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SOI VENT REFINED COAL (SRC) PROCESS

Annual Technical Progress Report for Period January—December 1979

Volume II—Part 3

November 1980

Work Performed Under Contract AC05-76ET10104

**Pittsburg & Midway Coal Mining Company
Englewood, Colorado**

**FOSSIL
FUEL
ENERGY**

U. S. DEPARTMENT OF ENERGY

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SOLVENT REFINED COAL (SRC) PROCESS

ANNUAL TECHNICAL PROGRESS REPORT
FOR THE PERIOD
JANUARY, 1979 THROUGH DECEMBER, 1979
VOLUME II - Part 3

THE PITTSBURG & MIDWAY COAL MINING CO.
Englewood, Colorado 80111

November 1980

PREPARED FOR THE
U. S. DEPARTMENT OF ENERGY
DIVISION OF COAL CONVERSION AND UTILIZATION
UNDER CONTRACT DEAC-0179-ET10104
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ABSTRACT

This report summarizes the progress of research and development tasks of the Solvent Refined Coal (SRC) project by the Pittsburgh & Midway Coal Mining Co. for the Department Of Energy for the period January 1, 1979 through December 31, 1979. A set of statistically designed, simulated recycle SRC-II experiments utilizing a bench-scale unit was completed; the objective was to study the effects of principle operating variables over wide ranges of conditions. Using data from four pilot plants, models have been developed which predict yields as a function of operating variables, describe unsteady state, three-phase convection, backmixing and generation of heat by reaction of hydrogen in the liquid phase of SRC-II reactors. A substantial amount of preparatory work was completed on a bench-scale reactor and laboratory which permits determining the effects of heavy media separation on response to coal liquefaction. Laboratory tests were completed to measure the effects of corrosion-erosion of coal slurries on various steels; the metal losses were found to be dependent on type of steel and conditions. A measure of coal reactivity was determined by correlating the effects of coal properties on product yields from a process development unit.

APPENDIX 5

GULF SCIENCE AND TECHNOLOGY COMPANY

Pittsburgh, Pennsylvania

MODELING AND SIMULATION OF THE
THERMAL BEHAVIOR OF SRC-II REACTORS

By

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Report No. 627RK017

October 3, 1979

File No. FT07-30-30

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SUMMARY

This report represents the results of a portion of the work done under Project 238-8500 and sponsored by Gulf Mineral Resources Company.

The objective of this particular task has been to develop a kinetic and hydrodynamic mathematical model for the adiabatic SRC-II reactor. The model and simulation results apply to pilot and large scale reactors. The thermal behavior of SRC-II reactors is the main response studied. The model has been developed for two kinds of operations: (1) Normal adiabatic reactor with no intrareactor quench, and (2) adiabatic reactor with the addition of an intrareactor quench. Computer simulation capability for SRC-II reactors based on this model will provide important impacts upon: (1) the scale-up to commercial-size reactors, and (2) the effect of various quench variables, such as the amount of quench, the quench temperature and the quench location on the performance of a commercial reactor, (3) the evaluation of reactor performance, (4) optimization of the operating conditions for the entire reactor system and (5) the information on minimum amount of quench needed under certain operating conditions for satisfactory operation.

The most important teachings from the simulations with this model are summarized in two parts: (1) the adiabatic case, and (2) the same type of reactor with one quench point:

I. Adiabatic Case

- Gas velocity reduction greatly increases the overall reactor temperature rise.
- Liquid velocity reductions also greatly increases the temperature rise.
- If both of the above variables were decreased simultaneously, an unusually large temperature rise would result.

- Feed temperature changes cause a gain of about two on the outlet reactor temperature.
- Increased recycle ash composition in the feed slurry reduces the reactor temperature rise.

II. Adiabatic Reactor with Quench

(Holding the inlet and outlet temperatures at constant values)

- The location of the one quench point along the reactor does not affect the flatness of the internal temperature profile very much.
- The amount of quench added has a large effect on the outlet temperature. (The outlet temperature is not fixed in this situation).
- The amount of quench required to hold a constant outlet temperature has been related to the hydrogen consumption for this model and it depended on the internal temperature profile.
- When either the gas or liquid velocity is decreased, large increases in quench are required. If both decreased simultaneously by about one-half their design values, a large and possibly excessive quench requirement is encountered.
- When the feed gas rate is decreased by one-third (12 to 4 cm/s), the actual quench rate must double.
- When the liquid (slurry) rate is decreased by about one-half, the quench rate must be tripled.
- The temperature profiles within the reactor cover a range of about 20° to 40°F temperature rise, and each rise is rather gradual from end to end.

Another important point which covers both types of reactor simulations, is that the models and their behavior have been shown to be in reasonable agreement with three different pilot plant runs. This provides some credence to our modeling concepts, and our estimates of the heat of reaction, the kinetics parameters, the thermal dispersion coefficient (Peclet number) and the three-phase holdups.

INTRODUCTION

This report presents the development of a model for an adiabatic SRC-II coal liquefaction reactor in two parts. In the first part of the report, a model for the adiabatic SRC-II reactor is presented. The linear correlation proposed by Schleppey⁽⁶⁾ is used in estimating the rate of hydrogen consumption. A study is made for evaluating the effects of various operating variables on the temperature profile within the reactor, the overall temperature rise, the hydrogen concentration profile and the overall hydrogen consumption. The parameters involved in the proposed model are varied so as to obtain a reasonable match between the experimental temperature distribution obtained at Ft. Lewis⁽⁵⁾ and that predicted by the model. The data for hydrogen consumption and temperature rise in adiabatic SRC-II coal liquefaction reactor at Ft. Lewis (reported by J. D. Naylor)⁽⁸⁾ were obtained for runs 78SR-19, 78SR-20 and 78SR-21 on Illinois #6 (River King Mine) coal.

In the formulation of the model, the overall heat of reaction is expressed as heat liberated per mole of hydrogen reacted. In other words, the rate of heat generation is assumed to depend directly on the rate of hydrogen consumption. A preliminary value of heat of reaction was obtained from the experimental data. This value was subsequently revised by matching the experimentally measured and predicted temperature profiles and hydrogen consumption data.

The model analyzed here assumes uniform gas velocity, liquid velocity, and gas and liquid holdups within the reactor. Thus, only hydrogen balance and the heat balance equations are involved. Although the model does

not consider the detailed kinetics and reactor hydrodynamics evaluated earlier by Shah and Parulekar,⁽¹⁾ it is believed that the present model will accurately predict the basic thermal behavior of a commercial coal liquefaction reactor under adiabatic conditions.

The simple mathematical model described in this report takes into account the effects of following primary reactor variables: temperature, pressure, nominal slurry space time, feed slurry composition consisting of coal, recycle mineral residue (or recycle ash), SRC recycle, and recycle distillate on the temperature distribution within the reactor. The model also illustrates the effects of scale-up variables such as superficial gas velocity, superficial liquid velocity, reactor diameter and length, and thermal Peclet number on the temperature distribution within the reactor. Since the model is based on a once-through operation, complete feed slurry composition must be stated or known. The feed temperature must also be specified as an initial condition.

In the second part, the proposed model considers the effects of an intrareactor gas quench on the reactor temperature distribution. It is a well known fact that hydrogenolysis and hydrocracking reactions taking place in a coal liquefaction reactor are exothermic (i.e., there is a temperature rise everywhere in an adiabatic reactor due to heat generation). Inasmuch as an increase in local temperature also increases the extents of all the reactions, it is essential to restrict the temperature rise within reasonable limits in order to maintain desired yields and to avoid temperature excursions and reactor instability. The analysis presented here reports the effects of an intrareactor gaseous quench on the temperature distribution and the hydrogen consumption in an adiabatic SRC-II reactor. The kinetic parameters and the heat of reaction for hydrogenation and hydrocracking used in this part were obtained by using a correlation similar to that proposed by Jones⁽⁷⁾ and these values were subsequently improved so as to get a reasonably good match between the experimental data⁽⁵⁾ and the model predictions. It is believed that the correlation proposed by Jones⁽⁷⁾ correlates the data reported for SRC runs very well.

In the SRC-II process, the reactor is operated under cocurrent upflow conditions wherein gas (mainly hydrogen), oils (of various boiling range fractions), and solids, (inert particulate materials and catalytic "ash") flow cocurrently upwards through the reactor. Several reactions take place in the liquid phase and some are catalyzed by the solid mineral matter. The reactions are accompanied by the consumption of hydrogen and generation of some gaseous, as well as liquid products. Most of the hydrogenolysis and hydrocracking reactions are exothermic and result in appreciable heat generation. The holdups and the velocities of the three phases (i.e. gas, liquid, and solid) are assumed to be constant along the reactor length in this study.

In order to restrict the outlet temperature within tolerable limits, use of gas "quench" is made in SRC-II reactors. The addition of quench results in reduction in temperature rise in the reactor. It also alters the dispersion (backmixing) characteristics of various phases. In this study, use of a single gas quench has been considered. Similar results can be anticipated for the case of multiple quenches. This study examines a steady state model. The results are generated for the operating conditions relevant to the commercial operation.

The model predictions for hydrogen consumption and temperature profile in the reactor have been compared with results obtained from Ft. Lewis operations for Illinois #6 coal.⁽⁵⁾ Comparisons have also been made between model predictions and the experimental data obtained from the above source for the case with intrareactor quench.⁽⁸⁾ Results indicate that scale-up variables such as length and diameter of the reactor, superficial gas and liquid velocities play important roles in the behavior of adiabatic SRC-II reactors. The reactor behavior is also very sensitive to operating conditions such as feed temperature, total pressure in the reactor, feed concentration of coal and recycle ash.

The temperature rise and the hydrogen consumption for an adiabatic SRC-II reactor with an intrareactor quench are dependent upon scale-up variables such as feed liquid velocity, feed gas velocity and reactor

length. Reactor diameter does not appear to have a significant effect on the amount of quench required to maintain the prescribed rise. Quench variables such as the amount of quench and the quench temperature affect the reactor performance. Surprisingly, within the range of operating conditions examined here, the quench location along the reactor length does not appear to affect significantly the temperature distribution within the reactor.

Model Development

The following assumptions are made in developing the mathematical model:

1. For the hydrogen balance, it is assumed that
 - (a) the gas moves in plug flow through the reactor
 - (b) it is consumed primarily in reactions involving the hydrogenation of coal liquids
2. For the energy balance, it may be assumed that:
 - (a) significant axial dispersion of heat exists
 - (b) there are no significant heat losses, i.e., the reactor is adiabatic
 - (c) heat is released during hydrogenation

As stated earlier, the present model illustrates the thermal behavior of the adiabatic coal liquefaction reactor. The detailed reaction kinetics and product distributions are not included within the scope of this work. The proposed dispersion model contains several hydrodynamic (e.g. axial dispersion of heat), kinetic, and heat of reaction parameters. The values of these parameters are adjusted such that predicted and measured temperature profiles agree under selected reaction conditions.

A. Reaction Pathways and Kinetics

The reaction paths and kinetics considered in this report are the same as those described earlier by Shah and Parulekar⁽¹⁾ except for the kinetics of the hydrogenation reaction (reaction 16 as referred by Shah and Parulekar).⁽¹⁾ In the first part of the report, the kinetics for reaction 16 (see nomenclature followed by Shah and Parulekar) is assumed to be the same as that reported earlier. In the second part, the kinetics for reaction 16 (hydrogen consumption reaction) is assumed to be described by the correlation proposed by Jones.⁽⁷⁾ The details of this correlation are discussed in Appendix C.

B. Development of Model

Part I. Normal Adiabatic Operation

An axial dispersion model for the reactor is developed based on the following assumptions: (1) there are no radial variations in either temperature or concentration of hydrogen and reacting species; (2) the backmixing of the slurry phase can be characterized by the standard axial dispersion model. The same model is assumed to be applicable for the heat balance; (3) the total pressure in the reactor is assumed to be approximately constant. Thus, the total molar concentration of gases in the reactor is inversely proportional to temperature anywhere in the reactor. The ideal gas law is assumed to be valid over the range of reactor operating conditions; (4) the gas and liquid superficial velocities as well as the holdups for the three phases are assumed to be constant everywhere in the reactor. The above assumptions are believed to be reasonable, based on the results obtained by earlier isothermal model analysis;⁽¹⁾ (5) since the solid particles are of the order of 3μ in diameter, a uniform distribution of the solid particles along the reactor length is assumed; (6) the specific properties, such as densities of solid and liquid phases, specific heats of the three phases, and the thermal dispersion coefficients of the three phases are assumed to be

independent of temperature; (7) the overall heat generation is assumed to be proportional to hydrogen consumption. Thus, the heat of reaction is expressed as kcal/kg-mole of hydrogen consumed. The heat of reaction is assumed to be independent of reactor temperature; (8) the gas density is assumed to be inversely proportional to reactor temperature and proportional to total reactor pressure; (9) the reactor is adiabatic (no significant heat loss).

Since the main objective of the present study is to evaluate temperature distribution and the hydrogen consumption within an adiabatic reactor, the key equations describing behavior of the reactor in the light of assumptions (4) and (7) are the hydrogen balance and the heat balance equations. At steady state they can be expressed in dimensionless form as shown below.

$$\frac{dH}{dz} = -R_{16} r H^{n_{16}} (1+B_{16}(ASR)) \epsilon_L \quad (1)$$

and

$$\frac{1}{Pe_\theta} \frac{d^2\theta}{dz^2} - (p_1 + p_2) \frac{d\theta}{dz} + \Gamma_R H^{n_{16}} (1+B_{16}(ASR)) \epsilon_L = 0 \quad (2)$$

where

$$z = x/L \quad (3)$$

$$\theta = (T-T_0)/T_0 \quad (4)$$

$$r = (U_{ol} / U_{og})_0 \quad (5)$$

$$R_{16} = K_{16} (C_T)_0^{n_{16}-1} (SRT) \exp(-E_{16}/RT_0 (1+\theta)) \quad (6)$$

$$P_1 = \frac{\rho_s C_{ps} (U_{os})_o}{(\rho_s C_{ps} (U_{os})_o + \rho_l C_{pl} (U_{ol})_o + (\rho_g)_o C_{pg} (U_{og})_o)} \quad (7)$$

$$P_2 = \frac{\rho_l C_{pl} (U_{ol})_o}{(\rho_s C_{ps} (U_{os})_o + \rho_l C_{pl} (U_{ol})_o + (\rho_g)_o C_{pg} (U_{og})_o)} \quad (8)$$

$$Pe_\theta = \frac{((\rho_g)_o C_{pg} (U_{og})_o + \rho_l C_{pl} (U_{ol})_o + \rho_s C_{ps} (U_{os})_o) L}{(D_{Hg} + D_{Hl} + D_{Hs})} \quad (9)$$

$$\Gamma_R = \frac{R_{16} \Delta H_R (U_{ol})_o (C_T)_o}{T_o ((\rho_g)_o C_{pg} (U_{og})_o + \rho_l C_{pl} (U_{ol})_o + \rho_s C_{ps} (U_{os})_o)} \quad (10)$$

and

$$SRT = L / (U_{ol})_o \quad (11)$$

In the above expressions, L is the length of the reactor, x is the distance from the inlet of the reactor, U_{og} , U_{ol} , and U_{os} are the superficial velocities of the gas, liquid and solid phases, respectively. T is the absolute temperature in the reactor; θ is the dimensionless temperature; $(C_T)_o$ is the total molar concentration in gas phase at reactor inlet (g-mole/cm³); K_{16} and E_{16} are the Arrhenius frequency factor and the activation energy for hydrogen consumption reaction (see nomenclature followed by Shah and Parulekar).⁽¹⁾ R is the universal gas constant; ρ_s , ρ_l , and ρ_g are the densities of solid, liquid and gas phase respectively; C_{pg} , C_{pl} , and C_{ps} are

the specific heats of gas, liquid, and solid phase respectively. n_{16} and B_{16} are the order of the hydrogen consumption reaction with respect to hydrogen concentration and the coefficient of recycle ash in the rate expression for the hydrogen consumption reaction, respectively (see nomenclature followed by Shah and Parulekar). D_{Hg} , D_{Hl} , and D_{Hs} are the thermal dispersion coefficients for gas, liquid, and solid phase respectively; ASR and SRT are the weight fraction of recycle ash in the feed slurry and slurry space time, respectively; ΔH_R is the overall heat of reaction expressed as kcal/kg-mole hydrogen consumed, and H is the dimensionless concentration of hydrogen in gas phase. Subscript o in expressions (3) through (11) refers to conditions at the dissolver (reactor) inlet. Detailed derivations of equations (1) and (2) are given in Appendix A.

Part II Adiabatic Operation with Intrareactor Gas Quench

The assumptions (1) through (9) listed in Part I earlier are also applicable in this case. The additional assumptions are listed below.

(10) At the conditions of operation of SRC-II reactor, it is assumed that addition of quench does not result in significant changes or differences in the flow patterns of various phases in the pre-quench and the post-quench sections of the reactor. The quench is evenly distributed across the cross section at the point of the entry.

(11) In the case of appropriate mass and/or energy flux balances where significant backmixing may be present, there is no sudden discontinuity in either concentration or temperature or both at the quench location. This assumption has been verified from the experimental results obtained in partially backmixed tubular reactors. (8)

The main objectives of this analysis are the same as those in Part I. Once again because of the assumptions (4) and (7) listed earlier, the key equations describing the behavior of the adiabatic reactor in this case are the hydrogen and the heat balance equations. As mentioned earlier, the kinetic expressions for the hydrogen consumption reaction assumed in this part were different from heat in Part I. With the kinetics proposed by Jones (7), the relevant equations can be expressed in dimensionless forms as

$$\frac{dH}{dz} = -R_{16} \cdot r \cdot H^{n_{16}} (1+B_{16}(ASR)) \epsilon_L (1+\theta)^{n_{16}} \quad (12)$$

$$\frac{1}{Pe_\theta} \frac{d^2\theta}{dz^2} - (p_1 + p_2) \frac{d\theta}{dz} + \Gamma_R H^{n_{16}} (1+\theta)^{n_{16}} (1+B_{16}(ASR)) \epsilon_L = 0 \quad (13)$$

where

$$r = U_{ol}/U_{og} \quad (14)$$

$$R_{16} = K_{16} (C_T)_o^{n_{16}-1} (SRT)_o^{n_{16}} \exp(-E_{16}/RT_o(1+\theta)) \quad (15)$$

All other quantities are the same as previously defined in equations (3), (4), and (7) through (11). Equations (12) and (13) are applicable to both pre and post quench zones of the reactor.

C. Boundary Conditions

Part I

Equations (1) and (2) are subjected to the following boundary conditions:

$$\text{At } z = 0^+$$

$$H = H_0 \quad (16)$$

$$\frac{1}{Pe_\theta} \frac{d\theta}{dz} = (p_1 + p_2) (\theta - \theta_0) \quad (17)$$

$$\text{At } z = 1^-$$

$$\frac{d\theta}{dz} = 0 \quad (18)$$

Where H_0 refers to dimensionless concentration of hydrogen in gas phase at reactor inlet. H_0 can be calculated from reactor operating conditions using equations (35) through (38) of Shah and Parulekar.⁽¹⁾

$$H_0 = 1 - \left(\frac{K_1 P_T^{n_1}}{M_a} + \frac{K_2 P_T^{n_2}}{M_b} + \frac{K_3 P_T^{n_3}}{M_p} + \frac{K_4 P_T^{n_4}}{M_h} \right) \frac{rC_{coal}}{(C_T)_0} \quad (19)$$

where K_1 , K_2 , K_3 , and K_4 are the distribution coefficients for the formation of light gases, naphtha, by-products and water, respectively, from coal; n_1 through n_4 are reaction orders for formation of light gases, naphtha, by-products and water, respectively; M_a , M_b , M_p , and M_h are the molecular weights of light gases, naphtha, by-products and water respectively, and P_T is the total pressure in the reactor, C_{coal} is the concentration of coal in slurry. The details of equation (19) are given by Shah and Parulekar.⁽¹⁾

Part II

The initial and boundary conditions for equations (12) and (13) are the same as those mentioned in equations (16) through (18).

Various additional conditions at quench location have to be specified in order to relate various concentrations and temperature in the pre and post quench zones. These conditions can be derived from overall and component mass and energy flux balances. In order to evaluate the role of gas quench, a total gas phase mass flux balance, a hydrogen flux balance and a heat flux balance at the quench location has to be considered. These additional conditions which are required to be satisfied from the point of conservations of mass and energy are discussed below. Detailed derivations of these conditions are given in Appendix A.

Let the quench be added at $z = \eta$. Let m denote the ratio of mass flow rate of quench added to mass flow rate of gas in the mainstream at $z = \eta$. Then total mass flux balance gives the relation between superficial gas velocities in the prequench and the post-quench section which is shown below.

$$(U_{og})_2 = (m+1) (U_{og})_0 \quad (20)$$

Hydrogen flux balance results in the following equation

$$(H)_{n+} = \frac{(H)_{n-} + \frac{H U_q}{q} / (U_{og})_o}{1+m} \quad (21)$$

Balance on heat flux gives us the following equation

$$-\frac{1}{(Pe_\theta)_1} \frac{d\theta}{dz} \Big|_{n-} + \frac{P_q (1+\theta)_q}{(1+\theta)_{n-}} + P_3 + (P_1 + P_2) (1+\theta)_{n-} = \frac{-1}{(Pe_\theta)_2}$$

$$\frac{d\theta}{dz} \Big|_{n+} + P_3 (1+m) + (P_1 + P_2) (1+\theta)_{n+} \quad (22)$$

$$\theta_{n+} = \theta_{n-} \quad (23)$$

where

$$(Pe_\theta)_1 = \frac{(\rho_g C_{pg} (U_{og})_o + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os}) L}{(D_{Hg} + D_{Hl} + D_{Hs})_1} \quad (24)$$

$$(Pe_{\theta})_2 = \frac{((\rho_g)_o C_{pg} (U_{og})_o + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os}) L}{(D_{Hg} + D_{Hl} + D_{Hs})_2} \quad (25)$$

$$P_3 = \frac{(\rho_g)_o C_{pg} (U_{og})_o}{((\rho_g)_o C_{pg} (U_{og})_o + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os})} \quad (26)$$

$$P_q = \frac{m(\rho_g)_o C_{pg} (U_{og})_o}{((\rho_g)_o C_{pg} (U_{og})_o + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os})} \quad (27)$$

Condition (23) simply states that there will not be any discontinuity in temperature as is observed in the case of use of quench in the plug flow reactors. In expressions (20) through (27) subscripts 1 and 2 denote conditions in the prequench and the post-quench sections, $(\rho_g)_o$ denotes the gas density of the mainstream gas at feed conditions, M_{H_2} is the molecular weight of hydrogen, θ_q is the dimensionless temperature of quench, U_q and H_q are the quench velocity based on the dissolver cross-section and the dimensionless hydrogen concentration in quench respectively. Subscripts η^- and η^+ refer to the conditions just before and just after the quench location respectively. The quench ratio based on feed gas, m' (amount of quench/amount of feed gas) is related to m and dimensionless temperature at the quench location as shown below.

$$m' = m/(1+\theta_{\eta^-}) \quad (28)$$

The above equation assumes $U_{og}|_{\eta^-} = U_{og}|_o$ i.e. constant gas velocity. This is believed to be a reasonable assumption. It also assumes that molecular weight of gas at the quench point is the same as that of the gas at the reactor inlet. This is in general, a questionable assumption

because the molecular weight of gas produced is higher than that of hydrogen (feed gas mainly consists of hydrogen). The correct m' is equal to m' obtained from above equation (28) multiplied by the ratio [mol. wt of gas at reactor inlet/mol. wt of gas at the quench location]. For simplicity, in the present study this ratio is assumed to be unity.

D. Solid Phase Distribution.

Equations (29) and (30) of Shah and Parulekar⁽¹⁾ were used to calculate the solid distribution within the reactor. Since the particles are of 3μ size, the solid concentration profile within the reactor is found to be essentially flat. Hence, in the computer programs included in Appendix C, the solid distribution is taken to be a constant.

Velocity of solid at reactor inlet $(U_{os})_o$ can be related to $(U_{ol})_o$. For the case under consideration, we have assumed

$$(U_{os})_o = (U_{ol})_o \quad (29)$$

E. Estimation of Holdups for the Three Phases Gas

1. Gas Holdup (ϵ_g)

The gas holdup in a bubble column is dependent upon the gas velocity (U_{og}), diameter of the column (D), and the surface tension of the liquid (σ_l). The relation for gas holdup used in this report is the same as equation (48) in the report by Shah and Parulekar.⁽¹⁾

$$\epsilon_g = \left(\frac{1}{(\sigma_l)^{0.1}} \right) D^{-0.00} (0.18 \ln U_{og} - 0.05) \quad (30)$$

Solid Holdup (ϵ_s)

Equation (50) in the report by Shah and Parulekar⁽¹⁾ has been used to evaluate the solid phase holdup.

Liquid Holdup (ϵ_l)

Once gas and solid holdups are known, the liquid phase holdup is obtained from the relation

$$\epsilon_l = 1 - \epsilon_g - \epsilon_s \quad (31)$$

F. Estimation of Overall Thermal Dispersion Coefficient

A value of the overall thermal dispersion coefficient can be obtained by matching the calculated temperature rise with the one measured experimentally.⁽⁵⁾ In this study, since the thermal dispersion coefficient for the gas phase, D_{Hg} , is usually much smaller than the thermal dispersion coefficients for liquid and solid phases, D_{Hl} and D_{Hs} , respectively, its importance was neglected. Also, thermal dispersion coefficients, D_{Hl} and D_{Hs} were assumed to be nearly equal since the respective mass dispersion coefficients, E_{2l} and E_{2s} are nearly equal for the liquid-solid slurry containing fine solid particles.

The combined thermal dispersion coefficient, $(D_{Hg} + D_{Hl} + D_{Hs})$ can be related to the actual combined dispersion coefficient (which has units of diffusivity, cm^2/sec) $(D_{Hg}'' + D_{Hl}'' + D_{Hs}'')$ and densities and specific heat of the gas, liquid and solid phase, respectively, as shown below.

$$(D_{Hg} + D_{Hl} + D_{Hs}) = (\rho_s C_{ps} + \rho_l C_{pl} + (\rho_g / \rho_{pg}) C_{pg}) (D_{Hg}'' + D_{Hl}'' + D_{Hs}'') \quad (32)$$

Due to the same reasoning, we have

$$(D_{Hg}' + D_{Hl}' + D_{Hs}') = (D_{Hl}' + D_{Hs}') \quad (33)$$

and

$$(D_{Hl}' + D_{Hs}') = \bar{M} E_{zl} \quad (34)$$

where $\bar{M}$ is a factor which is used to relate dispersion coefficients for heat and mass. Magnitude of $\bar{M}$ was estimated by trial and error such that the model prediction matched the experimental data. For Part I the value of $\bar{M}$ was found to be 0.45 while for Part II it was found to be 0.25.

Thus, we get the following correlation for the overall thermal dispersion coefficient.

$$(D_{Hg} + D_{Hl} + D_{Hs}) = \bar{M} E_{zl} (\rho_s C_{ps} + \rho_l C_{pl} + (\rho_g)_o C_{pg}) \quad (35)$$

It should be noted that the relation (34) is purely an empirical correlation. The value of coefficient, $\bar{M}$, may change if we use it for some other type of coal. But it is based on the results obtained by earlier investigators which showed that the thermal and mass diffusivities (or dispersion coefficients (cm^2/sec)) are of the same order of magnitude at conditions close to a CSTR (which is true in the case of SRC-II reactors where the mass Peclet number for liquid phase is around 0.5).

