1.0 INTRODUCTION

Coal liquefaction will be an important source of transportation fuels in the future, and can be accomplished by both a direct route (hydrogenation of coal in a donor solvent) or by an indirect route (gasification of coal followed by the Fischer-Tropsch reaction).

The product selectivity of the Fischer-Tropsch reaction has been the focus of extensive research for many years, yet still remains a prime target for technical innovation. Fischer-Tropsch technology, as it is currently practiced commercially for liquid fuels production, provides a broad range of hydrocarbon products which require costly downstream refining.

Selectivity can be influenced by variations in the catalyst composition and process conditions. Yet, in spite of the extensive effort devoted to this problem, a suitable catalyst has not previously been developed for producing a narrow range hydrocarbon product, such as gasoline or diesel fuel, without the coproduction of lighter and heavier undesirable products.

The Fischer-Tropsch reaction is exothermic, and improved heat transfer would also be expected to have a major beneficial effect on product selectivity. Slurry phase reactor operation improves heat transfer and temperature control, and results in greater selectivity to liquid products, usually through lower methane production. However, considerable differences have been reported in the space-time yield, catalyst life and ease of operation of slurry phase reactors.

In addition to improved product selectivity, slurry phase operation offers the advantage of ease of scale-up and the ability to directly utilize the carbon monoxide-rich synthesis gas produced by coal gasifiers. The full potential of the slurry phase Fischer-Tropsch process has not yet been realized, and its further development is an important part in our country's program to establish a viable technology for converting coal to hydrocarbon fuel.

Therefore, Air Products (APCI), under contract to the DOE, has undertaken a program in catalyst and reactor development for a slurry phase Fischer-Tropsch process. This contract spans 36 months and is divided into four major tasks. This report describes the work accomplished during the seventh quarter.

2.0 OBJECTIVE

The overall objective of this program is to evaluate catalysts and slurry reactor systems for the selective conversion of synthesis gas into transportation fuels via a single stage, liquid phase process.

Task 1 - To establish a detailed Project Work Plan.

Task 2 - To evaluate and test catalysts for their potential to convert synthesis gas to gasoline, diesel fuel, or a mixture of transportation fuels suitable for domestic markets, and to quantify catalyst activity, selectivity, stability and aging with a target process concept involving a single stage, liquid phase reactor system.

Task 3 - To evaluate through the use of cold-flow reactor simulators the flow characteristics and behavior of slurry reactors for the production of hydrocarbons from synthesis gas. This includes (1) defining heat, mass and momentum transfer parameters which effect the design of slurry reactors, (2) establish operating limits for slurry reactors with respect to system physical parameters, (3) developing or confirming correlations for predicting the flow characteristics and heat/mass transfer of slurry reactors, and (4) defining the necessary requirements for the design of larger scale reactors.

Task 4 - To develop a preliminary design for a pilot plant slurry phase Fischer-Tropsch reactor.

3.0 SUMMARY AND CONCLUSIONS

3.1 Task 1 - Project Work Plan

This task is complete.

3.2 Task 2 - Slurry Catalyst Development

3.2.1 Subtask 2a - Background Studies

A computerized survey of available literature and patents dealing with the conventional and slurry phase Fischer-Tropsch processes and the hydrodynamics of three phase slurry reactors was continued.

3.2.2 Subtask 2b - Bench-Scale Reactor Set-Up

This subtask is complete.

3.2.3 Subtask 2c - Catalyst Preparation and Slurry Reactor Testing

(a) Catalyst Preparation and (b) Gas Phase Screening Tests

These sections contain potentially patentable material and have therefore been issued in a supplementary report marked "Not for Publication."

(c) Slurry Tests

Baseline Catalyst

A second test of the baseline catalyst, sintered Fe_2O_3 promoted with 2-3% Al_2O_3, 0.5-0.8% K_2O and 0.7-1.2% CaO, was carried out in the 1,000 mL reactor. Using only CO rich syngas, with CO/H_2 ratios of 1.4 and 2.8, the stir speed and space velocity were systematically varied over a range of temperatures, with a total continuous run time of 766 hours.

Conversion increased rapidly with temperature and at 250°C with 1.4:1 CO/H_2, the product approximated a straight line Schulz-Flory distribution with $\alpha \sim 0.78$. Activity for the water gas shift reaction was high, and at 280°C, with $\alpha \sim 0.81\text{-}0.85$, the syngas usage ratio closely matched the feed ratio. However, catalyst deactivation was also observed at temperatures >250°C, primarily with 1.4:1 CO/H_2, and the total activity decreased by 83% over the period of the test.

