

SECTION I

MODELING OF WILSONVILLE INTEGRATED
TWO-STAGE LIQUEFACTION (ITSL) PROCESS

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Summary

Direct coal liquefaction involves the production of liquid fuels by increasing the hydrogen to carbon ratio and simultaneously removing the heteroatoms (N, S and O) and mineral matter from coal. Conventional liquefaction processes which include SRC-I and SRC-II (Solvent Refined Coal), H-Coal and EDS (Exxon Donor Solvent) are single stage processes, which considerably reduces process flexibility in terms of product quality and hydrogen utilization efficiency. The Wilsonville coal liquefaction facility first consisted of a single stage based on the SRC-II process. The reactor was a bubble column slurry reactor, which was modeled in the first year of this project (Brainard et al., 1984). A second stage was later added at the Wilsonville liquefaction facility to improve three performance criteria, which affect the overall economics; process flexibility, product quality and hydrogen utilization efficiency. The second stage consisted of an ebullated bed catalytic reactor based on the H-Coal reactor concept. This process was then called the Integrated Two-Stage Liquefaction (ITSL) process. The objective of this project was to develop a model for the ebullated bed reactor so that models for both reactors in the ITSL process could be in place. The reactor model took into account the unexpected phenomenon of bed contraction in a three phase fluidized bed by utilizing the hydrodynamic model of Darton and Harrison (1975) which is based on the wake concept. The kinetic model used was developed for the catalytic liquefaction of bituminous Elkhorn No. 3 coal (Gollakota et al., 1985). The plug flow model was used for both gas and slurry phases to describe their flow behavior. The program was written in FORTRAN in a modular form so that modifications can be easily made.

Introduction

Direct liquefaction of coal involves the production of liquid fuels by increasing the hydrogen to carbon ratio and simultaneously removing the heteroatoms (N, S, and O) and ash from coal. The two main methods for direct coal liquefaction are: (a) catalytic hydrogenation and (b) non-catalytic solvent extraction. The catalytic hydrogenation of coal was originated by Bergius in 1913; the process allows a slurry of coal in oil to be hydrogenated over active catalysts. In the 30's Pott and Broche found that coal could be extracted and dissolved at 10-15 MPa and 700 K by coal-derived solvent or hydrogen donor solvents. In more recent years a number of direct coal liquefaction processes have been developed. Typical operating conditions and product distributions of these processes are summarized in Table I-1. All these processes consist of a single stage and are thus limited in process flexibility. For instance, in the SRC process, the production of recycle solvent in sufficient quantities to maintain solvent balance is critical for process feasibility. The dissolver, thus, has to be operated at relatively high severity conditions. This has the undesirable effect of increasing the gas yields and reducing the efficiency of hydrogen utilization. At the Wilsonville coal liquefaction facility the addition of a second hydrotreater stage had a major impact on three process performance criteria which affect the overall economics: process flexibility, product quality, and hydrogen utilization efficiency.

Table I-1. Comparison of Major Coal Liquefaction Processes
(Ledakowicz et al., 1984)

Operating Conditions	Process			
	SRC-I	SRC-II	EDS	H-Coal
Pressure, MPa	10	13	10	12
Temperature, K	724	730	722	726
Residence time, min.	40	60	40	30-70
Catalyst matter	mineral matter	mineral matter	Ni-Mo Ni-Mo	Co-Mo
Type of reactor	upflow column reactor	upflow column reactor	upflow column reactor	ebullated bed reactor
Product distribution (wt% of maf coal)				
C ₁ -C ₄ hydrocarbons	6.9	17.6	7.0	12.3
C ₅ -473K distillate	4.9	13.0	37.2	14.2
473-800K distillate	11.7	25.8		19.7
+800K distillate	60.1 SRC	26.5 SRC	40.1	34.9
H ₂ O, H ₂ S, NH ₃ , CO, CO ₂	9.2	10.8	15.7	11.6
unreacted coal	<u>7.2</u>	<u>6.3</u>	<u>-</u>	<u>7.3</u>
total	100	100	100	100
H ₂ reacted	2.3	4.8	4.3	3.8

The purpose of the present work is to model the second stage of the Wilsonville Integrated Two-Stage Liquefaction (ITSL) process. Modeling of complex physical and chemical processes has become one of the key factors in the successful design of engineering systems. Modeling refers to the description of a phenomenon in terms of a mathematical model which can simulate the observed output from the system. The rationale for mathematical modeling lies in its ability to rapidly and thoroughly examine such questions as (Seinfeld and Lapidus, 1974):

- a. extrapolation of the process to operating ranges not being employed.
- b. controllability and stability of the process
- c. sensitivity of the process to changes in operating variables, and
- d. optimal economic operating conditions of the process.

A mathematical model is inherently more reliable than a model derived solely by statistical techniques ("yield" models). Statistical models adopt a "black-box" approach to reactor modeling and merely correlate the product distribution from the reactor as a function of process variables such as temperature, pressure, feed rates, feed concentrations etc. (Martin, 1985). Such models cannot be used for extrapolation.

Two-Stage Liquefaction Processes

As mentioned earlier, the two principal routes for the direct hydrogenation of coal to form a liquid involve:

- (a) Addition of hydrogen directly from the gas phase
- (b) Addition of hydrogen from a donor solvent.

The first route is called catalytic liquefaction or hydroliquefaction while the second route is called solvent extraction. Though both methods

involve direct hydrogenation, the difference lies in the catalytic hydrogenation stage.

a. Solvent Extraction:

This is essentially a two-step process involving a mild hydrogenation extraction stage at temperatures up to 500°C to produce a solid/liquid extract which may be subsequently converted to liquid fuels and/or chemical feedstocks via a catalytic hydrogenation step. The solvent extraction stage can be carried out either directly under H₂ pressure or without H₂ in the dissolver, the solvent being hydrogenated in a separate step before being returned to the extraction stage. The EXXON Donor Solvent (EDS), Solvent Refined Coal (SRC) and National Coal Board (NCB) processes are classified as solvent extraction processes. Bubble column slurry reactors are used for these processes.

b. Catalytic Liquefaction:

This involves stronger hydrogenation over active catalysts in a fixed, ebullating or trickle bed reactor to produce hydrocarbon products directly and rehydrogenation of solvent occurs in-situ. The H-Coal process is an example of this type.

Each process involves removal of ash, mineral matter and unconverted coal after the first hydrogenation stage. A general diagram to distinguish these processes is shown in Figure I-1 (Pullen, 1983).

In two-stage liquefaction processes, extraction and hydrogenation take place in separate reactors. Conditions for each stage can thus be optimized. A summary of the various two-stage liquefaction (TSL) processes is given in Table I-2.