The axial dispersion coefficient (cm^2/sec) for the liquid phase, E_{zl} , can be calculated by using the correlation proposed by Deckwer, et. al. (4)

$$E_{zl} = 2.7 (D)^{1.4} (U_{og})^{0.3} \quad (36)$$

where D is the diameter of column in cm.

From the above equation, it is seen that the liquid phase axial dispersion coefficient, E_{zl} , is a function of the superficial gas velocity. Hence, E_{zl} will be different in the pre-quench and the post-quench sections respectively.

$$(E_{zl})_1 = 2.7 D^{1.4} (U_{og})_o^{0.3} \quad (37)$$

$$(E_{zl})_2 = 2.7 D^{1.4} (U_{og})_2^{0.3} \quad (38)$$

G. Hydrogen Consumption

Part I: Normal Adiabatic Operation

Once the hydrogen concentration at the reactor outlet is obtained by solving the model equations (both steady state and unsteady state model equations), hydrogen consumption in the reactor (gm/gm mf coal) is obtained from the following relation

$$Y_{H_2} = M_{H_2} (C_T)_o (H_o - H_1) / r C_{coal} \quad (39)$$

where M_{H_2} and H_1 are the molecular weight of hydrogen and the dimensionless concentration of hydrogen at the reactor outlet respectively, Y_{H_2} is the hydrogen consumption, C_{coal} is the concentration of moisture-free coal in feed slurry.

Part II: Adiabatic Reactor with Quench

Once the hydrogen concentration at the reactor outlet is obtained by solving the model equations, hydrogen consumption (g/g mf coal) is obtained from the following relation

$$Y_{H_2} = M_{H_2} (C_T)_o (H_o + \frac{U_q}{(U_{og})_o} H_q - H_1 (1+m)) / (r)_1 C_{coal} \quad (40)$$

$$\text{where } (r)_1 = U_{ol} / (U_{og})_o \quad (41)$$

H. Reaction Constants and Physical Properties

Part I Normal Adiabatic Operation

Reaction constants n_{16} , B_{16} , and E_{16} reported by Shah and Parulekar⁽¹⁾ have been used in this analysis. Other physical properties used in this study are listed below in Table I.

TABLE I

Physical Properties and Kinetic Parameters

$$C_{pg} = 0.89 \text{ cal/g}^\circ\text{K}$$

$$C_{pl} = 0.63 \text{ cal/g}^\circ\text{K}$$

$$C_{ps} = 0.28 \text{ cal/g}^\circ\text{K}$$

$$\rho_g = 0.044 \text{ g/cm}^3 \text{ at } 410^\circ\text{C}$$

$$\rho_l = 0.9 \text{ g/cm}^3$$

$$\rho_s = 1.5 \text{ g/cm}^3$$

$$D_p = 3\mu \text{ (particle diameter)}$$

$$(\text{ASR})_{\text{inlet}} = 0.09 \text{ g/g mf coal}$$

$$\text{Viscosity} = 0.4 \text{ cp}$$

$$\Delta H_R = 11687 \text{ cal/g-mole or } 6493 \text{ Btu/lb-mole or } 58.6 \text{ Btu/SCF H}_2$$

$$K_{16} = 24000 \text{ hr}^{-1}$$

$$E_{16} = 12545 \text{ cal/g-mole or } 6970 \text{ Btu/lb-mole}$$

$$B_{16} = 0$$

$$M_a = 30$$

$$M_b = 115$$

$$M_p = 32$$

$$M_h = 18$$

$$n_1 = n_2 = 0.85$$

$$n_3 = n_4 = 0$$

$$B_8 = 0.07$$

$$B_9 = 0.116$$

Distribution Coefficients

$$K_1' = 0.0254 (P_T/15.4)^{n_1}$$

$$K_2' = 0.02584 (P_T/15.4)^{n_2}$$

$$K_3' = 0.042$$

$$K_4' = 0.0567$$

$$K_5' = 0.0595$$

$$K_6' = 0.069$$

$$K_7' = 0.394$$

$$K_8' = 0.246 (1+B_8(ASR))$$

$$K_9' = 0.08 (1+B_9(ASR))$$

$$SUM = \sum_{i=1}^9 K_i'$$

$$K_i = K_i' / SUM$$

The frequency factor, K_{16} , and the heat of reaction ΔH_R were varied over a limited range until the model predictions and the experimental data matched with each other within reasonable limits.

The frequency factor, K_{16} , for Illinois coal is around 20% higher than the frequency factor, K_{16} , for Kentucky coal evaluated earlier by Shah and Parulekar.⁽¹⁾

Part II Adiabatic Operation with Quench

Reaction parameters K_{16} , n_{16} , B_{16} , E_{16} , and ΔH_R were estimated using correlation proposed by Jones⁽⁷⁾ and adjusting the same so as

to get satisfactory comparison between the experimental data and the model predictions. The other physical properties used in this study are the same as those listed in Table I. Quench temperature was assumed normally to be 30°C and the quench was assumed to consist of pure hydrogen. Although in this report we have used kinetic parameters for Illinois coal, the results should be applicable to other coals as well.

The final estimates of the kinetic constants are shown below.

$$0.804$$

$$K_{16} = 800 \text{ (CI)} \quad (42)$$

and

$$E_{16} = 15500 \text{ cal/g-mole} \quad (43)$$

$$\Delta H_R = 40 \text{ BTU/SCF H}_2^* \text{ or } 7978 \text{ cal/g-mole} \quad (44)$$

$$n_{16} = 0.0804 \quad (45)$$

$$B_{16} = 1.7965 \quad (46)$$

The overall thermal dispersion coefficient was related to the liquid phase mass dispersion coefficient, E_{zl} as

$$(D_{Hg} + D_{Hl} + D_{Hs}) = 0.25 ((\rho_g) C_{pg} + \rho_l C_{pl} + \rho_s C_{ps}) E_{zl} \quad (47)$$

* This is a net, lumped parameter for all chemical and physical changes releasing (consuming) heat based on the hydrogen consumption.

I. Solution Technique

Part I Normal Adiabatic Operation

Equations (1) and (2) along with the accompanying boundary conditions were solved by two techniques. In the first technique, equations were solved in the same form as they are. Integration in z was done by using Euler method. Equations (1) and (2) were solved by starting integration at $z = 1$ and marching backwards till $z = 0$ is reached. The initial values at $z = 1$ were improved successively by Newton Raphson method. Another approach used was that of formulating the unsteady state hydrogen balance and heat balance equations. The resulting equations are described in Appendix A.

The resulting equations were converted into finite difference form. The coefficients of the unknown quantities form a tridiagonal matrix. The derivation of these equations is illustrated in Appendix B. These equations were solved by Thomas's algorithm. Details of both the solution techniques are well illustrated in Appendix B.

Part II Adiabatic Reactor with Quench

Equations (12) and (13) are a set of coupled ordinary differential equations. They describe the behavior of the reactor at steady state. These were solved in the form they are by using the numerical technique described in Part I earlier. Details of the technique are given by McGinnis⁽³⁾ and the application of the same in modeling of adiabatic SRC-II reactor is discussed in Appendix B.

RESULTS AND DISCUSSION

Part I Normaladiabatic Operation

Typical dimensionless hydrogen concentration and temperature rise ($^{\circ}\text{F}$) profiles within the reactor predicted by the present model are shown in Figure 1. From this figure we see that the model prediction and the experimental data for the temperature distribution within the reactor match with each other very well. The magnitudes of various parameters, namely K_{16} , ΔH_R , and m were varied within limited range in order to obtain a close match between model predictions and experimental data. The final values of these parameters (K_{16} , ΔH_R , and m) have been listed earlier.

In this study, effects of feed temperature, total pressure, superficial gas velocity, superficial liquid velocity, reactor diameter, reactor length, recycle ash percentage in feed slurry, and percentage of moisture-free coal in feed slurry on the hydrogen consumption and the overall temperature rise were examined. The results illustrating these effects under typical operating conditions are described in Figures 2 through 5.

The results shown in Figure 2 indicate that an increase in weight fraction of coal (mf basis) in feed slurry does not significantly affect the temperature rise across the reactor. This is because the rate of hydrogen consumption and hence the rate of heat generation are not affected by the change in feed coal concentration. Since the consumption of hydrogen is based on the amount of moisture-free coal entering the reactor, the hydrogen consumption decreases with an increase in weight fraction of mf coal in the feed slurry.

The effect of an increase in feed temperature is to increase the rate of reaction of hydrogen and, hence, the rate of heat generation. Hence, as shown in Figure 3 both hydrogen consumption and the overall temperature rise are found to increase with feed temperature.

An increase in recycle ash content (ASR) increases the solid phase holdup and thus causes a reduction in the liquid phase holdup at a fixed gas

phase holdup. Thus, the local reaction rates are reduced due to a decrease in the liquid phase holdup, which in turn reduces the heat generation and the local temperature rise. Thus, both the hydrogen consumption and the overall temperature rise are reduced when the ash content is increased. A typical range of liquid phase holdup for the conditions shown in Figure 4 is 0.69-0.83. (The former value corresponds to ASR of 0.14 and the latter corresponds to ASR of 0.04).

Referring to equation (C-5) of Shah and Parulekar,⁽¹⁾ one can observe that the kinetic constant K_{16} defined in (C-5) has units of $\text{hr}^{-1} (\text{MPa})^{-n_{16}}$. The value of K_{16} obtained from the CSTR model proposed by Schleppy⁽⁶⁾ was used and subsequently improved to get reasonable match between observed and predicted hydrogen consumption. Hence, while using K_{16} obtained from CSTR model, one has to modify the definition of R_{16} and define it as $R_{16} = K_{16} (\text{SRT})$ where K_{16} has units of hr^{-1} . K_{16} obtained from the CSTR model may be termed as a pseudo rate constant. This makes the dimensionless rate constant, R_{16} , independent of total reactor pressure and thus the local reaction rate does not depend on reactor pressure. An increase in total pressure, however, causes an increase in total gas phase concentration, $(C_T)_0$ which, therefore, causes an increase in hydrogen consumption as can be seen from equation (39) and Figure 5. An increase in total reactor pressure also causes a change in $(U_{og})_0$, which increases the thermal Peclet number and hence the rate of heat generation and temperature rises as shown in Figure 5.

Reactor diameter plays a significant role on the extent of liquid phase backmixing. Hence, as shown in Figure 6, the overall temperature rise is reduced when the diameter is increased due to increased thermal backmixing. Because of the assumed plug flow characteristics of the gas phase, the reactor diameter does not have any strong influence on hydrogen consumption as shown in Figure 6.

An increase in liquid velocity results in a decrease in the extent of backmixing and also a decrease in slurry space time. These two have counteracting effects on the hydrogen consumption and the temperature rise. For the operating conditions considered in obtaining the results shown in

Figure 7, the effects of latter parameter (i.e. space time) dominates over that of the former one. Thus, both hydrogen consumption and overall temperature rise are lowered with an increase in liquid velocity.

An increase in the reactor length decreases the extent of backmixing and increases the slurry space time. As shown in Figure 8, and as one would expect, both of these phenomena increase hydrogen consumption and the temperature rise.

An increase in superficial gas velocity decreases the hydrogen concentration gradient and also the time spent by a molecule of hydrogen in the reactor and, hence, it causes hydrogen consumption to decrease. At the same time it increases the backmixing and thereby decreases the temperature rise within the reactor which contributes partly to the decrease in hydrogen consumption. The typical results illustrating these effects are shown in Figure 9.

In this study, the effect of liquid velocity (and corresponding diameter) on the temperature rise for the constant liquid throughput rate is also examined. These results are described in Figure 10. It is observed that as the liquid velocity is increased, overall temperature rise goes up initially, at certain liquid velocity it is maximum and any further increase in liquid velocity results in a decrease in temperature rise. As explained earlier, effect of liquid velocity is two-fold. In the first part of the curve, an increase in liquid velocity and corresponding decrease in reactor diameter decrease backmixing which has a dominant effect on the overall temperature rise as compared to the effect of decrease in SRT on the same. In the latter part of the curve, the effect due to the decrease in SRT plays a dominant role and causes a decrease in temperature rise.

Both the steady state model equations (1) and (2) and the unsteady state equations (A1-6) and (A1-7) were solved to obtain the above results. Since equations (1) and (2) represent two coupled equations wherein values of one or two variables have to be guessed to start the integration, it is found that steady state solution is obtained economically and faster. Unsteady state equations yield a steady state solution after an appreciable amount of time.

TABLE I

SUMMARIZED RESPONSES TO 8 REACTOR VARIABLES, PART I

<u>Variables Studied</u>	<u>Basis Value*</u>	<u>Responses Due to an Increase in Variable</u>	
		<u>Hydrogen Consumption (G/G MF Coal)</u>	<u>Temperature Rise, °F</u>
MF Coal Conc.	30%	Decreases	Decreases slightly
Recycle Ash Conc.	9%	Decreases	Decreases
Feed Temperature	788°F	Increases	Increases
Reactor Pressure	14 MPA	Increases	Increases
Reactor Diameter	60 cm (1.97 ft)	No effect	Decreases
Length	900 cm (29.53 ft)	Increases	Increases
Velocity of Liquid	.3 cm/sec (.59 ft/hr)	Decreases	Decreases
Gas	3.0 cm/sec (5.9 ft/hr)	Decreases	Decreases

*Approximate Ft. Lewis Conditions.
Variables changed one at a time.

Part II Adiabatic Operation with Intrareactor Gas Quench

In this part of the study the effect of quench location and amount of quench added on the overall adiabatic temperature rise and the hydrogen consumption are analysed.

Figure 11 shows some typical temperature profiles for various quench locations (ranging from very near the inlet to very near the outlet). It can be seen that the adiabatic temperature rise is nearly the same for all the quench locations. It is also seen that more the quench location is near the reactor outlet, more is the temperature build-up in the reactor. Since the operating conditions were such that the liquid phase is nearly totally back-mixed, an addition of quench does not change the dispersion characteristics significantly. Hence the only major effect of the quench is to cause "sensible cooling," which affects the heat generation and thus reduces the temperature rise. For the same amount of quench added at various locations, the cooling effect is more when quench is added more towards the reactor inlet than when it is added more towards the reactor outlet. Hence, the temperature profile gradually builds up in the earlier portion of the reactor as quench location is moved from reactor inlet to reactor outlet. For the conditions considered in Figure 11, the hydrogen consumption did not change significantly.

For a typical set of commercial reactor variables, Figure 12 shows the effect of amount of quench on the overall temperature rise for a fixed reactor inlet temperature. The temperature rise decreases as amount of quench added is increased. This is because the addition of quench causes "cooling," the effect of which is carried all over the reactor due to dispersion. Since rate of hydrogenation reaction and rate of heat generation depend on local temperature, both the temperature rise and hydrogen consumption are affected due to addition of quench. Hydrogen consumption for various amounts of quench is illustrated in Figure 13.

In further discussion, let m_{cr} denote the minimum amount of quench needed under given operating conditions to maintain reactor outlet temperature at 460°C. Figure 14 shows the effect of feed liquid velocity on critical quench ratio (m'_{cr}) and corresponding hydrogen consumption. A decrease in liquid velocity results in increase in average space time of the liquid phase and also decrease in Peclet number for liquid phase. For the conditions considered in Figure 14, the former effect is dominating and hence the overall temperature rise and the hydrogen consumption increase in the case of an adiabatic reactor with no quench. Hence it is obvious that the minimum amount of quench required (as indicated by m'_{cr}) also increases as is shown in Figure 14. The hydrogen quench plays a dual role. First, it provides cooling effect and thereby reduces the temperature everywhere in the reactor which in turn reduces the reaction rate constant; secondly it increases the amount of hydrogen available for the reaction in the post-quench section, which tends to increase the rate of hydrogenation reaction. These two effects seem to be equally important in this case and thus hydrogen consumption increases as feed liquid velocity is decreased.

Decrease in feed gas velocity decreases the backmixing, increases the average space time for the gas phase, and increases the liquid phase holdup (due to corresponding decrease in the gas phase holdup due to reduction in gas velocity) in the case of adiabatic reactor with no quench. This results in increase in hydrogen consumption and increase in temperature rise. It is expected that the critical quench ratio (m'_{cr}) or in other words the minimum amount of quench required will be increased as feed gas velocity is reduced. The results in Figure 15 illustrate this expected trend. Hydrogen consumption increases as feed gas velocity is decreased. Arguments in support of this are the same as those mentioned in the earlier paragraph. The results are once again illustrated in Figure 15.

Figure 16 illustrates the effect of reactor length on critical quench ratio and the corresponding hydrogen consumption. It is known that an increase in reactor length increases the Peclet number for mass (liquid) and heat and also the average residence time of each phase. This increases the extent of hydrogenation reaction. Thus the hydrogen consumption and the

adiabatic temperature rise both increase with increase in reactor length in the case of adiabatic reactor with no quench. The minimum amount of quench required (m'_{cr}) thereby also increases with an increase in reactor length.

We have also considered the case where the quench temperature was varied between room temperature (300°K) and 400°K. As expected we found that critical amounts of quench required increased with increase in quench temperature. Hydrogen consumption was also found to increase. This is believed to be due to the increase in amounts of hydrogen (due to increase in amounts of quench needed) which in turn increases the rate of hydrogenation. The results are illustrated in Figure 17.

Finally, it was found that for the commercial reactor conditions examined in this report, the dependence of critical quench ratio on the reactor diameter was mild. The quantitative results illustrating this effect are therefore not shown. Typical temperature profiles at critical quench ratio for various feed gas velocities are illustrated in Figure 18. It is seen that higher gas velocities result in more thermal backmixing which causes the temperature profile to become flatter.

Figure 19 illustrates typical temperature profile in the reactor for various liquid velocities at critical quench ratio. As the liquid velocity is reduced, there is increase in the degree (importance) of backmixing (as indicated by decrease in Pe_L and Pe_0) which flattens the temperature profile more and more. The results in Figure 19 follow this expected trend.

The influence of reactor length on temperature profile in the reactor at the critical quench ratio is shown in Figure 20. It is seen that as the length is increased, the temperature gradient increases everywhere in the reactor. Again, this is due to increase in Peclet numbers for liquid and heat, which makes the temperature profile become steeper.

Comparisons between the model predictions and the experimental data were also made for the reactor with an intrareactor quench. Table II shows conditions for these runs.

TABLE II

Typical Operating Conditions For Adiabatic Reactor With And
Without Intrareactor Quench

Run	78SR-19 (IL coal)	78SR-14 (Pitt Seam Coal)	Test Run (IL coal)
Furnace Outlet Temp (°F)	807	804	806
Reactor Outlet T_o (°F)	861*	871*	859**
Temp. Rise in Reactor	54	67	76
"O" Position Temperature (°F)	733*	809	783
Quench Ratio (m)	0.51	0.46	--- (no quench)
H ₂ Consumption % MF coal	3.28	3.96	3.4
H ₂ Consumption % MF coal (model)	3.35	4.18	3.5
Quench Location (n)	0.05	0.55	---
C ₁ (gm/cm ³ slurry)	0.328	0.328	0.328
ASR (gm/gm slurry)	0.08	0.08	0.08
H ₂ Flow Rate (Preheater) (lb/hr)	247	256	---
H ₂ Flow Rate (Quench) (lb/hr)	125.2	117	---
Total Gas Rate (lb/hr)			
(1) Feed	734	479	---
(2) Quench	372	219	---
Diameter (cm)	60	60	60
Length (cm)	900	900	900
SRT (hr)	1	0.9	1

*Temperature sensor near quench injector questionable.

**See Figure 21 for temperature profile data.

From the results shown in Figure 21 and for runs 78-SR-14 and 78SR-19 those listed in Table II it can be seen that the outlet temperature and the hydrogen consumption predicted by the model and the corresponding ones observed experimentally match each other well. But the temperature profile in the reactor predicted by the model is in one case somewhat different from the measured one. It indicates two facts. One is that in the future runs more temperature data should be taken near the entrance region of the reactor and the other is that more runs are needed to test the validity of the dispersion model proposed in this study.

CONCLUSIONS

Part I Normal Adiabatic Operation

The model for an adiabatic coal liquefaction reactor presented in this report appears to predict the effect of various operating variables on the hydrogen consumption and the reactor temperature rise reasonably well. The model could be used for further analysis of the adiabatic coal liquefaction reactor. The solution to steady state model equations is obtained faster and more economically than the solution to unsteady state model equations. Unless the number of boundary value problems to be solved is large, the use of steady state model equations is recommended without any reservations.

Part II Adiabatic Operation with Intrareactor Quench

Location of quench does not seem to affect the overall temperature rise and hydrogen consumption significantly for the ranges of operating conditions considered. Increased amounts of quench reduces both the overall temperature rise and the hydrogen consumption.

The minimum amount of quench required (as indicated by the parameter, m'_{cr}) is strongly dependent on feed liquid velocity, feed gas velocity and reactor length. The critical quench ratio also depends on quench temperature.

RECOMMENDATIONS

This report should be mainly helpful in understanding the temperature distribution in an adiabatic coal liquefaction reactor. The model results obtained here involved estimations of several key parameters such as heat of reaction, Peclet number for heat, etc. In that sense the model is still more or less at the development stage. Although the model predictions do not differ from the experimental data significantly, there are still some differences such as shown in Figure 17 for run 78SR-19. There is still uncertainty about the shape of temperature profile near the initial entrance region of the reactor. More data should be taken in that region in future experiments.

Since the quench location does not seem to affect the reactor performance, the quench location in design may be determined by emergency control considerations. It is also recommended that along with the three-phase fluidized model, a two-phase (dense phase which consists mainly of solid and liquid and bubble phase which consists mainly of gas) model should also be considered. It may give better insight in the flow behavior within the reactor and closer match for the temperature profiles observed in the case of reactor where intrareactor quench is used. It is necessary that more data for the temperature distribution for the intrareactor quench system be available so that validity of the dispersion model could be more critically tested.

Finally, since the predictions of the model depends very strongly upon the values for the heat of reaction and Peclet number for heat, a program for independent measurements of these parameters should be undertaken.

NOMENCLATURE

A, B, C	Coefficient matrix in Thomas Algorithm
a, b, c	Defined in equations (B-29) through (B-31)
AS	Weight fraction of inert ash in mf coal
ASR	Weight fraction of recycle ash in slurry (gm/gm slurry)
B ₈ , B ₉ , B ₁₆	Coefficient of recycle ash concentration in rate expressions for reactions 8, 9, and 16, respectively (Shah and Parulekar ⁽¹⁾)
C ₁ , C ₂	Initial values at z = 1 defined in (B-1)
C ₁ [*] , C ₂ [*]	Improved estimates of C ₁ and C ₂ (equation (B-17))
C	Defined in equation (A1-8)
C _{coal}	Concentration of mf coal in feed slurry (gm/cm ³ slurry)
C _{H2}	Concentration of hydrogen (g-moles/cm ³)
CI, ASR, T, SRT, P _{H2}	Defined in (A2-12)
C _p	Specific heat (cal/gm°C)
C _T	Total gas phase concentration (g-moles/cm ³)
D, d	Right hand sides in finite difference equations

D	Reactor diameter (cm)
D_H	Thermal dispersion coefficient (cal/cm sec °C)
D'_H	Eddy thermal diffusivity (cm ² /sec)
E_{zl}	Axial dispersion coefficient for liquid phase (cm ² /sec)
E_{zs}	Axial dispersion coefficient for solid phase (cm ² /sec)
E_{16}	Activation energy for hydrogen consumption reaction (cal/g-mole)
f	Defined in (A2-14)
g	Defined in (A2-36) and (A2-37)
H	Dimensionless hydrogen concentration, $C_{H_2}/(C_T)_0$
ΔH_R	Heat of reaction (cal/g-mole H ₂ consumed)
K_1 through K_9	Distribution coefficients for fast reactions, reactions 1 through 9, respectively (Shah and Parulekar ⁽¹⁾)
K_{16}	Arrhenius factor for hydrogen consumption reaction
K_{16}^*	Reaction constant for hydrogen consumption reaction (hr ⁻¹)
L	Reactor length (cm)
$\bar{m}$	Defined in (34)
m	Ratio of the amount of quench to the amount of gas in mainstream at quench location

m'	Ratio of the amount of quench to the amount of the feed gas
m'_{cr}	Value of m' for fixed reactor inlet and outlet temperatures.
M_a	Molecular weight of light gases (gm/g-mole)
M_b	Molecular weight of naphtha (gm/g-mole)
M_p	Molecular weight of by-products (gm/g-mole)
M_h	Molecular weight of water (gm/g-mole)
M_{H_2}	Molecular weight of hydrogen (gm/g-mole)
N	Number of increments in z
n_1 through n_4	Reaction orders for reactions 1 through 4 respectively
n_{16}	Reaction order for hydrogen consumption reaction
P_1, P_2	Defined equations (7) and (8)
P_3	Defined in (26)
P_q	Defined in (27)
Pe_θ	Peclet number for heat
P_T	Total reactor pressure (MPa)
R	Universal gas constant (cal/g-mole °K)

r	Defined in equations (5) and (14)
R_{16}	Dimensionless reaction constant for hydrogen consumption reaction
SRT	Slurry residence time (hr)
t	Time (hr)
T	Reactor temperature ($^{\circ}\text{C}$)
U_o	Superficial velocity (cm/sec)
U_q	Superficial velocity of quench based on the reactor cross-section area (cm/s)
V_1, V_2, V_3, V_4	Defined in equations (B-2)
W	Defined in (B-36)
x	Distance from the reactor inlet (cm)
Y_{H_2}	Hydrogen consumption (gm/gm mf coal)
z	Dimensionless distance from the reactor inlet
Δz	Dimensionless distance increment

Greek Symbols

ρ	Density (gm/cm^3)
ϵ	Holdup
β	Dimensional distance of quench location from reactor inlet (cm)
θ	Dimensionless temperature, $(T-T_0)/T_0$
Γ_R	Dimensionless heat generation parameter
τ	Dimensionless time
$\Delta\tau$	Dimensionless time increment
σ	Surface tension (dyne/cm)
η	Dimensionless distance of quench from reactor inlet

Subscripts

cr	Critical
g	Gas phase
i	Grid point i
l	Liquid phase

o **Feed conditions**

s **Solid phase**

1 **Reactor outlet conditions**

1, 2 **Pre-quench and post-quench section conditions respectively**

Superscripts

old **Value at earlier time increment**

REFERENCES

1. Shah, Y. T. and S. J. Parulekar, "A Model for the SRC-II Coal Liquefaction Reactor," report submitted to Dr. N. L. Carr, Report No. 624RJ041, FT07-30-30, October, 1978.
2. Fox, L., "The Numerical Solution of Two-Point Boundary Problems in Differential Equations," Oxford, London, England (1957).
3. McGinnis, P. H., Jr., Chem. Eng. Progress Symp. Ser., 61 (1965), 2.
4. Deckwer, W. D., R. Burckhart, and G. Zoll, "Mixing and Mass Transfer in Tall Bubble Columns," Chem. Eng. Sci., 29, 2177 (1974).
5. Naylor, J. D., "Process Evaluation Progress Report for February 1978," report submitted to R. A. Berry, Ft. Lewis, WA, March, 1978.
6. Schleppy, R., Jr., Private Communication, April, 1978.
7. Jones, G. L., Private Communication, May, 1979.
8. Naylor, J. D., Process Evaluation Progress Report for February, 1978, dated March 8, 1978.

