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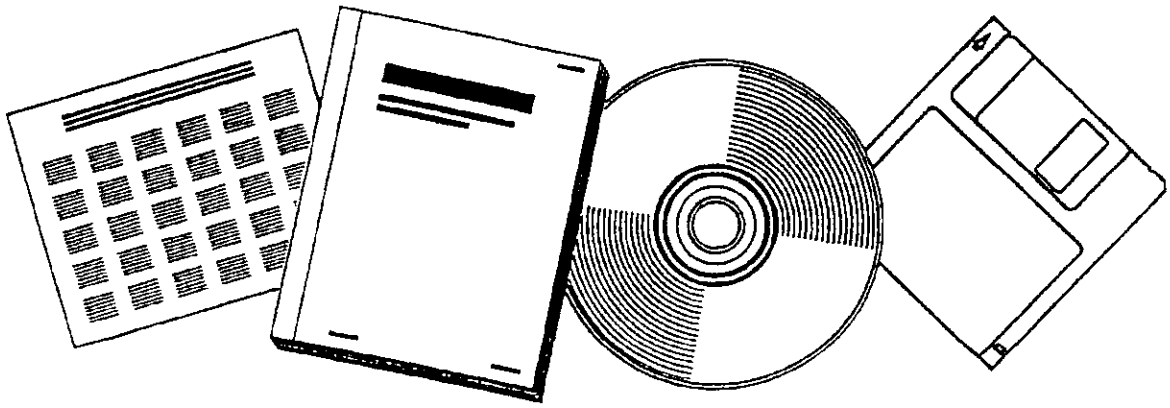

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Fischer-Tropsch Synthesis in Slurry Reactor Systems

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I. SUMMARY

In slurry reactors as used for Fischer-Tropsch synthesis or liquid phase methanol synthesis an important design factor is the effect of solids loading on gas-liquid mass transfer. Little information is available for organic liquids, which differ significantly from water in their behaviour. A detailed study has now been completed of the influence of solid particles upon the global mass transfer parameters, $k_L a$ and a, as determined in a mechanically stirred, one-liter autoclave. The interfacial area, a, was evaluated by the unsteady state absorption with simultaneous reaction in the fast-reaction regime of CO_2 with cyclohexylamine in a 90% toluene and 10% isopropanol mixture. The overall mass transfer coefficient, $k_L a$, was determined by the unsteady state desorption of helium from a helium-saturated solution of cyclohexylamine in the toluene and isopropanol mixture into a nitrogen purge stream.

Experiments were conducted at near-ambient conditions. Mixtures of 6-8% CO_2 in N_2, a superficial gas velocity of 0.75 cm/s, and solutions of 0.25 M cyclohexylamine were used. Stirring speeds ranged from 350-1750 rpm. The solid properties investigated were particle concentration (0-45 volume %), size (35-200 μm), density 0.7-4.5 g/ml), and composition (glasses of several densities, polytetrafluoroethylene, and polypropylene).

To evaluate the mass transfer parameters, the liquid and solid phases were modelled as a single homogeneous slurry phase behaving as a CSTR, while the gas phase was modelled as a PFR with recycle. Varying the recycle ratio, R, allowed the entire spectrum of gas phase mixing possibilities (CSTR to PFR) to be modelled. Uncertainty in the gas phase RTD and the high reaction rate of the amine

carbamation, however, precluded the unambiguous determination of $\underline{a}$. Criteria were established which indicate when $\underline{a}$ can be determined by absorption with simultaneous reaction independent of any gas phase assumption.

The overall mass transfer coefficient and the interfacial area decreased linearly with inert solids loading. The decrease in $\underline{k_L a}$ could be attributed to the decrease in $\underline{a}$: $\underline{k_L}$ was independent of solids loading for the conditions of this study.

Both $\underline{k_L a}$ and $\underline{a}$ were independent of particle size in this study. Both were also independent of particle density. Stirring speed was shown to be an appropriate basis for comparison of mass transfer parameters.

At high solids loadings $\underline{k_L a}$ and $\underline{a}$ became dependent upon particle composition. Particles which were more nonwetting caused a larger decrease in $\underline{k_L a}$ and $\underline{a}$. A mechanism for enhanced bubble coalescence was postulated.

A detailed report is appended.

