

Diffusion Studies

Our diffusion studies had the following objectives: (1) to design and construct an apparatus to measure molecular diffusivities of Fischer-Tropsch reaction products in supercritical propane and hexane at the Fischer-Tropsch reaction conditions; (2) to develop a technique to measure the effective diffusivities of the same products at the same conditions in the pores of the iron based Ruhrchemie LP 33/81 catalyst; (3) to develop a predictive equations for *a-priori* determination of the molecular diffusivities and the effective diffusivities of solutes in supercritical fluids.

In order to model the supercritical phase Fischer-Tropsch reaction data, effective diffusivities (D_{eff}) in the catalyst pores are needed. The effective diffusivities are related to the molecular diffusion coefficients. Using the relationship

$$D_{eff} = \frac{\epsilon_p}{\tau} D_{12} \quad (1)$$

if the tortuosity τ and particle porosity ϵ_p were known, only the molecular diffusion coefficient D_{12} at the reaction conditions would be needed. Although the tortuosity and porosity of each catalyst particle must be determined independently, if ϵ_p/τ is determined at one set of conditions D_{eff} can then be calculated at any other set of conditions provided that D_{12} is known or can be estimated. Hence the focus of this objective of the project was on *a-priori* prediction of D_{12} .

We have used the Taylor dispersion technique (Taylor, 1953; Aris, 1956; Erkey and Akgerman, 1990, 1991; Alizadeh et al., 1980) to measure the molecular diffusion coefficients in supercritical fluids and a tracer response technique (Levenspiel and Smith, 1957; Wakao and Kugei,

1982; Erkey and Akgerman, 1990) to measure effective diffusivities. The predictive equation was developed using the extension of rough hard sphere theory to supercritical fluids.

The details of the experimental technique used are explained in our publications (Noel et al., 1994; Eaton et al., 1995) given in Appendix IV. In the experimental technique, the supercritical fluid was allowed to flow through stainless steel tubing to a preheater in the furnace which is temperature was controlled to $\pm 1^\circ\text{C}$. The supercritical fluid then passes through an injection valve to a stainless steel column with an approximate diameter of 0.635 cm packed with Ruhrchemie LP 33/81 catalyst (100 Fe/5 Cu/4.2 K/25 SiO₂ on mass basis), or through a 15.84 m long Taylor dispersion coil, or through a bypass line. This switching between the apparatus was completed by two zero dead volume connections that could be unconnected and reconnected without added dispersion. The bypass was employed to measure the amount of dispersion incurred in the system (minus the packed column or the dispersion coil) due to flow and most important due to the cooling length necessary, since the detector could not handle the high temperature fluid. After the column or the dispersion coil, the supercritical fluid passed to a high pressure UV detector (ISCO V⁴) with a dead volume of 0.25 μl . The system pressure was set by a back pressure regulator placed after the UV detector. A second back pressure regulator at 54.4 atm reduced pulsations in the system by utilizing the double expansion technique developed in our laboratories (Erkey and Akgerman, 1990). The system pressure was measured by an internal pressure transducer in the syringe pump calibrated to a precision of ± 1 bar.

The Taylor dispersion tubing was coiled to a diameter of 0.28 m to allow it to fit into the furnace. The maximum flow rate that can be used in the diffusion coil depends on many criteria which are summarized by Erkey and Akgerman (1991), and flow rates less than 9 ml/h were used.

If the flow rate is above the criteria's maximum, then results will scatter mostly because of secondary flow effects (Erkey and Akgerman, 1991). A set of six experiments were completed at each temperature and pressure condition for both the Taylor dispersion coil and the bypass in order to obtain an accurate measurement of the molecular diffusion coefficients and to confirm the reproducibility of the experiments.

