KINETICS OF COAL HYDROGENATION

IN A

CONTINUOUS FLOW STIRRED TANK REACTOR

by

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ABSTRACT

The non-catalytic hydrogenation of a Kentucky No. 9 coal using a synthetic recycle solvent, consisting of 45% tetralin, 38% 2-methylnaphthalene and 17% p-cresol, was studied in a continuous flow stirred tank bench scale reactor. It was found that the overall conversion of coal could be modeled using a first order pseudo irreversible expression. An activation energy of 25.4 kcal/gmol was calculated. In addition the yield of products was shown to be adequately described by the following mechanism:

$$\begin{tikzcd}
\text{Coal} \arrow[r, "k_1"] \arrow[d, "k_2"'] & \text{Preasphaltenes} \arrow[dl, "k_3"] \\
\text{Asphaltenes} \arrow[r, "k_4"'] & \text{Oil}
\end{tikzcd}$$

Reactions 1 and 2 gave activation energies of 30.1 and 21.5 kcal/gmol respectively. When the rate constants were composed with those arrived at by Shalabi, in a batch system, a difference of several orders of magnitude was found in the coal to preasphaltene and coal to asphaltene reactions. The rate constants for the conversion of coal to THF solubles were compared and found to be several orders of magnitude different. The Activation Energies, however, were comparable. Qualitative comparisons between batch and flow reactor data indicated that a slightly lighter product distribution

was obtained with the CSTR.

It was also found that the reaction of coal to products is nearly complete at 430°C and 10 minutes, thus indicating that if rate data are to be collected at high temperatures, it must be at very short residence times. It was also found that the asphaltene and preasphaltene yields varied little at times greater than 10 minutes for all temperatures.

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INTRODUCTION

Lately there has been considerable concern about the "energy shortage". This is not a shortage of total energy, but rather a shortage of the energy used as liquid motor fuels. The interest in a source for liquid fuels from other than petroleum goes back to the first part of this century. Early work to produce liquid fuels from coal was pioneered by Berguis. Germany, which has no natural petroleum source, fueled much of their war effort during World War II by direct hydrogenation of coal. The plants operated successfully technically, but not necessarily economically during the war. Following World War II the United States Government formed a department to investigate the German developments in the area of coal liquefaction, with an eye toward filling the gaps in domestic crude oil production with a crude made from coal. The discovery in the early 1950's of the large middle east oil fields with their huge resources of cheap crude killed further research into coal liquefaction in this country. Currently, however, with the formation of OPEC and the price increases in crude which followed, interest has renewed in a source of liquid fuel from raw materials other than petroleum.

Coal is a natural choice to investigate for the production of a synthetic crude since there is an abundant domestic supply which can be easily mined. The basic mechanics of the process for high-pressure hydrogenation are fairly well understood, that is mix the ground coal with a liquid medium and heat in the presence of hydrogen. The results, depending on process conditions, are a liquid product which can be upgraded to a refinery feed-stock and a solid which can be used to generate hydrogen or burned as a boiler fuel. Areas not well understood include the effects of the solvent, the effect of catalyst (when used), the kinetics of the overall reactions and a method by which the best coal can be chosen. All of these areas provide quite a challenge to the scientific community because of the nature of the starting material and the complex relationships which can exist within a reactor. Briefly let us look at what coal is and what is thought to happen within the coal and the reactor.

Coal is composed of partially decomposed plant and vegetable matter which has been compacted while being subjected to an increased temperature over a long period of time. The result of this "coalification process" is a hydrocarbon which is high in carbon. The atomic carbon to hydrogen ratio increases from 0.6 to 1.0 as the rank increases from lignite through subbituminous, bituminous to anthracite. The product of the coalification process is far from a homogenous substance. First it is composed of the metamorphosed vegetable matter, which forms the hydrocarbon portion of coal, and second it has dispersed throughout mineral matter, which once was dirt and dissolved salts. The coal seam will vary in chemical and physical properties from top to bottom and side to side such that wide differences in reactivities may exist within a single deposit.

The three analyses used to characterize coals are ultimate, proximate and petrographic. The ultimate analysis gives the percentages of C, H, N, S and O in a coal so that the sum is 100. The proximate analysis gives the 1)moisture, 2)volatile matter, 3)fixed carbon, and 4)ash. Both of these are reported on an as-received and a dry basis. A petrographic analysis consists of the identification of groups of macerals. Macerals correlate to plant structures, see Fig. 1.

As has been seen, coal is made up of vegetable matter which has been altered. The resulting hydrocarbon is one which is substantially aromatic in nature depending on rank and petrographic composition. The coalification process is the process of rejecting oxygen and hydrogen such that the farther along a coal is in this process, the more condensed it becomes. This coalification process gives rise to a

Maceral Group	Maceral	Origin: Source	Origin: Process	Appearance: Color in Thin Section	Appearance: Reflected Light	Chemistry	Technological Behavior: Carbonization	Technological Behavior: Liquefaction
VITRINITE	Telinite (cell walls) Collinite (cell fillings, structureless vitrinite	Woody tissues, bark, leaves, etc.	Mummification	Red-brown	Intermediate grey	Intermediate hydrogen content and volatiles	Principal reactive constituent in coking coal	Susceptible to liquefaction
LIPTINITE (OR EXINITE)	Resinite	Resins	Resistant remains	Yellow	Dark grey	Higher hydrogen content and volatiles; more aliphatic	Reactive during carbonization	Susceptible to liquefaction
	Sporinite	Spore exines						
	Cutinite	Cuticles						
	Alginite	Algae						
	Fluorinite	Plant Oils, Fats			Black			
	Bituminite	Bacterial lipoids, Fats, Proteins	Migration		Between Vitrinite & Sporinite			
	Exudatinite	Exudates from Liptinite & Vitrinites			Black			
INERTINITE	Micrinite (massive & granular	Plant materials	Degradation products	Opaque	White, yellowish, light grey	Lower hydrogen content and volatiles; more aromatic	Generally inert during carbonization	Generally resistant to liquefaction
	Fusinite	Woody tissues, etc.	Fire; biochemical oxidation					
	Semifusinite	Woody tissues, etc.	Intermediate between vitrinite and fusinite					
	Sclerotinite	Fungal sclerotia, hyphae	Resistant remains					

Figure 1. Coal Macerals

general molecular structure for coal of a given rank, however there is no absolute coal molecule. As an example of the different types of molecular structures see fig. 2. A look at fig. 3 gives an idea of what a coal macro molecule looks like, based on indirect structural evidence. As can be seen, there exist clusters of aromatic ring compounds which are cross linked by sulfur, oxygen and aliphatic groups, such that the entire picture is one of a random polymer.

The object of coal liquefaction is to take solid coal and convert it into a liquid form. This can be done by increasing the atomic H/C ratio. Most coals of interest for liquefaction have a H/C ratio of about .8 compared with the H/C ratio for crude oil of about 1.5. This can be accomplished by one of two methods: rejecting some of the excess C, a process known as pyrolysis or by the addition of molecular hydrogen, termed direct liquefaction. This study is concerned with direct liquefaction, in a hydrogen-donor solvent. In the direct liquefaction process what is desired is to reduce the size of the macro molecule while introducing hydrogen into the structure to increase the H/C ratio. This is done best by thermally rupturing the most labile bonds in the macro molecule and thereby producing a molecule which is considerably smaller. The most easily broken bonds are given by Mayo (1977) as:

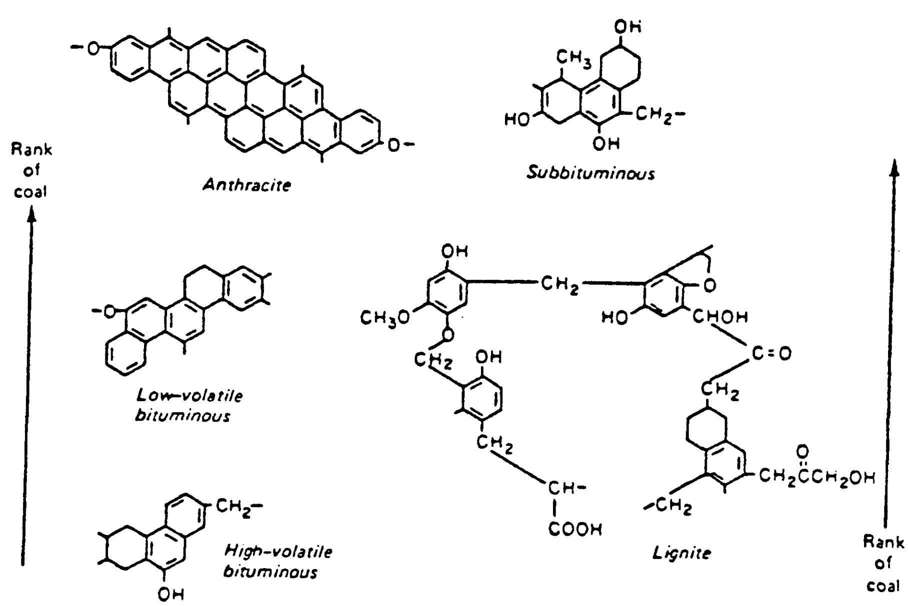


Figure 2. Representative Coal Structures

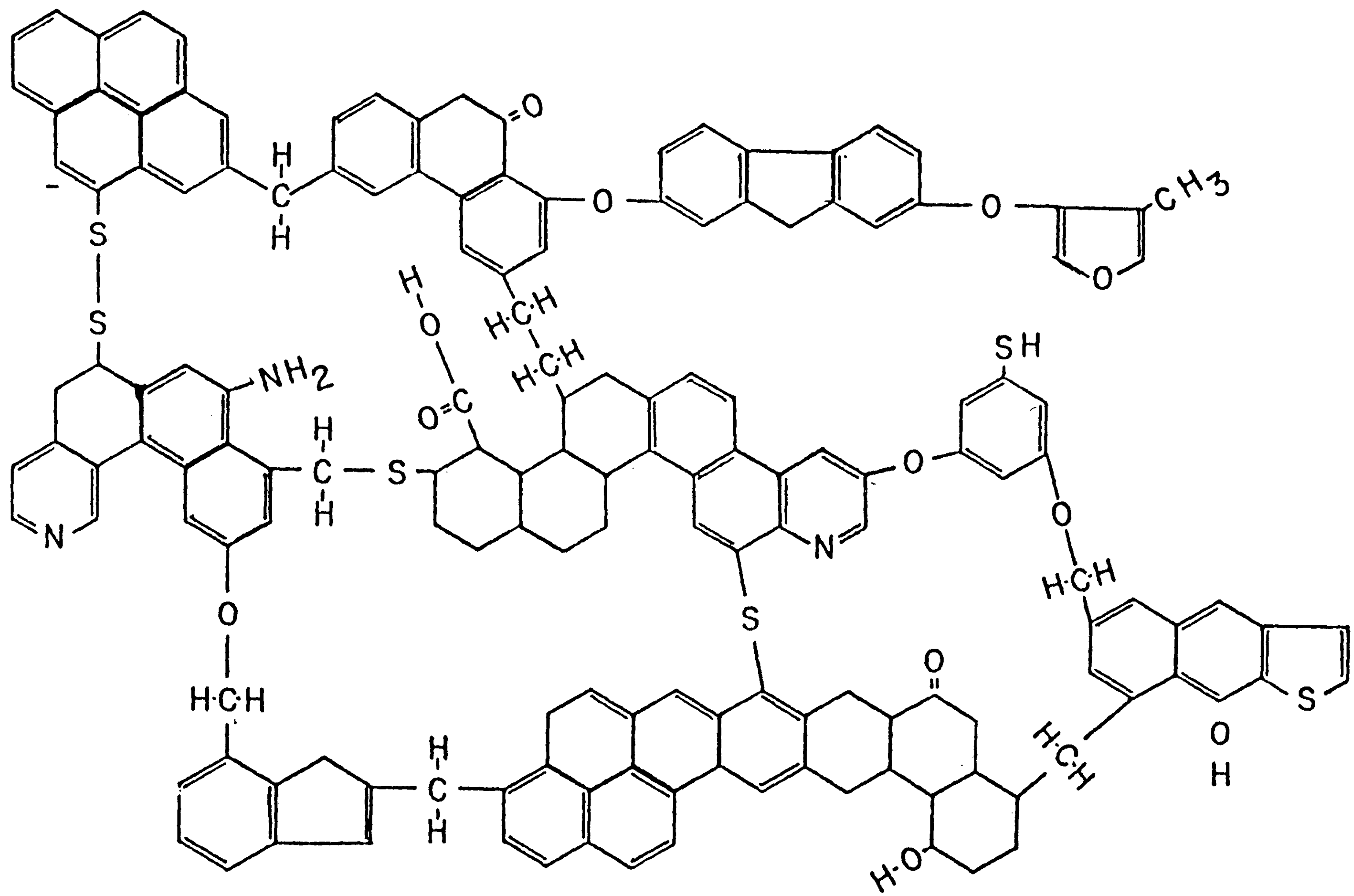


Figure 3. Representative Bituminous Coal Structure

$Ar\text{-}CH_2\text{-}Ar$
$Ar\text{-}(CH_2)_n\text{-}Ar$
Ar-O-Ar
R-O-Ar
R-OR
Ar-S-Ar
R-S-Ar
R- SR

Graphically, some examples of these areas for sission can be seen at points A,B,C, and D in fig. 4.

The reaction mechanism for the direct liquefaction process is thought to follow a free radical route. The initiation step is considered to be thermal cleavage, leaving highly reactive species. During the progation step there can occur a molecular rearrangement which results in a new radical of a different size and possibly a soluble product or a new radical and a gas molecule. The termination steps are where the free radical is capped with hydrogen, or combines with other radicals in the solution. This capping can be done by either molecular hydrogen in solution, or a hydrogen atom from a hydrogen donor solvent. Radical recombination reactions may lead to products of increased molecular weight, and are generally termed regressive reactions. Obviously what is desired is to have the free radical react with a hydrogen molecule so that the

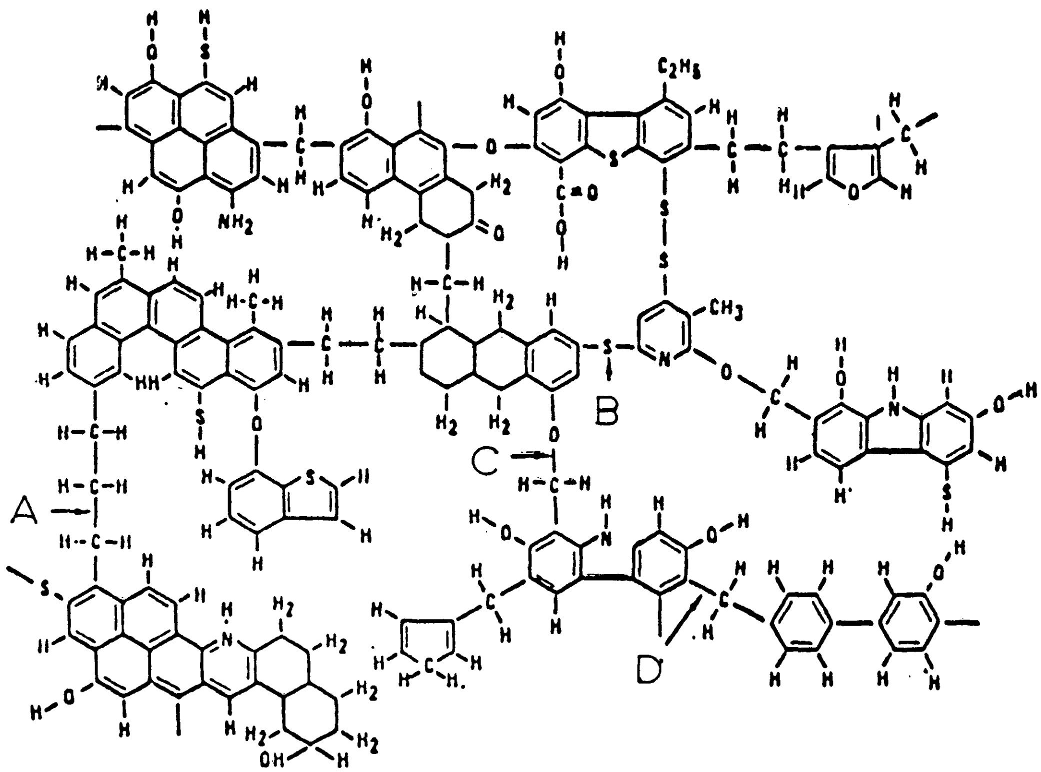


Figure 4. Critical Points of Cleavage of Coal Structure

resulting species is large enough so as not to be a gas, but small enough to be a liquid. The process is neither simple nor straight forward. It is also not a simple coal $\rightarrow$ liquid reaction, but one in which there are many intermediate steps. These steps need to be considered so that an overly simple scheme is not considered, however, since they are not well defined steps they must be considered in a general way.

The nature of the reactions involved brings into consideration several variables in any coal liquefaction study. Some of the important variables are listed below.

Temperature: the effects of temperature are very complex. Some of the areas involved are the possible thermal initiation of the reactions, the physical changes which occur in coals upon heating such as swelling and the observed minimum temperature necessary to dissolve coals in solvents;

Pressure: the pressure affects the amount of hydrogen which is dissolved in the solvent and also can have an important role in vapor liquid equilibrium considerations;

Solvent: the ability of the solvent to donate hydrogen to the reacting coal molecule is of primary importance in direct liquefaction;

Residence time: the time which the coal spends at the reaction conditions is of primary importance in determining the distribution of products from direct hydrogenation.

The products produced by the liquifaction process are defined by their solubility in selective solvents. The oil fraction is that portion which is soluble in pentane or hexane. The asphaltenes are those which are soluble in benzene or toluene but insoluble in pentane. Preasphaltenes are those products insoluble in benzene (toluene) and soluble in tetrahydrofuran or pyridine. The asphaltene and preasphaltene fractions are usually solids at room temperature, and comprise a large portion of what is considered Solvent Refined Coal. When the desired product is an oil the asphaltene and preasphaltenes are considered to be intermediates. A look at the mechanism proposed by Squires (1978), fig. 5 , shows the complex nature of the reactions which exist between the parent coal and the product oil. Referring back to the figures which depict the general structure of the coal molecule, one sees that the asphaltenes and preasphaltene would best be described as fragments of the parent coal or fragments of fragments. Weinberg and Yen (1980) even suggest that asphaltene and preasphaltene like molecules exist in the parent coal. This would tend to lead one to conclude that there exists a "maximum" conversion for a given coal where increasing the

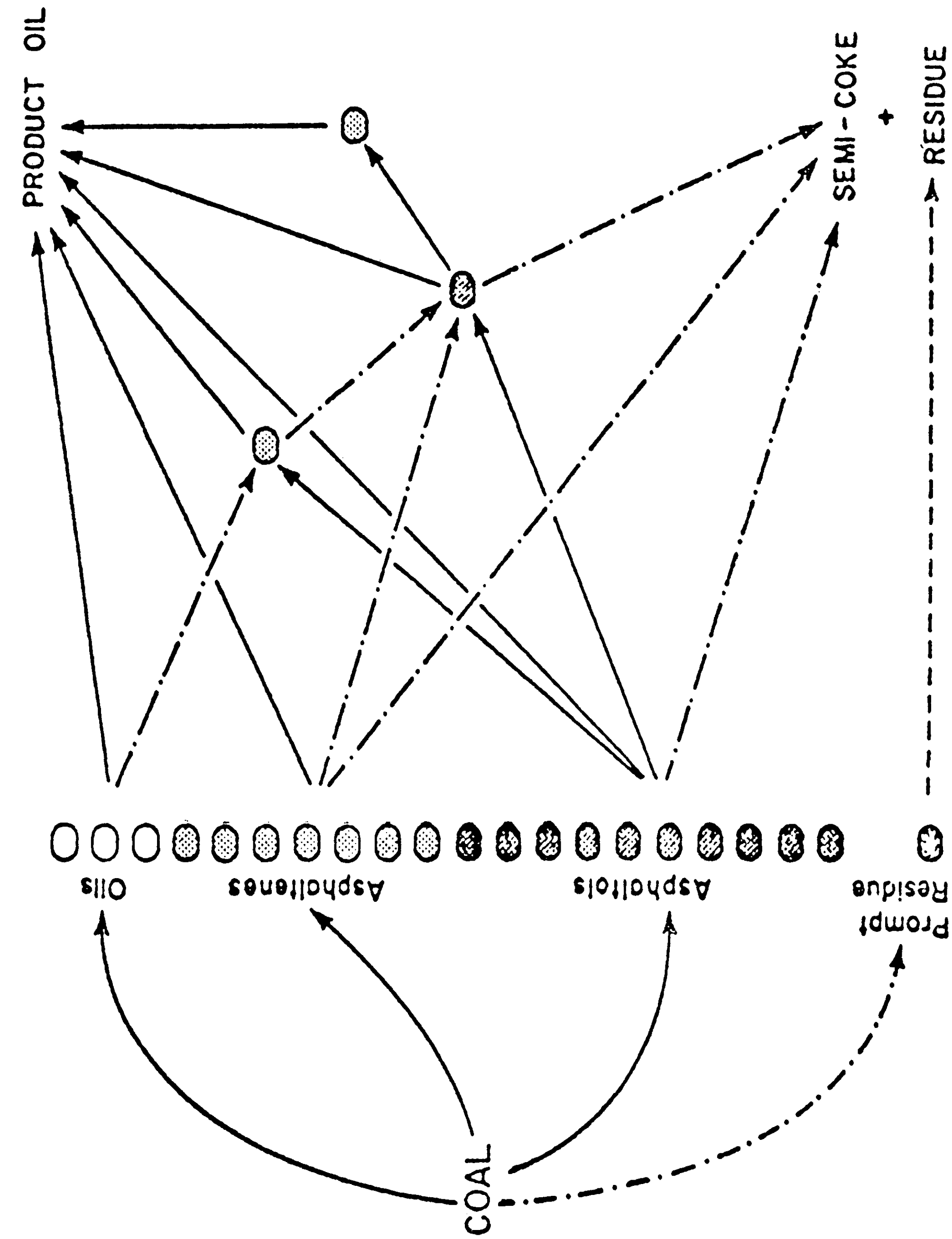


Figure 5. Squires Mechanism

severity of conditions would not have a significant effect.

The objective of this study is to look at one coal in a flow reactor system (CSTR). The information derived from this study will be used as baseline data for the reactor system. Additionally, this study will determine the rate constants for an assumed reaction mechanism. As an ancillary objective, the rate of reaction of coal to products from this study will be compared with that arrived at for a similar coal in a batch system. The comparison will be between product compositions on a qualitative basis since the systems are not identical.

LITERATURE SURVEY

The study of the kinetics and mechanism of coal conversion goes back to the 1940's and continues to this day. The studies which have used batch apparatus are abundant.