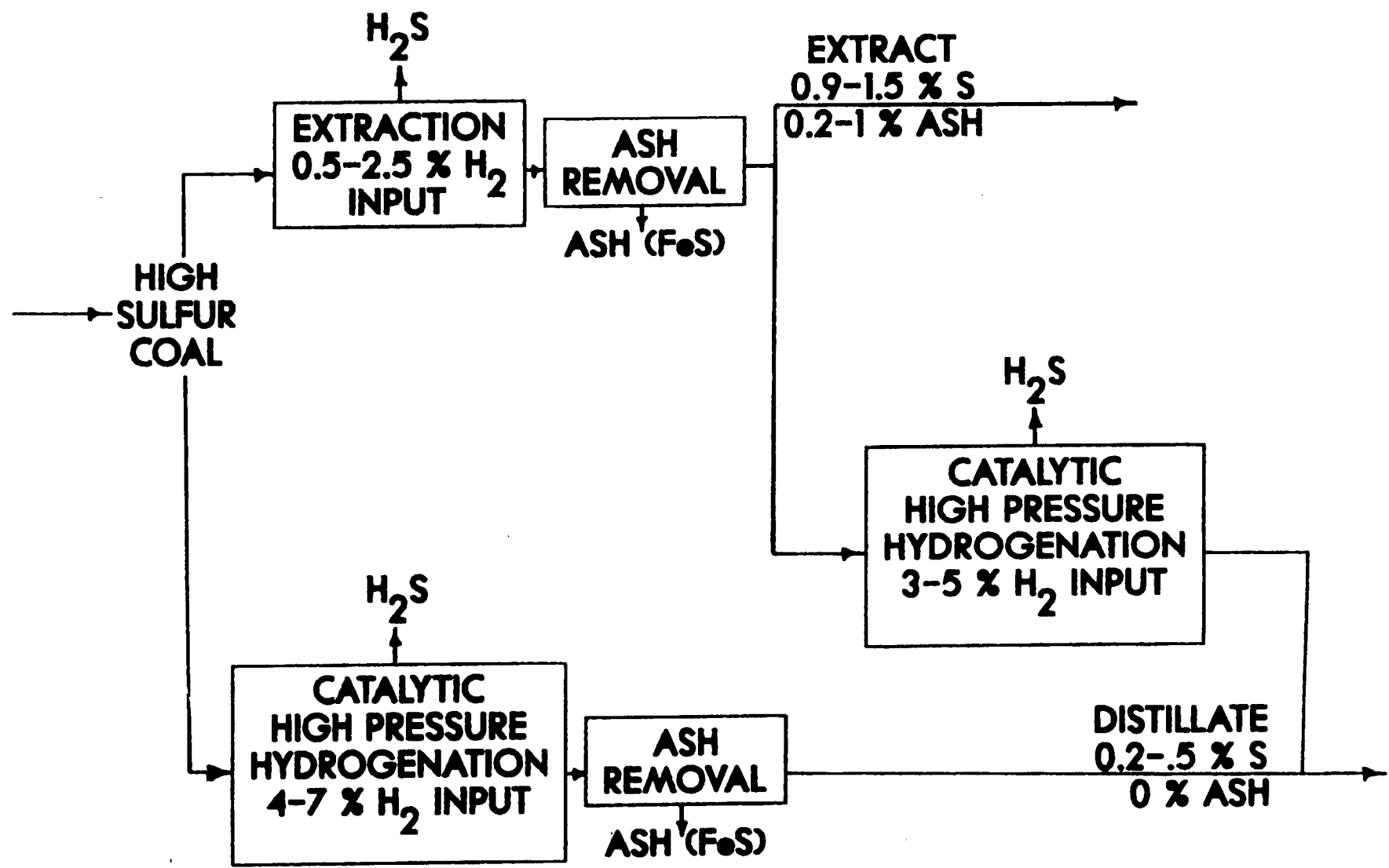


Figure I-1: Alternative Routes for Direct Coal Liquefaction (Pullen, 1983).

TABLE I-2: Summary of TSL Processes

Process	Extraction Pressure (atm)	Catalyst	Hydrogenation Environment	Reactor Type
Chevron	100-170	Co-Mo, Ni-Mo or Ni-W	Digest	Fixed Bed
Lummus	165	Ni-Mo	Solution	Expanded Bed
Wilsonville	140	Ni-Mo	Solution	Ebullated Bed
NCB Liquid Solvent Extraction	15	Co-Mo	Solution	Fixed Bed

c. Wilsonville Two-Stage Liquefaction Process

Emphasis of this work is on modeling the second stage of the Wilsonville Integrated TSL process. The original facility at Wilsonville consisted of a single-stage thermal process (SRC-I). A Critical Solvent Deashing process was installed in 1978 and a second stage catalytic hydrogenation unit began operation in 1981. The second stage consists of an ebullated bed catalytic reactor based on the H-Coal concept. A block diagram of the ITSL process is shown in Figure I-2. The salient features of the various process units are shown below.

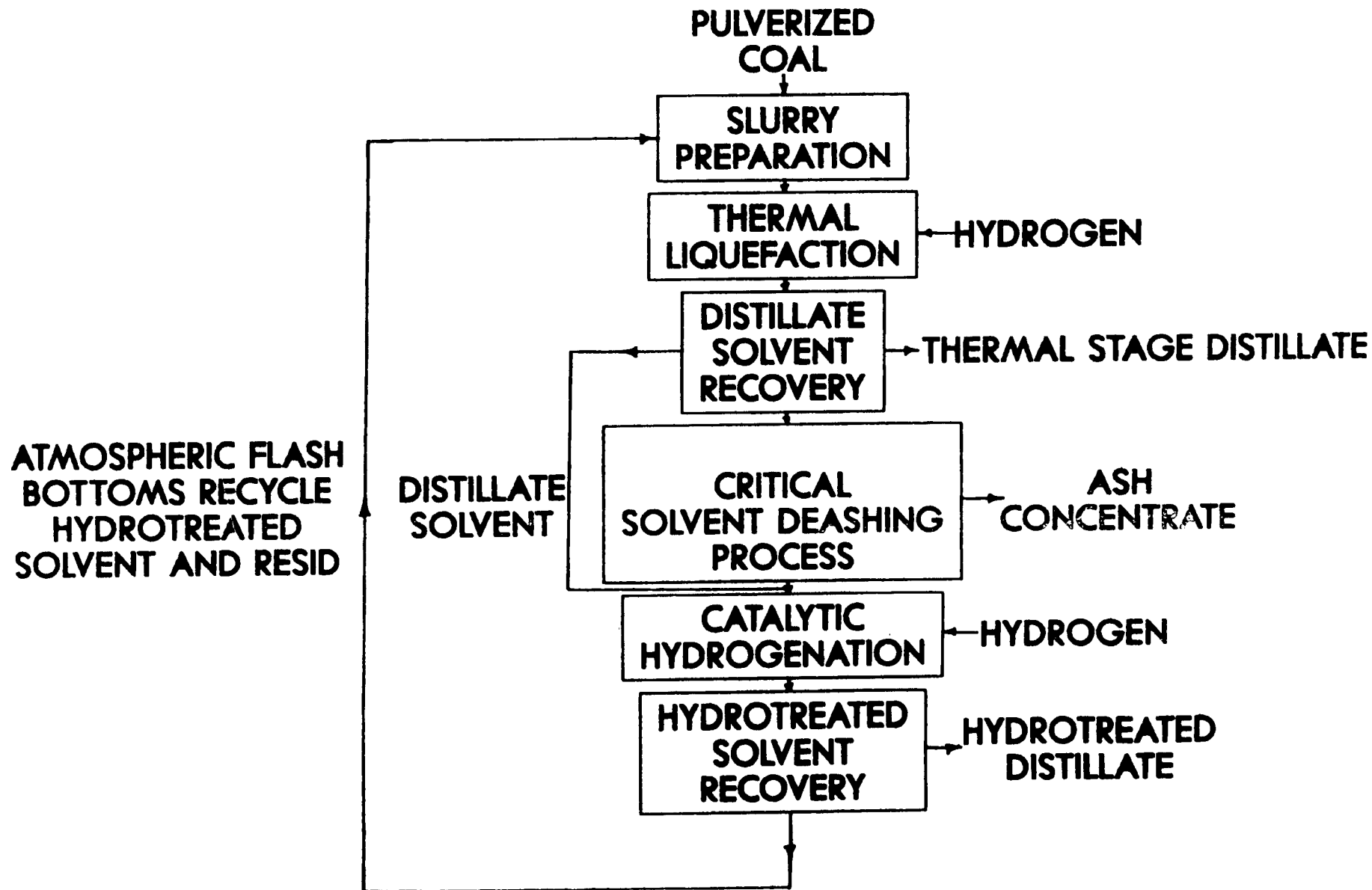


Figure I-2: Schematic Representation of Wilsonville Integrated Two-Stage Liquefaction (ITS) Process.