The use of 2.8:1 CO/H_2 syngas with partially deactivated catalyst gave non-standard product distributions, with CH_4 as low as 4.7 wt %, increased C_2-C_5, and near uniform carbon number weight fractions in the C_{10}-C_{30} range, at $\alpha = 0.93$.

Increases in slurry level due to the buildup of heavier hydrocarbons were observed throughout the test. Slurry oil was periodically withdrawn from the reactor via a 5 μm filter to maintain a constant level, and the high melting point wax samples thus obtained were analyzed and quantitatively included in the mass balances for each sample point. Over the test period, the original slurry oil was essentially replaced by C_{22-35} Fischer-Tropsch product n-alkanes.

Data from this run is currently being analyzed in terms of a totally backmixed gas and liquid reactor model, to distinguish mass transfer and chemical rate resistances. Preliminary results show that the simple pseudo first-order H_2 dependent kinetic expression is successful for CO-rich syngas, but a more complete kinetic treatment is required for H_2 rich syngas because of the effects of the water gas shift reaction. At T >250°C, measureable stir speed and space velocity dependent mass transfer limitations were observed.

This test shows conclusively that the slurry reactor system can operate with high CO ratio syngas, produce low CH_4 yields and accommodate, with no interruption in operation, the formation of high molecular weight hydrocarbons. The deactivation rate of a standard Fe_2O_3 Fischer-Tropsch catalyst is very dependent on the process conditions.

3.2.4 Subtask 2d - Metal Cluster Catalyst Preparation and Screening Tests

This section contains potentially patentable material and has therefore been issued in a supplementary report marked "Not for Publication."

3.3 Task 3 - Slurry Reactor Design Studies

The majority of measurements carried out in the 5" column this quarter were made on the water/0-5 µm silica and water/90-115 µm silica systems. Using the manometer tube method, it was found that the gas holdup varied with position in the column for the 90-115 µm silica system. The gas holdup profiles became less uniform with increasing solids loading, and more uniform with increasing gas velocity; a behavior that was consistent with the variation in solid concentration profiles. Although non-uniform solid dispersions were observed in the water/90-115 µm silica system, the non-uniformity was much less than in the equivalent isoparaffin system, where much of the silica remained undispersed at the bottom of the column.

Gas to liquid mass transfer coefficients and liquid dispersion coefficients were also measured for these two systems.

Mass transfer coefficients were found to decrease with increasing solid loading and with decreasing particle size. This may be due to variations in the gas/liquid interfacial area caused by solid dependent slurry viscosity and bubble size effects. Both gas holdup and mass transfer coefficients were statistically correlated for the larger silica system.

Liquid dispersion coefficients were measured by matching smoothed experimental data curves, obtained at various points in the column, with a series of curves generated from an analytical solution of the general Fick's Law equation. A higher dispersion coefficient was determined above the distributor plate than elsewhere in the column, but this may be partially due to a non-coincidence of the tracer inlet position between the model and the experimental location.

Construction of the 12" column was completed and the system subjected to a hazards review. Shakedown runs are expected to begin in July.

4.0 ACKNOWLEDGEMENTS

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5.0 RESULTS AND DISCUSSION

5.2 Task 2 - Slurry Catalyst Development

5.2.3 Subtask 2c - Catalyst Preparation and Slurry Reactor Testing

(a) Catalyst Preparation and (b) Gas Phase Screening Tests

These sections contain potentially patentable material and have therefore been issued in a supplementary report marked "Not for Publication."

(c) Slurry Reactor Tests

Test No. 7075-12-B1 - Baseline Catalyst

A second slurry test of the baseline catalyst, sintered Fe_2O_3, promoted with 2-3% Al_2O_3, 0.5-0.8% K_2O and 0.7-1.2% CaO, was carried out in the 1,000 mL reactor. Using 1.4:1 CO/H_2 and 2.8:1 CO/H_2, the stir speed and space velocity were systematica varied over a range of temperatures to give further information about mass transfer limitations, product distribution and catalyst activity with CO-rich syngas.

The gas phase activation and loading of the slurry catalyst are described in Section 6.2.3.

Table 1 summarizes the parameter range of the samples and lists the feed and usage ratios of the syngas, and the CO, H_2 and CO + H_2 conversions. Taken in conjunction with the previous slurry baseline test carried out at a constant 0.45:1 CO/H_2 ratio (5871-38-B1, October-December 1981, Quarterly Report), the results provide a comprehensive study of a standard Fischer-Tropsch catalyst operated in the slurry phase.

