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**FISCHER TROPSCH SYNTHESIS IN SUPERCRITICAL FLUIDS**

DE-FG22-92PC92545

**QUARTERLY TECHNICAL PROGRESS REPORT**

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## **I. Objectives for the Third Quarter, Year 3:**

### *A. Fischer-Tropsch (FT) Reaction Related Studies*

Our objective for this quarter was to study the effect of co-feeding a 1-olefin on the Ruhrchemie catalyst activity and selectivity, during both conventional Fisher-Tropsch synthesis (FTS) and FTS under supercritical conditions. We used propane as the supercritical fluid and 1-dodecene ( $1-C_{12}H_{24}$ ) in this test. Motivation for this study was the work of Fujimoto and co-workers (ACS Meeting in San Diego, 1994, and Topics in Catalysis, Vol. 2, No. 1-4, 1995) who reported that suppression of methane and enhancement of high molecular weight hydrocarbons selectivities occurs with co-feeding of 1-olefins (1-heptene, 1-tetradecene, or 1-hexadecene) during FTS under supercritical conditions, but not during the conventional FTS (Co-La catalyst supported on silica in supercritical n-pentane).

### *B. Diffusion Coefficients of F-T Products in Supercritical Fluids*

Our objective for this quarter was to measure the molecular diffusion coefficients and effective diffusivities at more conditions to get a better understanding of the exact value of the tortuosity to porosity ratio. We would like to develop the methodology to determine the tortuosity for this catalyst and thus be able to calculate effective diffusivities from molecular diffusion coefficients without dual experimentation. The next phase is to develop a theoretical/semi-empirical model to predict the molecular diffusion coefficients to a high degree of accuracy so that the molecular diffusion coefficients and the effective diffusivities can be predicted *a priori*.

## **II. Accomplishments and Problems, Third Quarter, Year 3:**

### *A. Fisher Tropsch Reaction Related Studies*

Fischer-Tropsch studies with supercritical propane and co-feeding of 1-dodecene on the Ruhrchemie catalyst (Run FA-1075)

During this quarter, we completed a test (Run FA-1075) with the Ruhrchemie LP 33/81 catalyst at both conventional and supercritical conditions (using propane as the supercritical fluid) and with or without co-feeding of 1-dodecene. The reduction was conducted using the procedure recommended by the manufacturer, i.e. : the catalyst was reduced with hydrogen at 220°C, atmospheric pressure and a linear superficial gas velocity of 150 cm/s for 1 h. Following the reduction and 24 h conditioning period, during which the reaction temperature was increased slowly to 250°C, the catalyst was tested at the baseline process conditions of

250°C, 200 psi (1.48 MPa) and synthesis gas feed rate of 2 NL/g-cat/hr, with synthesis gas with the H<sub>2</sub> to CO molar feed ratio of 0.67.

Table 1 summarizes the process conditions for Run FA-1075. In Period 1, the reaction was conducted at the baseline conditions. In Period 3, 1-dodecene (1-C<sub>12</sub>H<sub>24</sub>) was introduced at a feed rate of 1.67 cm<sup>3</sup>/h, which corresponds to 4 mol% of CO feed rate. Reaction conditions during Period 3 were maintained at the baseline conditions. In Period 5, the feed rates of synthesis gas and 1-dodecene were maintained at the same values as in Period 3, while propane was introduced at total system pressure of 800 psi (5.5 MPa). (The critical temperature and pressure for propane are 96.7°C and 608 psi, respectively.) In Period 7, the flow of 1-dodecene was terminated, and propane and synthesis gas were introduced at 800 psi (5.5 MPa). In Period 8, FT synthesis was carried out at the baseline conditions to investigate deactivation of the catalyst.

During the run, wax and liquid products were collected daily for better estimation of the wax/liquid production rates. The amount of propane produced during supercritical Fischer-Tropsch (SFT) synthesis could not be determined directly by gas chromatography due to the presence of large quantity of propane in the feed. The propane production rate was estimated by assuming that the propylene/propane ratio during the SFT is the same as that obtained during conventional FTS at the same process conditions, and it was calculated from the measured amount of propylene formed during operation under the supercritical conditions. This estimated propane production rate was used in the calculation of overall hydrocarbon product distribution.

#### *Activity*

Figures 1 and 2 show changes of (H<sub>2</sub>+CO) conversion and apparent reaction rate constant with time and process conditions. (The apparent reaction rate constant was calculated by assuming a first order reaction with respect to hydrogen.) In Period 1 (22 to 70 h on stream), conventional FT synthesis was conducted at the baseline conditions. The (H<sub>2</sub>+CO) conversion and apparent reaction constant were about 59% and 202 mmol/g-Fe/hr/MPa, respectively. These values are similar to those obtained in runs FB-1644 and FA-2984 over the same catalyst at the same conditions (59% and 208 mmol/g-Fe/hr/MPa - in run FB-1644; 60% and 207 mmol/g-Fe/hr/MPa - in run FA-2984).

In Period 3 (71 to 127 h on stream), FT synthesis was conducted at the baseline

conditions with 1-dodecene co-feeding at a rate of 1.67 cm<sup>3</sup>/h. During this period the (H<sub>2</sub>+CO) conversion and apparent reaction rate constant decreased to 52% and 178 mmol/g-Fe/hr/MPa, respectively.

In Period 5 (128 to 218 h on stream), SFT synthesis was conducted in the presence of propane and 1-dodecene at 800 psi and 250°C. The (H<sub>2</sub>+CO) conversion and apparent reaction rate constant were 54% and 215 mmol/g-Fe/hr/MPa, respectively. The increase of the apparent reaction rate constant during operation under supercritical conditions was also observed in runs FA-1724 (SFT with propane) and FA-2984 (SFT with hexane).

In Period 7 (219 to 296 h on stream), FTS was conducted with supercritical propane, only. The 1-dodecene feed was discontinued during this period. The (H<sub>2</sub>+CO) conversion and the apparent reaction rate constant were 57% and 231 mmol/g-Fe/hr/MPa, respectively.

In Period 8 (297 to 331 h on stream), conventional FT synthesis was resumed at the baseline conditions. The (H<sub>2</sub>+CO) conversion (46%) and the apparent reaction rate constant (160 mmol/g-Fe/hr/MPa) were lower than those in Period 1 (59% and 202 mmol/g-Fe/hr/MPa) at the same process conditions, indicating catalyst deactivation.

The rate of water-gas-shift (WGS) reaction is related to H<sub>2</sub> to CO usage ratio. In general, the usage ratio increases with decreasing WGS reaction. During this run, the usage ratio increased with decreasing (H<sub>2</sub>+CO) conversion. The same trend was also observed in previous tests (runs FA-1724, 2984 and 3194).