Flow rates of the solvent varied from 25 to 100 ml/h with an accuracy of $\pm 4\%$ for effective diffusivity measurements. The injection valve contained a 10 μl sample of solute dissolved in supercritical fluid. This sample was produced by injection of 3 ml of solute into a saturation system, with a volume of 9 ml, placed before the injection valve. Supercritical fluid was then put into the saturator and left for sufficient time to dissolve the solute injected. A column frit was placed before the saturator to prevent entrainment of the solute fluid. The 10 μl sample was injected into the column, which was filled with catalyst, and the response was measured on-line with the UV detector and recorded in one second intervals by means of an Intel 486 SX computer. This procedure was completed three times at each flow rate, pressure, and temperature condition to obtain an accurate result. The catalyst was prepared by crushing and sieving particles to a size of approximately 250-295 μm . The catalyst was then calcined at a temperature of 673.15 K for a period of four hours and re-sieved to eliminate any particles which were reduced in size during the calcining process. The particle porosity as well as the mean pore size and the specific surface area were determined by standard nitrogen adsorption techniques, completed independently. The particle density was determined by pycnometer analysis. Bed porosity was determined from the mass of a known volume of particles.

Our results are given in our publication (Eaton et al., 1995) in Appendix IV. For all measurements D_{12}/D_{eff} was 9.72 ± 1.22 , indicating that ϵ_p/τ was ~ 0.103 and was independent of temperature, pressure, and diffusing species as expected. Thus, if D_{12} can be predicted, one can easily determine D_{eff} at any condition.

The predictive equation was based on the rough hard sphere theory. The theory and the development of the predictive equation are given in our publication (Eaton and Akgerman, 1997) presented in Appendix V. The final equation developed does not have any adjustable parameters, although it includes two fitted parameters. The final form of the equation is given by

$$D_{12} = \beta \sqrt{T} \left(\frac{\sigma_1}{\sigma_2} \right)^\gamma \left[\frac{m_1 + m_2}{m_1 m_2} \right]^{1/2} \left(\frac{V_0}{\sigma_{12}^2} \right) \left[\left(\frac{V}{V_0} \right)^\alpha - b \right] \quad (2)$$

where

$$\alpha = \frac{\sigma_2}{\sigma_1} - \frac{1}{3} \quad b = \left[-0.2440 \left(\frac{\sigma_2}{\sigma_1} \right)^2 + 0.8491 \left(\frac{\sigma_2}{\sigma_1} \right) + 0.6001 \right] \left(\frac{m_1}{m_2} \right)^{-0.03587} \quad (3)$$

in this equation σ_1 and σ_2 are the effective hard sphere diameters of the solute and the solvent, respectively, calculated from Purkait and Majumdar (1981) equation, σ_{12} is the arithmetic average of the two hard sphere diameters, m_1 and m_2 are the molecular masses, V is the molar volume, V_0 is the close packed hard sphere volume, and T is the absolute temperature. The two parameters β and γ were postulated to be universal constants and were fitted from our data on diffusion coefficients of 1-octene in supercritical ethane, propane, and hexane in the temperature range 314 - 563 K and pressure range 44 - 124 bar yielding a solvent density range of 70 - 500 kg/m³. They were

determined as

$$\beta = 4.486599 \times 10^{-29} \left[\frac{m}{s} \sqrt{\frac{g \text{ gmol}}{K}} \right] \quad \gamma = 1.7538 \quad (4)$$

Tables 6 - 8 give our measured data on 1-octene diffusion in supercritical ethane, propane and hexane as well as the absolute error of prediction using the above equation. The parity plot for the predictions is given in Figure 5.

