SYNTHESIS OF OCTANE ENHANCERS DURING SLURRY-PHASE FISCHER TROPSCH. QUARTERLY TECHNICAL PROGRESS REPORT NO. 1, SEPTEMBER 26-DECEMBER 31, 1990

ALTAMIRA INSTRUMENTS, INC.
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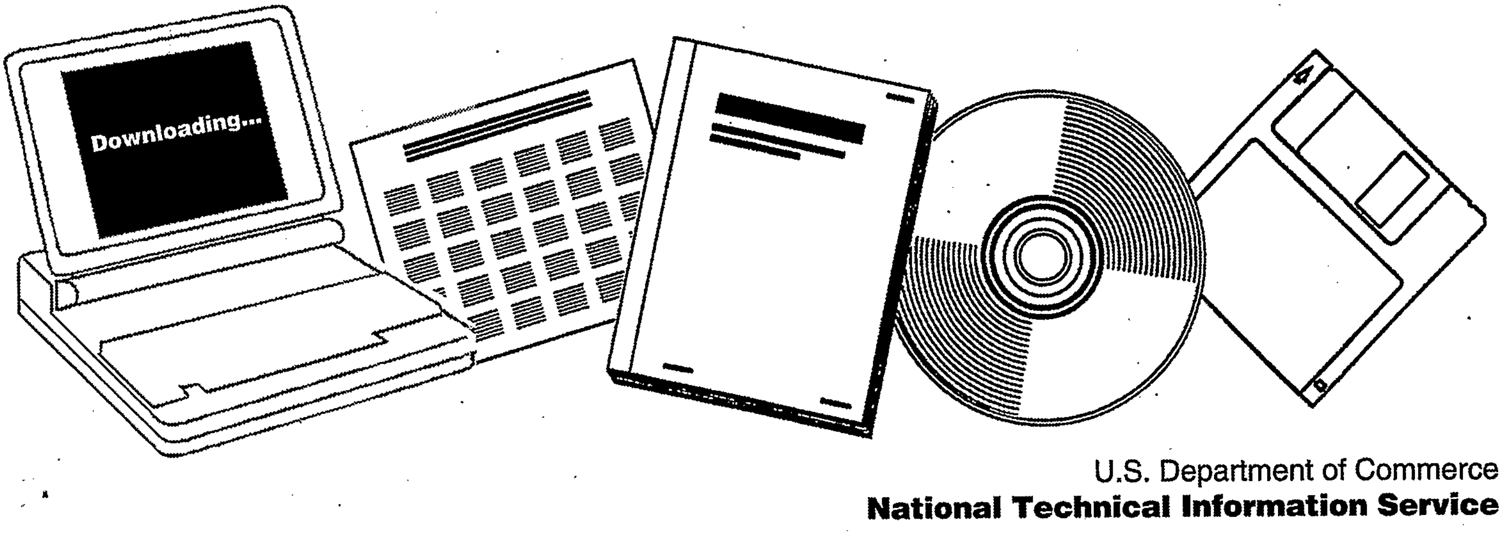

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QUARTERLY TECHNICAL PROGRESS REPORT No. 1

Covering the Period September 26 to December 31, 1990

SYNTHESIS OF OCTANE ENHANCERS DURING SLURRY-PHASE FISCHER TROPSCH

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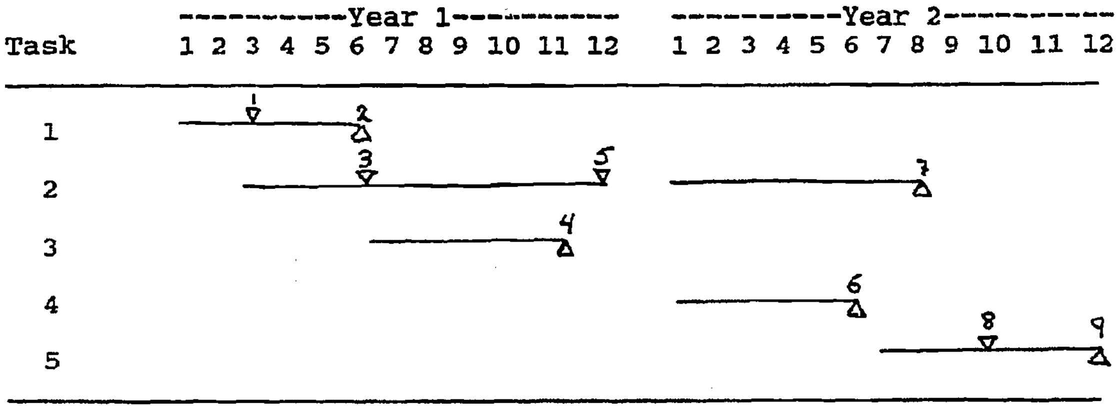
PLANNED TASK AND MILESTONE SCHEDULE



M = denotes milestone

<u>List of Milestones</u>

Milestone Number	Description
M1	Finalize design of slurry bubble column reactor (SBCR).
M2	Finalize construction and successful testing of SBCR. Topical report prepared.
M3	Completion of catalyst screenings for study on isobutylene addition during formation of alcohols. Decision made on catalysts to be studied in SBCR.
M4	Completion of slurry reaction of isobutylene addition during formation of alcohols.
M5	Completion of catalyst screenings for study on isobutylene addition to FT liquid products using acid catalysts. Decision made on catalysts to be studied in SBCR.
M6	Completion of slurry reaction of isobutylene addition to FT liquid products using acid catalysts.
M7	Completion of catalyst screenings.
M8	Completion of slurry-phase study of alcohol addition during iso-olefin synthesis.
M9	Final report issued.

OBJECTIVES

The objective of this project is to investigate three possible routes to the formation of ethers, in particular methyl tert-butyl ether (MTBE), during slurry phase Fischer-Tropsch (FT) reaction. The three routes to be investigated are:

- Addition of isobutylene during the formation of methanol and/or higher alcohols directly from CO and H_2 during slurry-phase Fischer-Tropsch.
- Addition of isobutylene to FT liquid products including alcohols in a slurry-phase reactor containing an MTBE or other acid catalyst.
- Addition of methanol to slurry phase FT synthesis making iso-olefins.

WORK ACCOMPLISHED THIS QUARTER

Work conducted during the first quarter has concentrated in the design of a laboratory-scale bubble column slurry reactor (BCSR) capable of operating at suitable temperatures and pressures for each of the three routes defined above. For design purposes the reactor has been configured as a one-inch diameter bubble column reactor for conversion of synthesis gas and operating with a wax paraffin (C_{30}+) liquid medium. This design has been finalized, thereby reaching milestone M1.

FIRST QUARTER'S TECHNICAL WORK

BACKGROUND -- IMPORTANT DESIGN PARAMETERS

HYDRODYNAMICS

A primary consideration in BCSR design is the hydrodynamics at actual operating conditions. Hydrodynamics represent a complex interaction of the component physical properties, column configuration and column operating conditions (feed rates, temperature and pressure). The column hydrodynamics and resulting mass transfer influence the reaction rate and overall conversion to product.

Many studies have been reported relating to bubble column hydrodynamics and the important design parameters (Shah et al., 1982). However, most of these studies concern hydrodynamic systems under cold flow conditions and correlations derived from these studies may not be relevant to the actual behavior at operating conditions. Differences in liquid properties, although appearing quite similar in viscosity and density, result in substantially different hydrodynamic properties (Buker et al., 1987a, Kuo et al., 1983). The primary difference lies in impurities in the liquid which can substantially change the hydrodynamic behavior specifically at the gas-liquid interface. The additional effects on viscosity of temperature and the presence of solids lead to further changes in the hydrodynamic behavior.