The test was run for a total of 766 hr, because of initial problems with the gas mass flow controllers, and the reactor operated continuously over this period. Increases in the slurry level were monitored by the differential pressure gauge, and heavier hydrocarbons that did not distill from the reactor were periodically withdrawn, via a 5 μm stainless steel sinter immersed in the slurry and a heated transfer line and ball valve, to the external slurry reservoir. By recording the rate of increase in slurry level and weighing and analyzing the wax samples filtered from the reactor, the heavier hydrocarbons that were retained in the slurry oil were quantitatively included in the mass balances obtained for each sample point listed in Table 1.

The total product distributions obtained for representative samples are shown in Tables 2-46 and Figures 1-30.

With 1.4:1 CO/H_2 at 220 and 250°C, samples 14-35, the conversion increased rapidly with temperature, but stir speed had little effect and no catalyst deactivation was observed under these conditions. At 220°C, the yield of C_2-C_5 olefins was high, but at 250°C the hydrocarbon product approximated a straight line Schulz-Flory distribution, with $\alpha \sim 0.78$.

At 280°C, the value of α increased to 0.81-0.85 with an increased production of higher molecular weight hydrocarbons, samples 47-55. A greater degree of water gas shift conversion brought the syngas usage ratio U close to the feed ratio S (Table 1). Some indication of the onset of rate limitations due to gas to liquid mass transfer was also observed at this temperature; an increase in conversion with increasing stir speed, and an increase in activity with space velocity. However, catalyst deactivation also occurred, since on returning to 250°C after a period of 167 hr at 280°C, the activity had decreased by 56%, samples 35 and 50.

With 2.8:1 CO/H_2 at 250°C, the hydrocarbon distributions showed increased yields of C_2-C_5, and near uniform weight fractions in the C_{10}-C_{30} region, with $\alpha \sim 0.93$ in this range, samples 62-68. No further deactivation occurred on increasing the CO/H_2 ratio at this temperature and no effect of stir speed was observed, although an increase in space velocity did increase the overall activity.

At 280°C with 2.8:1 CO/H_2, the hydrocarbon product distributions remained similar with low methane yields of 4.7-5.3 wt%, samples 71-74. Variations of the stir speed produced little effect, but the catalyst continued to exhibit less than 60% of the activity observed previously at 280°C with 1.4:1 syngas, samples 47 and 74.

Returning to 1.4:1 CO/H_2 at 280°C, further catalyst deactivation occurred and the overall conversion decreased to 13.9%. The increase in higher molecular weight hydrocarbons in the product continued, with C_{10}+ equal to 52 wt %, sample 52.

Finally the initial conditions of test were repeated, sample 84, and a reduction in the activity of the catalyst by 83% over the period of the test was measured. Evaluation of the results indicates that this deactivation occurred only at temperatures >250°C, and primarily with the 1.4:1 CO/H_2 syngas.

During the test a total of 140.9 g of wax were filtered from the reactor. Upon dismantling the reactor at the end of the run, a further excess of 97.8 g of slurry was recovered. The spent catalyst and oil are currently being analyzed. A sample of the spent slurry was filtered through a 1 μm filter and analyzed by GC. Figure 31 shows a comparison of the spent oil with the initial slurry oil, and indicates the buildup in the reactor and the replacement of the original oil over the period of the test with C_{22-35} n-alkanes.

Preliminary analysis of these results show that, with CO-rich syngas, the use of a simple pseudo first-order H_2 dependent kinetic expression gives a rate constant and activation energy for T ≦250°C that are in good agreement with previous workers.[1,2] For T >250°C, there is evidence of measureable stir speed and space velocity dependent mass transfer limitations. A more complex kinetic treatment is required, however, for the H_2 rich syngas results because of the effects of the water gas shift reaction.

5.2.4 Subtask 2d - Metal Cluster Catalysts Preparation and Screening Tests

This section contains potentially patentable material and has therefore been issued in a supplemntary report marked "Not for Publication."