Introduction

Three phase slurry reactors find increasing use in catalytic reaction engineering. Excellent temperature control and heat recovery characterize both the mechanically stirred vessel and the bubble column. These systems also provide a means of using smaller or more friable catalysts not amenable to other types of reactors. Hydrogenation of edible oils and a wide variety of chemicals typify the kinds of reactions for which they are utilized. Recent reviews have been published by Chaudhari and Ramachandran (1980) and Kurten and Zehner (1979).

Gas-liquid mass transfer often represents the major limitation to optimal conversion in these reactors. Catalyst particles usually are less than 300 μm in diameter, and a size range of 50-100 μm is common. Bubbles, though, range from 1 mm in mechanically stirred vessels to larger than 10 cm in some bubble columns. Even with a solids holdup one tenth of the gas holdup, the interfacial area available for mass transfer from the liquid to the outside catalyst surface is typically one hundred times or more greater than the interfacial area available for transfer from the gas to the liquid. Consequently, mass transfer resistance, if present, is at the gas-liquid interface.

The calculation of relevant mass transfer parameters for these reactors is still highly uncertain. Frequently, a three phase slurry reactor is modelled as a two phase system, gas and slurry, in which the solid-liquid mixture is treated as a homogeneous phase. If gas-liquid mass transfer could be adequately predicted, based upon a liquid with the same hydrodynamic characteristics as the slurry, the three phase problem would be removed. But the extent to which this assumption is valid has not been

fully tested.

This assumption is clearly inadequate under one set of circumstances. Since the solid particles are catalytic, mass transfer can be enhanced if the effective diffusion length from the gas-liquid interface to the particle surface is reduced. In terms of film theory, the effective diffusion length can be reduced by penetration into the liquid film of catalyst particles, an effect most noticeable with particles smaller than the film thickness. Pal et al. (1982) have demonstrated enhanced absorption of oxygen into sodium sulfide solutions in which 1 and 4 μm carbon particles were suspended. Very little enhancement was observed for 60-85 μm particles, which exceeded the film thickness of approximately 20 μm. Typical catalyst particles, though, are larger than 50 μm to facilitate separation from the liquid carrier. Enhancement by this mechanism is possible but would not normally be sought, although it could occur as a result of catalyst attrition in the liquid.

Catalytic properties of the particles aside, their effect upon gas-liquid mass transfer, other than through changing the bulk hydrodynamics of the pseudo-liquid slurry, has not yet been fully tested. Without this knowledge underdesign of slurry reactors is certainly possible. In a pilot plant bubble column reactor at Sasol in South Africa which employed a paraffinic wax for the Fischer-Tropsch reaction at 3.04 MPa pressure and 200-300 ^{o}C, Dry (1983) attested that increasing catalyst loading eventually reduced gas holdup and conversion. The observed reaction rate eventually changed from a kinetically-controlled regime to a mass transfer-controlled one. Similar adverse results have been reported by Kurten and Zehner (1979) for interfacial area: increased solids loading resulted in a reduction of the overall bubble surface area available for mass transfer in a

bubble column reactor in which air was sparged through an aqueous sulfite solution.

Other studies indicate that the assumption of a pseudo-liquid is an oversimplification. Joosten et al. (1977) reported a decrease in the mass transfer coefficient in a stirred vessel with increased solids loading, at high particle loadings. Reduced to a relative viscosity basis, however, the effect varied with the composition and density of the solid employed. Godbole et al. (1983) noted that gas holdup in a three phase bubble column varied with the particle composition. These observations have not been placed yet within a unifying framework.

An additional problem in slurry reactors, and indeed in gas-liquid reactors in general, is that experimental or pilot plant mass transfer studies are often conducted with fluids not representative of the ultimate industrial application. Water has been most frequently used because it is safe and also because aqueous systems are of intrinsic interest for some applications. However, aqueous systems often behave substantially differently than organic systems.

The ubiquitous presence of ions in aqueous systems, either through contamination or present deliberately, can cause the gas bubbles to be virtually noncoalescing and thus bubble sizes to be very small (Reith and Beek, 1970; Farritor and Hughmark, 1980). A double layer of electrolyte forms at the bubble surface and thus reduces bubble interactions. Froment and Bischoff (1979) noted that in electrolyte systems interfacial areas an order of magnitude larger than in pure liquids can be generated. Both the bubble size distribution and the coalescence characteristics are poorly representative of many systems employing organic liquids.