Kinetics in Batch Reactors

Storch, et al(1940) studied hydrogenation of Bruceton coal (Pittsburg seam) with tetralin as the solvent in the temperature range of 310 - 415^{o}C. Their data fit a first order plot for benzene solubles with respect to coal remaining. The activation energies for time = 30 minutes were found to differ with temperature as shown below:

Temp.^{o}C	310-355	355-370	370-385	385-400	400-415
Activation Energy(kg cal)	6.6	32.0	56.0	65.0	62.0

Oele, et al(1951) using anthracene oil as the solvent studied the hydrogenation of Limburg, Dutch, coal. They assumed a first order dependence for coal conversion while assuming a zero order dependence on coal conversion for the thermal disintegration of the coal. The expression they arrived at was

$$\ln\left(1 - \frac{x}{a}\right) = k't$$

where a was the equilibrium conversion. This pseudo first order expression successfully modeled the data.

Weller, et al(1951a) studied the hydrogenation of hand picked anthraxylon from a Pittsburg seam coal. The work was done with added catalyst, no oil vehicle and a cold hydrogen pressure of 2500 psig. The temperature range was 400-440^{o}C. Their reaction mechanism was:

$$\begin{tikzcd}
\text{Gases} & & \text{Gases} & & \\
\text{Coal} \arrow[u, "k_1'"] \arrow[d, "k_1'''"] \arrow[rr, "k_1'"] & & \text{Asphalt} \arrow[u, "k_2''"] \arrow[d, "k_2'''"] \arrow[rr, "k_2'"] & & \text{Oil} \\
H_2O & & H_2O & &
\end{tikzcd}$$

The data was found to give a first order fit with respect to coal remaining. The k_1 constants were added to give a new rate constant k_1 and the k_2 constants were treated likewise. These new constants are tabulated below.

Temperature	k_1 Min^{-1}	k_2 Min^{-1}
400	0.027	0.00107
420	0.060	0.00503
430	0.126	0.00895
440	0.129	0.01282

No activation energy was extracted from the rate constants.

Weller, et al(1951b) also hydrogenated some asphalt (asphaltene), defined as hexane insoluble benzene soluble, from a pilot plant run on the hydrogenation of Bruceton coal. From these studies the following rate constants were developed:

Temperature	Pressure	k^1 Min^{-1}
400	2500	0.00107 ± 0.00011
420	2500	0.00503 ± 0.00036
430	2500	0.00895 ± 0.00009
440	2500	0.01282 ± 0.00029
430	1250	0.00440 ± 0.00030

an activation energy of 38.5 k cal/mole was obtained for this reaction.

Falkum and Glenn(1952) using a Spitsbergen coal have modeled the conversion as first order with respect to products of each of two reactions. The reaction scheme which they proposed was:

$$\begin{tikzcd}
\text{Coal} \arrow[dr] & & \\
& \text{hybitenes} \arrow[r] \arrow[dl] & \text{benzene solubles} \\
\text{benzene insolubles} & &
\end{tikzcd}$$

where the hybitenes were a highly reactive intermediate species which the coal had degraded into.

Fabuss, et al(1964) have shown that many cyclic hydrocarbons show a first order self-inhibiting rate effect, which can be modeled as pseudo second order.

Curran, et al(1967) did studies on a West Virginia Coal (Pittsburg seam) with tetralin as the solvent in a shaking autoclave heated by a sand bath. They found that the data could not be modeled by a simple first or second order reaction. Therefore they proposed a parallel first order reaction network:

$$\text{Coal} \underset{k_2}{\overset{k_1}{\rightrightarrows}} \text{Products}$$

where $k_1 > k_2$.

The rate expression used was $a-x = \gamma\ a \exp\{-k_1 t\} + (1-\gamma) a \exp\{-k_2 t\}$ where γ was the fraction of the faster reacting species. The fit to the data was adequate. An activation energy of 30.0 k cal/mole was arrived at for the fast reaction and 38.3 k cal/mole for the slow reaction. They also studied other hydrogen-donor solvents and found about the same amount of hydrogen transfer at equal time and temperature.

Researchers at the University of Utah, Hill, et al(1966), have modeled the dissolution of a Utah bituminous coal using tetralin as the solvent with a second order expression, first order with respect to reactive coal and first order with respect to solvent concentration near the reaction site

$$\frac{dx}{dt} = k(a-x)\ (b-x)$$

Here (a) represents the unreactive coal and (b) the active site. At longer times the reaction was modeled as first order with respect to coal remaining. This change was attributed to the enlarging of the coal pores which enabled the solvent to be in a large excess. They proposed a series mechanism to explain these observations.

$$\begin{array}{l} \text{Coal} + \text{tetralin} \rightarrow Ro + Lo + Go \\ Ro \quad + \text{tetralin} \rightarrow Ri + Li + Gi \\ \qquad\qquad \vdots \\ Rn\text{-}1 + \text{tetralin} \rightarrow Rn + Ln + Gn \end{array}$$

where Ri is a reactive species and Li and Gi are liquids and gases respectively.

Wen, et al(1974, 1975), working with non catalytic batch data from the University of Utah, modeled the dissolution of an Illinois coal in a coal derived solvent as first order with respect to unreacted coal. Their expression was:

$$\ln\left(1 - \frac{x}{a}\right) = -k\,\Theta$$

where Θ was a combination of reaction time, initial reactive coal concentration and solvent to coal ratio. The rate constant was found to be dependent on hydrogen partial pressure. An activation energy of 11 k cal/mole was computed.

Yoshida, et al(1976a, b), working with Sumiyoshi brown coal from Hokkaido, have postulated a mechanism with the parallel - series approach.

$$\text{Coal} \xrightarrow{k_3} \text{Oil } (S_1)$$

$$\text{Coal} \xrightarrow{k_1} \text{Asphaltene} \xrightarrow[k_2]{} \text{Oil } (S_2)$$

Their work was with a shaking type autoclave reactor using decrystallized anthracene oil as the vehicle and red mud as the catalyst. The temperature was 400°C, the pressure range was 19.6 - 21.6 MPa and the residence time was 7 - 120 minutes. One conclusion was that the S_1 oil production reaction was not seen in "foreign coals," however, no information is given as to the foreign coal used.

The rate constants calculated were:

	Min -1			
Coal	k_1+k_3	k_1	k_2	k_3
Taiheiyo	0.020	0.0037	0.0049	0.0170
Oyubari	0.013	0.0090	0.0044	0.0046

The mechanism suggests that the S_1 oil is produced immediately while the oil from asphaltene is produced more uniformly during the whole process.

Guin and Tarrer (1976c) have modeled batch conversion data by assuming that the coal dissolved by a first order dependence on the concentration of unreacted coal, and that the coal conversion proceeded as two parallel reactions. The rate equations formulated were:

$$r_{c_1} = -k_{c_1} \left(C_{c_1}\right) \left(C_{H_2}\right)^2$$

$$r_{c_2} = -k_{c_2} \left(C_{c_2}\right) \left(C_{H_2}\right)^2$$

where c_1 and c_2 are coal fractions of different reactivities and C_{H_2} is the concentration of dissolved hydrogen.
When doing batch reactor studies, with other than micro-reactors, there can be a problem with the determination of the actual reaction time due to the sometimes extended heat up and cool down periods required.

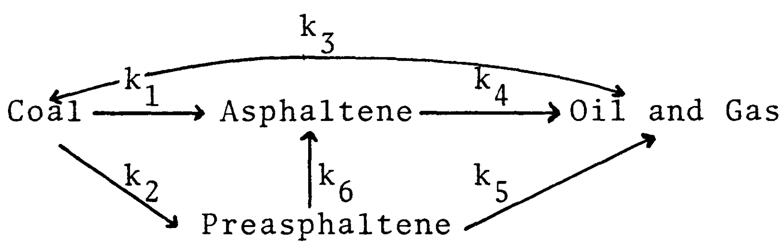
In an attempt to obtain more accurate reaction times Liebenberg, et al(1973) developed a procedure wherein a time zero sample was removed from the reactor when the desired temperature was reached. Chemically pure tetralin was used as the solvent, pressures ranged from 160 - 200 bar and temperatures from 380 - 440^{o}C. Again it was found that the benzene insoluble portion satisfied the requirements for first order kinetics. However, only about half the data is reported to have fit, which half is not reported. After failing to fit first a series and then a parallel mechanism with the data a parallel - series mechanism was postulated.

$$\text{Coal} \xrightarrow{k_1} \text{Asphalt} \xrightarrow{k_2} \text{Heavy oil}$$
$$\text{Coal} \xrightarrow{k_3} \text{Asphalt}$$
$$\text{Coal} \xrightarrow{k_4} \text{Heavy oil}$$

Here the heavy oil is the bottoms from a vacuum distillation of the benzene and n-hexane soluble product. No attempt was made to determine the constants k_1 - k_4.

The study of Shalabi, et al(1978) has produced an accurate zero reaction time. In their work a paste of coal and tetralin was injected into a stirred autoclave containing tetralin which was up to temperature and pressure. Reaction pressure was 2000 Psig and the temperature varied from 300 - 400°C.

The most adequate proposed mechanism was:

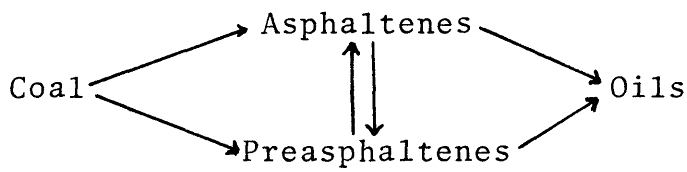


The rate constants were extracted from the rate data, and are given below.

TEMP	k_1	k_2	k_3 (hr-1)	k_4	k_5	k_6
400	.04546	.07150	.02646	.00279	.00284	.00385
375	.02697	.05202	.01870	≃0	.00183	.00225
350	.00789	.01214	.01214	.00081	.00269	≃0

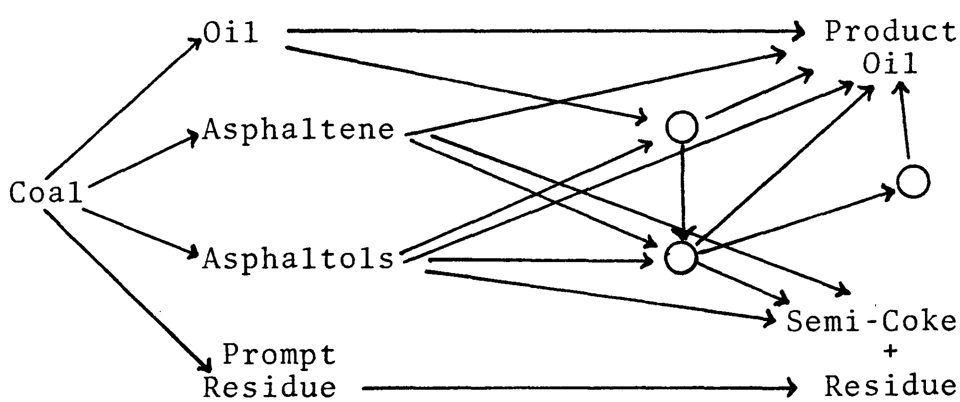
The fits of experimental points to a predicted trajectory are quite good with the exception of the gas and oil. The authors acknowledge that this may be due to the lumping of those two products.

Schwager and Yen (1978) have concluded from their work that the following mechanism is more probable than a straight series mechanism.



This conclusion was arrived at because the H/C ratio in the preasphaltenes was lower than in the parent coal, and that only a parallel - series mechanism can account for this phenomenon.

Squires (1978) has, by looking at the work of various authors, proposed a reaction mechanism where the various liquefaction reactions, including regressive reactions, are depicted as shown below:



Gun, et al(1979a, b) looked at the kinetics of the conversion of a coal to benzene solubles in three different systems: (1)solvent and catalyst, (2)solvent, and (3) catalyst. The temperature range was 390 - 410°C. Those runs done in the presence of a solvent were in a stirred autoclave. The catalyst only runs were done in a rocking autoclave. They found that the reaction order varied from about .5 to 2.0. A kinetic expression of the form

$$\frac{-dC}{dt} = k_1\{C\}^{n_1} + k_2\{C\}^{n_2} + k_3\{C\}^{n_3}$$

was arrived at where $n_1 = 1.0$, $n_2 = 1.5 - 2.0$, $n_3 = 0.5 - 1.0$. This indicates the interplay of multiple reactions.

They then continued using a free radical reaction scheme and the following mechanism

$$\text{Coal} \begin{array}{l} \nearrow \text{gas and benzene soluble products} \\ \\ \searrow \text{intermediates} \rightarrow \text{gas and benzene soluble products} \end{array}$$

to develop a series of rate equations which led to the development of the following overall rate equation

$$\frac{d\{Pm\}}{dt} = \beta_1\{C\} + \beta_2\{C\}^2 + \beta_3$$

where Pm is gas and benzene solubles

C is organic matter in coal

β's are constants.

Mori and Davis (1980) studied Kentucky #9 and #11 coals in a microautoclave using tetralin as the solvent and a Co - Mo/Al_2O_3 catalyst. The reaction time was 15 minutes. It was found that there was an apparent maximum conversion between 400 and 450^oC for the uncatalytic reaction. Also found was that the maximum conversion based on pyridine solubles was the same for Kentucky #9 and #11.

Gertenbach (1980), using a Kentucky #9 coal and an SRC Recycle solvent has found that some of the coal liquefaction reactions are reversible.

Whitehurst (1976) and Farcasiu, et al (1977) have found that preasphaltenes are the primary products of the disintegration of coal and that these are then in turn converted to asphaltene and oil by parallel reactions.

The regressive reactions have been noted by many of the investigators in the course of their work. In addition to these, Storch (1940) used the existence of regressive reactions to explain an observed decrease in conversion of a Pittsburg coal in tetralin at long residence times. Farcasiu, et al(1977) have reacted preasphaltenes and asphaltenes and produced all solvent fractions. Yen (1978) reacted an isolated oil fraction with tetralin and produced 10% asphaltenes. Whitehurst, et al(1979) have found that for bituminous coals there is negligible regression when adequate hydrogen donors are present.

Kinetics in Flow Reactors

Those studies which have utilized flow systems for the investigation of coal liquefaction kinetics are far less in number than the batch studies. The reason is obvious as the flow systems are more complicated and are more difficult to operate on a small scale than the batch systems.

Lewis (1976) working at the Wilsonville pilot plant has used a first order equation to model his plug flow conversion data. Lee, et al(1977, 1978) have also modeled data from the Wilsonville pilot plant, using a dispersion model comprised of previously developed hydrogenation, desulfurization and dissolution correlations.

Wen, et al(1974), Wen and Han (1975), Wen, et al(1978) and Wen (1978) from the University of West Virginia have demonstrated that conversion is a function of Reynolds Number in continuous units, due to a proposed coating of the coal particles with preasphaltenes and asphaltenes.

Rash and White (1978) have noted that continuous reactors give a much more saturated product than batch reactors when using a catalyst.

The investigators working at the Pittsburgh and Midway Coal Mining Company (1978) have used first order kinetics to describe the disappearance of vacuum residual material and the production of total-distillate-range material in a bench-scale flow reactor system.

Han, et al(1978) have used a first order reaction model developed from batch work to model tubular flow data from Pittsburg and Midway Coal Mining Company research laboratory in Merriam, Kansas, and the Pittsburg Energy Research Center to arrive at the following expression:

$$\ln (Xe - X) = k\theta$$

where X is the conversion and Xe is the conversion at equilibrium.

Wen, et al (1978) and Wen (1978) have expanded this model to include an intermediate in the form of asphaltene and have proposed a series reaction network of the form:

$$\text{Coal} \rightarrow \text{Asphaltenes} \rightarrow \text{Oils}$$

They then used this mechanism to predict, successfully, asphaltene and oil concentrations in the synthoil process.

In a departure from the products of liquefaction being denoted as oils, asphaltenes, and preasphaltene, Fant (1976) has attempted to correlate liquefaction data by grouping similar reacting species into "boiling pools" where

$$P_1 \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} P_2 \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} P_3$$

Fant (1977a), from Exxon Research, has developed a free radical mechanism for coal liquefaction:

$$\begin{aligned}
C &\xrightarrow{k_1} L + R + P \\
L + R &\xrightarrow{k_2} P \\
R + R &\xrightarrow{k_3} G + P \\
R + R &\xrightarrow{k_4} 2L \\
R + H_2 &\xrightarrow{k_5} L + H \\
R + H &\xrightarrow{k_6} L \\
2H &\xrightarrow{k_7} H_2
\end{aligned}$$

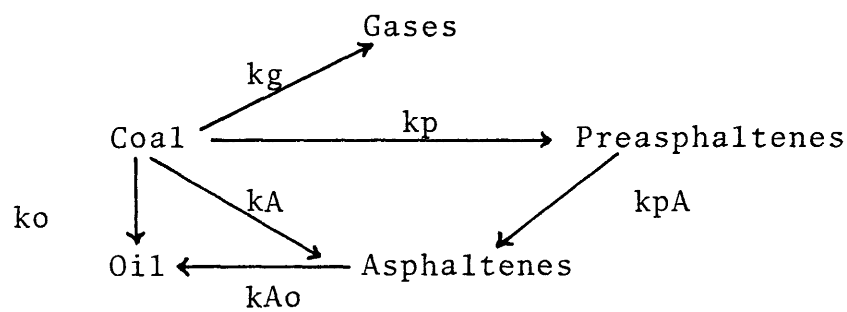
where R is reactant, P is product, L is liquid, G is gas and H is molecular hydrogen.

Fant (1978) and Brunson (1979) have continued with the idea of reacting species. Using rate data from an Illinois bituminous and a Wyodak subbituminous coal with an internally generated recycle solvent in a tubular reactor, they have proposed the following mechanism:

$$\begin{aligned}
\gamma &\xrightarrow{\text{instantaneous}} \text{Gas} \\
x_{\downarrow} &\xrightarrow[k_{x2}]{k_{x1} + k_{\beta}} \text{and} \\
\beta &\xrightarrow{k_{\beta}} \text{Liquid} \\
w &\quad \text{no reaction}
\end{aligned}$$

The β fraction is taken as the vapors evolved from the ASTM D=86 distillation procedure and the w is taken as those portions of the coal which are not liquefiable, ie. mineral matter, fusinite and micrinite.

Cronauer, et al(1978) have studied the kinetics of coal liquefaction in a continuous stirred tank reactor. Their work was done with a subbituminous coal from the Belle Ayr Mine using hydrogenated anthracene and hydrogenated phenanthracene as the vehicle. Hydrogen pressure of about 3000 Psig and temperatures of 450 - 470^{o}C were used. The space time varied from 5 - 40 minutes. The proposed mechanism was



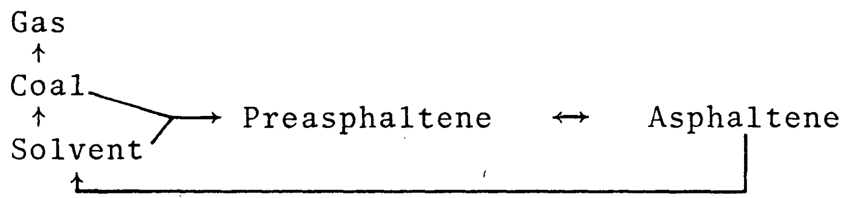
By using pseudo first order kinetics and solving for the rate constants the model predictions were compared with the experimental data to produce an adequate fit.

Thomas and Traeger (1979) have done low temperature (200 - 300^{o}C) studies in a flow reactor. Their conclusion is that at these temperatures the free radical process need not be invoked, but that liquefaction can be initiated by the solvent such that

Coal + Solvent $\rightarrow$ Preasphaltene

Thomas and Bickel (1980), working with an Illinois No. 6 coal and an untreated SRC-II heavy distillate in a tubular flow reactor, have postulated a mechanism where the solvent has an active role. The temperature range was 400 - 475^{o}C with a working pressure of 2000 Psi and gas flow rates 10 - 200 MSCF per ton of coal.

The mechanism is:



They have also ventured to give the stoichiometry for the reaction process, at 450^{o}C as:

$$\text{Coal} + 3\ \text{Solvent} \rightarrow \text{Preasphaltene}$$

$$\text{Preasphaltene} \rightarrow 2\ \text{Asphaltene}$$

$$\text{Asphaltene} \rightarrow 3\ \text{Oil}$$

Zielke, et al(1980), using a continuous stirred tank reactor with molten $ZnCl_2$ as the catalyst and a solvent which is aromatic but derived from petroleum, have modeled the data as a pair of first order reactions, one of which is fast and the other which is slow. From the expression for a series of n continuous stirred tanks where

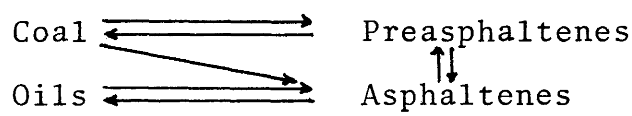
$$f = \frac{1}{(1+k\theta)^n}$$

they developed the expression

$$f = \frac{N}{1+k_1\theta} + \frac{1-N}{1+k_2\theta}$$

where f is the unconverted MAF coal, N is the fraction converted via the fast reaction, k_1 is the first order rate constant for the fast reaction, k_2 is the slow rate constant and θ is the residence time.

Gertenbach (1980) has modeled a continuous stirred tank reactor successfully. The coal used was a Kentucky #9 and the solvent was a recycle solvent from the Ft. Lewis Pilot Plant. Temperatures ranged from 340^{o} - 440^{0}C and 2000 Psig hydrogen provided the pressure. The mechanism developed was:



As can be seen, the regressive steps have been given much consideration in this reaction network.

Solvents

Neavel (1976) has described the initial dissolution of coal in the liquid vehicle as a physical dispersion, and has stated that an organic vehicle without hydrogen donating ability can dissolve coal as well as one with donating capacity. The hydrogen donating capacity of a vehicle becomes important when the hydrogenation process itself starts. The theory is that when free radicals are formed, labile hydrogen on a donor molecule will be easily abstracted producing a stabilized free radical and a hydrogen-deficient donator.

Thomas and Bickel (1980) suggest that solvent is a reactant with the coal in the early stages of the liquefaction process, and is in turn regenerated during the process.

Burke, et al(1981) studied recycle solvents from the Wilsonville SRC-1 pilot plant and found that as the solvent increased in saturates and mono-aromatic heteromolecules its quality as a liquefaction medium declined.

Kang, et al(1976) found when working with Black Mesa coal, a subbituminous coal, that the hydro-aromatics produced during the hydrogenation process tended to be better donors than tetralin.

Briggs, et al(1980) have found that tetralin can act as an antisolvent for the heavier products of liquefaction such as preasphaltenes and heavy asphaltenes.

Orchin and Storch (1948) found that liquefaction of coal in the presence of hydrogen proceeds equally well with an aromatic or hydro-aromatic compound but that the best results were obtained when the vehicle contained a hydroxyl group on an aromatic ring. They found that tetralin was enhanced as a liquefaction vehicle when cresol was added.

Kamiya, et al(1978) have found that phenolic compounds have a positive effect on coal liquefaction in the presence of tetralin. They suggest that the phenol acts in several ways. First, by being acidic, they can be involved in the rupture of methylene-aromatic bonds. Second, the polarity of the solvent can stabilize coal fragments. Third, phenols will penetrate the micropores of the coal molecule because of their affinity for oxygen-containing structures and promote swelling thus giving fast dissolution.