#### *Hydrocarbon product distribution*

Selectivities of CH<sub>4</sub>, C<sub>2</sub>-C<sub>4</sub> and C<sub>5</sub><sup>+</sup> hydrocarbons (as %C selectivity to hydrocarbons) are shown in Table 2. More detailed information on hydrocarbon product distribution, after the liquid and wax product collection and analysis, is given in Table A1 of Appendix A. Methane and gaseous hydrocarbon selectivities during conventional FT synthesis at the baseline conditions (Period 1) were: 5.8% CH<sub>4</sub> and 19.1% C<sub>2</sub>-C<sub>4</sub> hydrocarbons. During conventional FTS with co-feeding of 1-dodecene (Period 3), the selectivities changed slightly to: 5.7% CH<sub>4</sub> and 20% C<sub>2</sub>-C<sub>4</sub> hydrocarbons. In Period 5, the SFT synthesis with propane and co-feeding of 1-dodecene, the hydrocarbon selectivities were: 6.0% CH<sub>4</sub> and 17% C<sub>2</sub>-C<sub>4</sub>. In Period 7, SFT with propane only, the selectivities were: 5.7% CH<sub>4</sub> and 19% C<sub>2</sub>-C<sub>4</sub>. As can be seen from these results, gas phase hydrocarbon selectivities did not vary significantly from Period 1 to Period 7 (i.e. they were independent of the mode of operation). In Period 8, conventional FT

synthesis was resumed at the baseline conditions, and selectivities of  $\text{CH}_4$  and  $\text{C}_2\text{-C}_4$  were slightly higher than those in Period 1, due to deactivation of the catalyst.

#### *Olefin selectivity*

Figure 3 shows the total olefin selectivity during different periods of run FA-1075. At a given carbon number, the olefin selectivity follows the order of: SFT with propane > SFT with propane and 1-dodecene > conventional FTS with 1-dodecene > conventional FTS. Figure 4 shows the 2-olefin selectivity during different periods of run FA-1075. At a given carbon number, the 2-olefin selectivity was generally in the order of: conventional FTS > conventional FTS with 1-dodecene > SFT with propane and 1-dodecene > SFT with propane.

The observation of enhanced selectivity of the primary FTS reaction products (1-olefins) under SFT conditions is in agreement with results obtained in previous tests (runs FA-0844, FA-1724, FA-2984 and FA-3194). The presence of 1-dodecene during the conventional FTS (Period 3) also enhanced the selectivity of 1-olefins, but the effect was not as profound as that during operation with supercritical propane. This may be attributed to lower surface concentrations of high molecular weight olefins formed by FTS in the presence of a large amount of 1-dodecene which adsorbs on the surface (competitive chemisorption).

#### *B. Diffusion Coefficients of F-T Products in Supercritical Fluids*

We previously had reported on the methodology to extract molecular diffusion coefficients from experimental data in Taylor dispersion at high temperatures and the method for determining the effective diffusivities from tracer response data. In both these methodologies we used the method of subtraction of moments. The mass transfer in a catalyst bed is governed by a set of three partial differential equations. In these equations the film mass transfer coefficient  $k_f$  and the axial dispersion coefficient  $D_{ax}$  are system dependent parameters (column dimensions, packing type, hydrodynamics, etc.) whereas the effective diffusivity  $D_{eff}$ , the adsorption equilibrium constant  $K_A$ , and the adsorption rate constant  $k_a$  are intrinsic parameters for a given catalyst. From these equations the effective diffusivity and axial dispersion coefficient of the packed bed column may be obtained from the first and second moments (residence time and variance) of the peak which are given by:

$$t_r = \mu_1 - \mu_{II} = \frac{L_t}{U} (1 + \delta_0) \quad (1)$$

$$\sigma_m^2 = \mu_2 - \mu_{II} = \frac{2L_t}{U} \left[ \delta_1 + D_{ax} (1 + \delta_0)^2 \frac{1}{U^2} \right] \quad (2)$$

where:

$$\delta_0 = \frac{1 - \varepsilon_b}{\varepsilon_b} [\varepsilon_p + \rho_p K_A] \quad (3)$$

$$\delta_1 = \frac{1 - \varepsilon_b}{\varepsilon_b} \left[ \frac{\rho_p K_A^2}{k_a} + (\varepsilon_p + \rho_p K_A)^2 \left( \frac{1}{5D_{eff}} + \frac{1}{k_f R_t} \right) \frac{R_t^2}{3} \right] \quad (4)$$

In the above equations,  $\mu_1$  and  $\mu_2$  are the first and second moments, respectively, from the experiments completed with the packed bed of catalyst, whereas  $\mu_I$  and  $\mu_{II}$  are the moments with the packed column removed from the system, i.e. moments obtained by flowing through the bypass line. Normally a real time domain fitting of the model equations would yield the parameters, but there is a very large change in density (hence the residence time and variance) due to cooling from temperatures at experimental conditions to room temperature before the detector. The subtraction of moments procedure eliminates any extra dispersion caused by the cooling coil, as well as the UV detector dead volume, the injection valve, and any non zero dead volume connections. The first and second moments are calculated from the experimental data.

The adsorption equilibrium constant is the only parameter in the first moment equation which is unknown. From the slope of a plot of the residence time versus  $L/U$  the adsorption equilibrium constant can be determined. Figure 5 is a representative plot. The adsorption equilibrium constant can be determined from the slope of the lines. The catalyst bed properties and the adsorption equilibrium constants extracted from the first moments are given in Tables 3 and 4, respectively.

The second moment (equation 2) involves four additional parameters that must be

determined. In order to extract the effective diffusivity, some assumptions are made. First, it was estimated that the external mass transfer coefficient was much larger than the effective diffusivity in this study. Thus, term  $1/(k_f R_p)$  in equation (4) is much smaller than  $1/(5 D_{eff})$  and can be neglected. This is based on calculations using a correlation by Lim et al. (1989) for mass transfer coefficients. A second simplification was to neglect the contribution of the rate of physical adsorption to peak dispersion. Adsorption rates are typically very fast, i.e.  $k_a \rightarrow \infty$ , and the contribution of the first term in equation (4) becomes negligible. With these simplifications equations 2-4 reduce to:

$$\sigma_m^2 = \frac{2L_t}{U} \left[ \frac{1 - \epsilon_b}{\epsilon_b} \left( \epsilon_p + \rho_p K_A \right)^2 \left( \frac{R_t^2}{15 D_{eff}} \right) + (1 + \delta_0)^2 \frac{D_{ax}}{U^2} \right] \quad (5)$$

If the axial dispersion coefficient is assumed to be constant over the range of Reynolds numbers studied, then a plot of  $(\sigma_m^2 U)/(2 L_t)$  with respect to  $1/U^2$  should be linear and the catalyst effective diffusivity and the bed axial dispersion coefficient can be determined from the intercept and the slope, respectively. Figure 6 gives a representative plot and the values of the effective diffusivities and the Peclet Number  $Ud_p/D_{ax}$ , are summarized in Table 5. The Peclet numbers are reported although they are system dependent hydrodynamic parameters.

Results for molecular diffusion coefficients and the  $D_{12}/D_{eff}$  ratio for the octene - ethane system are presented in Table 6. The variation of the diffusion coefficient and the effective diffusivity with respect to the solvent density is displayed in Figure 7. As density of the fluid increases, both the molecular diffusivity and the effective diffusivity decrease. The ratio of the molecular diffusion coefficient to the effective diffusivity,  $D_{12}/D_{eff}$ , should be a constant equal to  $\tau/\epsilon_p$ . Figure 8 shows that this ratio is nearly constant which is also indicative of consistency of experimental measurements and data reduction procedures. The  $D_{12}/D_{eff}$  ratio in Table 6 specifies a value of  $9.72 \pm 1.22$ .