<u>Unit</u>	<u>Salient Features</u>
<u>First Stage</u> Thermal Liquefaction Unit (TLU)	<ul style="list-style-type: none"> • dissolver or short contact time (SCT) • disposable catalyst may be utilized • 90-95% coal conversion (Cresol solubles)
Critical Solvent Deashing (CSD) Unit	<ul style="list-style-type: none"> • proprietary extraction process • conditions near critical point of deashing solvent • capable of fractionating coal extract • very efficient deashing achieved
<u>Second Stage</u> Hydrotreating (HTR)	<ul style="list-style-type: none"> • ebullated bed reactor • commercial supported catalyst utilized • catalyst addition/withdrawal capability • wide range of stable operating conditions

The first stage is conventional SRC technology. In the second stage, the SRC is catalytically hydrocracked in the presence of hydrogen. Catalysts are used in the second stage of TSL processes to enhance distillate yields; improve product quality by removal of S, N and O; increase H/C ratios of products and rehydrogenate the recycle solvent. The catalysts used are similar to petroleum hydroprocessing catalysts and normally consist of Mo with Ni or Co as a promoter on an alumina support. In the hydrocracking step, the SRC is selectively cracked to gases and distillate fuels. A major portion of the sulfur and some nitrogen and oxygen are converted via hydrogenation to H_2S , NH_3 , and H_2O . Table I-3 gives a summary of catalytic reactions involved in coal conversion.

TABLE I-3: Catalytic Reactions in Coal Conversion (Cusumano et al., 1978)

Process	General Reactions	Specific Reactions/Products
Direct Liquefaction	Hydrogenation Cracking Hydrofining	Aromatic Liquids Hydrodesulfurization (HDS) Hydrogenitrogenation (HDN)
Liquids Refining and Upgrading	Cracking Reforming Hydroforming	Hydrogenation Dehydrogenation Dehydrocyclization Isomerization Hydrogenolysis HDS, HDN

Three-Phase Fluidized Bed Reactors

The first stage in the Wilsonville ITSL process is a thermal liquefaction unit, which consists of a bubble column slurry reactor. This reactor has been modeled in the first year of this project (Brainard et al., 1984). Though this reactor consists of three separate phases (gas, solvent, and coal) the slurry of coal and solvent is approximated for modeling purposes, as a pseudo-homogeneous liquid and the reactor is modeled as a two-phase system. However, the second stage which is the hydrotreating step consists of an ebullated bed reactor. Since a distinct solid phase (catalyst) is present in this reactor, the ebullated bed reactor is classified as a three-phase fluidized bed reactor. The mode of operation of three-phase fluidized beds is quite different from that of a slurry reactor as pointed out by Epstein (1981) and Muroyama and Fan (1985) in recent review articles. Some of these differences are shown in Table I-4.

TABLE I-4: Characteristics and Applications of Three-Phase Processes (Darton, 1985)

	<u>Three-Phase Fluidized Bed</u>	<u>Slurry Reactor</u>
Continuous Phase	Liquid	Liquid
Solids Suspended by flow of	Liquid	Gas
Solids Concentration Gradient	No	Yes
Typical Solids Holdup	10-50% vol.	< 10% vol.
Typical Particle Size	0.1-5 mm	< 0.5 mm
Applications	Heterogenous reactions particularly hydrogenation of coal; catalytic reactions such as hydroprocessing; Fischer-Tropsch reaction. Biological processes such as fermentation and hydrogenation of fats.	

The dynamics of three-phase fluidized beds are quite different from those of a slurry bed and equations developed to describe the hydrodynamic behavior of a slurry bed are not quite applicable to a three-phase fluidized bed (Epstein, 1981). Ebullated bed fluid dynamics for the H-Coal process have been studied by Schaefer et al. (1983).

Modeling of Ebullated Bed Reactor

The ebullated bed reactor, which was developed and patented by Hydrocarbon Research Inc. is the heart of the second stage of the Wilsonville Integrated Two-Stage Liquefaction (ITSL) Process. A schematic of the ebullated bed reactor is shown in Figure I-3. The catalyst particles are maintained in the form of an expanded bed by the continuous flow of slurry and hydrogen through the reactor. The liquid phase forms a continuous medium and the hydrogen is dispersed in the form of bubbles. A part of the slurry is recycled in order to obtain the necessary liquid velocity to fluidize the bed. The major advantages in using ebullated beds in place of fixed beds are: on stream catalyst replacement, fouling-free operation and a small reactor temperature gradient.

Modeling of the ebullated bed requires a detailed understanding of the fluid dynamics of the complex reacting system. Factors affecting the performance of the reactor and information needed for the design and modeling include the following:

- A) Catalyst bed expansion
- B) Phase holdups of gas, slurry and catalyst

H-Coal PDU Reactor

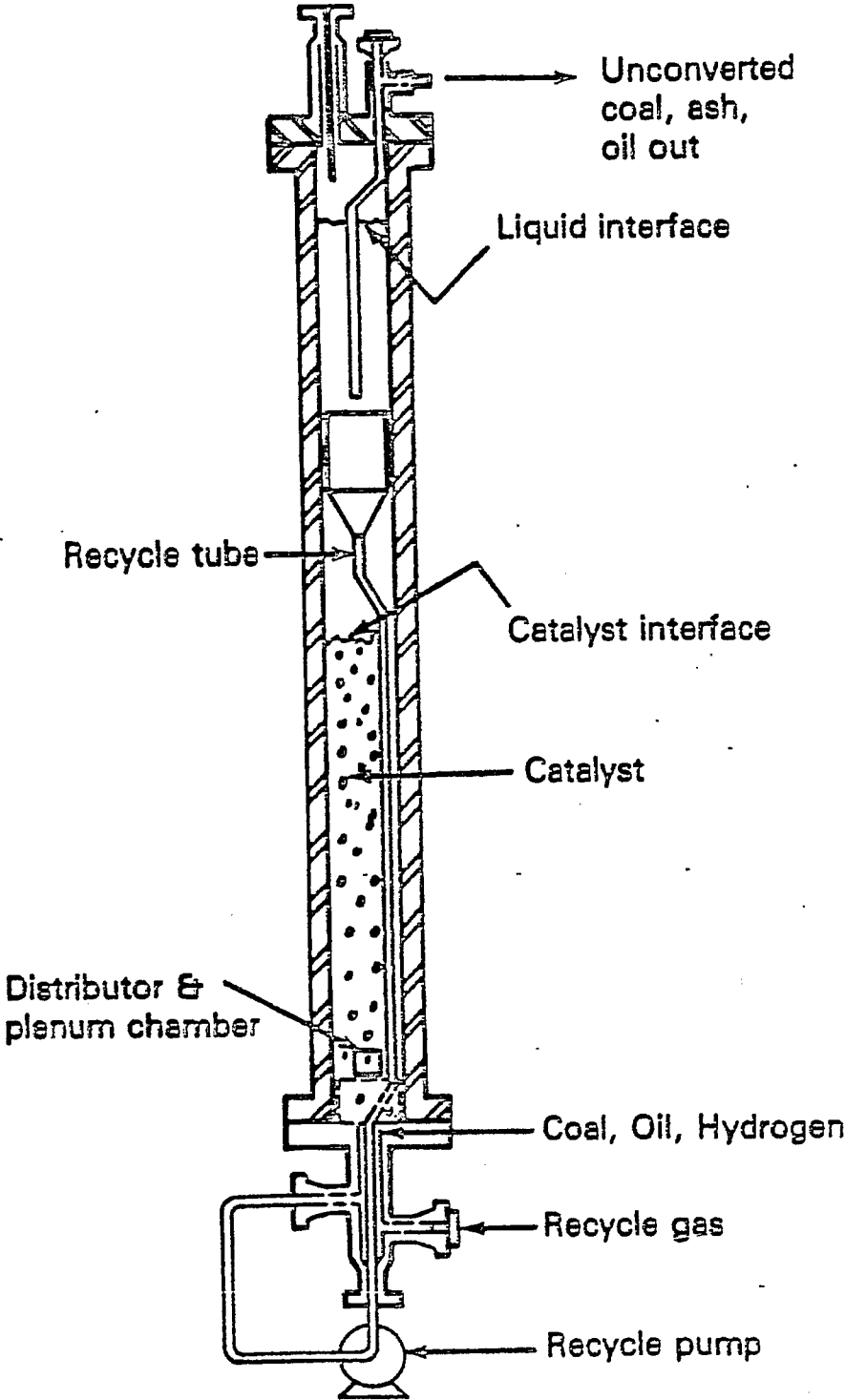


Figure I-3: Schematic of Ebullated Bed Reactor

- C) Mixing parameters, axial dispersion of gas, slurry and catalyst phases.
- D) Transport parameters: gas-liquid and liquid-solid mass transfer coefficients and gas-liquid interfacial area.
- E) Reaction data: kinetics, conversion and product yields.
- F) Thermodynamic parameters: vapor-liquid thermodynamic data, specific heats, thermal conductivities.