Pott and Broche (1934) found that the best solvent was a mixture of tetralin and low temperature tar phenols. The next best solvent was 40 percent tetralin, 20 percent phenols and 40 percent naphthalene.

Whitehurst, et al(1976) have developed a solvent which has a minimum number of components and still matches as closely as possible the important properties of pilot plant recycle solvents. They found that there was no coal conversion difference between their solvent and recycle solvent. The solvent developed had the following composition:

Wt%	Component
43%	Tetralin
38%	2-methylnaphthalene
17%	P-Cresol
2%	γ-Picoline

EQUIPMENT

Continuous Reactor

The process equipment used in this study was built and tested by Barker (1976) and later modified by Gertenbach (1980). The reader is referred to the above thesis for detail regarding the reactor system employed. Several areas within the system have been modified during this study, which are described below.

The system can be operated as either a tubular flow reactor or as a continuous flow stirred tank reactor. The unit has a maximum coal throughput of 0.6 kg/hr. The entire unit is enclosed within an explosion barricade with walls of a metal-plywood-metal laminate construction which is attached to the concrete floor and ceiling and to the external brick walls. The walls are essentially designed to stop projectiles and the room has an external window which acts as a blow-out panel in the event of an explosion. The unit is operated from an external control room in which all the necessary controls are located and where all the sampling can be accomplished. The sub sections of the unit are:

- gas feed system
- slurry feed system
- preheaters and reactor
- high pressure separators and liquid sampling system
- low pressure separator and gas sampling system
- gas clean up system

Figure 6 shows the schematic of the entire continuous process unit. Abbreviations and notations can be found in Table 1.

Gas Feed System

The gas feed system is shown in fig. 7. Gas is supplied to the system by high pressure industrial compressed gas cylinders (k-size). A Hoke regulator provides an adjustable inlet pressure to the suction of an Aminco diaphram compressor, model 46-13411. The gas flow rate is controlled by regulating the inlet pressure to the compressor. Figure 8 gives the compressor calibration curve. Gas flows from the compressor to a 2 liter surge tank to dampen oscillations in the compressor outlet. From the surge tank, gas can be delivered to the stirred tank reactor, to the bottom of the tube flow section or to the entrance of the fluidized sand bath preheater (the last was used in this study). A Mercoid pressure switch, separated from the gas by a Mercoid diaphram pressure transmitter, monitors the compressor discharge pressure and will shut down the compressor in the event of an overpressure. All tubing in the gas feed and delivery system is 316 stainless, 0.25 inch O.D., with 0.049 inch wall thickness.

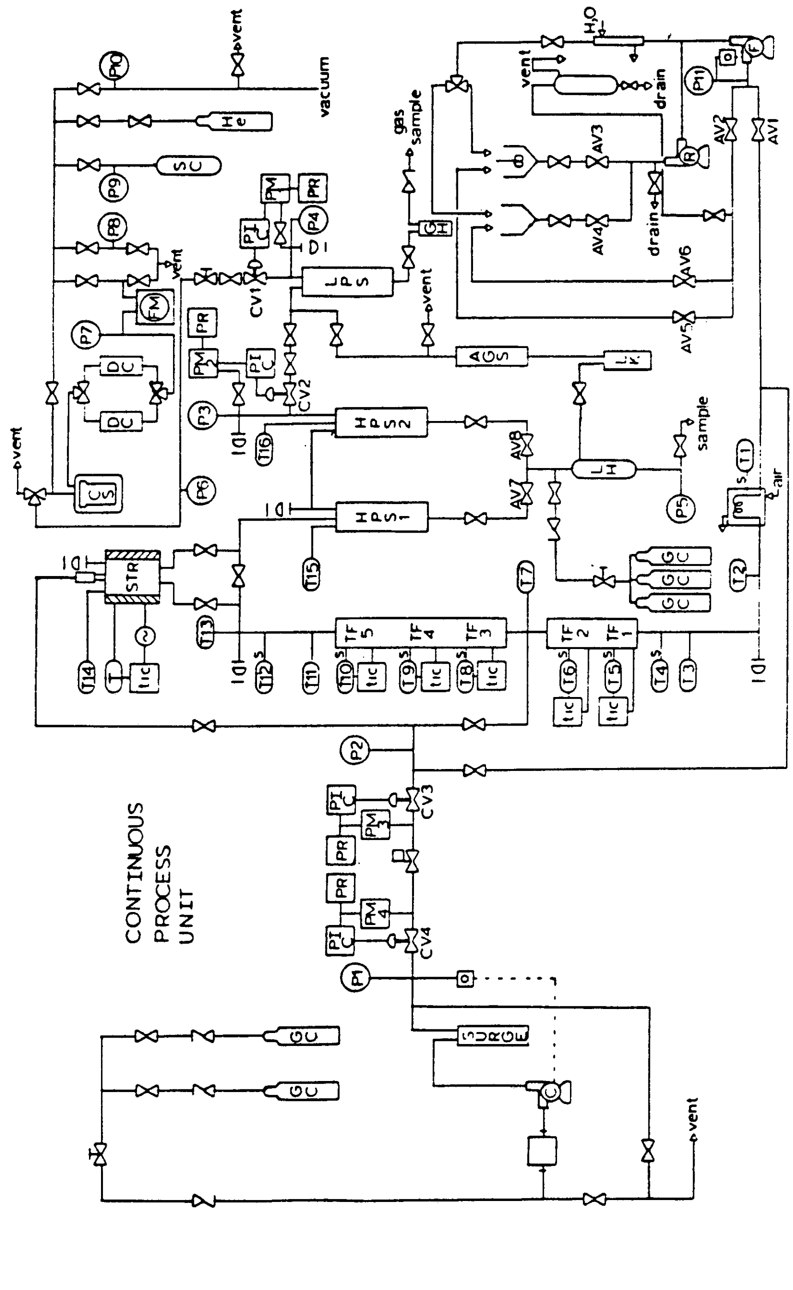
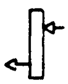
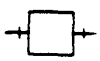


Figure 6. Continuous Process Unit

TABLE 1

ABBREVIATIONS AND NOTATIONS

	Compressor
	Feed Pump
	Recycle Pump
	Rupture Disc
	Manual Valve
	Check Valve
	Metering Valve
	Heat Exchanger
	Line Filter
	Inline Thermocouple
	Surface Thermocouple
	Fluidized Bed Preheater
	Pressure Switch
	Magnetic Stirrer
	Stirrer
	Heater
	Regulator Valve

GC	Gas Cylinder
He	Helium Gas
FM	Flow Meter
SC	Sample Cylinder
AV	Air Valve
CV	Control Valve
GH	Gas Holding
LK	Liquid Knock-out
LH	Liquid Holding
PM	Pressure Measuring Device
PIC	Pressure Indicating Controller
PR	Pressure Recorder
P	Pressure Guage
DC	Dessicant Column
CS	Caustic Scrubber
AGS	Acid Gas Scrubber
TIC	Temperature Indicating Controller
TF	Tube Flow Heater Section
STR	Stirred Tank Reactor
HPS	High Pressure Separator
LPS	Low Pressure Separator

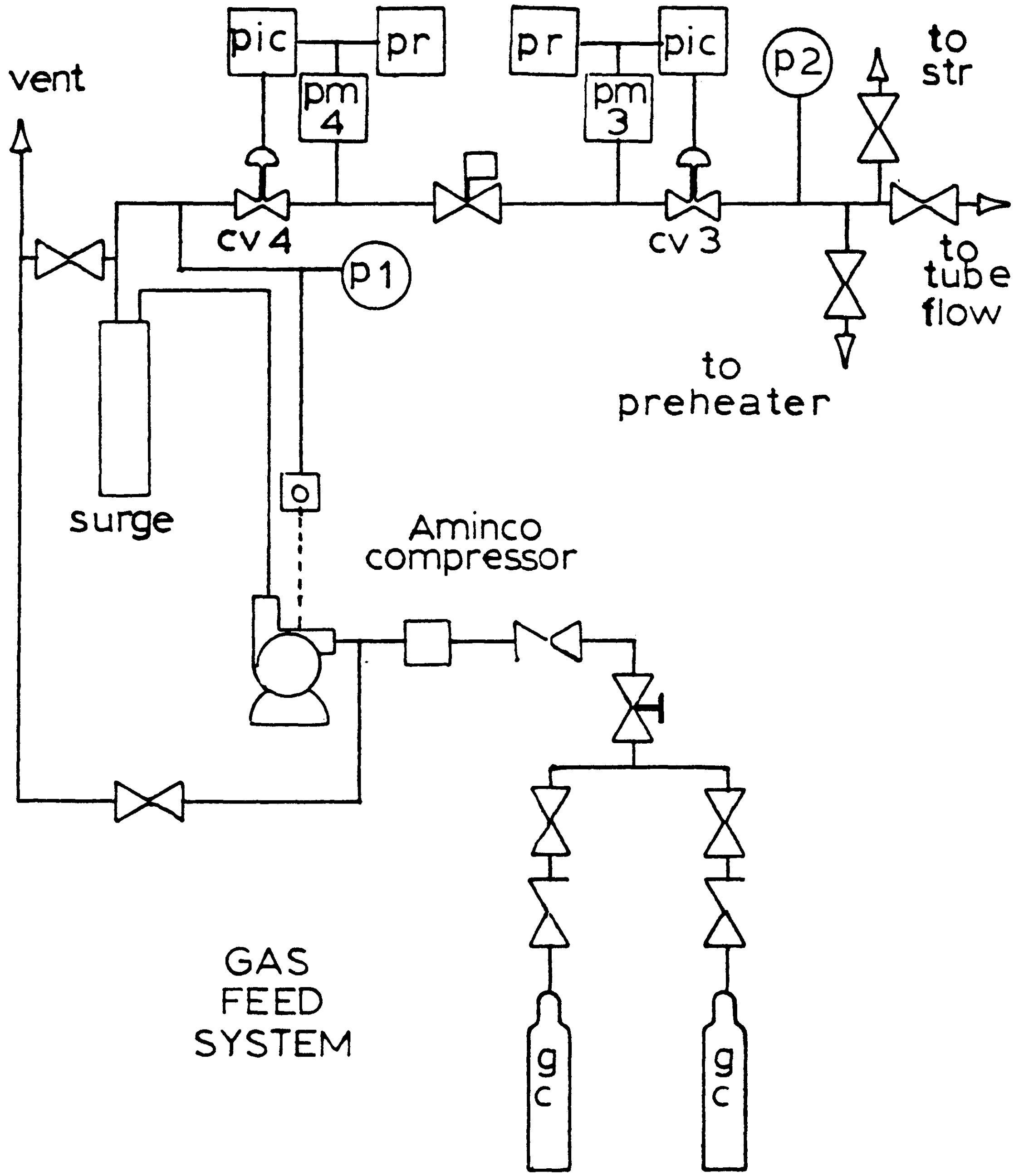


Figure 7. Gas Feed System

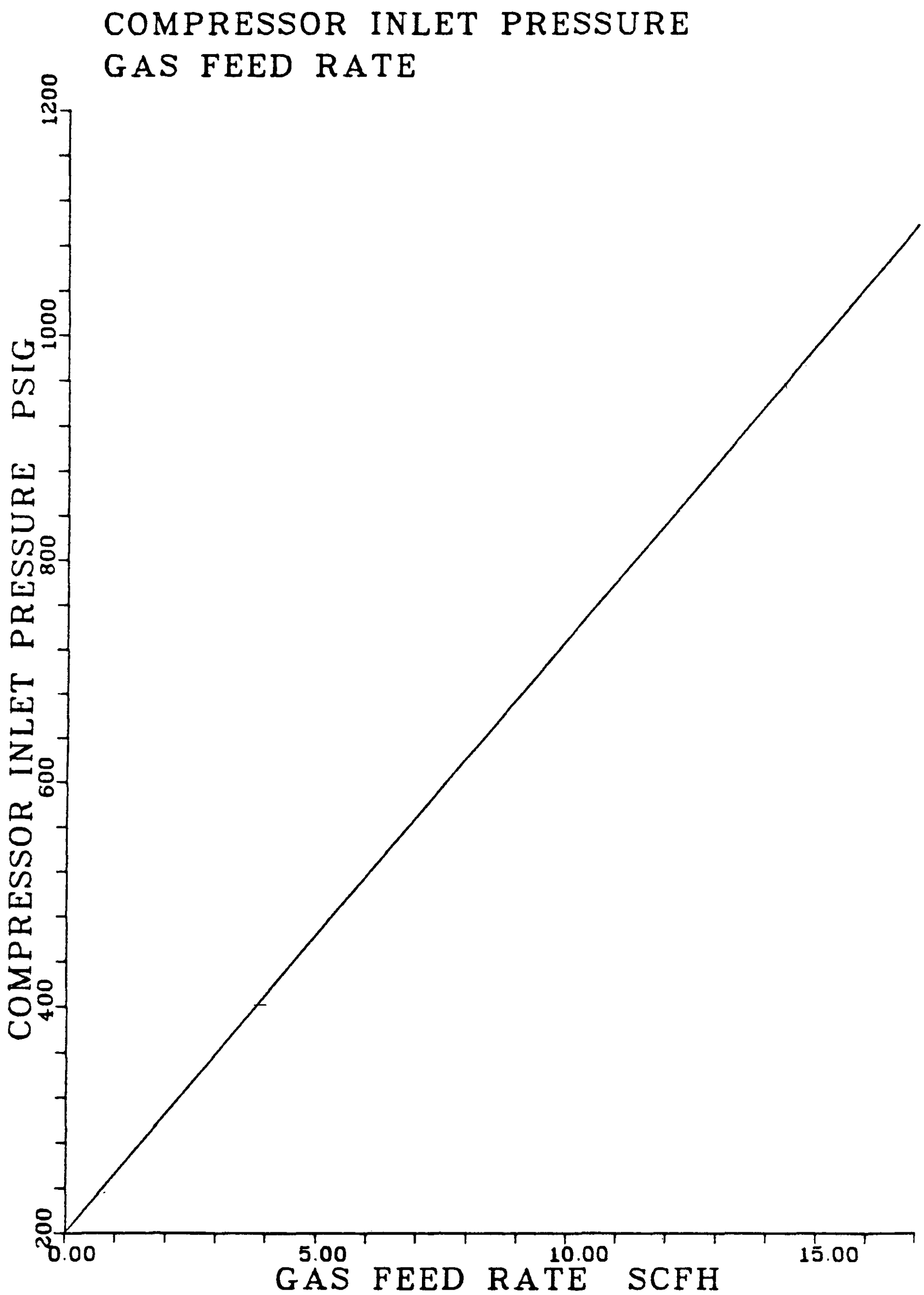


Figure 8. Compressor Calibration Curve

Slurry Feed System

The slurry feed system, Figure 9, delivers the oil-coal mixture to the unit at system pressure. Two tanks are provided, one for slurry which contains a variable speed mixer and the other for solvent. The slurry is continuously recycled past the inlet to the feed pump by an Eastern, model 483542-EW, centrifugal pump, providing a positive suction head. A heat exchanger is provided in the recycle line to prevent heating of the slurry. The feed pump is a Milton Roy, model "C", plunger pump with an adjustable stroke. The calibration for the feed pump is shown in Figure 10. The feed pump can be operated in either a recycle mode, to return the liquid back to the feed tanks, or to supply the reactor system. A blow down system is provided to relieve the pressure trapped between valves 1 and 2 and the feed pump upon a shut down. A Mercoid pressure switch, isolated from the slurry by a Mercoid pressure transmitter, will shut the feed pump off in the event of an overpressure. Valves 3 and 4, controlling the liquid lines under atmospheric pressure, are Whitey air-operated ball valves. Valves 1 and 2, controlling the liquid under system pressure, are Autoclave Engineers high pressure air operated valves. The tubing in the recycle portion of the slurry feed system is 316 stainless, 0.375

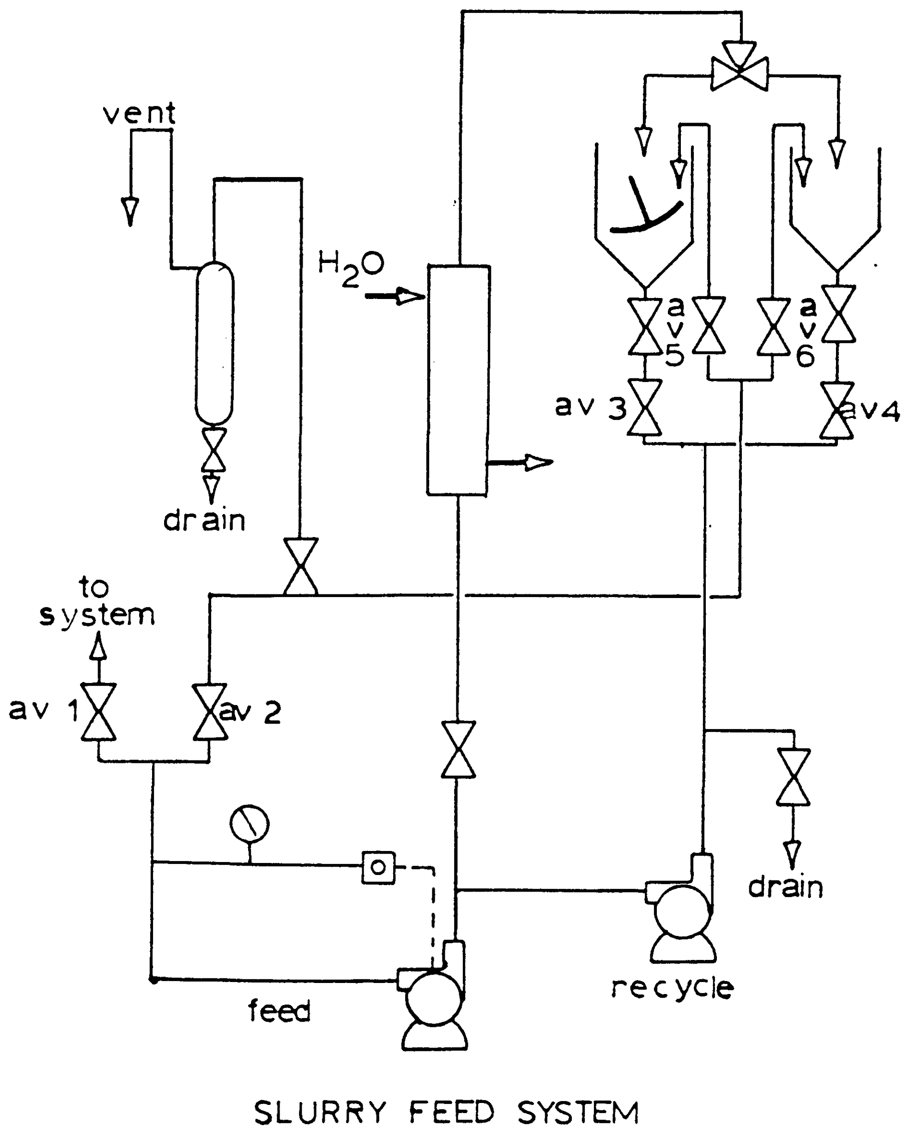


Figure 9. Slurry Feed System

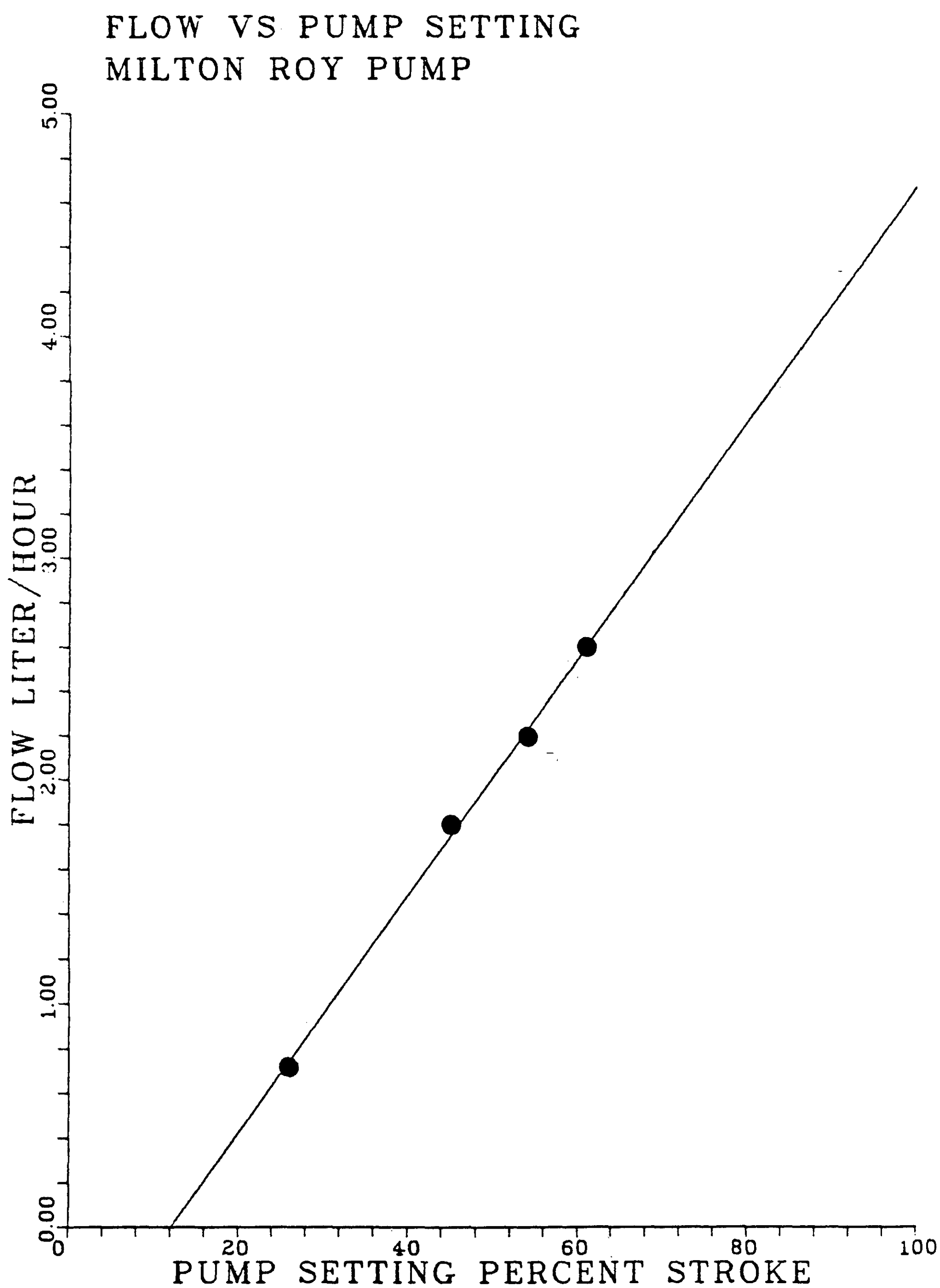


Figure 10. Feed Pump Calibration Curve

inch O.D., with 0.049 inches wall thickness. The tubing in the high pressure section is 316 stainless, 0.375 inch O.D., with 0.086 inch wall thickness.