### III. Plans for the Fourth Quarter, Year 3:

#### A. Fischer-Tropsch Reaction Related Studies

In the fourth quarter we will compare performance of the Ruhrchemie catalyst in different modes of operation: fixed bed reactor (conventional and supercritical mode of operation), and stirred tank slurry reactor.

### *B. Diffusion Coefficients of F-T Products in Supercritical Fluids*

We will measure the molecular diffusion coefficients and effective diffusivities with different solvent-solute pairs to get a better understanding of the interaction of Fischer-Tropsch synthesis products. We then will develop a model to predict the molecular diffusion coefficients based on the rough hard sphere theory.

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## Notation

$C$  = concentration in the fluid phase, mol/m<sup>3</sup>  
 $D_{12}$  = molecular diffusion coefficient, m<sup>2</sup>/s  
 $D_{ax}$  = axial dispersion coefficient, m<sup>2</sup>/s  
 $D_{eff}$  = effective diffusivity, m<sup>2</sup>/s  
 $d_p$  = particle diameter, m  
 $K_A$  = adsorption equilibrium constant, m<sup>3</sup>/kg  
 $k_a$  = adsorption rate constant, m<sup>3</sup>/kg<sup>3</sup> s  
 $k_f$  = external mass transfer coefficient, m/s  
 $L$  = length of Taylor dispersion tube, m  
 $L_t$  = length of packed catalyst column, m  
 $R$  = inner radius of Taylor dispersion tube, m  
 $R_c$  = radius of Taylor dispersion coil, m  
 $R_t$  = inner radius of packed catalyst column, m  
 $t$  = time, s  
 $t_r$  = residence time, s  
 $U$  = interstitial velocity in packed catalyst column, m/s  
 $n$  = number of points obtained for curve  
 $i$  = point number

## Greek letters

$\varepsilon_p$  = catalyst particle porosity  
 $\varepsilon_b$  = catalyst bed porosity  
 $\tau$  = tortuosity  
 $\rho_p$  = catalyst particle density, kg/m<sup>3</sup>  
 $\sigma_m^2$  = variance, s<sup>2</sup>  
 $\mu_1$  = first moment of response curve, s  
 $\mu_2$  = second moment of response curve, s<sup>2</sup>  
 $\mu_I$  = first moment of input signal, s  
 $\mu_{II}$  = second moment of input signal, s<sup>2</sup>

Table 1. Experimental Conditions for Run FA-1075a.

| Period | Time on Stream (h) | P (psi) | Type of Operation               | (H <sub>2</sub> +CO) Feed Rate |                      | 1-Dodecene Feed Rate cm <sup>3</sup> /h | Propane Feed Rate |                      |
|--------|--------------------|---------|---------------------------------|--------------------------------|----------------------|---|-------------------|----------------------|
|        |                    |         |                                 | NL/g-cat/h                     | cm <sup>3</sup> /min |   | NL/g-cat/h        | cm <sup>3</sup> /min |
| 1      | 22 to 70           | 200     | Conventional FT                 | 2.0                            | 117                  |   |                   |                      |
| 3      | 71 to 127          | 200     | Conventional FT with 1-dodecene | 2.0                            | 117                  | 1.67                                    |                   |                      |
| 5      | 128 to 218         | 800     | SFT with propane and 1-dodecene | 2.0                            | 117                  | 1.67                                    | 6.0               | 350                  |
| 7      | 219 to 296         | 800     | SFT with propane                | 2.0                            | 117                  |   | 6.0               | 350                  |
| 8      | 297 to 331         | 200     | Conventional FT                 | 2.0                            | 117                  |   |                   |                      |

a. The reaction temperature, synthesis gas partial pressure and H<sub>2</sub> to CO feed ratio were maintained at 250°C, 200 psi and 0.67, respectively.

Table 2. Summary of Results, Run FA-1075.

| Period  | 1         | 3                         | 5                               | 7                | 8         |
|---|-----------|---------------------------|---------------------------------|------------------|-----------|
| TOS, h  | 60        | 120                       | 210                             | 280              | 330       |
| Total pressure, psi                               | 200       | 200                       | 800                             | 800              | 200       |
| Type of operation                                 | normal FT | normal FT with 1-dodecene | SFT with propane and 1-dodecene | SFT with propane | normal FT |
| H <sub>2</sub> conv, %                            | 57.8      | 54.0                      | 54.7                            | 55.7             | 49.8      |
| CO conv, %  | 59.4      | 51.3                      | 53.1                            | 58.1             | 44.2      |
| (H <sub>2</sub> +CO) conv, %                      | 58.8      | 52.4                      | 53.7                            | 57.2             | 46.4      |
| H <sub>2</sub> /CO usage ratio                    | 0.65      | 0.70                      | 0.69                            | 0.65             | 0.75      |
| Mol % <sup>a</sup> CH <sub>4</sub>                | 5.79      | 5.66                      | 5.96                            | 5.68             | 6.62      |
| Mol % <sup>a</sup> C <sub>2</sub> -C <sub>4</sub> | 19.1      | 20.0                      | 17.2                            | 18.9             | 24.7      |
| Mol % <sup>a</sup> C <sub>5</sub> <sup>+</sup>    | 75.1      | 74.3                      | 76.8                            | 75.4             | 68.7      |
| k, mmol/g-Fe/h/MPa                                | 202       | 178                       | 215                             | 231              | 160       |

<sup>a</sup> : from gas phase composition

SFT - supercritical Fischer-Tropsch synthesis.

**Table 3. Properties of the Packed Catalyst Bed**

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|                       |                        |
|-----------------------|------------------------|
| Bed Length            | 0.254 m                |
| Bed Diameter          | 0.003175 m             |
| Bed Porosity          | 0.359                  |
| Particle Radius       | 0.000245 m             |
| Particle Porosity     | 0.628                  |
| Particle Density      | 1050 kg/m <sup>3</sup> |
| Specific Surface Area | 295 m <sup>2</sup> /g  |

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**Table 4. Adsorption Equilibrium Constants For 1-Octene/Ethane**

| Temperature<br>(K) | Pressure<br>(bar) | Density *10 <sup>-3</sup><br>(kg/m <sup>3</sup> ) | K <sub>A</sub> *10 <sup>3</sup><br>(m <sup>3</sup> /kg) |
|--------------------|-------------------|---|---|
| 523                | 62.0527           | 0.04569   | 23.821  |
| 523                | 82.7369           | 0.06192   | 18.146  |
| 523                | 103.4212          | 0.07839   | 14.25   |
| 523                | 124.1054          | 0.09488   | 9.437   |
| 523                | 144.7896          | 0.11116   | 6.209   |
| 533                | 62.0527           | 0.0446  | 17.419  |
| 533                | 82.7369           | 0.060337  | 15.480  |
| 533                | 103.4212          | 0.07626   | 12.806  |
| 533                | 124.1054          | 0.092186  | 7.785   |
| 533                | 144.7896          | 0.107906  | 6.136   |
| 543                | 62.0527           | 0.04357   | 15.447  |
| 543                | 82.7369           | 0.058848  | 14.620  |
| 543                | 103.4212          | 0.07428   | 12.378  |