APPENDIX A

DERIVATION OF MODEL EQUATIONS

Part I Normal Adiabatic Operation (No Quench)

Derivation of Transient Material and Heat Balance Equations

The material and energy balance equations can be derived by taking shell balance on a reactor element of thickness dx at a distance x from the reactor inlet.

Mass flux of hydrogen at x

$$= (U_{og} C_{H_2})_x$$

Heat Flux at x

$$= (\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os}) T|_x \\ - (D_{Hg} + D_{Hl} + D_{Hs}) \frac{dT}{dx} |_x$$

Mass flux of H_2 at $x + dx$

$$= (U_{og} C_{H_2})_{x+dx}$$

Heat flux at $x + dx$

$$= (\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os}) T|_{x+dx}$$

$$- (D_{Hg} + D_{Hl} + D_{Hs}) \frac{dT}{dx} \Big|_x + dx$$

H₂ reacted in the shell

$$= K_{16} * C_{H_2}^{n_{16}} (1 + B_{16} (ASR)) \epsilon_l dx$$

Heat generated in the shell

$$= K_{16} * C_{H_2}^{n_{16}} (1 + B_{16} (ASR)) \Delta H_R \epsilon_l dx$$

H₂ accumulation in shell

$$= \frac{\partial (C_{H_2} \epsilon_g)}{\partial t} dx$$

Heat accumulation in the shell

$$= \frac{\partial}{\partial t} [(\rho_g C_{pg} \epsilon_g + \rho_l C_{pl} \epsilon_l + \rho_s C_{ps} \epsilon_s) T] dx$$

Thus, the material and heat balance equations are:

$$(U_{og} C_{H_2}) \Big|_x - (U_{og} C_{H_2}) \Big|_{x+dx} - K_{16} * C_{H_2}^{n_{16}} (1 + B_{16} (ASR))$$

$$\epsilon_l dx = \frac{\partial (C_{H_2} \epsilon_g)}{\partial t} dx \quad (A1-1)$$

and

$$\begin{aligned}
 & (\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os}) T|_x \\
 & - (D_{Hg} + D_{Hl} + D_{Hs}) \frac{dT}{dx} \Big|_x - (\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} \\
 & + \rho_s C_{ps} U_{os}) T|_{x+dx} + (D_{Hg} + D_{Hl} + D_{Hs}) \frac{dT}{dx} \Big|_{x+dx} \\
 & + K_{16}^* C_{H_2}^{n_{16}} (1 + B_{16} \text{ (ASR)}) \Delta H_R \epsilon_l dx \\
 & = \frac{\partial}{\partial t} [(\rho_g C_{pg} \epsilon_g + \rho_l C_{pl} \epsilon_l + \rho_s C_{ps} \epsilon_s) T] dx \quad (A1-2)
 \end{aligned}$$

As $dx \rightarrow 0$, we have

$$\begin{aligned}
 & - \frac{\partial}{\partial x} (U_{og} C_{H_2}) - K_{16}^* C_{H_2}^{n_{16}} (1 + B_{16} \text{ (ASR)}) \epsilon_l \\
 & = \frac{\partial (C_{H_2} \epsilon_g)}{\partial t} \quad (A1-3)
 \end{aligned}$$

$$\begin{aligned}
 & (D_{Hg} + D_{Hl} + D_{Hs}) \frac{\partial^2 T}{\partial x^2} - \frac{\partial}{\partial x} [T (\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} \\
 & + \rho_s C_{ps} U_{os})] + K_{16}^* C_{H_2}^{n_{16}} (1 + B_{16} \text{ (ASR)}) \Delta H_R \epsilon_l \\
 & = \frac{\partial}{\partial t} [T (\rho_g C_{pg} \epsilon_g + \rho_l C_{pl} \epsilon_l + \rho_s C_{ps} \epsilon_s)] \quad (A1-4)
 \end{aligned}$$

$$K_{16}^* = K_{16} \exp(-E_{16}/RT) \quad (A1-5)$$

Equations (A1-3) and (A1-4) can be transformed into dimensionless equations with the help of assumptions made earlier.

$$-\frac{\partial H}{\partial z} - R_{16} \tau H^{n_{16}} (1 + B_{16} (ASR)) \epsilon_l = \tau \epsilon_g \frac{\partial H}{\partial \tau} \quad (A1-6)$$

and

$$\begin{aligned} \frac{1}{Pe_\theta} \frac{\partial^2 \theta}{\partial z^2} - (P_1 + P_2) \frac{\partial \theta}{\partial z} + \Gamma_R H^{n_{16}} (1 + B_{16} (ASR)) \epsilon_l \\ = C^1 \frac{\partial \theta}{\partial \tau} \end{aligned} \quad (A1-7)$$

where $\tau = t/SRT$

$$C^1 = \frac{(\rho_l C_{pl} \epsilon_l + \rho_s C_{ps} \epsilon_s) (U_{ol})_o}{[(\rho_g)_o C_{pg} (U_{og})_o + \rho_l C_{pl} (U_{ol})_o + \rho_s C_{ps} (U_{os})_o]} \quad (A1-8)$$

Boundary conditions at $z = 0$ can be derived as shown below:

Energy entering at $z = 0$

$$= (\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os}) T|_o$$

Energy leaving at $z = 0+$

$$= (\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os}) T|_{0+} \\ - (D_{Hg} + D_{Hl} + D_{Hs}) \frac{dT}{dx} |_{0+}$$

Equating the two expressions and using the assumptions made earlier and defining dimensionless quantities we can show that:

$$\frac{1}{Pe_0} \frac{d\theta}{dx} = (p_1 + p_2) (\theta - \theta_0) \quad \text{at } z = 0+ \quad (A1-9)$$

In equations (A1-3), (A1-4), and (A1-5), U_{og} , U_{ol} , U_{os} are the superficial velocities of gas, liquid, and solid phases, respectively, ρ_g , ρ_l , ρ_s are the densities of gas, liquid, and solid phases, respectively, ϵ_g and ϵ_l are the holdups for the gas and liquid phases, C_{H_2} is the hydrogen concentration (g-mole/cm³), T is the reactor temperature, x is distance from the reactor inlet and t is time, D_{Hg} , D_{Hl} , D_{Hs} are the thermal axial dispersion coefficients for gas, liquid, and solid phases, respectively, K_{16} , n_{16} , E_{16} , and B_{16} are the Arrhenius constant, reaction order, activation energy, and coefficient of ash for hydrogen consumption reaction.

All the other quantities have been defined previously.

Equations (1) and (2) are special cases of the more general equations (A1-6) and (A1-7) obtained by making right hand sides of the latter equations equal to zero.

Initial and Boundary Conditions

$$\text{At } t = 0, \quad z > 0, \quad H = 0, \quad \theta = 0 \quad (\text{A1-10})$$

$$\text{At } t = t, \quad z = 0+, \quad H = H_0$$

$$\frac{1}{Pe_\theta} \frac{d\theta}{dz} = (p_1 + p_2) (\theta - \theta_0) \quad (\theta_0 = 0) \quad (\text{A1-11})$$

$$\text{At } t = t, \quad z = 1-, \quad \frac{d\theta}{dz} = 0$$

Part II Adiabatic Operation with Quench

Derivation of equations (12) and (13) can be done by a manner similar to that shown in the earlier parts of this appendix. Hence it is not repeated. In the following discussion, additional boundary conditions at the quench location are derived.

Derivation of Additional Necessary Conditions at Quench

Location

Let the quench be added at $x = \beta$ from reactor (dissolver) inlet. The necessary conditions at quench location are obtained by taking flux balances for total gas phase, hydrogen, and heat.

Total mass balance can be represented as follows:

$$(\rho_g U_{og})_{\beta-} + \rho_q U_q = (\rho_g U_{og})_{\beta+} \quad (\text{A2-1})$$

where ρ_g and ρ_q represent densities of the mainstream gas and quench respectively, U_q represents superficial velocity of quench based on dissolver cross-sectional area, and the subscripts β^- and β^+ refer to conditions just prior to addition of quench and just after the addition of quench.

Mass flux balance on hydrogen can be represented as follows

$$(H_{og})_{\beta^-} + H_q U_q = (H_{og})_{\beta^+} \quad (A2-2)$$

where H_q is the dimensionless concentration of hydrogen in gas quench.

Finally heat flux balance at the quench location can be represented as follows

$$\begin{aligned} & - (D_{Hg} + D_{Hl} + D_{Hs})_{\beta^-} \frac{dT}{dx} \Big|_{\beta^-} + \{(\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} \\ & + \rho_s C_{ps} U_{os}) T\}_{\beta^-} + \rho_q C_{pq} U_q T_q \\ & = - (D_{Hg} + D_{Hl} + D_{Hs})_{\beta^+} \frac{dT}{dx} \Big|_{\beta^+} \\ & + \{(\rho_g C_{pg} U_{og} + \rho_l C_{pl} U_{ol} + \rho_s C_{ps} U_{os}) T\}_{\beta^+} \end{aligned} \quad (A2-3)$$

where C_{pq} and T_q represent the specific heat and absolute temperature of quench respectively.

Since the overall thermal dispersion coefficient ($D_{Hg} + D_{Hl} + D_{Hs}$), ρ_l , C_{pg} , C_{pl} , C_{ps} , U_{og} , U_{ol} , U_{os} are constant everywhere in the pre-quench and post-quench sections respectively, we could replace subscripts β^- and β^+ in those terms by 1 and 2 respectively. Converting the various dimensional quantities into dimensionless form with the help of appropriately defined dimensional basis values we can derive equation (22).

Dimensionless distance, η of the quench from the reactor inlet is defined as

$$\eta = \beta/L \quad (A2-4)$$

It has been experimentally observed and verified that in a multiphase flow reactor that there is concentration discontinuity in a phase at the location of quench if the phase is moving in a plug flow fashion (backmixing totally absent). Such a concentration discontinuity is found to be absent however when there is some backmixing. The same arguments are also applicable in the case of temperature (heat balance).

Since in the present case, there is significant thermal dispersion, the following condition holds true:

$$\theta_{\eta-} = \theta_{\eta+} \text{ (or } T_{\beta-} = T_{\beta+} \text{)} \quad (A2-5)$$

Making use of this assumption and converting equations (A2-1) through (A2-3) into dimensionless form we can derive equations (20) through (23).

Hydrogen Consumption

Hydrogen feed at the inlet of reactor

$$= M_{H_2} (C_{H_2})_0 (U_{og})_0 \text{ gm/cm}^2 \text{ sec} \quad (A2-6)$$

Hydrogen fed as part of quench

$$= M_{H_2} C_{H_2q} U_q \text{ gm/cm}^2 \text{ sec} \quad (A2-7)$$

Hydrogen unconverted (outlet) in reactor

$$= M_{H_2} C_{H_2} (U_{og})_o (1 + m) \text{ gm/cm}^2 \text{ sec} \quad (\text{A2-8})$$

Hence hydrogen consumed ($\text{gm/cm}^2 \text{ sec}$)

$$= M_{H_2} ((C_{H_2})_o (U_{og})_o + C_{H_2q} U_q - C_{H_2} (U_{og})_o (1 + m)) \quad (\text{A2-9})$$

Hence, hydrogen consumption based on moisture free coal entering the reactor is

$$Y_{H_2} = \frac{M_{H_2} (U_{og})_o}{(U_{of})_o C_{\text{coal}}} ((C_{H_2})_o + \frac{C_{H_2q} U_q}{(U_{og})_o} - C_{H_2} (1 + m)) \quad (\text{A2-10})$$

In expressions (A2-6) through (A2-10) subscript q refers to quench conditions. By rearranging equation (A2-10) in terms of basis for gas phase concentration, $(C_T)_o$ we can get equation (40) for hydrogen consumption.

The correlation proposed by Jones⁽⁷⁾ relates the hydrogen consumption in a CSTR to coal concentration, recycle ash concentration, partial pressure of hydrogen, mean slurry residence time and temperature as shown below.

$$\Delta H_2 = 0.437 \left(\frac{CI}{CI} \right)^{0.804} (1 + 0.1432 \left(\frac{ASR}{ASR} - 1 \right)) \left(\frac{P_{H_2}}{P_{H_2}} \right)^{0.0805}$$

$$\exp \left(\frac{15500}{R} \left(\frac{1}{T} - \frac{1}{T} \right) \right) \left(\frac{SRT}{SRT} \right) \quad (\text{A2-11})$$

In the above equation, (ΔH_2) represents the hydrogen consumption in g/100 g feed slurry. $\overline{CI}$, $\overline{ASR}$, $\overline{P_{H_2}}$, $\overline{T}$ and $\overline{SRT}$ are the mean values of coal concentration, recycle ash, partial pressure of hydrogen, temperature and slurry residence time. Jones⁽⁷⁾ has proposed the following values for these.

$$\overline{CI} = 0.296385$$

$$\overline{T} = 726.333^\circ K$$

$$\overline{P_{H_2}} = 12.5914 \text{ MPa} \quad (A2-12)$$

$$\overline{SRT} = 0.78 \text{ hr}$$

$$\overline{ASR} = 0.094078$$

The same values have also been used in this part of the study.

The rate expression in the differential reactor can be obtained using equation (A2-11) considering a differential element of a reactor as a stirred tank.

Equation (A2-11) can be expressed in another form by substituting values given in (A2-12) as

$$\Delta H_2 = 1.336 \times 10^5 (\overline{CI})^{0.804} (0.8568 + 1.5221 (\overline{ASR})) (\overline{SRT}) \exp(-7830.3/T) (\overline{P_{H_2}})^{0.0805} \quad (A2-13)$$

Actual rate is expressed as g-moles/cm³ liquid/hr which can be obtained by use of suitable conversion factors. The final correlation can be expressed as

$$r_{16} = K_{16} \exp(7830.3/T_o) (1 + \theta)^{n_{16}} (1 + \theta)^{n_{16}} (1 + B_{16}(\overline{ASR})) (C_T)_o^{n_{16}} T_o^{n_{16}} \quad (A2-14)$$

0.804

where: $K_{16} = 1871(\text{CI})$

and

$$B_{16} = 1.776542$$

(A2-15)

r_{16} is the rate of hydrogen consumption (expressed as g-moles of hydrogen consumed/cm³ liquid hr).

The values of frequency factor and activation energy were subsequently improved. Units for K_{16} are $\left(\frac{\text{g-mole}}{\text{cm}^3 \text{ liq-hr}}\right) \left(\frac{\text{cm gas}}{\text{g-mole}}\right)^{n_{16}}$.

APPENDIX B

Details of Solution Techniques

Part I Normal Adiabatic Operation (No Quench)

Equations (1) and (2) have been solved by two techniques. In the iterative technique, equations (1) and (2) are solved assuming an initial for θ and H at $z = 1^-$ and improving the initial guesses of hydrogen concentration and temperature by Newton-Raphson method. This approach has been discussed in detail by Fox⁽²⁾ and McGinnis.⁽³⁾ The other approach is to solve equations (A1-6) and (A1-7) along with conditions (A1-10) and (A1-11) with respect to time. At large time, the solution approaches steady state solution.

1. Iterative Solution

Solution to (1) and (2) is inherently stable when integration is started at $z = 1$. At $z = 1$, H_{1-} and θ_{1-} are unknown, we have to guess these values. Let us denote them by C_1 and C_2 , respectively.

$$\text{Thus } H_{1-} = C_1 \text{ and } \theta_{1-} = C_2 \quad (\text{B-1})$$

define additional variables

$$\begin{aligned} v_1 &= \frac{\partial H}{\partial C_1} \\ v_2 &= \frac{\partial H}{\partial C_2} \\ v_3 &= \frac{\partial \theta}{\partial C_1} \\ v_4 &= \frac{\partial \theta}{\partial C_2} \end{aligned} \quad (\text{B-2})$$

Hence at $z = 1$

$$v_1 = v_4 = 1, \quad v_2 = v_3 = 0 \quad (B-3)$$

Also

$$\left. \frac{d\theta}{dz} \right|_{1-} = 0$$

Thus

$$\left. \frac{dv_3}{dz} \right|_{1-} = \left. \frac{dv_4}{dz} \right|_{1-} = 0 \quad \text{at } z = 1- \quad (B-4)$$

Differentiating equations (1) and (2) with respect to C_1, C_2 we get a set of four additional equations.

$$\begin{aligned} \frac{dv_1}{dz} = & -R_{16} n_{16} H^{(n_{16}-1)} v_1 (1+B_{16}(ASR)) \epsilon_l \\ & - \frac{\partial R_{16}}{\partial C_1} H^{n_{16}} (1+B_{16}(ASR)) \epsilon_l \end{aligned} \quad (B-5)$$

$$\begin{aligned} \frac{dv_2}{dz} = & -R_{16} n_{16} H^{(n_{16}-1)} v_2 (1+B_{16}(ASR)) \epsilon_l \\ & - \frac{\partial R_{16}}{\partial C_2} H^{n_{16}} (1+B_{16}(ASR)) \epsilon_l \end{aligned} \quad (B-6)$$

$$\frac{1}{Pe_\theta} \frac{d^2 v_3}{dz^2} - (p_1 + p_2) \frac{dv_3}{dz} + \frac{\partial \Gamma_R}{\partial C_1} H^{n_{16}} (1 + B_{16}(ASR)) \epsilon_\ell$$

$$+ \Gamma_R H^{(n_{16}-1)} n_{16} v_1 (1 + B_{16}(ASR)) \epsilon_\ell = 0 \quad (B-7)$$

$$\frac{1}{Pe_\theta} \frac{d^2 v_4}{dz^2} - (p_1 + p_2) \frac{dv_4}{dz} + \frac{\partial \Gamma_R}{\partial C_2} H^{n_{16}} (1 + B_{16}(ASR)) \epsilon_\ell$$

$$+ \Gamma_R H^{(n_{16}-1)} n_{16} v_2 (1 + B_{16}(ASR)) \epsilon_\ell = 0 \quad (B-8)$$

Since

$$R_{16} = K_{16} (C_T)_O^{(n_{16}-1)} \exp(-E_{16}/RT_O (1 + \theta))$$

we have

$$\frac{\partial R_{16}}{\partial C_1} = \frac{E_{16}}{RT_O} \times \frac{R_{16}}{(1+\theta)^2} v_3 \quad (B-9)$$

$$\frac{\partial R_{16}}{\partial C_2} = E_{16} R_{16} v_4 / RT_O (1+\theta)^2$$

since $\Gamma_R = R_{16} \Delta H_R (U_{ol})_O (C_T)_O / T_O$ (B-10)

we have

$$\frac{\partial \Gamma_R}{\partial C_1} = \frac{\Gamma_R}{R_{16}} \frac{\partial R_{16}}{\partial C_1} \quad (B-11)$$

and

$$\frac{\partial \Gamma_R}{\partial C_2} = \frac{\Gamma_R}{R_{16}} \frac{\partial R_{16}}{\partial C_2} \quad (B-12)$$

Integration of equations (1), (2) and (B-5) through (B-8) is done by standard integration techniques till $z = 0^+$ is reached.

At $z = 0^+$ $H = H_O$

$$\frac{d\theta}{dz} = Pe_\theta (p_1 + p_2) \theta \quad (B-13)$$

Thus, assuming that we are always within the radius of convergence, we can use Taylor's series (first order approximation) for estimating the improved values.

Thus

$$H_O = H + (C_1^* - C_1) \frac{\partial H}{\partial C_1} + (C_2^* - C_2) \frac{\partial H}{\partial C_2} \quad (B-14)$$

Let $f = \frac{\partial \theta}{\partial z} - Pe_\theta (p_1 + p_2) \theta$

$$\text{and} \quad \frac{\partial f}{\partial C_1} = \frac{dv_3}{dz} - Pe_\theta (p_1 + p_2) v_3 \quad (B-15)$$

$$\frac{\partial f}{\partial C_2} = \frac{dv_4}{dz} - Pe_\theta (p_1 + p_2) v_4$$

Then

$$0 = f + (C_1^* - C_1) \frac{\partial f}{\partial C_1} + (C_2^* - C_2) \frac{\partial f}{\partial C_2} \quad (B-16)$$

Solution of equations (B-14) and (B-16) can be represented in matrix form as shown below.

$$\begin{bmatrix} C_1^* \\ C_2^* \end{bmatrix} = \begin{bmatrix} C_1 \\ C_2 \end{bmatrix} - \begin{bmatrix} v_1 & v_2 \\ \frac{\partial f}{\partial C_1} & \frac{\partial f}{\partial C_2} \end{bmatrix}^{-1} \begin{bmatrix} H - H_0 \\ f \end{bmatrix} \quad (B-17)$$

where C_1^* and C_2^* are improved estimates of C_1 and C_2 .

When the equations are not coupled as in the present case, we can solve energy balance equation independently and the problem is reduced to solving main equation and the auxilliary equation simultaneously.

2. Solution of Transient Equations

Equations (A1-6) and (A1-7) can be converted into finite difference form for any intermediate point i in a mesh of $(N+1)$ points between the interval $(0,1)$. Note $\Delta z = 1/N$ in this case. Thus

$$\begin{aligned}
& - \frac{(H_{i+1} - H_i - 1)}{2\Delta z} - (R_{16} H^{n_{16}})_i [(1 + B_{16} (ASR)) \epsilon_L]_i \\
& = \frac{r\epsilon_g}{\Delta\tau} (H_i - H_i^{old})
\end{aligned} \tag{B-18}$$

$$\begin{aligned}
& \frac{(\theta_{i+1} + 1 + \theta_i - 1 - 2\theta_i)}{(\Delta z)^2} - (p_1 + p_2) \frac{(\theta_{i+1} - \theta_i - 1)}{2\Delta z} \\
& + [\Gamma_R H^{n_{16}} (1 + B_{16} (ASR)) \epsilon_L]_i = \frac{C^1}{\Delta\tau} (\theta_i - \theta_i^{old})
\end{aligned} \tag{B-19}$$

where θ_i^{old} and H_i^{old} refer to values for the previous iteration (old time).

Equations (B-18) and (B-19) can be rearranged as shown below.

$$\begin{aligned}
& - \frac{H_i - 1}{2\Delta z} + \frac{r\epsilon_g}{\Delta\tau} H_i + \frac{H_{i+1} - 1}{2\Delta z} = \frac{r\epsilon_g}{\Delta\tau} H_i^{old} \\
& - (R_{16} H^{n_{16}} (1 + B_{16} (ASR)) \epsilon_L)_i
\end{aligned} \tag{B-20}$$

$$\begin{aligned}
& \left(\frac{1}{Pe_\theta (\Delta z)^2} + \frac{p_1 + p_2}{2\Delta z} \right) \theta_{i+1} - \left(\frac{2}{Pe_\theta (\Delta z)^2} + \frac{C}{\Delta\tau} \right) \theta_i \\
& + \left(\frac{1}{Pe_0 (\Delta z)^2} - \frac{p_1 + p_2}{2\Delta z} \right) \theta_{i-1} = - \frac{C^1}{\Delta\tau} \theta_i^{old} \\
& - [\Gamma_R H^{n_{16}} (1 + B_{16} (ASR)) \epsilon_L]_i
\end{aligned} \tag{B-21}$$

Equations (A2-20) and (A2-21) can be represented in the form

$$A_i X_{i-1} + B_i X_i + C_i X_{i+1} = D_i \quad (B-22)$$

where A_i , B_i , C_i , and D_i 's are as shown below.

For equation (B-20)

$$A_i = -\Delta t/2$$

$$B_i = r\epsilon_g \Delta z \quad (B-23)$$

$$C_i = \Delta t/2$$

$$D_i = r\epsilon_g \Delta z H_i^{\text{old}} - [R_{16} H^{n_{16}} (1 + B_{16} (\text{ASR})) \epsilon_L]_i$$

$$\times \Delta z \Delta \tau$$

and for equation (B-21)

$$A_i = \Delta \tau / Pe_\theta + (p_1 + p_2) \Delta z \Delta \tau / 2$$

$$B_i = -2\Delta \tau / Pe_\theta - C' (\Delta z)^2 \quad (B-24)$$

$$C_i = \Delta \tau / Pe_\theta - (p_1 + p_2) \Delta z \Delta \tau / 2$$

$$D_i = -C' (\Delta z)^2 \theta_i^{\text{old}} - (\Gamma_R H^{n_{16}})_i^{\text{old}} (1 + B_{16} (\text{ASR})) \epsilon_L$$

At $z = 0^+$

$$H_1 = H_0, \quad A_1 = 0, \quad B_1 = 1, \quad C_1 = 0, \quad D_1 = H_0$$

$$\left. \frac{d\theta}{dz} \right|_{z=0^+} = Pe_\theta (p_1 + p_2) \theta$$

$$\text{Thus } \frac{\theta_2 - \theta_1}{\Delta z} = \text{Pe}_\theta (p_1 + p_2) \theta_1$$

$$\text{or } \theta_2 = \theta_1 [1 + \text{Pe}_\theta (p_1 + p_2) \Delta z] \quad (\text{B-25})$$

$$A_1 = 0, \quad B_1 = (1 + \text{Pe}_\theta (p_1 + p_2) \Delta z), \quad C_1 = -1.0$$

At $z = 1^-$, mesh point $(N + 1)$

$$\frac{\partial H}{\partial z} = \frac{H_{N+1} - H_N}{\Delta z}$$

Thus at mesh point $(N + 1)$ we have

$$\begin{aligned} - \left(\frac{H_{N+1} - H_N}{\Delta z} \right) &= (R_{16} H^{n16})_{N+1} (1 + B_{16} (\text{ASR})) \epsilon_L \\ &= \frac{r\epsilon_g}{\Delta \tau} (H_{N+1} - H_{N+1}^{\text{old}}) \end{aligned}$$

$$\begin{aligned} \text{or } (r\epsilon_g \Delta z + \Delta \tau) H_{N+1} - H_N \Delta \tau &= r\epsilon_g \Delta z H_{N+1}^{\text{old}} \\ &- (R_{16} H^{n16})_{N+1} (1 + B_{16} (\text{ASR})) \epsilon_L \end{aligned}$$

$$\text{Thus } A_{N+1} = -\Delta \tau, \quad B_{N+1} = r\epsilon_g \Delta z + \Delta \tau \quad (\text{B-26})$$

$$C_{N+1} = 0, \quad D_{N+1} \text{ is same as in equation (B-23)}$$

At $z = 1^-$, substituting $\theta_{N+2} = \theta_N$ we have

$$\begin{aligned} (2/\text{Pe}_\theta) \Delta \tau \theta_N - [(2/\text{Pe}_\theta) \Delta \tau + C' (\Delta z)^2] \theta_{N+1} \\ = -C' (\Delta z)^2 \theta_1^{\text{old}} - [\Gamma_R H^{n16} (1 + B_{16} (\text{ASR})) \epsilon_L]_1 (\Delta z)^2 \Delta \tau \end{aligned} \quad (\text{B-27})$$

Hence,

$$A_{N+1} = (2/Pe_0) \Delta \tau$$

$$B_{N+1} = - (2/Pe_0) \Delta \tau - C' (\Delta z)^2 \quad (B-28)$$

$$C_{N+1} = 0$$

$$D_{N+1} \text{ is same as in equation (B-24)}$$

Thomas Algorithm

Consider an example of three simultaneous equations containing three unknowns x_1 , x_2 , and x_3 .

$$B_1 x_1 + C_1 x_2 = D_1 \quad (B-29)$$

$$A_2 x_1 + B_2 x_2 + C_2 x_3 = D_2 \quad (B-30)$$

$$A_3 x_2 + B_3 x_3 = D_3 \quad (B-31)$$

From (A2-29)

$$x_1 = \frac{D_1}{B_1} - \frac{C_1}{B_1} x_2$$

$$\text{Let } w_1 = C_1 / B_1, \quad g_1 = D_1 / B_1$$

$$x_1 = g_1 - w_1 x_2 \quad (B-32)$$

Substituting in equation (A2-30) we have

$$A_2 (g_1 - w_1 x_2) + B_2 x_2 + C_2 x_3 = D_2$$

$$x_2 + \frac{C_2 x_3}{(B_2 - A_2 W_1)} = \frac{(D_2 - A_2 g_1)}{(B_2 - A_2 W_1)} = g_2 \quad (B-33)$$

substituting (A2-33) in (A2-31) we solve for x_3 to obtain

$$x_3 = (D_3 - A_3 g_2) / (C_3 - W_2 A_3) \quad (B-34)$$

The above scheme can be generalized for a system of N simultaneous equations of the form

$$A_i x_{i-1} + B_i x_i + C_i x_{i+1} = D_i$$

for $i = 1, 2, \dots, N$

$$\text{for } i = 1, \quad W_1 = C_1 / B_1, \quad g_1 = D_1 / B_1 \quad (B-35)$$

$i = 2, 3, \dots, N$

$$W_i = C_i / (B_i - W_{i-1} A_i) \quad (B-36)$$

$$\text{and } g_i = (D_i - g_{i-1} A_i) / (B_i - W_{i-1} A_i) \quad (B-37)$$

$$\text{for } i = N, \quad x_N = g_N$$

$$\text{and } x_i = g_i - W_i x_{i+1} \quad \text{for } i = 1, 2, \dots, N-1 \quad (B-38)$$

Part II. Adiabatic Operation with Quench

Equations (12) and (13) can be solved by a treatment very similar to that already described earlier in this appendix.

