SEPARATION OF SOLID RESIDUES
FROM A SYNTHETIC LIQUID FUEL

by

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CHAPTER I

INTRODUCTION

The aims of this work were: first, to recognize and define the applicability and the deficiency of the existing solid-liquid separation technologies for the removal of solid residues from liquefied coal; second, to determine the conditions of liquefaction which would lead to easier separation; third, to improve the existing theories and/or design equations relating to solid-liquid separations; and finally, to make recommendations on the direction of future research.

Chapter II contains the survey of the recent developments in the field of solid-liquid separation. Special emphases are given to filtration and centrifugation. In those two techniques, some theoretical considerations leading to the design equations are presented. This chapter also includes the results of pilot plant and/or bench scale studies with coal liquids by other investigators on the separation techniques including filtration, centrifugation, separation by hydroclones, sedimentation, floatation, and magnetic separation. The conditions of maximum efficiency, the extent of separation, and the limitations of the above techniques are also discussed. Chapter II also discusses briefly new separation concepts, such as semi-fluidized bed filtration and cross flow filtration, that could have possible applications in coal liquefaction processes.

Chapter III and Chapter IV contain the experimental portion of this work. In Chapter III, experimental data of the atmospheric liquefaction of a Texas lignite through the solvolysis process are presented. The effect of the reaction conditions on the yields of product liquids and gases and residual solids is discussed. Chapter IV presents results of the filtration study with the liquefied lignite slurries obtained in the work described in Chapter III.

Chapter V describes a computer simulation of a continuous liquefied coal filtration process. The simulation has been performed with filtration parameters determined in the work given in Chapter IV. Chapter V also presents an efficient numeric scheme for solving systems of highly coupled and stiff partial differential equations frequently encountered in moving boundary problems.

Finally, future research areas relating to the work presented here are recommended in Chapter VI.

CHAPTER II

SOLID-LIQUID SEPARATION IN COAL LIQUEFACTION

INTRODUCTION

In spite of recent advances in coal liquefaction processes, all of
them including Synthoil, COED, SRC, H-Coal and CSF have a common barrier
toward commercialization, that is, solid residue removal from the product
stream is costly. Batchelor and Shih (1975) estimated the cost of solids
separation to be in the range of $1.53 to $3.24 per barrel of coal liquid
based on a 15% discounted cash flow rate of return on capital investment.

The difficulty in separation arises from the high viscosity of the
coal liquid, the high solids concentration, and the high concentration of
small residue particles. For example, the so-called solvent refined coal
is a solid at room temperature; and 50 number % of the solids in the H-Coal
liquid have diameters less than 0.11 microns while 50 volume % have diameters
less than 0.98 microns (Oak Ridge National Laboratory, 1975b). Therefore,
to effectively remove the solids, the separation processes must be performed
at an elevated temperature and pressure which lead to high cost.

Solids removal is essential in order for coal liquids to satisfy the EPA
requirements of 0.96% Sulfur and 0.15% ash for a 16,000 BTU/lb (3.7×10^7 J/Kg)
pollution-free solid combustion product (Rodgers and Westmoreland, 1976).
In other words, solids removal eliminates the need for stack gas clean-up.

This paper surveys the recent literature and the state-of-the-art on
the solid residue-liquid product separation in coal liquefaction processes.
Theoretical background leading to the design equations is discussed, and
separation techniques used in different coal liquefaction processes are
described.

COAL LIQUEFACTION PROCESSES

It is not the primary purpose of this report to exhaustively review the available coal liquefaction processes, as numerous review articles have been written on the subject (e.g. Friedman, et. al., 1974; Taylor and Hall, 1975; ERDA, 1975; Huebler, 1974; Squires, 1974; Klass, 1975; Wen, 1974). However, a brief summary of the major liquefaction processes will be given to facilitate the understanding of the associated solids separation problems.

Coal liquefaction processes can generally be classified into four categories: pyrolysis, indirect hydrogenation, direct hydrogenation, and solvent extraction. Pyrolysis processes are those that pyrolyze coal to obtain gas, liquid, and char. As expected, the liquid yield of the pyrolysis process, though significant, is not as high as that of the gas product. The liquid product generally accounts for 15-30% of the total product BTU's (Klass, 1975). Some of the available pyrolysis processes are COED, Coalcon, TOSCO, and Garret.

In indirect hydrogenation processes, steam and hot coal are reacted to produce carbon monoxide and hydrogen, and carbon monoxide is then hydrogenated in the presence of catalysts to form a mixture of aliphatic hydrocarbons via the Fischer-Tropsch synthesis. The most successful commercial operation of the indirect hydrogenation process is the Synthol process operated by the South African Coal, Oil and Gas Corporation.

In the direct hydrogenation processes, coal is slurried in a process derived liquid and liquefied in the presence of a catalyst. Synthoil and H-Coal are two direct hydrogenation processes.

Distinction between the direct hydrogenation and solvent extraction processes is vague. In an extraction process, coal is dissolved in the absence of a catalyst by a process derived solvent. The process derived solvent may

be catalytically hydrogenated before recycling; however, no direct contact between coal and catalysts is made. Solvent Refined Coal, Consol Synthetic Fuel, Exxon Donor Solvent, and Kyushu-Koshi Solvolysis are solvent extraction processes. Operating conditions of major coal liquefaction processes are summarized in Table 1.

FILTRATION

Theory

Flow of filtrate through the accumulated cake can be visualized as flow of liquid through numerous pores, with the pressure drop through the cake equal to the sum of all drag forces on the pores (McCabe and Smith, 1956). Incorporation of the definition of friction factor, f, in a force balance on the pores will yield the following relationship:

$$f = \frac{(P_a - P_b)g_c r_H}{L\rho v} \tag{1}$$

where

$P_a - P_b$ = pressure drop between a and b as shown in Figure 1.

g_c = conversion factor

r_H = average hydraulic radius

L = cake depth or thickness

ρ = density of filtrate

v = average velocity through the pores

For a bed with a given porosity of ϵ, the average hydraulic radius, r_H, is defined as the total void volume divided by the total surface area,

$$r_H = \frac{N v_p \epsilon/(1-\epsilon)}{N S_p} \tag{2}$$

where

N = total number of particles

v_p = volume per particle

S_p = surface area per particle

Rearrangement of equation (2) results in

$$r_H = \frac{\varepsilon v_p}{(1-\varepsilon)S_p} \quad . \tag{3}$$

Substitution of equation (3) and the relationship between v and the specific velocity, u,

$$v = \frac{u}{\varepsilon}$$

into equation (1) yields

$$f = \frac{(P_a - P_b)g_c \varepsilon^3 v_p}{L\rho u^2 (1-\varepsilon)Sp} \quad . \tag{4}$$

This known as the Kozeny-Carman Equation (McCabe and Smith, 1956). Since the Reynolds number is generally defined as

$$Re = \frac{v\rho r_H}{\mu}, \tag{5}$$

we have

$$Re = \frac{u\rho v_p}{\mu Sp(1-\varepsilon)} \quad .$$

For a flow at a low Reynolds number, the friction factor is inversely proportional to it (Bird, et. al., 1960), i.e.,

$$f \propto \frac{1}{Re} \quad . \tag{6}$$

Substituting equations (5) and (6) into equation (4) and rearranging the resultant expression, we obtain

$$\frac{dp}{dL} = \frac{k\mu u(1-\varepsilon)^2 (S_p/v_p)^2}{g_c \varepsilon^3} \tag{7}$$

where k is a proportionality constant. For randomly packed particles of definite size and shape, k is 5 (McCabe and Smith, 1956).

Filter depth can be related to the weight of the cake accumulated as follows:

$$dm = \rho_p(1-\varepsilon)AdL \tag{8}$$

where p_p is the density of the particles. Substituting equation (8) into equation (7) and rearranging the resultant expression we obtain the following equation:

$$dP = \frac{k\mu u(S_p/v_p)^2(1-\varepsilon)}{g_c\rho_p A\varepsilon^3} \, dm \quad . \tag{9}$$

For incompressible cake,

$$\Delta P_c = \frac{k\mu u(S_p/v_p)^2(1-\varepsilon)m_c}{g_c\rho_p A\varepsilon^3} \tag{10}$$

where

$\Delta P_c = P' - P_a$, pressure drop across the cake as shown in Figure 1

m_c = mass of the accumulated cake

For compressible cake, ε, ρ_p, k, s_p, and v_p vary within the cake. These are lumped into a single variable termed the local specific cake resistance,

$$\alpha_L = \frac{k(S_p/v_p)^2(1-\varepsilon)}{\varepsilon^3\rho_p} \tag{11}$$

which depends only on pressure drop. Substitution of this result into equation (9) gives

$$dP = \frac{\mu u\alpha_L}{g_c A} \, dm \quad . \tag{12}$$

Since

$$d(P - P_a) = dP$$

we then have

$$\frac{d(P - P_a)}{\alpha_L} = \frac{\mu u}{g_c A} \, dm \tag{13}$$

where

P_a = pressure at the upstream cake face as shown in Figure 1.

Integration of equation (13) over the accumulated cake yields

$$\int_0^{\Delta P_c} \frac{d(P - P_a)}{\alpha_L} = \frac{\mu u}{g_c A} \int_0^{m_c} dm$$

$$= \frac{\mu u m_c}{g_c A} , \tag{14}$$

The average specific cake resistance, α, is defined as follows:

$$\frac{\Delta P_c}{\alpha} = \int_0^{\Delta P_c} \frac{d(P - P_a)}{\alpha_L} \tag{15}$$

and equation (14) can be written as

$$\frac{\Delta P_c}{\alpha} = \frac{\mu u m_c}{g_c A} . \tag{16}$$

The filter medium resistance is defined analogous to the cake resis-

tance as

$$\frac{P' - P_b}{R_m} = \frac{\Delta P_m}{R_m}$$

$$= \frac{\mu u}{g_c} \tag{17}$$

where

$P' - P_b$ = pressure drop across the medium as shown in Figure 1

R_m = filter medium resistance.

Equations (16) and (17) can be combined to find the pressure drop through

the cake and the medium:

$$\Delta P = \Delta P_c + \Delta P_m$$

$$= \frac{\mu u}{g_c} \left(\frac{m_c \alpha}{A} + R_m \right) . \tag{18}$$

The specific velocity, u, of the filtrate can be expressed in terms of the volume of the filtrate collected as

$$u = \frac{dV/d\theta}{A} \tag{19}$$

where

V = volume of filtrate collected

θ = time

A = filter area

Substitution of equation (19) into equation (18) and subsequent rearrangement result in a form of Ruth's equation:

$$\frac{d\theta}{dV} = \frac{\mu}{Ag_c \Delta P} \left(\frac{\alpha c V}{A} + R_m \right) \tag{20}$$

where

$c = m_c/V$, the mass of particles deposited in the filter per unit

volume of filtrate.

For constant pressure filtration, as in most of the tests made in coal lique-faction, equation (20) can be integrated and rearranged to obtain

$$\frac{\theta}{(V/A)} = \frac{\mu}{g_c \Delta P} \left[\frac{c\alpha}{2} \left(\frac{V}{A} \right) + R_m \right] . \tag{21}$$

Equation (21) is used to find the average specific cake resistance and it also serves as a design equation. In the determination of the average specific cake resistance from experimental data obtained at constant temperature and pressure, $\frac{\theta}{V/A}$ is plotted against V/A, as shown in Figure 2; the slope is $\frac{\mu c\alpha}{2\Delta P g_c}$, and the intercept is $\frac{\mu R_m}{\Delta P g_c}$. With experimental measurements of μ, ΔP and c in hand, both α and R_m can be calculated.

Tiller (1962) has shown that for most compressible cakes, the average specific cake resistance, α, can be expressed by

$$\alpha = \alpha_o \Delta P^s \text{ for } \Delta P > \Delta P_i \qquad (22)$$

and

$$\alpha = \alpha_i$$
$$= \alpha_o \Delta P_i^s \text{ for } \Delta P \leq \Delta P_i \qquad (23)$$

where

α_o = particle size constant

ΔP = pressure drop across the cake and medium

ΔP_i = critical pressure

s = compressibility

The average specific cake resistance, as represented by equations (22) and (23), is shown in Figure 3 as a function of pressure drop. The compressibility, s, of the cake ranges between 0 and 1, with the compressibility of an incompressible cake equal to 0.

Applications in Liquefaction Processes

Only a few of the commercial filters presently available can operate at the conditions required by coal liquefaction processes. Rotary precoat drum filters and precoat leaf filters have been closely studied in many liquefaction pilot plants. Some have been tested at temperatures as high as 700° F (371° C) and pressures as high as 200 psig (14.6 atm.). The size of these pilot plant filters in terms of filter area ranged approximately from 5 sq ft (0.46 m^2) to 80 sq ft (7.43 m^2). The average highest sustained filtration rate of approximately 10 gal/(hr - ft^2) (0.41 m/hr) was observed (Oak Ridge National Laboratory, 1975a; Rodgers, et. al., 1976).

Filtration tests conducted for some coal liquefaction processes are sum-marized in Table 2. In the Char Oil Energy Development (COED) process, solids concentration of 3∿17 wt% in the feed was consistently reduced to 0.01∿0.09 wt% in the filtrate with a Goslin-Birmingham rotary precoat drum filter. The filtration rate which varied from 4.1∿9.5 gal/hr-ft^2 (0.17∿0.39 m/hr) was dependent on the type of coal liquefied as shown in Table 3 (Schoemann, et al, 1974). A similar filter used in the H-Coal process resulted in a filtration rate of 160 lb/hr-ft^2 (781 kg/hr-m^2) based on the submerged area, which is equivalent to 9.7 gal/hr-ft^2 (0.40 m/hr) (Katz, et. al., 1976a).

In the Consol Synthetic Fuel (CSF) process, a Dorr-Oliver rotary drum filter was studied at 150 psig (11.2 atm) and 600° F (316° C) (Oak Ridge National Laboratory, 1975a). Unlike Goslin-Birmingham rotary precoat drum filters used in most liquefaction processes, the Dorr-Oliver rotary drum filter has an inside-out flow pattern which made observation of cake build-up and cutting blade advancement impossible. This and other mechanical problems in addition to the fact that the equipment could not operate under leak-free conditions caused the filtration studies to be terminated (Wheeler Corp., 1971; Consolidation Coal Co., 1973).

In the Solvent Refined Coal (SRC) process, (Rodgers, et. al., 1976; Oak Ridge National Laboratory, 1975a), rotary drum filters, one with a filter area, of 40 sq ft (3.7 m^2) and the other with a filter area of 80 sq. ft. (7.4 m^2), are expected to be operated at 100∿200 psig (7.18∿14.6 atm) and 500°∿700°F (288°∿371°C). No data were reported due to minor mechanical problems. These are the largest filters in testing. It is believed that the results from these units can be used in direct scale-up to commericial liquefaction

plants with filter areas as large as $500 \sim 700$ sq ft ($46.5 \sim 65$ m^2) per filter. A Funda horizontal leaf filter with a filter area of 54 sq ft (5.0 m^2) was also tested at the same conditions as the two Goslin-Birmingham filters. The Funda filtering process consisted of 90 minute cycles, each including 40 minutes of filtration and 50 minutes of cleaning and precoat. Filtration rates of $12 \sim 14$ gal/hr-ft^2 ($0.49 \sim 0.57$ m/hr) based on actual filtration time was reported. This is equivalent to rates obtained with rotary drum filters on a per-cycle basis. Ash and Sulfur concentrations were reduced to 0.11% and 0.82%, respectively (Oak Ridge National Laboratory, 1975a; Wright, 1975; Lewton, 1975; Rodgers, et. al., 1976). Problems with screen tearing were encountered. Although the filtration rate of a Funda leaf filter was similar to that of the corresponding rotary drum filter, the capital cost of the former is higher than that of the latter. Batchelor and Shih (1975) showed that the cost of solids removal to be 22% higher for leaf filters. Design parameters of filtration for the SRC process was determined by Katz and Rodgers (1976). Filtration data, plotted according to equation (21), are shown in Figure 2. For filtration approximately at $300°$ F ($150°$ C), the compressibility of the filter cake as defined by equation (22) was determined to be 0.49, and the particle size constant, α_o, was determined to be 2.5 hr-ft^4/gal-in-Cp-lb$^{\frac{1}{2}}$ (92 m-hr^2/kg$^{\frac{3}{2}}$). Akhtar et. al. (1974) reported that centrifugation is effective in removing ash from liquefied coal of the Synthoil process. The early filtration studies were, therefore, aimed at improving the centrifuged product to an ultra-low-ash gas turbine fuel. In recent studies, however, direct filtration of solids from liquefied coal has been investigated. Weintraub, et. al. (1976) reported the success of direct filtration in consistently reducing the ash content from 5.7% to below 0.1%.

Similar problems were encountered in all processes discussed above. For example, mechanical failures were experienced due to thermal stress;

leak-free systems were hard to maintain; angle and advancement of the cake cutting knife were difficult to control. These problems, however, do not appear to be insurmountable. What should be of concern here is that the high filtration cost be reduced to a level where commercialization of liquefaction plants is possible.

Methods of improving the filtration rate, which lead to lower filtration cost, are being investigated. The work being carried out at the Oak Ridge National Laboratory has lead to two approaches of improving solids removal from coal liquids (Rodgers and Westmoreland, 1976; Katz and Rodgers, 1976b). The first involves the substitution of ground coal for diatomaceous earth as precoat and body feed. Rodgers and Westmoreland (1976) reported the effectiveness of using ground coal as a precoat. In their laboratory filtration tests, filtration rates obtained with coal precoat were consistently higher than those obtained with a standard diatomaceous earth precoat as shown in Figure 4. The maximum coal precoat particle size which will still produce a filtrate satisfying EPA requirements for a 16,000 BTU/lb (3.7×10^7 J/kg) solid fuel appears to be 100 to 120 mesh. One limitation of using a bituminous coal precoat is that coal liquids can only be filtered at a temperature no higher than 450°F (232°C) due to the softening characteristics of bitiminous coals. Fortunately, most liquefaction process filtrations can be performed at or below this temperature. For those that require higher process temperatures, it was suggested that anthracite coal or coke be used. The addition of coal as body feed also increased the filtration rate as can be seen in Figure 5. The most efficient method of increasing the filtration rate, however, is to maintain an ultra-thin cake. It was shown that the filtration rate doubled as cake thickness was reduced from 1/4 inch to 1/8 inch and that the rate

increased ten times when the cake thickness was reduced to "zero". An ultra-thin cake can be achieved by advancing the blade of a rotary drum filter at a rate equal to or slightly greater than the rate of solids deposition. The use of coal as a precoat and body feed will permit the filtration process to be operated at "zero" cake thickness without creating contamination problems, as diatomaceous earth would, when solids are fed to a gasifier to produce hydrogen and carbon monoxide. With the low cost of coal (coal is only one tenth as expensive as diatomaceous earth) and increased filtration at "zero" cake thickness, Rodgers and Westmoreland (1976) calculated a 90% reduction in solids removal cost.

The other approach of Rodgers and Westmoreland (1976) and Katz and Rodgers (1976b) in improving solid-liquid separation is the addition of solvents. They found that the filtration rates could be increased by the agglomeration of solids by toluene, the addition of process solvent, and the settling of the unfiltered oil before filtration. In both optical micrograph observation and settling rate measurements, agglomerates of 100 particles or more were confirmed for a mixture of 20% toluene and 80% SRC unfiltered oil. As a result of this agglomeration, an increase in the filtration rate of three and one-half times was measured for a 5% toluene/ 95% SRC unfiltered oil mixture as compared to that of the SRC unfiltered oil alone in tests at 100°C (212°F) and 50 psi (3.4 atm). Significant increases were also observed when the SRC process derived solvent was added to the SRC unfiltered oil prior to filtration. For example, a thirty percent dilution with process derived oil approximately doubled the filtration rate. Similar results were also observed in the Synthoil product diluted with light oil (Newman, et. al., 1976).

In filtration tests with the upper 20 to 30% portion from a sedimentation column, and increase in the filtration rate of up to 30 times was observed. This increase was attained only when sedimentation was carried out at 250° ˜ 310°C (482° ˜ 590°F), showing its temperature dependence.

CENTRIFUGATION

Theory

A particle settling in a constant force field has a terminal velocity given by Stoke's solution (see, e.g., Bird, et. al., 1960)

$$v_\infty = \frac{D_p^2 \, f(\rho_s - \rho)}{18\mu} \tag{24}$$

where

D_p = diameter of the particle

f = force field

ρ_s = density of the particle

ρ = density fo the fluid

μ = viscosity of the fluid

The force field, f, is replaced by g, the gravitational acceleration, for sedimentation.

Although in a centrifuge the force on a particle is increasing as the particle travels away from the axis of rotation and thus never reaches the terminal velocity, equation (24) can still be used to estimate the instantaneous settling velocity of a particle at a distance, r, from the axis of rotation:

$$v_\infty = \frac{D_p^2 \, \omega^2 r(\rho_s - \rho)}{18\mu} \tag{25}$$

where

ω = angular velocity, rad./time

The design equation for a tubular centrifuge can be developed as follows (Perry, 1973):

When a dilute suspension of uniform particles is fed to a centrifuge, the time, t, in which half the solids would settle is given by

$$t = \frac{s/2}{v_\infty} \tag{26}$$

where s is the liquid thickness, provided that the liquid thickness is thin. For a continuous process this would correspond to a feedrate of

$$q = \frac{V}{t}$$
$$= \frac{2V v_\infty}{s} \tag{27}$$

where V is the volume of liquid in the centrifuge. Substitution of equation (25) into equation (27) gives the rate at which half the solid is removed:

$$q = \frac{(\rho_s - \rho) \; D_p^{\;2} \; V \; \omega^2 R}{9\mu s} \tag{28}$$

where R is the radius of the centrifuge bowl.

For a slurry of non-uniform particles being bed to a centrifuge at a constant rate q, the critical diameter, D_{sc}, is obtained by the rearrangement of equation (28):

$$D_{sc} = \sqrt{\frac{9q\mu s}{(\rho_s - \rho) \; V \; \omega^2 R}} \tag{29}$$

Most particles with diameters larger than D_{sc} will be in the settled cake; most particles with diameters smaller than D_{sc} will stay in the effluent; and particles with diameter D_{sc} will be divided equally between the effluent and settled cake. With the particle size distribution known, equation (29) can be sued to establish a flow for the desired separation.

It should be noted that an accurate determination of all the parameters and variables in the equations presented in the preceding sections is extremely difficult, if not impossible, for a complex mixture of the solid residue and product oil from any coal liquefaction process.

Applications in Liquefaction Processes

Applications of centrifugation in coal liquefaction processes were not investigated as thoroughly as were applications of filtration. The reason is that solids separation in early centrifugation tests was not satisfactory. In all but the Synthoil process, filtration has been considered as the primary separation process. For example, in the COED process no testing with the centrifuge was reported.

In the CSF process, a 6-in. Bird continuous solid-bowl centrifuge was tested at 100 psig (7.8 atm) and 600° F(316° C), however, no useful data were obtained due to the seal problem (Wheeler Corp., 1971). In the SRC process, a centrifuge system was included in the pilot plant design (Pittsburg and Midway Coal Mining Co., 1971). The design included a primary nozzle-disc centrifuge which was intended to deliver a solid-free coal solution, and a secondary nozzle-disc centrifuge and a solid-bowl centrifuge, both for concentration of solids in the underflow from the primary centrifuge. The nozzle-disc centrifuge was selected because it has the highest separating power of any centrifuge available in the size range considered. In an in-house test made by the Sharples Centrifuge Company, centrifugation of the SRC liquid at 200°F (93°C) showed poor solids separation (Oak Ridge National Laboratory, 1975a). This and other factors caused the centrifuge system to be eliminated from the plans for the construction of the pilot plant in which a filtration system was selected for solid-liquid separation (Pittsburgh and Midway Coal Mining Co., 1975).

