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I am submitting herewith a thesis written by Richard E. Edwards, Jr. entitled "Evaluation and Analysis of Coking in Coal Liquefaction Preheaters." I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

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EVALUATION AND ANALYSIS OF COKING IN COAL LIQUEFACTION PREHEATERS

A Thesis

Presented for the

Master of Science

Degree

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Richard E. Edwards, Jr.

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ABSTRACT

The deposition of carbonaceous solids (coke) in direct liquefaction fired preheaters is a common technical problem experienced by many of the liquefaction processes of interest [including the Solvent Refined Coal Processes (SRC-I and SCR-II), the Hydrocarbon Research Process (H-Coal), and the Exxon Donor Solvent Process (EDS)], yet the causes for such behavior are not fully understood. This study is aimed at providing an insight into coking behavior by evaluating the influence of process operational conditions and coal-solvent properties on the deposition of coke in preheater coils. The Wilsonville, Alabama SRC-I pilot plant, having started operations in 1974, is the largest and most complete source of data for runs during which both coking did and did not occur in fired preheaters. Using, as a source of guidance, the mostly qualitative results obtained from a survey of the literature on coke formation from some coal-oils but primarily petroleum liquids, and a proposed incipient coking correlation based on coking occurring when the concentration of key coking precursors reaches its solubility limit, the nineteen coking data points obtained from the Wilsonville facility were correlated using multiple regression techniques with correlation coefficients (R^2-values) as high as 0.95 achieved depending on the combination of process condition factors and coal-solvent properties chosen. Developed incipient coking curves serve as a boundary between a non-coking domain and a coking domain. Those factors statistically indicated to influence coking tendencies are, in order of importance:

a) estimated preheater mean slurry residence time, b) inlet hydrogen partial pressure, c) combined coal oxygen and nitrogen content, d) coal vitrinite content, e) coal sulfur content, and f) solvent quality (short) as determined by the Wilsonville facility. Results indicate that increases in slurry residence time, combined coal oxygen and nitrogen content, or coal vitrinite content tend to promote coking tendencies, while increases in inlet hydrogen partial pressure or coal sulfur content tend to suppress coking tendencies. The reported value for solvent quality was usually statistically insignificant and thus its exact role, if it is important at all, is unclear. The inclusion of additional data indicated by the literature to influence coking, but not available from the Wilsonville facility, such as coal hydroxylic oxygen content and non-basic nitrogen content as well as complete coal petrographic data, are anticipated to further refine incipient coking correlations. Also, further refinements should be achieved as better methods to estimate slurry mean residence time in multi-phase flow through preheater coils are developed and as methods to calculate the hydrogen partial pressure locally in preheater coils, through the determination of vapor-liquid equilibria data for coal-derived multi-component solvents, are developed.

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CHAPTER 1

INTRODUCTION

Although many accomplishments have been made in the field of coal liquefaction in the last decade (McNeese, L.E., 1979), a number of technical problems have not been completely resolved. One such problem is the formation of coke (carbonaceous deposits which include volatiles and mineral material) in liquefaction process equipment. Each of the four major coal liquefaction processes receiving U.S. Department of Energy support [i.e., the Solvent Refined Coal Processes (SRC-I and SRC-II), the Hydrocarbon Research Coal Process (H-COAL), and the Exxon Donor Solvent Process (EDS)], each similar in many aspects, have experienced coke buildup in various processing units to some degree. The extent of coke buildup can vary from small deposits, which cause inaccuracies in process stream measurements, to large deposits, which can plug process equipment resulting in shutdown and extensive cleaning operations. The numerous difficulties reported by the major liquefaction facilities attest to the seriousness of coke deposition (see for example, SRC Process Report FE 2270-48, 1979 and EDS Process Report FE 2893-65, 1981).

At present, no reliable method is available to predict either the occurrence of coke deposition or the absence of coke deposition in relation to the operating conditions and process parameters which are typical of coal liquefaction processes. This current void is partially due to the unpredictability of coking which stems from the complex nature of both coal liquefaction and the coking process. Also, of major significance, is the lack of any organized coking data base with

which to compare and contrast the numerous process parameters as to their importance or lack of importance during coke formation. Therefore, an aim of this study is to establish an organized source of information consisting of process parameters and operating conditions during which coking did and did not occur.

The results of a survey of the coking data available from the coal liquefaction facilities and the literature relevant to coke formation, indicate the ability to characterize coking occurrences with a "semi-quantitative" correlation based on process conditions and coal properties. The largest source of coking data is from the operation of the coal liquefaction pilot plant at Wilsonville, Alabama (SRC-I). A description of the coal liquefaction process at Wilsonville is given in Chapter 2. The coking data from this facility consists primarily of process conditions during which coking occurred in the fired preheater. It is desired to consolidate this data in an attempt to quantify when coking occurs. Major variables which are considered of primary importance in attempting to correlate process variables with coking occurrences are: Residence time (not always known apriori), temperature, hydrogen partial pressure, solvent properties, feed slurry concentration, and coal type including mineral, heteroatom and petrographic composition.