Preheaters and Reactors

The preheaters and reactors are shown in Figure 11. The first section of this part of the unit is a fluidized sand bath, Tecem Model SBL-1, in which is a 20 foot coil of 0.250 inch O.D. 316 stainless steel tubing. Next are the tubular flow sections. These sections can either be 0.375 inch O.D., as used in this study, or 1.00 inch O.D. tubing. The tubing is encased within an aluminum sheath, to provide even heating and reduce hot spots. The tubular flow heaters are Thermo-line electrical resistance furnaces with 2 zones and 3 zones, respectively. Temperature control is provided by Athena, model 2121-P-O, proportional controllers which maintain a fixed wall temperature. Thermocouples monitor the fluid and the skin temperature as shown. The reactor used in this study was an Autoclave Engineers 1.0 liter stirred tank reactor. The volume in the reactor is maintained at 500 ml. by a dip tube, which serves as an exit for both the liquid and the gaseous effulent. The reactor was stirred at 1500 r.p.m. to ensure constant concentrations and to minimize mass transfer effects. Heat for the reactor is provided by

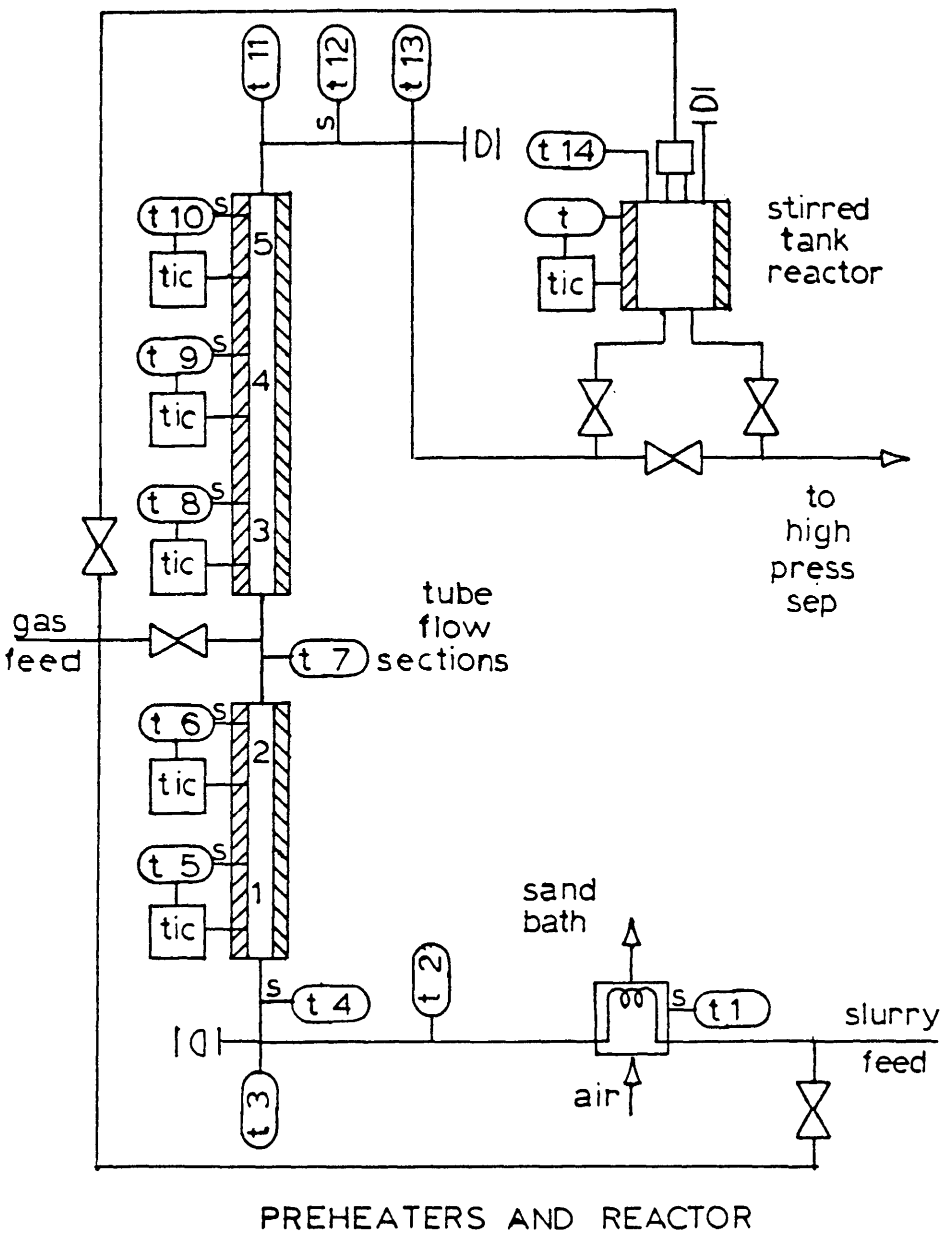


Figure 11. Preheaters and Reactors

a heating jacket controlled by a Honeywell, model R7355C-1025-1, controller. Liquid temperature is monitored by a thermocouple inserted into the reaction mass. The system can either be operated with or without the stirred tank reactor. All valves and fittings are Autoclave Engineers high pressure (20,000 psi, 1200^{o}F). Tubing is 0.375 inch O.D. with 0.086 inch wall thickness, 316 stainless steel.

Liquid Sampling System

The high pressure separators and liquid sampling system are shown in Figure 12. The separators are Autoclave Engineer 2.0 liter vessels, in which the liquid is disengaged from the gases. Liquid is collected in the separators until drained into the 1.0 liter liquid holding tank. This is a batch drain system and back pressure on the holding tank, about 1500 psig., is provided by helium cylinders. This is done to prevent excessive pressure excursions in the reaction system when the high pressure separators are drained. The pressure from the sampling system is let down through a liquid demister vessel filled with steel wool, through a dry acid gas scrubber and either vented to the atmosphere or to the low pressure gas system. Back-pressure is maintained on the system by a Research Control Valve (air to close) controlled by a Acco Bristol model OB5645C,

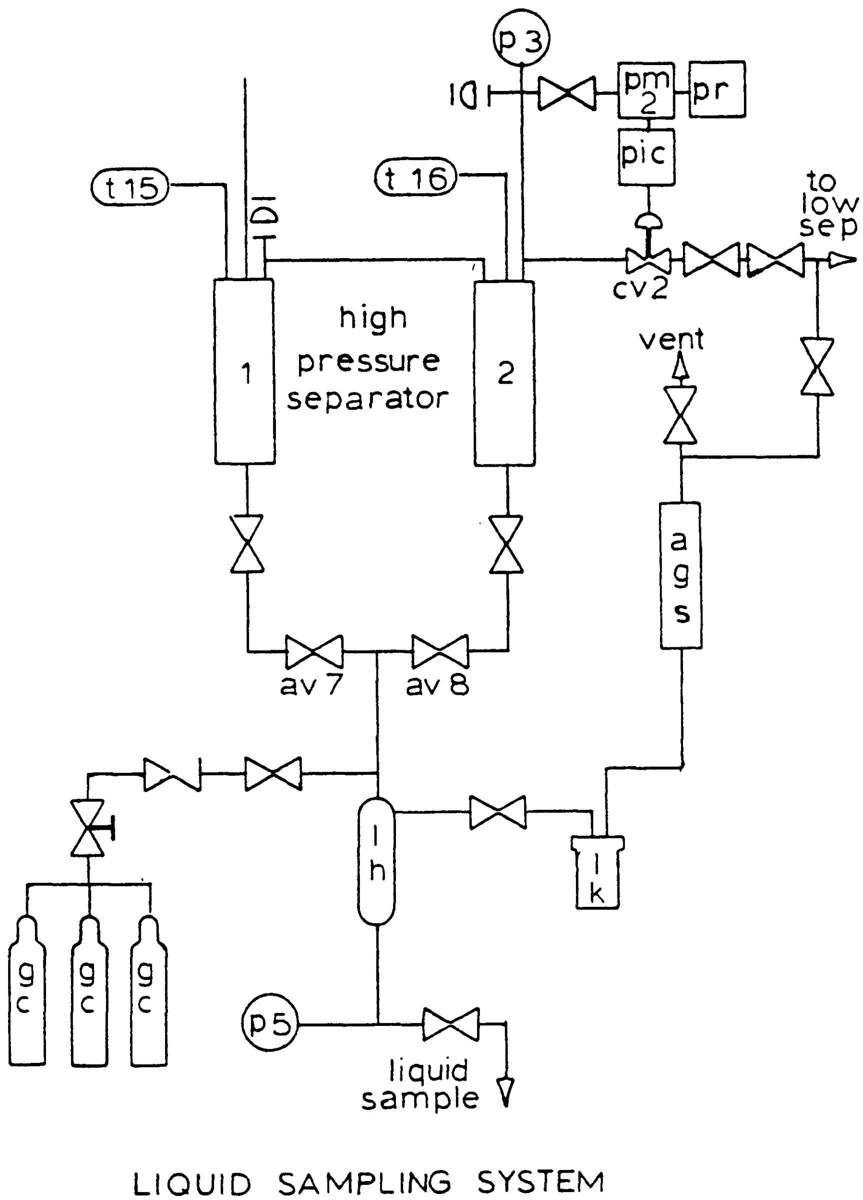


Figure 12. Liquid Sampling System

controller.

Gas Sampling System

Shown in Figure 13, the gas sampling system consists of a 2.0 liter Autoclave Engineers low pressure separator and a 500 ml. sample cylinder. The low pressure separator is used as a surge tank which collects product gases. The sample cylinder can be purged and evacuated then charged with the gases from the low pressure separator. Pressure on this section of the system is maintained by a Research Control, air-to-close, valve controlled by an Acco Bristol, model OBJ645C, controller at about 40 psig.

Gas Clean Up System

The gas clean up system, Figure 14, processes gases from the unit. The gases first go through a caustic scrub, to remove H_2S, then to a demister packed with glass wool. From there gases pass through a dessicant column to remove any moisture and to a dry gas meter, Rockwell model D75-S. Gases are then vented to the atmosphere.

Miscellaneous

The temperatures are recorded on an Acco Bristol 24 point temperature recorder. Pressures are recorded on

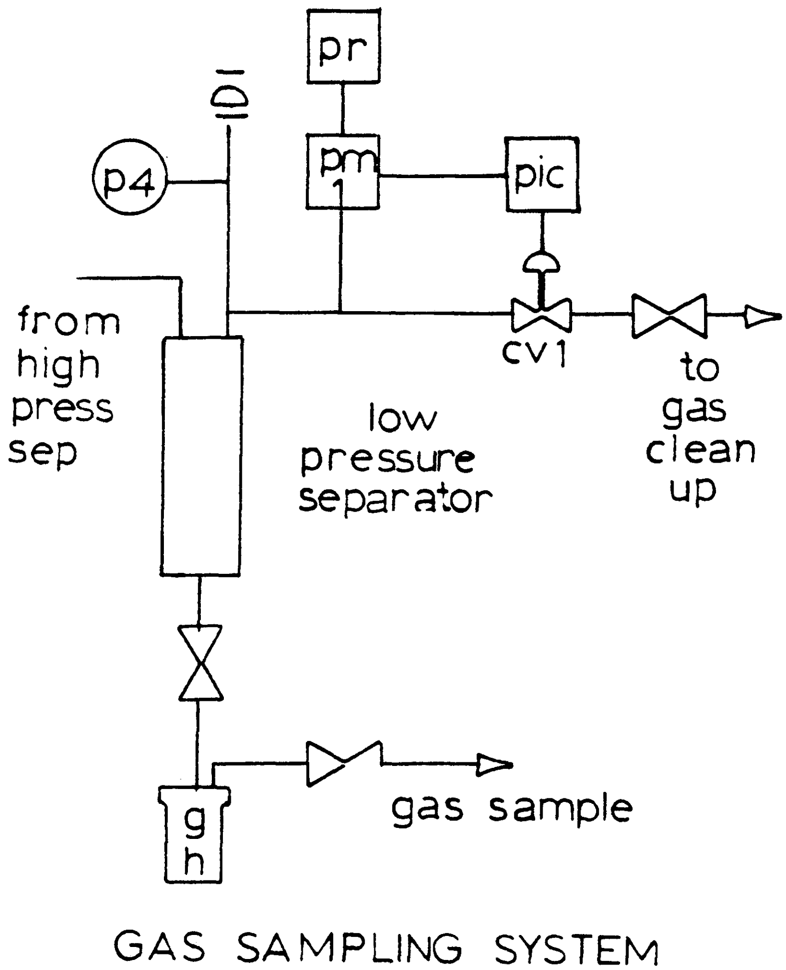


Figure 13. Gas Sampling System

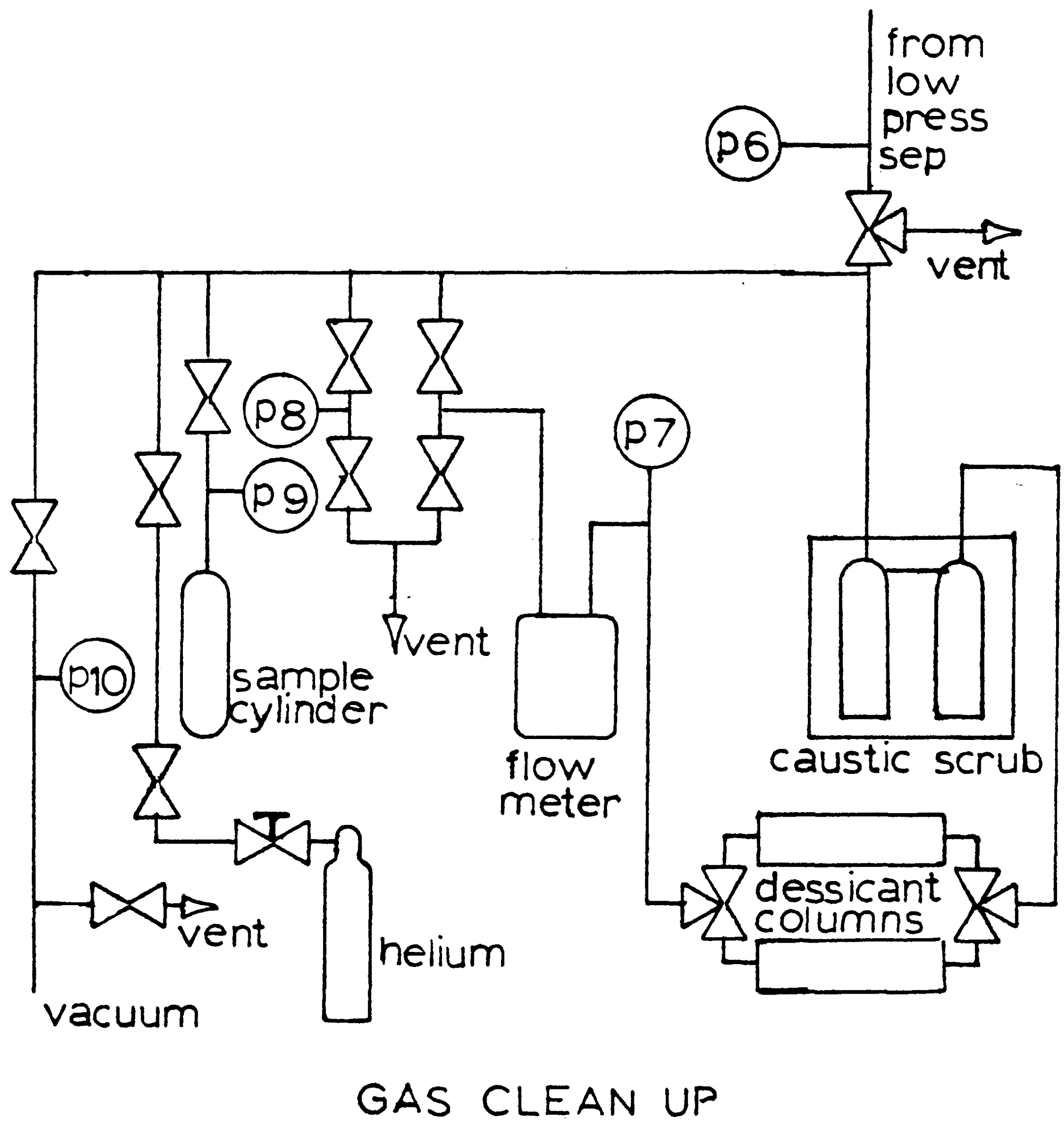


Figure 14. Gas Clean up System

Acco-Bristol pressure recorders. Pressures are also monitored on Maxisafe gauges and slurry pump discharge pressure on an Autoclave digital pressure indicator.

EXPERIMENTAL

Coal Preparation

A Kentucky No. 9 coal from the Pittsburg and Midway Coal Mining Company was used for this entire study. The ultimate and proximate analyses are given in Table 2. The petrographic analysis is shown in Table 3.

The coal was prepared for use by grinding in a ball mill and screening to -200 mesh. After screening the coal was thoroughly mixed, to insure constant physical and chemical properties, and stored in a plastic bag in a 55 gallon drum.

Solvent

The solvent used was developed by Whitehurst, et al (1976) to replace recycle solvents. The solvent is referred to as a synthetic recycle solvent. It contains pure compounds which are of the type found in recycle solvents, but not produced in the liquefaction process to any great extent. The solvent has the advantage of being 100% pentane soluble. The solvent was subjected to reaction conditions, that is 430^{o} C, 2000 psi H_2, and 30 minute space time, and was still found to be 100% pentane soluble. The gas chromatograph runs, Figures 15 and 16, show no significant differences.

TABLE 2

Proximate Analysis

Moisture:	Air Dry	Ø %
	Oven Dry	5.05%
	Total	5.05%

	As-Received	Dry Basis
% Volatile Matter	35.0	36.9
% Ash	8.71	9.18
% Fixed Carbon	51.2	53.9

Ultimate Analysis

	As-Received	Dry Basis
% Carbon	67.9	71.5
% Hydrogen	4.93	4.60
% Sulfur	3.40	3.50
% Nitrogen	1.40	1.47
% Oxygen	13.7	9.70
Sulfur Forms		
Sulfate		0.81
Pyritic		1.30
Organic		1.47

TABLE 3

Petrographic Analysis

Reactive Constituents	(volume percent)
Vitrinoids	
Type 5	7.1
Type 6	47.6
Type 7	16.3
Exinoids	7.7
Resinoids	1.5
Reactive Semifusinoids	0.9
Total	81.1

Inert Constituents	(volume percent)
Micrinoids, Total	8.7
Fusinoids	2.2
Inert Semifusinoids	1.8
Mineral Matter	6.2
Total	18.9

Mean Maximum Reflectance Ro%	0.66
Composition - Balance Index	0.80
Strength Index	2.74
Predicted A.S.T.M. Tumbler Stability	26

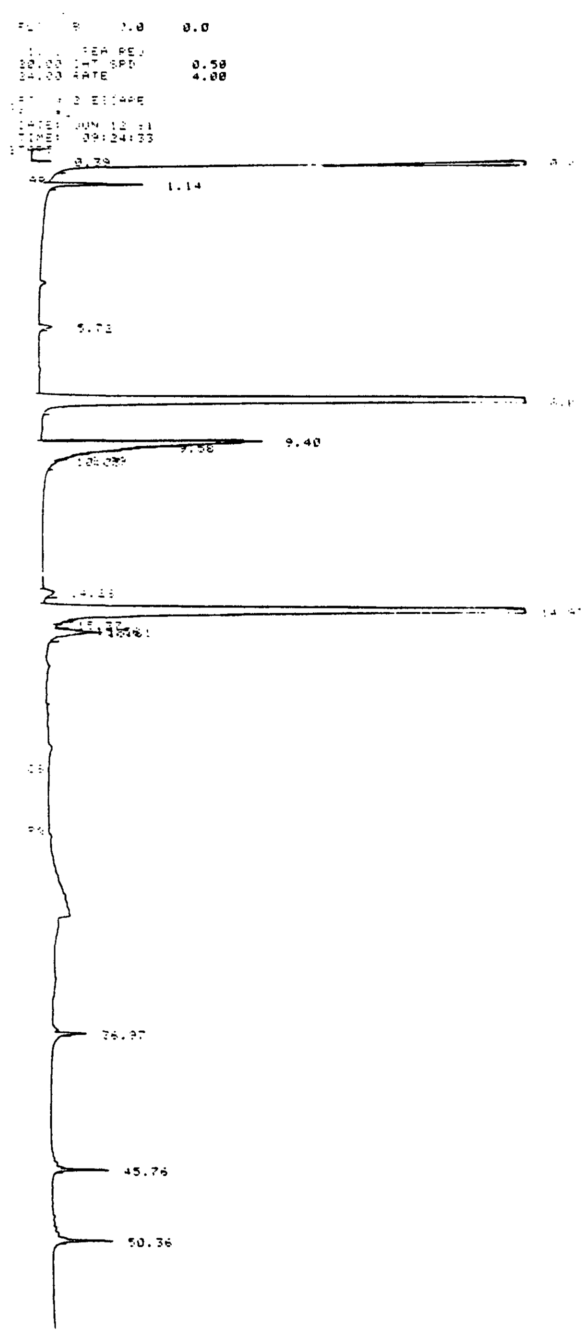


Figure 15. Raw Synthetic Solvent Chromatograph

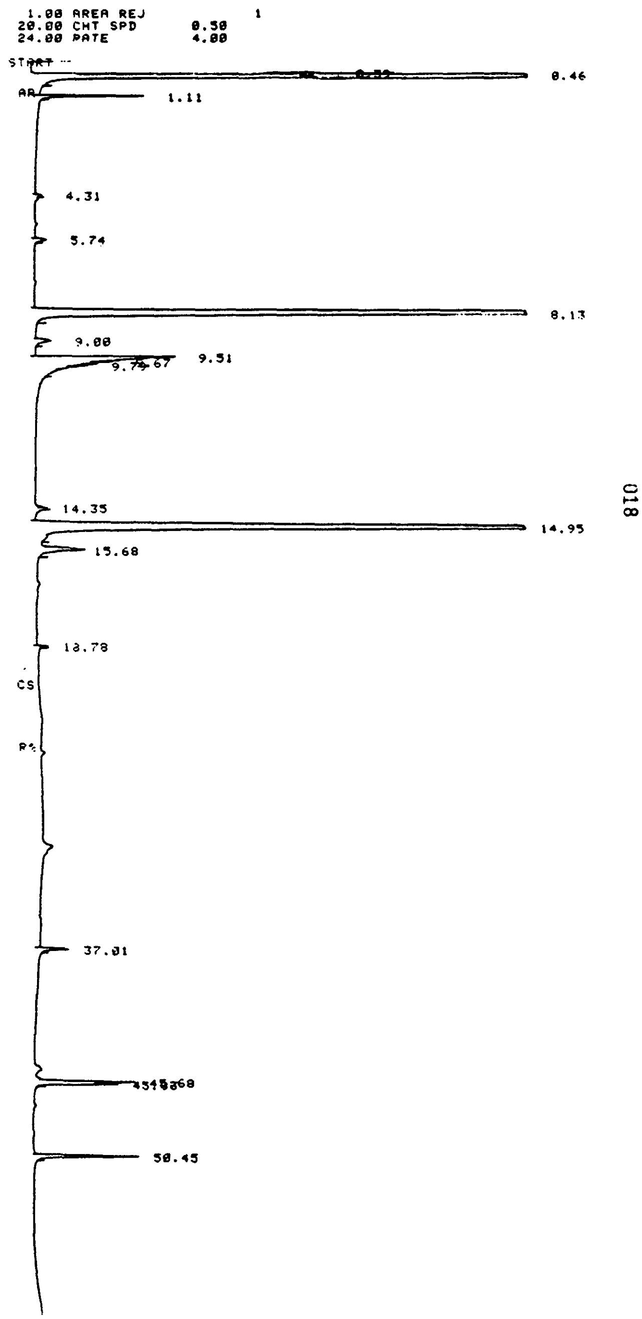


Figure 16. Treated Synthetic Solvent Chromatograph

Table 4 gives the composition of the recycle solvent used. It should be noted that the 2% γ-Picoline was deleted and the tetralin was increased to 45% due to mechanical seal problems.