Table 6. Diffusion Coefficients of 1-Octene in Ethane

T, K	P, bar	density kg/m ³	molar vol. m ³ /kmol	10 ⁹ x D ₁₂ m ² /s	prediction abs. error
322	124.1054	349.9	85.8703	16.26 ± 0.625	0.704
340	124.1054	299.9	100.1867	18.52 ± 0.940	5.84
357	124.1054	249.2	120.5698	22.67 ± 0.612	5.67
378	124.1054	199.9	50.3052	31.12 ± 0.346	4.63
414	124.1054	150.5	199.6412	37.61 ± 2.515	1.98
503	124.1054	100.9	297.7800	55.49 ± 4.476	1.60

Table 7. Diffusion Coefficients of 1-Octene in Propane

T, K	P, bar	density kg/m ³	molar vol. m ³ /kmol	10 ⁹ x D ₁₂ m ² /s	prediction abs. error
314	124.1054	500.7	88.0647	11.81 ± 0.288	10.70
354	124.1054	450.7	97.8345	14.31 ± 0.393	4.62
384	124.1054	401.1	109.9327	16.29 ± 0.746	4.67
408	124.1054	350.2	125.9109	22.70 ± 0.547	7.20
429	124.1054	300.6	146.6866	26.88 ± 0.843	3.98
453	124.1054	249.6	176.6587	24.59 ± 0.664	7.12
485	124.1054	200.6	219.8106	44.88 ± 0.640	9.33
544	124.1054	150.4	293.1782	54.65 ± 0.395	0.455
523	62.0527	73.64	598.7778	86.89 ± 1.610	0.560
533	62.0527	71.31	618.3425	88.77 ± 3.551	0.227
543	62.0527	69.18	637.3808	90.61 ± 0.451	0.960

Table 8. Diffusion Coefficients of 1-Octene in Hexane

T, K	P, bar	density kg/m ³	molar vol. m ³ /kmol	10 ⁹ x D ₁₂ m ² /s	prediction abs. error
483	124.1054	500.2	172.2711	18.50 ± 0.325	4.79
523	103.4212	437.7	196.8700	22.50 ± 0.110	2.54
523	82.7369	416.5	206.8908	26.22 ± 0.715	1.74
523	62.0527	381.6	225.8124	29.70 ± 1.521	1.82
523	44.8158	312.1	276.0974	38.97 ± 2.336	5.52
563	62.0527	257.2	335.0311	53.00 ± 2.755	5.08
563	44.8158	149.8	575.2336	82.10 ± 3.145	4.53

