c_L^2 \right) c_{CO} c_{H_2}}{\left(H_{CO}/c_L \right) c_{CO} + a \left(H_{H_2O}/c_L \right) c_{H_2O}} = \frac{k_o' c_{CO} c_{H_2}}{c_{CO} + a' c_{H_2O}} \tag{10}$$

Calculation of $k_o' \left(k_o H_{H_2}/c_L \right)$ and $a' \left(H_{H_2O}/H_{CO} \right)$ causes somewhat of a dilemma, in that the conversion of the rate constants to concentration units requires the use of Henry's constants, which as shown are functions of the average carbon number of the molten wax. If 52 is used, the constants in (10) are: k_o = 1650 cm^3/g-cat h, and a = 0.35; and if 30 is used, then they are: k_o = 1548 cm^3/g-cat h, and a = 0.90. This is a difference of 6.2 % for k_o and 160 % for a. These values are based on the correlations for H_i given above and correlations for c_L given in [20]. The effect of variations in wax composition and reaction rate on bubble column slurry reactor design is illustrated next.

Effect of Solubility on the Design of F-T Bubble-Column Slurry Reactors

The bubble column slurry reactor model developed by Prakash and Bendale [7] can be used to demonstrate the effect of wax composition on reactor performance. Input data used for this example are given in Table 3. The Henry's constants used in their original model were developed for a wax with an average carbon number of 36.4. The kinetic expressions used for both the F-T synthesis and associated water-gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) are based on regression of the data of Zimmerman and Bukur [16], and are expressed in terms of the partial pressures of reactants and products. The model was modified to incorporate the Henry's constants correlations given in Tables 1 and 2 into solubility calculations and to convert kinetic rate expressions from partial pressure based to moles per unit volume based concentrations. Changes in wax composition will also affect other properties such as density, viscosity, etc. *These effects have not been included in the*

present analysis. It is also worth noting that the correlation developed by Prakash and Bendale predicts values for the Henry's constant of H_2 which are roughly 1.5 % higher than those predicted here. Predictions for the other synthesis gas components vary as well.

Table 3: Bubble Column Slurry Reactor Design Data

Diameter	4.8 m	Inlet H_2/CO Ratio	0.64
Length	11.5 m	Catalyst Loading	34 %
Pressure	28 atm	Catalyst Diameter	25 μm
Superficial Gas Velocity	15.5 cm/s	Catalyst Density	3.01 g/cc

Three sets of operating conditions were used to show the effects of wax composition. These were based on the F-T product distributions reported by Kuo [10,30] for three different operating temperatures of Mobil's bubble column slurry reactor. The hydrocarbon products from the precipitated iron catalysts employed in Mobil's reactor are characterized by two distinct chain growth probability factors (a). These correspond to slopes on a plot of logarithm of mole fraction versus carbon number (i.e. Schulz-Flory plot). The values used for these slopes were determined by an analysis done by Fox and Tam [6]. The average carbon numbers of the molten wax phase present in the reactor are based on the calculations of Marano and Holder [5]. These values are included in Table 4. *For the purposes of this analysis, it will be assumed that these hydrocarbon product distributions remain the same for the reactor described in Table 3.* In reality, it is likely they will be somewhat different due to changes in mixing and mass transfer characteristics between the two bubble columns.

Table 4: Effect of Slurry Composition on Predicted Conversions

Catalyst from Run #	CT-256-3	CT-256-4	CT-256-5
Temperature (^{o}C)	260	256	244
a (C_{20-})	0.7900	0.8250	0.8500
a (C_{20+})	0.8693	0.9566	0.9765
Reactor Wax CN	27.8	41.6	58.4
H_2 Conversion (%)			
variable H_i	77.53	68.75	54.34
original model	75.59	70.00	56.77
	------------	------------	------------
difference	1.94	-1.25	-2.43
CO Conversion (%)			
variable H_i	79.82	76.39	62.40
original model	78.70	77.31	62.31
	------------	------------	------------
difference	1.12	-0.92	0.90

Results of the comparison are shown in Table 4, which reports the predicted conversions for H_2 and CO made with the original model and the model modified to use Henry's constants which are functions of carbon number. The effect is more pronounced for H_2. When the carbon number of the wax is less than 36.4, the original model under-predicts H_2 conversion, and when it is greater, it over-predicts the conversion. For the range of wax carbon numbers considered, 27.8 to 58.4, the difference in H_2 conversion from the two models is always less than about 2.4 % and spans a range of 4.4 (1.94- -2.43) %. This is much less than the difference between H_{H_2} , which varied by as much as 56 %, or the quantity H_{H_2}/c_L appearing in k_o above, which varied by as much as 8 %. The difference in CO conversions where about 1 % and spans a range of 2.0 %. The effect of carbon number on CO conversion is less predictable. While these differences may not be significant within the limits of accuracy of the model used, they do demonstrate a bias in the predicted conversions which can be easily accounted for. As more accurate kinetic expressions for the F-T synthesis and water-gas shift reaction are developed, and as improved bubble column slurry reactor models become available, it is appropriate that accurate solubility correlations be incorporated.

Conclusions

The correlations presented are useful for the design of separation and conversion processes. A related paper [5] describes how these expressions can be implemented in vapor-liquid equilibrium calculations. Correlations have been presented for predicting H_i^∞ for: H_2, CO, CO_2, and H_2O; and for predicting $\overline{V}_i^\infty$ for: H_2, CO, and CO_2 in high molecular-weight (C_{16}-C_{44}), pure n-paraffin solvents. Predictions made with these correlations for H_i^∞ are accurate over the range of temperatures and solvent carbon numbers for which they were developed. Predictions for $\overline{V}_i^\infty$ are much less accurate; however, they yield reasonable values when used to estimate the Poynting factor in equilibrium expressions. These correlations do not extrapolate well to very high carbon numbers and should not be used to predict solubilities in polyethylenes. The correlations for H_i^∞ and $\overline{V}_i^\infty$ can also be used to estimate solubilities in mixed solvents. For the latter, a number-average carbon number was used to apply the correlations to solvents which are F-T liquid mixtures. This procedure is in agreement with theory, and comparisons made with data for 30 solute-solvent pairs indicate it works reasonably well. It is preferable to earlier correlations which are only applicable for a specific mixture composition.

It has also been demonstrated how these Henry's constant correlations can be used to convert partial pressure based kinetic rate expressions for the F-T synthesis to concentration units and the uncertainty which may result. The impact of wax composition on design of a bubble column slurry reactor was shown using the model of Prakash and Bendale. Using a Henry's constant which is not composition dependent may result in errors in H_2 conversion of the order of a few percent. To improve accuracy when scaling-up from bench-scale stirred reactors to bubble columns, it is recommended the composition of the molten wax phase be predicted using appropriate VLE calculations, and the concentrations of the reactants be based on predicted solubilities in this wax phase.

Clearly, the data available for developing correlations for the solubility of synthesis gas in molten paraffin waxes, and in particular F-T waxes, are quite limited. Further experimental work is needed to obtain quality data from which more accurate correlations can be developed. Emphasis should be placed on obtaining data for water over a wider range of solvents and temperatures. Only scant data exist for predicting the effects of pressure, and this situation needs to be rectified. With additional data and improved correlations, it should be possible to improve the accuracy of kinetic rate expressions for slurry-phase F-T synthesis and subsequent predictions of performance for bubble column slurry reactors.

Acknowledgment

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