In the H-Coal process, clean liquid was obtained with a Westfalia-Centrico centrifuge operating in a batch mode at $250°\sim350°$ F ($121°\sim177°$ C). The solid concentrate contained oil and dry cake in the ratio of 1.3. Operating in a continuous mode with nozzle rejection of solids, 90% reduction in solids content was observed in the overflow. Operation with greater than 20% solids in the solid concentrate plugged the nozzles. Tests were also made with a Sharples 1660 Super-D-Canter horizontal conveyor type centrifuge with continuous slurry feed. The test slurry consisted of 10 wt% Illinois #6 coal ground to pass 100 mesh in 10.1° API TCC catalytic cracking syntower bottoms. The best result gave a solids reject containing 68.6% coal with overflow containing 0.9% coal (Hydrocarbon Research, Inc., 1968).

In the Synthoil process, a Sharples Supercentrifuge with a 4-in (0.10 m) -I.D. x 30-in. (0.76 m) long vertically placed bowl was tested. The centrifuge was capable of producing a separational force of 13,200 g (129,000 Newtons/Kg) at the wall at 15,000 rpm. Operating in a continuous mode, solids reduction of less than 50% was observed (Oak Ridge National Laboratory, 1975a). However, when operated in a batch mode, centrifuged liquid containing 0.2% sulfur and 0.1% ash was obtained for a feed oil containing 11.7% residue from a 4000 psi operation. Poorer separation was observed with the product from a 2000 psi operation. Centrifugation was conducted at 80°C with a load of $90\sim95$ lb. ($41\sim43$ Kg) of liquified coal per batch. Outlet from the centrifuge was continuously recirculated through the bowl at a rate of 1.5 gpm (0.34 m^3/hr). Thirty minutes of centrifugation was allowed per batch. Longer batch periods resulted in negligible increases in the amount of solids removed (Akhtar et al., 1974). A summary of the centrifugation test is shown in Table 4.

OTHER SEPARATION TECHNIQUES

Several solid-liquid separation techniques which have not been applied extensively in coal liquefaction processes are described in this section.

Hydroclone

Hydroclones are similar to centrifuges in that both utilize centrifugal force in separating solids from liquid. Unlike centrifuges, however, hydroclones have no moving parts; thus, they are not prone to mechanical failures. In general, hydroclones have much smaller separating forces compared to centrifuges.

In the CSF process, mechanical difficulties which plagued the filtration unit led to the abandonment of filtration and to the investigation of the separational capability of the mechanically simpler hydroclones. Early tests with a 3-in. Heyl and Patterson hydroclone at 500°∿600°F (260°∿316°C) indicated a satisfactory removal of solids. More specifically, an average solids concentration of 9.1% in the feed was consistently reduced to an average concentration of 1.3% in the overflow with the underflow containing an average of 17% of the feed liquid (Consolidation Coal Co., 1969; 1971). Typical inlet velocity of 30 ft/sec (32,900 m/hr) resulted in a separational force of about 200 g (1,960 Newtons/kg) (Shroeder and Associates, 1970).

A system of three hydroclones was installed and tested at 600°F (316°C). It consisted of two 3-in. hydroclones in parallel and a single 3-in. wash hydroclone. The overflow from the first two hydroclones

contained 0.5 to 1.0% solids which amounted to about 2% solids in the product oil with the removal of recycle solvent (Wheeler Corp., 1971). The underflow from the first two hydroclones then passes through the wash hydroclone for further concentration resulting in a bottoms slurry containing 55% solids (Shroeder and Associates, 1970).

In scaling up, efficiencies of the hydroclones are usually lowered. The so-called Consol correlations, which are the summarized results of CSF hydroclone experiments, show that the maximum acceleration of an 8-in. (0.2 m) hydroclone is 77% less than that of a 3-in. (0.08 m) hydroclone (Wheeler Corp., 1971). It was also observed that the hydroclone separated particulate solids on a density basis since the solids in the overflow contained only about half as much ash as the solids in the feed. Thus, with the lower acceleration in the larger hydroclones, the ash content in the overflow would be expected to increase, requiring a second stage removal. A commercial plant of 50,000 barrels/day (1950 m^3/day) would require an impractically large number of hydroclones.

Sedimentation

Solids separation by sedimentation is controlled by temperature and/or the addition of deasphalting solvent. The deasphalting solvent reduces the solubility of a small fraction of coal extract, mainly the asphaltenes, thereby producing agglomerates of asphaltene and residue which separate rapidly. Gorin et al. (1977A) considered n-decane, other n-paraffins, and cyclohexane to be effective deasphalting solvents; while toluene

and other aromatic hydrocarbons are recommended by Rodgers and Westmoreland (1976) for agglomeration of solids.

Gorin et al., (1977a and b) investigated the settling characteristics of several different coals liquefied by the CSF and H-Coal processes. They observed the optimum settling temperature to be 600°F (316°C), with coking taking place at higher temperatures and wall deposition at lower temperatures (500°F or 260°C). This seems to be in good agreement with the results obtained by Rodgers and Westmoreland (1976), where settling was observed to occur at 250°~310°C (482°~590°F) for the SRC oil with toluene added.

In their study, Gorin et al. (1977a) found that the highly caking Eastern coal required no deasphalting solvent while the non-caking Western coal required the addition of n-decane in the weight ratio of decane to extraction solvent between 0.1 and 0.3 to achieve the desirable separation in a continuous settler. They attributed the low settling rate of the Western coal to the smaller particle size and to the fact that unlike the Eastern coal, little or no extract precipitation occurred during cooling to 600°F (316°C). The settling rate was also seen to be a function of the extent of coal conversion. For example, the initial settling rate was reduced from 2.0 in/min (3.0 m/hr) to 0.4 in/min (0.6 m/hr) as conversion on a moisture-ash-free basis is increased from 77% to 86%. This could be due to the smaller particles produced at higher conversions.

Good separation was obtained with the continuous settlers. Average ash content of 0.2 wt.% was consistently observed in the clarified extract at an overflow rate of about 250 and 500 lb/hr-ft^2 (1220 and 2440 kg/hr-m^2) corresponding to solvent-to-coal ratios of 1.5 and 2.0 in the liquefaction reactor.

Floatation

Floatation solids removal is a process in which a gas is injected into a hot slurry of liquefaction product through a perforated plate, called the diffuser. As the gas bubbles travel through the slurry, they retain on their interfaces with the liquid some of the solids that come in contact with them; solids are carried by the bubbles to the surface of the liquid where a layer of foam is produced. Removal of the foam gives rise to removal of the solids that are retained in the foam.

Experiments were carried out to investigate solids removal from the coal liquefaction product by floatation (Kermode, 1975). A synthetic mixture composed of refinery light-cycle oil with 6% cresol and coal solids was used. The coal solid was the bottoms from a vacuum still used in a liquefaction process. It contained the ash from the original coal, unconverted coal and some high molecular weight liquefaction products. Thus, the synthetic mixture closely approximated the actual coal liquefaction product. CO_2 was used as the foaming gas. Tests were made at several different temperatures: 70°, 95°, 110°, 125°C, with different heating arrangements and different preheating times. It was found that 30 minutes of preheating resulted in the optimum separation; with shorter preheating times, poor separation was observed while at longer preheating times, no improvement in separation was observed as compared to the preheating period of 30 minutes. The tests also showed that the heating of CO_2 gas and the foam section resulted in poorer separation. No separation was achieved without the addition of cresol. The pore size of the diffuser was also a determining factor in the degree of separation. For example, with a 40 micron diffuser, a maximum of 60% ash removal was measured at 110°C and 30 minutes

of preheating; with the same conditions a 60 micron diffuser resulted in a maximum of 30% ash removed; a 4 micron and an 8 micron diffuser showed poorer separation, and diffusers with pore size greater than 150 micron resulted in no separation at all. Further tests such as the determination of particle size distribution of the ash removed need to be completed before the effectiveness of the floatation process can be evaluated. For example, if the particles to be removed are in the range of the sub-micron size, the floatation process, when used in conjunction with a process which can easily remove the larger particles, i.e. centrifugation, sedimentation, or separation by hydroclone, may increase its effectiveness.

Magnetic Separation

The high gradient magnetic separation technology was developed to remove micron size mineral particles from highly dispersed kaolin clay slurry. The separator is in essence an electromagnet. The electromagnet consists of an iron box enclosing the energyzing coils. The coils in turn enclose a cylindrical, highly magnetized working volume which is loosely packed with fine strands of filamentary magnetic material such as stainless steel wool. When these fibers become magnetized by the high intensity background magnetic field, capture sites of intense magnetic forces are created over the surfaces of the fibers. This acts as a magnetic filter (Oder, 1976).

Magnetic separation is being studied in the H-Coal process and the SRC process (Oak Ridge National Laboratory, 1975a; Johnson, 1976; Maxwell, et al., 1976). The basis of separation is the magnetic susceptibility of the solids to be eliminated. If the susceptibility is high, magnetic separation is feasible. The susceptibility of FeS_2 and FeS is relatively low.

However, when the average atomic ratio of Fe to S is approximately 1.0:1.1, i.e., Fe_7S_8, the magnetic susceptibility is improved by a factor of 100 (Oak Ridge National Laboratory, 1975a; Maxwell, et al., 1976). By controlling the process conditions, mainly the hydrogen pressure, the H-Coal process has been able to produce the desired ratio.

In tests made at 300°~350°F (149°~177°C) with a 20,000 gauges unit manufactured by the Pacific Electric Motor Company of Oakland, California, 80 to 90% of the inorganic sulfur and about 30% of the ash were removed from the SRC product (Johnson, 1976). It was observed that at this temperature range, capture sites were rapidly saturated for the less susceptible ash, while no significant decrease in inorganic sulfur removal was detected.

The degree of solids removal by magnetic separation is also a function of the temperature as shown by the substantial increase in magnetic susceptibility of Fe_7S_8 in the range of 500°~600°F (260°~316°C). Tests made in this temperature range showed a maximum reduction of about 60% ash and 50% sulfur (Maxwell, et al., 1976).

Other Systems

New separation systems that can have possible applications in liquefaction process are: cross (field) flow filtration, convertible (semifluidized) bed filtration, ultrasonic-aided filtration, and hot water washing with surface active agents.

In cross flow filtration (Henry, et al., 1976; Yang, et al., 1976; Porter, 1975; Lewton, 1975), a separation field and a filtration flux normal to an axial flow between two flat plates are established. A schematic drawing of a cross flow filter is shown in Figure 6. The most

important aspect of cross flow filtration is the migration of particles away from the filter due to fluid shear and the imposed gradient; thus, the cake build-up is minimized and filtration rate is maximized. The imposed field could be magnetic, electric, thermal, or gravitational in nature.

Convertible (Semifluidized) bed filters utilize the novel concept of semifluidization (Wen and Fan, 1977; Fan, et. al., 1959; 1961; 1968). In essence, the maximum filtration rate is maintained by careful, but simple, control of the cake thickness. This is accomplished by controlling the degree of fluidization in the filter (see Chapter VI). The device is mechanically simple, thus, easy to maintain, operate, and control. It has all the advantages of continuous leaf or rotary precoat filters but none of operation difficulties, such as screen tear, improper blade advancement, leakage problem, etc., that are associated with these costly filters. A more detailed description of the convertible or semifluidized bed filter is presented in Chapter VI.

The filtration rate of conventional filters can be significantly increased with the introduction of ultrasonic waves (Murry, 1975). Ultrasonic waves have no significant control on the thickness of the cake formed, but instead, ultrasound improves the filtration rate by its influence over the passage of filtrate through the cake.

Solids in liquefied coal may also be separated by hot water or steam washing. The addition of surface active agents may change the interfacial property of the interface between water and liquified coal such that solids may be preferentially retained on the interface, and thus may be easily removed.

CONCLUDING REMARKS

The present review indicates that much remains to be done to determine the suitability of different processes for separation of the solid residue from liquefied coal, and to derive governing and design equations for each separation process. This is due to the peculiar properties and complex structures of the solid residue-liquid product mixture and its components. It appears that no single separation technique can be effective and economical for the solid residue-liquid product separation in a coal-liquefaction process. Therefore, development of a hybrid or combined separation process containing more than one separation process by means of available system synthesis techniques is highly desirable.

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Table 1. Summary of Major Coal Liquefaction Processes

Classification	Process	Description	Investigator	References
Pyrolysis	COED (Char-Oil-Energy-Development)	Pulverized coal at 375°F enters a series of fluidized bed at 600°, 850°, 1000°, and 1600°F and 6-10 psig. Product gas and recycled char furnish the heat for second and third stages. Oils from the second stage are condensed and hydrogenated.	FMC	ERDA (1975); Jones, et al, (1970); Long, et al, (1975); Jones, et al, (1972); Scotti, et al, (1974).
	Coalcon	Ground coal is preheated to 325°C and fed to the reactor fluidized by hydrogen gas. Liquefaction occurs at 500-900 psig and 560°C	Coalcon	Morgan (1975).
Indirect Hydrogenation	Syothol	Synthesis gas produced by the gasification of coal is purified and fed to the Fischer-Tropsch synthesis plant to produce low and medium boiling range oils	South African Coal, Oil and Gas (SASOL)	Chan (1974).
Direct Hydrogenation	Synthoil	Slurry of coal and process derived solvent is fed, along with hydrogen, to a turbulent packed-bed catalytic reactor. Coal is liquefied at 2000-4000 psig and 400-500°C.	U.S. Bureau of Mines	Akhtar, et al, (1974); Yanorsky, et al, (1974); ERDA (1975).
	H-Coal	Coal slurried in process derived solvent, hydrogen, and catalysts is liquefied in an ebullated bed reactor operated at 2,700 psig and 850°F.	Hydrocarbon Research	Huebler (1974); Johnson, et al, (1974); Squires (1974); Stotler (1974); ERDA (1975).
Solvent Extraction	Donor Solvent	Coal, hydrogen, and process derived solvent are fed to the liquefaction reactor operating at 1450-2500 psig and 370-480°C. Spent solvent is regenerated by catalytic hydrogenation before being introduced to the reactor.	Exxon	Furlong, et al, (1975).

Table 1 (Continued)

SRC (Solvent Refined Coal)	Coal slurried in process derived solvent is extracted at 1000 psig and 850°F in the presence of hydrogen. No catalyst used	Pittsburg and Midway Coal Mining	Schmid (1974); Tingey, et al.(1973); Wen, et al.(1975); Pastor, et al.(1976); ERDA (1975); Taylor (1975).
CSF (Consol Synthetic Fuel)	Coal slurried in process derived solvent is extracted at 250-500 psig and 750°-800°F. After the removal of ash and undissolved coal, the extract is then catalytically hydrotreated to yield recycle solvent and product fuel oil	Consolidation Coal	Wheeler Corp. (1972); Wise (1971); Parsona Co. (1970); Consolidation Coal Co. (1973).
Solvolysis (Kyushu-Koshi Process)	Pulverized coal is slurried in hot asphalt. Extraction occurs at atmospheric pressure and 400-450°C.	Government Industrial Research Institute of Japan (Kyushu-Koshi)	Honda, et al,(1974); Kruse (1976); Wise (1971).

Table 2. Summary of Filtration Tests Made by Some Liquefaction Processes

Filter	Process Application	Operating Conditions	Filter Area ft^2	Highest Filtration Rates gal/hr-ft^2	Remarks	References
Goslin-Birmingham rotary drum	COED	12-29psig 290-340°F	6	9.5	Highest filtration rate depends on the type of coal liquefied. A rate of only 4.1 gal/hr-ft^2 was reported for Wyoming Big Horn coal	Schoemann, et al. (1974); Jones, et al. (1971); Merrill, et al. (1975); Scotti, et al. (1974).
	H-Coal	30psig 400°F	4.7	9.7		Oak Ridge National Laboratory (1975a); Hydrocarbon Research, Inc. (1968).
	SRC	100-200psig	40 and 80		A number of minor mechanical problems encountered. No sustained run was reported.	Rodgers and Westmoreland (1976); Oak Ridge National Laboratory (1975a); Lewton (1975).
	SYNTHOIL	200psig 350°C	4.7		Filtration is aimed at upgrading centrifuged product oil to an ultra-low-ash fuel suitable for fixing gas turbins. .	Akhtar, et al. (1975); Weintraub, et al. (1976); Oak Ridge National Laboratory (1975a)

Table 2 (Continued)

Dorr-Oliver rotary drum	CSF	150psig 600°F			Mechanical problems prevented satisfactory operation.	Consolidation Coal Co. (1968); Shroeder and Associates (1970); Wheeler Corp. (1971); Oak Ridge National Laboratory (1975a).
Funda horizontal leaf	SRC	100-200 psig 550-700°F	54	15	Process consists of a 90 minute cycle, 40 minutes for filtration, 50 minutes for washing. Problem arose with tear in the filter screens.	Lewton (1975); Rodgers and Westmoreland (1976); Oak Ridge National Laboratory (1975a).
Ronningen-Petter	SYNTHOIL	200psig 350°F	.78			Akhtar, et al. (1975); Weintraub, et al. (1976); Oak Ridge National Laboratory (1975a).

Table 3. Filtration Results on Various Coals
in COED Process (Schomann, et al., 1974)

	Colorado Bear coal	Wyoming Big Horn Coal	Illinois No. 6 seam coal
Period of operation	30 weeks	5 weeks	44 weeks
Oil filtered	1290 bbl	90 bbl	1800 bbl
Solids in feed	6-17 wt%	9-11 wt%	3-9.5 wt%
Solids in filtrate	0.01-0.09 wt%	0.03-0.04 wt%	0.01-0.09 wt%
Highest filtration rate	9.5 gal/hr-ft^2	4.1 gal/hr-ft^2	9.4 gal/hr-ft^2
Maximum number of precoats during one run	14	3	17

Table 4. Summary of Centrifugation Tests Made by Some Liquefaction Processes

| Centrifuge	Process Application	Test Slurry	Operating Conditions	Remark	References
Sharples 1660 Super-D-Canter Horizontal Conveyer type	H-Coal	10 wt% minus 100 mesh Illinois #6 coal in 10.1° API TCC catalytic cracking syntower bottoms.	250-350°F continuous feed	Best result gave a solids reject containing 68.6% coal with effluent containing 0.9% coal.	Hydrocarbon Research, Inc. (1968).
Sharples 4" i.D. x 30" long vertically place bowl	SYNTHOIL	unfiltered product oil	80°C batch process	Centrifuged liquid containing 0.1-0.8% ash and 0.2-0.5% sulfur was obtained with feed oil from a 4,000 psig reactor containing 12% solids.	Akhtar, et. al. (1974).
Sharples	SRC	unfiltered product oil	200°F	Tests made by Sharples Centrifuge Company showed poor separation of solids. No further testing was done.	Oak Ridge National Laboratory (1975a); Pittsburgh and Midway Coal Mining Co. (1971).
Westfalia-Centrico	H-Coal	unfiltered process oil	250°-350°F batch and continuous nozzle ejection	In batch operation, clean liquid was obtained with solid containing 1.3 lb of oil/lb of dry cake. With continuous nozzle ejection, 90% solids reduction in the liquid was achieved. Operation with greater than 20% solids in the reject plugged the nozzle.	Hydrocarbon Research, Inc. (1968).
6-In. Bird Continuous Solid-bowl	CSF	unfiltered product oil	100psig 600°F	No useful data obtained due to seal problem.	Wheeler Corp. (1971).
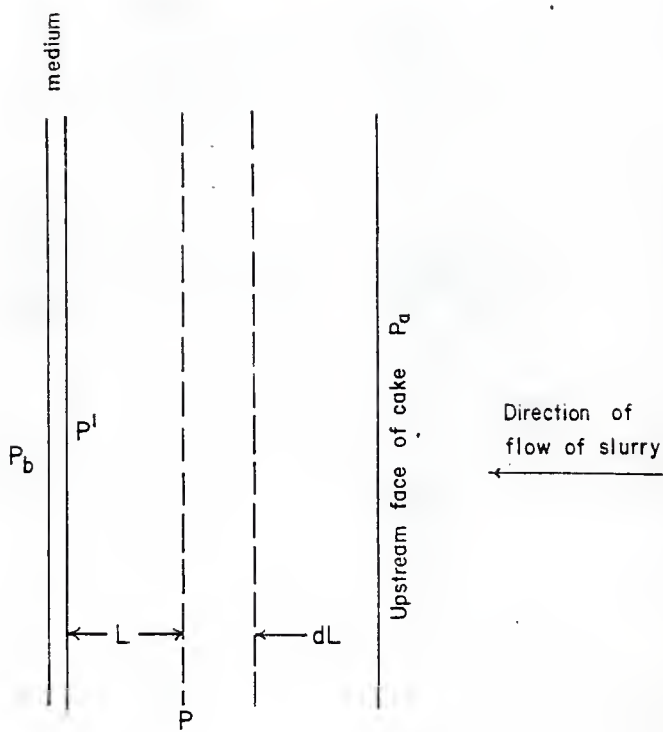
Figure 1.   Section through filter medium and cake (McCabe and
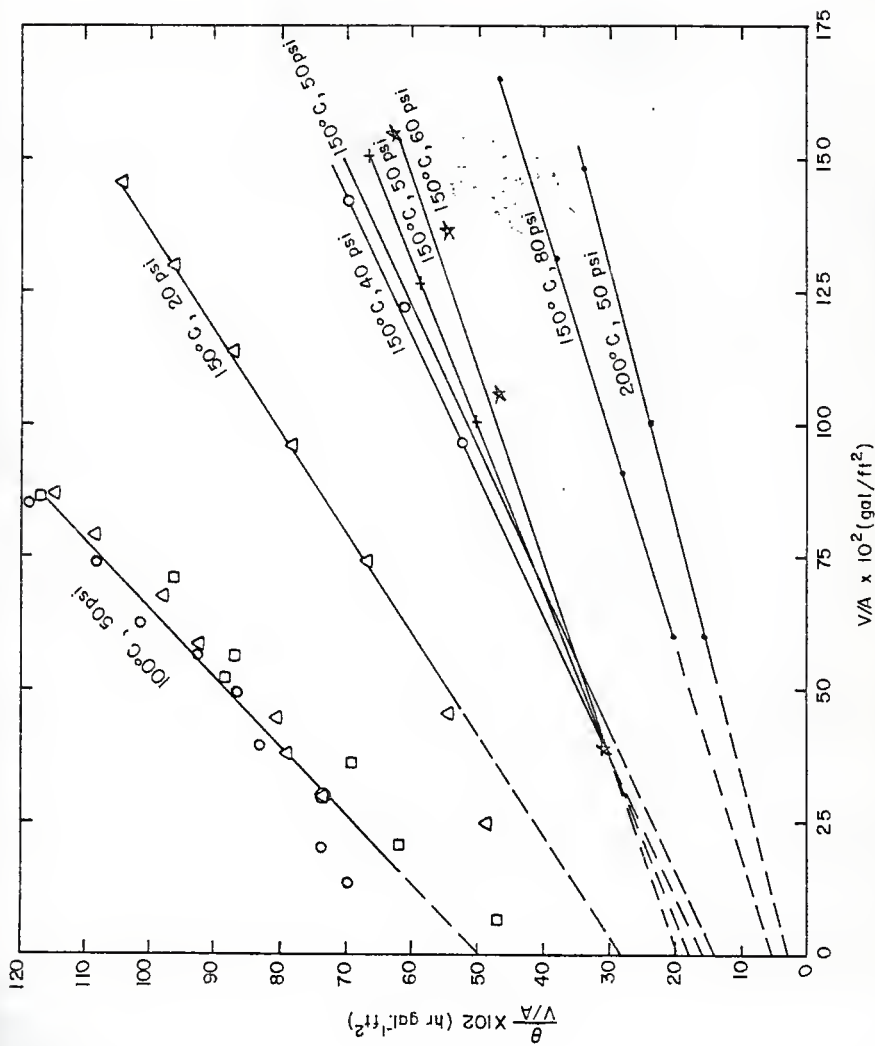   Smith, 1956).