APPENDIX C

Nomenclature Followed in Computer Programs

H, T	Current value of hydrogen concentration and temperature, respectively
HOLD, TOLD	Old value of hydrogen concentration and temperature, respectively
A, B, C	Elements of coefficient matrix in tridiagonal system of simultaneous linear algebraic equations
D	Vector containing right hand sides of above-mentioned equations
X	Solution vector
ZN12, ZN13	n_1 and n_2 as defined by Shah and Parulekar, ⁽¹⁾ respectively
N1	Number of increments in Z
ZMH2, ZMA ZMB, ZMP, ZMH	Molecular weights of hydrogen, light gases, naphtha, by-products, and water, respectively
D2	Increment in Z
B11, B8, B9	B_7 , B_8 , B_9 as defined by Shah and Parulekar ⁽¹⁾
RHOS	Solid density
DENS	Liquid density

DENS	Liquid density
RHOGO	Gas density at base temperature
CPG,CPL,CPS	Specific heats of gas, liquid, and solid phases, respectively
PMU	Viscosity of liquid
AS	Weight fraction of noncatalytic ash in feed coal (gm/gm mf coal)
DP	Particle diameter (cm)
ZN16,ZK16 E16,B16	Reaction order with respect to hydrogen, Arrhenius factor, activation energy, coefficient of recycle ash in rate expression for H ₂ consumption reaction.
CI	Weight fraction of mf coal in feed slurry
SO	Weight fraction of recycle ash in feed slurry
PT	Total pressure in reactor (MPa)
UOLO,UOL	Feed liquid velocity (cm/sec)
UOGO,UOG	Feed gas velocity (cm/sec)
D10,D0	Reactor diameter (cm)
ZLO,ZL	Reactor length (cm)
TEMP	Reactor temperature (°C)

DS	Soup density (gm/cm^3)
ASDO	Weight fraction of ash in slurry
TA	Absolute temperature at feed conditions ($^{\circ}\text{K}$)
RHOG	Gas density at actual feed temperature (gm/cm^3)
CI1	Weight fraction of mf coal in feed slurry
SRT	Slurry residence time (hr)
R	Ratio of liquid velocity to gas velocity
UT	Terminal settling velocity (cm/sec)
T1	Ratio of terminal settling velocity to feed liquid velocity
EZL	Axial dispersion coefficient for liquid phase
DH	Overall thermal dispersion coefficient ($D_{Hg} + D_{Hl} + D_{Hs}$)
HGO	Gas phase holdup
UOS	Solid velocity
QT	Peclet number for heat
CT	Total gas phase concentration ($\text{g mole}/\text{cm}^3$)
ZK1 thru ZK9	Distribution coefficients for reactions 1 through 9 as described by Shah and Parulekar ⁽¹⁾

DEN	Concentration of maf coal in slurry (gm/cm ³)
AO,BO,PO, YO,HO	Mole fractions of A, B, P.H, and H ₂ at reactor inlet
ZIO1	Weight fraction of IOM based on maf coal
ORGO	Weight fraction of IOM in feed slurry
S10	Weight fraction of heavy solids in feed slurry
S	Weight fraction of recycle ash in slurry
S1	Weight fraction of heavy solids in slurry
HLO,HS	Liquid and solid phase holdup
DHR	Heat of reaction (cal/g mole)
TIME	Time (hr)
DT	Time increment (hr)
R16,GAM	Dimensionless rate constant and heat generation parameter for hydrogen consumption reaction
C1	Initial guess of θ at $z = 1$
V2	$\frac{\partial \theta}{\partial C_1}$
DV2	$\frac{d}{dz} \left(\frac{\partial \theta}{\partial C_1} \right)$

DT	$\frac{d\theta}{dz}$
SDT	$\frac{d^2\theta}{dz^2}$
DGAM	$\frac{\partial \Gamma_R}{\partial C_1}$
SDV2	$\frac{d^2}{dz^2} \left(\frac{\partial \theta}{\partial C_1} \right)$
V1	f as defined in (A2-14)
DV1	as defined in (A2-14)
DH	gradient of hydrogen concentration
X5	hydrogen consumption (gm/gm maf coal)
RISE	temperature rise, °C
RISE1	temperature rise per unit hydrogen consumption, (°C) (gm maf coal)/gm
TEMPO	absolute temperature of quench
DQ	dimensionless distance of quench location (η)
QUE	same as η
PQ	same as p_q

Computer Programs

Part I Normal Adiabatic Operation

Program 1 = Solution to transient equations

Program 2 = Solution to steady state equations

Part II Adiabatic Operation with Quench

Program 3 = Solution to steady state equations

APPENDIX D

Program 1

Computer Listing For Unsteady State (Transient)
Solution - Adiabatic Reactor With No Quench

```
DIMENSION A(101),B(101),C(101),D(101),X(101)
DIMENSION H(201),HOLD(201),T(201),TOLD(201)
```

```
N1=100
```

```
ZN12=0.85
```

```
ZN13=0.85
```

```
ZMH2=2.0
```

```
ZN1=N1
```

```
ZMA=30.0
```

```
ZMB=115.0
```

```
ZMP=32.0
```

```
ZMH=18.0
```

```
D2=1.0/ZN1
```

```
B11=0.0
```

```
B8=7.0
```

```
B9=11.6
```

```
RHOB=1.5
```

```
DENS=0.9
```

```
RHOG=2.75/62.5
```

```
CPB=0.28
```

```
CPG=0.89
```

```
CPL=0.63
```

```
RHO=1.35
```

```
PMU=0.004
```

```
AS=0.09
```

```
DP=0.0003
```

```
ZN16=0.0
```

```
DO 510 J1=1,2
```

```
READ(5,*)CI
```

```
READ(5,*)SO
```

```
READ(5,*)PT
```

```
READ(5,*)UOL0
```

```
READ(5,*)D10
```

```
READ(5,*)UOG0
```

```
READ(5,*)ZL0
```

```
READ(5,*)TEMP
```

```
DS=1.1
```

```
ZL=ZL0
```

```
DO=D10
```

```
UOG=UOG0
```

```
ASDQ=AS*CI
```

```
TA=TEMP+273.0
```

```
RHOG0=2.75/62.5
```

```
RHOG=RHOG0*PT/TA+693.0/14.0
```

```
UOL=UOL0
```

```
CI1=(1.0-AS)*CI
```

```
SRT=ZL/UOL/3600.0
```

```
R=UOL/UOG
```

```
UT=981.0/18.0*DP*DP*(RHOB-DENS)/PMU
```

```
T1=UT/UOL
```

```
EZL=2.7*DO+1.4*UOG+0.3
```

```
S6=RHOG*CPG*DENS*CPL+RHOB*CPB
```

```
FACT=0.45
```

```
DM=EZL*S6*FACT
```

```
WRITE(6,*)DM
```

```
HG0=(0.15+ALOG(UOG)-0.04)/(DO+0.08)
```

```
UOS=UOL*(1.0-T1*(1.0-HG0))
```

```
WRITE(6,*)HG0
```

```
WRITE(6,*)UOS
```

```
QY=(RHOB*CPB*UOS+DENS*CPL*UOL+RHOG*CPG*UOG)*ZL/DM
```

```

TEMP2=1.8*TA-460.0
WRITE(6,600)TEMP2,80,PT
600 FORMAT(5X,12HTEMPERATURE=,G13.6,5X,4HABR=,G13.6,5X,9HPRESSURE=,G13.6)
1.6)
WRITE(6,38)SRT
38 FORMAT(5X,4HSRT=,G13.6)
WRITE(6,601)UOL,D0,UOG
601 FORMAT(5X,4HUOL=,G13.6,5X,9HDIAETER=,G13.6,5X,4HUOG=,G13.6)
WRITE(6,602)ZL,QT
602 FORMAT(5X,7HLENGTH=,G13.6,5X,23HPECKET NUMBER FOR HEAT=,G13.6)
ZK1=19890.0
READ(5,*)ZK16
Z16=6336.0
CT=PT/82.06/TA+9.868
CT0=14.0/82.0/(460+273.0)+9.868
ZK1=0.0294*(PT/15.4)**ZN12
ZK2=0.02683*(PT/15.4)**ZN13
ZK3=0.042
ZK4=0.0567
ZK5=0.0599
ZK6=0.069
ZK7=0.394*(1.0+B11*S0)
ZK8=0.246*(1.0+B8*S0)
ZK9=0.08*(1.0+B9*S0)
SUN=ZK1+ZK2+ZK3+ZK4+ZK5+ZK6+ZK7+ZK8+ZK9
ZK1=ZK1/SUN
ZK2=ZK2/SUN
ZK3=ZK3/SUN
ZK4=ZK4/SUN
ZK5=ZK5/SUN
ZK6=ZK6/SUN
ZK7=ZK7/SUN
ZK8=ZK8/SUN
ZK9=ZK9/SUN
DEN=C11*DS
A0=ZK1*DEN/CT/ZHA*R
B0=ZK2*DEN/CT/ZHB*R
P0=ZK3*DEN/CT/ZMP*R
Y0=ZK4*DEN/CT/ZMH*R
H0=1.0-A0-B0-P0-Y0
WRITE(6,*)H0
ZIO1=ZK5+S0/C11
ORG0=ZIO1*C11
S=80
S1=810
HS=(1.0-HG0)*DS/RHOS*(8+S1+ORG0+ABD0)
WRITE(6,*)HS
HLO=1.0-HS-HG0
WRITE(6,*)HLO
READ(5,*)CON
DHR=CON*359.0/1.8
WRITE(6,*)HLO,DHR
LT=70
TIME=0.0
DO 410 L=1,LT
IF(L,GT,10)GO TO 91
DT=1.0E-4
GO TO 59
91 IF(L,GT,20)GO TO 52
DT=1.0E-3

```

```

      GO TO 55
52  IF(L.GT.30)GO TO 53
      DT=1.0E-2
      GO TO 55
53  IF(L.GT.40)GO TO 54
      DT=1.0E-1
      GO TO 55
54  DT=3.0E-1
55  CONTINUE
      IF(L.GT.1)GO TO 5
      N5=0.0
      IF(J1.GT.1)GO TO 383
      N=N1+1
      DO 360 I=1,N
      T(I)=0.05
      H(I)=H0
360  CONTINUE
      GO TO 384
383  CONTINUE
      DO 385 I=1,N
      T(I)=TA0*(1.0+T(I))/TA=1.0
385  CONTINUE
384  CONTINUE
      H(I)=H0

5  CONTINUE
      N=N1+1
      DO 350 I=1,N
      HOLD(I)=H(I)
      TOLD(I)=T(I)
      R16=ZK16*EXP(-E16/TA/(1.0+T(I)))*8RT
      A(I)=-DT/2.0
      B(I)=R+HGO*D2
      C(I)=DT/2.0
      D(I)=R+HGO*H(I)*D2-R16*R+H(I)**2N16*HL0*(1.0+B16*8)*DT=D2
65  CONTINUE
      IF(I.GT.1)GO TO 10
      A(I)=0.0
      B(I)=1.0
      C(I)=0.0
      D(I)=H0
10  CONTINUE
      IF(I.LT.N)GO TO 12
      A(I)=DT
      B(I)=DT+R+HGO*D2
      C(I)=0.0
12  CONTINUE
350  CONTINUE
      CALL THOMAS(N,A,B,C,D,X)
      DO 120 I=1,N
      H(I)=X(I)
120  CONTINUE
      H(I)=H0
125  CONTINUE
      SUM=DENS*CPL*UOL+RHOS*CPB*UOS+RHOG*CPG*UOG
      P1=RHOS*CPB*UOS/SUM
      P2=DENS*CPL*UOL/SUM
      P3=RHOG*CPG*UOG/SUM
      DO 370 I=1,N
      TOLD(I)=T(I)

```

```

      R16=ZK16*EXP(-E16/TA/(1.0+T(I)))*8RT
      GAN=R16*DHR*UOL*CT/TA
      GAM=GAN/SUM
      A2=SUM/UOL
      SUM1=RHOS*CP3*HS+DENS*CPL*HL0
      A(I)=DT/QT+D2*DT*(P1+P2)/2.0
      B(I)=SUM1/A2+D2*D2=2.0*DT/QT
      C(I)=DT/QT-D2*DT*(P1+P2)/2.0
      D(I)=SUM1/A2+D2*D2*T(I)-GAM*H(I)**ZN16*(1.0+B16*8)*HL0+D2*D2*DT
370  CONTINUE
      A(I)=0.0
      B(I)=(1.0+QT*(P1+P2)*D2)
      C(I)=1.0

      A(N)=2.0*DT/QT
      B(N)=2.0/QT*DT-SUM1/A2*D2*D2
      C(N)=0.0

      D(1)=QTX(P1+P2)*D2*T(1)
      CALL THOMAS(N,A,B,C,D,X)
      DO 369 I=1,N
      Y(I)=X(I)
369  CONTINUE
      TIME=TIME+DT
      IF(J1,EQ,1)GO TO 410
      JS=L/5.0
      IF (JS,EQ,N5)GO TO 410
      REALT=TIME*8RT
      WRITE(6,515)REALT
      WRITE(6,520)
      DO 575 I=1,N,N1/10
      ATEMP=TA*(1.0+T(I))
      ATEMP1=TA*(1.0+TOLD(I))
      ATEMP=ATEMP+1.8-460.0
      ATEMP1=ATEMP1+1.8-460.0
      WRITE(6,525)H(I),ATEMP,HOLD(I),ATEMP1
575  CONTINUE
      NB=NS+1
410  CONTINUE
      IF(J1,GT,1)GO TO 528
      REALT=TIME*8RT
      TA=TA
      WRITE(6,515)REALT
515  FORMAT(5X,5HTIME=,G13.6,5HHOURS)
      WRITE(6,520)
520  FORMAT(10X,2HH2,15X,4HTEMP,12X,7HH2(OLD),10X,9HTEMP(OLD))
      DO 530 I=1,N,N1/10
      ATEMP=TA*(1.0+T(I))
      ATEMP1=TA*(1.0+TOLD(I))
      ATEMP=ATEMP+1.8-460.0
      ATEMP1=ATEMP1+1.8-460.0
      WRITE(6,525)H(I),ATEMP,HOLD(I),ATEMP1
525  FORMAT(4(5X,G13.6))
530  CONTINUE
528  X9=ZHM2*CT/R/DEN*(H0-H(N))*(1.0-A8)
      WRITE(6,706)X5
706  FORMAT(5X,15HH2 CONSUMPTION=,G13.6)
510  CONTINUE

```

END

```

SUBROUTINE THOMAS(N,A,B,C,D,X)
DIMENSION A(N),B(N),C(N),D(N),X(N)
DIMENSION W(201),G(201)
DO 5 I=1,N
  IF(I.GT.1)GO TO 3
  W(I)=C(I)/B(I)
  G(I)=D(I)/B(I)
  GO TO 5
3 W(I)=C(I)/(B(I)-W(I-1)*A(I))
  G(I)=(D(I)-G(I-1)*A(I))/(B(I)-W(I-1)*A(I))
5 CONTINUE
DO 6 J=2,N
  I=1+N-J
  X(N)=G(N)
  X(I)=G(I)-W(I)*X(I+1)
6 CONTINUE
RETURN
END

```

```

END      USER: PARULEKAR [114237,27340:]    JOB: GULF    SEQ: 12695    FINISH
*****

```

APPENDIX D

Program 2

Computer Listing For Steady State Solution -
Adiabatic Reactor With No Quench

DIMENSION M(101),T(101)

Z1=1.0E-7

ZN12=0.85

ZN13=0.85

N1=50

ZMH2=2.0

ZN1=N1

ZMA=30.0

ZMB=115.0

ZMP=32.0

ZMH=18.0

D2=1.0/ZN1

B11=0.0

B8=7.0

B9=11.6

RHOB=1.5

DENS=0.9

RHOG=2.75/62.5

CP8=0.28

CPG=0.89

CPL=0.63

RHO=1.35

PMU=0.004

AS=0.09

DP=0.0003

ZN16=0.0

DO 565 I9=1,17

READ(5,*)CI

READ(5,*)BO

READ(5,*)PT

READ(5,*)UOL0

READ(5,*)D10

READ(5,*)UOG0

READ(5,*)ZL0

READ(5,*)TEMP

DS=1.1

UOL=UOL0

ZL=ZL0

DO=D10

UOG=UOG0

ASDO=AS*CI

TA=TEMP+273.0

RHOG0=2.75/62.5

RHOG=RHOG0*PT/TA+693.0/14.0

CI1=(1.0-AS)*CI

BRT=ZL/UOL/3600.0

R=UOL/UOG

UT=981.0/18.0*DP*DP*(RHOB-DENS)/PMU

T1=UT/UOL

EZL=2.7*DO**1.4*UOG**0.3

S6=RHOG*CPG+DENS*CPL+RHO8*CP8

READ(5,*)FACT

DH=EZL*S6*FACT

WRITE(6,*)DH

HGO=(0.15*ALOG(UOG)-0.04)/(DO**0.08)

WRITE(6,*)HGO

UOS=UOL*(1.0-T1*(1.0-HGO))

WRITE(6,*)UOS

```

      GT=(RHOS*CPB*UOS+DENS*CPL*UOL+RHOG*CPG*UOG)*ZL/DH
      WRITE(6,600)TEMP,80,PT
600  FORMAT(5X,12HTEMPERATURE,G13.6,5X,4HABR,G13.6,5X,9HPRESSURE,G13.6)
      13.6)

      WRITE(6,601)UOL,D0,UOG
601  FORMAT(5X,4HUOL,G13.6,5X,9HDIAMETER,G13.6,5X,4HUOG,G13.6)
      WRITE(6,602)ZL,GT
602  FORMAT(5X,7HLENGTH,G13.6,5X,23HPECLET NUMBER FOR HEAT,G13.6)
      TA=TEMP+273.0
      ZK16=19890.0
      READ(5,*)ZK16
      E16=6336.0
      CT=PT/82.06/TA*9.868
      CT0=14.0/82.0/(460.0+273.0)*9.868
      ZK1=0.0254*(PT/19.4)**ZN12
      ZK2=0.02683*(PT/19.4)**ZN13
      ZK3=0.042
      ZK4=0.0567
      ZK5=0.0595
      ZK6=0.069
      ZK7=0.394*(1.0+B11*80)
      ZK8=0.246*(1.0+B8*80)
      ZK9=0.08*(1.0+B9*80)
      SUN=ZK1+ZK2+ZK3+ZK4+ZK5+ZK6+ZK7+ZK8+ZK9
      ZK1=ZK1/SUN
      ZK2=ZK2/SUN
      ZK3=ZK3/SUN
      ZK4=ZK4/SUN
      ZK5=ZK5/SUN
      ZK6=ZK6/SUN
      ZK7=ZK7/SUN
      ZK8=ZK8/SUN
      ZK9=ZK9/SUN
      DEN=CI1*DS
      A0=ZK1*DEN/CT/ZMA*R
      B0=ZK2*DEN/CT/ZMB*R
      P0=ZK3*DEN/CT/ZMP*R
      Y0=ZK4*DEN/CT/ZMH*R
      H0=1.0-A0-B0-P0-Y0
      WRITE(6,*)H0
      ZIO1=ZK5*80/CI1
      ORGO=ZIO1*CI1
      S=30
      S1=S10
      H8=(1.0-HG0)*DS/RHOS*(8+S1+ORGO+ASD0)
      WRITE(6,*)H8
      HLO=1.0-H8-HG0
      WRITE(6,*)HLO
      READ(5,*)CON
      DHR=CON*359.0/1.8
      WRITE(6,*)HLO,DHR
      SUM=DENS*CPL*UOL+RHOS*CPB*UOS+RHOG*CPG*UOG
      P1=RHOS*CPB*UOS/SUM
      P2=DENS*CPL*UOL/SUM
      P3=RHOG*CPG*UOG/SUM
      GT1=GT*(P1+P2)
      APRIME=GT*ZK16*8RT*DHR*CT/TA*UOL*(1.0+B16*8)*HLO
      WRITE(6,609)GT1
609  FORMAT(5X,23HMODIFIED PECLET NUMBER,G13.6)

```

```

WRITE(6,610)APRIME
610 FORMAT(5X,2HAN,013.6)
A2=SUM/UOL
N=N1+1
DO 350 L=1,100
IF(L.GT.1)GO TO 15
READ(5,*)C1
15 T(N)=C1
DT=0.0
V2=1.0
DV2=0.0
DO 360 J=1,N1
I=N-J+1
IF(T(I).GT.0.0)GO TO 20
T(I)=0.0
20 CONTINUE
R16=ZK16*EXP(-E16/(TA*(1.0+T(I))))*BRT
GAN=R16*DHRC/TA*UOL
GAM=GAN/SUM

SDT=GT*((P1+P2)*DT=GAM*M(I)**ZN16*(1.0+B16*B)*ML0)
DR16=R16*(E16/TA/((1.0+T(I))*2))*V2
DGAM=DR16*CT*DHRC*UOL/TA/(1.0+T(I))/SUM
SDV2=GT*((P1+P2)*DV2=DGAM*M(I)**ZN16*(1.0+B16*B)*ML0)
T(I=1)=T(I)-D2*DT+D2*D2*SDT/2.0
DT=DT+D2*SDT
V2=V2+D2*DV2+D2*D2*SDV2/2.0
DV2=DV2+D2*SDV2
IF(T(I=1).GT.0.0)GO TO 26
T(I=1)=0.0
26 CONTINUE
IF(T(I=1).LT.T(I))GO TO 32

T(I=1)=T(I)
32 CONTINUE
IF(DT.GT.0.0)GO TO 33
DT=0.0
33 CONTINUE

IF(I.GT.2)GO TO 360
V1=DT/GT/(P1+P2)=T(I)
WRITE(6,*)V1
IF(ABS(V1).LT.21)GO TO 375
DV1=DV2/GT/(P1+P2)=V2
C1=C1-V1/DV1
WRITE(6,*)C1,DV2

370 CONTINUE
360 CONTINUE
350 CONTINUE
375 CONTINUE
M(I)=M0
DO 410 I=1,N1
R16=ZK16*EXP(-E16/(TA*(1.0+T(I))))*BRT
R16=R16*CT0/CT
DHRC=R16*RH(M(I)**ZN16*(1.0+B16*B)*ML0)
M(I+1)=M(I)+D2*DH
IF(M(I+1).GT.0.0)GO TO 25
M(I+1)=0.0
25 CONTINUE

```

```

410 CONTINUE
    WRITE(6,520)
520 FORMAT(10X,2MH2,15X,4HTEMP)
    NDN1=1
    DO 530 I=1,N,N1/10
        RI=T(I)*TA
        RI=1.0*RI
        WRITE(6,525)M(I),RI
525 FORMAT(2(5X,013.6))
530 CONTINUE
510 CONTINUE
    XS=2MH2*CT/R/DEN*(H0-M(N))*(1.0-AB)
    WRITE(6,706)XS
706 FORMAT(5X,15MH2 CONSUMPTION=,013.6)
    RISE=TA-T(N)
    WRITE(6,*)RISE
    RISE1=RISE/XS
    WRITE(6,*)RISE1
565 CONTINUE
    END

```

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APPENDIX D

Program 3

**Computer Listing of Steady State Solution -
Adiabatic Reactor With One Quench Point**

```

DIMENSION H(101),T(101)
DIMENSION C(12),A(2,2),B(2)
REAL MP
Z1=1.0E-7
READ(5,*) Z1
READ(5,*) Z2
Z12=0.85
Z113=0.85
N1=50
ZMH2=2.0
ZM1=N1
ZMA=30.0
ZMR=115.0
ZMP=32.0
ZMH=18.0
D2=1.0/ZN1
B11=0.0
B8=7.0
B9=11.6
B16=2.2640804
RHOS=1.5
DEUS=0.9
RHOG=2.75/62.5
CPS=0.28
CPG=0.89
CPL=0.63
RHO=1.35
PMU=0.004
AS=0.09
DP=0.0003
ZM16=0.0805
MU=1.0

DO 565 I=1,17
  READ(5,*) CI
  READ(5,*) SO
  READ(5,*) PT
  READ(5,*) UOL0
  READ(5,*) D10
  READ(5,*) UOG0
  READ(5,*) Z10
  READ(5,*) TFP0
  READ(5,*) UOE
  READ(5,*) TFP0
  READ(5,*) DO
  WRITE(6,342) DO
342  FORMAT(5X,30HDISTANCE OF QUENCH FROM INLET=,G13.6)
  WRITE(6,343) UOE
343  FORMAT(5X,26HRAIO OF QUENCH TO FEED GAS=,G13.6)
  TQ=(TEMP0+273.0)/(TFP0+273.0)-1.0
  WRITE(6,344) TFP0
  WRITE(6,*) TQ
344  FORMAT(5X,22HTEMPERATURE OF QUENCH=,G13.6)
  ME=DO/D2+1
  DS=1.1
  UOL=UOL0
  ZL=ZL0
  DO=D10
  UOG=UOG0
  ASD0=AS*CI