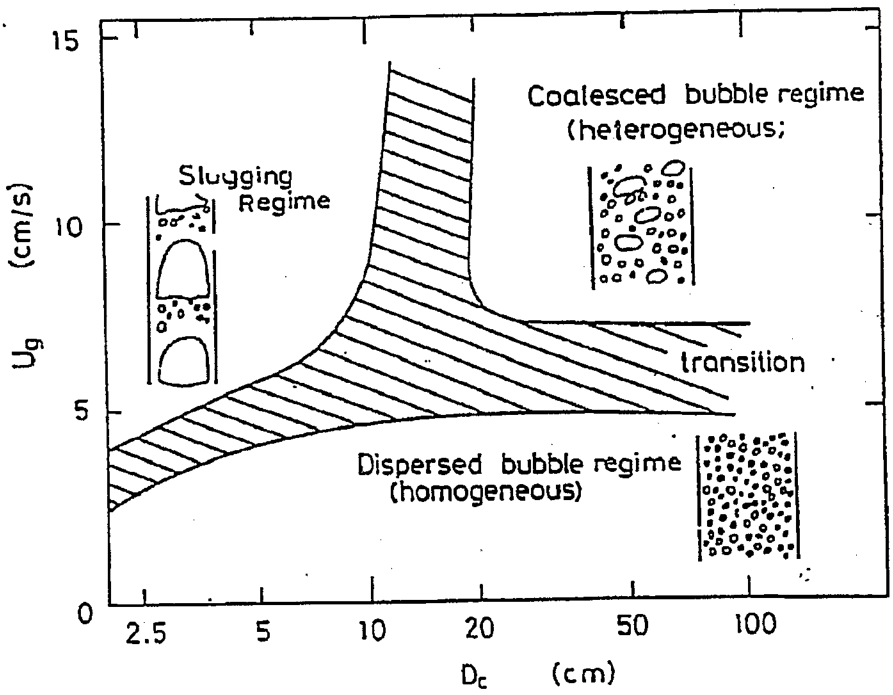
Flow Regime

The flow regime is the most important qualitative parameter and is determined by the superficial gas velocity and column diameter. Figure 1 presents a typical flow regime map as a function of column diameter. Small and large diameter columns exhibit substantially the same bubble size distribution in the homogeneous regime.

As gas velocity increases, the smaller bubble size remains the same, but the larger bubble size continues to increase for small diameter columns and the flow regime changes to slug flow as the wall effect of smaller diameter columns becomes important. The

Figure 1.

Flow Regime Map for Slurry Bubble Columns.
(From Deckwer et al. 1980)



larger diameter columns exhibit an increase in large bubble size as the regime changes to the heterogeneous regime. Wall effects are negligible.

Sauter Mean Bubble Diameter and Bubble Size Distribution

The Sauter bubble diameter is a volume-surface mean defined as:

$$d_s=[\Sigma(n_i d_{bi}^3)/[\Sigma(n_i d_{bi}^2)]$$

where: d_s is the mean Sauter bubble diamter,
d_{bi} is the equivalent bubble diameter and
n_i is the number of bubbles of a particular diameter.

Two types of bubble measurement are typically used resulting in either a bubble chord length or direct bubble size measurement. Bubble sizes follow a log-normal distribution (Fan, 1989). Significant radial distributions are also present. It should also be noted that systems exhibiting the same mean bubble diameter can have significantly different bubble size distributions.

Bubble size is dependent upon flow regime. In a homogeneous regime, the bubble size is small and increases slightly with the superficial gas velocity. In a heterogeneous regime, bubble size is large and increases only slightly with gas velocity. A maximum in bubble size is reached due to breakup from turbulent eddies formed in the liquid-solid suspension.

Liquid properties can have a significant effect on bubble size and bubble size distribution. Bubble coalescence and breakup affects the axial and radial distribution. Bubbles formed at the distributor begin to distribute in size through coalescence and breakup. As bubbles rise, coalescence or breakup occurs through interactions with other bubbles or particles and turbulent shear.

Gas Holdup

The gas holdup, e_g, is an important design parameter and can be correlated proportionally to the superficial gas velocity as U_g^n where n is dependent upon the flow regime. An example for an FT wax has been given by Deckwer et al. (1980) as:

$$e_g = 0.053(U_g)^{1.1}$$

where: e_g is the gas holdup,
U_g is the superficial gas velocity and
$U_g \leq 0.4$ cm/s.

It has been found that the gas holdup is also dependent upon the properties of the fluid such as density and viscosity (Bukur et al., 1987).

Gas holdup generally increases with increasing superficial gas velocity. The relationship can also depend upon the flow regime and distributor design. In coalesced systems (described later), gas holdup has been found to be proportional to superficial gas velocity with a single nozzle orifice distributor. At low superficial liquid velocities gas holdup is independent of the liquid velocity (Patel et al., 1990). Only a few correlations exist for small diameter columns (<0.1m). Most correlations exist where gas holdup is independent of column diameter and height. A column diameter greater than 0.15 m has been found to be sufficient to determine gas holdup for larger columns (Shah et al., 1982).

Superficial Velocity and Column Diameter

The superficial velocity U_g is based upon the column diameter and is determined by the operating conditions of feed flow rate, temperature and pressure. Thus once the column diameter and temperature and pressure conditions are set for the column operation, feed flow rate becomes the primary determination of the column hydrodynamics. The relation of superficial velocity with hydrodynamics can be qualitatively related to the flow regime which is related to the bubble size distribution, mean bubble size, and gas holdup. In addition, the liquid properties play an important part in the hydrodynamic behavior.

Interfacial Area

The gas-liquid interfacial area which is important for determining the overall mass transfer is determined from:

$$a = 6e_g/d_s$$

where: a is the interfacial area,

e_g is the average gas holdup, and
d_s is the mean bubble diameter.

Thus the interfacial area for gas-liquid mass transfer is dependent upon the mean bubble diameter and gas holdup. Any parameter which increases the hold-up or decreases the mean bubble diameter increases the interfacial area.

Liquid Properties

The hydrodynamic properties of various reactant hydrocarbons, although similar in physical properties, can lead to differences in gas hold-up, bubble size distribution, and mean bubble diameter. Liquid properties affect both bubble coalescence and bubble formation. Adding surfactants or oxygenates may lead to greater gas holdup (Shah et al, 1982, Bukur et al., 1987a).

The coalescing tendencies of the bubbles can be attributed to a "pseudo" viscosity at the gas-liquid interface. This interfacial viscosity determines the hydrodynamic behavior of the column at operating conditions. Liquid impurities present at the gas-liquid interface can result in different coalescing tendencies. Liquids which contain these surface active impurities supress coalescing and do not promote the formation of larger bubbles. Thus the gas holdup increases (Bukur et al., 1987a).

A non-coalescing tendency can also lead to foaming. Gas holdup increases substantially in the presence of foaming. Some F-T waxes exhibit a hysteresis effect. If the superficial gas velocity is increased from an initially low value, foaming occurs. However, if an initial high superficial velocity is used, foaming does not occur. This hysteresis is attributed to the distribution of the surface active impurities. When low superficial gas velocities are used, the impurities rise to the top of the column and promote foaming. Starting at high superficial velocity mixes the impurities throughout the liquid column and suppresses foaming (Bukur et al, 1987a).

Since temperature affects viscosity a decrease in temperature promotes coalescing leading to increased bubble size and lower gas holdup. Foaming may also be suppressed by decreasing the temperature.

Gas Properties

The density, viscosity and solubility of the gases are also involved in the hydrodynamic interactions. The density and viscosity of the gas are related to the terminal bubble rise velocity (Clift et al, 1978, see Fan, 1989).

The mean rise velocity is the interstitial gas velocity defined by:

$$U_g^* = U_g/e_g$$

where: U_g^* is the interstitial gas velocity,
U_g is the superficial gas velocity and
e_g is the average gas holdup.

Thus gas holdup is also dependent upon the bubble rise velocity. In the homogeneous and heterogeneous regimes, the bubble rise velocity distribution is narrow. For slugging, the bubble rise velocity is a broad multi-modal distribution (Fan, 1989).

Gas solubility is important in determining the concentration of the reactant species in the liquid phase. Differences in gas solubilities can lead to substantially different liquid and gas phase concentrations (discussed later). For most gases the solubility increases with increasing temperature and pressure and can often be represented by a Henry's law relation.