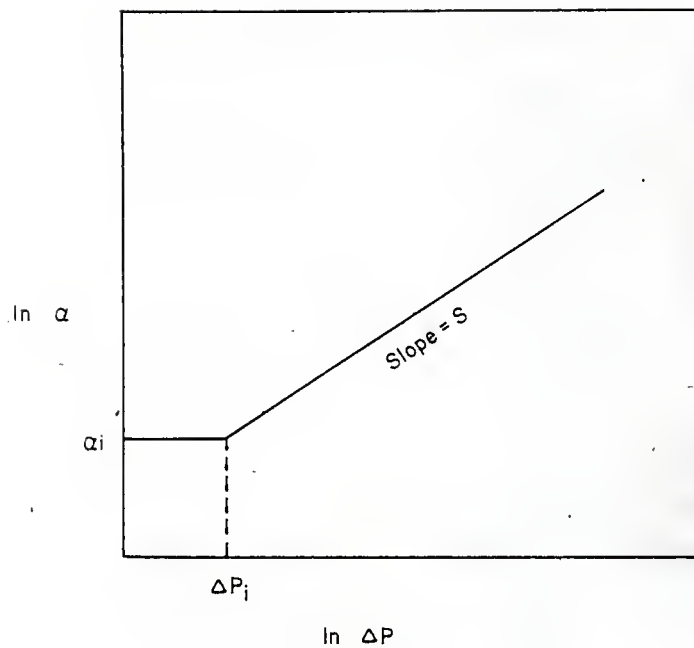Figure 2. Effect of temperature and pressure on precoat filtrations. (Katz and Rodgers, 1976)
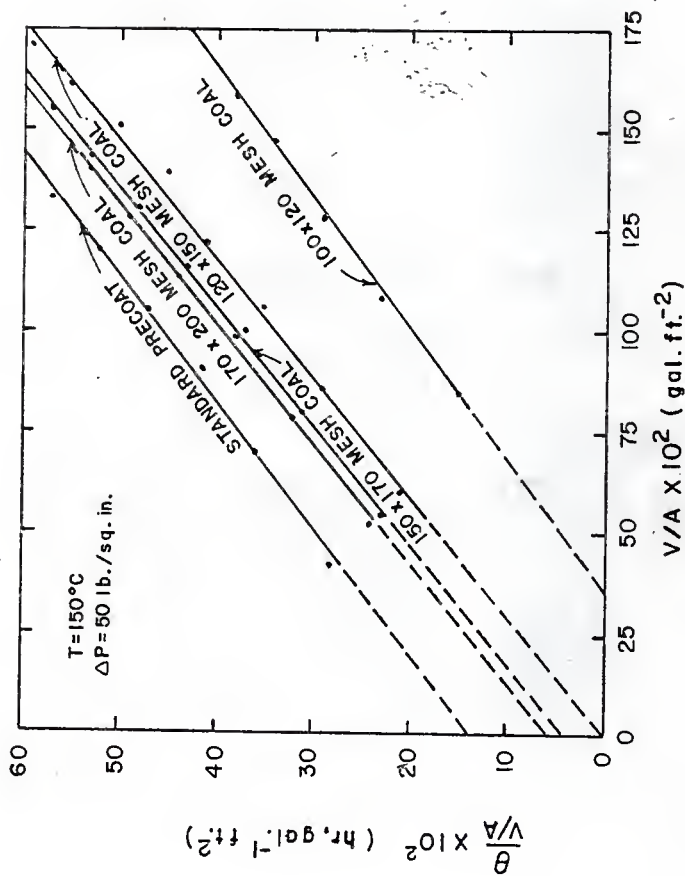
Figure 3. Specific cake resistance.

Figure 4. Effect of coal precoat particle size on filtration of SRC unfiltered oil. (Rodgers and Westmoreland, 1976)
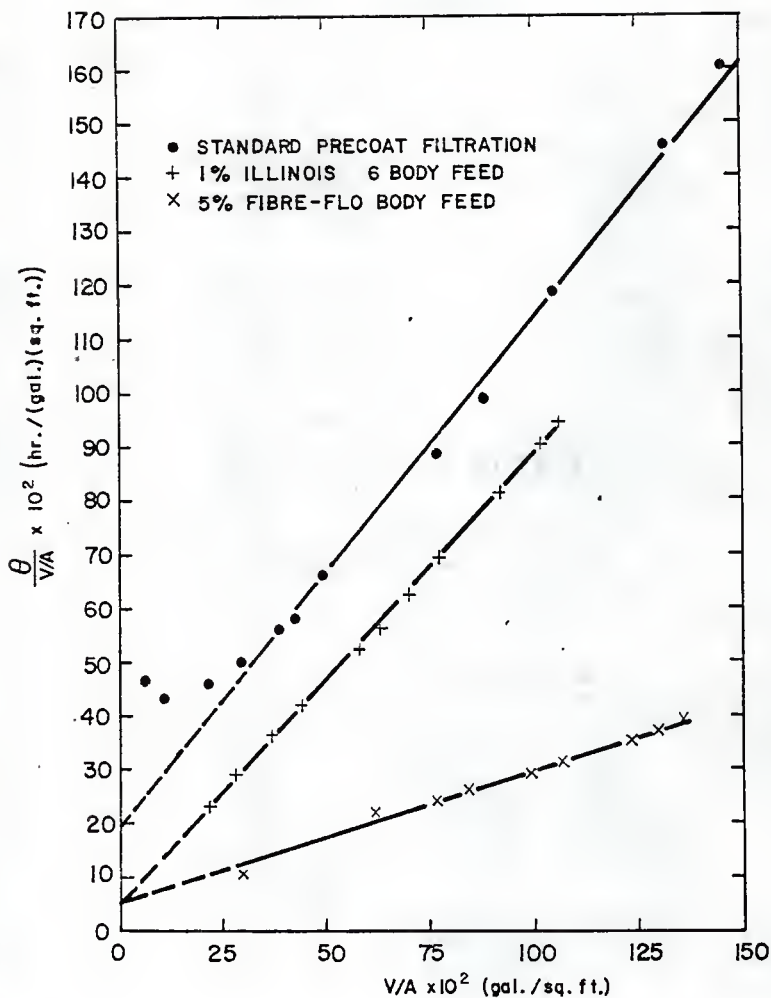
Figure 5.   Precoat filtrations of SRC unfiltered oil with body
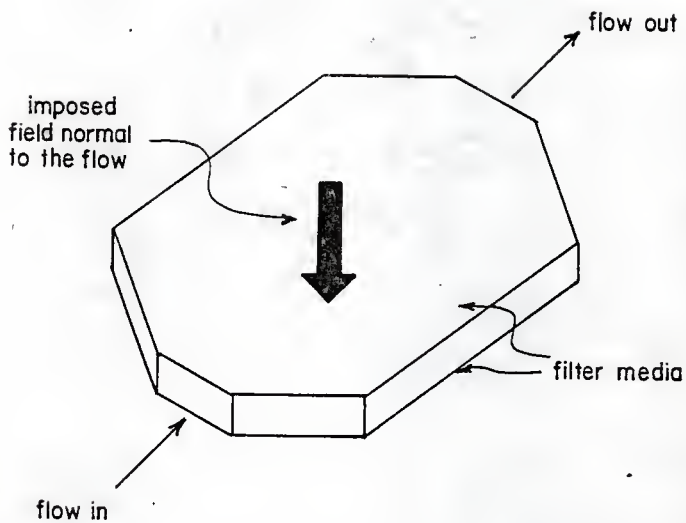   feed.   (Rodgers and Westmoreland, 1976)

flow out

imposed
field normal
to the flow

filter media

flow in

Figure 6. Cross Flow Filter.

CHAPTER III

SOLVOLYSIS LIQUEFACTION OF TEXAS LIGNITE:

An Experimental Study

INTRODUCTION

The Kyushu-Koshi solvolysis process of coal liquefaction (Honda and Yamada, 1974a; 1974b) involves atmospheric and non-catalytic dissolution of ground coal in a heavy solvent, e.g., petroleum derived oil such as vacuum residue, asphalt or coal tar. It is believed (Honda and Yamada, 1974a) that when the solvent is thermally treated at a temperature near 400°C (approx. 750°F), the long aliphatic chains not only undergo thermal cracking, but simultaneously, they also become polymerized. It is this thermal polymerization which produces ring and aromatic structured hydrocarbons that are necessary to liquefy the coal.

The solvolysis process has been found to be fairly specific in the type of coal liquefied (Osafune, et. al., 1976b). Osafune, et. al., (1976b) have reported the conversion of solid coal to liquid and gaseous products to be as high as 90% for a particular Japanese coal with 82-83% carbon. This compares favorably to other liquefaction processes in which both high hydrogen pressure and catalysts are needed (Wen and Han, 1975). However, for other coals, investigators (Osafune, et. al., 1976b; Kruse, 1976; Interess, et, al., 1977) have found much lower conversions.

In the present work, the conversion of solid Texas lignite to liquid or gaseous products by means of the solvolysis process was determined under a variety of different reaction conditions using asphalt as solvent. The facts that all previous works on the solvolysis process involved the use of sub-bituminous, bituminous or other higher rank coals, and that lignite deposits constitute a major portion of this country's readily usable energy reserve should make this study significant.

EXPERIMENTAL

The experimental apparatus and procedure employed in the present study are described below.

Apparatus

The experimental apparatus used in this work is shown in Figure 1. The set-up included: a 1000 ml glass reaction flask; a heating mantle rated at 650°C; a variable transformer to control the temperature of the mantle; a thermocouple, which was connected to a temperature recorder, to continuously monitor the reaction slurry temperature; a motor driven anchor-type stirrer; a constant-speed controller for the stirrer motor; reflux and water cooled condenser columns; and asbestos insulation.

Procedure

Lignite, from Hopkins County, Texas, was ground to -50 mesh (<300 μm), dried in a convective oven at 104-110°C, and then stored in air-tight containers. This lignite has a carbon content of approximately 55%.

Approximately 100 grams of dried lignite and 200 grams of Phillips 85-100 penetration asphalt from the Kansas City refinery were charged to the reaction flask. The mixture was then heated at a rate of 30°C/minute to the desired reaction temperature and held there for a pre-determined length of time. The slurry was continuously stirred at a rate of 100 rpm. The condensed portion, containing water and overhead oil, of the lighter components which evolved during heating and reaction, was collected and weighed. The non-condensed portion, containing gas, was permitted to escape to the atmosphere. At the end of the reaction, the reaction flask was cooled and its contents were removed. Finally, the reaction slurry was washed with benzene in a soxlet extractor to remove the benzene solubles.

The benzene insoluble residue was then dried at 104~110°C and weighed. Ash and moisture determinations were performed on representative samples of the feed lignite and on the benzene insoluble residue in accordance with ASTM D 3174-73 and D 3173-73 procedures.

The two largest sources of error were the control of reaction slurry temperature, $\pm$ 7°C ($\pm$13°F), and the extent of solid residue recovery. As a consistency test, 90% or better recovery of the tie component, ash, must be made for the run to be considered meaningful. Runs with less than 90% ash recovery were discarded.

The effects of reaction time, reaction temperature, and lignite-to-asphalt ratio on the conversion of solid lignite to liquid and gaseous products were determined.

RESULTS AND DISCUSSION

Experimental data obtained are shown in Figures 2 through 11. Figures 2 through 7 show the results of runs with a lignite-to-asphalt ratio of 1:2. Figures 8 and 9, on the other hand, show the results of runs with a lignite-to-asphalt ratio of 1:1. All calculations have been performed on a moisture-ash-free (maf) basis, and all yields expressed in terms of percentage, except those in Figures 10 and 11, refer to the quantity of maf lignite initially charged to the reaction flask. The yields in Figures 10 and 11 refer to the quantity of asphalt charged. The size of the data points in these figures, unless otherwise indicated, is an indication of experimental error due to uncertainties in the measurement and analysis. These, of course, do not reflect errors due to variations in the feed sample and errors due to failure to control the temperature.

The discussion given below includes: the effect of reaction temperature on the yields of benzene insolubles, overhead oil, gas, and water in 30 and 60 minute runs with a lignite-to-asphalt ratio of 1:2, shown in Figures 2 and 3; the effect of reaction time on the yields at 380 and 400°C with a lignite-to-asphalt ratio of 1:2, shown in Figures 4 through 7; and the effect of varying the lignite-to-asphalt ratio on the yields, shown in Figures 8 through 11.

Effect of Reaction Temperature

In Figure 2, the benzene insolubles, calculated with the formula on a maf basis (e.g., see, Weller, et. al., 1951; Ruether, 1977), i.e.,

$$\% \text{ Benzene Insolubles (BI)} = \frac{\text{wt. of BI from soxlet extractor}}{\text{wt. of lignite}} \times 100 \text{ ,}$$

is plotted against the reaction temperature, in the range of 300 ~ 410°C (approx. 575 ~ 775°F), for 30 minute and 60 minute reaction times. The

benzene insolubles consist of unreacted lignite, ash in the lignite and coke formed during the reaction. Because of coke formation, which occurred simultaneously while solid lignite was being converted to gaseous and liquid products, it was possible to obtain a greater amount of benzene insolubles than the initial lignite charge. This was the case with the 400°C, 60 minute run where the %BI was approximately 108. Coke formation was very pronounced at temperatures $\geq$ 400°C (approx. 750°F) as can be seen in the sharp rises in the curves of Figure 2. Coke formation was apparently catalyzed by lignite (Wright and Severson, 1972); little or no coke was formed when asphalt was heated under the conditions of this experiment. At lower temperatures, below 380°C (approx. 720°F), no appreciable amount of coke was formed as can be seen from the closeness in the amount of BI obtained in 30 minute and 60 minute runs. It appears that the amount of benzene insolubles obtained was a linearly decreasing function of reaction temperature in the range where coke formation was not significant. For higher temperatures (> 380°C), the extent of coke formation increased exponentially with the increase in the reaction temperature. The pseudo-conversion scale on the right hand side of Figure 2 is the extent of solid lignite conversion to liquid and gaseous products in terms of percentage based on the assumption that there was no coke formation. It can be seen in Figure 2 that the data were fairly reproducible.

Figure 3 shows the percent yield of overhead oil, gas, and water for reaction times of 30 and 60 minutes as functions of the reaction temperature. These percent yields were calculated as

(weight of sample/weight of maf lignite) x 100

For water,

weight of sample = weight of water collected - (% moisture)(weight of lignite).

The ranges of measurement uncertainties were typically ±1% for overhead oil, ±1.5% for gas, and ±1% for water. It appears that the quantity of water produced was a linear function of the temperature, and that the reaction time had no effect on the water yield. The latter observation was also verified in Figures 6 and 7. The yield of gas appears to be a linear function of the temperature for reactions below 350°C. For higher temperatures, gas yield became a mildly exponential function of the temperature. No appreciable quantity of overhead oil was produced in reactions below 350°C; above 350°C, the yields at 30 and 60 minute runs were sharp exponential functions of the temperature.

Effect of Reaction Time

Figures 4 and 5 show the yield of benzene insoluble residues as a function of the reaction time at 380°C (716°F) and 400°C (752°F), respectively. It is apparent that some conversion of lignite to products occurred during the heating-up period, that is, at the onset of reaction at the specified temperature, the amount of benzene insolubles was less than 100%. These two figures also give evidence of parallel and perhaps interacting reactions: one being the conversion of solid lignite to liquid and gaseous products, and the other being the conversion of the reaction slurry to coke. This may explain the existence of an optimal reaction period of approximately 25 minutes, during which the amount of benzene insolubles obtained was minimum, or during which the pseudo conversion was maximum. This observation can probably be extended to coal of other ranks when liquefied under similar conditions.

No significant difference could be detected when the quantities of benzene insolubles obtained at 380°C (716°F) with different reaction

times were compared, as can be seen in Figure 4. This is probably a good indication that no appreciable coking occurred at 380°C. In contrast, coking was very extensive at a higher temperature of 400°C. The relatively constant yield, about 75%, of benzene insolubles at 380°C, shown in Figure 4, corresponded to the minimum yield of benzene insolubles in the atmospheric solvolysis liquefaction of this Texas lignite.

Figures 6 and 7 show the yields of overhead oil, gas, and water as functions of the reaction time at reaction temperatures of 380°C and 400°C, respectively. The yield of water was, again, independent of the reaction time. The yield of gas was linearly dependent on reaction time for both temperatures. The yield of overhead oil at 400°C, again, was almost linear with respect to the reaction time; however, at 380°C, it asymptotically approached to 26% after proportionally increasing with the reaction time in the initial 60 minutes. This difference might be due to the fact that coking was predominant at 400°C while it was insignificant at 380°C, as can be observed in Figures 4 and 5.

Effect of Varying the Lignite-to-Asphalt Ratio

Figure 8 shows the yield of benzene insolubles for 30 and 60 minute runs in the temperature range of 350 ~ 400°C for a lignite-to-asphalt ratio of 1:1. In contrast to runs with a lignite-to-asphalt ratio of 1:2, no significant differences were observed between runs at different temperatures and with different reaction times. It also appears that coking, which was the predominant reaction at higher temperatures in runs with a lignite to asphalt ratio of 1:2, was insignificant here. The yield of benzene insolubles in runs with a lignite-to-asphalt ratio of 1:1 runs was $83 \pm 3.4\%$ of the initial lignite charged on a maf basis. The deviation of $\pm$ 3.4% was approximately within the range of measurement and analysis uncertainties.

Figure 9 shows the yields of overhead oil, gas, and water for 30 and 60 minute reaction runs in the temperature range of 350 ~ 400°C for a lignite-to-asphalt ratio of 1:1. General trends observed with a lignite-to-asphalt ratio of 1:2 (Figure 5) were also observed here, that is, the overhead oil and gas yields appear to be exponential functions of the temperature, and the yield of water was linearly dependent on the reaction temperature.

Figure 10 plots the yield of overhead oil, calculated on the basis of asphalt (i.e., weight of overhead oil collected/weight of feed asphalt), against reaction temperature; no significant difference can be observed among runs with different lignite to asphalt ratios. This suggests that overhead oil was a product from cracking of asphalt. However, no significant yield of overhead oil was obtained when asphalt was heated alone in this temperature range, thus showing the catalytic effect of lignite (Wright and Severson, 1972). On the other hand, Figure 11 shows that the yield of gas from runs with a lignite/asphalt ratio of 1:1 was significantly higher than those with a ratio of 1:2. This is a good indication that, unlike overhead oil, gas was the product of both asphalt cracking and coal conversion.

CONCLUSION

The results of the bench-scale experimental study indicate that the highest conversion of the Texas lignite to liquid and gaseous products obtained in the range of reaction condition studied was 23%. The results also show that parallel reactions which converted solid lignite to gaseous and liquid fuels, and coked the reaction slurry, interacted; however, coking predominated at higher temperatures, $\geq 400°C$ ($\geq 750°F$). Because of these two parallel reactions, there existed an optimal reaction time at which the yield of benzene insoluble residues was minimum. It also appears that overhead oil was produced from cracking of asphalt which was catalyzed by the presence of lignite. The presence of lignite also promoted coking which did not occur to any significant extent when asphalt was heated alone in the range of conditions studied. The amount of coking was also significantly reduced when the lignite-to-asphalt ratio was increased from 1:2 to 1:1; however, an increase in the lignite-to-asphalt ratio did not enhance the conversion of lignite to liquid and gaseous products under the optimal conditions. The results of the present study show that the solvolysis process may be suitable for producing low quality coke because of the catalytic effects of lignite and other coals (Wright and Severson, 1972).

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Osafune, K., Arita, S., Yamada, Y., Kakiyama, H., Honda, H., Tagawa, N., Abe, S., "Solvolysis of Coal by Petroleum Vacuum Residue II - The Influence of Coal Ranks on the Solvolysis Reaction," Nenryo-Kyokai-Shi, 55, 173 (1976b).