```

```

TA=TEMP+273.0
RHOG0=2.75/0.25
RHOG=RHOG0*PT/TA*0.93.0/14.0
CI1=(1.0-AS)*CI
SRT=ZL/UOL/3600.0
R=UOL/UG
UT=981.0/14.0*CF*DP*(RHUS=DENS)/PHU
T1=UT/UOL
EZL=2.7*DU**1.4*UG**0.3
S6=RHOG*CPG+DENS*CPL+RHUS*CPS
FACT=0.45

READ(5,*)FACT
DH=EZL*S6*FACT
DH1=DH*(1.0+QUE)**0.3

WRITE(6,*)DH
HGO=(0.15*ALOG(UOG)-0.34)/(D0**0.08)
QUE1=1.0+QUE
HGO1=HGO+0.15*ALOG(QUE1)/(D0**0.08)
WRITE(6,*)HGO
UOS=UOL*(1.0-T1*(1.0-HGO))
UOS1=UOL*(1.0-T1*(1.0-HGO1))
WRITE(6,*)UOS
QT=(RHUS*CPS*UOS+DENS*CPL*UOL+RHOG*CPG*UOG)*7L/UN
WRITE(6,600)TEMP,SD,PT
600  FORMAT(5X,12)TEMPERATURE=,G13.0,5X,4)MASP=,G13.0,5X,9)PRESSURE=,G13.0,
13.6)

WRITE(6,601)UOL,D,UG
601  FORMAT(5X,4)UOL=,G13.0,5X,9)DIAMETER=,G13.0,5X,4)HUG=,G13.0,
WRITE(6,602)ZL,GT
602  FORMAT(5X,7)LENGTH=,G13.0,5X,23)PECLET NUMBER FOR HEAT=,G13.0,
TA=TEMP+273.0
ZK16=2.25E10
READ(5,*)ZK16
E16=7830.303
READ(5,*)E16
CT=PT/82.06/TA*0.868
CT0=14.0/82.0/(0.60.0+273.0)*0.868
ZK1=0.0254*(PT/15.4)**2.12
ZK2=0.02683*(PT/15.4)**2.13
ZK3=0.042
ZK4=0.0567
ZK5=0.0595
ZK6=0.009
ZK7=0.394*(1.0+B11*SD)
ZK8=0.246*(1.0+D8*SD)
ZK9=0.08*(1.0+R9*SD)
SUN=ZK1+ZK2+ZK3+ZK4+ZK5+ZK6+ZK7+ZK8+ZK9
ZK1=ZK1/SUN
ZK2=ZK2/SUN
ZK3=ZK3/SUN
ZK4=ZK4/SUN
ZK5=ZK5/SUN
ZK6=ZK6/SUN
ZK7=ZK7/SUN
ZK8=ZK8/SUN
ZK9=ZK9/SUN
DEN=CI1*DS

```

```

AQ=ZK1*DEF1/CT/2.1A*P
BQ=ZK2*DEF1/CT/2.1B*P
CQ=ZK3*DEF1/CT/2.1D*P
YQ=ZK4*DEF1/CT/2.1H*P
H0=1.0-AQ-BQ-CQ-YQ
ZIO1=ZK5+S0/C11
ORGO=ZIO1AC11
S=S0
S1=S10
HS=(1.0-HG0)*DS/RHOS*(S+S1+ORGO+ASD0)
HLO=1.0-HS-HG0
HS1=(1.0-HG01)*DS/RHOS*(S+S1+ORGO+ASD0)
HLO1=1.0-HS1-HG01
READ(5,*)CON
DHR=CON*359.0/1.8
WRITE(6,*)HLO,DHR
SUM=DENS*CPL*UOL+RHUS*CPS*UOS+RHOG*CPG*JUG
RHOG=CT/(1.0+T0)*ZMH2
PG=UOL*UOG+RHOG*CPG/SUM
WRITE(6,*)PG
P1=RHOS*CPS*UOS/SUM
P2=DENS*CPL*UOL/SUM
P3=RHOG*CPG*UOG/SUM
QT1=Q1*(P1+P2)
APRIME=UT*ZK16*SRT*DHR*CT/TA*UOL*(1.0+B16*S)*HLO
QT2=QT*DH/DH1
QT=QT2
R=UOL/UOG/(1.0+UOL)
WRITE(6,609)QT2
609 FORMAT(5X,23#HMODIFIED PCLET NUMBER=,G13.0)
WRITE(6,610)APRIME
610 FORMAT(5X,2#A=,G13.0)
A2=SUM/UOL
N=N1+1
DO 350 L=1,100
IF(L.GT.1)GO TO 15
READ(5,*)C1(1),C1(2)
15 T(1)=C1(1)
H(1)=C1(2)
DT=0.0
V2=1.0
V3=0.0
W3=1.0
W2=0.0
DV2=0.0
DV3=0.0
HEAT=0.0
REAH=0.0
DO 360 J=1,N1
IF(J.LT.(N1+1-M))GO TO 30
QT=QT2*DH1/AM
R=UOL/UOG
30 CONTINUE
J=N-J+1
H0=1.0/(1.0+T0)
IF(J.EQ.M)GO TO 40
GO TO 41
40 CONTINUE
DT=DT1*(QT/QT2+PD*(T0-T(1))/(1.0+T(1)))

```



```

H(I)=H(I)*(1.0+QUE)-QUE*H0
DV2=QT*(DV2/QT2-PQ*V2/(1.0+T(I))-PQ*(T0-T(I))/(1.0+T(I))**2)*V2)
1)
DV3=QT*(DV3/QT2-PQ*V3/(1.0+T(I))-PQ*(T0-T(I))/(1.0+T(I))**2)*V3)
W2=W2*(1.0+QUE)
W3=W3*(1.0+QUE)

41 CONTINUE
20 CONTINUE
R16=ZK16*CI**0.804*(CT*TA)**ZN16/CT*SRT*CLP(-F16/(1.0+T(I)))
1)
GAN=R16*DHR*CT/TA*H0L
GAM=GAN/SUM

SDT=QT*((P1+P2)*DT-GAM*H(I)**ZN16*(1.0+B16*S)*HL0*(1.0+T(I))**ZN16)
1)
DH5=-R16*R*H(I)**ZN16*(1.0+T(I))**ZN16*(1.0+B16*S)*HL0
HEAH=PEAH-DH5
HEAT=HEAT+GAN*H(I)**ZN16*(1.0+B16*S)*HL0*(1.0+T(I))**ZN16

DR16=R16*F16/TA/((1.0+T(I))**2)*V2*(H(I)*(1.0+T(I))**ZN16
DR16=DR16+R16*ZN16*(H(I)*(1.0+T(I))**ZN16-1.0)*(1.0+T(I)
1) **V2)
DR161=R16*F16/TA/((1.0+T(I))**2)*V3*(H(I)*(1.0+T(I))**ZN16
DR161=DR161+R16*ZN16*(H(I)*(1.0+T(I))**ZN16-1.0)*(1.0+T(I))**V3)
1) **V3)
DGAM=DR16*CT*DHR*H0L/TA/SUM
DGAM1=DR161*CT*DHR*H0L/TA/SUM
GAM3=DHR*CT/TA*U06/SUM

SDV2=QT*((P1+P2)*DV2-DGAM*(1.0+B16*S)*HL0)
SDV3=QT*((P1+P2)*DV3-DGAM1*(1.0+B16*S)*HL0)
DH2=-DR16*R*(1.0+B16*S)*HL0
DH3=-DR161*R*(1.0+B16*S)*HL0
T(I-1)=T(I)-D2*D1+D2*D2*SDT/2.0
H(I-1)=H(I)-D2*DH5
DT=DT-D2*SDT
V2=V2-D2*DV2+D2*D2*SDV2/2.0
V3=V3-D2*DV3+D2*D2*SDV3/2.0
DV3=DV3-D2*SDV3
DV2=DV2-D2*SDV2
W2=W2-D2*DH2
W3=W3-D2*DH3
26 CONTINUE

IF(I.GT.2)GO TO 300

B(1)=DT/QT/(P1+P2)-T(1)
B(2)=H(1)-H0
A(1,1)=V2-DV2/QT/(P1+P2)
A(1,2)=V3-DV3/QT/(P1+P2)
A(2,1)=-W2
A(2,2)=-W3
C1(2)=C1(2)+(B(2)*A(1,1)-B(1)*A(2,1))/(A(2,2)*A(1,1)-A(1,2)*A(2,1))
1)
C1(1)=C1(1)+(B(1)*A(2,2)-B(2)*A(1,2))/(A(2,2)*A(1,1)-A(1,2)*A(2,1))
1)
IF (C1(1).GT.0.0)GO TO 120

```

```

      C1(1)=0.0
122 IF (C1(2).GT.0.0)GO TO 123
      C1(2)=0.0
123 IF (C1(2).LT.0)GO TO 124
      C1(2)=0
124 CONTINUE
      WRITE(6,*)C1(1),C1(2)
      WRITE(6,*)R(1),U(2)
      IF (ABS(U(1)).GT.21)GO TO 350
      IF (ABS(U(2)).GT.72)GO TO 350

      GO TO 410
370 CONTINUE
360 CONTINUE
350 CONTINUE
375 CONTINUE
      H(1)=H0
410 CONTINUE
      HP=QOE/(1.0+T(r))
      WRITE(6,540)HP
540 FORMAT(5X,12MHENCH/FEED=,G13.6)
      WRITE(6,520)
520 FORMAT(10X,2MH2,15X,4ITEMP)
      N=N1+1
      DO 530 I=1,N,N1/10
      RI=1(1)*TA
      RI1=RI
      RI=1.8*RI
      WRITE(6,525)H(1),RI
525 FORMAT(2(5X,G13.6))
530 CONTINUE
      WRITE(6,*)RI1
510 CONTINUE
      RTA=GAM3
      WRITE(6,700)RIA
700 FORMAT(5X,5ITHAX=,G13.6)
      XS=2MH2ACT/R/DEFH*(H0+H0*QOE=F(N)*(1.0+QOE))* (1.0-AS)
      WRITE(6,706)XS
      WRITE(6,*)HEAT
      WRITE(6,*)H(M-2),H(M-1),H(M),H(M+1),H(M+2)
706 FORMAT(5X,15MH2 CONSUMPTION=,G13.6)
      RISE=TA*T(1)
      WRITE(6,*)RISE
      RISE1=RISE/XS
      WRITE(6,*)RISE1
      WRITE(6,*)PEAD
565 CONTINUE
      END

```

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Figure 1

Comparison between predicted and experimental temperature profile.

H₂ Consumption:

(1) Model Prediction = 3.7%

(2) Experimental = 3.6%

Figure 2

Typical effects of feed coal concentration on temperature rise and hydrogen consumption.

Figure 3

Typical effects of feed temperature on temperature

Figure 4

Typical effects of recycle ash concentration on temperature rise and hydrogen consumption.

Figure 5

Typical effect of total pressure on temperature rise and hydrogen consumption.

Figure 6

Typical effects of reactor diameter on temperature rise and hydrogen consumption.

Figure 7

Typical effects of superficial liquid velocity on temperature rise and hydrogen consumption.

Figure 8

Typical effects of reactor length on temperature rise and hydrogen consumption.

Figure 9

Typical effects of superficial gas velocity on temperature rise and hydrogen consumption.

Figure 10
Temperature rise versus liquid velocity for a
fixed throughput.

Feed Temp. = 417°C

Pressure = 14 MPa

$U_{og} = 3 \text{ cm/sec}$

$U_{ol} D^2 = 1080 \text{ cm}^3$

CI = 30%

ASR = 9%

Length = 900 cm

Figure 11
Temperature profiles for various quench locations.

$$(U_{o\ell o}) = 1.0 \text{ cm/s}$$

$$(U_{og o}) = 12 \text{ cm/s}$$

$$L = 39.4 \text{ m}$$

$$D = 3.35 \text{ m}$$

$$CI = 0.3$$

$$ASR = 0.09$$

$$T_o = 420^\circ\text{C} (788^\circ\text{F})$$

$$P = 14 \text{ MPa}$$

See Figure 13 for

Corresponding H_2 Consumption

Figure 12

Effect of amount of quench on overall temperature rise.

Figure 13
Hydrogen consumption for various quench ratios.

Figure 14

Effect of liquid velocity on critical quench ratio.

[Holding outlet reactor temperature at about 460°C (860°F)]

Figure 15
Effects of feed gas velocity on critical quench ratio.
[Holding outlet reactor temperature at about 460°C (860°F)]

Figure 16
Effect of reactor length on critical quench ratio.
[Holding outlet reactor temperature at about 460°C (860°F)]

Figure 17
Effect of quench temperature on critical quench ratio
[Holding outlet reactor temperature at about 460°C (860°F)]

All other legends are same
as those in Figure 15

Figure 18

Temperature Profiles

For various gas velocities at the critical quench ratio.

Location of quench at the middle of the reactor

All other legends are same as
those in Figure 14

No.	1	2	3	4	5	6
$(U_{ol})_o$ (cm/s)	0.65	0.7	0.8	0.9	1	1.1
m'_{cr}	.33	.31	.24	.18	.12	.05

Figure 19
Temperature profiles for various feed liquid
velocities at the critical quench ratio.

Legends same as in Figure 16

No.	1	2	3	4	5	6
Length (m)	40	44	48	52	56	60
m'_{cr}	.07	.13	.2	.28	.32	.41

Figure 20
Temperature profiles for various reactor lengths
at the critical quench ratio.

Figure 21
Comparison between dispersion
Model predictions and experimental data for
the case of intrareactor quench.

Figure 21
Comparison between dispersion
Model predictions and experimental data for
the case of intrareactor quench.

A P P E N D I X 6

Analysis of the Thermal Stability of the
Adiabatic SRC Liquefaction Reactor to
Step Changes in Several Key Process
Variables

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FROM G.L. Jones AT Harmarville DATE February 6, 1980
TO N.L. Carr AT Harmarville REFERENCE 6270FT07-30-30
SUBJECT ANALYSIS OF THE THERMAL STABILITY OF THE 238-8575
ADIABATIC SRC LIQUEFACTION REACTOR TO
STEP CHANGES IN SEVERAL KEY PROCESS VARIABLES

SUMMARY

While there is currently no direct evidence from experiments or the pilot plants that the SRC-II reactor will undergo thermal instability or temperature runaway for a range of operating conditions, there is evidence from other reacting systems with exothermic reactions as well as theoretical evidence^{1,2} that changes in certain reactor variables will bring about temperature runaway or lead to a transition from a lower to a higher steady state temperature.

A theoretical analysis using a thermal model of the SRC reactor similar to those described previously by Y.T. Shah and Singh³ shows that for certain combinations of reactor variables multiple steady state temperatures exist. Singh's analysis also shows that under most conditions the steady states are far apart and, therefore, the transition to a new higher steady state temperature would appear as a temperature runaway. It was also of interest to determine the stability of the normal steady state to perturbations or step changes in specific variables. This report summarizes the time-temperature and hydrogen concentration profiles⁴ of the reactor predicted by the transient thermal model described previously when one of three input variables (slurry velocity, inlet coal concentration or inlet slurry temperature) undergoes a step change to a new level after achieving the "normal" or basis steady state conditions. The somewhat restrictive adiabatic reactor case was chosen in order to predict the stability behavior under the most severe conditions. Normally quench injection would provide a measure of control for these cases.

The results for the Demo Plant scale show that large step changes in inlet slurry temperature or inlet coal concentration bring about higher steady state temperatures which could not normally be tolerated in the plant but do not lead to temperature runaway. A reduction of slurry velocity from a basis value of 1.2 cm/sec does lead to temperature runaway. A reduction to 0.45 cm/sec leads to a neutral condition where a steady state may be achieved but it would be very high and require a very long time to reach. Below this velocity temperature runaway occurs. Above this velocity a steady state temperature is achieved. As slurry flow decreases, the time required to reach the steady state and the steady state temperature increase from 3 hours and 74°F at a velocity of 1.2 cm/sec to 69 hours and 596°F at 0.48 cm/sec. Reducing slurry flow to 0.6 cm/sec leads to an unacceptably high temperature rise of 155°F which is reached over a period of 11.5 hours.

This study is based on the premise that the reactor sees no recycle composition feedback; therefore the results of this work are to guide decisions about making further studies.

INTRODUCTION

Consumption of hydrogen in the SRC reactor releases heat which raises the temperature of the slurry and vapor phases which are in local thermal equilibrium. The reaction rate is a thermally activated hydrogenolysis occurring in the liquid phase to produce liquid and gaseous species and release heat.

Heat is removed by convection out of the reactor and by injection of cool quench gas at points along the reactor. For large diameter reactors heat loss through the reactor wall is normally negligible compared to these other terms.

However if a significant change occurs in one or more process variables which reduces the rate of heat removal or increases the rate of reaction, there is a potential for thermal instability or temperature runaway. The thermal model is a powerful tool in predicting what conditions may lead to runaway because it couples the hydrogen consumption and energy balance models and includes the effects of nearly all the important reactor variables. The following rather limited analysis using the thermal model focuses on the effects of very specific process variables which are normally closely controlled because of their important effect on the thermal behavior of the reactor.

Although temperature control is normally maintained in the reactor by means of quench injection at one or more axial points as well as by other means (i.e., inlet temperature), this study was limited to predicting behavior for somewhat more severe conditions without quench for control. The simulations were made using an adiabatic, transient co-current (upflow) model described in reference (4). Although changes in key variables from normal operating values are not tolerated for long before corrective action is taken, these simulations were made with step changes in one of three variables. The step change was applied until either convergence to a new steady state temperature was assured or divergence (runaway) was apparent. A number of criteria internal to the model algorithm assured sufficient time to achieve a steady state if convergence was indeed apparent (with one exception*). The dependence of the reaction rate on temperature is such that once the rate of change of temperature with time begins to accelerate rather than decelerate then divergence is assured and temperature runaway has occurred. In some cases probably unrealistically large step changes were imposed to rigorously test the range of thermal response for each. The variables chosen were those which were most likely to lead to a temperature increase either by increasing the rate of heat generation (increased coal concentration or temperature) by increasing the reaction rate or by decreasing the rate of heat removal (decreased slurry velocity, UL, or increased SRT). One other variable (total pressure) may contribute to an increased reaction rate but the effect is probably small in this model.

* UL = 0.448 cm/sec.

Each simulation begins with the conventional unity initial conditions for hydrogen density and slurry temperature which are the dependent variables in the thermal model. Starting from the unity conditions mentioned previously, the temperature and hydrogen evolve toward their normal steady state values over a period of three hours. With the normal steady state as the new initial condition, the model then predicts the transient temperature and hydrogen density response to a step change in a variable. In each case beginning with the same normal steady state, the process is repeated for successively larger step changes of each variable until the temperature diverges or the new steady state temperature becomes unacceptably large (a qualitative judgment).

There are many important processes occurring in the SRC plant outside the reactor which may affect reactor stability. These are outside the scope of the present thermal model and of this report. This analysis considers the reactor or combined preheater/reactor in isolation and does not consider effects of changes in the product, feed or recycle streams nor does it consider other physical processes such as vapor/liquid separation downstream of the reactor. Indeed this analysis does not even consider nonideal behavior either in flow, phase changes or side reactions which may occur in the reactor itself at higher temperatures which may lead to thermal instability. Not enough data are available at present to quantify these effects and incorporate them in the model.

The nearly linear dependence of the reaction rate of hydrogen on temperature (and the weak hydrogen partial pressure dependence) appears to enhance the stability of the steady state. A stronger temperature dependence such as an Arrhenius term (E/RT) would probably lead to predicted instabilities at less severe changes in conditions. This work should be continued should additional data reflecting instability or multiplicity of the steady state become available.

DISCUSSION

The results of the present study are shown in Table II and Figures 1-3 for basis conditions shown in Table I. Table II summarizes the final steady state temperature rise ($^{\circ}\text{F}$) and hydrogen consumption (g/g MAF coal basis) and the time required (TSS) to reach 99% of the ultimate value. Figures 1-3 illustrate the time/temperature response for each step change in each variable. The table and Figures 2 and 3 show that the steady states temperature increases with increasing CI (coal concentration) and (inlet slurry temperature) but the time required to reach it is approximately the same in each case. Although the new steady state temperatures are quite high, there is no tendency for the system to run away for changes in these variables. A slight oscillatory instability developed for high values of the coal concentration but the amplitude of each oscillation remained perfectly constant with time.

The sensitivity of the thermal response to slurry flow is strong (Figure 1). Indicative of a process which is approaching a runaway condition, the steady state temperature and the transition time both increase rapidly as UL decreases. The "neutral" flow rate between a converging steady state temperature rise and diverging run away temperature is shown in Figure 1. Ultimately the temperature rises to a high level where all the hydrogen is consumed near the reactor inlet and is therefore zero elsewhere in the reactor. Although this condition is never reached in the present analysis, it represents a theoretical and physical upper limit for the temperature runaway. In many cases hydrogen concentration does drop to zero at the reactor outlet. The results for reduced UL agree qualitatively with those of⁵ a previous memo which showed that even with quench injection for control, the slurry velocity could not be reduced below 0.4 cm/sec for the Demo Scale. It also compares with other reports^{4,6} which showed an unacceptably large temperature rise for a 50% reduction in UL for both the Ft. Lewis and the Demo Plant scale reactors.

As discussed previously^{4,5,7}, the dependence of the hydrogen consumption reaction rate on temperature and hydrogen partial pressure is the key to determining the temperature rise characteristics of the reactor. Other parameters such as thermal Peclet number appear to be of less importance although they may be strongly affected by the changes in process variables particularly slurry velocity.

Clearly we must continue to seek the best possible model for the hydrogen consumption because of its importance in determining the predicted thermal characteristics of the reactor. An accurate determination of the dependence of hydrogen consumption on temperature, pressure, recycle ash, coal concentration and SRT is of importance in any study of the thermal response of the reactor.

G.L. Jones

GLJ:clp

attachments

cc w/atts: HB-RGG

GLJ

HGM

UM-HT

WGM

MEP

YTS

Circ: PD&M Skill Group

REFERENCES

1. Aris, R., Introduction to the Analysis of Chemical Reactors, Prentice-Hall, Inc. 1965.
2. Levenspiel, Octave, Chemical Reaction Engineering, John Wiley, 1962.
3. Singh, Y.T. Shah, report number not yet assigned. Due to issue January, 1980.
4. Jones, G.L., "A Model for Adiabatic Countercurrent Flow SRC-II Liquefaction Reactor", C&M Division Report No. 6270FK016, August, 1979.
5. Jones, G.L. to N.L. Carr, "SRC-II Reactor Model Studies", dated December 26, 1979, Reference: 6270FT07-30.
6. Parulekar, S.J., Y.T. Shah, "Modeling and Simulation of the Thermal Behavior of SRC-II Reactors", C&M Report No. 627RK017, dated October 3, 1979.
7. Jones, G.L. to N.L. Carr, "Simplified Steady State Analysis of SRC Reactor Thermal Response and Hydrogen Consumption", not yet issued, Ref.: 6270FT07-30-30.

Table I

BASIS (INITIAL) CONDITIONS FOR STEP CHANGE RESPONSES

Scale: Demo Plant

Slurry Velocity: 1.2 cm/sec SRT: 0.869 hours

Gas Velocity: 12 cm/sec

Inlet Coal Conc.: 30%

Recycle Ash: 10%

Total Pressure: 13.79 mPa

Inlet Hydrogen Partial Pressure: 13 mPa

Slurry Inlet Temperature: 783°F

GR&DC
GLJ:clp
1/4/79

Table II

SUMMARY OF TRANSIENT THERMAL STABILITY ANALYSIS
FOR ADIABATIC SRC LIQUEFACTION REACTOR TO STEP CHANGES IN THREE VARIABLES

Variables Changed: Nominal Slurry Velocity, UL, 1.2, 0.60, 0.544, 0.484, 0.448, 0.40 cm/sec
 Slurry Inlet Temperature, T_{in} , 834, 884, 984, 1184°F
 Inlet Coal Concentration in Feed, CI, 0.50, 0.75 g/g Slurry Feed

Basis Conditions: Refer to Table I

Variable:		Steady State*		Time Required to
		Temperature	Hydrogen	Reach 99% of
		Rise	Consumption	Steady State ±
UL	cm/sec	°F	g/g MAF Coal	hours
	0.60	155	0.038	11.5
	0.54	254	0.054	~50
	0.48	596	0.110	~69
	0.45	-	-	insipient instability
	0.40	-	-	diverges-unstable
CI	g/g slurry			
	0.50	236	0.066	9.25
	0.75	383	0.068	2.85
T_{in}	°F			
	834	92	0.046	1.25
	884	120	0.060	2.05
	984	173	0.086	2.20
	1184	265	0.132	2.65

* Steady state defined as condition at which temperature is no longer changing at the level of 10^{-5} °F.

± Time required to reach 99% of new steady state temperature is defined from the start of the step change.

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APPENDIX 7

Gulf Science and Technology Company
Pittsburgh, Pennsylvania

EFFECTS OF COAL PROPERTIES ON SRC-II PRODUCT YIELDS

by

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Chemicals and Minerals Division
Report No. 627RK014
File No. FT07-50-20
Project No. 251-8370
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EFFECTS OF COAL PROPERTIES ON SRC-II PRODUCT YIELDS

I. SUMMARY

This report presents work performed to correlate SRC-II yield structure results from operation of the P99 coal liquefaction pilot plant. Special emphasis was given to the effects of coal properties on product yields.

Regression equations describing the product yield responses were formulated for each product component. A computerized stepwise regression program was used for this purpose. These equations, along with the statistical parameters relating to their goodness of fit, are presented in this report.

Six different coals have been run on P99 under various operating conditions. All of these coals have been included in the regression analysis. As a result of this analysis, product yield structures can be predicted for each coal at a set of base conditions. The resultant measure of coal reactivity is compared to measures of coal reactivity proposed by others.

II. INTRODUCTION

A. Coals Studied

The P99 SRC-II pilot plant has been operating successfully since 1976. During this time coals from six different mines have been run on the unit. They include one Kentucky coal (a blend of Kentucky Nos. 9 and 14 seams) and five Pittsburgh Seam coals (Blacksville No. 2, Ireland, Valley Camp No. 3, Robinson Run, and Powhatan No. 5). These coals, along with the run numbers during which they were used, are listed in Table I. Analyses on these coals, as performed at Harmarville, are given in Appendix A. Additional petrographic and associated analyses performed by Commercial Testing are listed in Appendices B and C.

B. Stepwise Regression

In the formulation of a regression equation to describe a certain dependent variable, it is first necessary to gather together a set of all possible independent variables which affect the dependent variable. Often, the number of possible independent variables can be so large as to be cumbersome and can make the regression model hard to understand. In this case, it is often convenient to determine a "best" set of independent variables. Generally, a computer program which determines this "best" set of variables will screen out variables which 1) may not be fundamental to the problem, 2) may be subject to large measurement errors, or 3) may effectively duplicate or be highly intercorrelated with other independent variables in the list.

The stepwise regression technique selected for this study is based on the F^* statistic. This selection procedure operates in the following manner.

- 1) All simple (single independent variable) regressions are calculated and the F^* statistic

$$F_k^* = \frac{MSR(X_k)}{MSE(X_k)} \quad (1)$$

is determined for each. MSR and MSE are the regression mean square and the error mean square, respectively. The independent variable with the largest F^* value is the candidate for first addition to the model. If its F^* value exceeds a certain predetermined level, the variable is added to the regression model. Otherwise, the program terminates.