**Table 5. Effective Diffusivity and Peclet Number**

| Temperature (K) | Pressure (bar) | Density *10 <sup>-3</sup> (kg/m <sup>3</sup> ) | D <sub>eff</sub> *10 <sup>8</sup> (m <sup>2</sup> /s) | Peclet Number |
|-----------------|----------------|--|---|---------------|
| 523             | 62.0527        | 0.04569  | 0.923 ± 0.200   | 0.030319      |
| 523             | 82.7369        | 0.06192  | 0.650 ± 0.175   | 0.025529      |
| 523             | 103.4212       | 0.07839  | 0.498 ± 0.100   | 0.022887      |
| 523             | 124.1054       | 0.09488  | 0.426 ± 0.210   | 0.020294      |
| 523             | 144.7896       | 0.11116  | 0.408 ± 0.132   | 0.013978      |
| 533             | 62.0527        | 0.0446   | 0.803 ± 0.140   | 0.01542       |
| 533             | 82.7369        | 0.060337                                       | 0.610 ± 0.152   | 0.016851      |
| 533             | 103.4212       | 0.07626  | 0.488 ± 0.200   | 0.018554      |
| 533             | 124.1054       | 0.092186                                       | 0.590 ± 0.276   | 0.013077      |
| 533             | 144.7896       | 0.107906                                       | 0.493 ± 0.205   | 0.022794      |
| 543             | 62.0527        | 0.04357  | 0.742 ± 0.175   | 0.012177      |
| 543             | 82.7369        | 0.058848                                       | 0.520 ± 0.154   | 0.018833      |
| 543             | 103.4212       | 0.07428  | 0.692 ± 0.212   | 0.020553      |

**Table 6. Molecular Diffusion Coefficients and D<sub>12</sub>/D<sub>eff</sub>**

| Temperature (K) | Pressure (bar) | Density *10 <sup>-3</sup> (kg/m <sup>3</sup> ) | D <sub>12</sub> *10 <sup>8</sup> (m <sup>2</sup> /s) | D <sub>12</sub> /D <sub>eff</sub> |
|-----------------|----------------|--|--|-----------------------------------|
| 523             | 62.0527        | 0.04569  | 7.03 ± 0.246   | 7.62                              |
| 523             | 82.7369        | 0.06192  | 6.10 ± 0.99  | 9.38                              |
| 523             | 103.4212       | 0.07839  | 4.99 ± 0.606   | 10.01                             |
| 523             | 124.1054       | 0.09488  | 4.49 ± 0.524   | 10.56                             |
| 523             | 144.7896       | 0.11116  | 4.37 ± 0.139   | 10.95                             |
| 533             | 62.0527        | 0.0446   | 6.91 ± 0.240   | 8.60                              |
| 533             | 82.7369        | 0.060337                                       | 5.90 ± 0.66  | 9.66                              |
| 533             | 103.4212       | 0.07626  | 5.71 ± 0.668   | 11.70                             |
| 533             | 124.1054       | 0.092186                                       | 5.27 ± 0.0676  | 8.13                              |
| 533             | 144.7896       | 0.107906                                       | 5.45 ± 0.0779  | 10.77                             |
| 543             | 62.0527        | 0.04357  | 6.70 ± 0.278   | 9.03                              |
| 543             | 82.7369        | 0.058848                                       | 6.00 ± 0.45  | 10.89                             |
| 543             | 103.4214       | 0.07428  | 6.29 ± 0.734   | 9.09                              |
|                 |                |  | Average:   | 9.72 ± 1.22                       |

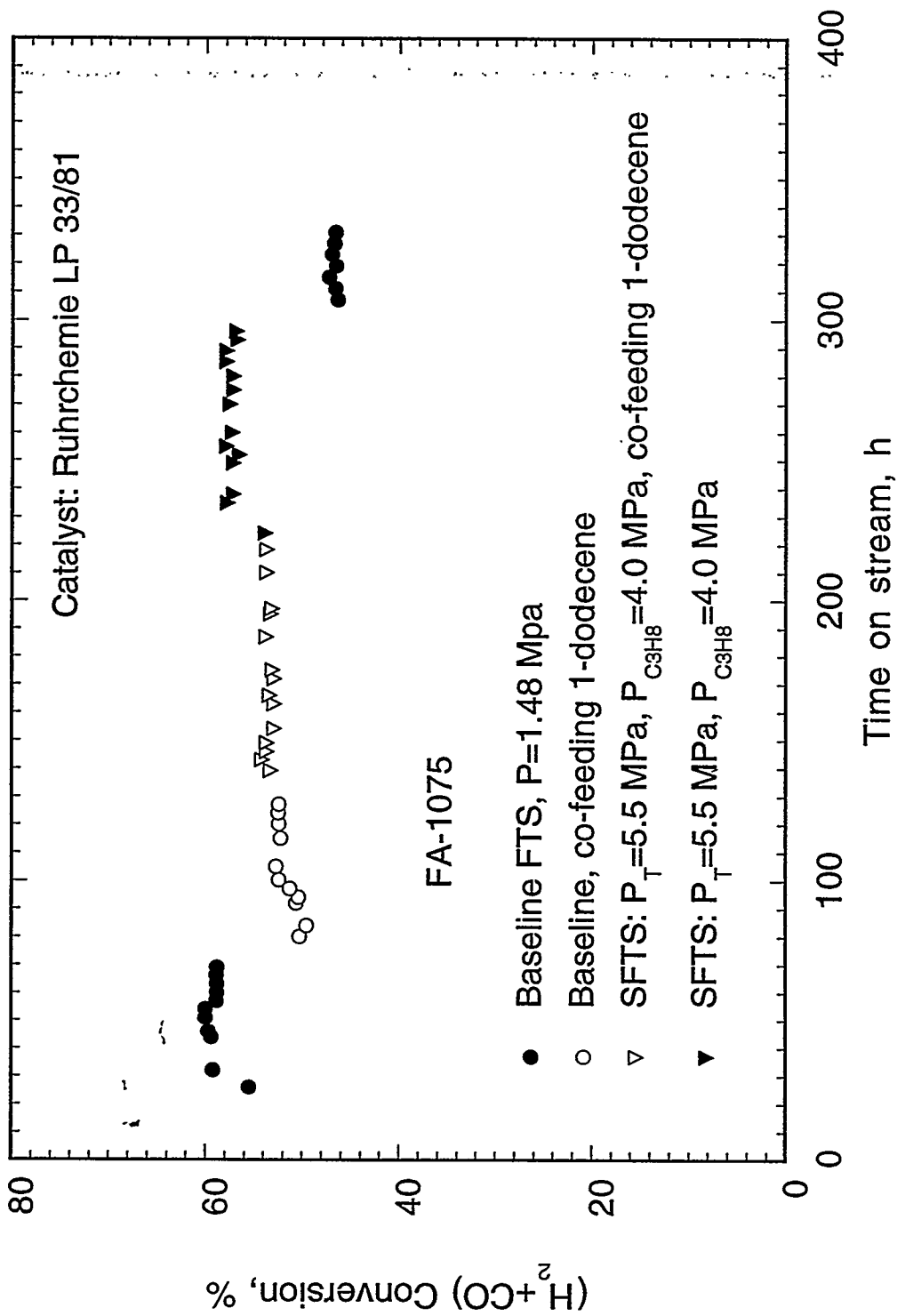


Figure 1. Variation in synthesis gas conversion with process conditions and time on stream during Run FA-1075