TABLE 4

Wt%	Component
45%	Tetralin
38%	2-Methylnaphthalene
17%	P-Cresol

Tetralin used was from Union Carbide, 98% pure. The 2-methylnaphthalene was from Howard Hall Company, 98% material with 2% 1-methylnaphthalene. The p-cresol was from the Merichem Company and contained 85% para and 15% meta cresol.

Gases

The gases used were industrial grade supplied by General Air of Denver.

Run Conditions

The reaction temperature was given by the thermocouple in the reaction mass in the stirred tank. The preheaters were used to supply heat sufficient to stay within the safe operating limits of the stirred tank heater. The amount of preheat varied depending on the reaction temperature. Tables 5 and 6 give the run conditions. Figure 17 is a map of the slurry temperature versus time in the unit at the maximum preheater profile. As can be seen, the slurry is at a maximum temperature of 350^{o} for a short time relative to the reactor conditions.

TABLE 5

RUN CONDITIONS

Fixed Parameters	
System Pressure	2000 psig
Gas	Hydrogen
Coal	Kentucky No. 9
Solvent	Synthetic Recycle
Solvent to Coal	4:1
Gas Treatment Rate	15,000 SCF/ton coal
Variable Parameters	
Temperature	350^{o}, 390^{o}, 430^{o}C
Space Time	10, 20, 30, 38 minutes
Compressor Inlet Pressure	400, 490, 585, 925 psi

TABLE 6

RUN CONDITIONS

Run	Space Time	Preheat	STR Temp.
20	30	25	350
21	30	175	390
22	30	340	430
26	20	200	350
27	20	210	390
28	20	290	430
29	10	260	350
30	10	325	390
31	10	350	430
33	38	250	390

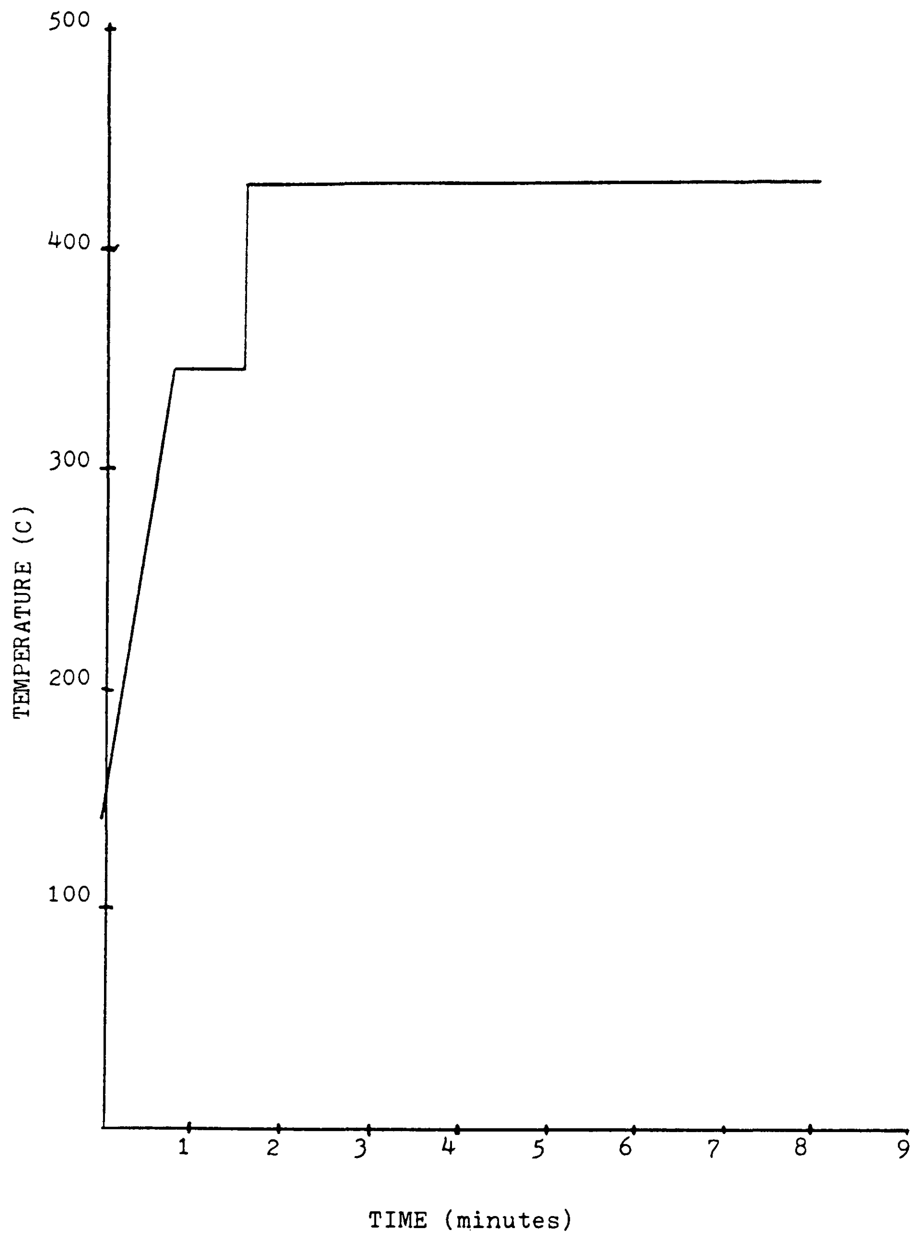


Figure 17. Slurry Preheat Curve

Continuous Experimental Procedure

An experimental run was conducted as follows:

1. The inlet pressure for the compressor was set for the desired gas feed rate.

2. The feed pump was set for the correct slurry flow rate.

3. The slurry and feed tanks are each filled, the stirrer is started in the slurry tank. Cooling water is turned on.

4. Solvent is recycled (valves 4, 6, and 2 open) to purge the system of all air. Valves 2 and 6 are closed and valve 1, to the system, is opened. The feed pump is started.

5. Gas feed is then introduced at the preheater to begin pressurizing the system.

6. The heaters are set and turned on.

7. When the temperature and pressure of the system approach reaction conditions, valve 4 is closed, valve 3 is opened and the recycle line is purged of solvent (not into the slurry tank).

8. A reading is taken periodically on the level gauge within the feed tank to obtain an accurate space time measurement.

9. The unit is sampled every space time to remove the entire contents of the high pressure separator. The

procedure is as follows:

a. All valves in liquid sampling system are closed.

b. The sample system is pressurized to 1500 psig.

c. Valve 7 is opened for 1 to 2 minutes.

d. The pressure is relieved from the sample system and the contents of the holding tank drained.

10. After the stirred tank reactor has reached a steady temperature profile for 5 space times a sample is taken every one-half a space time for as many samples as desired.

11. The gas holding pot is purged with helium and emptied by vacuum a minimum of 3 times. The valve between the low pressure separator and the holding pot is opened until the pressure equalizes to 40 psig. The gas sample is contained in the holding pot until it can be transferred to gas cylinders.

12. Gas cylinder contents were checked periodically and replaced when necessary. Slurry was replenished when needed.

13. Shut down proceeded by turning off all heaters, shutting down the gas feed and switching back to solvent. The feed pump rate was increased to about 3 liters/hour and solvent was pumped through the system for at least one hour. The system was allowed to cool to less than 200°C and totally

depressurized at which time at least 1.5 gallons of solvent was pumped through the open system with the recycle pump. The system is then allowed to cool to ambient and flushed with acetone.

14. The system was then given a thorough inspection and any servicing necessary was taken care of at this time.

Analytical Procedures

The liquid samples were mixed thoroughly and 10 gram samples were weighed into centrifuge tubes. These were subjected to the solvent fractionation scheme shown in Figure 18. The results of this analysis are an oil fraction (soluble in pentane), an asphaltene fraction (insoluble in pentane soluble in toluene), a preasphaltene fraction (insoluble in toluene, soluble in tetrahydrofuran) and an "unreacted" coal and ash fraction. The unreacted coal fraction is subjected to oxidation at 700^{o}C to determine the amount of ash in the sample. The asphaltene and preasphaltene fractions are stripped of their solvents (under vacuum) and then precipitated with pentane. The excess pentane is evaporated off and the samples are analyzed on a Carlo-Erba analyzer, model 1104, for carbon, hydrogen and nitrogen.

The gas samples are analyzed on a Carle, model 5001,

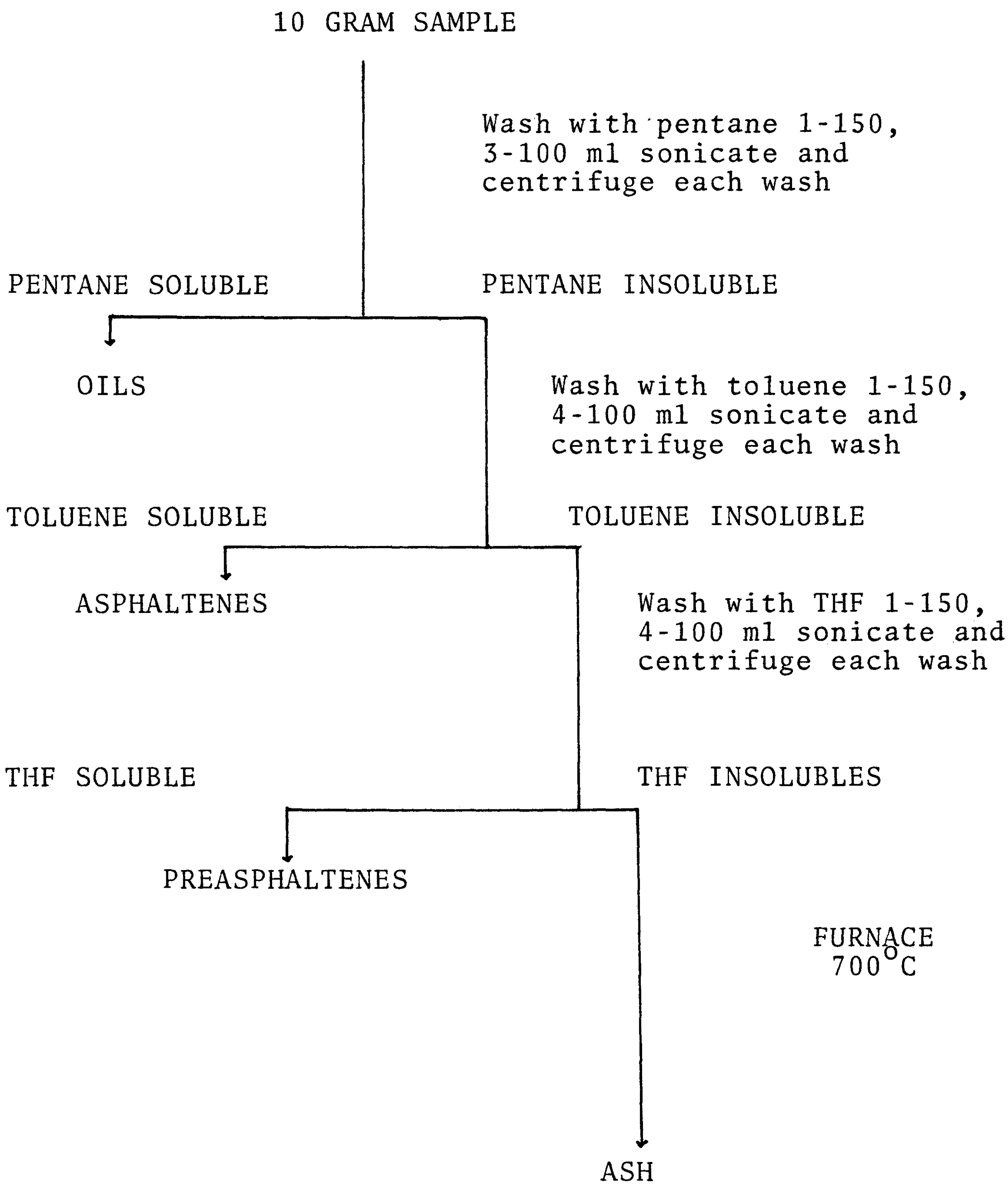


Figure 18. Solvent fractionation scheme.

gas chromatograph for hydrogen, carbon monoxide, carbon dioxide, hydrogen sulfide and various hydrocarbon gases.

RESULTS AND DISCUSSION

Reproducibility Tests

Four runs were made to test the reproducibility of the yields obtained from the same operating conditions. The results are tabulated in Table 7. All runs were done at a total pressure of 2000 psi. Sampling for run CR8 was started at 3.0 space times, after a constant temperature was attained in the reactor, and a sample was withdrawn every .5 space times until 4 samples had been accumulated. Sampling for run CR10 was begun at 4.5 space times, after a constant reactor temperature was attained, and a sample withdrawn every .5 space times thereafter for 4 samples. The small deviations in the conversion data indicate that samples were taken when the reactor was operating at a steady state.

Gas Analysis

Gas samples were taken and analyzed as previously noted. Due to a malfunction in the gas chromatograph the majority of the gas sample analyses are useless. Three analyses taken after repairs and recalibration are given in Table 8. These show the increase in gas made as the temperature increases, most notably in the light hydrocarbon range. However, due to some uncertainty in the absolute accuracy of the percent-

TABLE 7

REPRODUCIBILITY

Run	Temp	Space Time	% Conversion
CR7	350°C	35 min.	39.85 ± 1.27
CR9	350°C	35 min.	41.48 ± 2.15
CR8	430°C	10 min.	68.50 ± 1.76
CR10	430°C	10 min.	67.85 ± 1.38

TABLE 8

GAS ANALYSIS COMPOSITIONS (PERCENT)

Run	CR29	CR30	CR31
Space Time	10 min.	10 min.	10 min.
Temperature	350^{o}C	390^{o}C	430^{o}C
H_2	91.04	82.28	66.07
H_2S	5.13	8.36	8.68
CO	.18	.84	1.98
CO_2	3.32	5.09	5.82
CH_4	.33	1.94	9.78
C_2H_4	--	.06	.28
C_2H_6		.89	4.15
C_3H_6		.13	.47
C_3H_8		.42	2.12
$C\text{-}C_4$		--	.12
$n\text{-}C_4$		.02	.50

ages given, these cannot be used to give an exact gas make. These data can at best be used as a qualitative indication of the gases that were present in the system after reaction, and cannot be used to calculate degree of coal gasification.

Solvent Fractionation

Each product sample was subjected to the solvent fractionation scheme shown in Figure 18. From this analysis the yields of oils, asphaltenes, preasphaltenes and unreacted coal were determined. These results for each run in the experimental program are given in Table 9. Sample calculations are given in Appendix A. The error shown is the estimate of the uncertainty in a given fraction using the standard deviations of the samples at a given data point. When the value of the standard deviation was less than the average standard deviation of the reproducibility runs the higher value was used. These are to represent the true uncertainty in a given yield.

Elemental analysis was done on the asphaltene and preasphaltene fractions, and these results are tabulated in Appendix B. The elemental analysis for a set of asphaltene and preasphaltene fractions at a space time of 30 minutes are given in Table 10.

The trend shown in the H/C ratio in Table 10 indicates

TABLE 9

SOLVENT FRACTIONATION PERCENTAGES

Run	Oil	Asphaltene	Preasphaltene	Unreacted Coal
CR 20	9.2 ± 3.9	15.9 ± 1.4	16.2 ± .4	58.6 ± 2.1
CR 21	10.9 ± 6.0	18.7 ± 2.7	37.9 ± 1.4	32.6 ± 2.0
CR 22	28.2 ± 7.1	25.5 ± 3.0	27.5 ± 2.8	18.8 ± 1.7
CR 26	5.1 ± 2.0	12.8 ± .1	16.3 ± .3	65.8 ± 1.6
CR 27	10.7 ± 6.1	16.1 ± .6	34.1 ± .5	39.1 ± 5.0
CR 28	26.2 ± 10.3	20.6 ± 3.6	31.9 ± 3.2	21.3 ± 3.5
CR 29	1.4 ± 5.9	12.2 ± .9	9.9 ± 1.1	76.5 ± 5.7
CR 30	4.2 ± 15.2	14.8 ± 1.7	29.1 ± 5.0	51.9 ± 10.1
CR 31	18.1 ± 2.8	23.0 ± 1.0	34.0 ± .1	25.0 ± 1.7
CR 33	17.2 ± 2.0	20.7 ± .2	32.8 ± .3	29.3 ± 1.5

TABLE 10

SELECTED ELEMENTAL ANALYSIS

Sample	H	C	N	H/C	Temp.
CR 20 ASP	6.07	82.06	1.34	.89	350^{0}C
CR 20 PRE	5.69	76.48	1.64	.89	350^{0}C
CR 21 ASP	6.13	83.48	1.57	.88	390^{0}C
CR 21 PRE	5.54	76.07	1.71	.87	390^{0}C
CR 22 ASP	5.83	85.53	2.02	.82	430^{0}C
CR 22 PRE	5.20	78.18	2.10	.80	430^{0}C

that the solid residue left after hydrogenation is becoming a more highly condensed aromatic structure as the conditions become more severe. It is expected to find the preasphaltene H/C ratio to be less than the asphaltene. What is interesting is to note that the H/C ratio of these two fractions is about the same. This may indicate that the mechanism of hydrogenation is not at all simple or straight forward.

An analysis was done on a cold sample of slurry to give a value for the initial concentrations of asphaltenes and preasphaltenes. The results are:

Oil	0.0%
Asphaltene	3.97% ± .23
Preasphaltene	6.32% ± .49

Mathematical Solution to a System of Equations

The analysis of a continuous flow stirred tank reactor gives a series of algebraic equations. When the system has multiple dependent variables, one method of solution is to apply multiple linear regression using the sum of least squares technique.

A system of equations

$$Y_1 = B_1 X_1 + E_1$$
$$Y_2 = B_1 X_2 + E_2$$
$$\vdots$$
$$Y_n = B_1 X_n + E_n$$

can be represented by a system of matrices.

$$\underline{Y} = \underline{X}\ \underline{B} + \underline{E}$$

where $\underline{Y}$ is the matrix of observations,

$\underline{X}$ is the matrix of dependent variables

$\underline{B}$ is the matrix of parameters to be estimated,

$\underline{E}$ is the matrix of errors.

The normal equations for this system are:

$$\sum_{i=1}^{n} (Yi - biXi) = 0$$

$$\sum_{i=1}^{n} Xi\ (Yi - biXi) = 0$$

which can be represented by

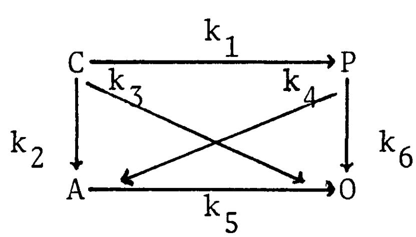
$$\underline{X}'\ \underline{X}\ \underline{b} = \underline{X}'\ \underline{Y}$$

where $\underline{X}'$ is the transpose of the matrix $\underline{X}$.

The solution of the normal equation for the matrix of parameters is then given by:

$$\underline{b} = (\underline{X}'\ \underline{X})^{-1}\ (\underline{X}'\ \underline{Y})$$

In the case of a CSTR analysis the parameters to be estimated are the rate constants. For an example mechanism



the equations to be solved are

$Y = B \quad X \quad + \quad E$

$$\frac{Xc}{T} = k_1\ (1-Xc) + k_2\ (1-Xc) + k_3\ (1-Xc)$$

$$\frac{\alpha-\alpha o}{T} = k_1\ (1-Xc) - k_4\alpha - k_6\alpha$$

$$\frac{\beta-\beta o}{T} = k_2\ (1-Xc) - k_4\alpha - k_5\beta$$

$$\frac{\gamma-\gamma o}{T} = k_3\ (1-Xc) + k_5\beta + k_6\alpha$$

The matrices describing this set of equations using two data points are shown in Figure 19. The Y's in the $\underline{Y}$ matrix are the observed rates of reaction. The X's in the $\underline{X}$ matrix are the observed yields of the various fractions. The k's are the rate constants to be evaluated.

The program MINITAB from Penn State University will perform this analytical technique. At present it is in the library of computer programs available at Colorado School of Mines. The print out includes the standard deviations for the coefficients and the sum of squares of the residuals and totals, for use in calculating the correlation coefficient of the regression equation. Figure 20 gives a sample printout. Appendix C shows a sample run and data file for MINITAB.

$$
\begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \\ y_5 \\ y_6 \\ y_7 \\ y_8 \end{bmatrix}
=
\begin{bmatrix}
x_{11} & x_{12} & x_{13} & 0 & 0 & 0 \\
x_{21} & 0 & 0 & x_{24} & 0 & x_{26} \\
0 & x_{32} & 0 & x_{34} & x_{35} & 0 \\
0 & 0 & x_{43} & 0 & x_{45} & x_{46} \\
x_{51} & x_{52} & x_{53} & 0 & 0 & 0 \\
x_{61} & 0 & 0 & x_{64} & 0 & x_{66} \\
0 & x_{72} & 0 & x_{74} & x_{75} & 0 \\
0 & 0 & x_{83} & 0 & x_{85} & x_{86}
\end{bmatrix}
\begin{bmatrix} k_1 \\ k_2 \\ k_3 \\ k_4 \\ k_5 \\ k_6 \\ \\ \end{bmatrix}
$$

$$\underline{y} \quad = \quad \underline{x} \quad \underline{b}$$

Figure 19. Matracies for Least Squares Analysis

-- REGRESS Y IN C1 ON 4 PRED. IN C2,C3,C4,C5

THE REGRESSION EQUATION IS
Y = + 5.82 X1 + 11.1 X2 - .0670 X3
+ 0.765 X4

	COLUMN	COEFFICIENT	ST. DEV. OF COEF.	T-RATIO = COEF/S.D.
NOCONSTANT				
X1	C2	5.821	0.570	10.22
X2	C3	11.133	0.596	18.69
X3	C4	-0.067	0.298	-0.22
X4	C5	0.765	0.224	3.41

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S = 0.2101
WITH (20- 4) = 16 DEGREES OF FREEDOM

ANALYSIS OF VARIANCE

DUE TO	DF	SS	MS=SS/DF
REGRESSION	4	62.74664	15.68666
RESIDUAL	16	0.70613	0.04413
TOTAL	20	63.45277	

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

DUE TO	DF	SS
REGRESSION	4	62.74664
C2	1	39.18223
C3	1	22.99137
C4	1	0.05937
C5	1	0.51367

ROW	X1 C2	Y C1	PRED. Y VALUE	ST.DEV. PRED. Y	RESIDUAL	ST.RES.
1	0.271	4.3650	4.5946	0.1257	-0.2296	-1.36
2	0.271	1.5750	1.5951	0.1259	-0.0201	-0.12
3	0.000	2.5810	2.6695	0.1249	-0.0885	-0.52
4	0.000	0.2040	0.3299	0.0967	-0.1259	-0.67
5	0.251	4.4850	4.2555	0.1164	0.2295	1.31
6	0.251	1.4910	1.4778	0.1164	0.0132	0.08
7	0.000	2.6350	2.4409	0.1176	0.1941	1.11
8	0.000	0.3590	0.3368	0.0987	0.0222	0.12
9	0.111	1.7780	1.8819	0.0515	-0.1039	-0.51
10	0.111	0.6200	0.6669	0.0757	-0.0469	-0.24
11	0.000	0.6500	0.9662	0.0757	-0.3162	-1.61
12	0.000	0.5060	0.2488	0.0729	0.2572	1.31
13	0.032	0.9680	0.5425	0.0148	0.4255	2.03R
14	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

Figure 20. MINITAB Information

Kinetic Analysis

The conversion of coal to products is a reaction which will proceed to an "equilibrium" condition. The "equilibrium" conversion is a function of the termperature of reaction and the inherent inertinite maceral content of the coal. In order to use irreversible kinetics, the fraction of unreacted coal at equilibrium must be normalized with respect to this unreactive fraction. The total conversion of coal to all products (1.0 - unreacted coal fraction) was plotted vs. space time and a smooth curve was drawn to estimate a value for the "equilibrium" conversion.