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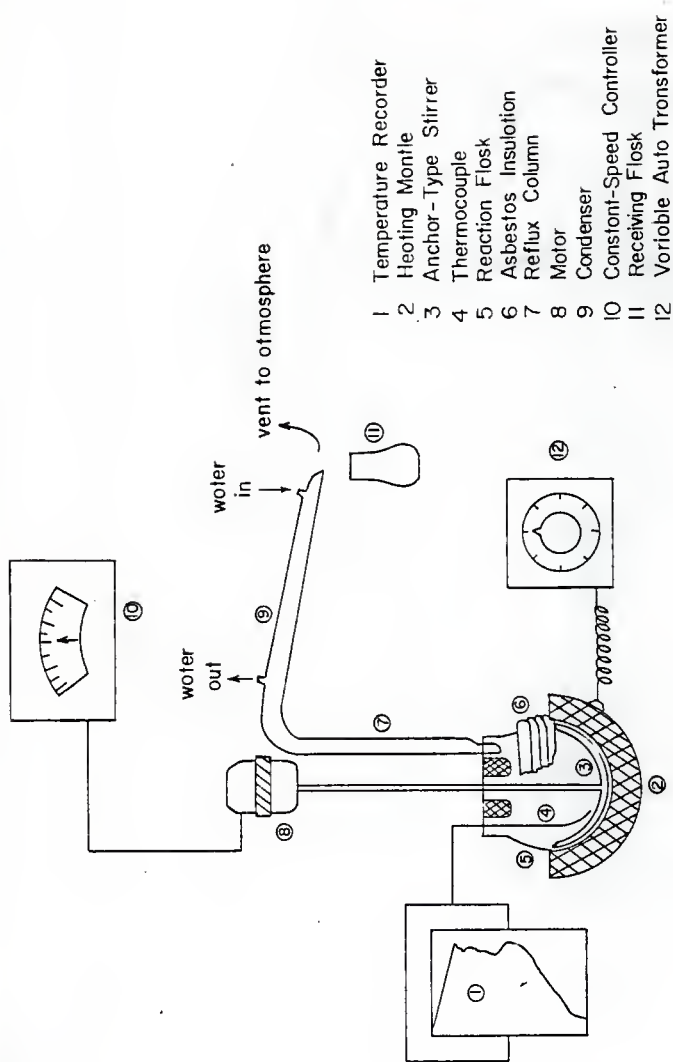
1. Temperature Recorder
2. Heating Mantle
3. Anchor-Type Stirrer
4. Thermocouple
5. Reaction Flask
6. Asbestos Insulation
7. Reflux Column
8. Motor
9. Condenser
10. Constant-Speed Controller
11. Receiving Flask
12. Variable Auto Transformer

Figure 1. Schematic Diagram of Experimental Apparatus
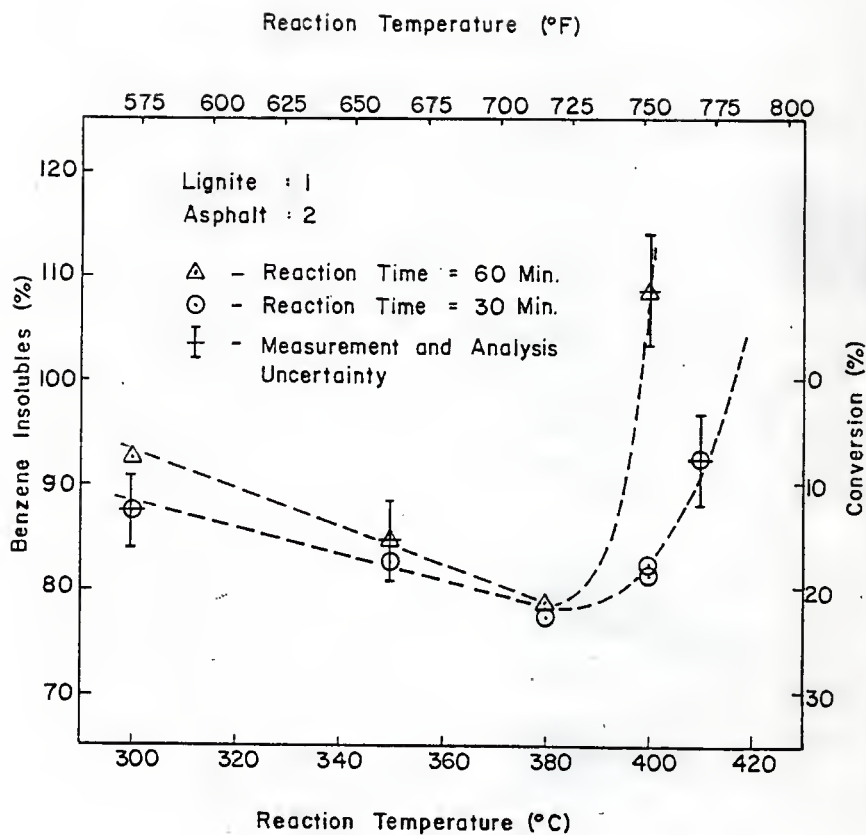
Reaction Temperature (°F)

Figure 2.   Yield of Benzene Insolubles (Residues) for 30 and 60
            Minute Runs at Various Reaction Temperatures
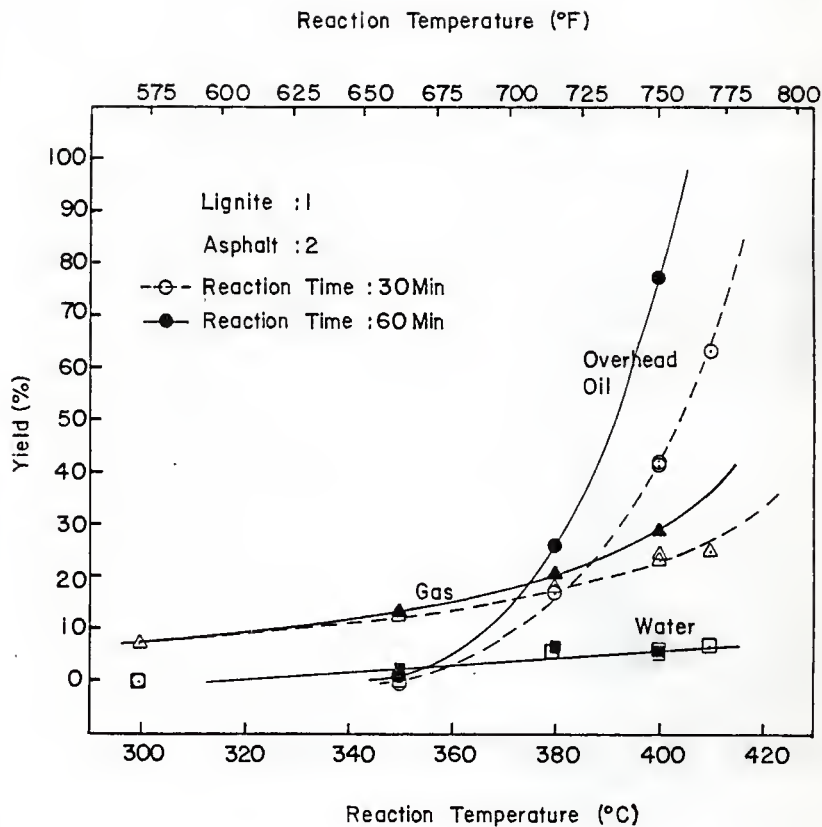   (Lignite/Asphalt = 1/2).

Reaction Temperature (°F)

Figure 3. Yield of Overhead Oil, Gas, and Water for 30 and 60 Minute Runs at Various Reaction Temperatures (Lignite/Asphalt = 1/2).
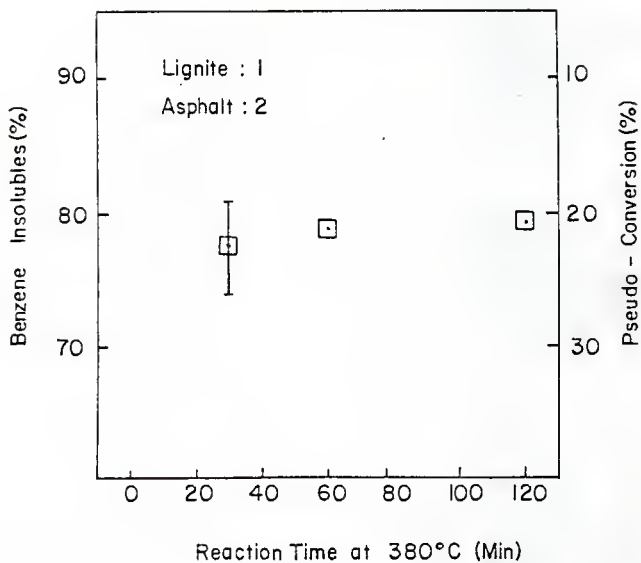
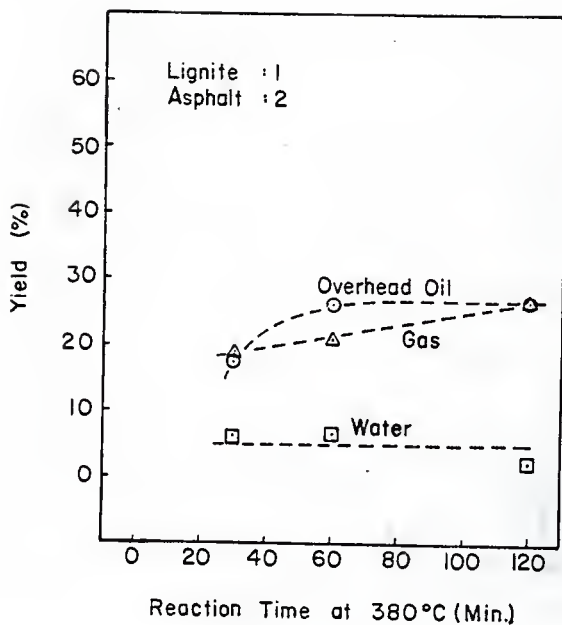Figure 4. Yield of Benzene Insolubles (Residue) at 380°C Under Different Reaction Times (Lignite/Asphalt = 1/2).
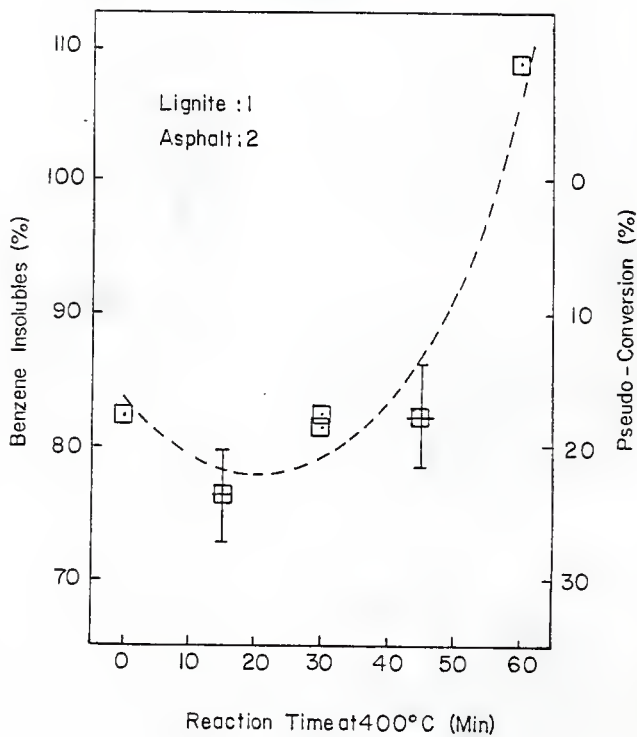
Figure 5. Yield of Benzene Insolubles (Residue) at 400°C Under Different Reaction Times (Lignite/Asphalt = 1/2).

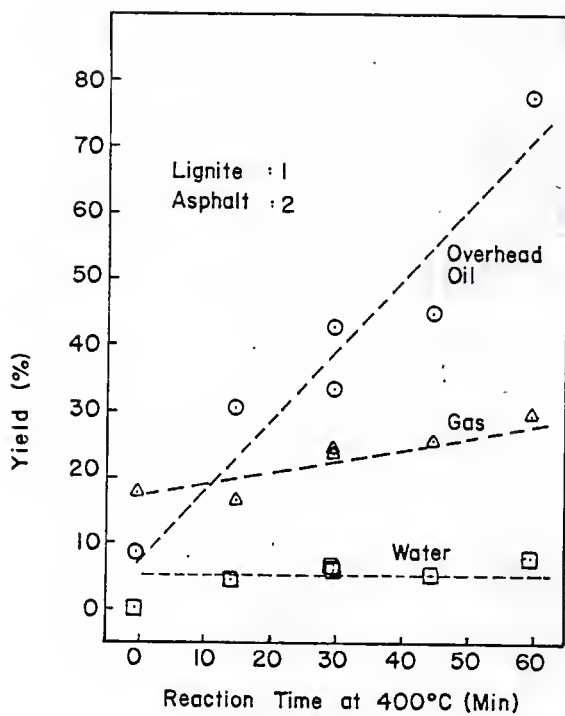Figure 6. Yields of Overhead Oil, Gas, Water at 380°C as Functions of Reaction Time (Lignite/Asphalt = 1/2).

Figure 7.   Yields of Overhead Oil, Gas, Water at 400°C as
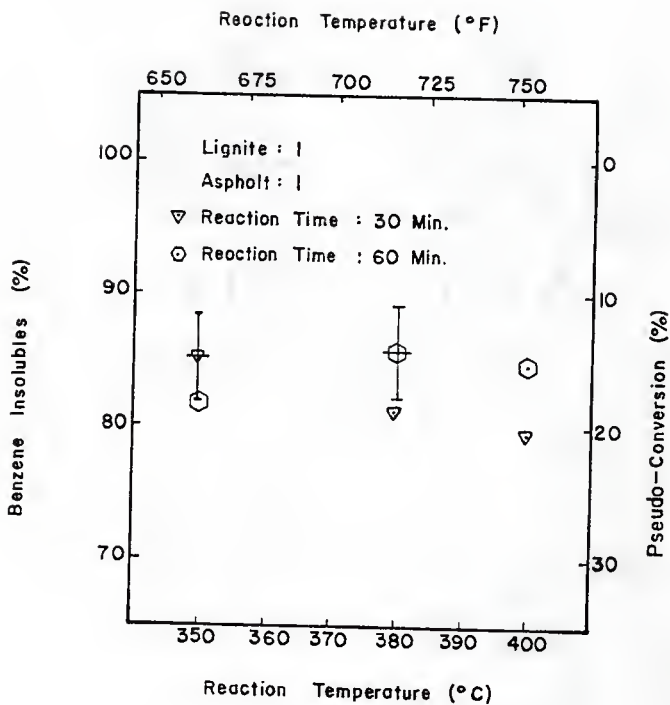   Functions of Reaction Time (Lignite/Asphalt = 1/2).

Figure 8. Yield of Benzene Insolubles (Residue) for 3ᵒ and 60
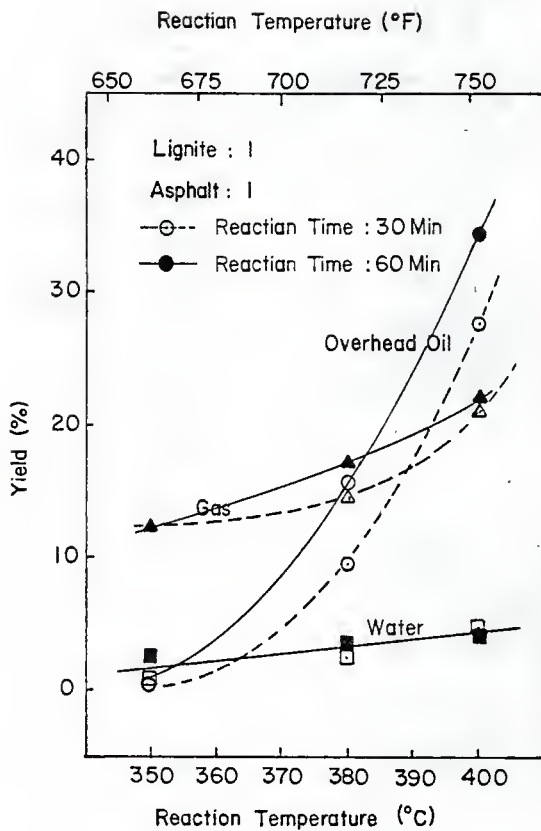Minute Runs at Various Reaction Temperatures
(Lignite/Asphalt = 1/1).

Figure 9. Yields of Overhead Oil, Gas, and Water for 30 and
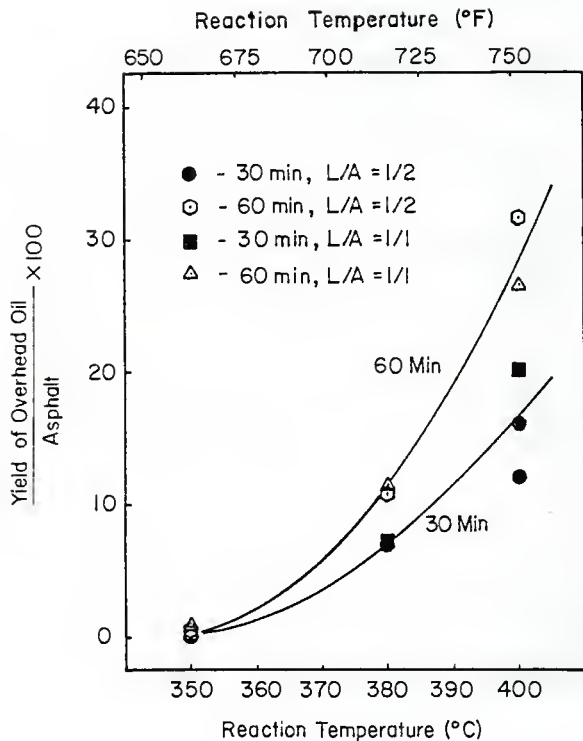60 Minute Runs at Various Reaction Temperatures
(Lignite/Asphalt = 1/1).

Figure 10. Yield of Overhead Oil (Expressed as % Feed Asphalt)
for 30 and 60 Minute Runs Under Different Lignite
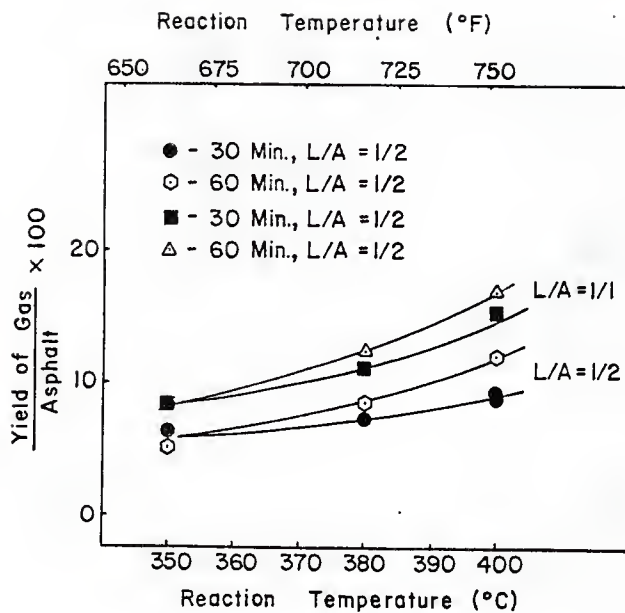to Asphalt Ratios and Different Temperatures.

Figure 11. Yield of Gas (Expressed as % Feed Asphalt) for
30 and 60 Minute Runs Under Different Lignite
to Asphalt Ratios and Different Temperatures.

CHAPTER IV

CONSTANT PRESSURE FILTRATION OF LIQUEFIED LIGNITE

INTRODUCTION

It is well-known that the separation of solid residues from liquefied coal constitutes the bottleneck in the commercialization of liquefaction processes (Batchlor and Shih, 1975; Oak Ridge National Laboratory, 1975; Rodgers and Westmoreland, 1976; also see Chapter II). Conventional solid-liquid separation systems, such as filtration, centrifugation, and sedimentation, have been found to be unsuitable because of the high cost and/or low efficiency in the removal of solids. Therefore, it is imperative that

1. a combination of the existing separation systems be determined so that the solid residues may be removed with relative ease;

2. a new separation system be developed; and/or

3. the conditions of liquefaction which will lead to easier separation be identified.

In the present work, the effect of reaction conditions on the separability of solid residues from lignite liquefied through the solvolysis process (Honda and Yamada, 1974) has been investigated. Filterability of liquefied lignite was chosen as the measure of the ease of separation.

The theory of constant pressure filtration has been adequately developed (see, e.g., McCabe and Smith, 1956; Tiller, 1966). The general filtration equation, stated as

$$\frac{\theta}{V/A} = \frac{\mu}{P} \left[\frac{c\alpha}{2} \left(\frac{V}{A}\right) + Rm\right] \tag{1}$$

where

θ = filtration time

V = volume of filtrate collected

A = filter area

μ = viscosity of filtrate

P = imposed filtration pressure

c = mass of solid particle deposited in the filter per unit volume of filtrate

α = average specific cake resistance.

R_m = resistance of the filter medium,

can be derived by considering all drag forces created as the filtrate flows around the cake solids (McCabe and Smith, 1956). Equation (1) indicates that $\frac{\theta}{V/A}$ is a linear function of V/A with a slope of $\frac{\mu c \alpha}{2P}$. Therefore, the magnitude of the slope is a measure of the difficulty of separation.

EXPERIMENTAL

The experimental apparatus, shown in Figure 1, included a Gelman pressure filtration funnel, an electric heat tape, asbestos insulation, a variable auto transformer, a thermocouple, a temperature recorder, a volumetric filtrate receiving flask, and a hot plate. The stainless steel batch filter had a capacity of 200 ml (0.053 gal) and an effective filter area of 9.62 cm^2 (0.010 ft^2). The filter could be operated at a pressure as high as 137.2 N/cm^2 (200 psi) and, because of the viton O-ring seal, at temperatures between -7°C (20°F) and 205°C (400°F). The filter medium used was made of glass fiber and had pore sizes 0.2 to 10 μm. The filter was wrapped with the electric heat tape and the asbestos insulating tapes. The thermocouple, which was located near the filter medium, was connected to the temperature recorder to monitor the filter temperature.

The liquefied lignite slurries used in the present study were obtained from a bench-scale investigation of the solvolysis liquefaction process (Honda, 1974; also see chapter II). In the investigation, experiments were carried out to determine the effects of the reaction temperature (300-410°C), the reaction time (0-120 min) and the lignite-to-solvent (asphalt) ratio ranging from 1:2 to 1:1 on the conversion of solid lignite to gaseous and liquid products.

The liquefied lignite slurry was first heated to the filtration temperature, 180°C (356°F), and was then introduced to the filter which was also maintained at the same temperature. The filter was then pressurized to 20 psi (13.7 N/Cm^2) with a nitrogen cylinder, and the accumulated filtrate volume was recorded as a function of filtration time.

RESULTS AND DISCUSSION

The results of filtration of liquefied lignite at 180°C (356 °F) and 13.7 N/cm^2 (20 psi) are shown in Figures 2 through 9.

Figure 2 shows the typical filtration data plotted according to equation (1). The plot will be henceforth referred to as a filtration curve. The highest (initial) filtration rates obtained in this study were in the range of 0.05-1.56 $m\ell/cm^2$-min (0.7-23.0 gal/ft^2-hr). These rates were comparable to those obtained by other investigators with the Solvent Refined Coal, 4-14 gal/ft^2-hr (Rodgers, et. al., 1976; Katz, et. al., 1975; Schoemann, et. al., 1974). Photographs of a typcial filter cake obtained is shown in Figure 3.

Effect of the Extent of Conversion on Separability

Figure 4 plots the degree of separation difficulties, expressed in terms of the slope of the filtration curve, against the quantity of benzene insolubles obtained under different liquefaction conditions. Intuitively, one would suspect the magnitude of the slope of the filtration curve to be inversely proportional to the extent of conversion of lignite to products; that is, as the extent of conversion increases (less benzene insolubles), the particle size decreases, and as particle size decreases, the degree of the binding of the filter rises, leading to a higher cake resistance and, therefore, a steeper slope. In Figure 4, however, no easily identifiable relationship exists between the difficulty of separation and the extent of conversion from solid lignite to liquid and gaseous products. This was probably due to many factors. Among them is the fact that the conversion of lignite to products through the solvolysis process was too low ($\leq$ 23%) to have an

appreciable reduction in particle size. It was also possible that other physical properties such as viscosity, had a greater effect than did particle size on the difficulty of separation. In general, the magnitude of the slope fell below 2 $Min/(Ml/cm^2)^2$ or 0.5 $Hr/(Gal/Ft^2)^2$, which corresponded to a relatively low cake resistance for an extractive coal liquid.

Effect of the Reaction Conditions on Separability

Figure 5 shows the effect of liquefaction temperature while Figure 6 shows the effect of liquefaction time on the difficulty of separation. No significant differences in the difficulty of separation were observed for lignite liquefied under various conditions with a lignite-to-asphalt (L/A) ratio of 1:1. For lignite liquefied with a L/A ratio of 1:2, separability of solid residues from liquefied lignite was highly dependent on the condition of liquefaction. For example, it appears that as the liquefaction time was increased, separation of solids became more difficult. This observation is particularly true for slurries obtained at a liquefaction temperature of 350°C (662°F) or lower. It also appears that solid-liquid separation was relatively easy for slurries obtained at a liquefaction temperature of 380-400°C (716-752°F). This temperature range corresponded to the maximum conversion of lignite to liquid and gaseous products.