Phase Holdups in Three-Phase Fluidized Beds

Models to predict phase holdups in three-phase fluidized beds have been reviewed by Muroyama and Fan (1985). The impetus to describe the internal structure of a three-phase fluidized bed followed the discovery of the phenomenon of bed contraction. Thus, although a particulate fluidized bed increases in volume as the fluid flow through it is increased, it is often found that a liquid-fluidized bed contracts when a gas is injected into it. Most models proposed to explain this phenomenon are based on the wake concept which considers the three phase fluidized bed to be composed of (1) the gas bubble region, (2) the wake region and (3) the solid-liquid fluidization region. The bubble wake consists of (a) the liquid wake immediately below the bubble and (b) a lower region of particles and liquid also apparently moving with the bubble. Bed contraction is primarily caused by the liquid wakes, which move through the bed at a relatively high speed causing a reduction in the liquid velocity through the particulate phase since the overall liquid flow-rate remains constant. The particulate phase therefore contracts and this can cause the whole bed to follow suit. The main differences among the various models lie in the assumptions for the solids concentration in the wake region, the correlations for the porosity in the liquid-solid fluidization

region and the correlations for the gas holdup or bubble velocity. In the present work, the solid-free wake model proposed by Darton and Harrison (1975) will be used.

a. Darton-Harrison Model

The Darton-Harrison model (Darton and Harrison, 1975) uses the correlation of Richardson and Zaki (1954) to describe the two-phase fluidization in the limit of zero gas flow:

$$\epsilon_L^n = \frac{U_L}{U_T} \quad (1)$$

The relationship between the hold-ups of gas and liquid is obtained in the following way. The flux of liquid in the wakes of the bubbles is assumed to be $\bar{K}U_G$ where \bar{K} is the mean value of (liquid-wake volume/bubble volume). The superficial liquid velocity in the particulate phase is then given as $(U_L - \bar{K}U_G)/(1 - \epsilon_G - \bar{K}\epsilon_G)$. The liquid hold-up in the particulate phase is $(\epsilon_L - \bar{K}\epsilon_G)/(1 - \epsilon_G - \bar{K}\epsilon_G)$ and equation (1) is then used to relate the holdup to the superficial velocity to give the following relation

$$\epsilon_L = (U_L/U_T - \bar{K}U_G/U_T)^{1/n} (1 - \epsilon_G - \bar{K}\epsilon_G)^{1-1/n} + \bar{K}\epsilon_G \quad (2)$$

The above equation is derived from the principle of continuity and assumes the solids to be particularly fluidized according to equation (1). An empirical correlation was obtained for \bar{K} from the experimental data on air-water as follows:

$$1 + \bar{K} = 1.4 (U_L/U_G)^{0.33} \quad (3)$$

In order to predict gas and liquid holdups, a second equation relating ϵ_L and ϵ_G is needed in addition to equation (2). Darton and Harrison (1975) used the drift flux approach to obtain the second relation. The drift flux of gas V_{CD} is defined as the volumetric flux of gas relative to a surface moving at the average velocity, i.e.

$$V_{CD} = U_S \epsilon_G (1 - \epsilon_G) \quad (4)$$

where U_S is the slip velocity, defined as the mean relative velocity:

$$U_S = \frac{U_G}{\epsilon_G} - \frac{U_L}{\epsilon_L} \quad (5)$$

Thus,

$$V_{CD} = U_G (1 - \epsilon_G) - \frac{U_L \epsilon_G (1 - \epsilon_G)}{\epsilon_L} \quad (6)$$

The authors calculated the drift flux from the data of Michelsen and Ostergaard (1970) and plotted the data as a function of ϵ_G (Figure I-4). The data fell into two regions; one in which the gas holdup increased rapidly with increasing drift flux, and one in which the increase was noticeably slower. These two regions correspond to the uniform bubbling and the churn turbulent regimes in gas-liquid flow. In the uniform bubbling regime, the bubbles tend to be of a similar size and the gas drift flux is a function only of the gas holdup and the rising velocity of an isolated bubble, U_{B0} . The drift flux in this regime was well correlated by the following expression:

$$V_{CD} = \epsilon_G U_{B0} \quad (7)$$

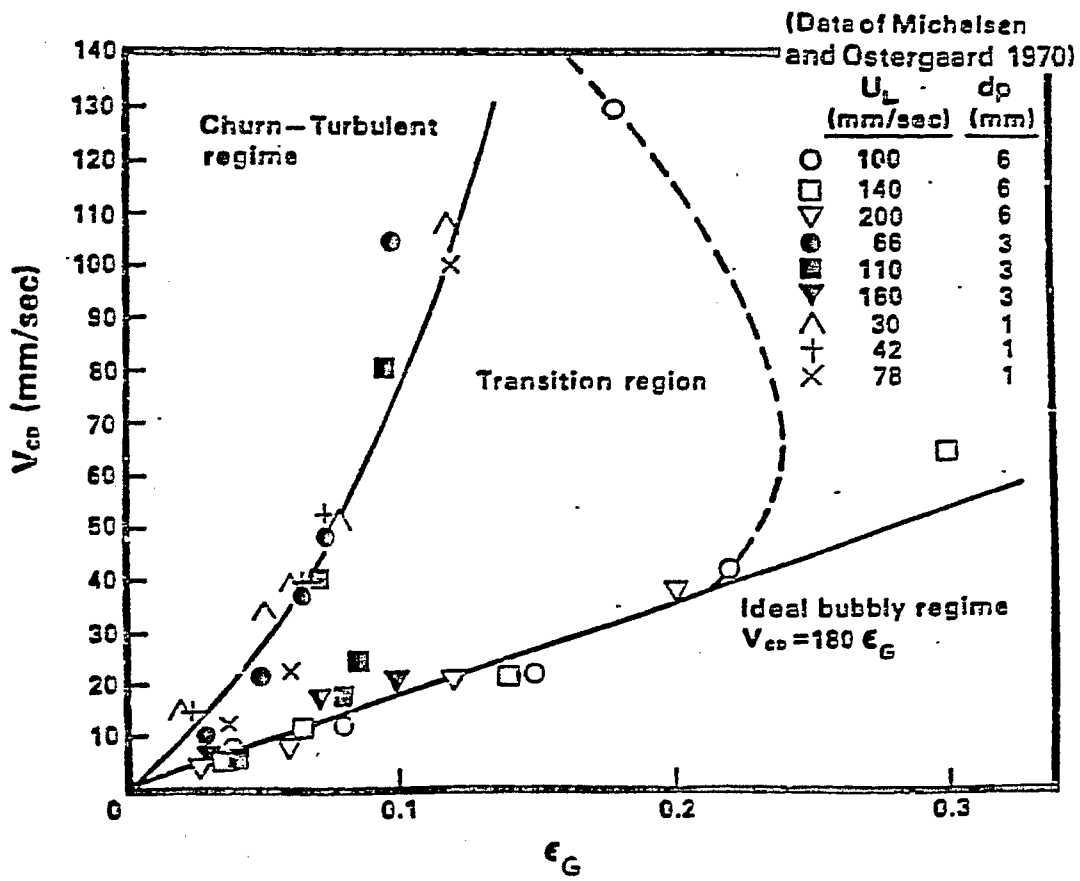


Figure I-4: Flow Regime Classification Using Drift-Flux Model

This equation suggests that the influence of the bubbles on each other is either neutral or such as to increase the mean speed of rise. Equation (7) can be solved simultaneously with equation (2) to give values of gas and liquid holdup. In the churn turbulent regime equations such as (7) do not apply and a graphical method has to be resorted to.

b. Comparison with Bhatia-Epstein Model:

Muroyama and Fan (1985) have recommended the generalized wake model developed by Bhatia and Epstein (1974) to be used in describing the individual phase holdups. The main difference between this model and the one developed by Darton and Harrison lies in the fact that whereas the latter authors characterized the bubble wakes with the single parameter \bar{K} , Bhatia and Epstein considered also the particulate region of the wake and introduced two variables; the wake size and porosity. However, Bhatia and Epstein found that, with the wake size estimated on an ad hoc basis, experimental hold-up data were best fitted assuming the wakes to be particle-free. Vasalos et al. (1980) also found that the solids concentration in the wake phase was zero from their cold flow studies for the H-coal reactor. A second point of difference lies in the use of the gas drift flux by Darton and Harrison.