- 2) If an independent variable is added in step 1 (let's call it X_1), the stepwise regression routine calculates all regressions with two independent variables, one of which is X_1 . The F^* statistic:

$$F_k^* = \frac{MSR(X_k | X_1)}{MSE(X_1, X_k)} \quad (2)$$

is obtained. The independent variable with the largest F^* value is the candidate for addition to the model at this stage. Again, if its F^* value exceeds a predetermined level, the variable is added to the regression equation. If not, the program terminates.

- 3) This procedure is repeated with three, four, etc., variables until the program terminates.

The stepwise regression process also allows for the removal of previously added independent variables which have become statistically insignificant due to the addition of other independent variables. This procedure is executed at the end of each step in the model formulation. This is done in the following manner. Assume that X_1 and X_2 have previously been added to the model and that X_3 has just been tested and selected for addition. Before beginning testing at the next level, in this case four variable regressions, the computer will recheck the significance of the variables X_1 and X_2 in light of the new regression containing X_1 , X_2 , and X_3 . This is done by evaluating the F^* statistics for the previously included variables based on the new regression model. For the above case these F^* values would be:

$$F_1^* = \frac{MSR(X_1 | X_2, X_3)}{MSE(X_1, X_2, X_3)} \quad (3)$$

and

$$F_2^* = \frac{MSR(X_2 | X_1, X_3)}{MSE(X_1, X_2, X_3)} \quad (4)$$

If either of these statistics are lower than a predetermined value, the corresponding independent variable is dropped. Otherwise, they remain in the regression equation. In both cases, the search for statistically significant independent variables continues.

SEQLS, a Gulf developed program, was utilized to perform the stepwise regressions presented in this report. In addition to performing the stepwise regression calculations, SEQLS allows the forcing of designated independent variables into the regression model. Information concerning the use and capabilities of this program can be found by consulting reference 1.

III. CORRELATIONS

A. Independent Variables

A total of five process operating variables and eight feed coal properties were offered to the stepwise regression program. The process variables included average dissolver temperature, nominal slurry residence time, average hydrogen partial pressure, percent coal in feed slurry, and percent recycle ash in feed slurry. The feed coal properties included percent iron, carbon-to-hydrogen weight ratio, total sulfur, organic sulfur, total oxygen, mean maximum reflectance of vitrinite, percent vitrinite, and percent vitrinite + exinite. A listing of the independent variables and their definitions is given in Table II. The range over which the independent variables vary for the P99 data set is shown in Table III.

Values for the coal properties and process variables, when available, were taken from the final data reduction printout for the P99 pilot plant. For coal properties not found in the final data reduction printout, i.e., petrographic data, analyses of the individual feed coals were used. In two cases, Kentucky and Ireland Mine coals, the petrographic analyses were not run on the same batch of coal as was used in the corresponding P99 pilot plant runs. For these cases, samples of similar coal from the same original mine were used to provide the petrographic data. Occasionally, coal properties were observed to vary from batch to batch within a particular coal type. The values of the coal properties used in this correlating effort are presented in Table IV.

B. Regression Equations

Regression equations were formulated for the P99 SRC-II pilot plant product yield responses. The models used were linear in nature and did not contain any second order or interactive terms. Throughout the modeling the independent variables were offered to the regression under the criteria of 0.900 minimum probability of significance for entering the variable and 0.875 minimum probability of significance for retaining the variable. Two different sets of regression equations have been generated. For one set, all of the independent variables were allowed to float in the variable pool (none were forced into the regression and all were evaluated by the stepwise regression program), while for the second set, the five process variables (dissolver temperature, percent coal, percent recycle ash, nominal slurry residence time, and average hydrogen partial pressure) were forced into the regression relationships and only the variables representing the coal properties were permitted to float.

P99 experimentation is divided into runs, each run being made up of several run periods. A run period typically lasts twenty hours. Experimental yields for each individual run period were used in the formulation of the regression equations. In this manner the data was more-or-less weighted. That is to say, in the opinion of the author, the runs having the most run periods represent the most reliable data. Data were included for all completed runs, 15 through 48, with the exception of runs 45 through 47. These runs were not included in the data base because of differences in their feed coal preparation.

The intercept and slope coefficients defining the generated linear yield response models are in Tables V and VI. Tables VII and VIII contain the statistical parameters (correlation coefficient, percent of variation explained, standard deviation, and standard deviation as a percent of the mean response) relating to these regressions. Parity plots of the experimentally observed responses versus their predicted responses for the floating variable case are in Appendix D.

As stated previously, the use of a stepwise regression technique can serve to screen out variables which are effectively duplicative or are highly intercorrelated with one another. With the use of historic data, such as the P99 pilot plant data analyzed herein, this screening may exclude some otherwise important variables. The potentially important variables may become intercorrelated due either to poor experimental design, bad luck, or both. The intercorrelation of the variables percent coal and percent recycle ash provides a classic example of confounded variables.

Generally, in P99 operation, the solids level in the feed slurry stream has been held in the neighborhood of 45% by weight. This solids level can be defined by the equation:

$$\% \text{ total solids} = \% \text{ coal} + \% \text{ recycle solids} \quad (5)$$

where

$$\% \text{ recycle solids} = \% \text{ IOM} + \% \text{ recycle ash} \quad (6)$$

Normally, the relationship

$$\% \text{ recycle ash} \approx 0.67 \times \% \text{ recycle solids} \quad (7)$$

also holds. These relationships can be rearranged to give:

$$\% \text{ total solids} = 45\% = \% \text{ coal} + 1.5 \times \% \text{ recycle ash} \quad (8)$$

It is by this constraint of operation that the percent coal and percent recycle ash, two variables which can (within limits) be varied independently, are forced into an intercorrelative relationship.

Several other independent variables are intercorrelated in the P99 data base. Table 9 lists these pairs of variables and their simple correlation coefficients.

IV. COAL PROPERTIES AS A GAUGE OF COAL REACTIVITY

Several authors have shown that coal properties can be linked, in a general way, to coal liquefaction behavior. A detailed review of all of these studies and an indepth analysis of their resultant findings is beyond the scope of this report. A brief summary of this work follows along with an index of coal reactivity generated by the presented regression analysis. The ranking of reactivities generated herein is then compared with similar yardsticks proposed by others.

A. Previous Work

Mukherjee and Chowdhury² have studied the effects of mineral matter constituents on the hydrogenation of a North Assam (India) coal. The major conclusions arrived at from this study were 1) conversion of the organic matter in coal increased with increasing mineral matter content in the coal and 2) conversion of the organic matter in the coal increased with increasing iron content in the coal. It appears from the discussion of their work that these two conclusions are not independent of one another.

Guin et al.³ have studied the effects of several mineral matter constituents on the hydrogenation of creosote oil, a coal pyrolysis liquid. Their experimentation was performed in the batch mode. An autoclave was first charged with 15 g of catalyst and 100 g of creosote oil. The reaction was then carried out at 425°C for two hours with an initial hydrogen partial pressure of 3000 psig. The total reactor pressure was monitored throughout the run. The final hydrogen partial pressure was used as a gauge of the hydrogenation activity of the catalyst. Guin's results are shown in Figure 1. As can be seen, the most catalytically active mineral matter constituent was found to be iron pyrite. Furthermore, the smaller sized iron pyrite fraction (-325 mesh) was found to be more active than the larger sized iron pyrite fraction (-80 + 150 mesh).

Mori et al.,⁴ in studies on the liquefaction behavior of several coals, found coal reactivity to be highly correlated with % volatile carbon. They defined % volatile carbon as:

$$\% \text{ volatile carbon} = \% \text{ carbon (maf)} \times \frac{\% \text{ fixed carbon}}{\% \text{ volatile matter} + \% \text{ fixed carbon}} \times 100 \quad (9)$$

Durie,⁵ in a review article relating to the liquefaction potential of Australian coals, points out the importance of the coals reactive maceral content and H/C atomic ratio.

Gray et al.,⁶ studying South African coals, have developed individual regression equations relating coal liquefaction conversion in anthracene oil to the feed coal properties - reactive macerals, R; volatile matter (maf), VM; and H/C atomic ratio. Gray's simple regression equations and their correlation coefficients are given below.

$$\text{Conversion} = 0.47 R + 48.0 \quad (10)$$

$$\text{Conversion} = 1.4 (\text{VM}) + 40.0 \quad (11)$$

$$\text{Conversion} = 106.6 (\text{H/C}) + 1.0 \quad (12)$$

The correlation coefficients are 0.92, 0.89, and 0.96 respectively. Gray also observed that coal liquefaction conversion increased with the iron pyrite content of the feed coal.

A statistical study of the effects of coal properties on coal liquefaction yield performed by Yarzab and Given⁷ is probably the most extensive study of its kind done to date. One hundred four high volatile bituminous coals were included in the study. Batch liquefaction experiments were performed in 35 ml tube bombs at 400°C using tetralin as the hydrogen donor solvent. Percent conversion was based on the amount of ethyl acetate soluble products plus gases. The coal property variables considered by this study included percent volatile matter, VM; percent carbon, C; mean maximum reflectance of vitrinite, Ro; calorific value; H/C atomic ratio; O/C atomic ratio; percent oxygen; percent total sulfur, S_t; percent organic sulfur; percent pyritic sulfur; vitrinite plus pseudo vitrinite, V; total reactive

macerals, TRM; and percent mineral matter. These variables were offered to a stepwise regression program similar to the one used in this report. The results of initial correlations showed that the coals clustered into three groupings, the groupings being mainly distinguished by the sulfur content of the coal. The groupings also generally split the coals along regional lines with group 1 representing Eastern province coals, group 2 representing Interior province coals with some Eastern coals, and group 3 representing Rocky Mountain province coals. The coals run on P99 can be successfully assigned to group 2. The groups were segregated and a separate stepwise regression was performed for each group. The resulting regression equations were:

Group 1:

$$\text{Conversion} = -34.8 \text{ Ro} + 50.7 \text{ H/C} + 0.16 \text{ V} + 30.5 \quad (13)$$

$$\text{Standard Deviation} = 3.30$$

$$\% \text{ Variation Explained} = 80.0$$

Group 2:

$$\text{Conversion} = 0.86 \text{ VM} - 22.8 \text{ Ro} + 1.39 \text{ S}_t + 39.0 \quad (14)$$

$$\text{Standard Deviation} = 2.95$$

$$\% \text{ Variation Explained} = 79.2$$

Group 3:

$$\text{Conversion} = 0.93 \text{ VM} + 0.28 \text{ TRM} - 1.7 \quad (15)$$

$$\text{Standard Deviation} = 3.12$$

$$\% \text{ Variation Explained} = 47.5$$

Finally, a reactivity index has been proposed by George Chenoweth⁸ at GRMC. This reactivity index is defined as:

$$\text{Reactivity Index} = \text{Organic Factor} \times \text{Catalytic Factor} \quad (16)$$

$$\text{Organic Factor} = \frac{\% \text{ Volatiles}}{\% \text{ Fixed Carbon} \times \% \text{ Oxygen in MAF coal}} \quad (17)$$

$$\text{Catalytic Factor} = \% \text{ Fe in MAF coal} \times \text{Washability Factor} \quad (18)$$

$$\text{Washability Factor} = \frac{\% \text{ Fe in ash when coal is washed to 5\% ash}}{\% \text{ Fe in ash when coal is washed to 10\% ash}} \quad (19)$$

The washability factor gives a qualitative measure of the size of the iron bearing particles in the coal. This reactivity index has been successfully used to rank the performance of coals run at P99, at Ft. Lewis, and at Merriam.

B. Present Work

The regression models proposed by this work allow not only for the ranking of the coals studied by their relative reactivity; the models also allow for the prediction of product yield structures for various sets of the independent variables. For the sake of comparison, a set of yield structures for each coal at a set of base processing conditions (Table X) are presented in Tables XI and XII. The particular set of operating conditions used was picked to be close to the conditions visualized for the demonstration plant.

If the coal conversion criteria suggested by Chenoweth is chosen,

$$\text{Conversion (\% maf coal)} = 100 - [900^\circ\text{F} + \text{organic matter}] \quad (20)$$

then Equation 21 (forced process variables) or Equation 22 (floating variables) can be used to determine the relative reactivity of the coals. (A word of warning: correlation does not necessarily imply causation.)

$$\text{Conversion} = 110.44 - 7.387 (C/H) + 0.8317 (Vit) \quad (21)$$

$$\text{Standard Deviation} = 2.39$$

$$\% \text{ Variation Explained} = 85.1$$

$$\text{Conversion} = 175.50 - 4.217 (C/H) - 3.840 S_t + 3.960 S_o - 53.511 R_o \quad (22)$$

Standard Deviation = 2.32

% Variation Explained = 85.9

The reactivity ranking determined using these equations, in order of descending reactivity, is: Kentucky > Valley Camp > Powhatan > Ireland > Robinson Run > Blacksville. It should be noted that the coals would be ranked differently if the production of C_5 -900°F liquids is the conversion criteria (Kentucky > Ireland > Powhatan > Valley Camp > Robinson Run > Blacksville.)

C. Comparison of Ranking Techniques

The reactivity rankings generated by using Equations 21 and 22 have been compared with the rankings generated by the Penn State correlations (Equation 14) and the Chenoweth reactivity index (Equation 16). The results of this comparison are presented in Table XIII. There is good agreement on which two coals are the worst (Robinson Run and Blacksville No. 2). However, the agreement of relative ranking for the most reactive four coals is not as good. For the Penn State correlation and the present correlation, where statistical parameters are available, this can be best explained by the fact that the methods cannot reliably rank coals whose reactivities are very similar. The most reactive coals used in this study lie well within a band of plus-or-minus two standard deviation units of one another.

V. CONCLUSIONS AND RECOMMENDATIONS

Several conclusions can be drawn from this study. They include:

- 1) Coal property regressions do supply a basis for comparison of SRC-II yield structures among coal types.
- 2) The reactivity ranking of coals derived from the regression correlation developed herein generally agrees with reactivity rankings observed by others.

- 3) Reactivity ranking can vary depending on how the term reactivity is defined.
- 4) Presently available reactivity rankings give only a gross estimate of coal reactivity.
- 5) The number of coals tested (6) is very small. Therefore, caution should be exercised in the application of the presented regression models developed above to other coals.

It is presently not clear just how much of the model deviations are attributable to failings in the process parameter portion of the model versus failings in the coal property portion. Perhaps a more detailed, proven model for the effects of the process parameters would help pull the coal parameter contributions more into line. Additional statistically sound studies, not based solely on historical data, would provide for a better evaluation of the effects of coal properties on SRC-II yields.

REFERENCES

1. Dzuna, A. E., and F. B. Smith, Jr., SEOLS. A Step-Wise Regression Program, File CN11, June 21, 19791.
2. Mukherjee, D. K., and P. B. Chowdhury, "Catalytic Effect of Mineral Matter Constituents in a North Assam Coal on Hydrogenation," Fuel, 55, 4 (1976).
3. Guin, J. A., A. R. Tarrer, J. W. Prather, D. R. Johnson, and J. M. Lee, "Effects of Coal Minerals on the Hydrogenation, Desulfurization, and Solvent Extraction of Coal," Ind. Eng. Chem. Process Des. Dev., 17, (2), 118 (1978).
4. Mori, I. M. Taniuchi, A. Kawashima, O. Okuma, and T. Takahashi, "Relationship Between Coal Characteristics and its Reactivity on Hydroliquefaction," preprints ACS Division of Fuel Chemistry, 24, (2), 12 (1979).
5. Durie, R. A., "The Characteristics of Australian Coals and their Implications in Coal Liquefaction," preprints ACS Division of Fuel Chemistry, 24 (2), 12 (1979).
6. Gray, D., G. Barrass, and J. Jezko, "Relationships Between Coal Liquefaction Behavior and the Composition of South African Coals," preprints ACS Division of Fuel Chemistry, 24 (2), 2 (1979).
7. Yarzab, R. F., and P. H. Given, "Dependence of Coal Characteristics on Coal Liquefaction Behavior-4. Cluster Analyses for Characteristics of 104 Coals," submitted to Fuel (1978).
8. G. E. Chenoweth to Coal Supply File, "Coal Reactivity," November 29, 1978, Ref. M0412.

FIGURE 1

Comparison of the Hydrogenation Activity of Catalysts
 (the lower the hydrogen partial pressure the more active the catalyst)³

TABLE I

Coals Used as SRC-II Feed by Pilot Plant P99

<u>Coal</u>	<u>Sample Number</u>	<u>Runs</u>
Kentucky Nos. 9 & 14	LR-22366	15-24
Blacksville No. 2	LR-24001	25-29, 33
Ireland	LR-22991	31-32
Powhatan No. 5	LR-24924 LR-25844	35-37 48
Valley Camp No. 3	LR-24925	38-39
Robinson Run	LR-25447	41-44

TABLE II

Independent Variables Used in Regression Modeling

Process Operating Conditions

<u>Variable</u>	<u>Description</u>
Dissolver Temperature	Weighted average dissolver temperature in degrees centigrade. Available from the P99 data reduction printout.
SRT	Nominal slurry residence time in the dissolver. Measured in hours. This number is based on the feed slurry flow alone and does not take the gas flow rate into account. Available from the P99 data reduction printout.
Average H_2 Partial Pressure	The average of the preheater inlet and dissolver outlet hydrogen partial pressures as reported in the P99 data reduction printout. These partial pressures are estimated to be the product of the total pressure and the percent (mole) hydrogen in the gas stream.
% Coal	The percent coal (weight basis) in the feed slurry. Available from the P99 data reduction printout.
% Recycle Ash	The percent recycle ash (weight basis) in the feed slurry. The percent pyridine insolubles in the feed slurry is reported in the P99 data reduction printout. The amount of ash in the pyridine insolubles is assumed to be in the same ratio as is found in the vacuum tower bottoms. This information is available from the P99 data reduction printout.

Table II (continued)

Coal Properties

<u>Variable</u>	<u>Description</u>
% Fe	Percent iron (weight basis) based on moisture and ash free (maf) coal. Calculated from Harmarville analyses as ash in coal x iron in ash.
C/H Ratio	Carbon-to-hydrogen weight ratio. Calculated using Harmarville analyses.
Total Sulfur	Percent total sulfur (weight basis) based on moisture free (mf) coal. Available from p99 data reduction printout.
Organic Sulfur	Percent organic sulfur (weight basis) based on maf coal. Calculated using Harmarville analyses.
Total Oxygen	Percent total oxygen (weight basis) based on mf coal. Available from p99 data reduction printout.
Mean Maximum Reflectance	Mean maximum reflectance of vitrinite macerals. From Commercial Testing petrographic analyses.
Vitrinite	Percent vitrinite (volume basis) based on maf coal. From Commercial Testing petrographic analyses.
Vitrinite & Exinite	Percent vitrinite plus exinite (volume basis) based on maf coal. From Commercial Testing petrographic analyses.

TABLE III
Range of Independent Variables Used in
Regression Modeling

<u>Variable</u>	<u>Low</u>	<u>High</u>	<u>Range</u>
Dissolver Temperature, °C	450	465	15
SRT, hr	0.7	1.3	0.6
Average H ₂ partial pressure, MPa	10.1	13.8	3.7
Coal in Feed Slurry, wt%	24.3	33.7	9.4
Recycle Ash in Feed Slurry, wt%	3.9	15.9	12.0
Fe, wt% maf coal	1.434	2.203	0.769
C/H Weight Ratio	13.93	15.27	1.34
Total Sulfur, wt% maf coal	2.68	4.38	1.70
Organic Sulfur, wt% maf coal	1.19	2.49	1.30
Total Oxygen, wt% maf coal	11.19	14.07	2.88
Mean Maximum Reflectance	0.69	0.82	0.13
Vitrinite, % maf coal	72.9	80.9	8.0
Vitrinite + Exinite, % maf coal	81.5	87.2	5.7

TABLE IV
Coal Properties Used in Regression Modeling

<u>Coal</u>	<u>Kentucky</u>	<u>Valley Camp</u>	<u>Powhatan</u>	<u>Ireland</u>	<u>Robinson Run</u>	<u>Blacksville</u>
Coal Properties						
Fe, wt% maf coal	1.702	1.434	1.674	2.203	1.965	1.445
C/H Weight Ratio	13.93	14.26	14.67	14.68	14.19	15.27
Total Sulfur, % mf coal	3.24	2.88	3.42	4.38	3.59	2.68
Organic Sulfur, % maf coal	2.07	1.35	1.99	2.49	1.42	1.19
Total Oxygen, % mf coal	13.80	11.19	12.67	14.07	12.88	12.41
Mean Maximum Reflectance	0.71	0.73	0.71	0.69	0.77	0.82
Vitrinite, % maf coal	78.7	79.0	80.9	79.0	72.9	77.0
Vitrinite + Exinite, % maf coal	87.2	85.6	86.3	85.5	81.5	83.6

TABLE V

Intercepts and Slopes for Regression Models (All Variables Floating)*

Parameter Response	Constant	Dissolver Temp.	SRT	Ave. H ₂ PP	% Coal	% Recycle Ash	% Fe	C/H Ratio	Total Sulfur	Organic Sulfur	Total Oxygen	Ro	Vitrinite	Vitri- nite + Exinite
H ₂ Consumption	28.202	-0.02553 (0.9484)	-2.222 (1.0000)	-0.1086 (1.0000)		-0.1265 (1.0000)					-0.2096 (1.0000)		0.09315 (1.0000)	-0.2489 (1.0000)
C ₁ - C ₄	-7.369		11.771 (1.0000)		-0.1728 (0.9849)		1.911 (0.9934)				1.176 (1.0000)			
Other Gases	14.312		0.6707 (1.0000)	0.03311 (0.9079)						2.080 (1.0000)	-0.1744 (1.0000)		-0.1595 (1.0000)	
Water	-68.373	0.08244 (0.9968)	0.5347 (0.9584)		-0.09295 (0.9847)	0.06919 (0.9674)	-2.602 (1.0000)	-0.7038 (1.0000)			0.6517 (1.0000)			0.5268 (1.0000)
C ₅ - 380 °F	-70.248	0.1483 (0.9922)	3.201 (0.9997)	0.2609 (0.9263)		0.2559 (1.0000)			1.098 (0.9550)					
380 - 550 °F	24.569		8.022 (1.0000)	0.6423 (0.9998)	-0.6162 (1.0000)			1.447 (0.9992)		-4.054 (0.9953)	1.808 (1.0000)	-57.492 (1.0000)		
550 - 900 °F	188.81	-0.3391 (0.9997)	-5.968 (0.9999)					-1.862 (0.9999)					0.1735 (0.9016)	
C ₅ - 900 °F	66.385		4.533 (0.9985)	1.286 (1.0000)		0.7639 (1.0000)		-1.724 (0.9991)				-36.480 (1.0000)		
380 - 900 °F	26.371			1.040 (0.9999)		0.6125 (1.0000)		-3.210 (1.0000)					0.4305 (0.9997)	
900 °F + Pyridine Soluble	154.67	-0.2790 (0.9474)	-16.472 (1.0000)		0.7934 (1.0000)			2.034 (0.9998)			-2.700 (1.0000)			
ICM	-194.98	0.4199 (1.0000)		-1.080 (1.0000)						-2.252 (0.9849)		36.558 (1.0000)		
900 °F + Organic	-32.856		-14.629 (1.0000)	-1.068 (0.9999)		-1.460 (1.0000)		4.217 (1.0000)	3.840 (0.9972)	-3.941 (0.9632)		53.571 (0.9985)		

* Slope or Intercept
(Probability of Significance)

TABLE VI

Intercepts and Slopes for Regression Models (Process Variables Forced)*

Parameter Response	Constant	Dissolver Temp.	SRT	Ave. H ₂ PP	% Coal	% Recycle Ash	% Fe	C/H Ratio	Total Sulfur	Organic Sulfur	Total Oxygen	Ro	Vitrinite	Vitri- nite + Exinite
H ₂ Consumption	27.655	-0.04522 (0.9965)	-2.280 (1.0000)	-0.1362 (1.0000)	0.03110 (0.8606)	-0.08282 (1.0000)		0.2041 (0.9996)	-0.1294 (0.9029)		-0.2192 (1.0000)			-0.09060 (1.0000)
C ₁ - C ₄	-6.454	-0.00448 (0.0542)	11.779 (1.0000)	0.1955 (0.8856)	-0.2560 (0.9811)	-0.05694 (0.5490)			1.149 (0.9979)		1.277 (1.0000)			
Other Gases	-18.852	0.04691 (1.0000)	0.7460 (1.0000)	0.06146 (0.9955)	-0.00666 (0.2774)	0.00525 (0.2930)		-0.3727 (1.0000)	0.7841 (1.0000)	0.6177 (0.9992)		2.873 (0.9663)		
Water	-33.997	0.1215 (1.0000)	0.6099 (0.9788)	0.04197 (0.6657)	-0.1139 (0.9963)	0.03156 (0.6824)	-5.779 (1.0000)	-0.9969 (1.0000)		2.744 (1.0000)	0.4835 (1.0000)			
C ₅ - 380 °F	-77.177	0.1751 (0.9967)	3.265 (0.9998)	0.2236 (0.8694)	-0.1646 (0.8023)	0.1756 (0.9554)			1.268 (0.9978)					
380 - 550°F	-30.481	0.09207 (0.6572)	7.772 (1.0000)	0.7272 (0.9999)	-0.3860 (0.9860)	0.1935 (0.9585)					0.8691 (0.9968)	-17.507 (0.9997)		
550 - 900°F	177.86	-0.3092 (0.9824)	-5.702 (0.9997)	0.3449 (0.8072)	0.4031 (0.9119)	0.4811 (0.9860)	-5.916 (0.9913)	-2.028 (0.9996)		1.770 (0.9172)				
C ₅ - 900°F	36.051	0.07619 (0.5043)	4.763 (0.9986)	1.230 (1.0000)	-0.1264 (0.4370)	0.7345 (1.0000)		-1.796 (0.9979)				-35.337 (1.0000)		
380 - 900 °F	289.37	-0.5199 (0.9997)	2.420 (0.8731)	1.036 (0.9999)	-0.1333 (0.4378)	0.4707 (0.9946)			-3.220 (0.9976)		1.411 (0.9988)	-57.737 (1.0000)		
Pyridine 900°F+ Soluble	204.83	-0.3788 (0.9783)	-16.635 (1.0000)	-0.2878 (0.7336)	0.4653 (0.9550)	-0.2720 (0.9297)		2.375 (0.9999)			-2.232 (1.0000)			
ICM	-89.116	0.3265 (1.0000)	0.5091 (0.4369)	-0.9701 (1.0000)	-0.03080 (0.1890)	-0.3675 (0.9991)						31.150 (1.0000)		-0.7142 (0.9997)
900 °F + Organic	222.93	-0.4000 (0.9997)	-14.728 (1.0000)	-1.205 (1.0000)	-0.1616 (0.5170)	-1.665 (1.0000)		7.387 (1.0000)					-0.8317 (1.0000)	

* Slope or Intercept
(Probability of Significance)

TABLE VII

Statistical Parameters for Regression Models
(All Variables Floating)

Statistical Parameter Response	Correlation Coefficient	% Variation Explained	Standard Deviation	Standard Deviation as a % of the Mean Value
H ₂ Consumption	0.935	87.5	0.20	4.1
C ₁ - C ₄	0.878	77.0	1.09	5.9
Other Gases	0.958	91.7	0.18	4.1
Water	0.973	94.6	0.38	5.9
C ₅ - 380°F	0.643	41.4	1.30	13.1
380 - 550°F	0.784	61.5	1.52	9.0
550 - 900°F	0.537	28.9	2.36	17.1
C ₅ - 900°F	0.824	67.9	2.19	5.4
380 - 900°F	0.696	48.4	2.36	7.7
900°F+ Pyridine Soluble	0.843	71.0	2.37	8.7
ICM	0.842	70.9	1.36	16.9
900 °F+ Organic	0.927	85.9	2.32	7.0

TABLE VIII

Statistical Parameters for Regression Models
(Process Variables Forced)

Response \ Statistical Parameter	Correlation Coefficient	% Variation Explained	Standard Deviation	Standard Deviation as % of the Mean Value
H ₂ Consumption	0.937	87.8	0.20	4.1
C ₁ - C ₄	0.883	77.9	1.08	5.8
Other Gases	0.958	91.7	0.19	4.3
Water	0.974	94.8	0.37	5.7
C ₅ - 380°F	0.651	42.4	1.29	13.0
380 - 550°F	0.761	58.0	1.58	9.4
550 - 900°F	0.585	34.2	2.32	16.8
C ₅ - 900°F	0.825	68.1	2.20	5.4
380 - 900°F	0.735	54.0	2.28	7.4
900°F Pyridine Soluble	0.850	72.2	2.35	8.7
ICM	0.860	73.9	1.30	16.2
900°F+ organic	0.922	85.1	2.39	7.2

TABLE IX
Single Correlation Coefficients*

<u>Variable Pair</u>		<u>Correlation Coefficient</u>
% Fe	- Total Sulfur	0.93
Ro	- Organic Sulfur	-0.91
Vitrinite	- Vitrinite + Exinite	0.88
% Coal	- % Recycle Ash	-0.77
Ro	- Vitrinite + Exinite	-0.71
Total Oxygen	- Organic Sulfur	0.69
Vitrinite + Exinite	- Organic Sulfur	0.69
Recycle Ash	- Vitrinite + Exinite	-0.69
% Coal	- Vitrinite + Exinite	0.68
Total Sulfur	- Organic Sulfur	0.67
% Fe	- Recycle Ash	0.66

* The variable pairs show increasing correlation as the absolute value of their correlation coefficients approaches a value of 1.00.