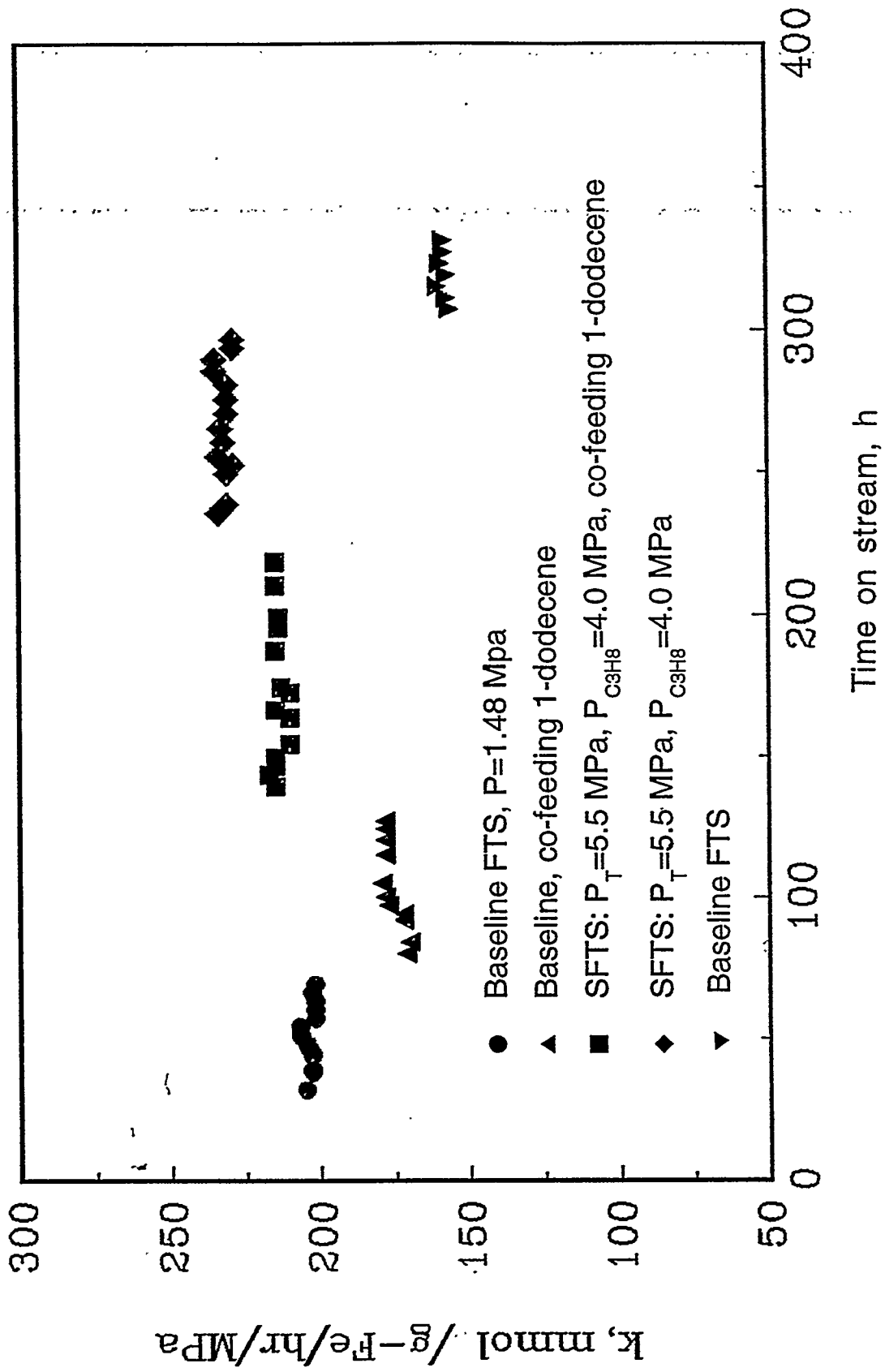


Figure 2. Variation in apparent reaction rate constant at different times on stream during Run FA-1075