Solids Properties and Loading

The important solids or catalyst hydrodynamic properties are particle density and diameter. These properties along with the liquid density, liquid viscosity, solids loading and gas flow rate are important in determining the critical superficial gas velocity for solids suspension in the column.

Critical gas velocity increases with increasing particle terminal velocity and solids loading. Several correlations exist for critical solids suspension and are dependent upon the superficial gas velocity, solids loading, gas-liquid densities, particle diameter and column diameter (Fan, 1989). For particles smaller than a given diameter under particular conditions, the terminal velocity is fairly constant with respect to gas velocity. Critical gas velocity has been found to be independent of column height. The critical gas velocity ratio to the particle terminal velocity generally ranges from 2 to 4 (Koide et al., 1983, see Fan 1989).

Confusion still exists as to whether critical gas velocity increases or decreases with increasing column diameter or more specifically the ratio of the particle diameter to column diameter. Increasing solids concentration increases the "pseudo" viscosity which promotes bubble coalescence resulting in larger bubbles and a decrease in gas holdup. In the heterogeneous regime gas holdup changes only slightly with increasing solids concentration (Deckwer et al., 1980).

Distributor Sizing

Distributor sizing and behavior in bubble column slurry reactors has led to many different conclusions especially for gas holdup. The differences in behavior may be attributed to the liquid properties, flow regime operation and differences in determining the proper sizing of holes and number of holes in the distributor. The proper design is based upon good distribution through all the holes and prevention of weeping of the continuous phase (Mersmann, 1978). The use of sintered metal plates has been found to increase the foaming tendency for non-coalescing liquids (Bukur et al, 1987a). Single or multi-hole distributors are used in the majority of designs.

Temperature

Many of the hydrodynamic parameters of the BCSR are affected by the operating temperature. An increase in temperature tends to decrease the gas holdup as the bubble rise velocity increases given that all other conditions remain constant. However, an increase in temperature also decreases the liquid viscosity which tends to decrease the coalescing tendency of the liquid leading to smaller bubbles and increased gas holdup. An increase in temperature can also lead to foaming as the coalescing tendency of the liquid decreases (Bukur, 1987a).

Pressure and Pressure Drop

An increase in operating pressure above 5 MPa has been found to decrease the bubble size (Idogawa et al., see Fan, 1989), while pressures up to 1.6 MPa have no effect on the bubble size and gas holdup (Kolbel et al., 1961, see Shah et al., 1982).

Dynamic pressure drop can be calculated from:

$$-dP/dz=\epsilon_s(\rho_s-\rho_l)g-\epsilon_g(\rho_l-\rho_g)g$$

where:
dP/dz is the pressure drop per unit length,
ϵ_g is the gas holdup,
ρ_g is the gas density,
ρ_l is the liquid density,
g is the gravitational constant, and
ϵ_s is the solids holdup expressed as:

$$\epsilon_s = W_s/(\rho_s AH)$$

where:
W_s is the total mass of solids,
ρ_s is the density of the solids,
A is the cross sectional area of the column, and
H is the effective bed height.

MASS TRANSFER

Both the mass tranfer limitation and the kinetic resistance have been determined to be important in determining the overall reaction rate. This difference has been attributed to the differences in hydrodynamic behavior and modeling (Bukur, 1983).

The overall mass transfer resistances are depicted in Figure 2. The overall resistances (including kinetic) can lead to substantially different concentrations in the liquid, gas and at the catalyst surface.

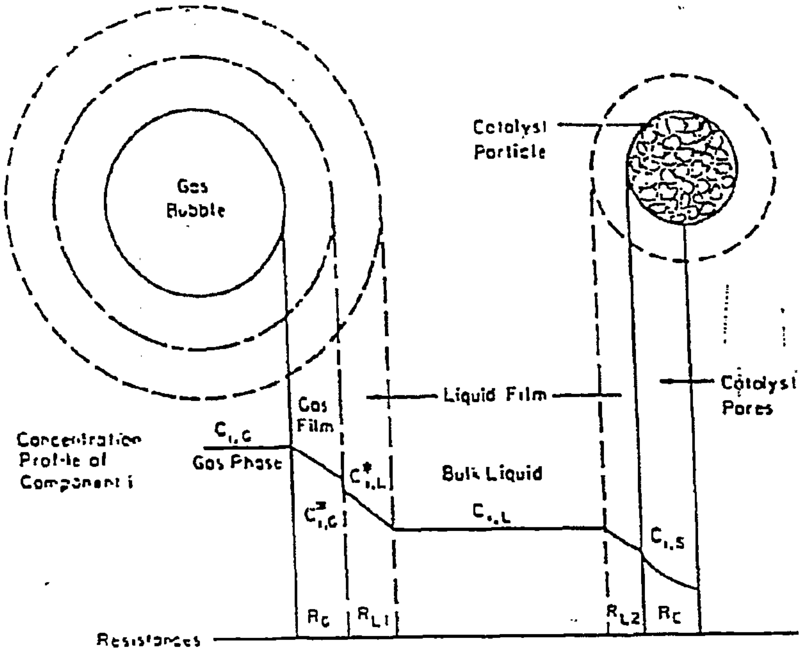
The overall importance of either the mass transfer resistance or the kinetic resistance can be defined by a relative resistance:

$$B = R_m/(R_m + R_k)$$

where:
B is the relative mass transfer resistance,
R_m is the mass transfer resistance and
R_k is the kinetic mass transfer resistance.

Figure 2.

Concentration Profile and Resistances in a Slurry Bubble Column.
(From Saxena et al., 1986)



Liquid Side

The liquid side mass transfer is usually the most important for gases of low solubility and slow chemical reaction. Many correlations exist for $k_l a$ of the form:

$$k_l a = b \cdot U_g^{\,n} \qquad \text{(Shah et al., 1982)}$$

where: $k_l a$ is the volumetric mass transfer coefficient,
b is a correlation constant and
$U_g^{\,n}$ is the superficial gas velocity.

All other hydrodynamic parameters which determine the interfacial area are important in determining the overall mass transfer coefficient specifically the mean bubble diameter and gas holdup.

Gas Side

Gas side mass transfer becomes important for highly soluble gases and fast chemical reaction. No correlations are known to exist for $k_g a$ (Shah et al., 1982). However, in FT reactions liquid side mass transfer is limiting for the relatively low soluble feed gases (Saxena et al., 1986).

Bulk Liquid

The diffusion of reactant to and product away from the catalyst surface is dominated by convection due to the high liquid and solid turbulence experienced in a dynamic bubble column. Consequently the resistance to diffusion is low in most situations, and the bulk liquid concentration is essentially constant except when considering liquid and solid axial dispersions (Saxena et al., 1986).

Catalyst Surface

Mass transfer resistance at the liquid film surrounding the catalyst is generally insignificant compared to the liquid film mass transfer resistance at the gas-liquid interface in view of the fact that the effective catalyst surface area is much larger than the gas bubble surface area (Saxena et al., 1986). The liquid-solid effectiveness factor ranged from 0.9 to 1.0 for a Fischer-Tropsch synthesis reaction using 50 to 200 micron particles (Deckwer, 1982).

Kinetic and Intraparticle

The kinetic resistance in relation to the mass transfer resistances is important in determining the overall reaction rate. The reaction rate is dependent upon the temperature, the activity of the catalyst, the specific surface area, the effectiveness factor and the reactant surface concentrations. The effectiveness factor is dependent upon the reactant diffusivity and particle porosity, tortuosity, diameter and density. Intraparticle mass transfer limitations are usually small because of the small size of catalyst particles typically used in bubble slurry columns (Saxena et al., 1986).

Temperature

An increase in temperature typically increases the mass transfer. The gas solubilities increase as well as the liquid diffusivity. Likewise, the reaction rate is dependent upon temperature and with increasing temperature a kinetically limited system may become mass transfer limited as the reaction rate increases with temperature.

Pressure

An increase in pressure can increase the solubility of the gas leading to increased reactant liquid phase concentrations.