Roles of Viscosity and Cake Resistance on Separability

In order to determine the magnitude of the average specific cake resistance, α, it was necessary to know the viscosity of the filtrate at a filtration temperature of 180°C. But, because of the limited amount of liquefied slurry and also because of the high temperature involved, it was not possible to measure the viscosity of the opaque lignite liquids directly. The viscosity of one specific lignite liquid, obtained at 380°C

with a lignite-to-asphalt ratio of 1:2 and a reaction time of 60 minutes, was measured at 120, 121 and 132°C. The viscosity at 180°C was then determined by extrapolation as illustrated in Figure 7. With viscosity known, it was possible to calculate the resistance of the filter medium, Rm, from the intercept of the filtration curve [see equation (1)]. The value of Rm for the glass fiber medium employed in this study was found to be $1.05 \times 10^{11} m^{-1}$ $(3.20 \times 10^{10} ft^{-1})$. Viscosity of lignite liquids liquefied at different conditions was then back calculated from the intercept of the filtration curve assuming a constant Rm of $1.05 \times 10^{11} m^{-1}$. This assumption would not be valid when working with precoat filters in which the resistance of the laid precoat would be highly variable. However, with laboratory filters that use relatively uniform filter media of controlled quality, the assumption of constant medium resistance at a given filtration condition should be acceptable. The following discussions are based on the assumption of constant filter medium resistance.

Figure 8 shows the viscosity, at 180°C (356°F), of the lignite liquid obtained under various liquefaction conditions, and Figure 9 shows the average specific cake resistance, α, of the liquefied lignite slurries filtered at 180°C (356°F) and 13.7 N/cm^2 (20 psi). The average specific cake resistance was determined from the slope of the filtration curve using the calculated viscosity. As a check, the viscosity of one lignite liquid liquefied at 300°C with a L/A ratio of 1:2 and a liquefaction time of 30 minutes was measured at 110, 116 and 122°C, and the viscosity at the filtration temperature of 180°C was then determined by extrapolation as shown in Figure 7. The value of viscosity thus obtained was 38.4 cp, while the value calculated from the filtration data shown in Figure 8 was 38.6 cp, showing an excellent

agreement. It appears that the viscosity of the liquefied lignite was highly dependent on the conditions of liquefaction. For example, the viscosity of the lignite liquids liquefied with a L/A ratio of 1:2 and a reaction time of 60 minutes showed no significant dependency on the liquefaction temperature. On the other hand, viscosity of the lignite liquids liquefied with the same L/A ratio but with a shorter reaction time of 30 minutes was parabolically dependent on the liquefaction temperature with a minimum in the 350-400°C range. The values of the average specific cake resistance were generally low and independent of liquefaction conditions. Exceptions to this were two runs liquefied with a L/A ratio of 1:2, a liquefaction time of 60 minutes and at temperatures below 380°C. The high values of the average specific cake resistance determined in these two runs contributed heavily to the large values of the slope of the filtration curve, as seen in Figure 5. Also in Figure 5, filtration of the lignite slurry, obtained with a temperature of 410°C, a liquefaction time of 30 minutes and a L/A ratio of 1:2, showed a high degree of difficulty in separation. This, on the other hand, was because of high viscosity of the lignite liquid, as can be seen in Figures 8 and 9.

CONCLUSION

The results of the present study on separability by filtration of lignite liquids obtained through the solvolysis process show that the ease of separating the solid residues from the product slurry was to some extent dependent on the condition of liquefaction. High average specific cake resistances were encountered in the filtration of lignite liquids obtained at the condition of 60 minute liquefaction time, a lignite-to-solvent ratio of 1:2, and liquefaction temperatures below 380°C (716°F). On the other hand, at high liquefaction temperatures, $\geq$ 410°C (770°F), separation of solids from the liquefied lignite slurry was hampered by high viscosity. It appears that separation was best accomplished when lignite was liquefied in the temperature range of 380~400°C (716~770°F) which was also the conditions of optimal conversion.

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    (1960).

1   N₂ Line
2   Filtration Chamber
3   Heat Tape
4   Asbestos Insulation
5   Thermocouple
6   Filter Medium
7   Volumetric Receiver
8   Hot Plate
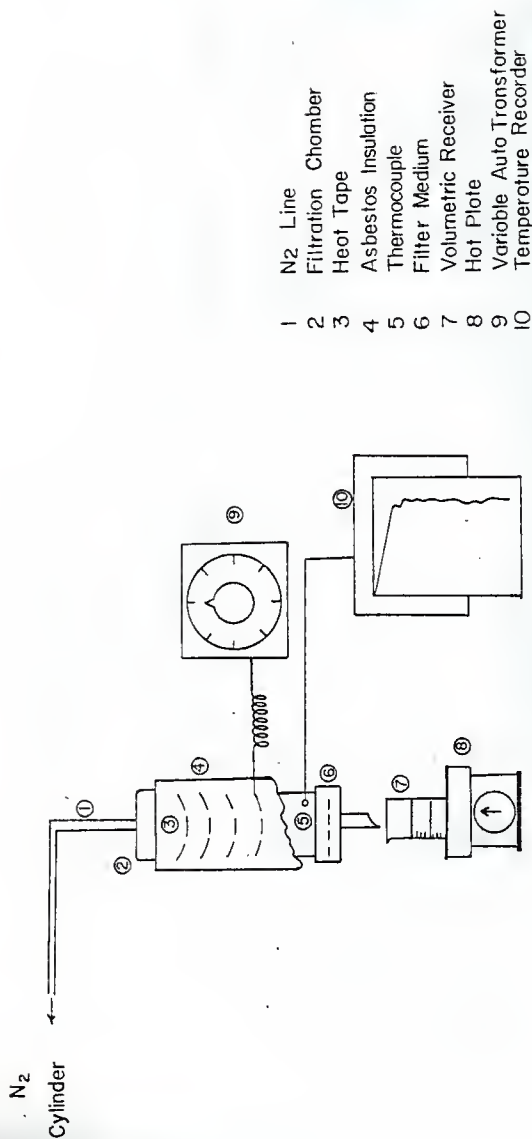9   Variable Auto Transformer
10 Temperature Recorder

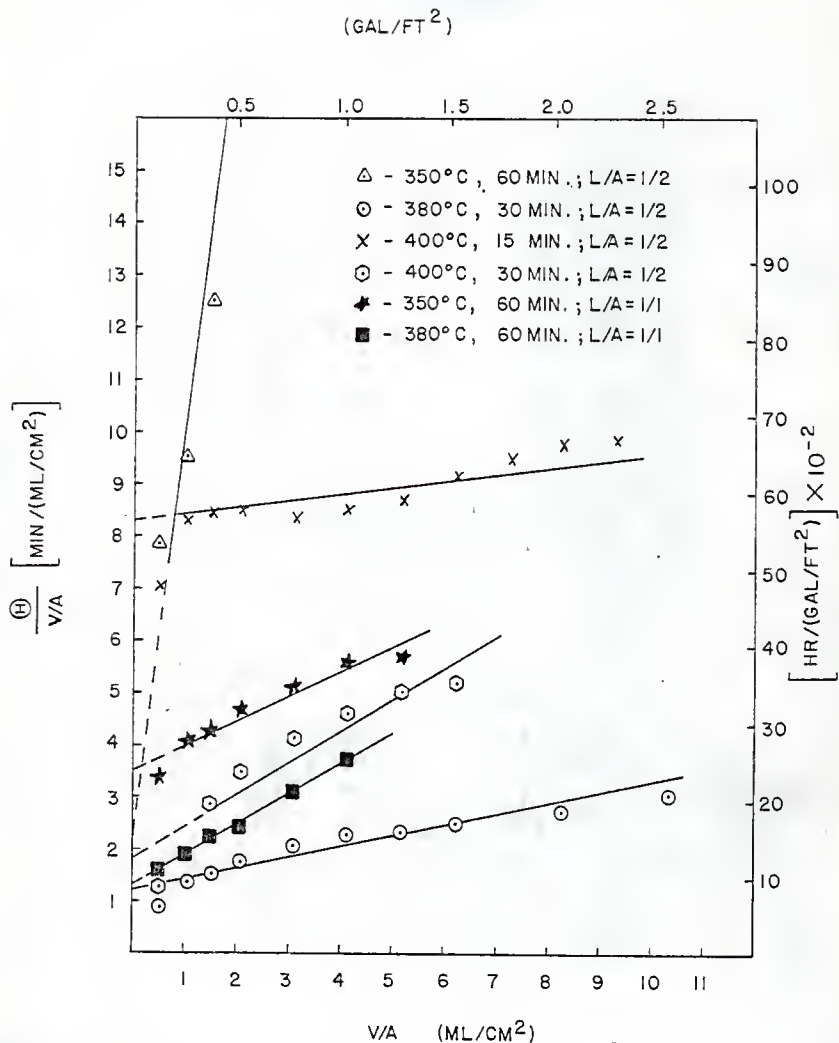Figure 1.   Schematic Diagram of Experimental Apparatus for the Filtration of Liquefied Lignite Slurry.

Figure 2. Typical Filtration Data at 180°C and 13.7 N/cm² of Lignite Slurry Liquefied in the Reaction Range of 300-410°C, 0-120 minutes and with the Lignite to Asphalt Ratio of 1/2 and 1/1.
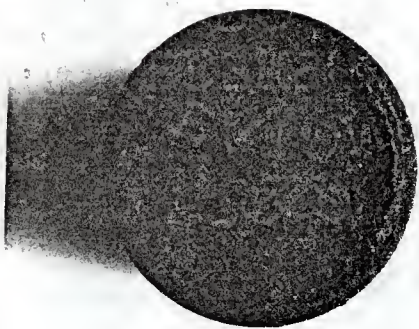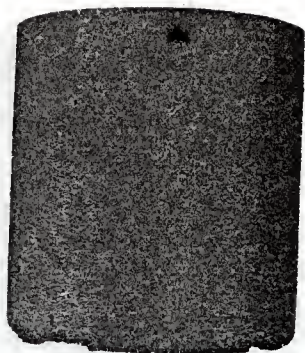
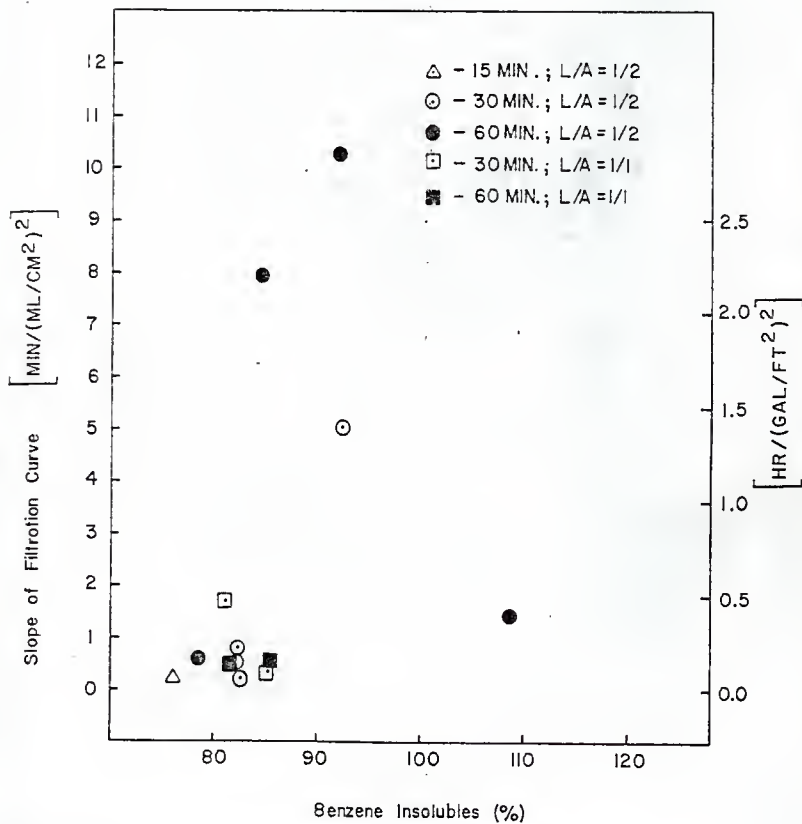Figure 3.   Photographs of a Typical Filter Cake Obtained in This
Study.

Figure 4. Degree of Separation Difficulties Expressed in Terms of
the Slope of the Filtration Curve as a Function of the
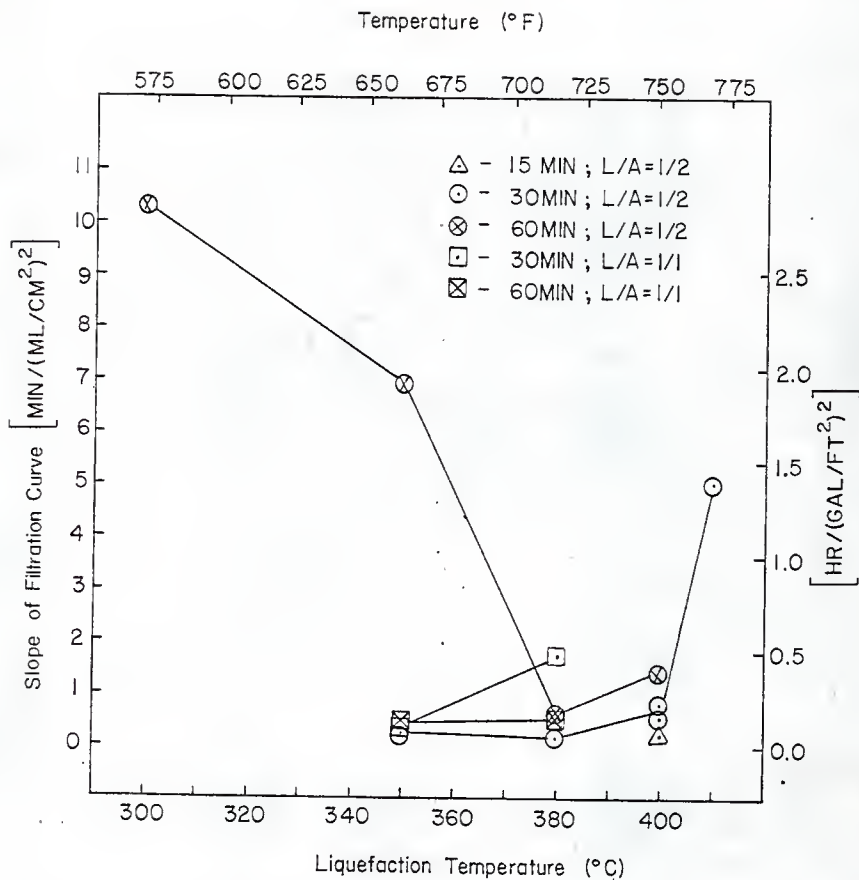Quantity of Benzene Insolubles obtained.

Figure 5. Degree of Separation Difficulties Expressed in Terms of the Slope of the Filtration Curve as Functions of Liquefaction Temperature with Liquefaction Time and Lignite to Asphalt Ratio as Addition Parameters.
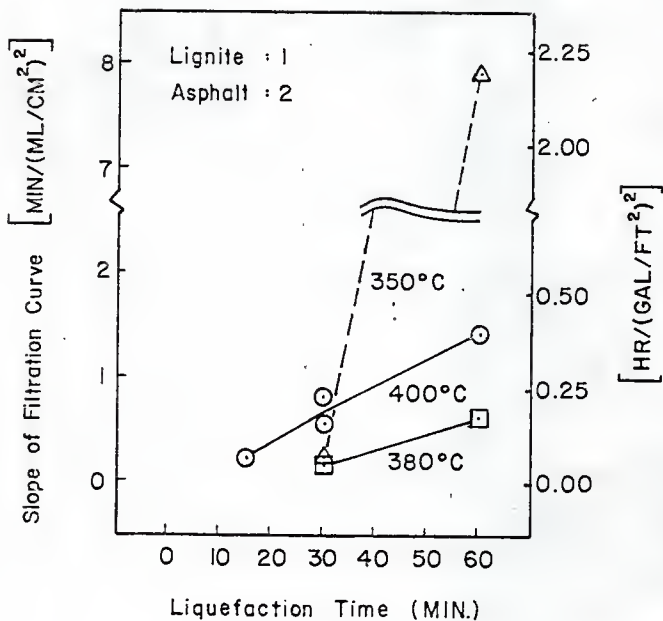
Figure 6.   Degree of Separation Difficulties Expressed in Terms of
the Slope of the Filtration Curve as Functions of
Liquefaction Time with Liquefaction Temperature
as the Parameter. Lignite to Asphalt ratio was
1/2.
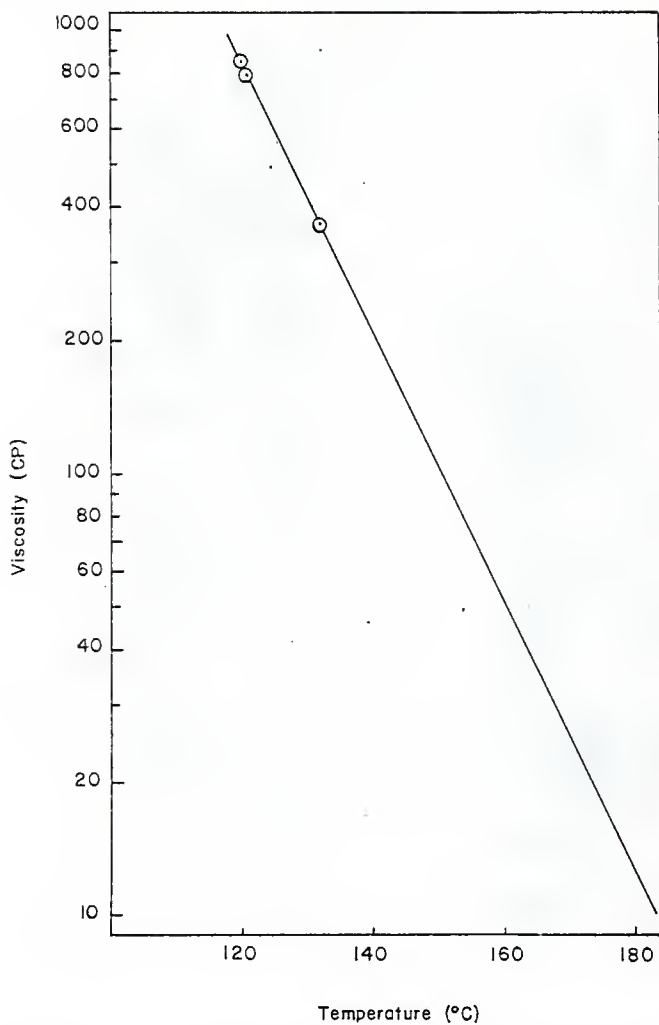
Figure 7.   Viscosity of Lignite Liquid Liquefied at 380°C with a Lignite to Asphalt Ratio of 1/2 for 60 Minutes.

Figure 8. Viscosity of Lignite Liquids at 180°C as Functions of Liquefaction Time and L/A Ratio as Additional Parameters.

Figure 9. Average Specific Cake Resistance Liquefied Lignite Slurry at 180°C and 13.7 N/cm² as Functions of Liquefaction Condition.

CHAPTER V

FILTRATION WITH VARIABLE SLURRY CONCENTRATION AND SLURRY
DISPERSION: Solution of a Moving Boundary Problem

INTRODUCTION

The development of filtration theories and models to date has been concentrated on constant pressure filtration (Tiller, 1966; 1977). Although several 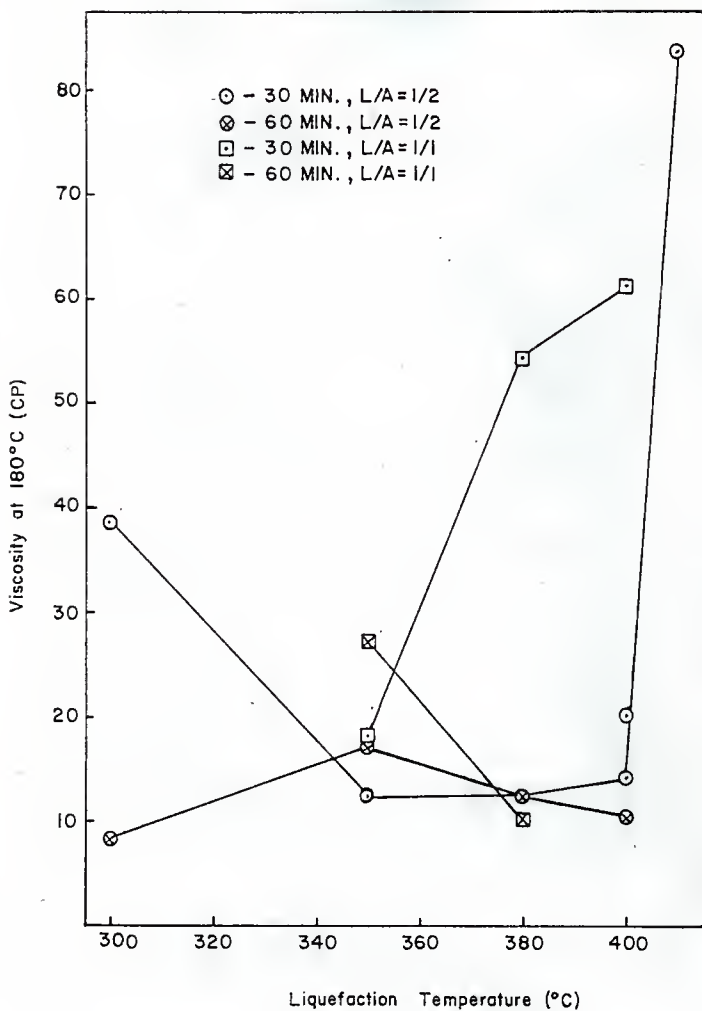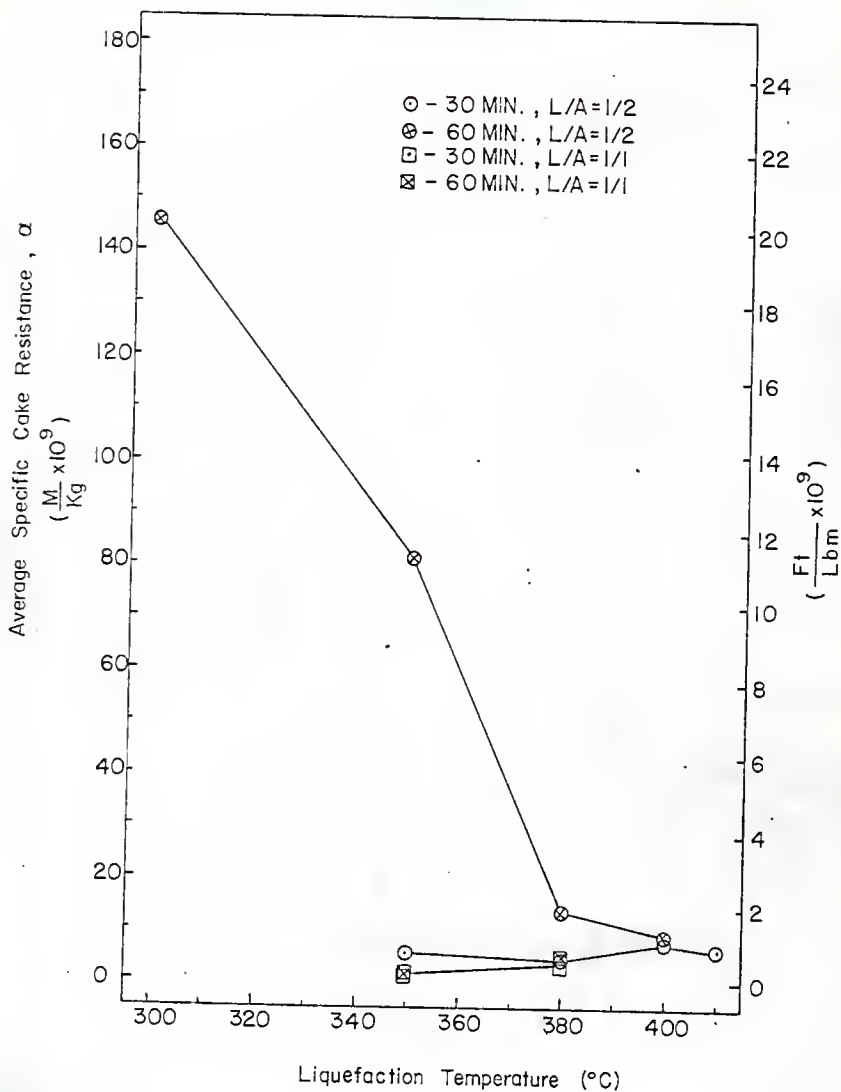works have been published on constant rate filtration (see, e.g., Machej, 1974; Silverblatt, et. al., 1974; Tiller and Crump, 1977), it appears that little has been published on variable pressure, variable rate filtration. Furthermore, previous works were almost entirely concerned with situations where slurry concentrations are maintained constant. It was not until recently that Tiller and Anantharamakrishnan (1977) presented their analysis of filtration involving variable slurry concentration.