Aqueous systems are also affected by surfactant-type impurities. They

can alter the surface tension of the liquid, and thus the size and coalescence characteristics of bubble swarms, and consequently cause overall mass transfer coefficients and interfacial areas different than those observed in their absence (Davies, 1963). Short chain alcohols in water can also reduce coalescence considerably without changing greatly the measured surface tension (Calderbank, 1958).

Mass transfer is often altered unpredictably for these systems. The total rate of mass transfer from gas to bubble interface and from interface to bulk liquid can be expressed as the product of a driving force and an overall mass transfer coefficient:

$$N_m a = k_g a(p - p_i) = k_L a(C - C_i) \qquad (1)$$

In many typical applications, the liquid-side transfer will be the dominating resistance. The corresponding mass transfer coefficient, $k_L a$, will experience two opposing effects from the presence of ions or organic solutes. The interfacial area per unit volume, a, will increase, often dramatically, because of a skewing of the bubble distribution toward smaller diameter bubbles. However, the individual liquid phase mass transfer coefficient, k_L, may decrease by as much as 70%, because of the reduction of turbulence at the bubble interface caused by the presence of solutes (Calderbank and Moo-Young, 1961). Whether $k_L a$, the product of k_L and a, ultimately increases or decreases can not always be predicted.

The present study was undertaken to investigate the effect of inert solids upon the mass transfer parameters a and $k_L a$ in an aerated and mechanically stirred vessel. Both parameters were sought since both are required for proper design and scale-up of a three phase slurry reactor. The experiments were conducted in an organic liquid mixture to avoid the

problems inherent in using an aqueous system. The results obtained were thus characteristic of liquids commonly encountered in industrial practice.

Measurement Technique

The interfacial area was determined by the so-called "chemical method" (absorption with simultaneous chemical reaction in the "fast-reaction regime"). Traditionally, the sulfite oxidation reaction has been used for this purpose. Oxygen is absorbed with reaction into a sodium sulfite solution, the reaction of oxygen and sulfite being homogeneously catalyzed by cobaltous ions (Co^{+2}). The rate constant can be varied over a thousand-fold range by varying the concentration of the catalyst. Several physico-chemical criteria are necessary for this method to be implemented (Table 1).

The sulfite method has been in use since the work of Cooper et al. (1944). Despite its long history, the kinetics are still not very well understood. Contamination of the water, homogeneous catalyst or sulfite salt can lead to incorrect and irreproducible results (Linek and Vacek, 1981). The main advantage is the ability to change the rate constant over a wide range. The sulfite method is clearly limited to aqueous solutions. The noncoalescent behavior of these ionic systems has led to the development of other reaction schemes for measuring interfacial area, but all suffer from the problem of an invariant rate constant. The reaction must be carefully chosen to ensure that the rate and other physicochemical constants satisfy the criteria for use. One class of reactions that has emerged is the carbamation of amines.

In the present study interfacial area was determined by the reaction of CO_2 with cyclohexylamine (CHA) in a 90% toluene and 10% isopropanol mixture, a reaction first investigated for this purpose by Sridharan and

Table 1

Physicochemical Criteria Required for Determination of a by Absorption with Reaction in the Fast Regime

Reaction: $A(gas) + zB(liquid) \longrightarrow products$

$$M = \frac{2D_A k_{mn} [A^*]^{m-1} [B_o]^n}{k_L^2 (m+1)}$$

Criteria to determine a:

(1) $$\sqrt{M} \ll 1 + \frac{[B_o]}{z[A^*]} \sqrt{\frac{D_B}{D_A}}$$

(2) $$k_g \gg k_L H^* \sqrt{M} = H^* [CHA_o] \sqrt{D_{CO_2} k_{12}}$$

(3) $$\sqrt{M} > 3$$

then $$R_A a = a[A^*] \sqrt{D_A k_{mn} [B_o]^n [A^*]^{m-1} \left(\frac{2}{m+1}\right)}$$

Sharma (1976). The kinetic expression was subsequently reevaluated by Alvarez-Fuster et al. (1980) and Imaishi et al (1981). The kinetics, rate constant, and physicochemical constants from Alvarez-Fuster et al. (1980) were used in the present study. The reaction and rate expression are as follows:

$$CO_2(gas) + 2CHA(liquid) \longrightarrow CHA.CO_2.CHA\ (liquid) \qquad (2)$$

$$R_k = k_{12}[CO_2^*][CHA_o]^2 \qquad (3)$$

Several other amine carbamations have been reported in the literature as available for use in organic liquids (Alvarez-Fuster et al., 1981). However, most amine mixtures are noncoalescent: indeed, severe foaming was encountered in preliminary work in the present study in an attempt to use the other amine reactions investigated by Alvarez-Fuster et al (1980, 1981). The amine system used here was the only one which visually exhibited coalescence similar to that of pure liquids.