KINETICS

The reaction kinetics are closely related to the hydrodynamics of the bubble column slurry reactor. Hydrodynamics determine to what extent the overall reaction rate is affected by the rate of mass transfer. The primary effect of the hydrodynamics other than the interfacial area for mass transfer is the gas, liquid, and solid dispersions which occur along the axial length of the column.

In determination of the overall importance between mass and kinetic resistance, modeling of the reaction and hydrodynamics has led to different conclusions as to the relative importance of each in the determination of the relative mass transfer resistances and the reactor sizing with respect to predicted conversions.

Kinetic models can be based on either a power law or a Langmuir-Hinshelwood model. Reaction parameters which affect the hydrodynamic reaction characteristics such as volume contraction or expansion and usage ratio of the feeds must be taken into account in modeling. Likewise, interfacial area and the axial dispersions determined by the hydrodynamics affect the reaction rate and conversion which in turn affects volume contraction or expansion. With consideration of the relative importances of mass transfer resistances the loop is closed for modeling.

Volume Contraction/Expansion

In modeling, accounting for the volume changes with increasing conversion is important for reactions involving a change in the number of moles. If volume contraction is not accounted for, significantly longer reactor heights are determined for FT synthesis reaction which involve a significant decrease in the number of moles at high conversion (Bukur, 1983).

Solids Dispersion

Both catalyst distribution and volume contraction during reaction must be taken into account. The effects of catalyst dispersion for varying volume systems show different characteristics depending upon the kinetics associated with the system. The type of reaction model determines this dependency (Bukur and Kumar, 1986).

The solids axial dispersion coefficient E_c can be correlated from (Kato et al., 1972, see Deckwer, 1982):

$$E_c = U_{mg} d_r (1+8Fr^{0.85})/13Fr,$$

where: E_c is the solids axial dispersion coefficient,

U_{mg} is the mean superficial velocity U_g/U_{go},

U_g is the superficial gas velocity,

U_{go} is the inlet superficial gas velocity,
d_r is the diameter of the column,
Fr is the Froude number and
$Fr = U_{mg}/(gd_r)^{0.5}$
where: g is the gravity constant.

It is evident from this correlation that an increase in the diameter of the reactor increases the axial dispersion coefficient.

For a power law model, the rate for a first order reaction is written as:

$$r(C_{L,1}) = kC_{L,1}^{n} \quad \text{(nth order)}$$

In nth order kinetics, the reaction rate decreases as the concentration decreases since the rate of disappearance is a product of catalyst concentration and the rate of reaction. When the catalyst is axially dispersed, the reaction rate and catalyst concentration decrease along column height.

The conversion is always lower than with uniform catalyst distribution. A reaction that is accompanied by an increase in moles (volume expansion) will give lower values of conversion than a reaction that proceeeds without any change in the number of moles due to shorter residence times of the gas (Bukur and Kumar, 1986).

For a Langmuir-Hinshelwood (L-H) reaction model the reaction rate can be expressed as:

$$r(C_{L,1}) = kC_{L,1}/(1 + KC_{L,1})^2$$

In this case, the reaction rate passes through a maximum as the reactant concentration decreases while catalyst concentration decreases with height (non-uniform distribution) or remains constant (uniform distribution).

Thus for a L-H model, it is possible to have an increase in reactor performance over that obtained with uniform catalyst distribution. For L-H kinetics, volume contraction can yield lower conversions than reaction accompanied by volume expansion. When high conversions are obtained at the exit (reactant concentration is small) the reaction will be decreasing over the length of the reactor, and the behavior will approach that of nth-order kinetics. Volume expansion then leads to an increase in the conversion. (Bukur and Kumar, 1986).

Liquid Dispersion

A small diameter column, under identical operating conditions as a large diameter column, yields a lower axial dispersion. This is due to lower axial backmixing of the liquid phase in the smaller column.

Hydrodynamic parameters have a strong effect on estimation of kinetic parameters by determining to what extent the overall reaction rate is affected by the rate of mass tranfer from the gas to the liquid. Two different models for liquid mixing are based on plug flow and perfect mixing of the gas (Bukur, 1983).

In the plug flow model, the liquid is not well agitated by rising bubbles, so that the reactant concentration in the gas as well as liquid phase varies along column height.

In the perfect mixing model, the liquid phase is completely mixed with the rising bubbles. The reaction concentration is uniform throughout the entire liquid but changes in the gas phase along the column height.

If the plug flow model is applicable, the reactor height calculated for a specific conversion is significantly less than the perfect mixing model especially at higher conversions.

The axial dispersion coefficient D_L can be correlated from:

$$D_L = 3.676U_{mg}^{0.32}d_r^{1.34}$$

(Deckwer et. al, 1980):

where: D_L is the axial dispersion coefficient,
U_{mg} is the mean superficial velocity U_g/U_{go},
U_g is the superficial gas velocity,
U_{go} is the inlet superficial gas velocity and
d_r is the diameter of the column.

and

$$N_L=D_Le_L/U_{go}L \quad \text{(Bukur, 1983)}$$

where: N_L is the axial mixing parameter,
D_L is the axial dispersion coefficient,
e_L is the liquid holdup and
L is the reaction column height.

For small values of D_L and large values of L, the axial mixing parameter will be small (D_L proportional to $d_r^{1.34}$). As the diameter increases, the axial dispersion also becomes important.

For small N_L, the problem reduces to a non-mixing or plug flow model. The aspect ratio L/D becomes important in determining whether the axial mixing is important. For small diameter columns with large aspect ratios (40 to 110), the simple plug flow model can be used. For large diameter columns with small aspect ratios, the axial liquid dispersion is important (Bukur, 1983).

Gas Dispersion

Gas phase dispersion is related to the change in bubble distribution along the axial length of the column. Gas dispersion has been correlated with the column diameter, superficial gas velocity and gas holdup (Shah et al., 1982). In modeling, the gas phase dispersion has not been used, and constant bubble size and gas holdup are usually assumed (Saxena et al., 1986).

Temperature

Temperature affects the reaction rate and equilibrium of the reaction via the reaction rate constant and the equilibrium constants. For the formation of ethers, the equilibrium constant decreases with increasing temperature.

Pressure

An increase in pressure favors those reactions which exhibit a decrease in the number of moles upon reaction. An increase in both FT synthesis and ether production is obtained at higher pressure.

HEAT TRANSFER

The primary benefit of bubble slurry column reactors is the excellent heat transfer available in the liquid slurry. The heat transfer is dependent upon the slurry heat transfer properties. Consequently, the reactor is easily held at an isothermal temperature except under conditions of low liquid backmixing and high conversion.

Heat Transfer Coefficient

The heat transfer can be correlated according to:

$$St = B(Re\ Fr\ Pr^2)^{-1/4}$$

where:
St is the dimensionless Stanton number,
Re is the Reynolds number,
Fr is the Froude number,
Pr is the Prandtl number and
B is a constant.

Deckwer et al. (1982) reported a heat transfer correlation for FT slurry:

$$St = 0.1\ Pr^{-0.5}(U_m^3 \rho_s/\mu_s g)^{-0.25}$$

where:
$St = h/\rho_s C_{p(s)} U_m$;
$Pr = C_{p(s)} \mu_s / k_s$;
h is the heat transfer coefficient at the wall;
μ_s is the viscosity of the slurry;
ρ_s is the density of the slurry;
$C_{p(S)}$ is the heat capacity of the slurry;
U_m is the mean superficial velocity, U_g/U_o;
U_g is the superficial gas velocity;
U_o is the inlet gas velocity;
k_S is the thermal conductivity of the slurry; and
g is the gravitational constant.

The heat transfer coefficient is independent of column height and diameter.

Heat Capacity

The heat capacity of the slurry can be calculated from:

$$\bar{C}_{p(S)} = w_s C_{ps} + w_1 C_{p1}$$

where:
w_s is the weight fraction of solids,
C_{ps} is the heat capacity of the solids,
w_1 is the weight fraction of the liquid and
C_{p1} is the heat capacity of the liquid.