The study of variable concentration filtration is important in view of the semi-continuous industrial filters where a layer of precoat is layed and a filtration cycle is initiated with clear liquid in the filtration chamber (Perry and Chilton, 1973; Himes, et. al., 1977). As the slurry feed is introduced, the solids concentration in the chamber increases simultaneously. Tiller and Anantharamakrishnan (1977), have derived analytical expressions relating the filtrate volume and the filtration time for both slug (or plug) flow and completely mixed flow systems. The present work deals with the constant pressure filtration system with longitudinal dispersion of slurry. This gives rise to the filtration chamber with a temporally and spatially variable slurry concentration. The resultant governing equation of the parabolic partial differential equation type, together with its boundary conditions and the coupled filtration equation, yields a unique and complex moving boundary problem; the governing equation contains a convective term with variable coefficients. The convective terms

are usually missing or remain constant in conventional moving boundary problems, e.g., those encountered in dealing with heat and mass transport accompanied by phase changes or chemical reaction of solid substances (Bankoff, 1964; Wilcox, 1967; Chalmers, 1964). Whereas Tiller and Anantharamakrishnan were able to obtain analytical solutions, it appears that we have to resort to an approximate analytical or numerical method to solve the present problem.

THEORY

The filter cake is viewed as a separate entity as shown in Figure 1 which depicts only the slurry section of the filtration chamber. The volume of the cake increases, and the length of the slurry section of the filtration chamber decreases from the initial value of L to ℓ with the increase in filtration time. A solids material balance around a differential volume between z and $z + \Delta z$ in the slurry section of the filtration chamber yields the following partial differential equation under the assumption that the contents in the chamber are continuous and homogeneous (Tojo, et. al., 1975):

$$\frac{\partial C_s}{\partial t} = D \frac{\partial^2 C_s}{\partial z^2} - u_\ell(t) \frac{\partial C_s}{\partial z} \tag{1}$$

where

C_s = volume fraction of solids

t = time

$u_\ell(t)$ = the convective velocity of the slurry

z = axial coordinate

D = dispersion coefficient of the solids

The initial condition is

$$C_s = 0 \qquad \text{at} \qquad t = 0$$

The following boundary conditions are obtained under the assumption that no dispersion of the solids occurs outside the slurry section of the filtration chamber (Levenspiel and Bishoff, 1963; Wen and Fan, 1975);

$$u_\ell C_{Sin} = u_\ell C_s \Big|_{z \to 0+} - D \frac{\partial C_s}{\partial z} \Big|_{z \to 0+} \qquad \text{at} \qquad z = 0 \tag{3}$$

and

$$\frac{\partial C_s}{\partial z} \Big|_{z=\ell} = 0 \qquad \text{at } z = \ell \tag{4}$$

where

C_{sin} = volume fraction of the solids in the feed slurry.

A solids balance at the slurry-cake interface gives

$$u_\ell C_s \Big|_{z=\ell} = -(1 - \epsilon) \frac{d\ell}{dt} \tag{5}$$

where

ϵ = average porosity of the cake

ℓ = position of the slurry-cake interface or the length of the slurry section.

Equation (5) can be integrated to give the position of the slurry-cake interface at any time t as

$$\ell(t) = 1 - \frac{1}{(1 - \epsilon)} \int_0^t u_\ell C_s \Big|_{z=\ell} dt \tag{6}$$

The slurry velocity, u_ℓ, is also the filtration rate. It can be determined from the Ruth filtration equation (McCabe and Smith, 1956) in the form of

$$u_\ell = \frac{p}{\mu \left(\frac{m_c \alpha}{A} + R_m\right)} \tag{7}$$

where

p = applied filtration pressure

μ = viscosity of liquid

m_c = mass of the accumulated cake

α = average specific cake resistance

A = filter area

R_m = resistance of the filter medium (or the precoat)

For constant pressure, constant temperature filtration, p, μ, α, and R_m remain constant.

The mass of the accumulated cake, m_c, can be expressed as

$$m_c = \rho_s \ (1 - \varepsilon) \ A \ (L - \ell) \tag{8}$$

where ρ_s is the density of the solids, and $(L - \ell)$ is the thickness of the cake. Substituting equation (8) into equation (7) yields

$$u_\ell = \frac{p}{\mu \ [\rho_s \ (1 - \varepsilon) \ \alpha \ (L - \ell) + R_m]} \tag{9}$$

The normalized forms of equations (1) through (4) are, respectively,

$$\frac{\partial C}{\partial \theta} = -u \ \frac{\partial C}{\partial \xi} + \frac{1}{N_{pe}} \ \frac{\partial^2 C}{\partial \xi^2} \tag{10}$$

$$\text{I.C.} \ \ C = 0 \qquad \text{at} \qquad \theta = 0 \tag{11}$$

$$\text{B.C.'s} \ \ uC_{in} = uC \big|_{\xi \to 0+} - \frac{1}{N_{pe}} \ \frac{\partial C}{\partial \xi} \bigg|_{\xi \to 0+} \qquad \text{at} \qquad \xi = 0 \tag{12}$$

$$\frac{\partial C}{\partial \xi} \bigg|_{\xi = \beta} = 0, \qquad \text{at} \qquad \zeta = \beta \tag{13}$$

and those of equations (6) and (9) are, respectively,

$$\beta = 1 - \int_0^\theta uC \big|_{\xi = \beta} \ d\theta \tag{14}$$

$$u = \frac{a}{b(1 - \beta) + a} \tag{15}$$

The dimensionless groups in these expressions are defined as

$$C = \frac{C_s}{1 - \varepsilon}, \qquad\qquad C_{in} = \frac{C_{sin}}{1 - \varepsilon},$$

$$\theta = \frac{u_o t}{L}, \qquad\qquad \xi = \frac{z}{L},$$

$$u = \frac{u_\ell}{u_o}, \qquad\qquad \beta = \frac{\ell}{L}, \tag{16}$$

$$N_{pe} = \frac{u_o L}{D} \ .$$

Here u_0 is the initial filtration rate and can be determined from equation (9) with $\ell = L$:

$$u_0 = \frac{p}{\mu R_m} \tag{17}$$

The constants, a and b, in equation (15) are, respectively,

$$a = \mu R_m, \tag{18}$$

and

$$b = \rho_s \mu \alpha L \ (1 - \varepsilon) \tag{19}$$

Note that the present transient model of filtration accompanied by the longitudinal dispersion of slurry gives rise to a moving boundary problem of the very general and complex type. This is the consequence of the advancing slurry-cake interface and increased cake resistance with the progress of the filtration process.

SOLUTION

In solving the highly coupled equations (10), (14) and (15), a finite difference method has been employed. Discretization of equation (10) and its initial and boundary conditions is made with the following forward-difference approximation for the first-order derivative and the center-difference approximation for the second-order derivative (see, e.g., Ames, 1977):

$$\frac{\partial C}{\partial \xi} \cong \frac{C_{i+1} - C_i}{\Delta \xi}$$

$$\frac{\partial^2 C}{\partial \xi^2} \cong \frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta \xi^2} \tag{20}$$

where C_i's and $\Delta \xi$ are depicted in Figure 2. With these substitutions, equations (10), (12) and (13) become, respectively,

$$\frac{dC_i}{\partial \theta} = -u \left(\frac{C_{i+1} - C_i}{\Delta \xi} \right) + \frac{1}{N_{pe}} \left(\frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta \xi^2} \right),$$

$$i = 1, 2, \ldots, N-1$$

$$\frac{dC_0}{d\theta} = \frac{dC_N}{d\theta} = 0, \tag{21}$$

$$uC_{in} = u_0 C_0 - \frac{1}{N_{pe}} \frac{C_1 - C_0}{\Delta \xi} \tag{22}$$

and

$$C_N = C_{N-1}, \tag{23}$$

where N is the number of ordinary differential equations resulting from discretization. Since the length of the dispersion chamber decreases as cake solids accumulate, N also decreases from the original value of $1/\Delta \xi$.

A trapezoidal rule approximation is used in evaluating the integration in equation (14). It can be written as

$$\beta(\theta) = 1 - \left(\frac{\Delta \theta}{2} \right) \sum_{j=1}^{M} \left([uC|_{\xi=\beta}]_j + [uC|_{\xi=\beta}]_{j-1} \right), \tag{24}$$

$$M = \frac{\theta}{\Delta \theta}$$

where $\Delta \theta$ is the time increment.

The numerical scheme employed in this work to solve the simultaneous equations is shown in Figure 3. In essence, the values of β, position of the slurry-cake interface, and u, the filtration rate, determined in the θ_{j-1}'s calculation are used as constants during numerical integration of equations (21) at time θ_j. It is worth noting that the solution scheme involves a direct solution of the governing equations and that this numerical scheme did not invoke quasi-steady state assumptions nor a preliminary transformation of the original equations that are typical in the solution of moving boundary problems (Bankoff, 1964). The widely available software packages GEAR and/or

GEARB (Hindmarsh, 1974; 1975) can be used to solve the system of stiff ordinary differential equations, equation (21). The packages offer variable order methods, automatic time-step, error control, and they are particularly known for their efficiency in solving stiff problems (Gear, 1971).

RESULTS AND DISCUSSION

Calculations have been executed with the following values for constants: $C_{in} = 0.2$, $a = 1.58$, $b = 33.9$. Values of a and b correspond to an average specific cake resistance, α, of 1.99×10^9 ft/lbm (1.41×10^{10} m/kg) and a medium resistance, R_m, of 3.20×10^{10} ft^{-1} (1.05×10^{11} m^{-1}) which were experimentally determined during pressure filtration of liquefied lignite at 356°F and 20 psi (180°C, 1.38×10^5 N/m^2).

Time increments of 0.1 and spatial mesh of 50 (i.e., N is initially 50) are used. The results of the calculations are shown in Figures 4 through 9.

Figures 4 through 8 show the solids concentration profile in the filtration chamber at various times and for the Peclet number, N_{pe}, of 0.001, 1.0, 10.0, 50.0, and 100.0. Initially, there are no solids in the chamber. With the assumption of constant porosity of the filter cake, the dimensionless solids concentration in it has a constant value of unity. Therefore, the slurry-cake interface is represented by a vertical line extending from $C\big|_{\xi=\beta^-}$ to 1. It appears that the rate of cake formation becomes weakly dependent on the Peclet number when $\theta \geq 2.0$ and that about 20% of the filtration chamber becomes occupied by the cake when θ reaches 4.0.

Figure 4 indicates that the concentration profile is essentially flat when the Peclet number is small as 0.001; in contrast, Figure 7 or 8 shows that the concentration profile resembles that of a slug (plug) flow system when the Peclet number becomes large. It is well known (Levenspiel and Bischoff, 1963) that the dispersion model approximates the behavior of a

completely mixed flow system at one extreme of having an infinitely large dispersion coefficient and that it approximates the behavior of the plug flow system at the other limit of having a negligibly small dispersion coefficient. Often analytical solutions of the completely mixed flow and the slug (plug) flow systems are attainable. For this particular problem, analytical solutions were presented by Tiller and Anantharamakrishnan (1977). Their solutions are in close agreement with those of the present work obtained at the upper and lower bounds of the Peclet number, as shown in Figure 9 where the accumulated filtrate volume is plotted against time. The filtrate volume curves for the dispersion model are calculated with a trapezoidal rule approximation of the following integral:

$$\text{Filtrate Volume } (\theta) = \int_{0}^{\theta} u d\theta \tag{25}$$

The oscillation observed in Figure 8 is quite common in numerical solutions of partial differential equations (see, e.g., Carver, 1976). Its appearance is caused by the inability of the numerical methods to handle "sharp" functions such as those resulting from a step change. Oscillation also frequently indicates the onset of instability. Once the oscillatory wake has passed, the solution stabilizes to its normal value. In the present work, the oscillation is eliminated when the spatial mesh is increased from 50 to 100, as can be seen in Figure 8. Generally, increasing the number of spatial meshes (i.e., reducing $\Delta\xi$) will stabilize the solution; however, this is done at the cost of increased computational time. In most moving boundary problems, the Peclet number is usually small enough so that stability is not a problem when an adequate number of spatial meshes is employed.

GEAR and GEARB (Hindmarsh, 1974; 1975) are generally considered as the most efficient available packages for solving highly stiff differential

equations such as those commonly encountered in the chemical engineering field (Heydweiller and Sincovec, 1976). The capability of these software packages does not diminish appreciably when coping with systems with a large number of differential equations. An example of such a system is the freezing of multicomponent liquid, in which each component gives rise to a single partial differential equation. The present numerical solution scheme should be applicable to systems with more than one differential equation.

CONCLUDING REMARKS

A mathematical model of the transient filtration process accompanied by the dispersion of solids in the slurry section of the filtration chamber has been presented. The model takes into account the temporal variation of solids concentration distribution which develops in the filtration chamber. The model naturally reduces to those of the ideal slug (or plug) flow and completely mixed flow systems. The model also gives rise to a moving boundary problem of the very general type which has been solved numerically. It appears that a similar numerical scheme can be applied to a variety of hitherto unsolved moving boundary problems or to those solved by imposing quasi-steady state assumptions (see, e.g., Wilcox, 1967, Bankoff, 1964).

NOMENCLATURE

A = filter area

a = constant

b = constant

C = dimensionless solids concentration

C_{in} = dimensionless solids concentration in the feed slurry

C_s = volume fraction of solids

C_{sin} = volume fraction of solids in the feed slurry

D = dispersion coefficient of solids in liquid

L = length of filtration chamber

ℓ = position of the slurry-cake interface, or the length of the slurry section.

m_c = mass of the accumulated cake

N = number of discretized equations

N_{pe} = Peclet number

p = filtration pressure

R_m = filter medium resistance

t = time

u = dimensionless filtration rate or the dimensionless slurry velocity

u_ℓ = filtration rate or the slurry velocity

u_o = initial filtration rate

z = spatial coordinate

Greek Symbols

α = average specific cake resistance

β = dimensionless position of the slurry-cake interface

ε = average porosity of the filter cake

μ = viscosity of liquid

ξ = dimensionless spatial coordinate

ρ_s = density of solids

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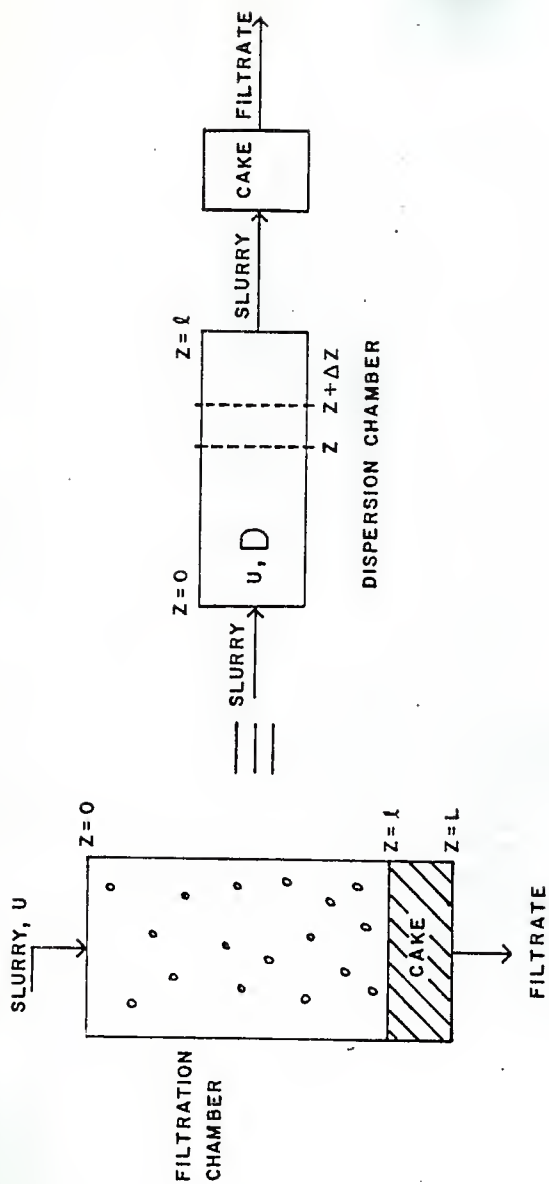
Figure 1. Diagramatic Representation of the Modeling Scheme.
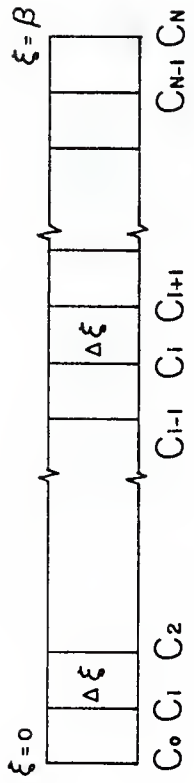
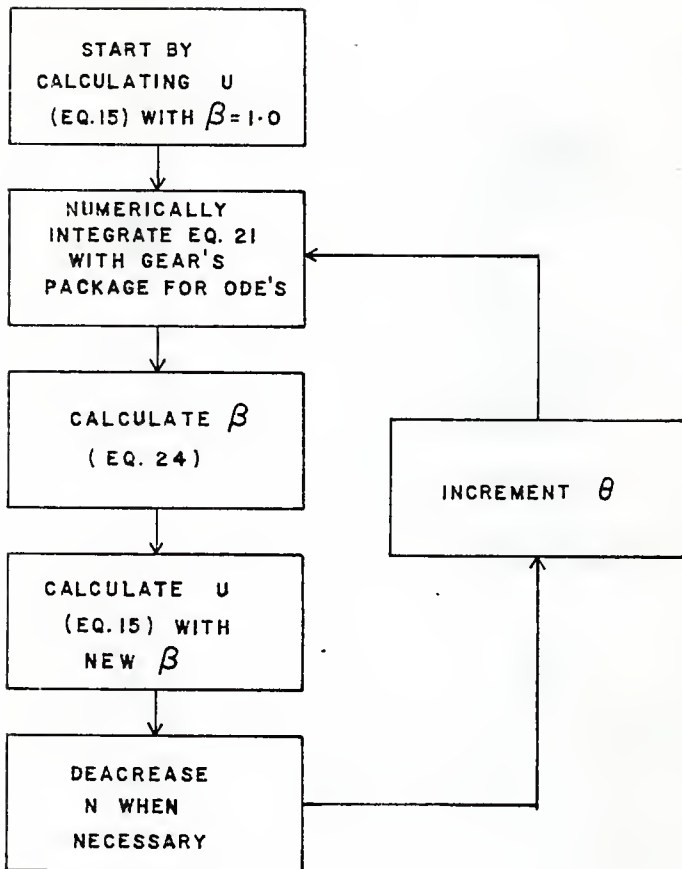Figure 2. Discretization of a Continuous Dispersion Chamber.

Figure 3.   Numerical Scheme for the Solution of a Moving
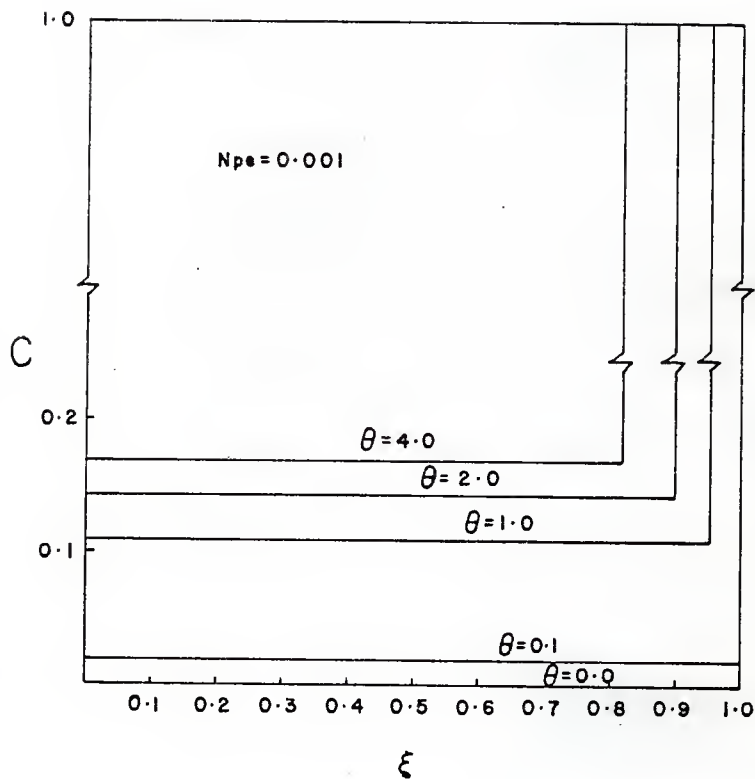   Boundary Problem.

Figure 4. Solids Concentration Profile in the Filtration
Chamber with N_{Pe} = 0.001.

Figure 5. Solids Concentration Profile in the Filtration
Chamber with N_{Pe} = 1.0.