The material balance for a continuous flow stirred tank reactor is:

$$Q\,Co \quad QC + rV = 0$$

where Q = volumetric flow rate $\frac{\text{liter}}{\text{minute}}$

C = mass concentration $\frac{\text{grams}}{\text{liter}}$

V = volume of reactor liter

r = rate of reaction

for the mechanism of

$$\text{Coal} \xrightarrow{k} \text{Products}$$

where the reaction is assumed to be first order with respect to coal remaining, the rate of reaction is given by

$$\text{rate} = -k\,C$$

the material balance becomes

$$\frac{x}{a} - T\,k\,(1 - \frac{x}{a}) = 0$$

where
$$T = V/Q$$
$$C = Co\,(1 - \frac{x}{a})$$
$$a = \text{equilibrium conversion}$$

Solving for k and substituting in the values for the total conversion a set of rate constants were calculated, as shown in Table 11. The errors given are the standard deviations from the average values.

TABLE 11

Rate Constants

Temperature ^oC	k (overall) coal→products Hr^{-1}
350	6.02 ± 2.66
390	19.27 ± 8.96
450	68.71 ± 6.7

Figure 21 shows the experimental values superimposed on the plots of the values predicted by these rate constants. The fit is fairly good. Figure 22 shows the Arrhenius plot of these constants for which the fit is surprisingly good. An Arrhenius activation energy of 25.4 k cal/g mole results

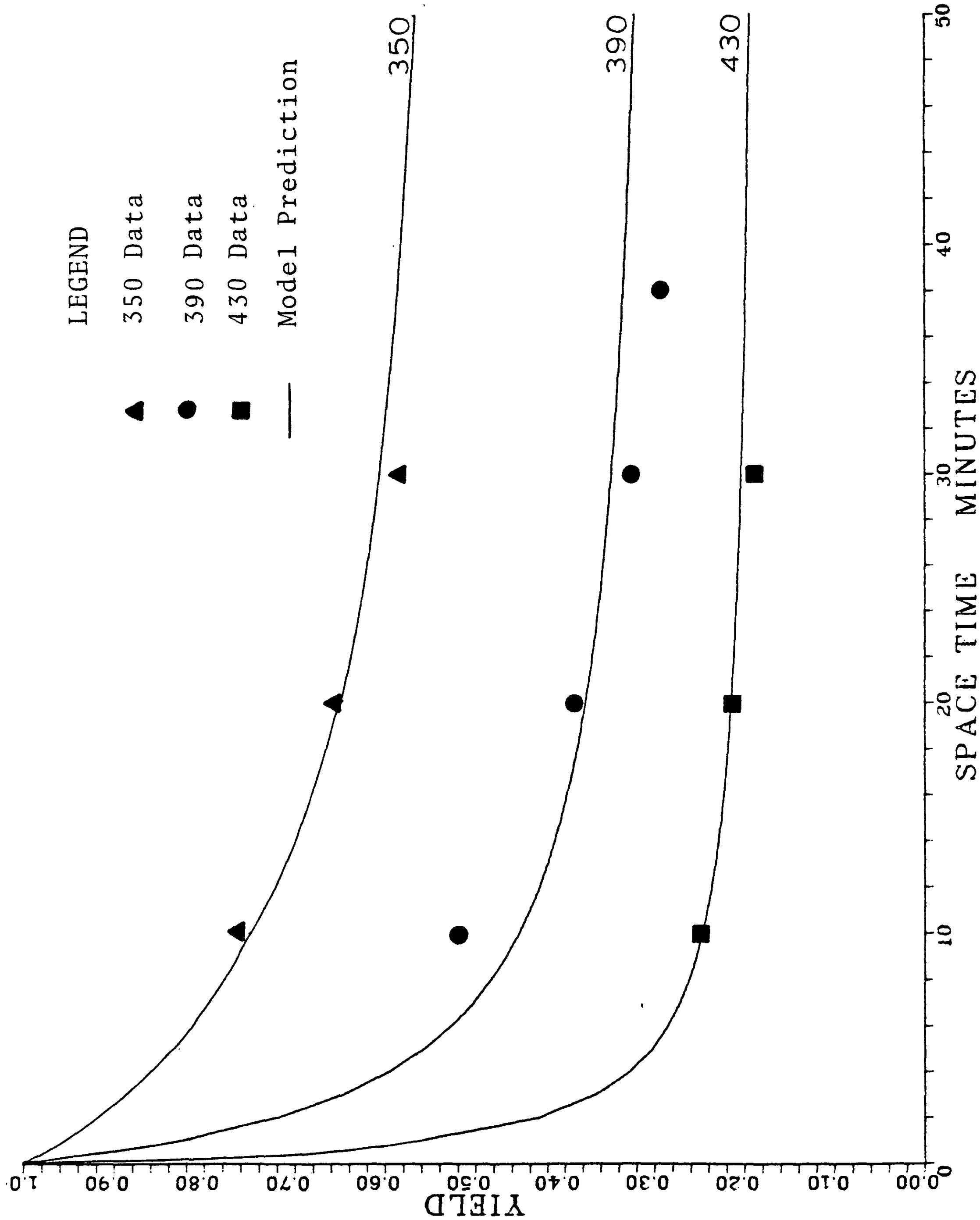


Figure 21. Coal to Products Model

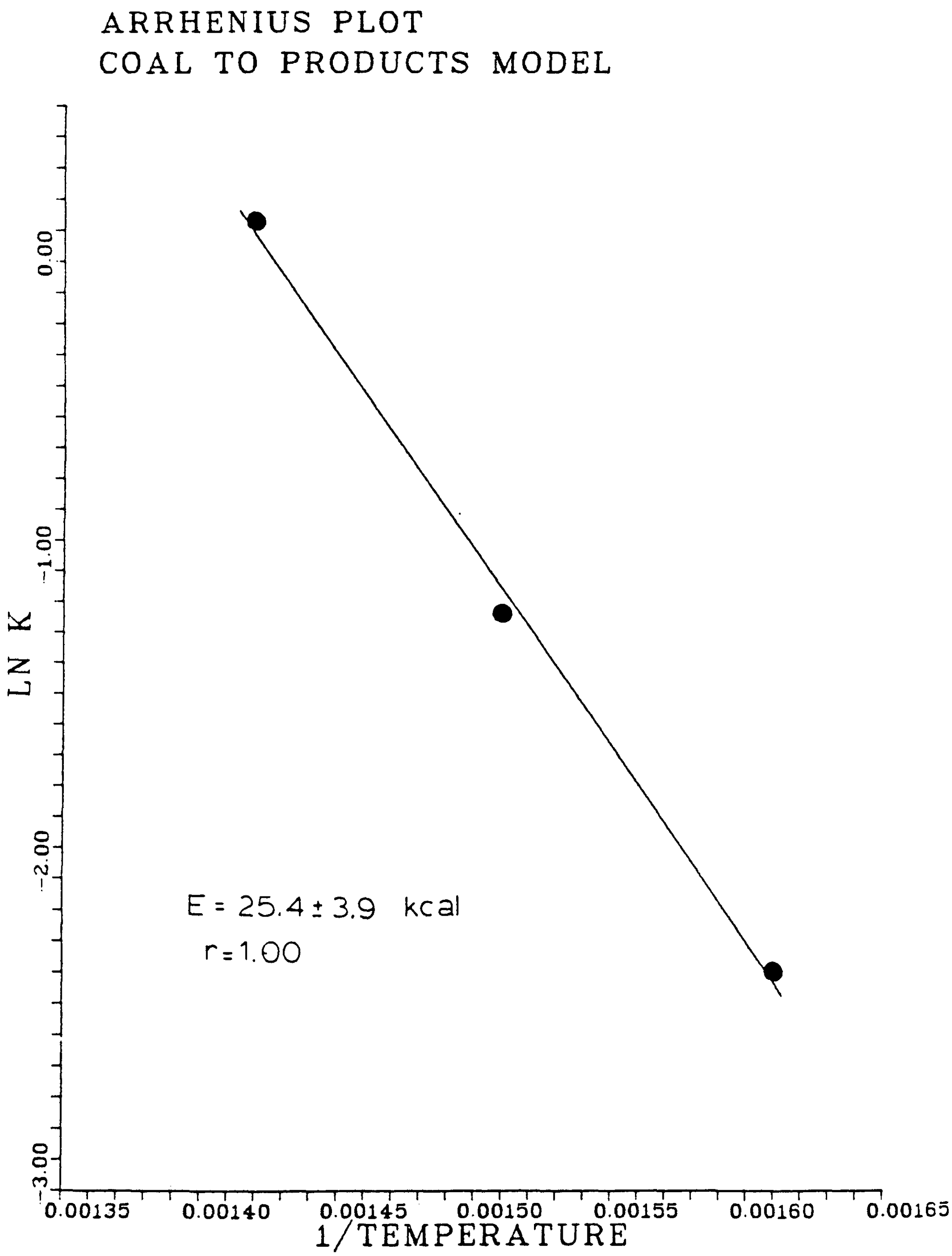


Figure 22. Arrhenius Plot Coal to Products Model

from this set of rate constants.

The following mechanism was postulated to determine the coal to products rate constants using a different technique.

$$\begin{tikzcd} \text{Coal} \arrow[rr, "k_1"] \arrow[d, "k_2"'] \arrow[drr, "k_3"] & & \text{Preasphaltene} \\ \text{Asphaltene} & & \text{Oil and Gas} \end{tikzcd}$$

By assuming the reactions of coal to oil, coal to asphaltenes and coal to preasphaltenes are all first order irreversible with respect to coal remaining, the CSTR material balance becomes

$$C_o \qquad C \qquad T\ C\ (k_1 + k_2 + k_3) \ = \ 0$$

Using the library program MINITAB to solve for k_1, k_2 and k_3 gave the results in Table 12. Comparing the summed rates with those in Table 11 shows almost identical results. Figure 23 shows the Arrhenius plot of the summed k's. The fit is quite good and the activation energy from the lumped k's is comparable with that calculated from the averaged k's.

It was desired to investigate different mechanisms for coal hydrogenation in order to arrive at an adequate mechanistic model for the observed kinetics. Accordingly, pure series and series - parallel mechanisms were developed, inserted into the mass balances, and the rate constants

TABLE 12

RATE CONSTANTS FOR COAL TO PRODUCTS

Temperature	Rate Constants Hr^{-1}			
^{o}C	k_1	k_2	k_3	$\Sigma k's$
350	2.04±.38	2.48±.38	0.861±.38	5.38±1.14
390	7.27±1.34	3.73±1.34	1.99±1.34	12.99±4.02
430	27.0±4.88	19.1±4.88	19.6±4.88	65.7±14.64

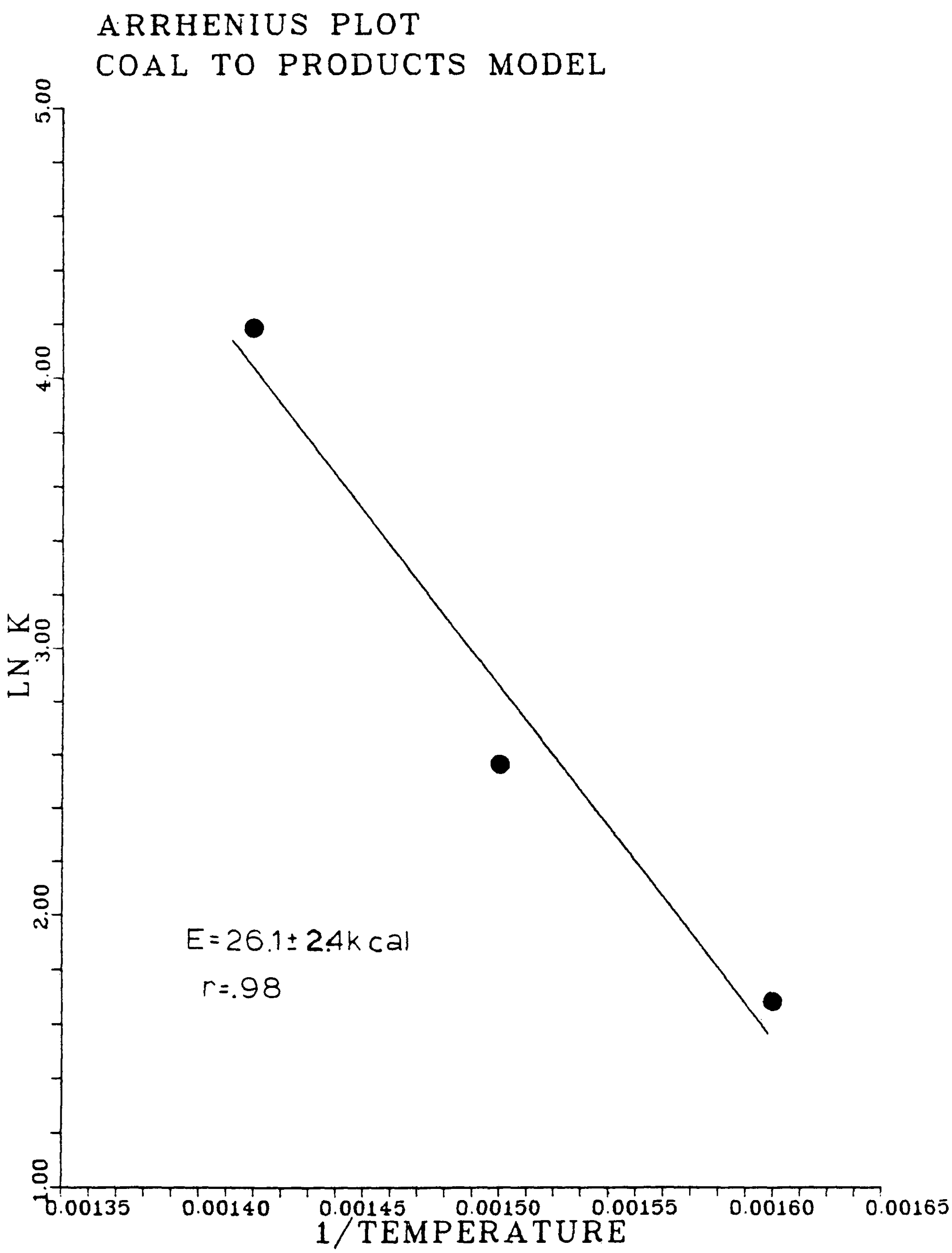


Figure 23. Arrhenius Plot Coal to Products Model
Rate Constants from Regression

solved for by multiple linear regression.

The first mechanism investigated was a straight series model:

$$\text{Coal} \xrightarrow{k_1} \text{Preasphaltene} \xrightarrow{k_2} \text{Asphaltene} \xrightarrow{k_3} \text{Oil}$$

The reactions were assumed to be first order irreversible in the species remaining. All the yield data have been normalized with respect to the "equilibrium" conversions for each temperature. The normalized values used for all the calculations are in Appendix D. Using the material balance for a CSTR and the rate equations for the various products the following equations were developed.

$$\begin{array}{lll} Co & C + T\{-k_1 C\} = \emptyset \\ Po & P + T\{k_1 C \quad k_2 P\} = \emptyset \\ Ao & A + T\{k_2 P \quad k_3 A\} = \emptyset \\ Oo & O + T\{k_3 A\} = \emptyset \end{array}$$

where

$$C = Co\,(1 - Xc)$$

$$P = Co\,\alpha$$

$$A = Co\,\beta$$

$$O = Co\,\gamma$$

Here, α, β and γ are the normalized fractions of preasphaltene, asphaltene and oils respectively and Xc is the normalized total conversion (X/a). Rearranging these mass balances gave the following set of simultaneous equations:

$$\frac{X_c}{T} = k_1 \; (1 - x_c)$$

$$\frac{\alpha - \alpha o}{T} = k_1 \; (1 - x_c) - k_2 \; \alpha$$

$$\frac{\beta - \beta o}{T} = k_2 \; \alpha \qquad k_3 \; \beta$$

$$\frac{\gamma}{T} = k_3 \; \beta$$

This set of equations was solved by multiple linear regression for k_1, k_2 and k_3 using MINITAB. The resulting rate constants are given in Table 13.

Figures 24 through 26 show the conversions predicted with the experimental points superimposed. As can be seen the overall conversion fits fairly well which is expected since the values for k_1 are close to those for the coal to products model. It should be noted that the preasphaltene concentration by this model builds quickly as the coal is converted and then declines slowly during the remainder of the process. The experimental data fails to show this trend. The asphaltene concentration fits fairly well indicating that it is being used and produced at the same time. The oils follow the predicted values generally, however due to the large error inherent in the oil calculation method it is difficult to evaluate the fit. What is obvious, however, is that the straight series mechanism should be replaced by a parallel - series. The Arrhenius plot for the series model is found in Figure 27.

TABLE 13

RATE CONSTANTS FOR SERIES MODEL

Temperature	Rate Constants Hr^{-1}		
^oC	k_1	k_2	k_3
350	4.66 ± .729	3.09 ± 1.14	0.69 ± 1.07
390	11.1 ± 1.59	1.13 ± .732	0.66 ± 1.30
430	59.6 ± 7.34	4.34 ± 1.20	3.09 ± 1.47