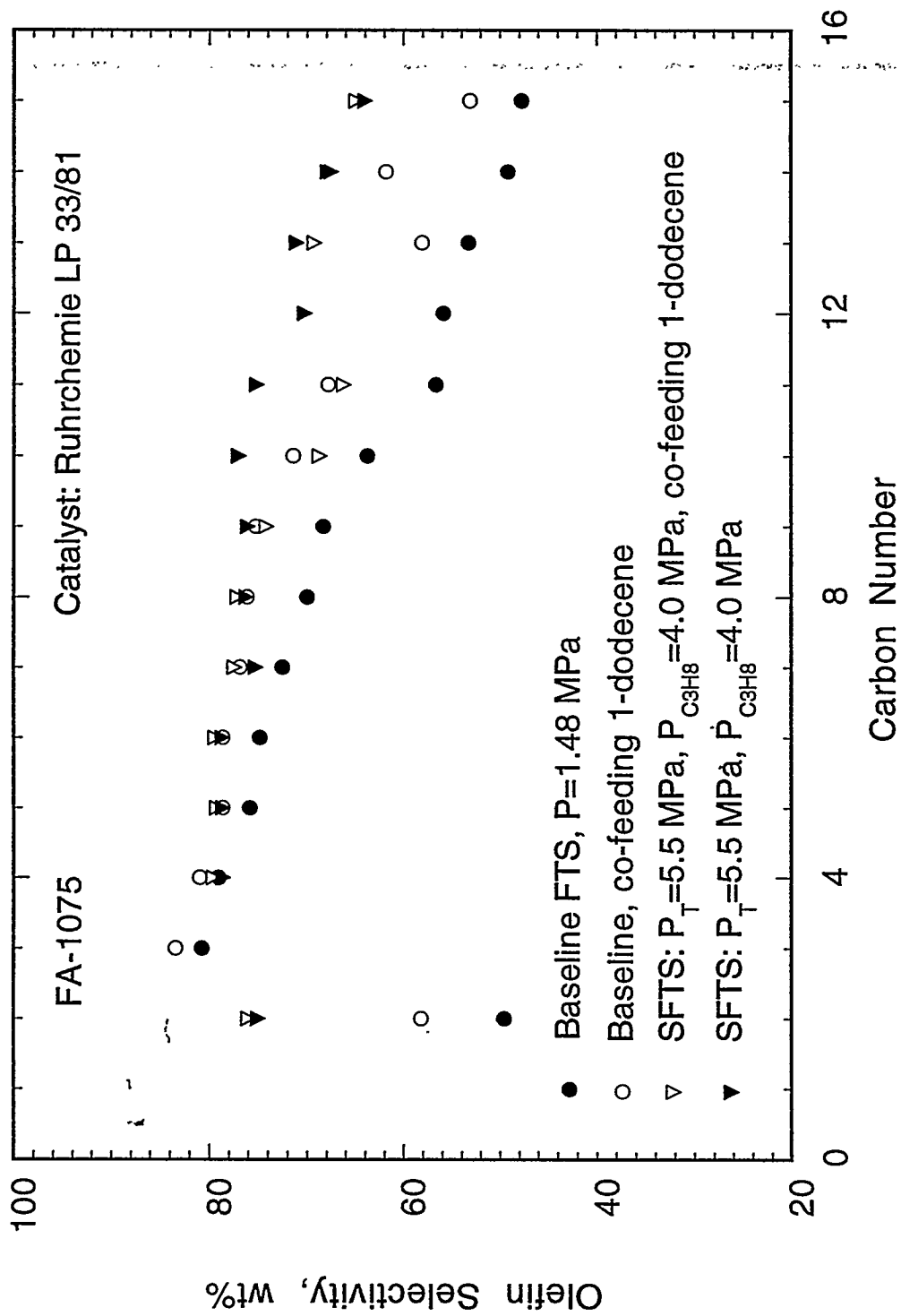


Figure 3. Olefin selectivities during different periods of Run FA-1075



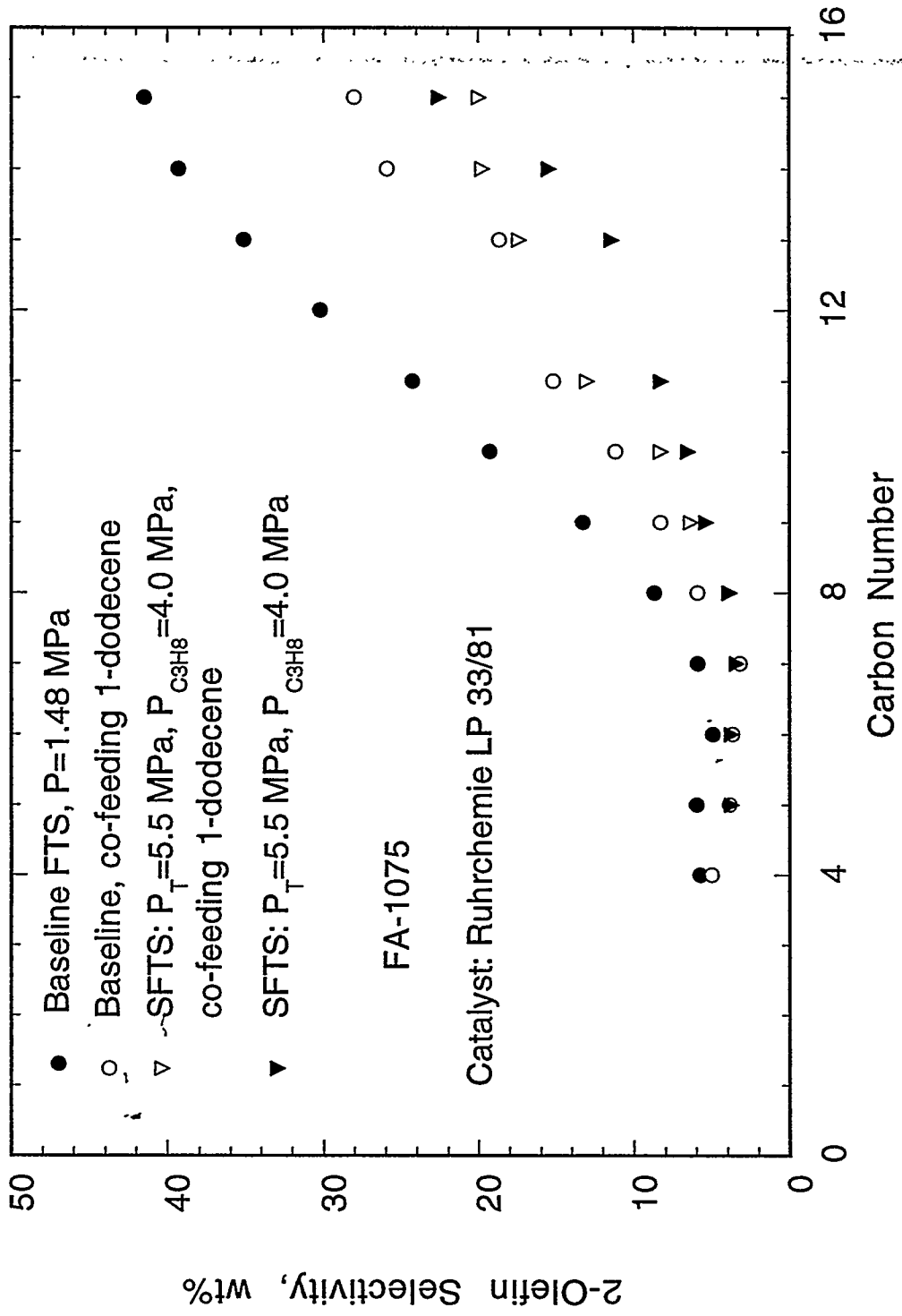


Figure 4. 2-olefin selectivities during different periods of Run FA-1075

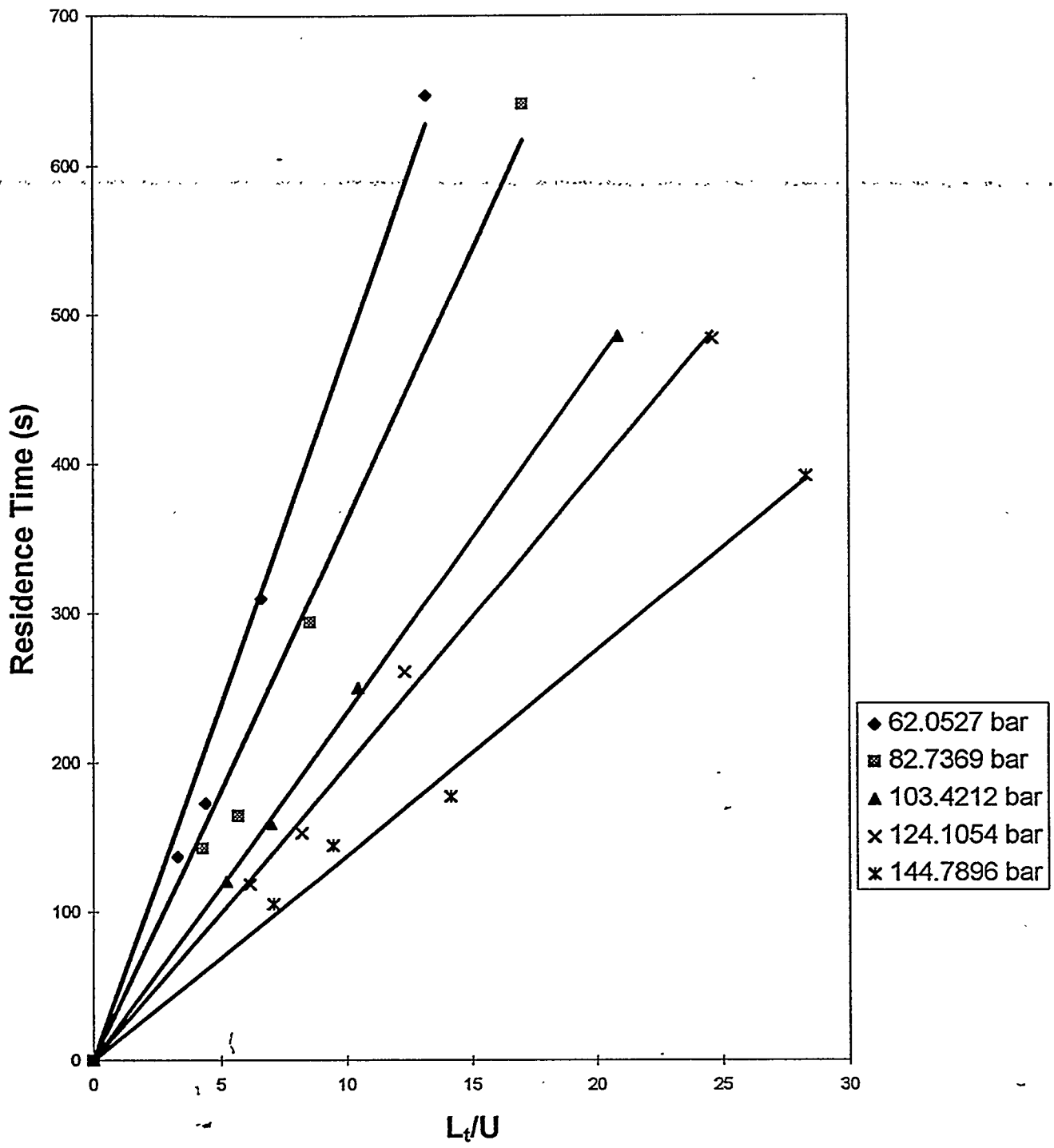