The overall mass transfer coefficient, $k_L a$ was determined by the unsteady state desorption of a sparingly soluble gas (helium) from a helium-saturated liquid into a nitrogen purge stream, similar to the system used by Joosten et al (1977). The liquid used was the cyclohexylamine in toluene and isopropanol mixture used for determining interfacial area. The effect of inert solids upon the degree of conversion was also measured in a mechanically-stirred slurry reactor in which the Fischer-Tropsch synthesis was occurring under partially mass transfer-controlled conditions.

Experimental Apparatus

Both a and $k_L a$ were determined using CHA in toluene and isopropanol in identically shaped vessels. The interfacial area was determined in a one-liter, stainless steel, stirred autoclave (Autoclave Engineers, Inc.)

depicted in Figure 1. It had a diameter (d_t) of 7.6 cm and was equipped with both a propeller and six-bladed impeller (d_i = 3.2 cm) mounted on the shaft. This configuration was shown by Huff (1982) to be more effective in keeping solids suspended than a single impeller. A four-bladed baffle (d_f = 0.75 cm) was used to prevent vortexing. A machined polyethylene plug was seated above the gas-liquid-solid dispersion to minimize dead volume in the reactor. Gas was sparged into the vessel via an inlet tube mounted flush to the bottom (0.10 cm ID). The reactor was maintained at 20 ^{o}C by a constant temperature bath.

A glass replica of the one-liter autoclave was used to determine $k_L a$. All dimensions and internals were identical to the stainless steel autoclave. Gas holdup could be measured visually and complete solids suspension was confirmed at every stirring speed and solids loading. An inlet gas flow rate of 35 ml(STP)/s (u_g = 0.75 cm/s) and a liquid plus slurry volume of 400 ml was used throughout this study. Gases were metered with calibrated rotameters and flows checked by a bubble meter. Stirring speeds ranged from 350 to 1750 rpm. Solids used in this study are listed in Table 2. Sieved fractions of solids were used in all experiments. The particle size indicated in any $k_L a$ or a measurement thus includes a maximum deviation of ±9%.

The reactor used in the Fischer-Tropsch studies was a one-liter, stirred autoclave (Autoclave Engineers, Inc.) identical to that used to determine a. Gas was fed into the vessel via an inlet tube in the bottom. An impeller and propeller combination was driven by a hollow shaft to agitate the liquid. The propeller and impeller were 5.08 cm in diameter, 45% larger than those used in the unsteady state a and $k_L a$ studies. A two-bladed baffle was used to prevent vortexing and a cooling coil was mounted