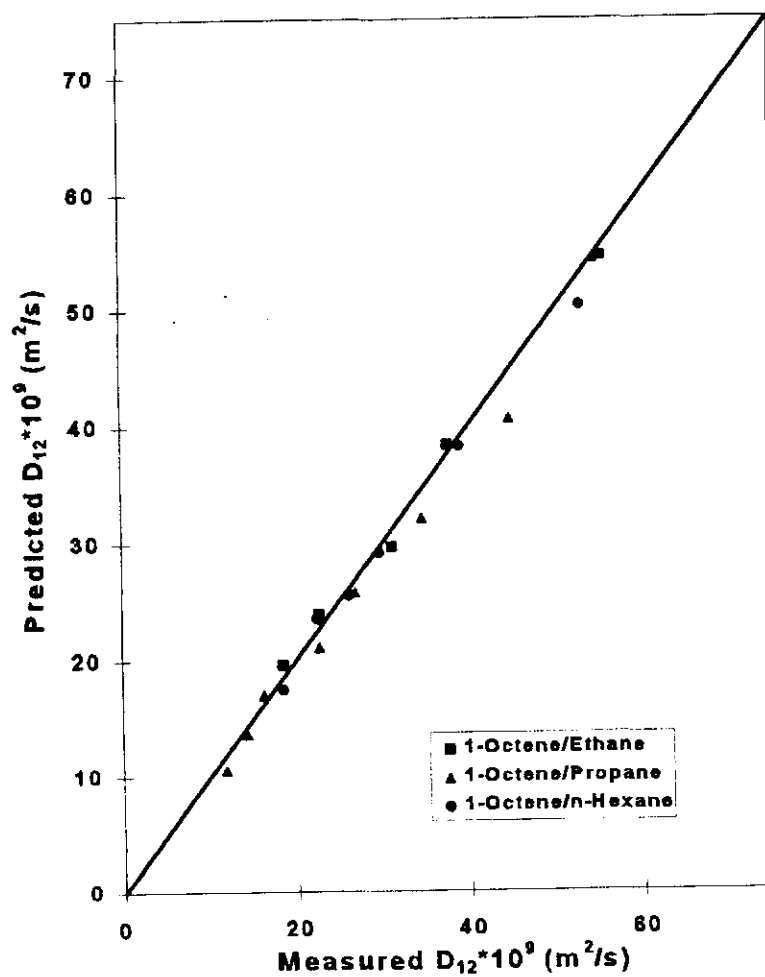


Figure 5. Comparison of experimental and predicted diffusivities for data presented in Tables 6-8.

Using the above values of β and γ we attempted to predict all the available data on diffusion in supercritical fluids in the literature. The self diffusion data ($\sigma_1=\sigma_2$ and $m_1=m_2$) can be predicted with an average absolute deviation of 3.64% as shown in Figure 6.

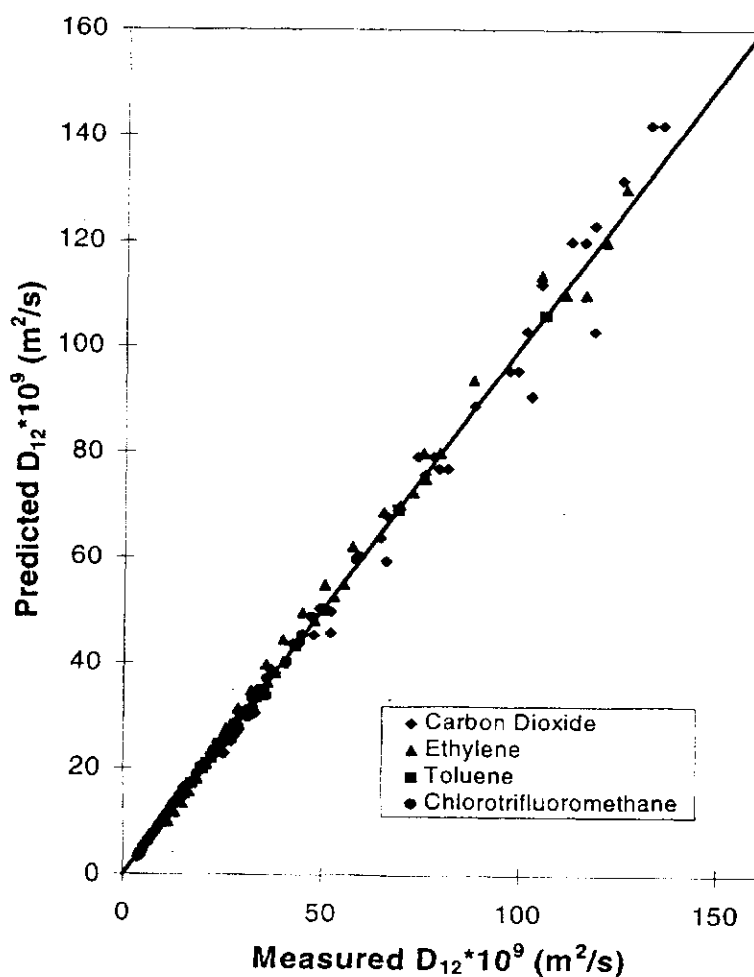


Figure 6. Prediction of self diffusion coefficients of supercritical carbon dioxide, ethylene, toluene and chlorotrifluoromethane.

The predictive equation uses the Purkait and Majumdar (1981) method for estimation of the hard sphere diameters which necessitates the critical temperature and critical volume of the species. These values are not available for some compounds and were estimated using available correlations (Eaton and Akgerman, 1997). Some estimates may have a large error resulting in large uncertainty in prediction of the diffusion coefficients. On the other hand, our predictions of all the data in the literature (101 systems and over 1500 data points), excluding our data, has an average absolute deviation of 15.08%. For systems where the critical properties (T_c and V_c) of the solute and the solvent are known, our average absolute deviation reduces to 9.62%. The data and predictions are presented in Appendix V.