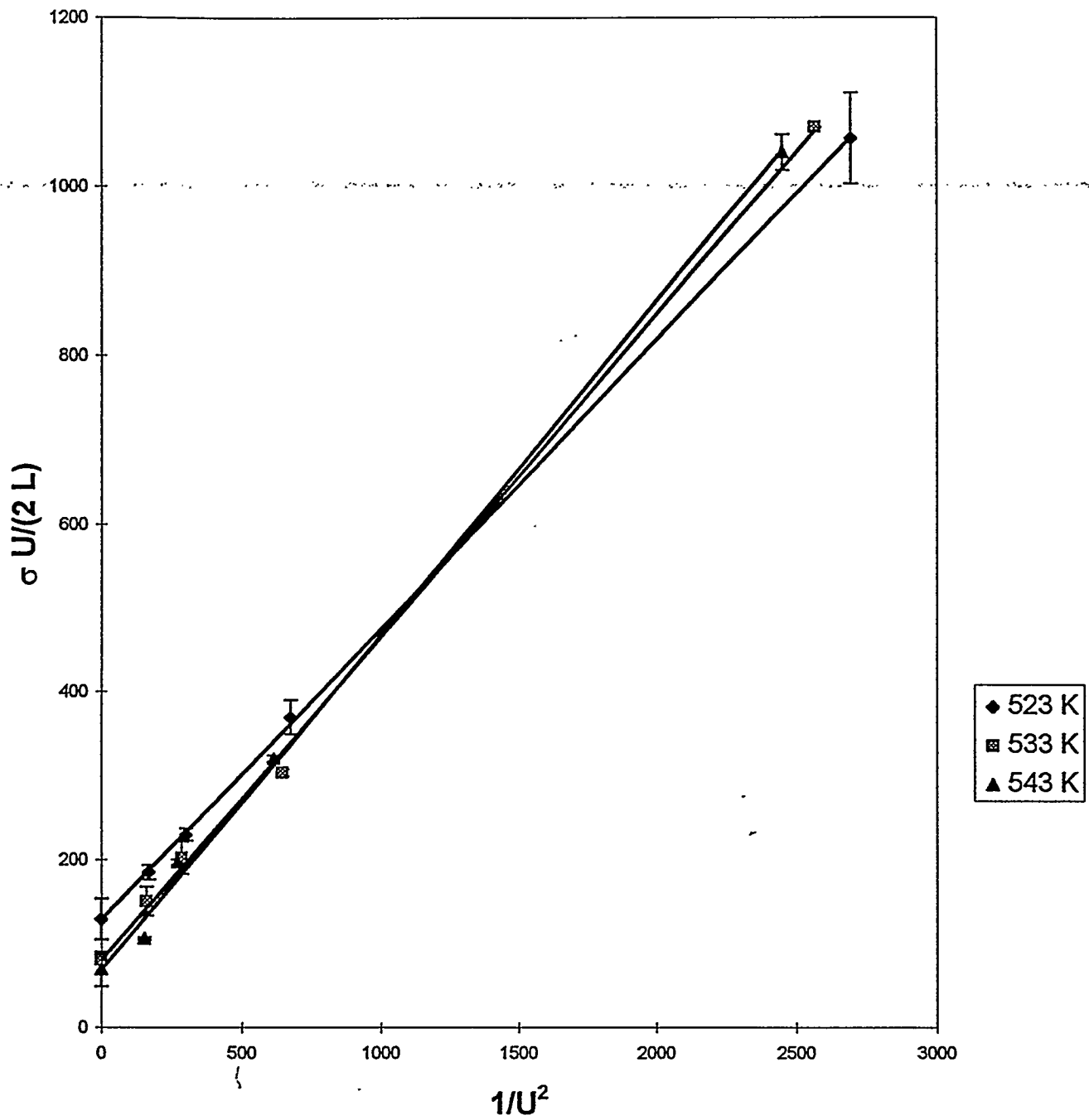


Figure 5. Determination of  $K_A$  in 1-octene/ethane  
 ( $P_{re} = 1.25-2.91$ ;  $T_{re} = 171.-1.78$ )



**Figure 6. Determination of  $Pe$  and  $D_{eff}$  in 1-octene/ethane (523-543 K: 62-144 bar) ( $P_{re} = 1.25-2.91$ ;  $T_{re} = 1.71-1.78$ )**