The generalized wake model was used by Vasalos et al. (1980) and Schaefer et al. (1983) to describe holdup data both for the cold model and Process Development Unit (PDU) runs for the H-coal process, primarily due to the fact that it could quantitatively describe operation both in the ideal bubbly and churn turbulent regimes. However, since most of the PDU runs lie in the bubbly flow regime, it is simpler and adequate to use the Darton-Harrison model with a direct estimate of the liquid-wake volume.

c. Calculation of Phase Volume Fractions

The following equations apply for the calculation of phase volume fractions in three-phase fluidized beds:

Identity Relationship:

$$\epsilon_G + \epsilon_{Lf} + \epsilon_S = \epsilon_{LG} + \epsilon_S = 1.0 \quad (8)$$

For the case where the fluidizing medium is a homogeneous slurry,

$$\epsilon_{Lf} = (\epsilon_L + \epsilon_f) \quad (9)$$

Catalyst Mass Balance

$$H_{mf}(1 - \epsilon_{mf}) = H_{LG}(1 - \epsilon_{LG}) = H_{LG}\epsilon_S \quad (10)$$

If the voidage at minimum fluidization, ϵ_{mf} , is unknown, then a value of 0.43 may be used for any smooth cylindrical catalyst (Blum and Toman, 1977). Once ϵ_G and ϵ_L are calculated from equations (2) and (7), the height of the three phase fluidized region can be calculated from the equation

$$H_{LG} = \frac{H_{mf}(1 - \epsilon_{mf})}{(1 - \epsilon_{LG})} \quad (11)$$

The H-Coal ebullated bed reactor contains at least four discrete components: gas, liquid, catalyst and unconverted coal. For purposes of modeling, liquid and unconverted coal are treated as a pseudo-homogeneous slurry.

Liquid Phase Dispersion

Liquid phase dispersion measurements were carried out by Schaefer et al. (1983) and they have proposed the following correlation

$$Pe_L = 5.05 + 42.91 \exp(-35.48 U_G) \quad U_G \text{ in ft/sec} \quad (8)$$

$$\text{where } Pe_L = \frac{U_Z L}{D_L}$$

Gas-Liquid Mass Transfer Coefficient

Muroyama and Fan (1985) do not recommend any specific correlation and note that literature correlations for $k_L a$ lack generality and can be employed only for very limited conditions. Lee et al. (1978) have shown that for the SRC dissolver, mass transfer of hydrogen was not the rate-controlling step, rather, the SRC reactor was found to operate in a kinetically limited regime. In the case of catalytic liquefaction, however, Feldman et al. (1972) concluded from their studies on the hydrogenation of coal tar and a coal-coal tar slurry using a Co-Mo catalyst, that the rate of hydrogenation was limited by the diffusion of hydrogen from the gas phase to the liquid phase rather than by inter or intraphase diffusion involving the catalyst. Thus a knowledge of gas-liquid mass transfer coefficient is needed for an accurate model of the ebullated bed. In the absence of directly applicable correlations, the correlations developed by Dhanuka and Stepanek (1980) for the system $CO_2/N_2/Na_2CO_3-NaHCO_3$ buffer will be used. The correlations were obtained in the range $U_G = 2 - 8$ cm/sec and $U_L = 6.1 - 13.8$ cm/sec and for glass beads of 1.98, 4.08 and 5.86 mm diameter. They are of the form:

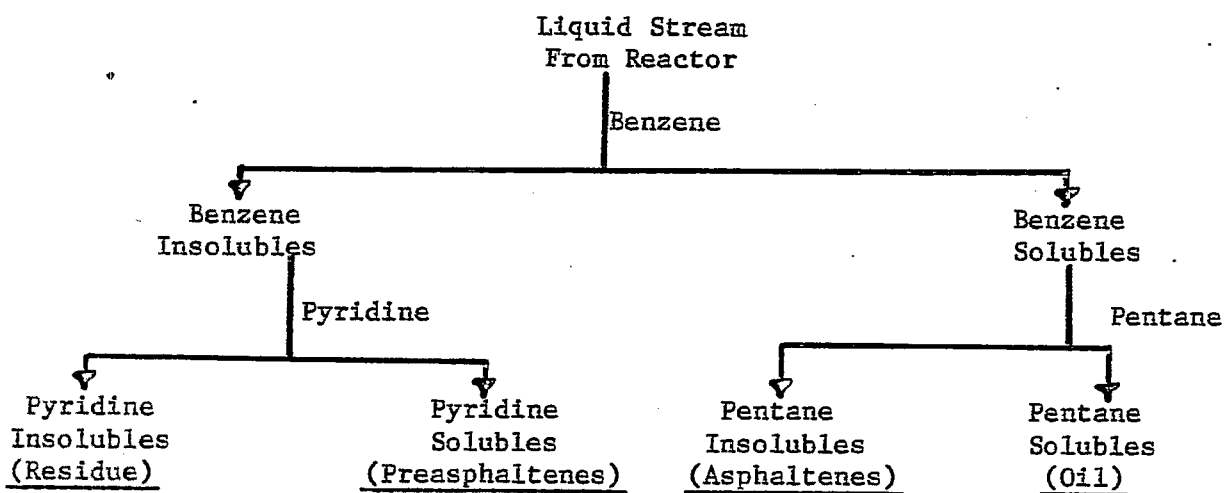
$d_p = 1.98 \text{ mm}$	$k_L a = 2.37 \times 10^{-3} U_G U_L^{0.45}$	(for pure CO_2)
	$k_L a = 3.23 \times 10^{-3} U_G U_L^{0.55}$	(for pure N_2)
$d_p = 4.08 \text{ mm}$	$k_L a = 3.41 \times 10^{-2} U_G^{0.4077}$	
$d_p = 5.86 \text{ mm}$	$k_L a = 2.52 \times 10^{-2} U_G$	

Liquid-Solid Mass Transfer Coefficient

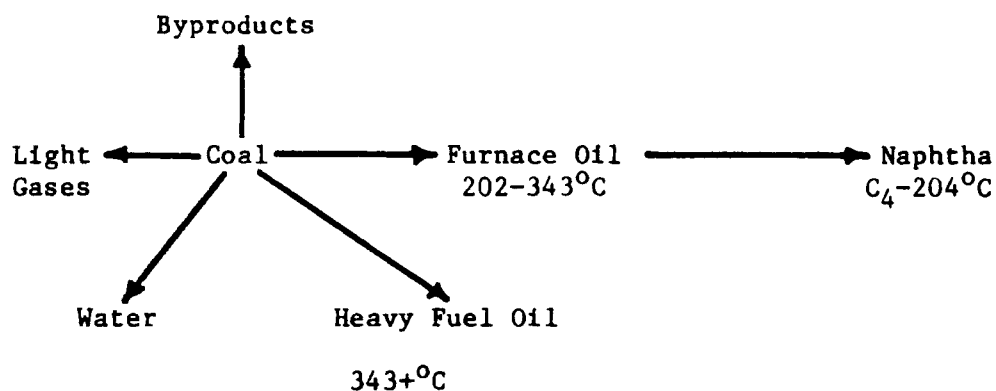
Lee et al. (1974) neglected liquid-solid mass transfer in modeling a three-phase fluidized bed. Ermakova et al. (1977) have given a correlation for the liquid-solid mass transfer coefficient for a liquid fluidized bed.