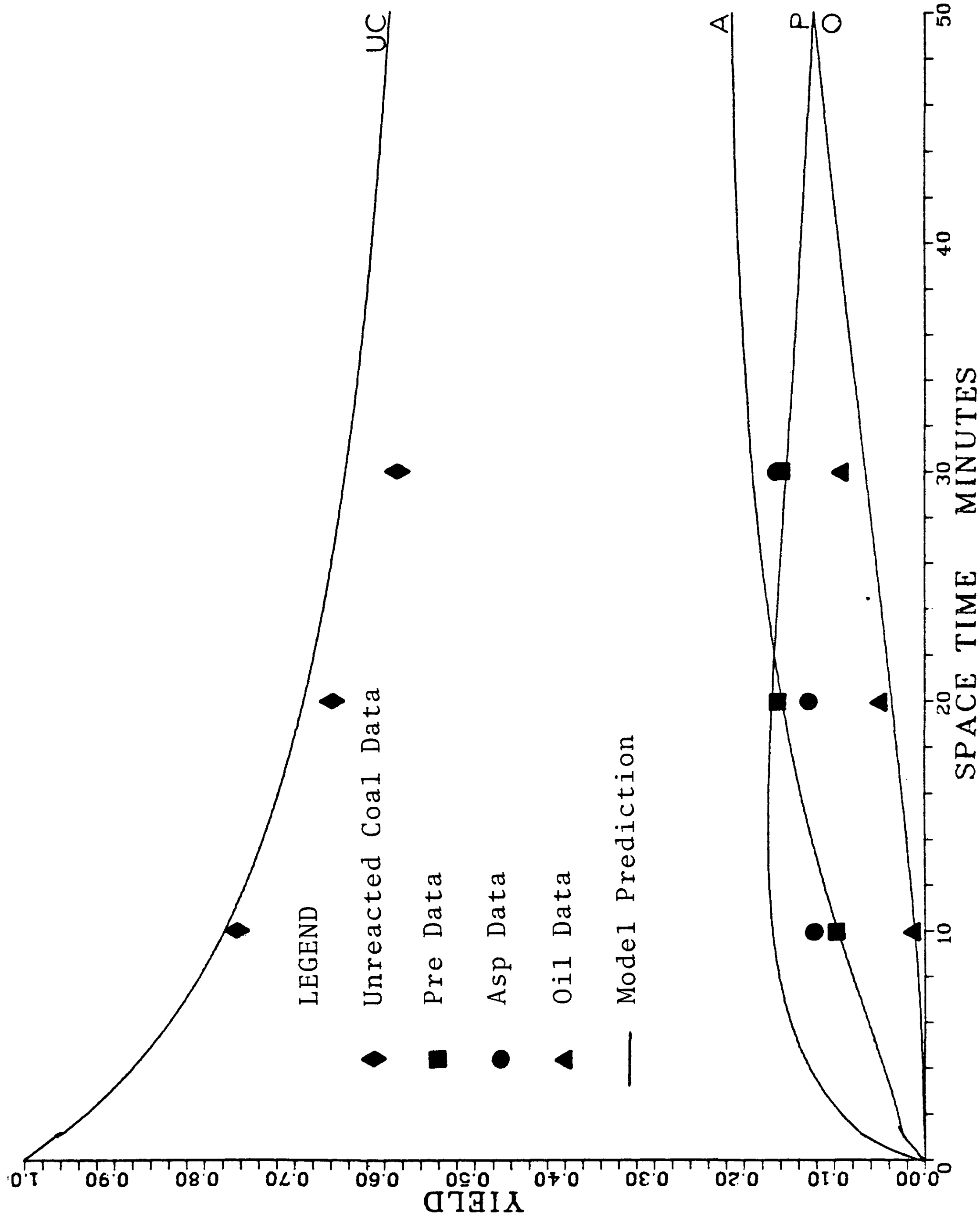


Figure 24. Pure Series Model Yields at 350^{o}C

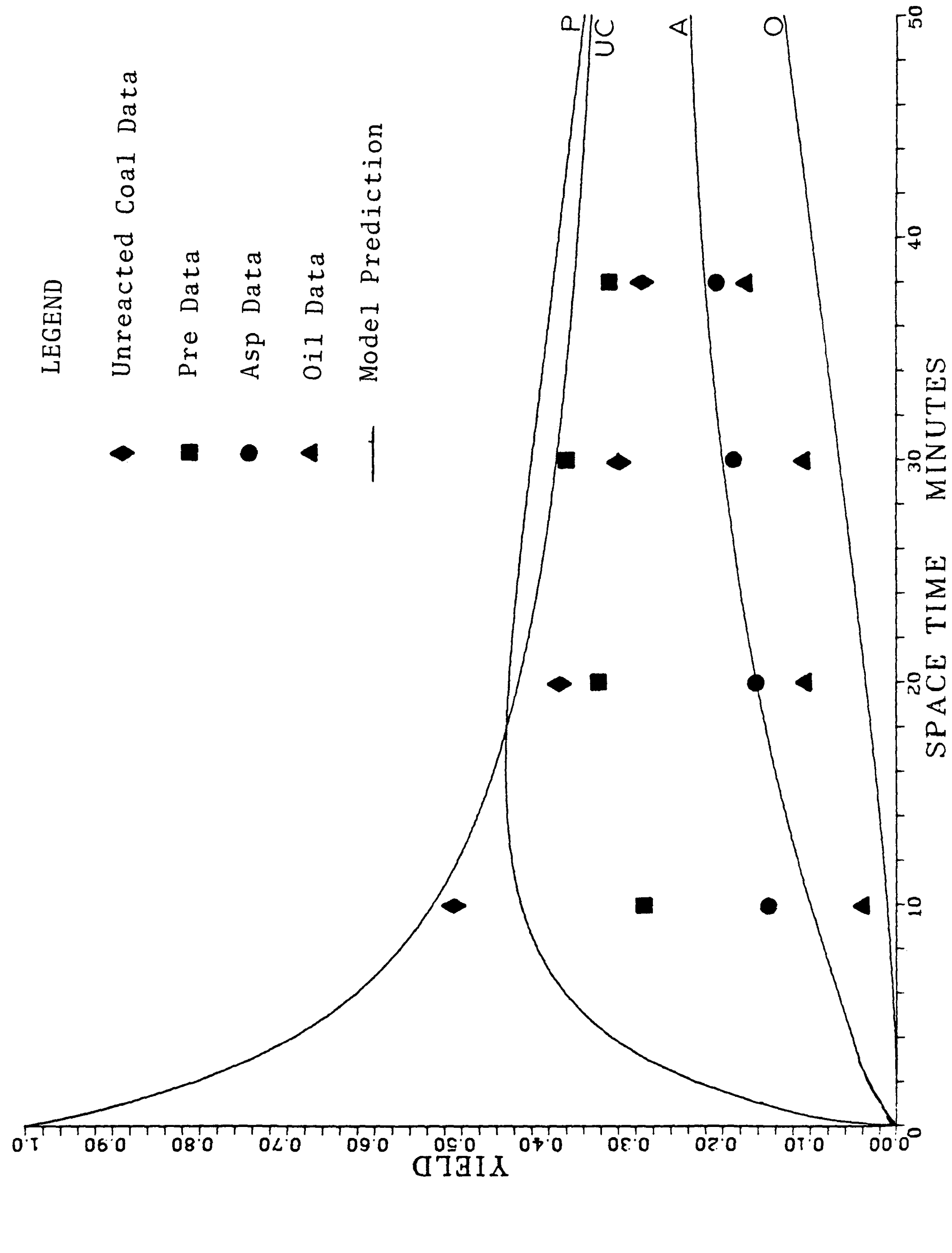


Figure 25. Pure Series Model Yields at 390°C

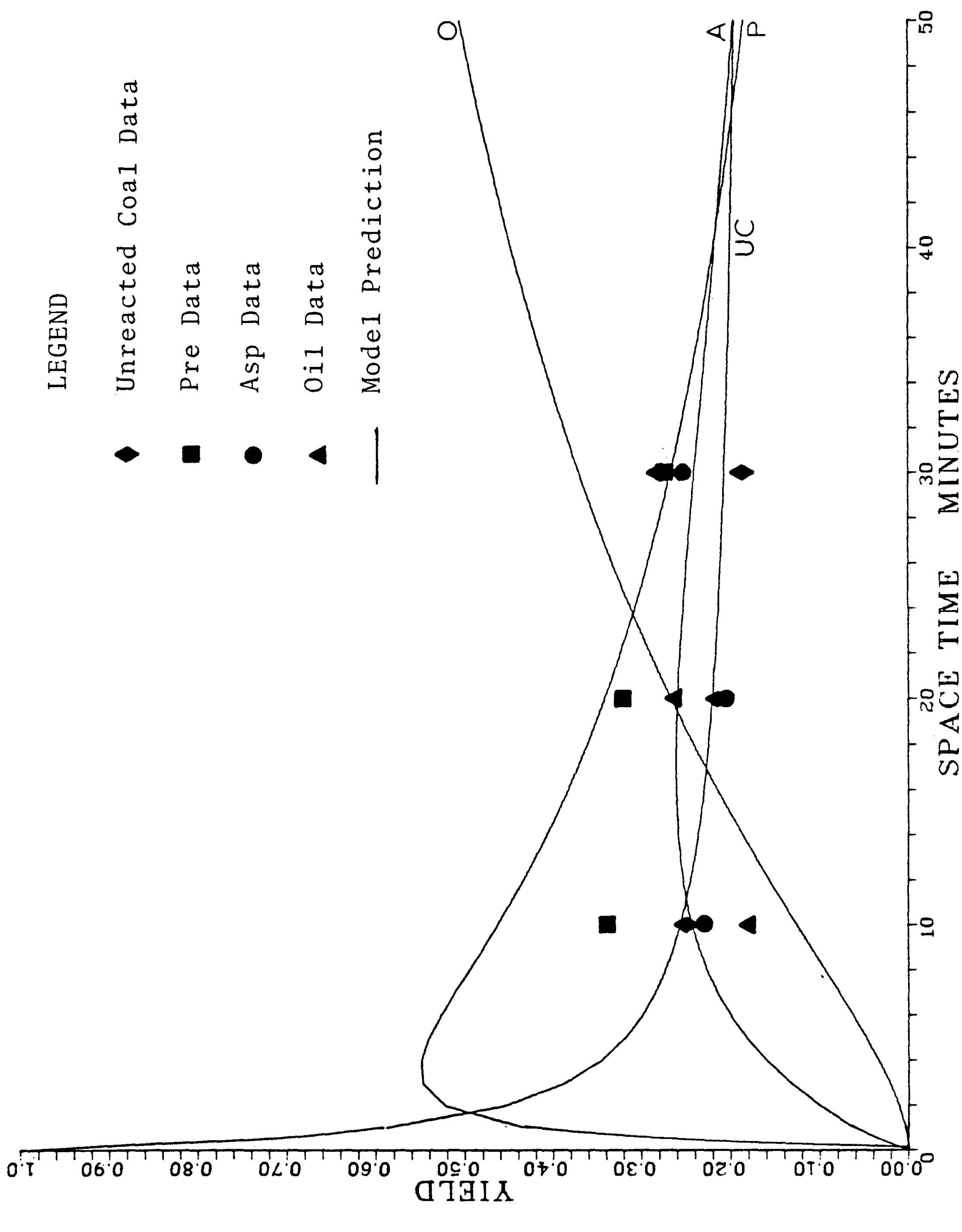


Figure 26. Pure Series Model Yields at 430°C

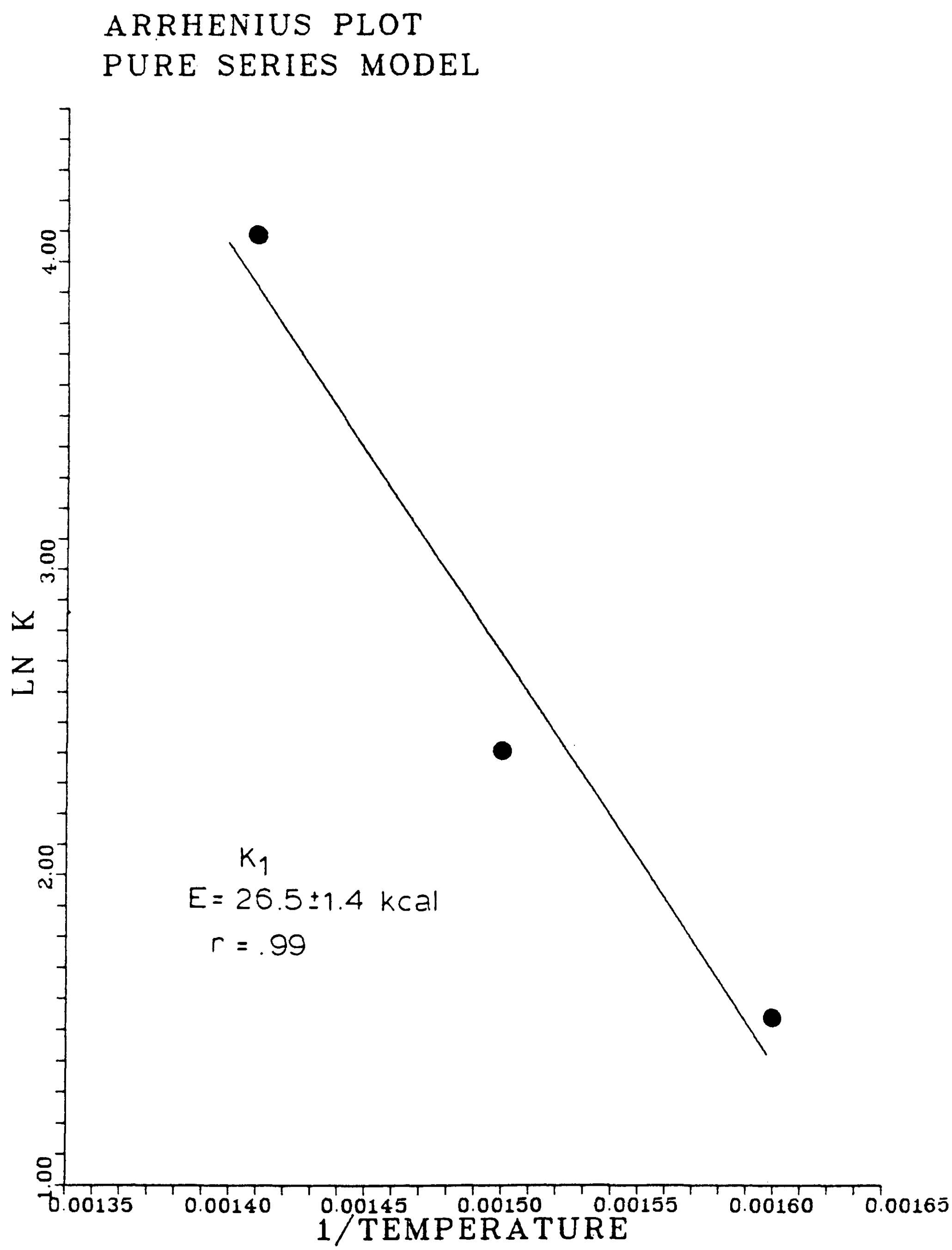


Figure 27. Arrhenius Plot Pure Series Model

Several parallel - series models were tried before the following was settled upon.

$$\begin{tikzcd}
\text{Coal} \arrow[r, "k_1"] \arrow[d, "k_2"'] & \text{Preasphaltene} \arrow[dl, "k_3"'] \\
\text{Asphaltene} \arrow[r, "k_4"] & \text{Oil}
\end{tikzcd}$$

The CSTR material balance equations for this mechanism are as follows:

$$Co \quad C \; + \; T\{-k_1\, C \quad k_2\, C\} \; = \; \emptyset$$

$$Po \quad P \; + \; T\{\, k_1\, C \quad k_3\, P\} \; = \; \emptyset$$

$$Ao \quad A \; + \; T\{\, k_2\, C \quad k_4\, A\} \; = \; \emptyset$$

$$Oo \quad O \; + \; T\{\, k_4\, A\} \; = \; \emptyset$$

where:

$$C = Co\,(1 - Xc)$$

$$P = Co\,\alpha$$

$$A = Co\,\beta$$

$$O = Co\,\gamma$$

Combining and rearranging gives:

$$\frac{Xc}{T} = k_1\,(1 - Xc) + K_2\,(1 - Xc)$$

$$\frac{\alpha - \alpha o}{T} = k_1\,(1 - Xc) \quad k_3\,\alpha$$

$$\frac{\beta - \beta o}{T} = k_2\,(1 - Xc) + k_3\,\alpha - k_4\,\beta$$

$$\frac{\gamma}{T} = k_4\,\beta$$

Solving for k_1, k_2, k_3 and k_4 simultaneously using MINITAB gave the rate constants found in Table 14. The k_3 constant for 350 and 390°C are both very small and close to zero. The k_4 constants for the same temperatures are both essentially equal.

Plots of the predicted conversions are given in Figures 28 through 30 along with the experimental data points. As may be seen, the predicted total conversion curve fits the data well. Here the sum of rate constants k_1 and k_2 falls within the range of the rate constants found for the coal to products model. The preasphaltenes fit the predicted values fairly well, as do the asphaltenes. The Arrhenius plots of the rate constants are given on Figure 31.

This mechanism fits the observed data fairly well and has the advantage of having some physical significance as well. The chemistry of hydrogenating coal dictates that the pathways need not be simple. It is realistic to expect that when the coal structure is being reacted, it will be broken at random so that preasphaltene as well as asphaltene size molecules be produced.

Table 15 gives the correlation coefficients for the regression equations giving the rate constants for the various models. It can be seen that the fits are fairly good for the parallel - series and coal to products models. The

TABLE 14

RATE CONSTANTS FOR PARALLEL - SERIES MODEL

Temperature ^{o}C	Rate Constants Hr^{-1} k_1	k_2	k_3	k_4
350	2.11±.65	3.21±.66	0.014±.87	1.089±.57
390	7.61±1.53	4.97±1.52	-0.042±.61	0.833±.88
430	37.9±10.9	25.6±10.8	1.43±1.54	3.13±1.19