TABLE X

Base Process Conditions
for Reactivity Comparison

Average Dissolver Temperature	455°C
Nominal Slurry Residence Time	1.0 hour
Average Hydrogen Partial Pressure*	11.6 MPa
Percent Coal in Feed Slurry	30.0%
Percent Recycle Ash in Feed Slurry**	10.7%

*Based on 1350 psig inlet partial pressure of hydrogen (P-99 Powhatan coal runs).

**Based on 46% total solids in the feed slurry. % Recycle Ash = $0.67 \times (\% \text{ Total Solids} - \% \text{ Coal})$

TABLE XI
Predicted Product Yields
(All Variables Floating)

<u>Coal</u>	<u>Kentucky</u>	<u>Valley Camp</u>	<u>Powhatan</u>	<u>Ireland</u>	<u>Robinson Run</u>	<u>Blacksville</u>
Yields, Wt% maf Coal						
*H ₂ Consumption	-5.5	-4.6	-4.9	-5.1	-4.5	-4.5
*C ₁ -C ₄	18.7	15.1	17.3	20.0	18.1	16.6
*Other Gases	4.7	3.6	4.4	5.5	4.4	4.0
*Water	8.3	6.2	6.7	5.8	3.9	5.2
C ₅ -380°F	9.8	9.4	9.9	11.0	10.1	9.1
380-550°F	17.5	15.0	16.8	18.5	15.4	14.1
550-900°F	<u>16.3</u>	<u>15.7</u>	<u>15.3</u>	<u>14.9</u>	<u>14.8</u>	<u>13.5</u>
* C ₅ -900°F	44.1	42.8	42.8	43.5	41.5	37.8
380-900°F	34.2	33.2	32.7	31.9	30.8	29.1
900°F+ Pyridine Solubles	26.1	33.8	30.7	26.9	29.1	32.6
ICM	<u>4.8</u>	<u>7.2</u>	<u>5.0</u>	<u>3.2</u>	<u>8.5</u>	<u>10.8</u>
* 900°F+ Organic	25.6	29.5	29.7	30.4	33.8	38.4
Calculated Material Balance	95.9	92.6	96.0	100.1	97.2	97.5

*Used in the calculated material balance.

TABLE XII
Predicted Product Yields

<u>Coal</u>	<u>Kentucky</u>	<u>Valley Camp</u>	<u>Powhatan</u>	<u>Ireland</u>	<u>Robinson Run</u>	<u>Blacksville</u>
Yields, Wt% maf Coal						
*H ₂ Consumption	-5.2	-4.4	-4.7	-5.1	-4.5	-4.2
*C ₁ -C ₄	18.6	14.9	17.4	20.3	17.8	16.2
*Other Gases	4.5	3.7	4.3	5.3	4.4	3.3
*Water	7.9	5.9	6.6	5.6	3.9	5.0
C ₅ -380°F	9.4	8.9	9.6	10.8	9.8	8.7
380-550°F	17.7	15.1	16.7	18.3	15.8	14.5
550-900°F	<u>18.1</u>	<u>17.7</u>	<u>16.6</u>	<u>14.3</u>	<u>14.8</u>	<u>15.3</u>
* C ₅ -900°F	43.7	42.7	42.4	43.1	41.1	37.4
380-900°F	36.3	32.7	34.2	34.2	30.4	29.8
900°F+ Pyridine Solubles	25.8	32.4	30.1	27.0	28.5	32.1
IQM	<u>3.7</u>	<u>5.4</u>	<u>4.3</u>	<u>4.3</u>	<u>9.6</u>	<u>9.7</u>
* 900°F+ Organic	27.0	29.2	30.6	32.3	33.8	38.3
Calculated Material Balance	96.5	91.7	96.6	101.5	96.5	96.0

*Used in the calculated material balance.

TABLE XIII
Reactivity Ranking Comparison

	Floating (Equation 22)	Fixed (Equation 21)	Penn State (Equation 14)	Chenoweth (Equation 16)
Kentucky	74.4 (1)	73.0 (1)	66.1 (2)	12.5 (1)
Valley Camp	70.5 (2)	70.8 (2)	64.1 (4)	5.6 (4)
Powhatan	70.3 (3)	69.4 (3)	65.9 (3)	8.2 (3)
Ireland	69.6 (4)	67.7 (4)	67.9 (1)	9.8 (2)
Robinson Run	66.2 (5)	66.2 (5)	63.8 (5)	3.7 (5)
Blacksville	61.6 (6)	61.7 (6)	59.8 (6)	2.0 (6)

APPENDIX A
Coal Properties - Hammarville

Table A-1

ANALYSES OF KENTUCKY COAL (LR-22366)*

Date of Analysis	6-21-76	6-22-76	6-28-76	6-24-76	9-21-76	9-11-76		3-21-77	5-17-77	8-20-77
Elemental Analysis:										
Carbon	70.61	70.45	71.13	70.44	70.87	70.14	71.53	70.98	66.94	71.93
Hydrogen	5.28	5.35	5.36	5.42	5.26	5.35	5.20	5.17	4.91	5.25
Nitrogen	1.53	1.51	1.54	1.49	1.54	1.50	0.015	1.51	1.53	1.55
Oxygen	15.4	16.6	14.7	15.5	18.4	21.2	15.2	17.3	14.1	20.0
Sulfur	3.30	3.27	3.11	3.28	3.28	2.85	3.04	3.14	3.11	2.91
Moisture	3.33	3.29	3.26	3.36	2.92	4.88	2.44	1.88	2.43	2.03
Ash	9.73;10.1	8.94	8.69	9.10	9.06	8.32	8.70	8.61	8.64	8.03
Ash-Sulfur	1.09; 1.13	1.07	0.93	1.02	0.96	0.85	0.65	1.09	0.85	1.94
Ash-Oxygen	41.1 ;54.5	49.6	41.0	40.2	58.8	63.3	47.9	39.1	38.3	19.0
Sp Ash Analyses										
Ash	9.26	-	-	-	9.23	8.48	9.29	8.83	8.70	8.03
Sp Ash Anal, % Ash										
Al	15	-	-	-	10	15	15	15	15	15
Ba	Present	-	-	-	Present	Present	Present	Present	Present	Present
B	0.09	-	-	-	0.1	0.2	0.1	0.2	0.06	0.1
Ca	1	-	-	-	1	1	1	1	1	0.6
Cr	0.05	-	-	-	0.09	0.06	0.05	0.05	0.03	0.03
Cu	0.008	-	-	-	0.009	0.009	0.007	0.01	0.006	0.006
Fe	20	-	-	-	20	20	15	15	0.8	15
Mg	0.9	-	-	-	1	1	0.5	0.8	0.7	1
Mn	0.1	-	-	-	0.2	0.2	0.2	0.09	0.1	0.06
Ni	-	-	-	-	0.03	0.02	-	0.02	-	-
K	1	-	-	-	1	2	1.0	1.4	1.4	1.6
Si	15	-	-	-	20	20	20	20	30	20
Na	0.3	-	-	-	0.3	0.4	0.08	0.4	0.1	0.6
S	0.1	-	-	-	0.1	0.1	0.07	0.08	0.06	0.08
Ti	1	-	-	-	1	1	1	1	0.9	0.8
Va	0.1	-	-	-	0.2	0.1	0.1	0.1	0.1	0.1
Part Size Dist, wt %										
>200 mesh	21.0	7.7	6.1	7.2	30.7	-	5.2	8.7	6.7	2.9
200-325 mesh	21.6	28.5	26.1	25.8	17.3	-	23.2	26.4	26.6	18.7
325-625 mesh	33.9	35.9	37.2	35.8	24.9	-	39.8	35.5	38.7	39.2
<625 mesh	23.5	27.9	30.6	31.2	27.1	-	31.7	29.4	28.0	39.2
Proximate Analyses										
Moisture	-	-	-	-	1.89	-	-	1.13	1.07	0.89
Ash	-	-	-	-	9.05	-	-	8.61	8.50	8.35
Volatile	-	-	-	-	51.12	-	-	23.76	37.87	36.13
Sulfur Types										
Pyritic Sulfur	-	-	-	-	1.46	-	-	0.93	0.96	0.99
Sulfate Sulfur	-	-	-	-	0.08	-	-	0.34	0.32	0.22
Organic Sulfur	-	-	-	-	1.79	-	-	1.87	1.83	1.70
Inorganic Sulfur	-	-	-	-	1.54	-	-	1.27	1.28	1.21
Total Sulfur	-	-	-	-	3.33	-	-	3.14	3.11	2.91
Chlorine	-	-	-	-	-	-	-	<0.0008	0.04	0.18

*Obtained from the No. 9 and 14 seams of Pittsburgh & Midway Coal Mining Co.'s Colonial Mine, ground and dried by Empire Coke Co.

GS&TC CR&CD HCM:WPC 7/24/79

Table A-2

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ANALYSIS OF PITTSBURGH SEAM COAL FROM BLACKSVILLE MINE (LR-24001)*

Date of Analysis	9-7-77	10-14-77	2-15-78	2-21-78	3-6-78
Elemental Analysis					
Carbon	69.08	72.47	70.46	73.35	71.33
Hydrogen	4.79	4.94	4.67	4.94	4.82
Nitrogen	1.34	1.38	1.36	1.40	1.37
Oxygen	13.4	12.5	13.1	11.9	13.0
Sulfur	2.64	2.80	2.84	2.62	2.67
Moisture	1.66	0.57	0.89	0.98	0.68
Ash	17.3;8.39	12.9	13.4	11.7	13.0
Ash-Sulfur	1.27	2.70	2.73	2.47	2.22
Ash-Oxygen	52.0	55.6	46.0	43.4	46.0
Chlorine	0.13	-	-	-	-
Spectral Ash Analysis					
Ash, wt %	17.3	12.9	13.7	11.7	13.0
Spectral Ash Analysis, wt % of Ash					
Al	15	15	20	10	10
Ba	Present	Present	Present	0.1	-
B	0.1	0.1	0.1	0.1	0.1
Ca	2	3	6	4	4
Cr	0.02	0.03	0.04	0.02	0.03
Cu	0.004	0.005	0.006	0.003	-
Fe	9	10	20	10	10
Pb	-	-	0.2	-	-
Mg	2	1	1	1	-
Mn	3	0.2	0.2	0.2	0.1
K	0.7	0.8	0.9	0.6	0.2
Si	30	20	1	20	20
Na	0.5	0.7	0.5	0.6	0.2
Sr	0.09	0.1	0.2	0.1	0.1
Sn	0.2	0.08	-	-	-
Ti	1	0.7	1	1	1'
V	-	-	-	-	0.06
Zn	0.009	-	-	-	-
Proximate Analysis As Received, wt %					
Moisture	1.25	0.69	0.24	1.09	1.16
Ash	14.19	13.82	13.50	11.5	13.17
Volatile	35.63	34.26	33.07	-	33.14
Sulfur Forms, D2492					
Pyritic Sulfur	1.47	1.47	1.73	1.73	1.36
Sulfate Sulfur	0.06	0.07	0.25	0.05	0.17
Inorganic Sulfur	1.53	1.54	1.98	1.78	1.53
Organic Sulfur	1.12	1.26	0.86	0.84	1.14
Total	2.65	2.80	2.84	2.62	2.67
Particle Size Distribution, wt %					
>80μ	8.6	0.1	0	0	0
75μ	26.1	3.5	4.9	2.9	6.4
46μ	13.7	17.9	16.7	16.5	18.9
20μ	17.2	34.6	34.8	39.8	35.4
<20μ	34.4	43.9	43.6	40.8	39.3

*Obtained from Consolidation Coal Co.'s Blacksville No. 2 Mine; ground and dried by Empire Coke Co.

SCT/ep; C&MD; GS&TC; 7/24/79

Table A-3

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ANALYSIS OF PITTSBURGH SEAM COAL FROM THE IRELAND MINE (LR-22991)

	<u>Bin #25</u>	<u>30T Hopper 1-29-78</u>	<u>30T Hopper 3-10-78</u>
Elemental Analysis, wt %			
Carbon	68.24	67.40	67.13
Hydrogen	5.01	4.65	4.78
Nitrogen	1.12	1.20	1.18
Sulfur	4.44	4.37	4.25
Oxygen	12.3	15.0	13.6
Chlorine	-	0.36	0.55
Ash	14.2	15.1	14.5
Ash-Sulfur	1.10	1.07	1.06
Ash-Oxygen	37.6	46.5	65.5
Moisture	0.15	0.52	0.95
Spectral Ash, wt %	12.5	15.1	14.8
Spectral Ash Analysis, wt % Ash			
Al	15	15	10
Ba	-	Present	Present
B	0.06	0.2	0.1
Ca	1.3	1	2
Cr	0.04	1	0.03
Cu	0.004	0.003	0.004
Fe	15	15	15
Mg	0.9	0.9	1
Mn	0.2	0.1	0.1
K	1.1	0.6	1.1
Si	20	20	25
Na	0.25	0.3	0.6
Sr	0.9	?	0.1
Ti	0.8	1	1
V	-	0.1	-
Proximate Analysis, wt %			
Moisture	0.25	1.07	0.92
Ash	-	15.24	14.6
Volatile	-	34.85	36.25
Sulfur Types			
Pyritic Sulfur	2.36	2.28	2.35
Sulfate Sulfur	<0.02	0.05	0.14
Inorganic Sulfur	2.36	2.33	2.49
Organic Sulfur	2.07	2.03	1.81
Total Sulfur	4.43	4.36	4.30
Particle Size Distribution, wt %			
>80 mesh	0%	0.1%	0%
75 μ	5.8	2.7	5.6
45 μ	26.1	14.9	23.5
20 μ	35.8	40.6	36.4
<20 μ	32.3	41.7	34.5

HGM:WPC

C&MD

GS&TC

7/24/79

ANALYSIS OF PITTSBURGH SEAM COAL FROM VALLEY CAMP NO. 3 MINE (LR-24925)*

<u>Coal Sample</u>	<u>Bin #8</u>	<u>6-2-78</u>
<u>Basis</u>	<u>As Rec'd</u>	<u>As Rec'd</u>
Elemental Analysis, wt %		
Carbon	75.11	73.73
Hydrogen	5.30	5.15
Nitrogen	1.46	1.45
Sulfur	2.95	2.94
Oxygen	11.9	10.1
Chlorine	-	-
Ash, wt %	8.42	8.95
Sulfur, wt % of Ash	0.37	0.64
Oxygen, wt % of Ash	57.9	31.4
Moisture, wt %	0.73	0.70
Spectral Ash Analysis		
Ash, wt %	8.69	9.0
Metals, wt % of Ash		
Al	15	15
Ba	Present	Present
B	0.1	0.8
Ca	-	0.9
Cr	0.1	0.08
Cu	0.007	0.008
Fe	15	15
Mg	0.8	0.9
Mn	0.1	0.2
Mo	0.06	-
Ni	-	0.02
K	1.0	0.7
Si	25	25
Na	0.4	0.2
Sr	0.08	0.1
Ti	1	1
P	-	-
Proximate Analysis, wt %		
Moisture	0.65	0.62
Ash	8.79	8.88
Volatile	38.23	37.32
Sulfur Types, wt %		
Pyritic Sulfur	1.53	1.74
Sulfate Sulfur	0.03	0.11
Inorganic Sulfur	1.56	1.85
Organic Sulfur	1.41	1.12
Total Sulfur	2.97	2.97
Particle Size Distribution, wt %		
>80 mesh	0	0
75 μ	7.1	5.7
45 μ	25.1	20.8
20 μ	35.4	35.3
<20 μ	32.4	38.2

*Obtained from Valley Camp Coal Sales Company's No. 5 mine; dried and ground by Empire Coke Co.

Table A-5

ANALYSIS OF PITTSBURGH SEAM COAL FROM POWHATAN NO. 5 MINE (LR-24924)*

<u>Coal Sample</u>	<u>Bin #1</u>	<u>Bin #14</u>	<u>Bin #33</u>	<u>5-25-78</u>
<u>Basis</u>	<u>As Rec'd</u>	<u>As Rec'd</u>	<u>As Rec'd</u>	<u>As Rec'd</u>
<u>Elemental Analysis, wt %</u>				
Carbon	Lost Sample	72.39	73.42	72.61
Hydrogen	Lost Sample	5.13	5.10	5.21
Nitrogen	1.30	1.26	1.25	1.31
Sulfur	3.54	3.40	3.54	3.35
Oxygen	13.0	11.6	12.4	14.2
Chlorine	0.56	0.42	0.48	0.40
Ash, wt %	9.47	9.55	9.44	9.21
Sulfur, wt % of Ash	0.92	0.66	1.27	0.71
Oxygen, wt % of Ash	43.9	51.1	48.7	35.7
Moisture, wt %	0.39	0.93	1.00	1.07
<u>Spectral Ash Analysis</u>				
Ash, wt %	9.4	9.6	9.4	9.3
Metals, wt % of Ash				
Al	15	10	10	15
Ba	Present	Present	Trace	Trace
B	0.2	0.1	0.08	0.1
Ca	0.8	0.7	0.3	2
Cr	0.03	0.02	0.02	0.04
Cu	0.005	0.006	0.009	0.02
Fe	15	15	15	15
Mg	0.8	0.5	0.4	0.7
Mn	0.1	0.1	0.05	0.2
Ni	0.01	-	-	-
K	0.8	1.0	0.9	0.7
Si	25	20	20	25
Na	0.3	0.4	0.5	0.2
Sr	0.09	0.06	0.04	0.1
Ti	-	-	-	-
<u>Proximate Analysis, wt %</u>				
Moisture	0.90	0.83	1.01	0.54
Ash	9.30	9.25	9.28	9.17
Volatile	38.50	37.88	39.05	37.08
<u>Sulfur Types, wt %</u>				
Pyritic Sulfur	1.70	1.79	1.68	1.64
Sulfate Sulfur	0.02	0.01	0.01	0.07
Inorganic Sulfur	1.72	1.80	1.69	1.71
Organic Sulfur	1.73	1.57	1.82	1.64
Total Sulfur	3.45	3.37	3.51	3.35
<u>Particle Size Distribution, wt %</u>				
>80 mesh	0	0	0	0
75 μ	6.3	6.3	5.2	6.1
45 μ	23.6	24.6	23.2	23.3
20 μ	35.9	37.8	38.1	34.1
<20 μ	34.2	31.3	33.5	36.5

*Obtained from North American Coal Company's Powhatan No. 5 mine; dried and ground by Empire Coke Co.

Table A-6

35

ANALYSIS OF PITTSBURGH SEAM COAL FROM POWHATAN NO. 5 MINE (LR-25844)*

<u>Coal Sample</u>	<u>Bin #30</u>	<u>Bin #24</u>	<u>Bin #39</u>	<u>3-26-79</u>
<u>Basis</u>	<u>As Rec'd</u>	<u>As Rec'd</u>	<u>As Rec'd</u>	<u>As Rec'd</u>
Elemental Analysis, wt %				
Carbon	68.88	68.39	67.37	68.62
Hydrogen	4.78	4.90	4.79	5.11
Nitrogen	1.24	1.31	1.24	1.23
Oxygen	18.0	15.0	14.8	14.3
Sulfur	3.36	2.19	3.38	3.31
Chlorine	0.03	0.06	0.06	-
Ash, wt %	11.8	11.5	11.4	11.7
Sulfur, wt % of Ash	1.54	1.51	1.47	1.23
Oxygen, wt % of Ash	-	53.2	45.5	39.4
Moisture, wt %	1.02	1.73	1.71	1.52
Spectral Ash Analysis				
Ash, wt %	11.9	11.6	11.7	11.9
Metals, wt % of Ash				
Al	10	10	10	15
Ba	0.2	Trace	Trace	Trace
B	0.07	0.1	0.1	0.1
Ca	1.0	0.9	1.0	0.6
Cr	0.03	-	-	0.02
Cu	0.06	0.04	0.04	0.004
Fe	10	15	15	15
Mg	1	1	1	0.9
Mn	0.1	0.1	0.1	0.09
Ni	0.01	-	-	0.02
K	1.0	1.0	0.9	1.0
Si	25	25	25	20
Na	0.2	0.2	0.2	0.2
Sr	0.09	-	-	0.06
Ti	1.0	1.0	1.0	0.5
V	0.1	-	-	0.08
Proximate Analysis, wt %				
Moisture	2.08	1.73	1.98	0.96
Ash	11.91	12.69	11.68	11.71
Volatile	34.0	32.18	38.13	37.08
Sulfur Types, wt %				
Pyritic Sulfur	1.08	0.92	1.01	1.14
Sulfate Sulfur	0.59	0.55	0.53	0.54
Inorganic Sulfur	1.69	1.47	1.54	1.68
Organic Sulfur	-	0.72	1.84	1.62
Total Sulfur	-	2.19	3.38	3.30
Particle Size Distribution, wt %				
>80 mesh	0	0	0	0
75 μ	8.4	30.7	8.8	12.6
45 μ	49.0	20.9	28.5	32.6
20 μ	35.8	26.8	34.7	29.2
<20 μ	6.8	21.6	28.0	25.6

*Obtained from North American Coal Company's Powhatan No. 5 mine; dried and ground by Empire Coke Co.

ANALYSIS OF PITTSBURGH SEAM COAL FROM THE ROBINSON RUN MINE (LR-25447)

<u>Coal Sample</u>	<u>Bin 25</u> <u>8-9-78</u>	<u>Bin 5</u> <u>8-9-78</u>
<u>Basis</u>	<u>As Rec'd</u>	<u>As Rec'd</u>
Elemental Analysis, wt %		
Carbon	68.72	68.00
Hydrogen	4.89	4.77
Nitrogen	1.29	1.28
Sulfur	3.42	3.68
Oxygen	13.3	13.3
Chlorine	0.05	0.05
Ash	16.0	16.8
Ash-Sulfur	2.38	2.36
Ash-Oxygen	48.2	47.3
Metals	7.91	8.46
Moisture	0.88	1.01
Spectral Ash Analysis, Metals, wt % of Ash		
Al	15	15
Ba	Trace	Trace
B	0.1	0.09
Ca	3	3
Cr	0.03	0.02
Cu	0.006	0.008
Fe	10	10
Mg	2	2
Mn	0.2	0.1
K	1.3	1.3
Si	20	20
Na	0.4	0.4
Sr	0.2	0.2
Ti	1	1
Proximate Analysis, wt %		
Moisture	0.9	1.0
Ash	16.0	16.8
Volatile	34.4	34.4
Sulfur Types		
Pyritic Sulfur	2.66	2.31
Sulfate Sulfur	0.09	0.10
Inorganic Sulfur	2.75	2.41
Organic Sulfur	1.27	1.27
Total Sulfur	3.42	3.68
Particle Size Distribution, wt %		
>80 mesh	0	0
75 μ	4.4	3.4
45 μ	21.4	19.9
20 μ	35.0	36.4
<20 μ	39.2	40.3

SCT:ep
GS&TC
C&MD
7/24/79

APPENDIX B

Coal Properties - Commercial Testing

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 220 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 726-8484

Reply to
Instrumental Analysis Division
14335 West 44th Avenue
Golden, Colorado 80401

Phone: 303-278-9521

To: Mr. W. Gall
Gulf Research & Development
P.O. Drawer 2038
Pittsburgh, PA 15230

Date: November 22, 1978

Purchase Order: GRL-13095-B78

IAD No: 97-B836-277-07

Sample ID: LR 22366 Kentucky 9/14

* PROXIMATE ANALYSIS	As received	Dry basis	* ULTIMATE ANALYSIS	As received	Dry basis
% Moisture	3.03	--	Moisture	3.03	--
% Ash	8.58	8.85	Carbon	70.27	72.47
% Volatile	39.81	41.05	Hydrogen	4.83	4.98
% Fixed Carbon	48.58	50.10	Nitrogen	1.16	1.20
	100.00	100.00	Chlorine	0.01	0.01
Btu	12449	12838	Sulfur	3.01	3.10
% Sulfur	3.01	3.10	Ash	8.58	8.85
% Alk. as Na ₂ O			Oxygen (diff)	9.11	9.39
				100.00	100.00
* SULFUR FORMS			MINERAL ANALYSIS	% Wt.	
% Pyritic Sulfur	0.71	0.73		Ignited Basis	
% Sulfate Sulfur	0.54	0.56	Silica, SiO ₂	44.69	
% Organic Sulfur	1.76	1.81	Alumina, Al ₂ O ₃	21.21	
% Total Sulfur	3.01	3.10	Titania, TiO ₂	0.95	
			Ferric oxide, Fe ₂ O ₃	21.85	
* WATER SOLUBLE ALKALIES			Lime, CaO	3.12	
% Na ₂ O =	.003	.003	Magnesia, MgO	0.81	
% K ₂ O =	.004	.004	Potassium oxide, K ₂ O	2.42	
			Sodium oxide, Na ₂ O	0.24	
SILICA VALUE =	63.42		Sulfur Trioxide, SO ₃	3.20	
T250 =	2380 °F		Phos. pentoxide, P ₂ O ₅	0.16	
* FREE SWELLING INDEX =	2½		Strontium oxide, SrO	0.00	
			Barium oxide, BaO	0.00	
* Analyzed at Alternate			Manganese oxide, Mn ₃ O ₄	0.04	
CT&E Laboratory			Sum	98.69	

Approved by:
M. L. Jacobs, Ph.D., Mngr.
Instrumental Analysis Div.