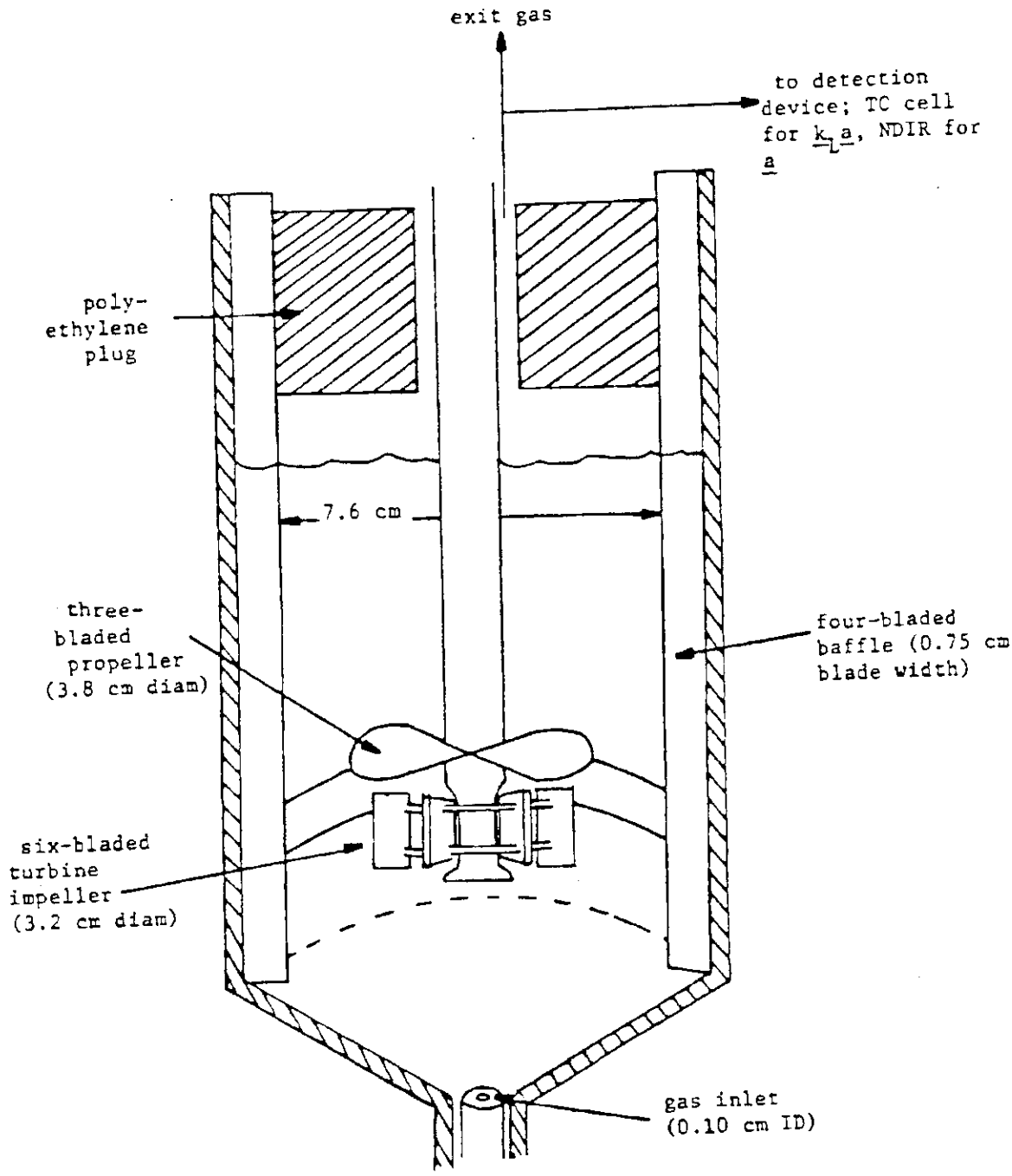

Figure 1. One-liter mechanically stirred vessel for unsteady state determination of $k_L a$ and a.

Table 2

Physical Properties of Inert Solids
Used in This Study

Particle Composition	Supplier	Designation	Shape	Density g/ml	Size Range microns
polypropylene	Polysciences	6068, 4342	granular	1.0	30-180
polytetrafluoro-ethylene	Polysciences	1344	flat	2.0	350-550
soda-lime silica glass	Potters Industries	P-004, -006, -007, -008	spherical	2.5	30-220
barium titanate glass	Potters Industries	H-002, -003, -005, -008	spherical	4.5	30-220
soda-lime silica glass	Ferro Corp.	MS-M	spherical	2.5	30-180
silicone-coated soda-lime silica glass	Ferro Corp	MS-ML-W	spherical	2.5	30-120
glassy alumina-silica fly ash (fillite)	Fillite, Inc.	200/7	spherical	0.7	30-180

about the shaft of the stirrer (Figure 2). Full details on the operation of the reactor and analysis of the reaction products can be found in Huff and Satterfield (1982) and Huff et al (1983).

The catalyst used in this study was a triply-promoted (Ca, K, Al) fused-iron (ammonia synthesis) catalyst. The slurry carrier was octacosane, a linear C-28 parafin. The catalyst charge (45-90 μm particles) of 75 g for each of two runs studied was reduced in a separate vessel at 400 °C for 50 hours under hydrogen flow of about 1 liter/min. The reduced catalyst was then slurried with 450 g of octacosane. Complete details on materials used and catalyst reduction procedure are in Huff and Satterfield (1982). The conditions of operation of both runs are indicated in Table 3.

Experimental Procedure

The bubble area, a, and the mass transfer coefficient, $k_L a$, were both determined by an unsteady state measurement. For bubble area determination the slurry charge was placed into the reactor, the reactor sealed, and a nitrogen stream introduced to establish a steady state concentration in the reactor, at a pressure approximately 15 kPa above ambient. At the beginning of the measurement, this stream was exchanged with a gas mixture of 6-8% CO_2 in N_2. The CO_2 concentration in the outlet gas was continuously monitored by a nondispersive infrared analyzer (NDIR) and the outlet displayed on a chart recorder. The inlet gas composition was set by combining metered streams of N_2 and CO_2, and the composition verified by gas chromatography.