Slurry Density

Slurry density can be calculated from:

$$\rho_s = w_s\rho_s + w_l\rho_l$$

where: ρ_s is the density of the slurry

ρ_l is the density of the liquid,

ρ_s is the density of the solid,

w_s is the weight fraction of solids and

w_l is the weight fraction of the liquid

An increase in solids concentration increases the slurry density, viscosity and thermal conductivity increasing the heat transfer in the system.

INTERACTION OF SYSTEM PARAMETERS

A number of interrelations must be considered in bubble column slurry reactor design. These interrelations can be divided into two primary areas: the hydrodynamics and the kinetics. Hydrodynamics is primarily dependent upon the liquid properties, the gas properties, the catalyst hydrodynamic properties and the column configuration. The demarcation for the hydrodynamics lies in the flow regime which qualitatvely separates the overall behavior of the column. The kinetics is dependent upon the particular reaction, the catalyst properties and the various mass transfer properties. Tying the hydrodynamic properties and the kinetic properties together are the liquid and solids dispersions which are based on the column hydrodynamic characteristics, the hydrodynamic mass transfer characteristics and the conversion to product. Finally relating the hydrodynamics and the kinetics is the temperature and heat transfer.

It is also evident that all of the interactions must be carefully considered in modeling and designing the bubble column slurry reactor. Proper modeling and correlation is required if a viable method of scale-up is to be developed for laboratory small diameter columns to industrial large diameter columns.

RELATIONSHIP OF LAB SCALE TO INDUSTRIAL SCALE BCSR

FLOW REGIME

The primary difference between small diameter laboratory scale reactors and large diameter industrial scale reactors is the operating flow regime. Large diameter reactors are normally operated in the heterogeneous bubble regime while small diameter columns are operated in the homogeneous bubble regime. At low velocities both small and large diameter columns operate in the homogeneous regime, and many hydrodynamic correlations can be used to determine gas hold-up, bubble distribution, and gas-liquid interfacial area.

At higher velocities, the small diameter column enters the slug flow regime and the larger diameter column enters the heterogeneous regime. Correlations from the homogeneous regime are no longer valid. However, the hydrodynamic behavior in the homogeneous regime is useful in determining the overall behavior such as the liquid properties, reaction kinetics, and the mass transfer limitations.

BUBBLE DIAMETER TO COLUMN DIAMETER

At a column diameter to mean bubble diameter ratio greater than 100, wall effects can usually be neglected. (Quicker and Deckwer, 1981, see Deckwer and Serpemen, 1982). Wall effects become important at higher velocities in small diameter columns where the wall introduces slugging as the bubbles increase in diameter and meet the wall. At higher velocities in large diameter columns, larger bubbles are only formed by coalescence unassisted by the wall, and a heterogeneous regime is obtained.

COLUMN DIAMETER TO PARTICLE DIAMETER

A column diameter to particle diameter ratio of 100 is usually sufficient to neglect particle to wall interactions (Fan ,1989). Most BCSRs are operated with catalyst diameters less than 50 microns. Thus, for all but very small diameter columns (< 1 cm), particle wall interactions can be neglected.

COLUMN HEIGHT TO COLUMN DIAMETER

The column height to diameter ratio (L/D) is important in determining both the solid and liquid axial dipersions. For large aspect ratio columns (L/D > 40), a plug flow or nonmixing model can be assumed, and the axial liquid dispersion is not important. For industrial large diameter columns where there is a low aspect ratio, the axial liquid dispersion becomes important (Bukur, 1983).

Both large and small diameter columns are likely to be operated with dispersed catalyst; however, under identical operating conditions, large diameter columns yield greater axial catalyst dispersion than smaller diameter columns due to higher backmixing in the larger diameter columns (Bukur and Kumar, 1986).

PARAMETER ESTIMATIONS

The main difficulties and uncertainties of designing slurry-phase reactors are concerned with the estimation of parameters involved in the design equations, i.e. physicochemical properties, kinetic data, and hydrodynamic parameters (Deckwer et al. 1982).

Although extensive reports on slurry bubble column hydrodynamics can be found in the literature, the majority of these studies relate to air-water mixtures or to pure liquids. Even systems having similar physical properties can have vastly different holdups and/or bubble size distribution (Quicker and Deckwer 1981). The gas holdup time and gas interfacial area are often very sensitive to the liquid media and the number of correlations proposed indicates that no single unified expression is available. Thus, the correlations obtained using systems different from FT synthesis cannot be used for design and scaleup of SBCR for use in FT applications.

Some studies on bubble column hydrodynamics relevant to this project do exist. Most notably, Bukur et al. (1986, 1987, 1990) have studied the hydrodynamics of slurry column reactors using actual FT synthesis operating conditions and actual FT-type wax medium.

The reactor design described in this report has been arrived at by using a number of correlations described in the literature which were obtained using conditions very close to the actual environment in which we will be operating. These correlations are tabulated in Tables 1 and 2.

DESIGN OF THE BENCH-SCALE BSCR

MATHEMATICAL MODELS

A number of mathematical models for FT synthesis in slurry reactors have been developed by various research groups. A comparison between seven of these models is presented in Table 3. The differences between the various models arise primarily from the pattern assumed to describe the mixing in the different phases.

The bench-scale BCSR will have a nominal column diameter of one inch (2.54 cm) and a height not to exceed 1.2 m. This diameter is imposed primarily due to the cost of gases required to maintain proper bubble column conditions. It will also be operating at about six times the critical gas velocity. Under these conditions it can be assumed that there will be uniform catalyst dispersion throughout the reactor. Hence the mathematical model of Deckwer et al. (1981) can be used to predict conversions.

The basic assumption in the Deckwer model is that the liquid is not well agitated by rising bubbles so that the hydrogen concentration in the gas as well as in the liquid varies along the height of the bubble column reactor. Other important assumptions are:

1. Temperature and pressure are constant throughout the reactor.
2. The kinetics of FT synthesis is first order with respect to hydrogen concentration and zeroth order with respect to CO concentration.

TABLE 1. CORRELATIONS FOR ESTIMATION OF PARAMETERS FOR SLURRY REACTOR DESIGN.

Parameter (reference)	Medium	Correlation
VISCOSITY (Deckwer 1980)	molten wax	$\mu_L=0.052\exp(-6.905+3266/T)$
	catalyst suspended in wax	$\mu = \mu_L(1. + 4.5\ v_{cat})$ where v_{cat} is the volume fraction of catalyst in suspension, i.e., $\rho_l W_{cat}/(\rho_{cat}-W_{cat}(\rho_{cat}-\rho_L))$ and W_{cat}=conc. of catalyst in suspension
DENSITY (Deckwer 1980)	molten wax	$\rho_L = 0.758-0.555 \times 10^{-3}(T-373)$
	catalyst suspension	$\rho_s = V_{cat}\rho_{cat} + (1-V_{cat})\rho_L$
DIFFUSIVITY OF H_2 IN WAX (Satterfield and Huff 1980)		$D_{L,H} = 7.35 \times 10^{-3}\exp(-2285/T)$
HENRY'S CONSTANT (Peter and Weinert 1955)		$H_C = 2.291 \times 10^7\exp(-1.2326+(583/T))$
HEAT CAPACITY (Peter and Weinert 1955)	wax-catalyst mixt.	$C_p = w_{cat}\ C_{p,cat} + (1-w_{cat})C_{p,L}$
GAS HOLDUP (Deckwer 1980)	Sasol wax	$\epsilon = 0.053\ u_G^{1.1}$, for $u_G \leq 4$ cm/sec and T> 250°C
(Bukur 1987)	Mobil reactor wax	$\epsilon = 94\ u_G^{0.41}$, for $0.1 < u < 0.7$ m/s

TABLE 1. CORRELATIONS FOR ESTIMATION OF PARAMETERS FOR SLURRY REACTOR DESIGN. (Cont.)