MLJ/mw

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 220 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 726-8484

Reply to
Instrumental Analysis Division
14335 West 44th Avenue
Golden, Colorado 80401

Phone: 303-278-9521

To: Mr. W. Gall
Gulf Research & Development
P.O. Drawer 2038
Pittsburgh, PA 15230

Date: November 22, 1978

Purchase Order: GRL-13095-B78

IAD No: 97-B836-277-07

Sample ID: LR 24001 Blacksville

* PROXIMATE ANALYSIS	As received	Dry basis	* ULTIMATE ANALYSIS	As received	Dry basis
% Moisture	1.15	--	Moisture	1.15	--
% Ash	11.70	11.84	Carbon	72.23	73.07
% Volatile	36.23	36.65	Hydrogen	4.72	4.77
% Fixed Carbon	50.92	51.51	Nitrogen	1.11	1.12
	100.00	100.00	Chlorine	0.08	0.08
Btu	13055	13207	Sulfur	2.70	2.73
% Sulfur	2.70	2.73	Ash	11.70	11.84
% Alk. as Na ₂ O			Oxygen (diff)	6.31	6.39
				100.00	100.00
* SULFUR FORMS				% Wt.	
% Pyritic Sulfur	1.33	1.35	MINERAL ANALYSIS	Ignited Basis	
% Sulfate Sulfur	0.10	0.11	Silica, SiO ₂	45.05	
% Organic Sulfur	1.27	1.27	Alumina, Al ₂ O ₃	21.08	
% Total Sulfur	2.70	2.73	Titania, TiO ₂	0.88	
			Ferric oxide, Fe ₂ O ₃	15.37	
* WATER SOLUBLE ALKALIES			Lime, CaO	7.49	
% Na ₂ O =	.026	.026	Magnesia, MgO	1.25	
% K ₂ O =	.004	.004	Potassium oxide, K ₂ O	1.68	
			Sodium oxide, Na ₂ O	1.02	
SILICA VALUE =	65.14		Sulfur Trioxide, SO ₃	7.84	
T250 =	2420°F		Phos. pentoxide, P ₂ O ₅	0.45	
* FREE SWELLING INDEX =	8½		Strontium oxide, SrO	0.00	
			Barium oxide, BaO	0.07	
			Manganese oxide, Mn ₃ O ₄	0.07	
			Sum	102.25	

*Analyzed at Alternate CT&E
Laboratory

MLJ/nw

Approved by:
M. L. Jacobs, Ph.D., Mngr.
Instrumental Analysis Div.

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 838 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 728-8484

Reply to

Instrumental Analysis Division
14335 West 44th Avenue
Golden, Colorado 80401

Phone: 303-278-9521

To: Mr. W. Gall
Gulf Research & Development
P.O. Drawer 2038
Pittsburgh, PA 15230

Date: November 22, 1978

Purchase Order: GRL-13095-878

IAD No: 97-8836-277-07

Sample ID: LR 22991 Ireland

* PROXIMATE ANALYSIS	As received	Dry basis	* ULTIMATE ANALYSIS	As received	Dry basis
% Moisture	1.62	--	Moisture	1.62	---
% Ash	13.77	14.00	Carbon	68.01	69.13
% Volatile	37.93	38.55	Hydrogen	4.72	4.80
% Fixed Carbon	46.68	47.45	Nitrogen	1.46	1.48
	100.00	100.00	Chlorine	0.02	0.02
Btu	12316	12519	Sulfur	4.56	4.64
% Sulfur	4.56	4.64	Ash	13.77	14.00
% Alk. as Na ₂ O			Oxygen (diff)	5.84	5.93
				100.00	100.00
*SULFUR FORMS			MINERAL ANALYSIS	% Wt.	
% Pyritic Sulfur	2.22	2.26		Ignited Basis	
% Sulfate Sulfur	0.18	0.18	Silica, SiO ₂	41.86	
% Organic Sulfur	2.16	2.20	Alumina, Al ₂ O ₃	21.48	
% Total Sulfur	4.56	4.64	Titania, TiO ₂	0.90	
WATER SOLUBLE ALKALIES			Ferric oxide, Fe ₂ O ₃	25.11	
% Na ₂ O =	.038	.039	Lime, CaO	3.53	
% K ₂ O =	.004	.004	Magnesia, MgO	0.82	
			Potassium oxide, K ₂ O	1.92	
SILICA VALUE =	58.69		Sodium oxide, Na ₂ O	0.59	
T250 =	2410 °F		Sulfur Trioxide, SO ₃	3.02	
* FREE SWELLING INDEX =	6½		Phos. pentoxide, P ₂ O ₅	0.38	
			Strontium oxide, SrO	0.00	
			Barium oxide, BaO	0.04	
			Manganese oxide, Mn ₃ O ₄	0.04	
			Sum	99.69	

*Analyzed at Alternate
CT&E Laboratory

Approved by:

M. L. Jacobs, Ph.D., Mngr.
Instrumental Analysis Div.

MLJ/nw

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 228 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 736-8434

Reply to Instrumental Analysis Division
14335 West 44th Avenue
Golden, Colorado 80401

Phone: 303-278-9521

To: Mr. W. Gall
Gulf Research & Development
P.O. Drawer 2038
Pittsburgh, PA 15230

Date: November 22, 1978

Purchase Order: GRL-13095-B78

IAD No: 97-B836-277-07

Sample ID: LR 24925 Valley Camp

* PROXIMATE ANALYSIS	As received	Dry basis	* ULTIMATE ANALYSIS	As received	Dry basis
% Moisture	1.50	--	Moisture	1.50	--
% Ash	10.82	10.98	Carbon	73.06	74.17
% Volatile	38.48	39.07	Hydrogen	5.03	5.11
% Fixed Carbon	49.20	49.95	Nitrogen	0.72	0.73
	100.00	100.00	Chlorine	0.02	0.02
Btu	13156	13356	Sulfur	3.28	3.33
% Sulfur	3.28	3.33	Ash	10.82	10.98
% Alk. as Na ₂ O			Oxygen (diff)	5.57	5.66
				100.00	100.00
* SULFUR FORMS				% Wt.	
% Pyritic Sulfur	1.72	1.75	MINERAL ANALYSIS	Ignited Basis	
% Sulfate Sulfur	0.02	0.02	Silica, SiO ₂	30.53	
% Organic Sulfur	1.54	1.56	Alumina, Al ₂ O ₃	16.10	
% Total Sulfur	3.28	3.33	Titania, TiO ₂	0.74	
			Ferric oxide, Fe ₂ O ₃	47.73	
WATER SOLUBLE ALKALIES			Lime, CaO	1.96	
% Na ₂ O =	.018	.018	Magnesia, MgO	0.43	
% K ₂ O =	.004	.004	Potassium oxide, K ₂ O	1.30	
			Sodium oxide, Na ₂ O	0.46	
SILICA VALUE =	37.35		Sulfur Trioxide, SO ₃	1.30	
T250 =	2150°F		Phos. pentoxide, P ₂ O ₅	0.16	
* FREE SWELLING INDEX =	7		Strontium oxide, SrO	0.03	
			Barium oxide, BaO	0.06	
* Analyzed at Alternate			Manganese oxide, Mn ₃ O ₄	0.10	
CT&E Laboratory			Sum	100.90	

Approved by:

M. L. Jacobs, Ph.D., Mngr.
Instrumental Analysis Div.

MLJ/nw

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 226 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 736-8484

Reply to

Instrumental Analysis Division
14335 West 44th Avenue
Golden, Colorado 80401

Phone: 303-278-9521

To: W. Gall
Gulf Research & Development
P.O. Drawer 2038
Pittsburgh, PA 15230

Date: January 3, 1979

Purchase Order: GRL-13095-B78

IAD No: 97-C022-277-01

Sample ID: LR 24924 Powhatan

*PROXIMATE ANALYSIS	As received	Dry basis	*ULTIMATE ANALYSIS	As received	Dry basis
% Moisture	1.89	----	Moisture	1.89	----
% Ash	9.09	9.27	Carbon	72.07	73.46
% Volatile	39.16	39.91	Hydrogen	4.95	5.05
% Fixed Carbon	49.86	50.82	Nitrogen	1.40	1.43
	100.00	100.00	Chlorine	0.09	0.09
Btu	13021	13272	Sulfur	3.27	3.33
% Sulfur	3.27	3.33	Ash	9.09	9.27
% Alk. as Na ₂ O	-----	-----	Oxygen (diff)	7.24	7.37
*SULFUR FORMS			% Wt.		
% Pyritic Sulfur	1.49	1.52	MINERAL ANALYSIS	Ignited Basis	
% Sulfate Sulfur	0.04	0.04	Silica, SiO ₂	41.22	
% Organic Sulfur	1.74	1.77	Alumina, Al ₂ O ₃	22.27	
% Total Sulfur			Titania, TiO ₂	0.91	
*WATER SOLUBLE ALKALIES			Ferric oxide, Fe ₂ O ₃	25.87	
% Na ₂ O =	----	0.018	Lime, CaO	2.87	
% K ₂ O =	----	0.004	Magnesia, MgO	0.64	
SILICA VALUE =	58.39		Potassium oxide, K ₂ O	1.77	
T250 =	2330 °F		Sodium oxide, Na ₂ O	0.46	
*FREE SWELLING INDEX =	4 1/2		Sulfur Trioxide, SO ₃	1.80	
			Phos. pentoxide, P ₂ O ₅	0.20	
			Strontium oxide, SrO	0.00	
			Barium oxide, BaO	0.00	
			Manganese oxide, Mn ₃ O ₄	0.05	
			Sum	98.06	

*Tests performed at alternate
CT&E Laboratory

Approved by:

M. L. Jacobs, Ph.D., Mngr.
Instrumental Analysis Div.

MLJ/nw

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 226 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 726-8484

Reply to

Instrumental Analysis Division
14335 West 44th Avenue
Golden, Colorado 80401

Phone: 303-278-9521

To: W. Gall
Gulf Research & Development
P.O. Drawer 2038
Pittsburgh, PA 15230

Date: January 31, 1979

Purchase Order: GRL-13095-878

IAD No: 97-C117-277-01

Sample ID: LR25844 Powhatan

PROXIMATE ANALYSIS			ULTIMATE ANALYSIS		
	As received	Dry basis		As received	Dry basis
% Moisture	1.19	-----	Moisture	1.19	-----
% Ash	10.19	10.31	Carbon	71.66	72.52
% Volatile	40.03	40.51	Hydrogen	5.02	5.08
% Fixed Carbon	48.59	49.18	Nitrogen	1.10	1.11
	100.00	100.00	Chlorine	0.06	0.06
Btu	13015	13172	Sulfur	3.32	3.36
% Sulfur	3.32	3.36	Ash	10.19	10.31
% Alk. as Na ₂ O			Oxygen (diff)	7.46	7.56
				100.00 % Wt.	100.00
SULFUR FORMS			MINERAL ANALYSIS		
% Pyritic Sulfur	1.42	1.44		Ignited Basis	
% Sulfate Sulfur	0.16	0.16	Silica, SiO ₂	43.76	
% Organic Sulfur	1.74	1.76	Alumina, Al ₂ O ₃	22.66	
% Total Sulfur			Titania, TiO ₂	1.01	
WATER SOLUBLE ALKALIES			Ferric oxide, Fe ₂ O ₃	23.76	
% Na ₂ O =		0.007	Lime, CaO	2.05	
% K ₂ O =		0.004	Magnesia, MgO	0.59	
			Potassium oxide, K ₂ O	1.81	
SILICA VALUE =	62.37		Sodium oxide, Na ₂ O	0.28	
T250 =	2395°F		Sulfur Trioxide, SO ₃	1.26	
FREE SWELLING INDEX =	4		Phos. pentoxide, P ₂ O ₅	0.14	
			Strontium oxide, SrO	0.00	
			Barium oxide, BaO	0.00	
			Manganese oxide, Mn ₃ O ₄	0.03	
			Sum	97.35	

M. L. Jacobs (ss)
Approved by:
M. L. Jacobs, Ph.D., Mngr.
Instrumental Analysis Div.

MLJ/nw

COMMERCIAL TESTING & ENGINEERING CO.

GENERAL OFFICES: 938 NORTH LA SALLE STREET, CHICAGO, ILLINOIS 60601 • AREA CODE 312 756-8494

Reply to
Instrumental Analysis Division
14335 West 44th Avenue
Golden, Colorado 80401

Phone: 303-278-9521

To: Mr. W. Gall
Gulf Research & Development
P.O. Drawer 2038
Pittsburgh, PA 15230

Date: November 22, 1978

Purchase Order: GRL-13095-B78

IAD No: 97-8836-277-07

Sample ID: LR 25447 Robinson Run

*PROXIMATE ANALYSIS	As received	Dry basis	*ULTIMATE ANALYSIS	As received	Dry basis
% Moisture	1.35	--	Moisture	1.35	--
% Ash	15.57	15.78	Carbon	68.21	69.14
% Volatile	36.13	36.62	Hydrogen	4.64	4.70
% Fixed Carbon	46.95	47.60	Nitrogen	1.33	1.35
	100.00	100.00	Chlorine	0.02	0.02
Btu	12459	12609	Sulfur	3.51	3.56
% Sulfur	3.51	3.56	Ash	15.57	15.78
% Alk. as Na ₂ O			Oxygen (diff)	5.37	5.45
				100.00	100.00
*SULFUR FORMS				% Wt.	
% Pyritic Sulfur	2.14	2.17	MINERAL ANALYSIS	Ignited Basis	
% Sulfate Sulfur	0.07	0.07	Silica, SiO ₂	44.13	
% Organic Sulfur	1.30	1.32	Alumina, Al ₂ O ₃	20.36	
% Total Sulfur	3.51	3.56	Titania, TiO ₂	0.84	
			Ferric oxide, Fe ₂ O ₃	18.47	
*WATER SOLUBLE ALKALIES			Lime, CaO	5.21	
% Na ₂ O =	.038	.039	Magnesia, MgO	1.42	
% K ₂ O =	.009	.009	Potassium oxide, K ₂ O	2.39	
			Sodium oxide, Na ₂ O	0.70	
SILICA VALUE =	63.74		Sulfur Trioxide, SO ₃	5.63	
T250 =	2380°F		Phos. pentoxide, P ₂ O ₅	0.56	
*FREE SWELLING INDEX =	7½		Strontium oxide, SrO	0.00	
			Barium oxide, BaO	0.13	
			Manganese oxide, Mn ₃ O ₄	0.06	
			Sum	99.90	
*Analyzed at Alternate CT&E Laboratory					

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APPENDIX C

Petrographic Analyses - Commercial Testing

Introduction to Coal Petrography

Coal is a complex mixture of organic and inorganic constituents (macerals and minerals). Macerals may be microscopically distinguished from one another in incident light by differences in morphology and relative reflectance. Individual macerals may be lumped into Maceral Groups, based on similarities in composition and behavior.

A schematic of coal composition is presented below.

Although the various macerals may occur in coals of any rank, maceral properties change with rank. For this reason, a petrographic analysis must measure both coal composition and coal rank.

Petrographic analyses are performed on representative coal samples that are crushed to - 20 mesh, mixed with epoxy and pelletized. The coal pellets are then polished to create a planar, scratch-free surface suitable for examination in incident light.

The Maceral Analysis is performed to determine coal composition on a volume percent basis. It consists of a point count on 1000 points, 500 counts on each of 2 pellets per sample. In a routine analysis, the macerals sporinite, cutinite, alginite, exudatinite, fluorinite and bituminite are counted as 'exinite', and sclerotinite is counted as fusinite. Other macerals are counted as they occur.

The Vitrinite Group macerals normally dominate coal composition. In addition, the reflectance of vitrinite particles in incident light increases with increasing rank and correlates well with rank parameters such as Volatile Matter and % Carbon. The Reflectance Analysis then, may be used to indicate coal rank. It consists of a determination of the maximum reflectance on 100 vitrinite particles, 50 on each of 2 pellets per sample.

The distribution of vitrinite reflectance readings may be expressed in histogram form or, more concisely, as percentages in reflectance categories or 'V-types'. Each V-type spans a 1% reflectance range. For example, V-9 includes all readings between 0.9 and 0.99% reflectance.

The petrographic data on composition and rank characterize or 'fingerprint' a coal and may be used for purposes such as seam correlation, quality control or prediction of coal behavior in industrial processes.

LAD Batch #: 97-C519-277-02

Report of Analysis on Sample: LS 8629-A
Kentucky Coal

MACEPAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

<u>MACEPAL</u>		<u>MACEPAL GROUP</u>	
Vitrinite	71.4	Vitrinite	78.7
Pseudovitrinite	7.3		
Exinite	7.6	Exinite (Liptinite)	8.5
Resinite	0.9		
Semi-Fusinite	5.0		
Semi-Macrinite	0.2		
Fusinite	3.5	Inertinite	12.8
Macrinite	0.3		
Micrinite	3.8		
TOTAL	100%		100%

Comments: Mineral matter appears to be dominated by disseminated Pyrites.

IAQ Batch: # 97-C519-277-02
 Report of Analysis on Sample: LS 8629-A Kentucky Coal

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.71

Distribution of Vitrinite Reflectance Readings:

%Ro

161
 Number
 of
 Counts
 (Total =
 100)

V-Type Table for Vitrinites (=100%)

V-6	V-7	V-	V-
34%	66%		

V-Type Table for Vitrinites (= 78.7%)

(Adjusted to = Maceral % of Reactive Vitrinites)

V-6	V-7	V-	V-
26.8%	51.9%		

IAD Batch #: 97-B395-277-03

Report of Analysis on Sample: LR 24001 Blackville

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

<u>MACERAL</u>		<u>MACERAL GROUP</u>	
Vitrinite	65.3	Vitrinite	77.0
Pseudovitrinite	11.7		
Exinite	6.1	Exinite	6.6
Resinite	0.5	(Liptinite)	
Semi-Fusinite	3.2		
Semi-Macrinite	0.6		
Fusinite	4.9	Inertinite	16.4
Macrinite	1.9		
Micrinite	5.8		
TOTAL	100		100%

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.82

Distribution of Vitrinite Reflectance Readings:

%Ro

V-Type Table for Vitrinites (=100%)

<u>V- 7</u>	<u>V- 8</u>	<u>V- </u>	<u>V- </u>
23	77		

V-Type Table for Vitrinites (= %)

(Adjusted to = Maceral % of Reactive Vitrinites)

<u>V- </u>	<u>V- </u>	<u>V- </u>	<u>V- </u>

IAD Batch #: 97-C510-277-01

Report of Analysis on Sample: LS 8628
Ireland Mine Coal

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

<u>MACERAL</u>		<u>MACERAL GROUP</u>	
Vitrinite	66.5	Vitrinite	79.0
Pseudovitrinite	12.5		
Exinite	5.3	Exinite (Liptinite)	6.5
Resinite	1.2		
Semi-Fusinite	5.6		
Semi-Macrinite	0.5		
Fusinite	4.1	Inertinite	14.5
Macrinite	0.9		
Micrinite	3.4		
TOTAL	100%		

Comments: Mineral Matter appeared to be dominated by Pyrites and Clays.

IAD Batch: # 97-C510-277-01

Report of Analysis on Sample: LS 8628

Ireland Mine Coal

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.69

Distribution of Vitrinite Reflectance Readings:

%Ro

165
Number
of
Counts
(Total =
100)

V-Type Table for Vitrinites (=100%)

<u>V-6</u>	<u>V-7</u>	<u>V-</u>	<u>V-</u>
56	44		

V-Type Table for Vitrinites (= 79.0%)

(Adjusted to = Maceral % of Reactive Vitrinites)

<u>V-6</u>	<u>V-7</u>	<u>V-</u>	<u>V-</u>
44.2	34.8		

IAD Batch #: 97-B395-277-03

Report of Analysis on Sample: LR 24925 Valley Camp

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

<u>MACERAL</u>		<u>MACERAL GROUP</u>	
Vitrinite	70.1	Vitrinite	79.0
Pseudovitrinite	8.9		
Exinite	6.0	Exinite	6.6
Resinite	0.6	(Liptinite)	
Semi-Fusinite	3.0		
Semi-Macrinite	0.5		
Fusinite	4.3	Inertinite	14.4
Macrinite	1.4		
Micrinite	5.2		
TOTAL	100%		100%

IAD Batch: # 97-B395-277-03

Report of Analysis on Sample: LR 24925 Valley Camp

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.73

Distribution of Vitrinite Reflectance Readings:

167
Number
of
Counts
(Total=
100)

V-Type Table for Vitrinites (=100%)

V-6	V-7	V-8	V-
34	55	11	

V-Type Table for Vitrinites (= %)

(Adjusted to = Maceral % of Reactive Vitrinites)

V-	V-	V-	V-

IAD Batch #: 97-B395-277-03

Report of Analysis on Sample: LR 24924 Powhatan

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

<u>MACERAL</u>		<u>MACERAL GROUP</u>	
Vitrinite	70.1	Vitrinite	80.5
Pseudovitrinite	10.4		
Exinite	5.2	Exinite	6.1
Resinite	0.9	(Liptinite)	
Semi-Fusinite	3.2		
Semi-Macrinite	0.6		
Fusinite	3.0	Inertinite	13.4
Macrinite	1.9		
Micrinite	4.7		
TOTAL	100%		100%

IAD Batch: # 97-B395-277-03
 Report of Analysis on Sample: LR 24924 Powhatan

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.73

Distribution of Vitrinite Reflectance Readings:

V-Type Table for Vitrinites (=100%)

<u>V- 6</u>	<u>V- 7</u>	<u>V- 8</u>	<u>V- 9</u>
24	65	11	

V-Type Table for Vitrinites (= %)

(Adjusted to = Maceral % of Reactive Vitrinites)

<u>V- 6</u>	<u>V- 7</u>	<u>V- 8</u>	<u>V- 9</u>

IAD Batch #: 97-B995-277-02

Report of Analysis on Sample: LR 25844 *Powhatan*

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

<u>MACERAL</u>		<u>MACERAL GROUP</u>	
Vitrinite	72.3	Vitrinite	77.9
Pseudovitrinite	5.6		
— Exinite	4.3	Exinite	5.4
Resinite	1.1	(Liptinite)	
— Semi-Fusinite	3.8		
— Semi-Macrinite	0.4		
Fusinite	4.2	Inertinite	16.7
Macrinite	1.2		
Micrinite	7.1		
TOTAL	100%		100%

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.68

Distribution of Vitrinite Reflectance Readings:

%Ro

171
 Number
 of
 Counts
 (Total=
100)

V-Type Table for Vitrinites (=100%)

<u>V-5</u>	<u>V-6</u>	<u>V-7</u>	<u>V-</u>
1	62	37	

V-Type Table for Vitrinites (= %)

(Adjusted to = Maceral % of Reactive Vitrinites)

<u>V-</u>	<u>V-</u>	<u>V-</u>	<u>V-</u>

IAD Batch #: 97-C519-277-02

Report of Analysis on Sample: LS 8629-B
Powhatan Coal

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

<u>MACERAL</u>		<u>MACERAL GROUP</u>	
Vitrinite	77.5	Vitrinite	84.6
Pseudovitrinite	7.1		
Exinite	3.1	Exinite (Liptinite)	3.9
Resinite	0.8		
Semi-Fusinite	4.9		
Semi-Macrinite	0.3		
Fusinite	2.9	Inertinite	11.5
Macrinite	0.1		
Micrinite	3.3		
TOTAL	100%		100%

Comments: Some Coke Contamination (less than 0.5%). Mineral matter appears to consist of clays and disseminated pyrites.

IAQ Batch: # 97-C519-277-02

Report of Analysis on Sample: LS 8629-B Powhatan Coal

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.71

Distribution of Vitrinite Reflectance Readings:

%Ro

173
Number
of
Counts
(Total =
100)

V-Type Table for Vitrinites (=100%)

<u>V-6</u>	<u>V-7</u>	<u>V-8</u>	<u>V-</u>
35%	64%	1%	

V-Type Table for Vitrinites (= 84.6%)

(Adjusted to = Maceral % of Reactive Vitrinites)

<u>V-6</u>	<u>V-7</u>	<u>V-8</u>	<u>V-</u>
29.6%	54.1%	0.9%	

IAD Batch #: 97-B782-277-01

Report of Analysis on Sample: LR 25447 Robinson Run

MACERAL ANALYSIS
(Volume Percent)
(Mineral-Matter Free Basis)

<u>MACERAL</u>		<u>MACERAL GROUP</u>	
Vitrinite	66.0	Vitrinite	72.9
Pseudovitrinite	6.9		
Exinite	6.9	Exinite	8.6
Resinite	1.7	(Liptinite)	
Semi-Fusinite	5.5		
Semi-Macrinite	0.8		
Fusinite	2.4	Inertinite	18.5
Macrinite	1.8		
Micrinite	8.0		
TOTAL	100%		100%

Comments: Mineral-Matter appears to consist of Shale and Pyrite. Pyrite occurs as disseminated framboids and euhedra, as cell fillings in fusinite, and in large massive to dendritic forms.

IAD Batch: #97-B782-277-01

Report of Analysis on Sample: LR 25447 Robinson Run

REFLECTANCE ANALYSIS

Mean-Maximum Vitrinite Ro- 0.77

Distribution of Vitrinite Reflectance Readings:

V-Type Table for Vitrinites (=100%)

<u>V-6</u>	<u>V-7</u>	<u>V-8</u>	<u>V-9</u>
8	62	28	2

V-Type Table for Vitrinites (=72.9%)

(Adjusted to = Maceral % of Reactive Vitrinites)

<u>V-6</u>	<u>V-7</u>	<u>V-8</u>	<u>V-9</u>
5.8	45.2	20.4	1.5

APPENDIX D

Parity Plots

FIGURE D - 1
Hydrogen Consumption Parity Plot
(standard deviation: $s = 0.20$)

FIGURE D - 2

C₁ - C₄ Gas Yield Parity Plot

(standard deviation: $s = 1.09$)

FIGURE D - 3
Other Gases (CO , CO_2 , H_2S , NH_3) Parity Plot
(standard deviation: $s = 0.18$)

FIGURE D - 4
Water Yield Parity Plot
(standard deviation: $s = 0.38$)

FIGURE D - 5

C₅ - 380° F Liquid Yield Parity Plot
(standard deviation: $s = 1.30$)

FIGURE D - 6

380 - 550° F Liquid Yield Parity Plot
(standard deviation: $s = 1.52$)

FIGURE D-7

550-900°F Liquid Yield Parity Plot
(Standard Deviation: $S = 2.36$)

FIGURE D-8

C₅-900°F Liquid Yield Parity Plot
(Standard Deviation: $S = 2.19$)

FIGURE D-9

380-900°F Liquid Yield Parity Plot
(Standard Deviation: $S = 2.36$)

FIGURE D-10

900°F+ Pyridine Soluble Product Yield Parity Plot
(Standard Deviation: $S = 2.37$)

FIGURE D-11

Insoluble Organic Matter (IOM) Yield Parity Plot
(Standard Deviation: $S = 1.36$)

FIGURE D-12

900°F+ Organic Matter Yield Parity Plot
(Standard Deviation: $S = 2.32$)