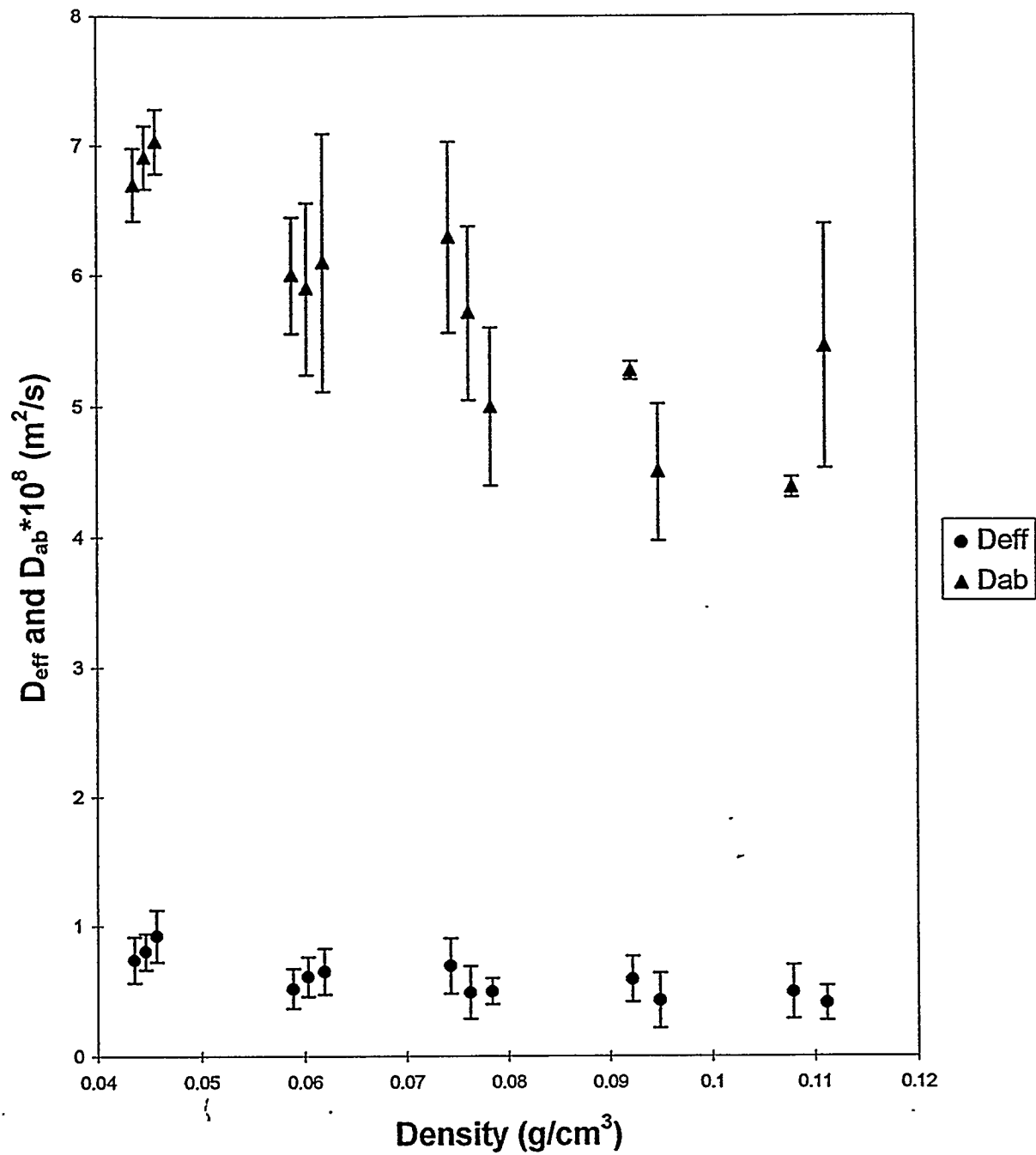


Figure 7. Variation of  $D_{eff}$  and  $D_{ab}$  in 1-octene/ethane (523-543 K; 62-144 bar) ( $P_{re} = 1.25-2.91$ ;  $T_{re} = 1.71-1.78$ )

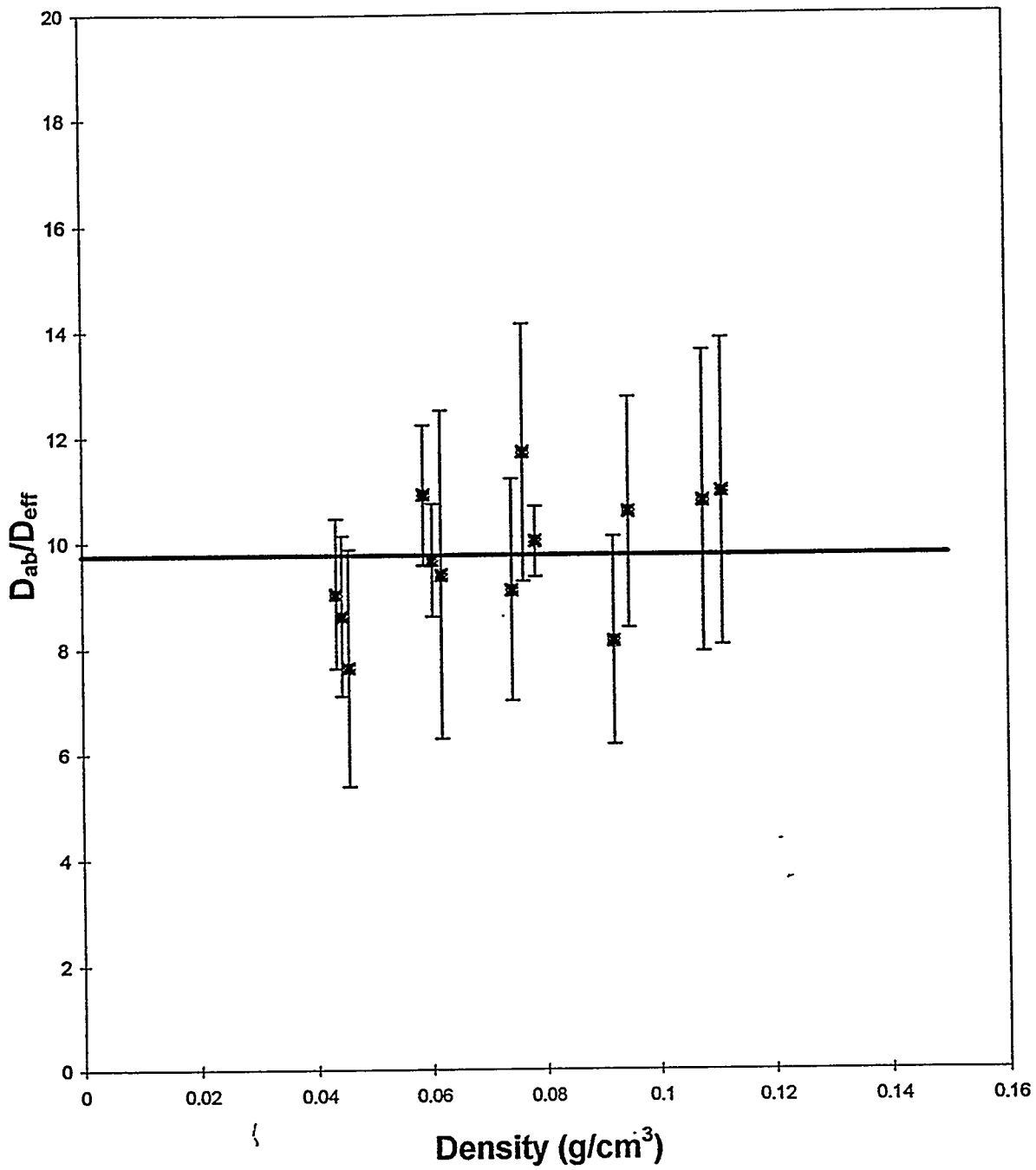


Figure 8. Variation Of  $D_{ab}/D_{eff}$  in 1-octene/ethane  
(523-543 K; 62-144 bar) ( $P_{re} = 1.25-2.91$ ;  $T_{re} = 1.71-1.78$ )