Kinetic Model

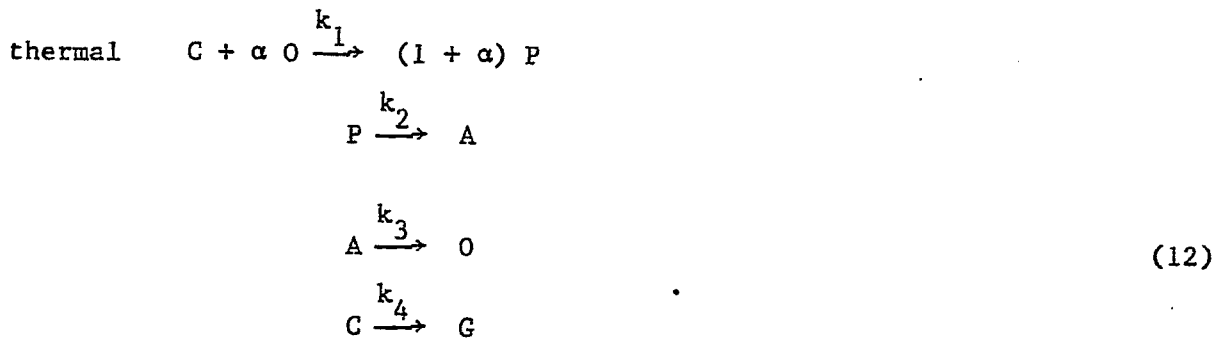
The kinetics of thermal liquefaction of coal have been reviewed by Albal et al. (1983). Most of the kinetic models consider liquefaction to be a multi-step process and the various products are classified according to their solubilities in different organic solvents. The following scheme is most commonly used in classifying products of coal liquefaction.



Shah et al. (1978) studied the kinetics of catalytic liquefaction of Big Horn Coal in a segmented bed reactor. The products were defined on a boiling range basis rather than solubility. They proposed the following reaction mechanism:



Gollakota et al. (1985) determined the influence of pore diffusion and the relative selectivity of thermal/catalytic reaction pathways in the catalytic liquefaction of Elkhorn No. 3 coal. Their studies were conducted in batch microreactors in the presence of a coal-derived solvent, hydrogen and a Co-Mo/Al₂O₃ supported catalyst. The details of their kinetic model will be set forth since their model is particularly relevant here as pelleted high surface area catalysts are used in the second stage ebullated bed. Due to the presence of large molecular sizes in the preasphaltene and asphaltene fractions of coal-derived liquids, pore diffusion limitations can exist. The following reaction model was proposed by these workers:



where C = Coal, O = oils, P = preasphaltenes

A = asphaltenes, and G = gases

The authors define α to be a stoichiometric parameter; however, since the reactions are written on a mass rather than a molar basis, α has to be defined as some sort of an adduction parameter. The error in assigning α to be a stoichiometric parameter carried into their mass balances. They determined α from a fit of the kinetic data to be 0.2. The thermal and catalytic reactions were assumed to proceed in parallel in the presence of a catalyst. The rate of disappearance of each component in a batch reactor can thus be written as the sum of thermal (homogeneous) and catalytic reaction rates.

$$\frac{dC}{dt} = -k_1 CO - k_4 C \tag{14}$$

$$\frac{dP}{dt} = k_1 (1 + \alpha) CO - k_2 P + N_P|_{z=L} W^2 \tag{15}$$

$$\frac{dA}{dt} = k_2 P - k_3 A + N_A|_{z=L} W^2 \tag{16}$$

$$\frac{dO}{dt} = -k_1 \alpha CO + k_3 A + N_O|_{z=L} W^2 \tag{17}$$

$$\frac{dG}{dt} = k_4 C \quad (18)$$

In the above equations, N_p , N_A and N_O are the mass fluxes at the surface of the catalyst pellet and W^2 is the catalyst external surface area per unit volume of liquid. The catalytic reaction fluxes were determined by assuming a slab geometry for the catalyst and analytically solving the diffusion-reaction equations. The equations (12), (13) and (14) could be then expressed as follows:

$$\frac{dP}{dt} = k_1 (1 + \alpha) CO - (k_2 + k_{2e})P \quad (19)$$

$$\frac{dA}{dt} = (k_2 + k_{2e}(1-\epsilon)) P - (k_3 + k_{3e}) A \quad (20)$$

$$\frac{dO}{dt} = -k_1 \alpha CO + (k_3 + k_{3e}) A + k_{2e} \epsilon P \quad (21)$$

where $k_{2e} = \frac{mk_2 \eta_1}{\rho}$ $k_{3e} = \frac{mk_3 \eta_2}{\rho}$

$$\eta_1 = \frac{\tanh \gamma L}{\gamma L}$$

$$\eta_2 = \frac{\tanh \beta L}{\beta L}$$

$$\gamma = \left[\frac{k_2}{D_p} \right]^{1/2}$$

$$\beta = \left[\frac{k_3}{D_A} \right]^{1/2}$$

$$\epsilon = \frac{1 - \eta_2/\eta_1}{1 - \gamma^2/\beta^2}$$

The above analysis shows that for a catalytic reaction with powder (small L) $\eta_1 \approx \eta_2 \approx 1$ and $\epsilon \approx 0$. Also, for a purely thermal reaction in the absence of a catalyst one has $k_{2e} = k_{3e} = 0$.

Reactor Model Development

The following assumptions are made in the development of the model for the ebullated bed reactor:

- 1) The ebullated bed operates at steady-state conditions. Nalitham et al. (1984) have shown that the relatively slow catalyst deactivation kinetics makes it feasible to maintain essentially steady performance in a discrete addition-withdrawal mode.
- 2) The gas phase moves in plug flow (Muroyama and Fan, 1985).
- 3) The slurry phase can also be modeled using the plug flow model. This assumption is valid if the reciprocal of the Peclet number is less than 1.0 (Kohler, 1986). In this particular study, this criterion was satisfied. Commercial H-coal reactors tend to be well-mixed (Li and Lin, 1981) due to the large diameters. The present analysis can still be used since the large recycle stream in conjunction with the plug flow reactor usually results in a CSTR performance (Levenspiel, 1972).
- 4) The reactor operates in an isothermal mode. This is a reasonable assumption in view of the observation of Li and Lin (1981) of not more than 8°C rise in axial reactor temperature. Van Driesen and Stewart (1964) also reported a virtually uniform temperature distribution throughout the H-Oil fluidized-bed reactor even when the heat of reaction was sufficient to raise the temperature of the entire feed by 56°C. The uniform temperature distribution within the H-Oil or H-Coal reactor is due primarily to the large recycle flow of the liquid.

- 5) The reaction phase components participating in the reactions (i.e., coal, preasphaltenes, asphaltenes and oils) are assumed to be relatively non-volatile so that mass transfer of these components to the gas phase can be neglected.
- 6) Mass transfer resistance from liquid to catalyst is negligible.

Based on the above assumptions, the following mass balance equations can be written:

Gas Phase:

$$\frac{dy_i}{dz} = \frac{-St}{m_i} (y_i - m_i c_i) \quad (22)$$

Liquid Phase:

$$\frac{dc_i}{dz} = \frac{St}{m_i} \cdot \frac{1}{U_r} (y_i - m_i c_i) - \tau r_i \quad (23)$$

The subscript i refers to the components and in the gas phase only one component is present (H_2). In the liquid phase, $i = H_2$ (liq), C (coal), P (preasphaltenes), A (asphaltenes) O (oil), and G (gases).