Parameter (reference)	Medium	Correlation
MEAN VELOCITY (Deckwer 1981)		$U_G=U_{G,i}(1 + 0.5\ \alpha\ X_{CO+H_2})$
DISPERSION COEFFICIENT (Kato 1972)		$D_C = -u\ d_R(1 + 8\ Fr^{0.85})/13Fr$, where $Fr = u_G/(gd_R)^{1/2}$, d_R is the reactor diameter
GAS-LIQUID MASS TRANSFER COEFFICIENT (Satterfield and Huff 1980)		$K_{L,H}=0.1165((\rho/\mu)\exp(-4570/T)^{1/2}$

TABLE 2

Correlations fot Gas-Liquid Interfacial Area for Various Waxes (Bukur et al. 1987)

	Temperature (°C)	
Medium	200	265
Mobil wax	$165\ U_g^{0.010}$	$300\ U_g^{0.010}$
Sasol wax	$492\ U_g^{0.256}$	$1000\ U_g^{0.25}$
FT 300 wax	$997\ U_g^{0.021}$	$2411\ U_g^{0.071}$

TABLE 3

COMPARISON BETWEEN VARIOUS MATHEMATICAL MODELS FOR FISCHER-TROPSCH REACTOR DESIGN

	Type of flow		Catalyst dispersion considered or not.	Effect of conversion on gas holdup ,bubble size and superficial velocity considere d or not.	H_2/CO usage ratio	Catalyst loading considered.	Remarks
	Slurry	Gas					
Calderbank et al. (1963)	Plug	Plug	No	Gas holdup & bubble size considered constant.	Same as H_2/CO in feed	No	
Satterfield (1980)	Back mixed	"	No	"	"	Yes	
Deckwer et al. (1981,b)	plug	"	"	Included the effect of conversion on bubble size & superficial velocity.	Can differ from H_2/CO as in feed.	Yes	
Bukur (1983)	Back mixed	"	"	"	"	No	
Stern (1983)	"	"	"	Gas contraction considered.	—	Yes	Mass of both H_2/CO considered. Included the resistance offered to the transport of product from bulk liquid to gas phase.
Deckwer et al. (1982,b)	"	"	Catalyst axial dispersion considered	"	Can differ from as in feed.	Yes	First one to consider liquid solid mass transfer and to include heat transfer in calculations effect.
Kuo et al. (1983)	"	"	"	"	"	Yes	Developed single & multiple component model.

3. The overall reaction rate is controlled by the rate of mass transfer from the gas bubbles to the bulk liquid and by the chemical reactions that occur at the catalyst surface.
4. The liquid phase hydrogen concentration at the gas-liquid interface obeys Henry's law.
5. The usage ratio (consumption of CO/consumption of H_2) is constant.

For this model the final design equation is:

$$-St = (1 + \alpha') \ln (1 - x_H{}^e) + \alpha' X^e$$

where:

α' is the modified contraction factor

$$= \alpha (1 + U)/(1 + I);$$

α is the contraction factor, defined as:

$$\frac{V_{g(X=1)} - V_{g(x=0)}}{V_{g(X=0)}} \quad ;$$

V_g = volumetric gas flow rate;
U = usage ratio $\Delta N_{CO}/\Delta N_{H_2}$;
N = molar flow rate;
I = CO and H_2 concentration ratio in the inlet gas;
X = fractional conversion of synthesis gas;
St = Stanton number, defined as:

$$k_o\ RTL/U_g{}^i\ m_H{}'' \quad ; \quad \text{and}$$

L = reactor length;
U_g^i = gas velocity at the reactor inlet;
m_H'' = Henry's law constant for H_2;
k_o = overall rate constant, defined as:

$$1/k_o = (1/ak_{L,H}) + (1/k_c\ \epsilon_L).$$

In the above equation:

a = gas-liquid interfacial area;
$k_{L,H}$ = mass transfer coefficient;
k_c = rate constant for H_2 consumption;
ϵ_L = liquid holdup.

The first and second terms on the right side of the above relation represent the mass and kinetic resistances, respectively.

The kinetic data of Schlesinger et al. (1954), shown graphically in Figure 4, was used to determine the reaction rate constants.

SUMMARY OF DESIGN ASSUMPTIONS AND CALCULATIONS

Physical Parameters

Column i.d.	= 1" (2.54 cm)
Reactor length	= 4' (1.2 m)
Operating temperature	= 220°C
Operating pressure	= 15 atm
Catalyst size	= 44µm
H_2/CO ratio	= 0.7
Catalyst bulk density	= 3.25 g/ml
Catalyst loading	= 20 wt%

Assumed Parameters

Contraction ratio, α = -0.5 (Deckwer 1982)
Usage ratio, U = 1 (Deckwer 1981)

Physical Properties

Using the correlations detailed in Tables 1 and 2 the following physical properties were determined:

Density of liquid medium = 0.69 g/cm
Mass fraction of catalyst = 0.167
Volume fraction of catalyst = 0.0407
Density of slurry = 0.792
Viscosity of liquid medium = 0.039 g/cm-sec
Viscosity of slurry = 0.046 g/cm-sec
Mass transfer coefficient = 0.0137 cm/sec
Henry's law coeff. for H_2 = 2.15×10^5 atm ml/g-mole
Modified contraction factor = -0.413
Particle terminal velocity = 0.069 cm/sec

Critical Gas Velocity

It has been determined experimentally that critical gas velocities (i.e. the minimum velocity required to keep the particle in suspended form) is 2 to 4 times the terminal velocity (Fan 1989).

Critical gas velocity, U_c = 0.14 to 0.27 cm/sec

Reactor Inlet Gas Velocity

High superficial gas velocity results in better catalyst dispersion and more interfacial area and holdups. However it also results in a smaller residence time. An inlet velocity of 1.5 cm/sec is thus selected and is expected to result in optimum catalyst dispersion and residence times.

Gas Consumption

Maintenance of a 1.5 cm/sec superficial gas velocity at the inlet will require a gas flow rate at STP = 4.5 l/min, with corresponding flow rates for H_2 and CO of 1.85 and 2.65 l/min, repectively.

Hydrogen Conversion

Estimates of hydrogen conversion are naturally dependent on the catalyst considered and exact temperature and pressure used. For purpose of reactor design, the above operating conditions were used in terms of the model of Deckwer et al. (1981) and using the kinetic data of Schlesinger et al. (1954). These data refer to an Fe catalyst for producing hydrocarbons from syngas. The predicted hydrogen conversion for such a system is ca. 11%.