5.3 Task 3 - Slurry Reactor Design Studies

5.3.1 5" Cold Flow Simulator

(i) Gas Holdup

Gas holdup profiles were obtained for the isoparaffin/ 45-53 μm silica, two-phase air/water, water/0-5 μm silica and water/90-115 μm silica systems, and are shown in Tables 47 and 50 and Figures 32 to 35, respectively. In Tables 47 and 50 "EG23" is the gas holdup between ports 2 and 3 as determined by the manometer tube method. Two gas holdup measurement methods were employed, the average method (1), and the manometer tube method (2), both of which are explained in Section 6.3.1 of this report. Because noticeable deviations in gas holdup with position in the column were observed in the 90-115 μm silica case, Figures 36-38 show the gas holdup profiles for 10, 20 and 30 wt % solids, respectively. The gas holdup profiles became less uniform with increasing solids weight loading, which is consistent with the observed solid concentration profiles. With increasing gas velocity the solid profiles became less observable, and the gas holdup profiles also approached the average value. The following expression gave an R^2 of 0.973 when correlating average gas holdup against weight % and gas velocity for the water/90-115 μm silica system:

$$\varepsilon_G/(1 - \varepsilon_G)^4 = 0.679V_G^{1.777}/W_S^{0.3061} \qquad (1)$$

where, ε_G = gas holdup
V_G = superficial gas velocity, ft/sec
W_S = weight fraction solid in slurry

(ii) Solid Dispersion

Solid concentration profiles were obtained for the water/0-5 μm and water/90-115 μm silica systems operated in the batch mode, and are shown in Figures 39, 40, 41, and 42, respectively. While the solids concentration decreased considerably with column height, in the water/90-115 μm silica case, the profiles were more uniform than in the isoparaffin system, where much of the silica remained undispersed at the bottom of the column. A more detailed comparison between the water and isoparaffin systems will await the accumulation of more data.

(iii) Mass Transfer

Mass transfer runs were carried out for the water/0-5 μm and 90-115 μm silica systems, and examples are shown in Figures 43 to 46. These O_2 concentration vs time curves were analyzed using:

$$K_L a = \frac{1 - \varepsilon_G}{t_2 - t_1} \ln \frac{C_1}{C_2} \qquad (2)$$

(see Section 6.3.1 for deviation and nomenclature), and the results are tabulated in Tables 49 and 50 and illustrated in Figures 47 and 48.

In Figures 43 to 46, except at the highest gas velocity, the two probes responses, from port 2 and port 4 spaced 26 inches apart, are superimposable. Thus, in relation to the time constant of 4.3 sec for the O_2 electrode, the system can be considered to be well mixed.

Figures 47 and 48 also show a literature comparison with two-phase correlations applied to the air/water system, Akita and Yoshida,[3]

$$K_La = 0.6 \frac{D_L}{D^2} N_{Sc}{}^{0.5} N_{Bo}{}^{0.62} N_{Ga}{}^{0.31} \varepsilon_G{}^{1.1} \qquad (3)$$

where $N_{Sc} = \mu_L/\rho_L D_L$

$N_{Bo} = gD^2\rho_L/\sigma$

$N_{Ga} = gD^3\rho_L{}^2/\mu_L{}^2$

D_L = 0_2 liquid diffusivity, cm^2/sec

D = column diameter, cm

and Hikita et al,[6]

$$K_La = \frac{14.9\ g}{v_G} {\frac{v_G\mu_L}{\sigma}}^{1.76} {\frac{\mu_L 4g}{\rho_L\sigma 3}}^{-0.248} {\frac{\mu_G}{\mu_L}}^{0.243} {\frac{\mu_L}{\rho_L D_L}}^{-0.604} \qquad (4)$$

For the water/air system with,

$\rho_L = 0.998\ g/cm^3$

$\mu_L = 0.961$ g/cm sec

$\mu_G = 0.0182$ g/cm sec

$\sigma = 72.3$ dyne/cm

$D_L = 2.22 \times 10^{-5}\ cm^2/sec$

$D = 12.7$ cm

equations (3) and (4) simplify respectively to,

$$K_La = 0.323\varepsilon_G{}^{1.1} \qquad (5)$$

$$K_La = 9.39 \times 10^{-3} v_g{}^{0.76} \qquad (6)$$

In Figure 47, the data for the 0-5 μm silica system lies mostly below the two, two-phase correlations. A decrease in K_La in going from 0 to 10 and from 10 to 20 wt % was observed in both silica sizes. However, a further decrease in K_La in going from 20 to 30 wt % was detected only for the large silica. A decrease in K_La at about the 20 wt % region was observed by Joosten et al,[7] using glass beads and finely divided polypropylene solids. Other workers, however, observed no such effect of solids on K_La.[8,9] A possible explanation for this effect would the same as for the decrease in gas holdup with greater weight loadings observed previously, i.e., increasing slurry viscosity yielding larger bubbles with a shorter residence time and hence a smaller interfacial area.