Also,

$$y_i = \frac{C_{G,i}}{C_{G,in}} \quad c_i = \frac{C_{L,i}}{C_{G,in}} \text{ (for } H_2) = \frac{C_{L,i}}{C_{tot}} \text{ (for other components)}$$

$$z = \frac{x}{L} \quad U_r = \frac{U_L}{U_G} \quad St = \frac{L k_L a}{U_G} \quad \tau = \frac{L \epsilon_L}{U_L}$$

$r_i =$ reaction rates for liquid phase components and are defined as below

$$r_{H_2(1iq)} = k_{H_2} C_{H_2}$$

$$r_C = k_1 C_C C_0 + k_4 C_C$$

$$r_P = (k_2 + k_{2e}) C_P - k_1 (1 + \alpha) C_C C_0$$

$$r_A = (k_3 + k_{3e}) C_A - (k_2 + k_{2e}(1 - \epsilon)) C_P$$

$$r_0 = \alpha k_1 C_C C_0 - (k_3 + k_{3e}) C_A - k_{2e} \epsilon C_P$$

$$r_G = -k_4 C_C$$

a. Method of Solution

The mass balance equations (22) and (23) constitute a set of ordinary, first-order, non-linear differential equations. These equations are numerically integrated using the Runge-Kutta fourth-order technique (Carnahan et al., 1969). The initial conditions for the slurry entering the reactor have to be obtained using a trial and error method. The reason becomes apparent on examining Figure I-3. The slurry entering the reactor consists of fresh feed and a recycle slurry stream. Thus, if one wishes to obtain the conversion obtained in the reactor, then the composition of the recycle stream is unknown. The method of successive substitution is used for obtaining the correct initial conditions. The method proceeds as follows:

- 1) Guess the composition of the recycle stream. The initial guess is the fresh feed composition.

The above parameters were obtained for only a single temperature (425°C) and hence the activation energies for the above reactions could not be obtained. This precludes the use of these kinetic parameters at any other temperature. From the values of the rate constants, it appears that the primary step in coal liquefaction, the rupture of coal to form lower molecular weight products, is predominantly thermal in nature. The data also revealed that the catalyst was relatively ineffective for the preasphaltene to asphaltene reaction probably due to the relatively large molecular size of the preasphaltenes which led to restricted diffusion rates in the pores of the pellet.

Diffusivity values for preasphaltenes and asphaltenes needed in the calculation of effective catalytic rate constants were obtained from the data of Curtis et al. (1986). They were as follows:

$$\text{Diffusivity of preasphaltenes} = 1.736 \times 10^{-6} \frac{\text{cm}^3}{\text{cm}_p \cdot \text{s}}$$

$$\text{Diffusivity of asphaltenes} = 2.18 \times 10^{-5} \frac{\text{cm}^3}{\text{cm}_p \cdot \text{s}}$$

b. Hydrogen Consumption Kinetics

Hydrogen consumption kinetics have been discussed by Albal et al. (1983). Rao et al. (1982) used multiple step-wise regression to correlate hydrogen consumption with the yields of SRC (Solvent Refined Coal) and distillates. The reaction model used here is a lumped kinetic model and is of the following form.

$$(-r_{\text{H}_2}) = k_o \exp\left(\frac{-E}{RT}\right) C_{\text{H}_2}$$

where $k_o = 2.1 \times 10^4$ (1/s)

$E = 5850$ cal/gmole

The solubility of hydrogen in the liquid phase is found using Henry's Law:

$$C_{H_2L} = \frac{C_{H_2G}}{M}$$

where $\frac{1}{M} = H = \bar{H} \exp\left(\frac{-\Delta H_s}{RT}\right)$

$\bar{H} =$ solubility constant = 1.2

$\Delta H_s =$ heat of dissolution = 770 cal/gmole

c. Slurry Properties

The physical properties of the slurry were obtained from the data of Schaefer et al. (1983). The properties for the different runs are reported in Appendix I.

Case Study

The ebullated bed reactor simulation was carried out for Run No. 43B (Appendix I-A). The gas holdup predicted by the hydrodynamic model of Darton and Harrison (1975) was in good agreement with the experimental values as can be seen from Table I-6.

Table I-6: Comparison of Experimental Holdup
 Values with those Predicted from
 Darton and Harrison's Model.

	Experimental Value	Predicted Value
Gas Holdup, ϵ_G	0.25	0.25
Slurry Holdup, ϵ_{Lf}	0.35	0.39
Catalyst Holdup, ϵ_C	0.40	0.36

The predicted value of slurry and catalyst holdups, however did not agree quite as well with the experimental values. While the gas holdup depends primarily on the bubble rise velocity, the Richardson-Zaki parameters U_T and n have a major effect on predictions of catalyst and slurry holdups. In fact, Schaefer et al. (1983) had to increase the viscosity of the slurry by a factor of 4 to obtain Richardson-Zaki parameters that predicted catalyst and slurry holdups which agreed well with experimental values. Thus the bubble rise velocity and Richardson-Zaki parameters are the critical parameters needed for the prediction of phase holdups in a three-phase fluidized bed reactor.

The model predicted a coal conversion of only 50%. The low conversion is not unexpected since the residence time of the slurry in the reactor was only 82.5 sec. Since the reaction model was specific for the catalyst system of Gollakota et al. (1985), comparisons with experimental PDU coal conversions could not be made. The concentration profiles for the reactants and products are shown in Figures I-5 and I-6. The liquid phase concentration profiles are not very steep despite the plug flow assumption. This can be attributed to