Figure 6. Solids Concentration Profile in the Filtration Chamber with N_{Pe} = 10.0.
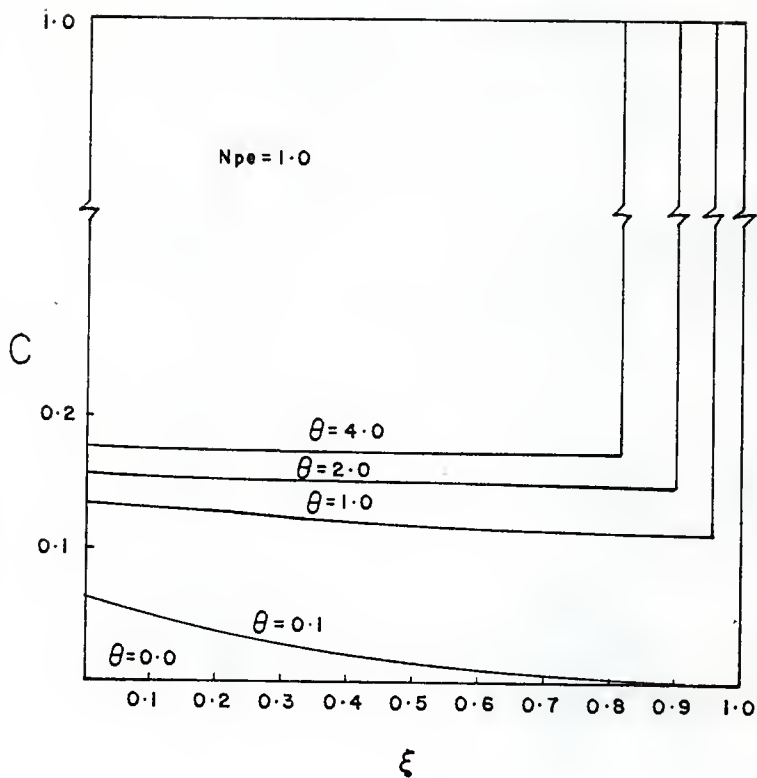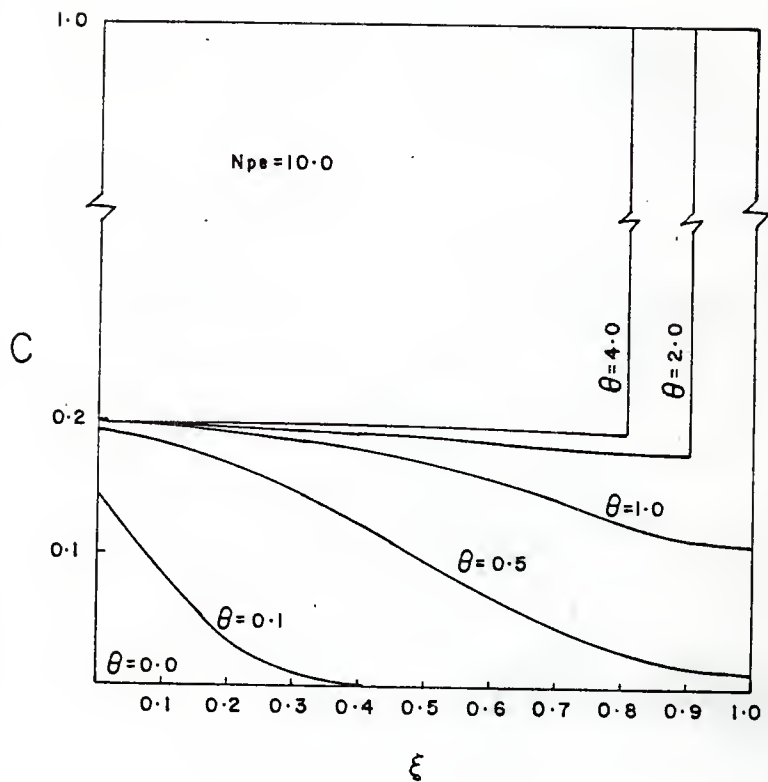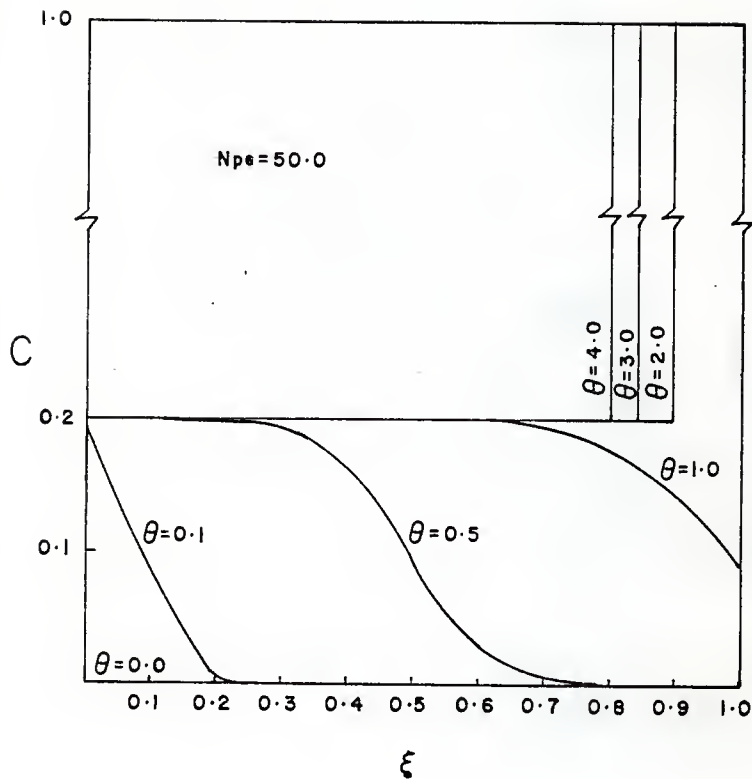
Figure 7.   Solids Concentration Profile in the Filtration
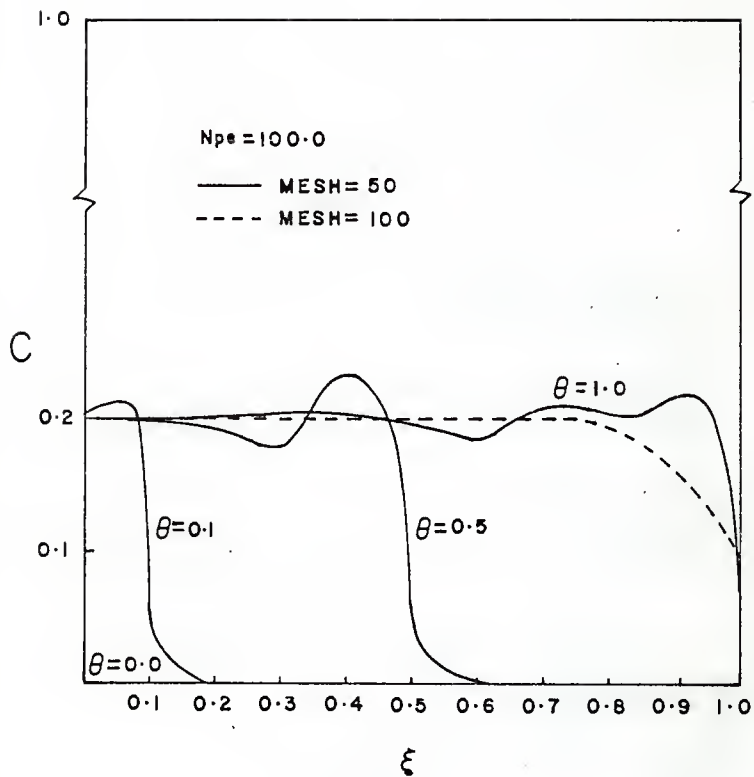   Chamber with N_{Pe} = 50.0.

Figure 8. Solids Concentration Profile in the Filtration Chamber with $N_{Pe} = 100.0$
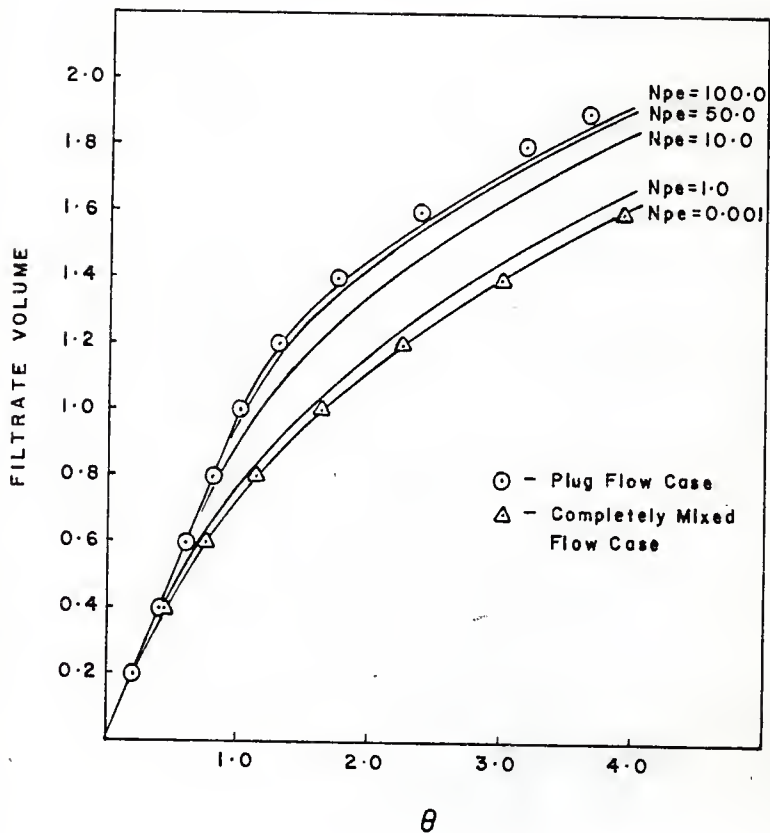
Figure 9. Comparison of the Accumulated Filtrate Volume Calculated with the Dispersion Model and that Calculated with the Plug Flow and Completely Mixed Flow Models of Tiller et. al.

APPENDIX 1.   DERIVATION OF THE DISPERSION EQUATION

Consider a material balance on a differential volume in the slurry section of the filtration chamber:

rate of solids in by convection at $z = u_\ell C_s \big|_z$ A,

rate of soids in by dispersion at $z = -D \dfrac{\partial C_s}{\partial z} \bigg|_z$ A,

rate of solids out by convection at $z+\Delta z = u_\ell C_s \big|_{z+\Delta z}$ A,

rate of solids out by dispersion at $z+\Delta z = -D \dfrac{\partial C_s}{\partial z} \bigg|_{z+\Delta z}$ A,

accumulation of solids in the idfferential volume $= \dfrac{\partial C_s}{\partial t}$ AΔz.

Summing all contributions, we obtain

$$\frac{\partial C_s}{\partial t} A\Delta z = u_\ell (C_s \big|_z - C_s \big|_{z+\Delta z}) \ A$$
$$- D \ (\frac{\partial C_s}{\partial z} \bigg|_z - \frac{\partial C_s}{\partial z} \bigg|_{z+\Delta z}) \ A$$

Dividing this equation by AΔz and taking the limit as $\Delta z \to 0$ gives the dispersion equation, we have

$$\frac{\partial C_s}{\partial t} = -u_\ell \ \frac{\partial C_s}{\partial z} + D \ \frac{\partial^2 C_s}{\partial z^2}$$

APPENDIX 2. DERIVATION OF BOUNDARY CONDITIONS

The equivalence relationship between compartments-in-series with the back-flow model and the dispersion model is (Wen and Fan, 1975)

$$\frac{fu_\ell}{\Delta z} \cong \frac{D}{\Delta z^2}$$

with

$$\frac{u_\ell}{\Delta z} = \frac{vN}{V}$$

where

f = fraction of back-flow

u = specific velocity in the dispersion model

z = axial coordinate of the dispersion model

D = dispersion coefficient

v = volumetric flowrate in the compartments-in-series with back-flow model

$\frac{V}{N}$ = volume of the individual compartments

This relationship and the compartments-in-series with the back-flow model depicted below will be used to derive the boundary conditions for the dispersion model. Closed-Entrance Boundary Condition at $z = 0$,
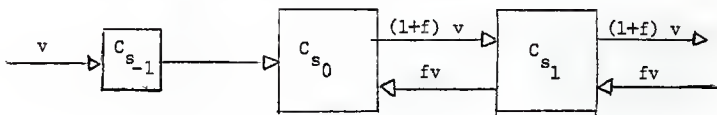
Material balance on the compartment, 0, yields

$$\left(\frac{V}{N}\right) \frac{dC_{s_0}}{dt} = v \, (C_{s_{-1}} - C_{s_0}) + fv \, (C_{s_1} - C_{s_0})$$

Applying the equivalence relationship, we have

$$\Delta z \frac{dC_{s_0}}{dt} \cong u_\ell \, (C_{s_{-1}} - C_{s_0}) + D \frac{C_{s_1} - C_{s_0}}{\Delta z} \quad .$$

Letting $C_{s_{-1}} = C_{sin}$, and taking the limit as $\Delta z \to 0$, the boundary condition becomes

$$u_\ell C_{sin} = u_\ell C_s \Big|_{z \to 0+} - D \frac{\partial C_s}{\partial z} \Big|_{z \to 0+} \quad .$$

Closed-Exit Boundary Condition at $z = \ell$
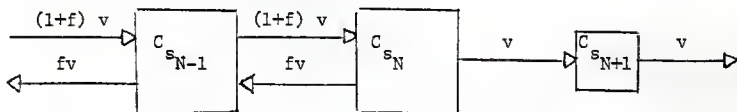
Material balance on the N-th compartment yields

$$(\frac{V}{N}) \frac{dC_{s_N}}{dt} = v \, (C_{s_{N-1}} - C_{s_N}) + fv \, (C_{s_{N-1}} - C_{s_N})$$

Applying the equivalence relationship, the above equation becomes

$$\Delta z \frac{dC_{s_N}}{dt} \cong u_\ell \, (C_{s_{N-1}} - C_{s_N}) + D \frac{C_{s_{N-1}} - C_{s_N}}{\Delta z}$$

Letting $C_{s_{N-1}} \to C_{s_N}$ and taking the limit as $\Delta z \to 0$, the boundary condition becomes

$$\frac{\partial C_s}{\partial z} \Big|_{z = \ell} = 0$$

CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

The following areas of research are suggested for future pursuit:

CONVERTIBLE (SEMIFLUIDIZED) BED FILTER

The results of the present work indicate that convertible
or semifluidized bed filters may have great potentials in solid–liquid
separation not only for synthetic fuel processes but also for other
industries where separations are carried out in severe conditions.

The convertible bed filter (Wen and Fan, 1977), which is based on the
principle of semifluidization (Fan, et al., 1959; 1961; 1968), consists of
a cylindrical bed section containing a distributor plate, the bed and a
sieve plate. The slurry to be filtered is dispersed and injected into the
bed through a conical shaped flow regulator at the bottom of the filter
bed. The bed is comprised of packing particles which are inert and serve
as a porous filter. The sieve plate located at the top of the bed permits
the passage of filtrate from the bed and retards the upward movement of
the bed particles once the fluid stream enters the chamber. The maximum
filtration rate is maintained in the convertible (semifluidized) bed by
maintaining an ultra-thin cake. A diagrammatical representation of the
filtration cycle is shown in Figures 1 through 4, and the following is a
description of the cycle.

Initially the bed is in a fixed configuration as the fluid stream
containing fines (solid or colloidal material to be removed) enters the
flow regulator and passes into the bed. The fines, upon entering the por-
tion of the bed adjacent to the distributor zone, are unable to penetrate
the bed to any great extent before being stopped by the bed particles.
Thus, a "cake" of fines begins to build up in this zone. The formation of
the cake produces an increased pressure drop as monitered via the pressure

taps at the distributor and at the top of the bed. This rise in the pressure drop activates a driving mechanism which raises the sieve plate. The mechanical movement of the sieve plate in conjunction with the . . forces being exerted by the fluid stream disrupts the formed cake of fines into small fragments. Cake disruption is also aided by the fluidized particles. In addition, the act of disruption of the existing cake causes more of the particles which are encased by the cake to become fluidized. Raising of the sieve plate continues while small fines in the stream are being trapped in the fixed bed. The amount of fixed bed gradually decreases with successive disruption of the formed cakes.

Continuation of this process results in the condition where the amount of fixed bed remaining can no longer function adequately as a filter. At this point, the fluid stream is stopped and the contents of the bed chamber may be purged or flushed by lifting the sieve plate to the very top of the column. Depending on which process is used for removal of cake and cake fragments, the bed column is returned to the initial conditions to restart the filtering process. The fines to be filtered can fill 80 to 90% of the volume of the column at the end of the operation. The column can be heated or pressurized to such a condition that the fluid density and viscosity are adjusted for easier flow through the packing. The filtration process described here using a convertible bed (semifluidized bed) may be suitable for removal of ash, sand and other particulates from liquefied coal and petroleum crude oil. Continuous filtration can be established by utilizing two or more beds.

SCALE-UP, DESIGN AND SYSTEM SYNTHESIS

To scale-up or design any of the separation processes that are reviewed in Chapter II, it is essential that a mathematical model be developed

which characterizes the performance of the process. This can be accomplished
best by adopting the so-called sequential mechanistic model building pro-
cedure (Box and Hill, 1967; also see Appendix 1). The procedure will
permit the fullest exploitation of the available data, the fundamental
theories and the existing models, and will enable the effective utilization
of new data yet to be obtained and of new mechanisms yet to be discovered.

The sedimentation-filtration test discussed in Chapter II and the observed
exponentially increasing effort required, in any given technique, to remove
the solids as their concentration diminishes seem to indicate a need for
more than one method of solid residue-liquid product separation for any
coal liquefaction process. In other words, there exists a combination of
different separation techniques which will be best suited for a particular
liquefaction process. Methods of finding such a combination or methods
of system synthesis are available (see Appendix 2).

Because of the extreme complexity of solid residue-liquid product
separation in any coal liquefaction process, even an optimally synthesized
separation system will probably not perform optimally in practice. The
final determination of the optimal operating conditions should be carried
out experimentally by employing a suitable experimental optimization pro-
cedure, e.g., EVOP (see Appendix 3).

COMPUTER SIMULATION

Researchers in the field of solid-liquid separation processes have been
relying heavily on linearization and other mathematical simplifications of
the governing equations of the processes in order to solve them analytically.
However, with the advanced continuous industrial filters, such

simplifications are often impractical and undesirable. Furthermore, computer simulation can now be easily accomplished with the development of the high speed computers and the highly sophisticated integrator software packages. Therefore, more sophisticated and realistic models should be developed to accurately simulate and predict the performances of solid-liquid separation systems.

PETROLEUM COKE

In the experimental study of the solvolysis process, it was seen that the lignite and asphalt slurry was subjected to coking under certain reaction conditions. It was also observed that extensive coking took place in a relatively short period of 0.5 ~ 1 hour. In the commercial production of petroleum coke where a coking time of 8 to 24 hours is usually required, this could mean a tremendous saving. Additional research is required to determine the conditions of carbonization which would lead to efficient production of a clean coke. This would encompass the identification of process variables such as:

1. minimum lignite (or coal)-to-asphalt ratio which would still result in fast production of coke,

2. heating conditions which would reduce the sulfur content in the coke.

STATISTICAL ANALYSIS OF INTERACTION AND NON-NEWTONIAN EFFECTS

The solvolysis and filtration data obtained in the present work and other future data should be statistically examined for interaction effects among any of the reaction conditions which are difficult to detect other-wise. The analysis of filtration data in Chapter IV was carried out on

the assumption that slurry remained newtonian. This assumption may not be completely valid. Re-analysis of the data based on a non-newtonian model may be desirable.

FURTHER STUDY ON THE SOLVOLYSIS PROCESS

A study should be conducted to determine the effects of catalysts, solvent pretreatment, and other solvents on the conversion of lignite to gaseous and liquid products.

It is also highly desirable to determine the suitability of the solvolysis process in the extraction of bitumen from oil shale and oil sands.

GASIFICATION OF LIGNITE

Circulating-type fluidized bed gasifiers are currently being developed in Japan to produce low BTU gas from municipal solid wastes which contain as much as 30 - 50% moisture. Such a process could efficiently produce synthetic fuel gases from moist lignite by eliminating the costly drying process.

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LIQUID OR
GAS OUTLET
(FILTRATE)

MOVABLE ROD

HEATING MEDIUM

SIEVE PLATE

PACKINGS

DISTRIBUTOR

SOLID PARTICLES
SUSPENDING IN
FLUID TO BE FILTERED

FIXED BED

FLUID CONTAINING PARTICULATES
TO BE FILTERED

Figure 1. Initial Stage of Semi-fluidized
Filtration.

(FILTRATE OUTLET)

CAKE FORMATION

FLUID IN

Figure 2. Cake of Fines Start to Form at the
Bottom of the Fixed Bed.

Figure 3. Top Sieve Plate is Gradually Lifted and a Fluidized Bed is Formed Making Flow and Filtration Easier.
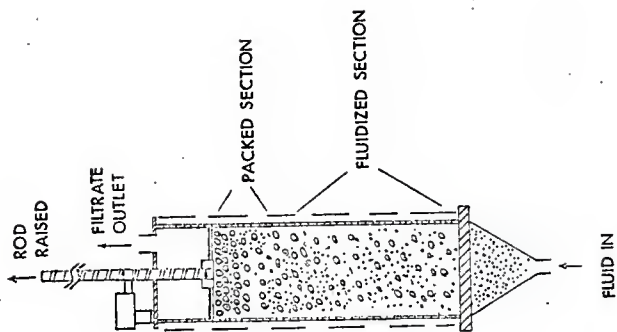
Figure 4. Final Stage of Filtration. Fines Collected Can Be Purged by Lifting the Sieve Plate and Washed by Suitable Fluid.
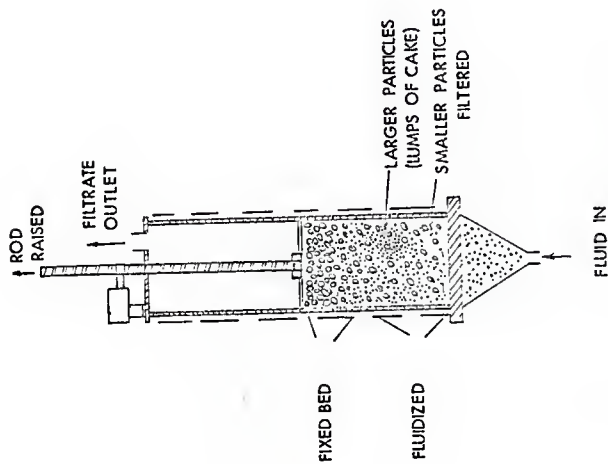
APPENDIX 1

MODEL DEVELOPMENT PROCEDURE

The mathematical form of a model can generally be written as

$$\eta = f(\theta; \xi)$$

where η is the dependent variable, or the response of the system to the independent (or, controllable) variables ξ, and the θ's are the parameters of the system. The procedure for building a mechanistic model can be roughly separated into two distinct stages, the specification and estimation stages (Hunter and Kittrell, 1967). In the specification stage, the problem is to search for an adequate mathematical function of the mechanistic model which appropriately describes the system behavior or response (Bruin, 1971). The techniques employed are: (a) model screening, (b) model discrimination, and (c) model modification. Although parameter estimation is often necessary to test the adequacy of any particular functional form at this stage, the estimation often does not need to be very precise. The estimation stage follows the specification stage, where attention is paid to the accurate estimation of the parameters within the chosen functional form.

At the onset of the specification stage, the model builder usually must select an appropriate functional form of the model from several forms which were derived from various proposed mechanisms. In case there is a large number of proposed models, the model builder might try to reduce the number of models to a minimum by applying preliminary screening techniques which include analysis of variance (Draper and Smith, 1966), test of residuals (Draper and Smith, 1966), and/or linear test of non-linear models (Kittrell, 1966) using sets of data generated through

a series of experiments with screening design (Kittrell, 1966). The

discrimination techniques, such as application of intrinsic parameters

(Kittrell and Mezaki, 1967), non-intrinsic parameters (Mezaki and Kittrell,

1966), and/or efficient model discrimination experiments (Hunter and

Reiner, 1965; Hill, 1966), are applied to the outcome of model screening

to choose the most adequate model. At this point it may happen that

the chosen model has a specific shortcoming under certain conditions.

The procedure of model modification (Box and Hunter, 1962; Hunter and

Mezaki, 1964) can be employed to eliminate the shortcoming until a satis-

factory form of the model is obtained.