Values of K_La for the 90-115 μm system are greater than those obtained in the 0-5 μm silica system. If K_L for the two systems is similar this points to an inverse relationship between particle size and interfacial area. Again, this could be accounted for by the slurry viscosity or bubble size effect mentioned earlier. Three phase bubble diameter measurements, to be conducted in the 12" column, will determine the effect of solid loading and size on bubble diameter. An R^2 of 0.888 was obtained when correlating K_La for the water/90-115 μm silica system against wt % and gas velocity by the following equation:

$$K_La = 0.0633V_G^{0.690}/W_S^{0.325} \tag{7}$$

(iv) Liquid Dispersion

Measurements to determine liquid dispersion coefficients were made for the water/0-5 μm and water/90-115 μm silica systems. Treatment of the data shows that the general Fick's Law equation:

$$\frac{\partial C}{\partial t} = E\frac{\partial^2 C}{\partial z^2} \tag{8}$$

where C = tracer concentration, mol/liter
t = time, sec
E = liquid axial dispersion coefficient, m^2/sec
z = distance up column

can accurately model bubble column liquid dispersion with possibly some variation of "E" with column height. The shape of the theoretical curves generated from an analytical solution of equation (8), see Figures 49 to 52, agreed well with the measured concentration versus time curves, see Figures 53 to 56.

One set of normalized data, smoothed as described in the previous quarterly report, was analyzed according to the procedure discussed in Section 6.3.1 of this report (Figure 57), giving average dispersion coefficients of 0.030, 0.023, 0.012 and 0.018 m^2/sec for ports 2 through 5, respectively. The variation is believed to be a consequence of the model, which assumes a slug of tracer introduced immediately above the distributor, whereas, in the experimental system, the tracer is actually introduced about two inches above the distributor. This causes the tracer, at time zero, to begin to spread out, both up the column and towards the distributor. Therefore at the detection port 3.5 inches above, the tracer appears to disperse very quickly, causing a larger apparent dispersion coefficient.

An alternative solution will be used in which the tracer injection can be at any point along the column. It should then be possible to obtain a true value of the dispersion coefficient at port 2.

5.3.2 12" Cold Flow Simulator

12" Column Construction

Construction of the 12" column has been completed, and the system has been subjected to a hazards review. Shakedown runs are expected to take place in July.

6.0 EXPERIMENTAL

6.2 Task 2 - Slurry Catalyst Development

6.2.3 Sub-Task 2c - Catalyst Preparation and Slurry Reactor Tests

(a) Catalyst Preparation

This section contains potentially patentable material and has therefore been issued in a supplemntary report marked "Not for Publication."

(b) Slurry Reactor Testing

Test No. 7075-12-B1 - Baseline Catalyst

The catalyst was first ground to less than 200 mesh, and reduced in a gas/solid tubular reactor with hydrogen at 450-455°C, 1 atm and a GHSV of 380 h^{-1} for 72 hr. The reduced, pyrophoric catalyst was then slurried in deoxygenated Edwards #16 oil, and transferred to the 1,000 mL slurry reactor under a N_2 atmosphere. The resultant reactor loading was 464.3 mL of 14.70 wt % slurry containing 73.45 g of reduced catalyst.

At a constant pressure of 450 psig, the slurry was then contacted with 1.4:1 CO/H_2 and 2.8:1 CO/H_2 using stirring rates of 800 and 1,600 rpm, space velocities of 144-147 and 285-312 h^{-1} while varying the reactor temperature from 220 through 250 to 280°C.

6.2.4 Subtask 2d - Metal Cluster Catalyst Preparation and Screening Tests

This section contains potentially patentable material and has therefore been issued in a supplementary report marked "Not for Publication."

6.3 Task 3 - Slurry Reactor Design Studies

6.3.1 5" Cold Flow Simulator

(i) Gas Holdup

There are two common methods for determining gas holdup in a two or three-phase system. Method 1, used reliably in the isoparaffin studies, entails measuring an expanded gas, liquid-solid, and settled, liquid-solid, slurry height. Gas holdup is then determined from the following equation:

$$\varepsilon_g = 1 - H_s/H_e \tag{9}$$

where ε_g = gas holdup

H_s = settled slurry height

H_e = expanded slurry height

Method 2 uses manometer tubes filled with the liquid phase. Referring to Figure 58, a force balance on each manometer tube yields,

$$\rho_L\ (h''-D) = \rho 3\phi\ (H_e - D) \tag{10}$$

$$\rho_L\ (h' - A - D) = \rho 3\phi\ (H_e - A - D) \tag{11}$$

where $\rho 3\phi$ = three phase density.