In the determination of $k_L a$ the liquid was first saturated with helium and then the gas flow and impeller turned off. The vapor space above the liquid was next cleared with a nitrogen purge. The impeller was turned on and a nitrogen flow admitted through the bottom of the reactor.

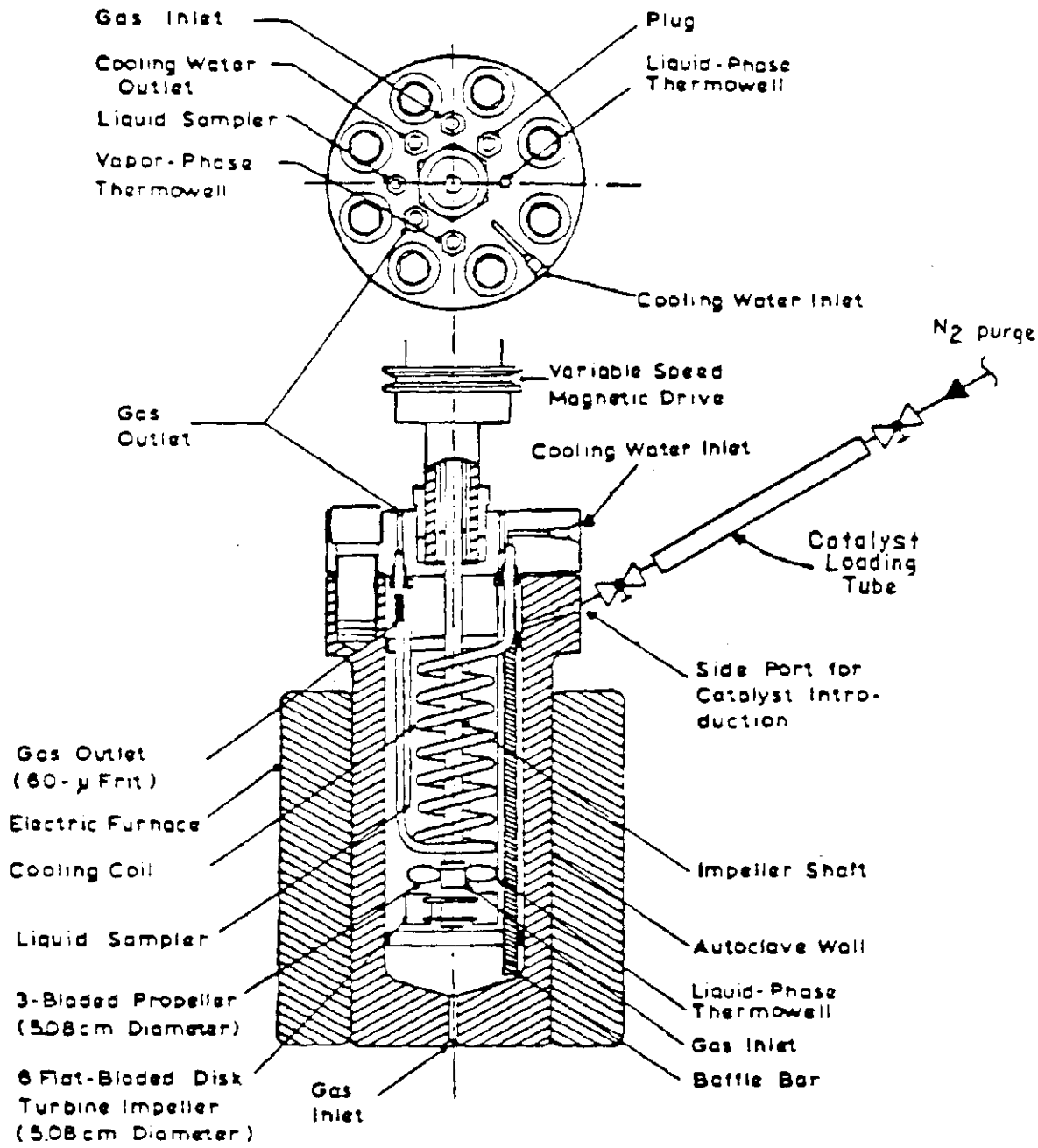

Figure 2. One-liter stirred autoclave reactor for Fischer-Tropsch reaction accompanied by mass transfer (Huff and Satterfield, 1982).