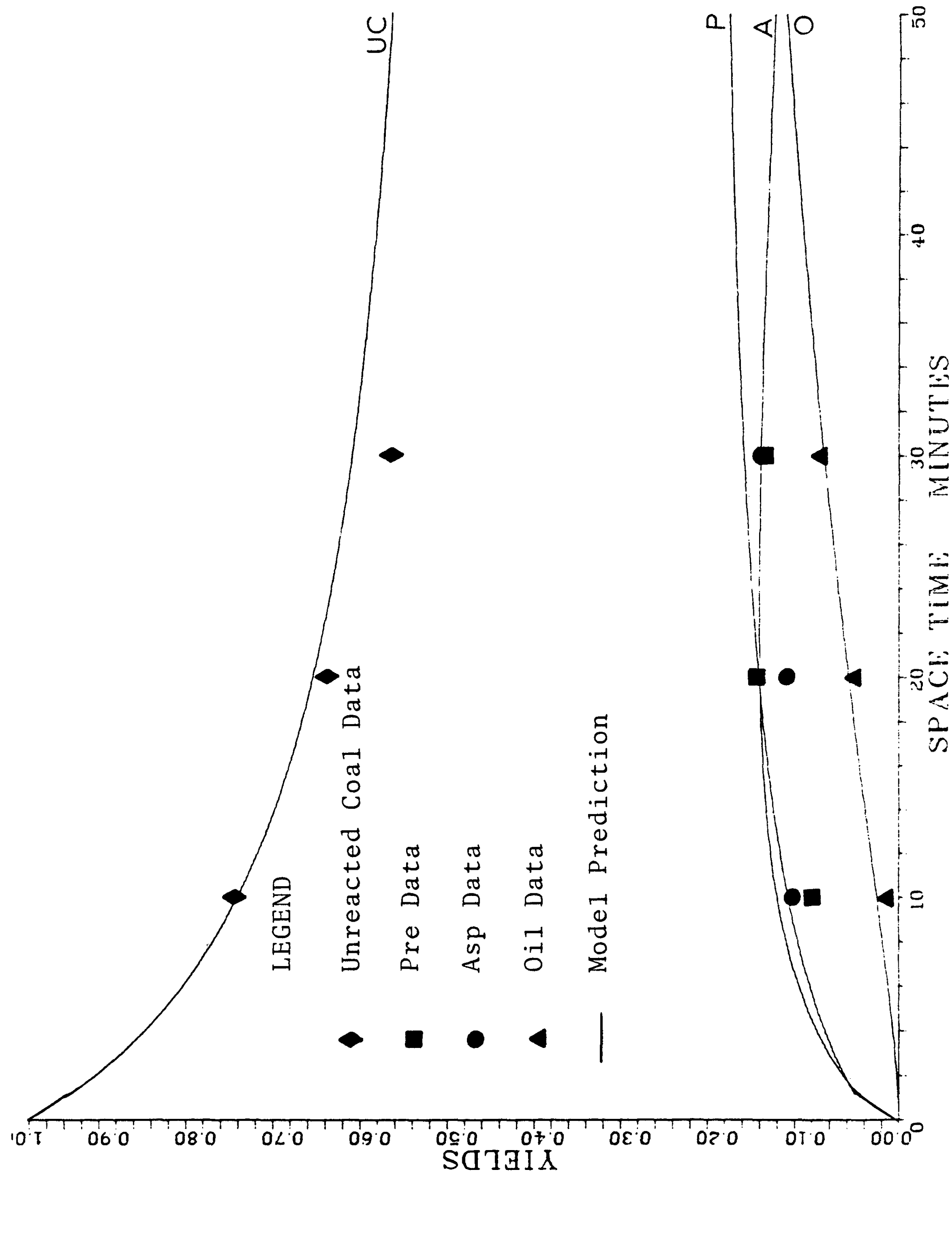


Figure 28. Parallel-Series Model Yields at 350°C

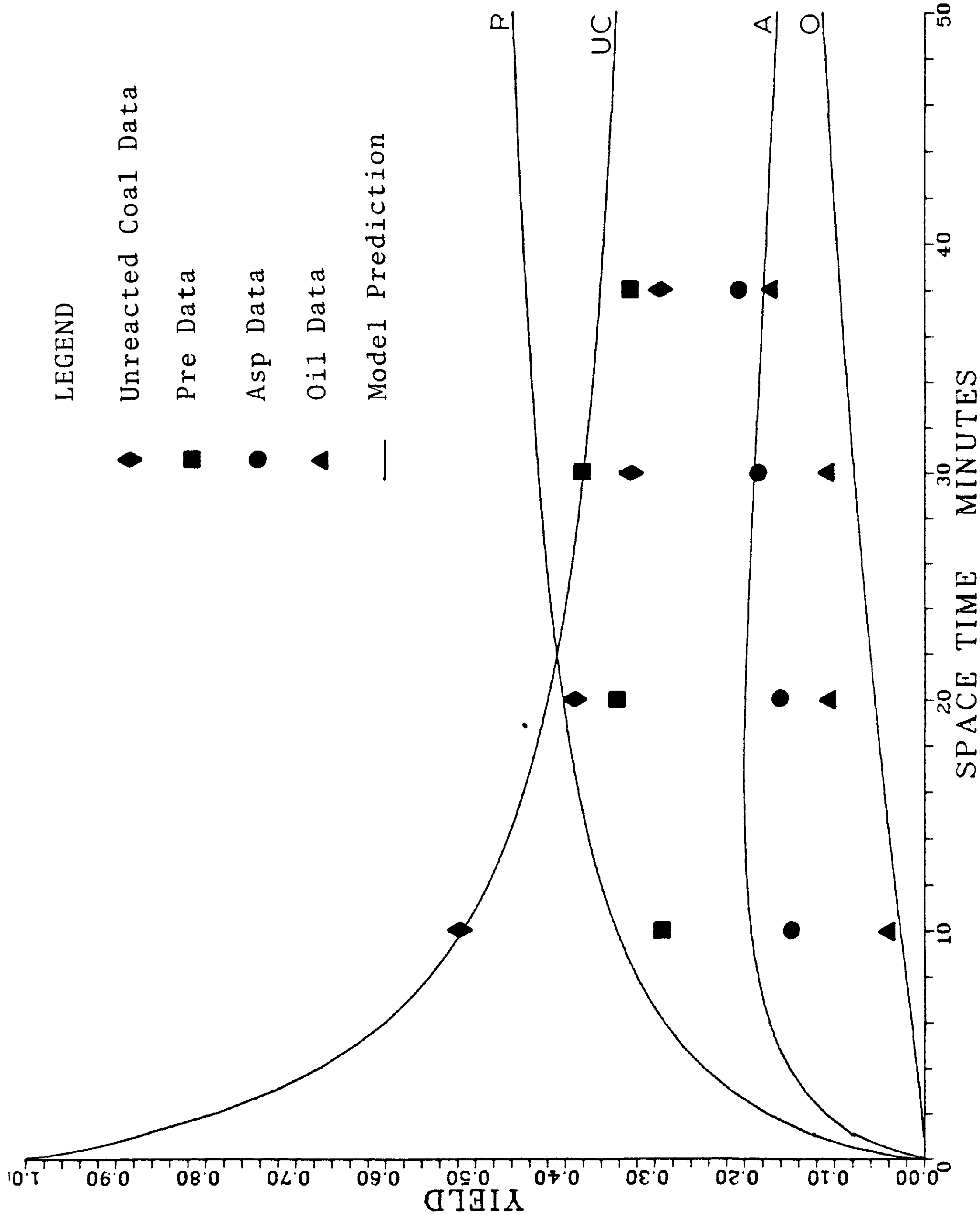


Figure 29. Parallel-Series Model Yields at 390°C

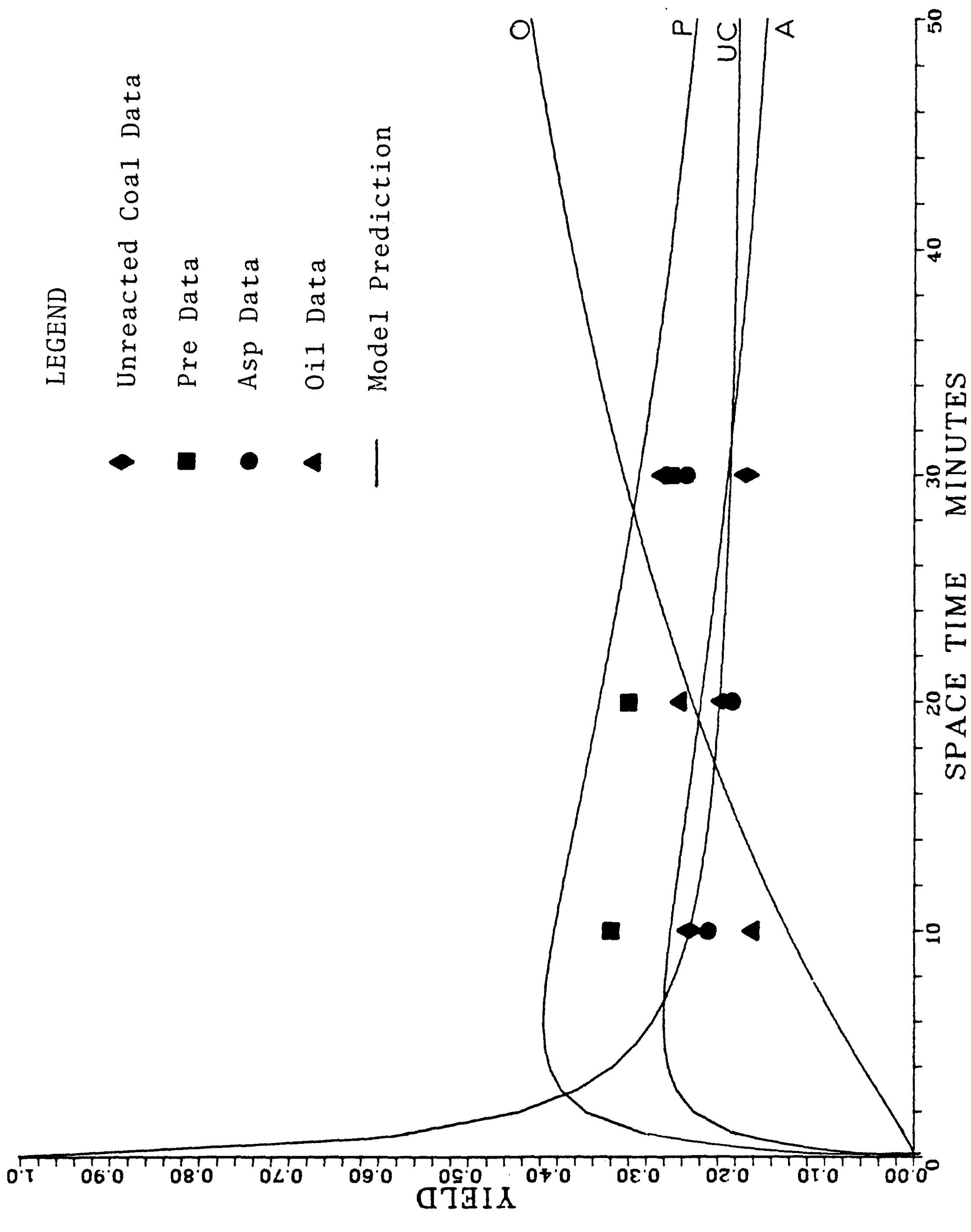


Figure 30. Parallel-Series Model Yields at 430^oC

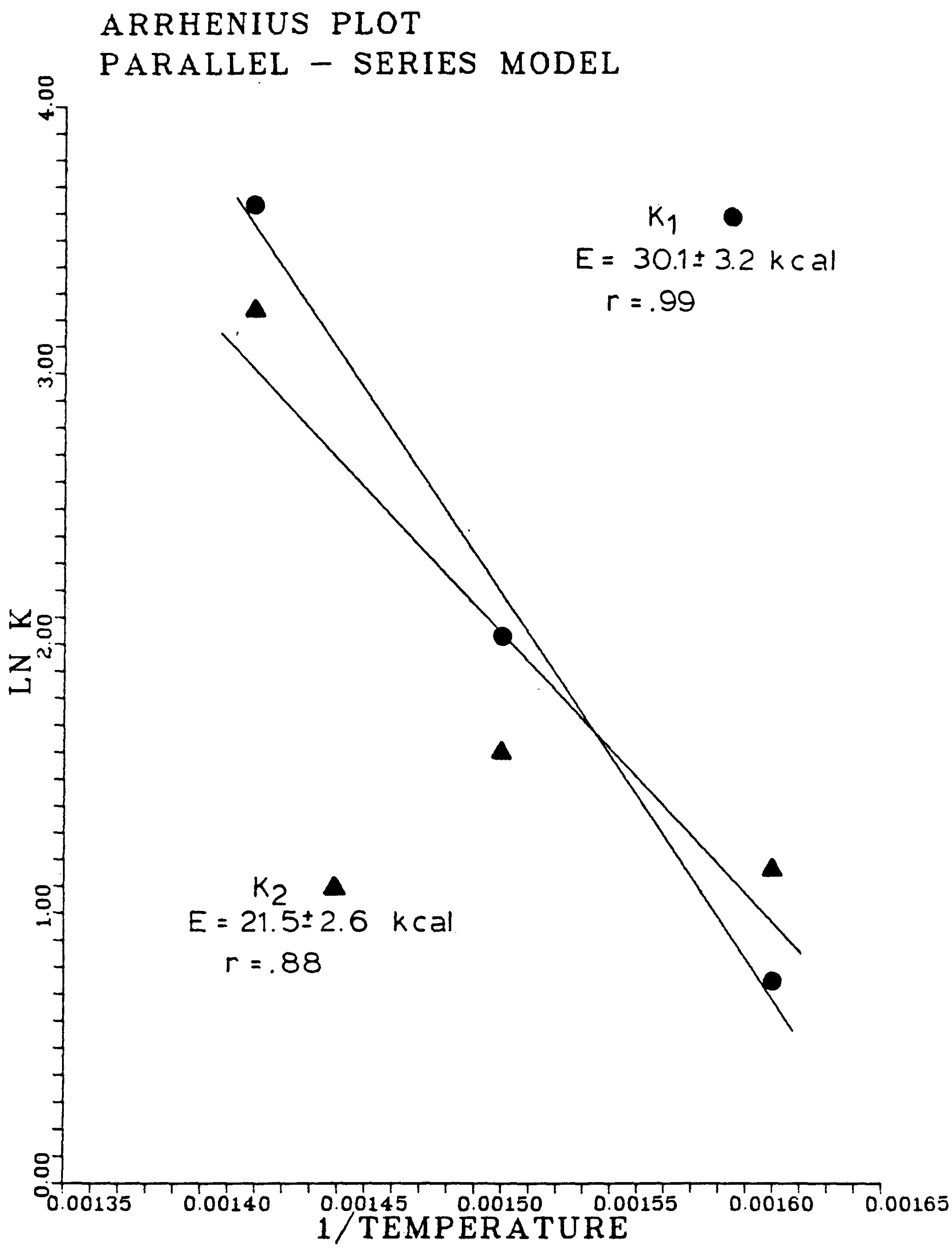


Figure 31. Arrhenius Plot Parallel-Series Model

TABLE 15

CORRELATION COEFFICIENTS

FOR REGRESSION EQUATIONS

Model	Temperature	R^2
Parallel - Series	350	.956
Parallel - Series	390	.874
Parallel - Series	430	.930
Coal to Products	350	.958
Coal to Products	390	.885
Coal to Products	430	.953
Series	350	.824
Series	390	.798
Series	430	.880

pure series model was found to have R^2 values less than both the other models. The coefficients for the 390^o regression equations are in all cases less than those given for the equations at 350 and 430^{o}C. It was this temperature which gave the slightly negative rate constant for k_3 and a k_4 which was almost the same as the 350^o value. The implication is that there may be a problem with some of this data.

There is a high degree of uncertainty in the rate constants determined by multiple linear regression due to the obvious nearness to completion of the coal/products reactions. The compositions of all products are almost at a steady state condition after 10 minutes of reaction, thus tending to create a large uncertainty in the calculation of reaction rates as the change in rates is small. Kinetic rates are best calculated in that region where the change in composition is the greatest with time. For this reason the area below 10 minutes needs to be investigated further. To do so would require a system modification which is beyond the scope of this study.

One of the objectives of this study was to compare the product distributions obtained with the results of Shalabi's batch studies. Table 16 shows the rate constants calculated for the coal to products mechanism (first-order, irreversible) from both this study and Shalabi's study. As can be seen, there exists no similarity in the rate constants.

Consideration of the two systems indicates that a direct comparison of the gross dissolution kinetics is not possible in this case. The batch study of Shalabi was conducted in a 10:1 by weight excess hydrogen donor vehicle, while this study used a solvent to coal ratio of 4:1, of which only 45% consisted of the hydrogen donating species, tetralin. Additionally, Shalabi's coal, while from the same mine, had a substantially different composition than the coal used for this study, especially in the inorganic fraction. Mineral catalysis by the large pyrite content of the coal used in the batch study may have thus strongly influenced the kinetics observed in the batch system. Next, the hydrogen partial pressures in the two studies were substantially different. The pressure contribution of the solvent is not as important in a flow system as in a batch reactor. In a flow system the vapors from the solvent are being swept away continuously with the hydrogen flow thus giving a higher hydrogen partial pressure.

TABLE 16

RATE CONSTANT COMPARISON

COAL TO PRODUCTS MODEL

This Study

Temperature ^oC	k Hr^{-1}
350	6.02
390	19.27
430	68.72

Shalabi's Data

350	.0322
375	.0977
400	.143

Finally, a look at the Arrenhius plot of the rate constants derived from the batch data for the coal to products model, Figure 32, shows a change in slope when going from the low temperature to the high temperature. This may indicate that the high temperature batch runs were operating in a mass transfer controlled regime, possibly due to the absence of a good dissolution solvent in the vehicle used for the batch study. If the kinetics were mass transfer controlled, obviously no comparisons can be made between the two studies.

Taking a qualitative look at the yield fractions of the two studies may at this point be the only effective comparitive technique. Table 17 gives the normalized yield fractions from Shalabi's work and the projected fractions from this work at the same temperatures. Noticeable differences in the trends appear in the oil and preasphaltene yields. The yields are higher for both these fractions in the present study (CSTR). This may indicate the importance of the presence of a good dissolution vehicle (cresol) in the solvent employed if light products (oils and asphaltenes) are the desired products of coal hydrogenation. Additionally a higher hydrogen partial pressure would have a tendency to produce a lighter product slate.

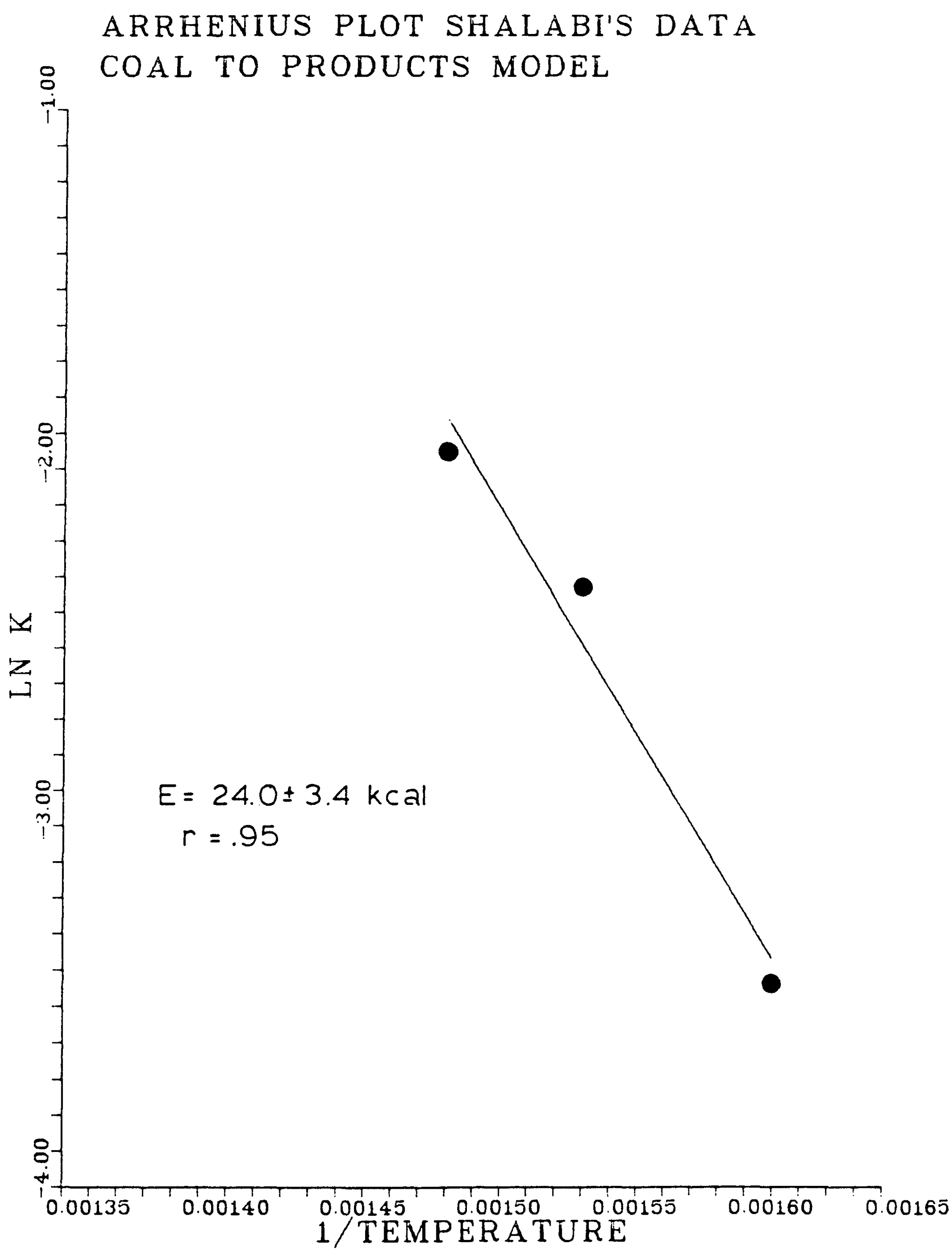


Figure 32. Arrhenius Plot Coal to Products Model, Shalabi's Data

TABLE 17

YIELD FRACTIONS

	Temp.	10 Min.		30 Min.	
		Shalabi	Present	Shalabi	Present
OIL	350	--	2.8	5.1	18.1
	375	7.0	6.	3.6	19
	400	4.7	10.	25	24
ASP	350	--	24.	27.4	31.8
	375	34.5	24.	47.6	30.
	400	43.5	25.	32.5	30.
PRE	350	--	19.4	21.2	31.3
	375	18.1	33.	28.6	45.
	430	25.6	41.	31.0	47.

CONCLUSIONS

1. The data has been modeled successfully as a first order pseudo irreversible reaction for conversion of coal to THF solubles where the rate expression is given by: Rate = $-k\ (1-x/a)$. Parameter "a" is the equilibrium conversion. The overall activation energy found was 25.4 kcal.

2. The data on product distribution was modeled successfully with the a parallel - series mechanism:

$$\begin{tikzcd}
\text{Coal} \arrow[rr, "k_2"] \arrow[d, "k_2"'] & & \text{Preasphaltenes} \arrow[dll, "k_3"] \\
\text{Asphaltenes} \arrow[rr, "k_4"'] & & \text{Oil}
\end{tikzcd}$$

   Activation energies of 30.1 kcal and 21.5 kcal were found for coal to preasphaltenes and asphaltenes respectively.

3. The synthetic recycle solvent developed by Whitehurst, et al has been found to be an efficient solvent in a flow system.

4. When the yield fractions were compared with those arrived at in a batch system the flow system produced more oils.

5. The activation energies for this study and for Shalabi's data, using the coal to products model, were comparable.

6. No correlation was found between the rate constants from batch and those from a CSTR.
7. At a space time of 10 minutes and a temperature of 430^{o}C the conversion of coal to products is almost complete.
8. The yields of asphaltenes and preasphaltenes varied little after 10 minutes for all temperatures.

RECOMMENDATIONS

1. Modify the sampling portion of the unit to obtain shorter residence times and reduce possible sampling errors.
2. Perform a comparative study using this solvent in a batch system.
3. Perform a tracer experiment to determine if the reactor is a true stirred tank reactor and determine the residence time distribution.
4. Check some of the data taken at 390^{o} to improve the rate constants in the parallel - series mechanism.

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APPENDICES

APPENDIX A

CONVERSION CALCULATION METHOD

(Sample wt) (.2) = Coal in Sample

(THFi - TARE) (% Ash in THFi) = Ash in Sample

Coal in Sample   Ash in Sample = MAF Coal in Sample

$$\frac{(Pi - Ti)}{MAF} \times 100 = \%\ \text{Asphaltene}$$

$$\frac{(Ti - THFi)}{MAF} \times 100 = \%\ \text{Preasphaltene}$$

$$\frac{(THFi - TARE - Ash)}{MAF} \times 100 = \%\ \text{Unreacted Coal}$$

100   % ASP - % PRE - % UC = % Oil

Pi = Pentane insoluble weight

Ti = Toluene insoluble weight

THFi = Tetrahydrofuran insoluble weight

TARE = TARE of Centrifuge tube

APPENDIX B

ELEMENTAL ANALYSIS

Run	Product	%C	%H	%N
CR20	ASP	82.06	6.07	1.34
CR20	PRE	76.48	5.69	1.64
CR21	ASP	83.48	6.13	1.57
CR21	PRE	76.07	5.54	1.71
CR22	ASP	85.53	5.83	2.02
CR22	PRE	78.18	5.20	2.10
CR29	PRE	77.93	5.57	1.71
CR30	ASP	82.12	6.03	1.44
CR30	PRE	77.03	5.36	1.78
CR31	ASP	83.20	6.00	1.77
CR31	PRE	79.91	5.44	2.11
CR33	ASP	83.22	6.04	1.57
CR33	PRE	81.45	5.62	2.09

APPENDIX C
MINITAB DATA FILE
AND PRINTOUT

```
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1.1976,0,.5392,0,.1939,-.2396,0
.1650,0,0,.5392,0,.2396,.1939
2.0094,.3302,.3302,.3302,0,0,0
.7668,.3302,0,0,-.3186,0,-.3186
.6324,0,.3302,0,.3186,-.2508
.3012,0,0,.3302,0,.2508,.3186
1.6244,.1878,.1878,.1878,0,0,0
.500,.1878,0,0,-.3130,0,-.3130
.5566,0,.1878,0,.3130,-.3183,0
.3620,0,0,.1878,0,.3183,.3130
```

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[20:02:54]
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.9942,0,.3324,0,.4043,-.2057,0
.3456,0,0,.3324,0,.2057,.4043
2.5374,.1542,.1542,.1542,0,0,0
1.2327,.1542,0,0,-.4739,0,-.4739
.5508,0,.1542,0,.4739,-.2236,0
.4449,0,0,.1542,0,.2236,.4739
1.8722,.0639,.0639,.0639,0,0,0
.9268,.0639,0,0,-.5264,0,-.5264
.4384,0,.0639,0,.5264,-.2592,0
.3014,0,0,.0639,0,.2592,.5264
1.5510,.0175,.0175,.0175,0,0,0
.6202,.0175,0,0,-.4558,0,-.4558
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.3778,0,0,.0175,0,.2874,.4558
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1.3206,0,0,.0849,0,.2808,.4143
2.8812,.0396,.0396,.0396,0,0,0
.9792,.0396,0,0,-.3894,0,-.3894
.6330,0,.0396,0,.3894,-.2510,0
.9600,0,0,.0396,0,.2510,.3894
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.5412,0,.0099,0,.3356,-.3106,0
.6800,0,0,.0099,0,.3106,.3356
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   READ 'DAT390.FOR'C1,C2,C3.C4.C5.\.\,C6,C7,^U
READ  DAT390.FOR'C1,C2,C3,C4,C5,C6,C7,\,\
COLUMN        C1           C2           C3           C4           C5           C6
COUNT         16           16           16           16           16           16
ROW
  1      4.00560     0.332400     0.332400     0.332400     0.000000     0.000000
  2      2.04780     0.332400     0.000000     0.000000    -0.404300     0.000000
  3      0.99420     0.000000     0.332400     0.000000     0.404300    -0.205700
  4      0.34560     0.000000     0.000000     0.332400     0.000000     0.205700
       .

COLUMN          C7
COUNT           16
     0.000000    -0.404300     0.000000     0.404300  .

   NO ERS
NOCONSTANT
-- NOBRIEF
   REGRESS Y IN C1 ON 3 PRED. IN C2,C3,C4

THE REGRESSION EQUATION IS
Y =   7.27 X1 +  3.73 X2 +  1.99 X3

                                          ST. DEV.     T-RATIO =
        COLUMN        COEFFICIENT         OF COEF.     COEF/S.D.
NOCONSTANT
X1      C2                 7.27             1.34          5.44
X2      C3                 3.73             1.34          2.79
X3      C4                 1.99             1.34          1.49

THE ST. DEV. OF Y ABOUT REGRESSION LINE IS
S =      0.5752
WITH (  16- 3) =  13 DEGREES OF FREEDOM

 ANALYSIS OF VARIANCE

 DUE TO        DF           SS         MS=SS/DF
REGRESSION      3      33.2383         11.0794
RESIDUAL       13       4.3007          0.3308
TOTAL          16      37.5391

FURTHER ANALYSIS OF VARIANCE
SS EXPLAINED BY EACH VARIABLE WHEN ENTERED IN THE ORDER GIVEN

 DUE TO        DF           SS
REGRESSION      3      33.2383
C2              1      28.4808
C3              1       4.0218
C4              1       0.7358

             X1            Y     PRED. Y     ST.DEV.
ROW          C2           C1       VALUE     PRED. Y     RESIDUAL        ST.RES.
  1       0.332        4.006       4.320       0.445       -0.315        -0.86 X
  2       0.332        2.048       2.417       0.445       -0.369        -1.01 X
  3       0.000        0.994       1.241       0.445       -0.246        -0.68 X
  4       0.000        0.346       0.663       0.445       -0.318        -0.87 X
  5       0.154        2.537       2.004       0.206        0.533         0.99
  6       0.154        1.233       1.121       0.206        0.112         0.21
  7       0.000        0.551       0.576       0.206       -0.025        -0.05
  8       0.000        0.445       0.308       0.206        0.137         0.26
  9       0.064        1.872       0.831       0.085        1.042         1.83
 10       0.064        0.927       0.465       0.085        0.462         0.81
 11       0.000        0.438       0.238       0.085        0.200         0.35
 12       0.000        0.301       0.127       0.085        0.174         0.31
 13       0.018        1.551       0.227       0.023        1.324         2.30R
 14       0.018        0.620       0.127       0.023        0.493         0.86
 15       0.000        0.391       0.065       0.023        0.325         0.57
 16       0.000        0.378       0.035       0.023        0.343         0.60

R DENOTES AN OBS. WITH A LARGE ST. RES.
X DENOTES AN OBS. WHOSE X VALUE GIVES IT LARGE INFLUENCE.


   PRINT XTXINVERSE

               1             2             3
         5.40904
        -1.80301       5.40904
        -1.80301      -1.80301       5.40904

   REGRESS Y IN C1 ON 3 PRED. IN C2,C5C\C\,C6   .
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APPENDIX D

NORMALIZED DATA

Temperature $350^{o}C$
a .51

T(min)	α	β	γ	Xc
10	.1939	.2396	.0275	.4608
20	.3186	.2508	.1004	.6698
30	.3130	.3183	.1810	.8122

Temperature $390^{o}C$
a .72

10	.4043	.2057	.0576	.6676
20	.4739	.2236	.1483	.8458
30	.5264	.2592	.1507	.9361
38	.4558	.2874	.2393	.9825

Temperature $430^{o}C$
a .82

10	.4143	.2808	.2201	.9151
20	.3894	.2510	.3200	.9604
30	.3356	.3106	.3440	.9902