Dividing equation (2) by (1) gives:

$$\frac{H_e - A - D}{H_e - D} = \frac{h' - A - D}{h'' - D} \tag{12}$$

Solving for H_e,

$$H_e = \frac{h''\ (D + A) - h'D}{h'' - h' + A} \tag{13}$$

Inserting into the average gas holdup equation:

$$\varepsilon_g = 1 - H_s/H_e \tag{14}$$

gives the final equation

$$\varepsilon_g = 1 - \frac{H_s(h'' - h' + A)}{h''(D + A) - h'D} \tag{15}$$

The manometer tube method was investigated for the following reasons. Firstly, gas holdup profiles up the column can be obtained by using multiple manometer tubes instead of just an average gas holdup. Since solid concentration profiles have been determined, a reliable method to determine gas holdup profiles could better characterize the column. Secondly, in method 2, measurement of expanded height is not required, a major source of inaccuracy in method 1.

(ii) Mass Transfer

For mass transfer of O_2 from a liquid volume, $V(1 - \varepsilon_g)$, to a gas volume, $V\varepsilon_G$, two differential mass balances can be set up, one for each phase[10]

$$(\varepsilon_G)dy/dt = \varepsilon_G E_g d^2y/dz^2 - v_G dy/dz + K_L a\ (C - C^*) \tag{16}$$

$$(1 - \varepsilon_G)dC/dt = (1 - \varepsilon_G)E_L d^2C/dz^2 + v_L dC/dz - K_L a\ (C - C^*) \tag{17}$$

where y = gas phase concentration of O_2, lb-mol/ft^3
t = time, sec
v = volumetric flow rate, ft^3/sec
V = volume, ft^3 reactor
z = column height, ft
ε_G = gas holdup
K_L = mass transfer coefficient, ft/sec
a = specific interfacial area, ft^2/ft^3 reactor

C = liquid phase concentration of O_2, lb-mol/ft^3 slurry

C* = liquid phase concentration of O_2 in equilibrirm with the gas phase, lb-mol/ft^3 slurry

E = axial dispersion coefficient, ft^2/sec

subscript,

G = gas phase

L = liquid stream

For a batch system, $v_L = 0$, and equation (17) simplifies to,

$$(1 - \varepsilon_G)dC/dt = (1 - \varepsilon_G)E_L d^2C/dz^2 - K_La(C - C^*) \qquad (18)$$

In the transient method to determine K_La the gas feed of air is instantaneously changed over to nitrogen. Because a large amount of nitrogen is used to strip out part per million quantities of O_2 from the liquid phase, the gas phase O_2 concentration is essentially zero. Thus dy/dt = 0 in equation (16), and C* = 0 in equation (18). With the following assumptions:

a) the liquid is well mixed,

b) the gas phase is well mixed, and

c) the response time of the dissolved O_2 electrode is fast compared to the rate of mass transfer between liquid and gas,

the first term on the right hand side of equation (18) equals zero, and equation (18) can be integrated directly to yield:

$$K_La = \frac{1 - \varepsilon_G}{t_2 - t_1} \ln \frac{C_1}{C_2} \qquad (19)$$

where C_1 and C_2 are dissolved O_2 concentrations at t_1 and t_2.

The validity of the assumptions, particularly assumption (c), will subsequently be tested and K_La values will be recalculated if necessary.

(iii) Liquid Dispersion

Residence time distribution (RTD) curves generally are obtained at four locations in the column; at 3.5, 14.75, 25.75, and 44.58 inches above the distributor plate. Figures 49 and 52 show a family of theoretical RTD curves generated from the approximate analytical solution of Ohki and Inoue,[11]

$$C/C_E = 1 + 2 \sum_{n=1}^{100} [\cos(n\pi Z/L)\exp(-n^2\pi^2 Et/L^2)] \qquad (20)$$

where C/C_E = normalized tracer concentration
Z = port location, m
L = extended bed height, m
E = liquid axial dispersion coefficient, m^2/s
t = time

Experimental dispersion coefficients were obtained by matching the theoretical dispersion curves to the maxima of the data curves.

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