SCHEMATIC DIAGRAM OF LABORATORY SCALE BCSR

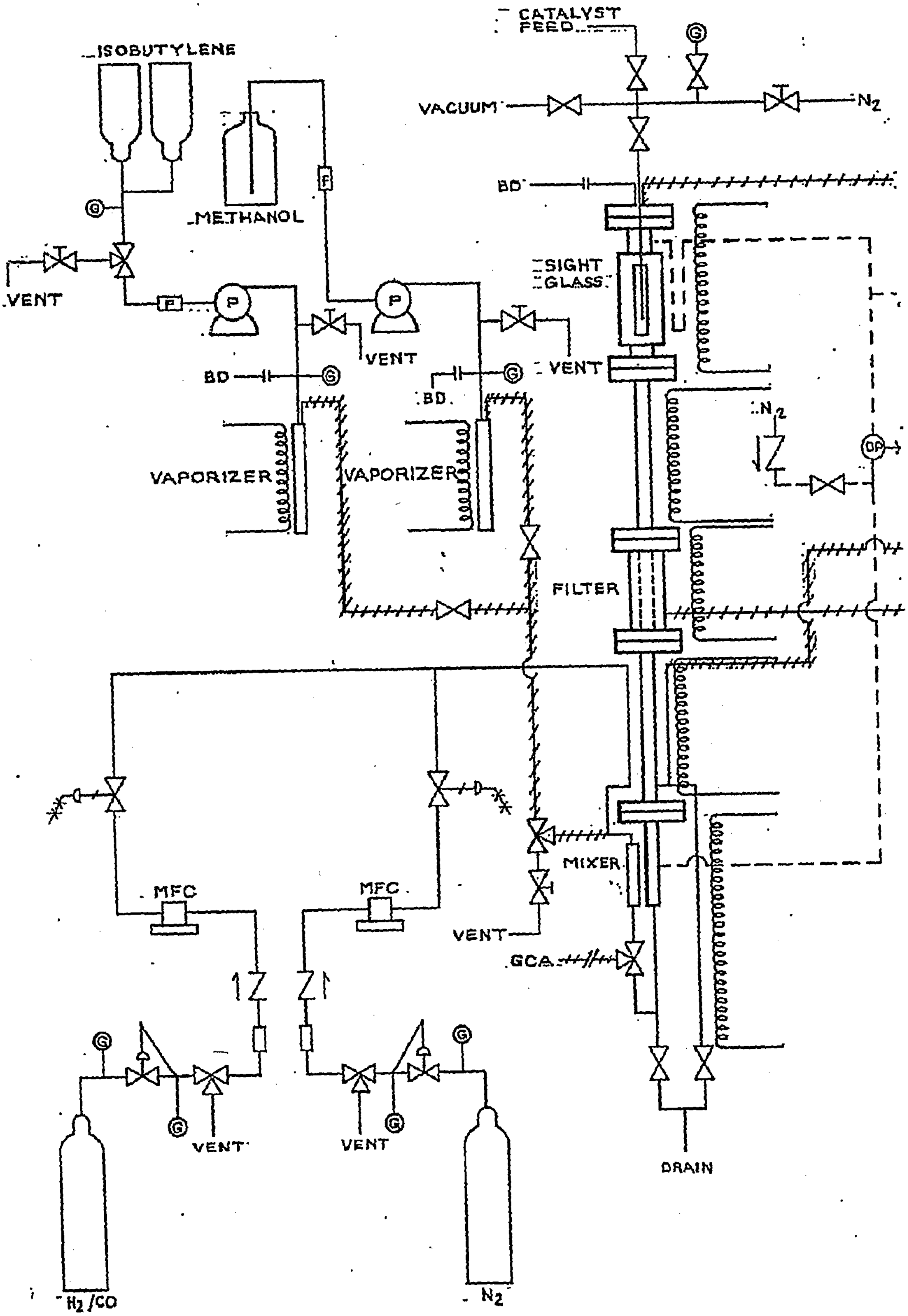
A schematic diagram of the laboratory BCSR system showing the reactor as well as all necessary ancillary equipment is shown in Figure 3. The reactor itself will be constructed of one-inch stainless-steel pipe in four flanged sections for easy assembly and modification. Syngas and inert gas feeds will be controlled via electronic mass flow controllers capable of operating to 1500 psig at a flow of 0 to 5 Std.L/min. Liquid feed pumps will be used for delivery of isobutylene and other liquid feeds when necessary. An additional section of the reactor, consisting of a 2-inch diameter sight glass will serve as a disengaging zone for the solids and will allow the direct observation of the liquid medium. In addition, provisions for the incorporation of a differential pressure cell for measurement of the liquid level inside the reactor are included in the design. A thermowell will be located in the internal periphery of the reactor for temperature measurement via a movable thermocouple.

A filter section will be located approximately half-way along the slurry reaction zone of the reactor. This filter consists of a double wall six-inch length of stainless steel tube with the inner wall consisting of a 2 µm porous stainless steel one-inch internal diameter pipe. The outer wall is piped through a liquid drain valve to a liquid collection vessel.

Gaseous product will be analyzed gas chromatographically in-line. Liquid product will be collected and analyzed ex-situ. Reactor by-pass lines are also available for direct analyses of the reaction mixtures.

An external fixed bed zone will also be available for catalyst pretreatment.

Temperature and mass flow control, as well as logging and reporting of temperature, pressure, and GC analysis will be carried out using proprietary interfaces and control/analysis software.


CATALYST FEED
G
VACUUM
N2
ISOBUTYLENE
METHANOL
F
G
VENT
F
P
P
VENT
VENT
BD
SIGHT GLASS
BD
G
BD
G
VENT
VAPORIZER
VAPORIZER
N2
DP
FILTER
MIXER
MFC
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VENT
GCA
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DRAIN
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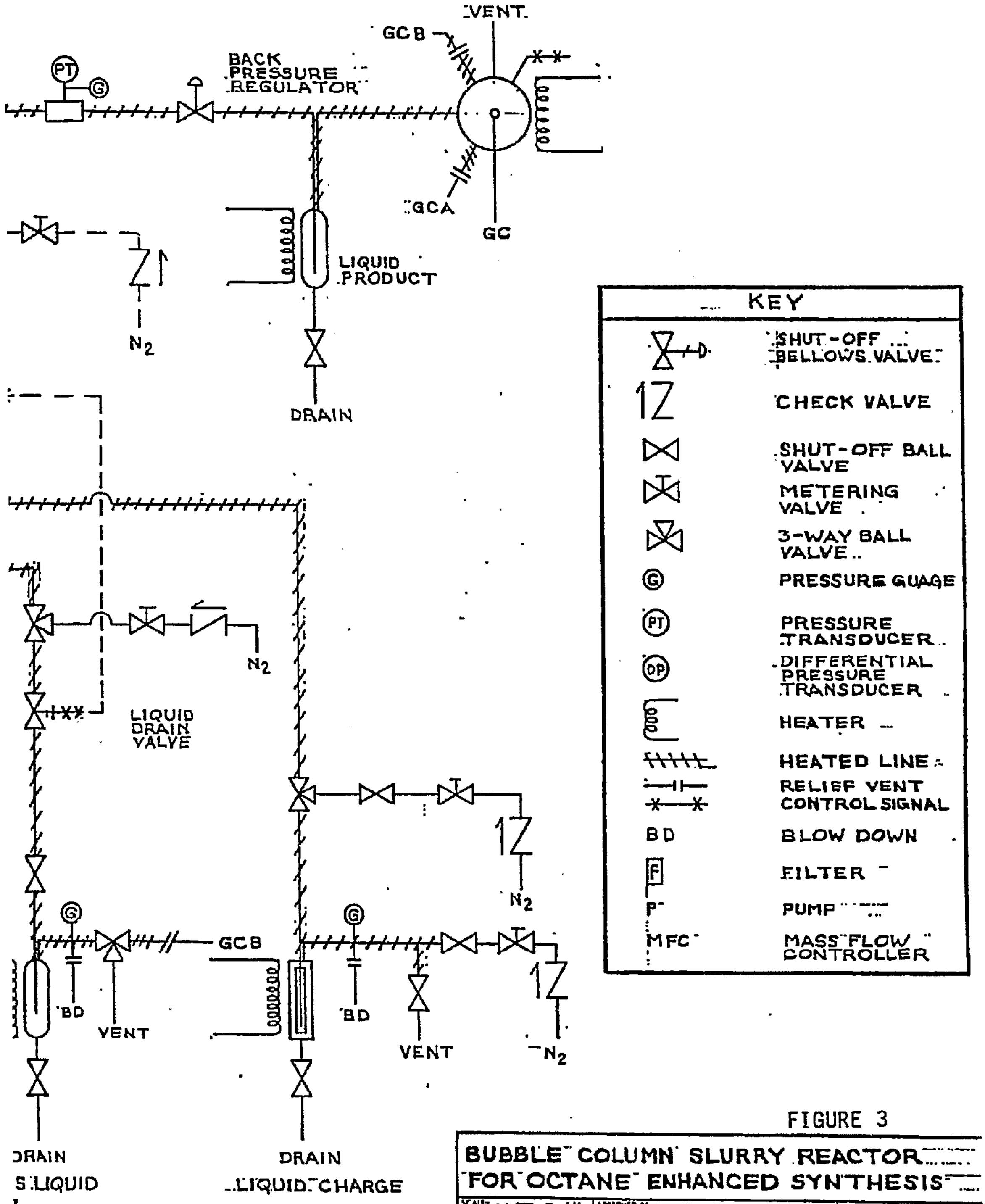

FIGURE 3

BUBBLE COLUMN SLURRY REACTOR FOR OCTANE ENHANCED SYNTHESIS		
SCALE: N.T.S.	APPROVED BY:	DRAWN BY: A.COHEN
DATE: 1-14-91	--	REVISED: 1-14-90
ALTAMIRA INSTRUMENTS INC.		DRAWING NUMBER

REFERENCES

Bukur, D.B., "Some Comments on Models for Fischer-Tropsch Reaction in Slurry Bubble Column Reactors," Chem. Eng. Sci., 38 (3), 44 (1983).