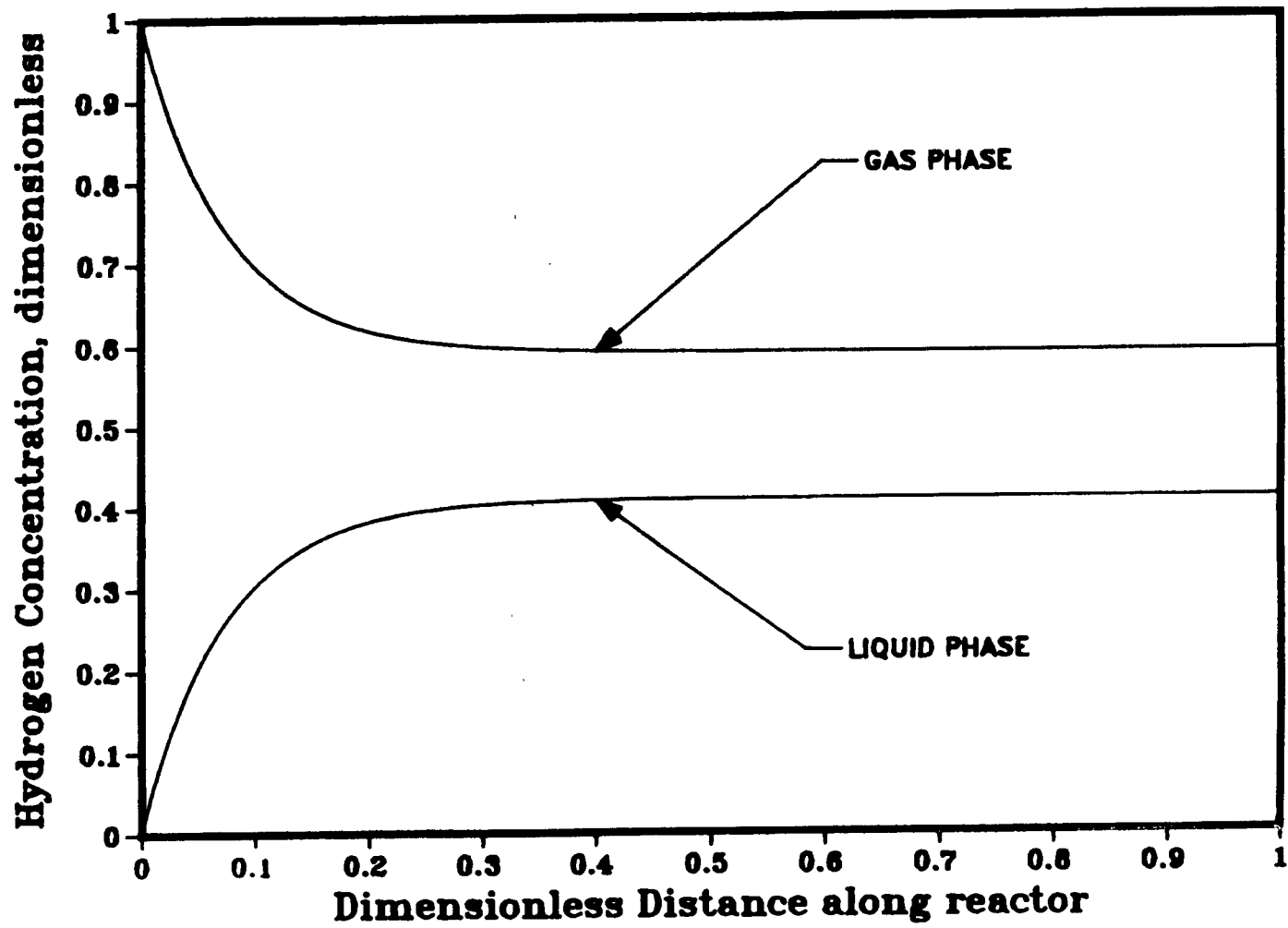


Figure I-5: Hydrogen Concentration Profile in Reactor

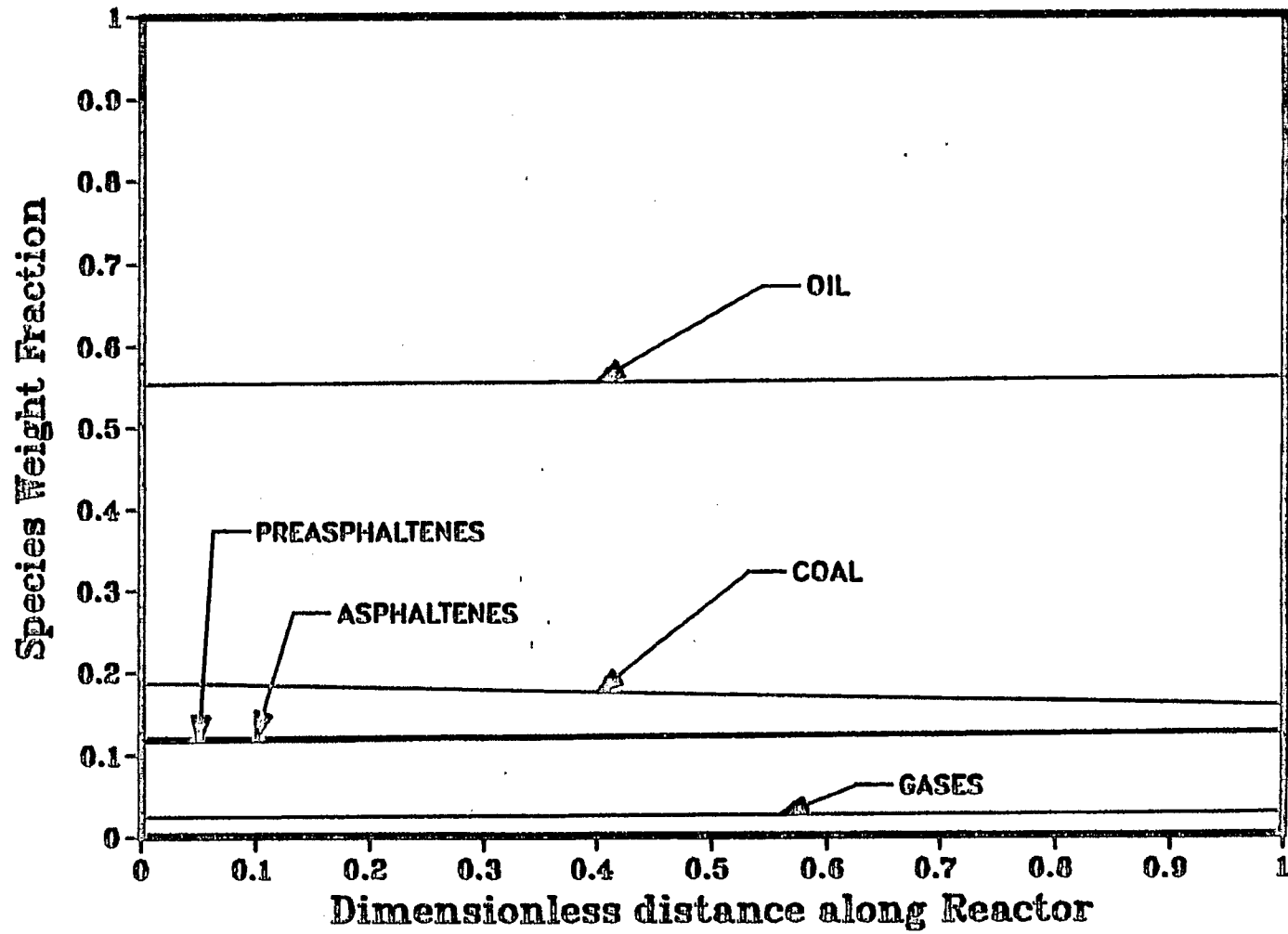


Figure I-6; Concentration Profiles of Liquid Phase Reactants and Products in Reactor

the relatively slow kinetics and the large recycle ratio (5.2), which tends to make the entire reactor behave as a CSTR (Levenspiel, 1972; Rao et al., 1982).

In the present study, mass transfer of hydrogen from the gas phase to the liquid phase was relatively unimportant since the mass transfer resistance ($1/k_L a = 30$) was much lower than the kinetic resistance ($1/k_{H_2} \epsilon_{Lf} = 2419$). The kinetic constant for the hydrogen consumption reactions used in this study is not truly representative of catalytic reactions and for the case of highly active catalysts, the kinetic constant can become high enough for mass transfer limitations to set in. This was the case observed by Feldman et al. (1971) for the hydrogenation of a coal tar.

Conclusions

A reactor model was developed for the second stage ebullated bed reactor of the Wilsonville ITSL process. This completes reactor model development for both stages. The first stage was modeled in a previous report (Brainard et al, 1984). The reactor model takes into account the thermal and catalytic reactions taking place in the reactor by using the kinetic model developed by Gollakota et al (1985) for the catalytic liquefaction of bituminous Elkhorn No. 3 coal. The hydrodynamic model of Darton and Harrison (1975) predicted values of gas holdup which were in good agreement with the experimental value. The predicted values of slurry and catalyst holdup were strong functions of the Richardson-Zaki parameters. Due to the absence of a distributed kinetic model for second stage liquefaction, comparison of experimental and predicted species concentration could not be performed. This reveals the need to develop a reliable kinetic model along with the reactor model development.

Notation

$C_{G,i}$	gas phase concentration of component i , kmol/m ³
$C_{G,in}$	inlet gas phase concentration, kmol/m ³
c_i	dimensionless concentration of component i in liquid phase
$C_{L,i}$	liquid phase concentration of component i , gm/cc slurry
C_{tot}	total liquid phase concentration, gm/cc slurry
d_p	pellet diameter, cm
D_L	liquid phase dispersion coefficient, m ² /s
D_p, D_A	effective diffusivity of preasphaltenes and asphaltenes, cm ³ /(cm _p .s)
H_{mf}	height of fluidized bed at minimum fluidizing conditions, m
H_{LG}	height of gas-liquid fluidized bed at operating conditions
k_1-k_4	reaction rate constants for thermal reactions (first order, 1/s)
\bar{k}_2, \bar{k}_3	first order rate constants for catalytic reactions, cm ³ /(cm _p ³ .s)
$k_L a$	gas-liquid mass transfer coefficient, 1/s
K	ratio of liquid-wake/bubble volume
n	Richardson-Zaki expansion index
L	effective reactor height, m
m	catalyst loading, gm/cc
m_i	solubility coefficient for component i
r_i	reaction rates
Pe_L	liquid phase Peclet number
St	Stanton number
U_G	superficial gas phase velocity, m/s
U_L	superficial liquid phase velocity, m/s
U_z	linear liquid phase velocity, m/s
U_T	particle terminal velocity, m/s
U_s	slip velocity of gas relative to liquid, m/s

U_{BO} rising velocity of isolated bubble in stagnant fluid, m/s
 V_{CD} gas drift flux, m/s
 x distance along reactor, m
 y_i dimensionless gas phase concentration of component i
 z dimensionless reactor distance

Greek

ϵ_L liquid phase holdup
 ϵ_G gas phase holdup
 ϵ_{Lf} homogeneous slurry phase holdup
 ϵ_f volume fraction of solids in slurry
 ϵ_{mf} void fraction at minimum fluidization conditions
 ρ catalyst pellet density, gm/cc
 τ slurry phase residence time, sec
 η_1, η_2 effectiveness factors

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