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

A precipitated iron catalyst (100 Fe/5 Cu/4.2 K/25 SiO₂ on mass basis, prepared by Ruhrchemie AG) was tested in a fixed bed reactor under a variety of process conditions during conventional Fischer-Tropsch synthesis and supercritical Fischer-Tropsch synthesis. It was found that total olefin content decreased and 2-olefin content increased with either decrease in gas space velocity or increase in H₂/CO molar feed ratio, whereas olefin selectivities were essentially independent of reaction temperature (235-265°C).

Results from bed residence time effect studies in both modes of operation indicate that α -olefins are the dominant primary products of FTS. Normal paraffins are primary products also, and their fractional content on the Ruhrchemie catalyst was approximately 20%. Selectivity of n-paraffins and 2-olefins increases, whereas α -olefin selectivity decreases with increase in carbon number, due to secondary reactions of α -olefins.

Bed residence time and carbon number (molecular weight) effects were more pronounced during conventional FTS than during supercritical FTS. During conventional FTS high molecular weight products (C₈+ hydrocarbons) leave the reactor preferentially in the liquid state, and their residence time is longer than that of either the gas phase products, or the products formed during supercritical FTS. Diffusivities of high molecular weight α -olefins in the liquid hydrocarbon wax are significantly lower than the corresponding diffusivities in the supercritical propane, and hence the pore residence time of these products is longer during the conventional FTS. Longer residence time in the reactor and/or catalyst pores increases probability for secondary readsorption of α -olefins, and results in secondary formation of n-paraffins and 2-olefins. Also, desorption rates of heavy α -olefins are higher in supercritical propane than in liquid filled pores during conventional FTS, which results in higher selectivity of primary products. At high syngas conversions (~80%), selectivities of high molecular weight α -olefins during SFTS were significantly higher than those

obtained during conventional operation. These results indicate that SFTS is a potentially attractive route for synthesis of high molecular weight alpha olefins from the synthesis gas.

Results with n-hexane as a supercritical fluid were qualitatively similar to those obtained with supercritical propane. Olefin selectivities obtained during were nearly the same as those obtained during SFTS with supercritical propane. α -olefin selectivity was higher during FTS at subcritical conditions than during conventional FTS, but the effect was less pronounced than during operation at higher partial pressure of n-hexane (SFTS).

Catalyst activity decreased during both conventional FTS and SFTS (propane as supercritical fluid) upon introduction of 1-dodecene. In contrast to the work of Fujimoto et al. (1995), on supported cobalt catalyst, we did not observe suppression of methane selectivity and enhancement of selectivity of high weight molecular hydrocarbons, during SFTS with co-feeding of 1-dodecene. Perhaps this is due to the fact that 1-olefin readsorption is significantly smaller on the iron than on the cobalt.

Major conclusions from tests in different modes of operation (conventional FTS in a fixed bed reactor, SFTS in a fixed bed reactor, and conventional FTS in a stirred tank slurry reactor - run SB-1370) at baseline process conditions: 250°C, 2 NI/g-cat/h, syngas partial pressure of 1.48 MPa, and synthesis feed gas with H₂/CO molar ratio of about 0.67, are as follows.

In the fixed bed reactor tests activity of the Ruhrchemie catalyst was slightly higher (~5%) in the supercritical mode of operation with propane as supercritical fluid, and about 33% higher in supercritical n-hexane. This is attributed to higher diffusivities of reactants in supercritical fluids relative to conventional mode of operation (pores filled with liquid hydrocarbon wax). Catalyst activity in a stirred tank slurry reactor was lower than in a fixed bed reactor (conventional FTS). It is believed that low catalyst activity in run SB-1370 is due to low degree of iron reduction in the STSR.