Bukur, D.B., and V.R. Kumar, "Effect of Catalyst Dispersion on Performance of Slurry Bubble Column Reactors," Chem. Eng. Sci., 41 (6), 1435 (1986).

Bukur, D.B., S.A. Patel and R. Matheo, "Hydrodynamic Studies in Fischer-Tropsch Derived Waxes in a Bubble Column," Chem. Eng. Comm., 60, 63 (1987a).

Bukur, D.B. et al, "Hydrodynamics of Fischer-Tropsch Synthesis in Slurry Bubble Column," Final Report DOE Contract No. DE-AC22-84PC70027 (1987).

Calderbank, P.H., F. Evans, R. Farley, G. Jepson, and A. Poll, "Rate Processes in the Catalysis-Slurry-Fischer-Tropsch Reaction," Catalysis in Practice, 66 (1963).

Clift, R., J.R. Grace and M.E. Weber, Bubbles, Drops and Particles, Academic Press (1978).

Deckwer, W.D., Y. Louisi, A. Zaidi and M. Ralek, "Hydrodynamic Properties of Fischer-Tropsch Slurry Process," Ind. Eng. Chem. Process Des. Dev., 19 699 (1980).

Deckwer, W.D., Y Serpemen, M. Ralek and B. Schmidt, "On the Relevance of Mass Transfer Limitations in the Fischer-Tropsch Slurry Process, Chem. Eng. 36, 765 (1981).

Deckwer, W.D., Y Serpemen, M. Ralek and B. Schmidt, "Modeling the Fischer-Tropsch Synthesis in the Slurry Phase," Ind. Eng. Chem. Process Des. Dev., 21, 231 (1982).

Fan, L.S., Gas-Liquid-Solid Fluidization Engineering, Butterworths, Boston (1989).

Idogawa, K., K Ikeda, T. Fukuda and S. Morooka, Int. Chem. Eng., 26 (3), 468 (1986).

Koide, k., T. Yasudo, S. Iwamoto and E. Fukuda, J. Chem. Eng. Japan, 16, 7 (1983).

Kolbel, H., E. Borchers and H. Langemann, "Grossenverteilung der Gasblasen in Blasensaulen," Chem. Ing. Tech., 33, 668 (1961).

Kuo, J.C.W., et al., "Slurry-Fischer/Mobil Two Stage Process of Converting Syngas to High Octane Gasoline," Final Report DOE Contract No. DE-AC22-80PC30022 (1983).

Kuo, J.C.W., et al., "Two Stage Process for Conversion of Synthesis Gas to High Quality Transportation Fuels," Final Report DOE Contract No. DE-AC22-83PC60019 (1985).

Mersmann, A., "Design and Scale-Up of Bubble and Spray Columns," Ger.Chem. Eng., 1, 1 (1978).

Patel, S.A., J.G. Daly and D.B. Bukur, "Bubble-Size Distribution in Fischer-Tropsch Derived Waxes in a Bubble Column," AIChE J., 36 (1), (1990)

Quicker, G. and W.D. Deckwer, " A Further Note on Mass Transfer Limitations in the Fischer-Tropsch Slurry Process," Chem. Eng. Sci., 36, 1577 (1981).

Satterfield, C.N. and G.A. Huff, "Mass Transfer Limitations in Fischer-Tropsch Slurry Reactors," Chem. Eng. Sci., 36, 790 (1981).

Saxena, S.C., M. Rosen, D.N. Smith and J.A. Reuther, "Mathematical Modeling of Fischer-Tropsch Slurry Bubble Column Reactors," Chem. Eng. Comm., 40, 97 (1986).

Schlesinger, M.D., H.E. Benson, E.M. Murphy and H.H. Storch, "Chemicals from the Fischer-Tropsch Synthesis," Ind. Eng. Chem., 46, 1322 (1954).

Shah, Y.T., B.G. Kelkar, S.P. Godbole and W.D. Deckwer, "Design Parameters Estimations for Bubble Column Reactors," AIChE J., 28 (3), 353 (1982).

Stern, D., A.T. Bell and H. Heinemann, " Effects of Mass Transfer on the Performance of Slurry Reactors Used for Fischer-Tropsch Synthesis," Chem. Eng. Sci., 38, 597 (1983).

APPENDIX A
DISTRIBUTOR DESIGN

Gas is introduced into the reactor by passing through a distributor plate. Good distribution can be achieved only if the fluid passes uniformly through all the orifices in the distributor. According to Mersman (1978), this condition is satisfied only if the Weber Number, We, based on the hole diameter and density of the gas is equal to or greater that 2. i.e.,

$$We = U_j^2 \, d_o \, \rho_g / \sigma \geq 2 \qquad (1)$$

where d_o = orifice diameter;
ρ_g = gas density;
σ = surface tension of liquid medium; and
U_j = jet velocity, defined as:

$$U_j = U_g \, d_c^2 / n \, d_o^2 \qquad (2)$$

where U_g is the superficial gas velocity,
d_c is the diameter of the column,
n is the number of holes in the distributor plate, and
d_o is the orifice diameter.

Equation (1) is valid for orifices with diameters less than the critical diameter, $d_{o(Cr)}$, i.e.:

$$d_o \leq d_{o(Cr)} = 2.32(\sigma/\rho_l \, g)^{1/2}(\rho g/\rho_l - \rho_g)^{5/8}$$

where ρ_l and ρ_g represent the density of the liquid medium and the density of the gas, respectively.

DESIGN BASIS:

Gas pressure = 15 atm.
Gas temperature at distributor inlet = 110^oC

H_2/CO mole ratio = 0.7
Surface tension of liquid medium, σ = 0.026 N/m
Density of liquid medium, ρ_l = 700Kg/m^3

For a 0.7 H_2/CO mole ratio, the percentages of hydrogen and CO in the feed are 41.1 and 58.9%, respectively. Using these values and the ideal gas law densities of the gases, a gas density for the syngas mixture can be calculated.

Density of the syngas, ρ_g = 0.0081 g/cm^3

Using these values in equation 3, the calculated critical orifice diameter is: $d_{o(cr)}$ = 0.255 cm. Thus the orifice diameter on any hole in the distributor should be less that 2.55 mm.

Solving equation (2):

$$U_j = 1.5\ (2.54)^2/\ nd_o^2 \quad = \quad 9.68/nd_o^2$$

Substituting in equation (1):

$$We = (9.68/nd_o^2)^2\ d_o\rho_g/\sigma$$

$$= 0.029/n^2\ d_o^3$$

For stable flow,

$$We = 0.029/n^2 d_o^3 \quad \geq 2,\ \text{or}$$

$$d_o \leq (0.0145/n^2)^{1/3}$$

The following combination of number of holes and orifice diameters satisfy the above criteria:

Number of holes	Maximum diameter (mm)
1	2.4
2	1.5
3	1.2
4	1.0
etc.	

For uniform gas distribution and in order to achieve smaller size bubbles, a minimum of three holes are deemed to be necessary. Therefore a distributor with three holes of approximately 1 mm diameter each will be initially tested.

WORK PLANNED FOR NEXT REPORTING PERIOD

Work on the construction of the laboratory-scale bubble column reactor has begun. Most long lead-time items have been ordered and machine drawings are being prepared. It is expected that by the end of next quarter the construction will be complete and the BCSR ready for preliminary test runs.

Work on the various catalyst systems necessary for carrying out Task 3 is currently underway. Chemicals and supplies have been ordered and a small fixed-bed reactor system is being modified at the University of Pittsburgh for the preliminary screening experiments.

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