Table 3

Experimental Operating Conditions
for Mass Transfer with Reaction

Fischer-Tropsch Reaction (approximate)

$$13H_2 + 6CO \longrightarrow 2C_3H_7 + 6H_2O$$

Water-Gas Shift Reaction

$$H_2O + CO \longrightarrow H_2 + CO_2$$

	Run #1	Run #2
Run designation	FE21	FE22
Time on stream prior to k_La measurements (hrs)	593	390
Inlet flow (ml/s) (20 °C, 0.101 MPa)	13.7	13.2
Temperature (°C)	263	263
Pressure (MPa)	0.929	0.929
H_2/CO inlet ratio	0.74	2.19
Superficial gas velocity at reactor conditions (cm/s)	0.060	0.058
Measured usage ratio ($\Delta H_2/\Delta CO$)	0.63	0.78

A small fraction of the outlet purge stream was pumped through a calibrated thermal conductivity (TC) cell to determine the helium concentration. A metering piston pump located downstream of the TC cell maintained flow through the cell. As with the determination of α, the outlet concentration was continuously displayed on a high-speed chart recorder.

In the Fischer-Tropsch synthesis runs, experiments were begun in the kinetically-controlled regime at high stirring speeds (600-650 rpm). The stirring speed was then decreased to lower the overall mass transfer coefficient and reduce the conversion. Within this partially mass transfer-controlled regime, the overall resistance was the sum of a mass transfer resistance and a kinetic resistance. This was a steady state measurement and thus not prone to possible error caused by transients. Inert glass beads (75 μm diameter) were added to the reactor in increments under an inert nitrogen blanket, and conversion was measured after steady state had been reached after each solids addition. The stirring speed was periodically increased to the kinetically-controlled regime to ensure that catalyst deactivation had not occurred.

Data Analysis

In order to determine properly the mass transfer parameters in this study, an appropriate model for both the gas and liquid phase were required. In this study the liquid was modelled as a CSTR, which was justified by the short mixing times in the vessel (Mehta and Sharma, 1971). The gas phase was modelled as a PFR with recycle, which physically corresponds to surface aeration which may take place in the reactor (Topiwala, 1972). This one parameter model (R = recycle ratio) thus allowed the complete spectrum of mixing possibilities in the gas phase to be encompassed, from CSTR ($R = \infty$) to PFR ($R = 0$).

The interfacial area was calculated by fitting the outlet concentration curve to the solved mass balance equations for CHA and CO_2. The integrated mass balance equations for this reaction are as follows:

gas:
$$-(R + 1)G\int_{x_i'}^{x_o} \frac{dx}{R_r} = aV \tag{4}$$

liquid:
$$(1 - \varepsilon_s)V([CHA_o] - [CHA_o]_O) = -2G(R + 1)\int_0^t (x_i' - x_o)dt \tag{5}$$

$$[CO_2^*] = H^*P\left(\frac{x}{1 + x}\right) \tag{6}$$

$$x_i' = \left(\frac{x_i}{R + 1}\right) + \left(\frac{Rx_o}{R + 1}\right) \tag{7}$$

The equations were solved using the nitrogen flow rather than the total flow as a basis (Jukevar and Sharma, 1977) to take into consideration flow contraction over the length of the agitated vessel. The rate expression for the transfer of CO_2 into the liquid was as follows:

$$R_r a = \frac{k_g a([CO_2^*] - [CO_{2,eq}^*])[CHA_o]\sqrt{D_{CO_2}k_{12}}}{k_g + H^*[CHA_o]\sqrt{D_{CO_2}k_{12}}} \tag{8}$$

The appearance of k_g in the numerator and denominator is a consequence of criterion (2) from Table 1 not being completely satisfied. When $k_g >> H^*[CHA_o]\sqrt{D_{CO2}k_{12}}$, the denominator becomes dominated by k_g, and R_r becomes independent of k_g. In this study k_g at 20 °C was taken to be 0.008 kg.mole/m^2s-MPa based upon the work of Sharma and Mashelkar (1968). Gas phase resistance thus accounted for approximately 10% of the total resistance to reaction. The carbamation of cyclohexylamine was also found to be an equilibrium-limited process in this study, not an irreversible one