In any model building procedure, values of parameters in the model

have to be estimated through comparison between the predicted values

of system responses based on the model and the corresponding observed

values from the experiment. For a linear model using least square criteria,

estimation is quite straight-forward (Draper and Smith, 1966); however,

for non-linear models, estimation is generally more complicated and require

use of some iterative search procedures (Bard, 1967; Marquardt, 1963;

Fletcher and Powell, 1963) which minimize (or maximize) some appropriate

functions of residuals, such as least squares (Draper and Smith, 1966),

weighted least squares (Hill, 1966), maximum likelyhood (Bard, 1967),

and Bayesian (Box and Draper, 1965).

Once model discrimination has been accomplished, and the best model

is selected from a group of rival models, further experimentation can

be conducted to improve parameter estimation. Criteria for efficient

design of experiments to increase the preciseness of parameter estimates

have been developed (Kittrel et al., 1966; Box and Hunter, 1965; Box,

1970). The sequential mechanistic model building procedure is outlined

in Table A1-1.

TABLE A1-1. OUTLINE OF MECHANISTIC MODEL BUILDING

INITIAL STAGE

Derivation of Models

1. Understanding of the system through review of past experiences, survey of literature and/or exploratory experimentation

2. Proposal of possible mechanisms

3. Derivation of mechanistic models

SPECIFICATION STAGE

Model Screening

1. Experimental design for model screening

2. Analysis of data by using techniques of
Analysis of variance (test of lack of fit)
Analysis of residual
Linear Test of non-linear models

Model Discrimination

1. Use of diagnostic parameters

2. Experimental design for model discrimination

Model Modification

ESTIMATION STAGE

1. Experimental design for parameter estimation

2. Least square estimation

3. Maximum likelihood estimation

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APPENDIX 2

SYSTEMS SYNTHESIS METHODOLOGIES

The study of system synthesis, beginning in 1968, has developed into six major areas; the decomposition approach, the heuristic technique, evolutionary design, dynamic programming, branch and bound strategies, and the structural parameter integrated approach. How one classifies a particular application can be somewhat subjective since many papers use combinations of these basic techniques. To describe system synthesis, the guides for type assignment must be somewhat soft or flexible so that a single paper can be said to advance more than one concept of synthesis.

Decomposition Approaches

To decompose is to subdivide; to subdivide is to simplify. Rudd (1968) first formally stated the decomposition algorithm for the optimal design of a complicated or nonsolvable system as one of decomposing the original problem into smaller solvable problems. For the simplest case, one large system is decomposed into two smaller subsystems; or one large optimization, design problem is decomposed into two smaller less compli- cated and solvable optimization problems plus one problem of optimally combining the subsystems into the original system. The subsystems are optimized with respect to the independent variables associated with each subsystem; while the decomposition, recombination problem is optimized with respect to how the problem is decomposed and recombined.

Rudd describes a general philosophy of developing a design as one of decomposing a problem that cannot be solved with existing technology into a group of subproblems which can be solved with existing technology.

Several researchers have investigated how large sets of interconnected equations can be solved by decomposing the problem into smaller tasks and then combining the smaller problems into the original large problem.

Christenson et al. (1969) investigated decomposition of design equations for large systems with many recycle streams to obtain an optimal solution.

One of the most recent of these solution procedures, tearing algorithm papers, was that by Westerberg and Debrosse (1973). Again it presents a method to obtain a solution procedure for a system with many recycle streams and other complicated interconnections.

Decomposition procedures have been applied to the systems synthesis problem directly by Nishida et al. (1971), Kobayashi et al. (1971), Umeda and Ichikawa (1972), Menzies and Johnson (1972) and Osakada and Fan (1972).

In 1972, a symposium was held in Cambridge, England, on decomposition theory as applied to control theory, computer science, operations research, chemical engineering mathematics, and network theory. The notes of the symposium, edited by Himmelblau (1973), contained thirty-seven papers. About ten papers considered nonlinear systems, but only two of these papers presented complete applications of their proposed decomposition schemes. The first paper, by Westerberg, implied that the direct solution of a combined problem without decomposition could be obtained more quickly than the decomposed problem. Jung et al. (1973) also reported this result when he reviewed several decomposition schemes. The second paper from the symposium, by Sandbloom, illustrated the optimization of a highly decomposable system of equations with his proposed decomposition scheme. The results indicated that, again, the direct solution without decomposition was faster than the decomposed problem. The method also required that

the objective function and constraints were convex and differentiable functions. Of course, the equations normally encountered in systems synthesis studies may not be convex or differentiable.

Wilde (1972) computed the constrained derivative from each stage of a large interconnected system and then the entire system is constructed from the combination of the derivatives of each stage by the chain rule.

Umeda et al. (1972) has presented the concept of a feasible decomposition method. All decomposition procedures before this decomposed a problem by assigning a variable at one point in the procedure and at some later point in the solution procedure, an equality constraint was added. The effect is to require the production of infeasible regions. Umeda's method first requires that the number of coordination variables produced in a decomposition be less than the number of independent variables associated with all of the subproblem optimizations. Next, instead of relaxing an equality, the method uses one of the internal independent variables in the subsystem to fix a coordination variable. An iterative technique is then used to alternatively fix coordination variables by selecting internal independent variables associated with a subproblem and, secondly, by selecting the remaining independent variables to achieve the desired result in the objective function.

Heuristic Technique

A heuristic rule is a guideline. Usually, its validity has been found from experience as opposed to being rigorously proved. In engineering the existence of such rules is wide spread. Indeed, the most noticeable distinction between a practicing engineer and a new graduate entering the field is the heuristic-knowledge gap.

The heuristic approach has long been the only available technique for process systems synthesis. Heuristic rules are probably still being used more often than any other system synthesis technique. The systematic use of a set of heuristic rules and a learning technique in systems synthesis apparently was first attempted by Masso and Rudd (1969) in heat exchanger network design.

In applying the heuristic technique, several sets of possible heuristic rules are first developed. Weighting terms are then introduced for the purpose of determining which heuristic rule should be used. Each time a particular heuristic rule performs well, its respective weighting term is incremented; if the heuristic rule performs poorly, the weighting term is decremented. The value of the weighting term determines which heuristic rule will be used from that set during later iterations.

Thompson and King (1972) used the heuristic technique to generate separation sequencing solutions. The heuristic rules used in their study were developed by Heaven (1969) in his study on distillation sequencing.

Siirola and Rudd (1971) extended the heuristic technique so that, given a reaction sequence, a complete task identification procedure, including material and energy balances and utility estimates can be developed. In addition to the heuristic rules employed in the computer program, the provision for the interaction with the design engineer is also included. Siirola, Powers, and Rudd (1971) continued with this Adaptive Initial Design Synthesizer (AIDES) and developed a semi-automated design synthesizer. This final form performs the complete design problem from the reaction scheme to the final flow sheet with the complete equipment specification.

Since the work of Powers in 1972, no new techniques or papers have been proposed dealing with the heuristic technique.

Evolutionary Method

A basic design technique used by practicing engineers in industry is evolutionary design. The principle is to first start with a working system and improve it. Of course, how or where the improvements should be made is not obvious. Indeed, that is the challenge to industrial optimization, to find areas in a system where costs can be decreased.

This method of evolutionary design is also used in systems synthesis. Again, the starting point is a working, feasible design. From this point changes are made in the structure of the system and the effect on the objective function of the proposed system is observed. If the profit is increased by the change in structure, the new system replaces the original design.

Evolutionary design has been used by King et al. (1972) to reduce the ethylene loss from a demethanizing tower of a chemical complex. How and where the changes in structure were made were determined entirely by engineering judgement. They also carried out an available energy balance over the entire process. Those units that had the largest loss of available energy were then studied closely to determine possible structural changes in order to minimize the energy consumption per pound of liquified methane.

Ichikawa and Fan (1972) used the evolutionary process to design a reaction-separation system. In addition, they derived the necessary condition for an optimal system.

The dual feasible decomposition proposed by Lasdon (1970) was used by McGalliard and Westerberg (1972) to develop an evolutionary design procedure with which the effect of a structural change could be determined

without reoptimization of the entire system. Several heat exchanger net-
work designs were synthesized with satisfactory results.

Dynamic Programming

A waste treatment plant was synthesized using dynamic programming
by Shih and Krishnan (1973). The system synthesized by them had a primary
clarifier, a trickling filter, an aerated lagoon, an activated sludge reactor,
a coagulation settler, and a carbon adsorbent filter. A drawback in the
problem formulation was the lack of a recycle stream around the activated
sludge reactor. In practice, however, such systems are extremely rare.

Separation sequencing was first performed with dynamic programming
and list processing by Hendry (1972). The difference between a pure dynamic
programming solution and the inclusion of list processing was two-fold.
First, the number of possible sequences that had to be considered were
reduced by taking into account only those separations included in the list
processing scheme. In other words, only a single split could be obtained
for each separation. The second difference was that the list processing
scheme allowed all types of separations to be considered in the same dynamic
programming problem. Extraction, distillation, crystallization could all
be considered in the same separation sequencing problem.

Energy integration was added to the work of Hendry by Rathore et al.
(1974a,b). By using Hendry's method of separation sequencing and dynamic
programming for the heat exchanger network design, the integration was achieved.
In a second paper, the problem was extended to the sequencing problem with
distillation towers operating at pressures other than atmospheric. Branch
and bound was used for the heat exchanger network design in this second paper.
Optimal systems were obtained by both techniques but the relative savings
was small for systems without energy integration.

Branch and Bound

Heat exchanger network synthesis was performed by Lee and Masso (1970) using a branch and bound algorithm. By relaxing the network feasibility criteria of using a stream only once in a network, a branch and bound algorithm could be formulated. A cost matrix was constructed from the costs of individual exchangers and subsequent networks including the neces- sary utility costs of steam and cold water needed to accomplish the process. The step of filling the cost matrix was considered to be the simplest step in the design problem. Next, various branching strategies were de- veloped along with the appropriate bounding criteria. By the repeatedly branching and bounding, the original problem was transformed into many small problems, many of which need not be solved completely. The job of comparison was then drastically reduced.

The second application of branch and bound by Menzies and Johnson (1972) expanded Lee's basic method of heat exchanger network design by considering both the heat transfer problem and the pressure change problem. The system structure for the units other than the heat exchanger network was fixed for the entire problem.

Branch and bound was finally used by Rathore et al. (1974b) in his distillation sequencing and energy integration problem.

Feasible Matrix and Decision Tree Methods

A decision tree algorithm developed by Pho and Lapidus (1973) consi- ders only the feasible structures of heat exchanger network synthesis. By judiciously matching streams in a matrix representation, the assign- ment effort and the computational burden are reduced. The condition that allowed branch and bound to be used in heat exchanger network synthesis

was the relaxed constraint on the multiple use of a single stream. The tree structuring method can then be used to include the multiple use constraint and therefore reduce the required computation. For example, a four stream heat exchanger network requiring the evaluation of 4200 possible system structures can be reduced to a problem of requiring examination of only 24 structures.

Synthesis by Direct Optimization

The structural parameter of solution formulation was introduced and first used with a direct search by Ichikawa et al. (1969), and has been used broadly. Since the study of optimization has been so extensive, it would seem plausible that these techniques could be used directly in systems synthesis. This is the basis for the structural parameter method of solution formulation used with a direct search. The method begins by devising a system structure composed of all the reasonable combinations of units. Engineering judgment and basic heuristic rules must, of course, be used in order to devise both a general system and a system of moderate size. Structural parameters are employed at splitting points to determine the split fractions of the state variables to the various streams leaving the split point. After a solution procedure and the appropriate decision variables are obtained, the system can then be optimized with any existing nonlinear optimization technique.

Since structural parameters are merely splitting fractions, they can also be used in combination with a variety of systems synthesis techniques. Umeda and Ichikawa (1972) used structural parameters with a decomposition technique; Ichikawa and Fan (1972) used them with an evolutionary approach; and Umeda, Shindo, and Tazaki (1972) used them with a feasible decomposition technique.

Hybrid Methods in Synthesis

Combinations of methods is very common in systems synthesis. For example, Hendry and Hughes (1972) used both dynamic programming and list processing in order to accomplish his separation sequencing. Rathore et al. (1974a,b) added the branch and bound strategy devised by Lee et al. (1970) to integrate the energy and separation sequencing problems.

Ichikawa and Fan (1972) used the structural parameter method of solution formulation and an evolutionary approach to optimize a reactor-separation system. Osakada and Fan (1972) used the structural parameter method of solution formulation and a multilevel decomposition procedure to optimize a reaction-separation system.

Additional information on system synthesis methodologies are available in two earlier reviews, one by Fan and Osakada (1972) and the other by Hendry and Rudd (1973).

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APPENDIX 3

PROCEDURE FOR EXPERIMENTAL OPTIMIZATION

Evolutionary operation (EVOP) is a statistical method for process improvement which employs sequentially Response Surface Methodology (RSM). EVOP was developed by Box and his associates (Box, 1954; Box, 1969; Box and Draper, 1969; Box and Hunter, 1958; Box and Wilson, 1951). The basic philosophy of the method is that data collected routinely during the regular operation of a process can often be used to find new operating conditions to improve its performance.

In biological waste treatment processes, the influent conditions and the ambient temperature are seldom constant. Furthermore, the loading often increases with time because of increases in population and/or expansion of industrial activity. It is, therefore, frequently necessary to search for improved operating conditions.

The number of independent operating variables that can be optimized simultaneously using EVOP is not fixed. Box and Draper (1969) described in detail the procedures for treating two independent variables using a 2^2 factorial design and for treating three independent variables using a 2^3 factorial design. A 2^2 factorial design was employed in this work to optimize two variables, flow rate ratio and volume ratio, as shown in Figure A3-1.

A single performance at one of the five operating conditions in Figure A3-1 is called a run while a complete sequence of performances at these five sets of operating conditions is called a cycle. The order of experiments within a cycle should be randomized. After several cycles, statistically significant results become available and a new phase or new set of operating conditions can be selected.

After n cycles, the effects and their standard errors for a 2^2 design can be computed according to Table A3-1. The effects of flow rate ratio, volume ratio, and their interactions can be presented diagrammatically as shown in Figure A3-2. From this diagram and Table A3-1 the effect of a variable can be interpreted.

The sample standard deviation, s_j, at point j is calculated from the positive root of the sample variance as follows:

$$(s_j)^2 = \frac{\sum\limits_{i=1}^{N} (\bar{y}_j - y_{ij})^2}{N - 1} \tag{1}$$

where

s_j = sample standard deviation at point j

$\bar{y}_j = (\sum\limits_{i=1}^{N} y_{ij})/N$

    = average of the N observations at point j

y_{ij} = value of the ith observations at point j

n   = number of observations.

One can estimate s from preliminary experiments before initiating the EVOP search pattern or from the use of data obtained during EVOP experiments. In this work s was initially estimated using four observations from four successive days for each of the five operating conditions during cycle 1 of phase 1; that is, at point j:

$$(s_j)^2 = \frac{\sum\limits_{i=1}^{4} (y_j - y_{ij})^2}{3} \quad , \quad j = 1, 2, 3, 4, 5 \tag{2}$$

where

$y_j = (\sum\limits_{i=1}^{4} y_{ij})/4$

y_{ij} = observation on day i at point j

s_j = standard deviation at point j

The average of the five values is

$$s = \frac{\sum_{j=1}^{5} (s_j)}{5} \tag{3}$$

The estimation of s for phase 2 was slightly different from that of phase 1. First, the four standard deviations for the operating conditions 1, 2, 3, and 4 between cycles 1 and 2 of phase 1 were calculated by using equation (1); the standard deviation for 0 was computed based on the three data at this operating condition from cycles 1 and 2 of phase 1 and cycle 1 of phase 2. Second, the average of these five standard deviations was taken as the standard deviation for cycle 1 of phase 2.

After the standard deviation is obtained the standard error in Table A3-1 can be calculated. The effects, which can be calculated using the formulas in Table A3-1, and the 2 S.E. limits are used in constructing the EVOP information board. An information board generally consists of the functions of interest (objective function and other reference functions), requirement, running averages, 2 S.E. limits, phase mean, effects with 2 S.E. limits, and standard deviations for individual observations. The standard error is multiplied by two because this gives values which are approximately equivalent to a 95% confidence interval. Thus, the statistical significance of the effects is given in the information board. As the number of cycles increases, the standard error decreases. After several cycles, statistically significant results can usually be obtained. This property of the method makes it particularly useful for improving operation in processes where the standard deviation is relatively large or where one can afford to make only small changes in operating conditions.

TABLE A3-1

Computational Formulas for the Effects and Standard Errors for a 2^2
EVOP Design

Effect	Formula (Sequence Numbering)	Standard Error
Main effect of flow rate ratio ($\bar{Q}$)	$\frac{1}{2}(\bar{y}_2 + \bar{y}_3 - \bar{y}_4 - \bar{y}_1)^*$	$\frac{s\dagger}{\sqrt{n}}$
Main effect of volume ratio ($\bar{V}$)	$\frac{1}{2}(\bar{y}_2 + \bar{y}_4 - \bar{y}_3 - \bar{y}_1)$	$\frac{s}{\sqrt{n}}$
Interaction ($\bar{Q} \times \bar{V}$)	$\frac{1}{2}(\bar{y}_2 + \bar{y}_1 - \bar{y}_4 - \bar{y}_3)$	$\frac{s}{\sqrt{n}}$
Change in mean	$(\bar{y}_1 + \bar{y}_2 + \bar{y}_3 + \bar{y}_4 - 4\bar{y}_0)/5$	$0.89\frac{s}{\sqrt{n}}$

$^*\bar{y}_1$, $\bar{y}_2$, $\bar{y}_3$, $\bar{y}_4$ and $\bar{y}_0$ = process averages from the n cycles for operating conditions 1, 2, 3, 4, and 0, respectively.

†s = sample standard deviation calculated from the positive root of the sample variance. n = number of cycles performed.
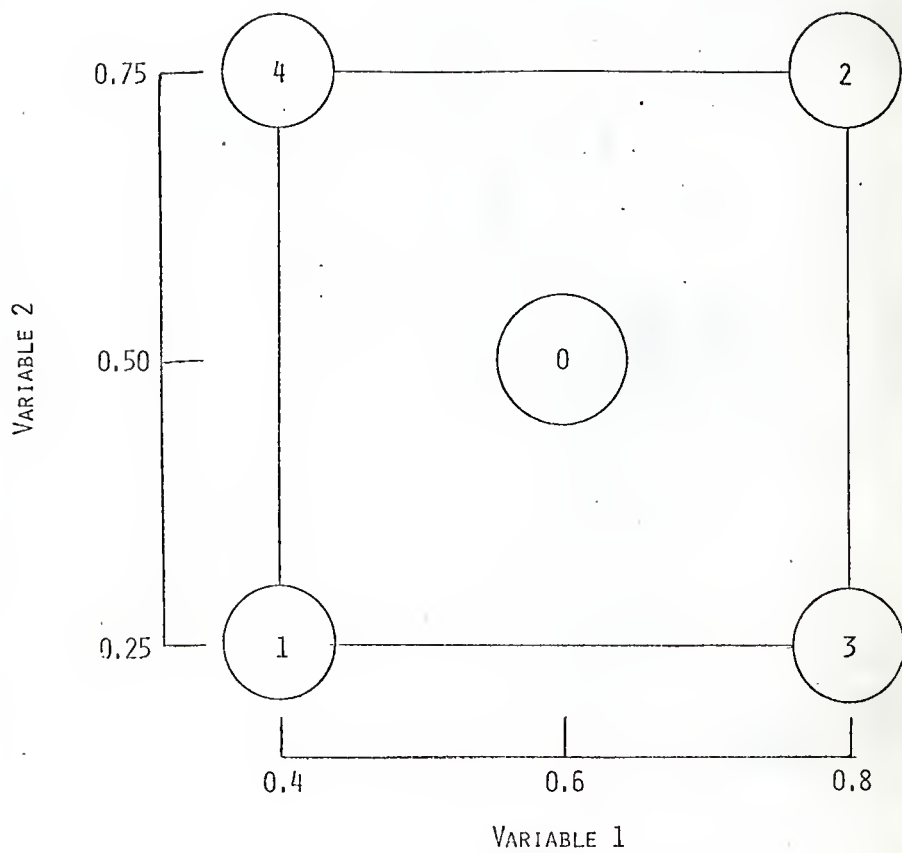
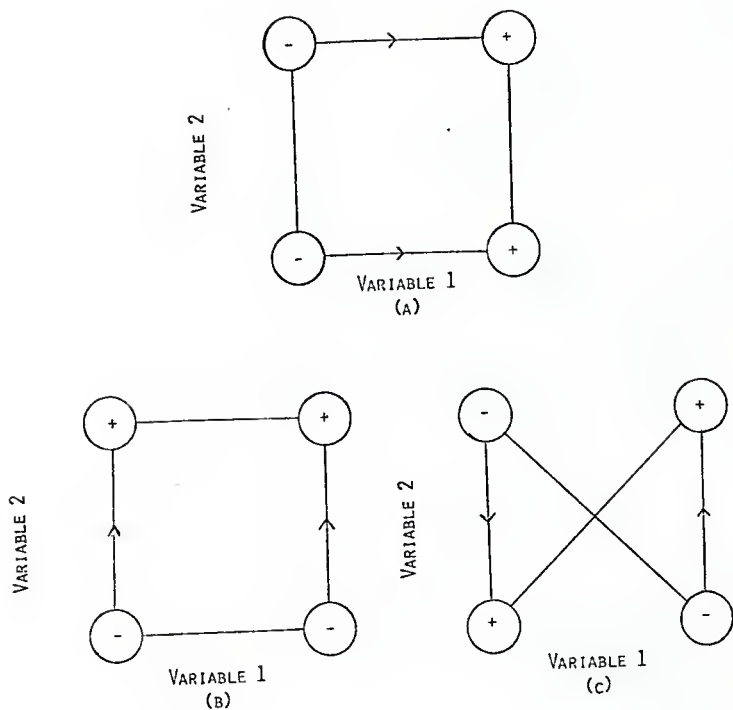Figure A3-1. Sequence of the Runs in a 2^2 EVOP Design.

Figure A3-2. Diagrammatic Representation of Effects for 2^2 EVOP Design:
(a) Variable 1 effect; (b) Variable 2 effect; (c) Inter-
action effect.

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SEPARATION OF SOLID RESIDUES
FROM A SYNTHETIC LIQUID FUEL

by

EDWARD H. HSU

B. S., Kansas State University, 1976

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AN ABSTRACT OF A MASTER'S THESIS

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Solid residue–liquid product separation techniques currently being tested for coal liquefaction processes were reviewed and summarized. The result indicates that no single technique, such as filtration, centrifugation, or sedimentation could effectively and economically remove the solid residues from liquefied coal.

Experimental study was then carried out to determine the effect of conditions during liquefaction on the ease of solid–liquid separation; liquefied Texas lignite slurries obtained through the solvolysis process under atmospheric pressure were filtered at 180°C (356°F) and 13.7 N/cm^2 (20 psi). The conversion of solid lignite to liquid and gaseous products through the solvolysis process with asphalt as the solvent was low (<25%). However, the difficulty of separation, measured in terms of filterability, was highly dependent on the liquefaction condition. The filtration rate varied from 0.05 to 1.56 $m\ell/cm^2$-min (0.7 to 23.0 gal/ft^2-hr). The experimental study also revealed that the solvolysis process might be an efficient process to produce petroleum coke.

The filtration parameters, such as the average specific cake resistance and filter medium resistance, determined in the experimental study were incorporated in a numerical simulation of a filtration process with variable slurry concentration. The resultant moving boundary problem was solved with a highly stiff Gear–type integrator. The result of the calculation indicates that the numerical scheme used ought to be applicable to other moving boundary problems.