Hydrocarbon selectivities in the fixed bed reactor were similar in both modes of operation. Methane selectivity in the STSR was lower than in fixed bed reactor tests (4.8 % vs. 6.2%), due to better temperature control in the former. Gasoline yield (C₅-C₁₁ hydrocarbons) was higher in the

STSR than in fixed bed reactors (29 % vs. 23.6 %), whereas the yield of high molecular weight hydrocarbons (C_{12}^+) was higher in the fixed bed reactor (53.5% vs. 50%).

Total olefin content was the highest, and the 2-olefin selectivity was the lowest in the supercritical mode of operation. This is attributed to higher diffusivities of high molecular weight 1-olefins in supercritical fluids than in the liquid filled pores during the conventional FTS in either the fixed bed or the stirred tank slurry reactor. The total olefin content was lower and the olefin isomerization activity was higher during conventional FTS in the fixed bed reactor than in the slurry reactor. These differences in olefin selectivities are partly caused by differences in conversion levels, since higher conversions favor secondary reactions (~61% syngas conversion in the fixed bed reactor, and 38% in the STSR).

Our reaction studies indicate the importance of higher diffusion rates and pore cleaning effects of supercritical fluids when used as the reaction media. We have developed a sound equation for prediction of diffusion coefficients in supercritical fluids and have proven its validity at a wide range of conditions. We have also shown that the calculation of effective diffusivity from molecular diffusivity is through a constant conversion factor (ϵ_p/τ). This conversion factor can usually be approximated by ϵ_p^2 (Satterfield, 1970) which is a known parameter for a given catalyst or can easily be measured. Thus the ability to calculate the molecular diffusivity enables prediction of the effective diffusivity with reasonable accuracy. The prediction of effective diffusion rates in different solvents would give at least a qualitative comparison of product selectivity in FTS using different solvents at various conditions enabling optimization of the process conditions.

Recommendations for Future Work:

1. Studies with different supercritical fluids are recommended, since this may lead to improved catalyst performance.

2. Studies with cobalt based FTS catalysts are recommended. 1-olefin readsorption seems to be significantly more pronounced on cobalt than on iron, and this may lead to improved selectivities (higher yields of high molecular weight products and suppression of methane yield) as demonstrated in the study by Fujimoto et al. (1995).

3. Development of mathematical models for chemical reaction with diffusion in a porous catalyst pellet coupled with convective effects for fluid flow along the reactor is needed to quantify the effects of intraparticle diffusion. Kinetic parameters for multistep reaction network would need to be determined experimentally from experiments in fixed bed or stirred tank slurry reactors.

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APPENDIX I

Effects of Inert Gas and Supercritical Propane on Fischer - Tropsch Synthesis over an Iron Catalyst in a Fixed Bed Reactor

Paper published in Industrial & Engineering Chemistry Research, Vol. 34, pp. 72-77 (1995).

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APPENDIX II

**Effect of Process Conditions on Olefin Selectivity during Conventional and Supercritical
Fischer - Tropsch Synthesis**

Manuscript accepted for publication in Industrial & Engineering Chemistry Research.

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APPENDIX III

Comparison of Catalyst Performance during Conventional FTS in Fixed Bed and Stirred Tank
Slurry Reactors and Supercritical FTS in a Fixed Bed Reactor

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APPENDIX IV

**Experimental Apparatus Used to Measure Molecular Diffusivities by
Taylor Dispersion and Effective Diffusivities by Tracer Response and
Data on Effective Diffusivities**

Manuscripts published in *Journal of Chemical and Engineering Data*, 1994 & 1995

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APPENDIX V

**Theory for Prediction of Diffusion in Supercritical Fluids and Prediction of
all the Data in the Literature (101 Systems over 1500 Data Points)**

Manuscript Published in *Industrial & Engineering Chemistry Research*, 1977

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