The primary sources of information for this study include (a) Chemical Abstracts, (b) American Petroleum Institute Data Base, (c) progress and topical reports from projects funded by the Department of Energy (DOE) and the Electric Power Research Institute (EPRI). A limited amount of information was also obtained from unpublished

documents, such as memoranda resulting from technical review meetings for major coal liquefaction projects. The searching and screening of pertinent literature focused on the following subject areas: (a) specific operating experiences dealing with coking in coal liquefaction process equipment and related studies, (b) properties and conditions affecting coke formation and coking rates (e.g., temperature, hydrogen partial pressure and solubility, residence time, coal properties, etc.), and (c) properties and factors affecting heat and mass transfer in process equipment, as they relate to coking behavior (e.g., transport properties including viscosity, thermal conductivity, and hydrogen diffusivity; geometry, flow rates and flow regimes).

The results of the literature survey, which are first preceded by a general discussion of direct coal liquefaction (Chapter 2), are subsequently discussed in two chapters. Chapter 3 contains a general discussion of the coking problems in coal liquefaction fired preheaters. This is followed by Chapter 4, which contains an evaluation of the literature pertinent to coking, and is to be used as a guide and technical base for correlating coking occurrences.

CHAPTER 2

BACKGROUND INFORMATION - DIRECT COAL LIQUEFACTION

The direct liquefaction of coal is not a relatively new concept. In 1913 Bergius and Billwiller demonstrated the ability to liquefy coal, when they obtained liquid products from coal under high pressure and temperature in the presence of hydrogen (Goldman,G.K., 1972). Due to an apparent shortage of petroleum reserves, which lasted from the mid-1920's through World War II, the commercialization of the Bergius' process soon followed. A coal hydrogenation plant, based on the Bergius' process, was constructed at Leuna, Germany, and started operations in April 1927. The Leuna plant hydrogenated brown coal and was used to produce gasoline and fuel oil.

With time, additional improvements in the original Bergius' process were made along with advances in indirect liquefaction, with the net result being the operation of twelve coal conversion plants in Germany by 1943. These facilities were hydrogenating brown and bituminous coal to supply 98% of the aviation gasoline, or 47% of the total hydrocarbon products consumed in Germany at that time (Wen,C.Y. and Lee,E.S., 1979). However, at the end of World War II, economic reasons along with post war presures caused the shutdown of most of the German liquefaction facilities.

Shortly thereafter, an interest in coal liquefaction was spawned in the United States. With the fantastic increase in the consumption of petroleum products and the reduced rate in the discovery of petroleum reserves throughout the 1940's, a growing concern about the

future supply of petroleum led to the passage of the Synthetic Liquid Fuels Act in 1944 and to the creation of the Office of Synthetic Liquid Fuels within the U.S. Bureau of Mines. A good deal of research and development in the field of coal liquefaction was conducted, and in 1949 a coal hydrogenation demonstration plant at Louisiana, Missouri was completed (Markovits,J.A., 1949). The demonstration plant utilized modern United States engineering practices along with the operating experience and technology of the German facilities. Unfortunately, with the discoveries of Middle East petroleum reserves increasing at a rapid rate in the early 1950's , and with the change in administration in the United States government in 1953, the development of coal liquefaction was discontinued at that time.

In the last decade, however, a number of factors have brought about renewed interest in the direct liquefaction of coal as a viable energy source for the United States. A partial list of these contributory factors include (a) the increasing cost of imported petroleum which currently accounts for approximately 35% of the United States consumption (Balzhiser,R.E., 1982), (b) the heavy burden imported petroleum places on the United States balance of payments and the value of United States currency, (c) the need for clean, easily transportable fuels to satisfy the transportation sector, which currently consumes over one-half of the liquid fuels in the United States, and (d) the vast supplies of coal in the United States, which contain more energy than the Middle East oil reserves (Brennan,J.P. and others, 1977).

Currently, four major direct liquefaction processes are in operation on a pilot plant scale in the United States. These consist of (a) the Solvent Refined Coal Process (SRC-I) at Wilsonville, Alabama, (b) the Solvent Refined Coal Process (SRC-I and SRC-II) at Fort Lewis, Washington, (c) the H-Coal Process at Catlettsburg, Kentucky, and (d) the Exxon Donor Solvent Process (EDS) at Baytown, Texas. Each of these processes are similar in that a slurry of coal in a process-derived oil is subjected to fairly severe liquefaction conditions in the presence of hydrogen. An individual discussion of each of these processes follows.

2.1 Solvent Refined Coal Processes (SRC-I and SRC-II)

The Solvent Refined Coal Process was developed by the Pittsburgh and Midway Coal Mining Company which is a subsidiary of the Gulf Oil Corporation.

2.1.1 SRC-I

In the SRC-I process, shown schematically in Figure 2.1, process coal is slurried with a process-derived solvent and is pumped through a fired preheater into a dissolver. Hydrogen is added both upstream and downstream of the preheater. Liquefaction takes place primarily in the dissolver where conditions are in the general range of 800-900 ^{o}F, around 2000 psig, and a residence time of 20-60 minutes. About 90% of the organic material in the coal is dissolved with the remaining solids consisting of ash-forming inorganic material and some undissolved carbon. There is no catalyst other than the catalytically-active mineral matter associated with the coal.

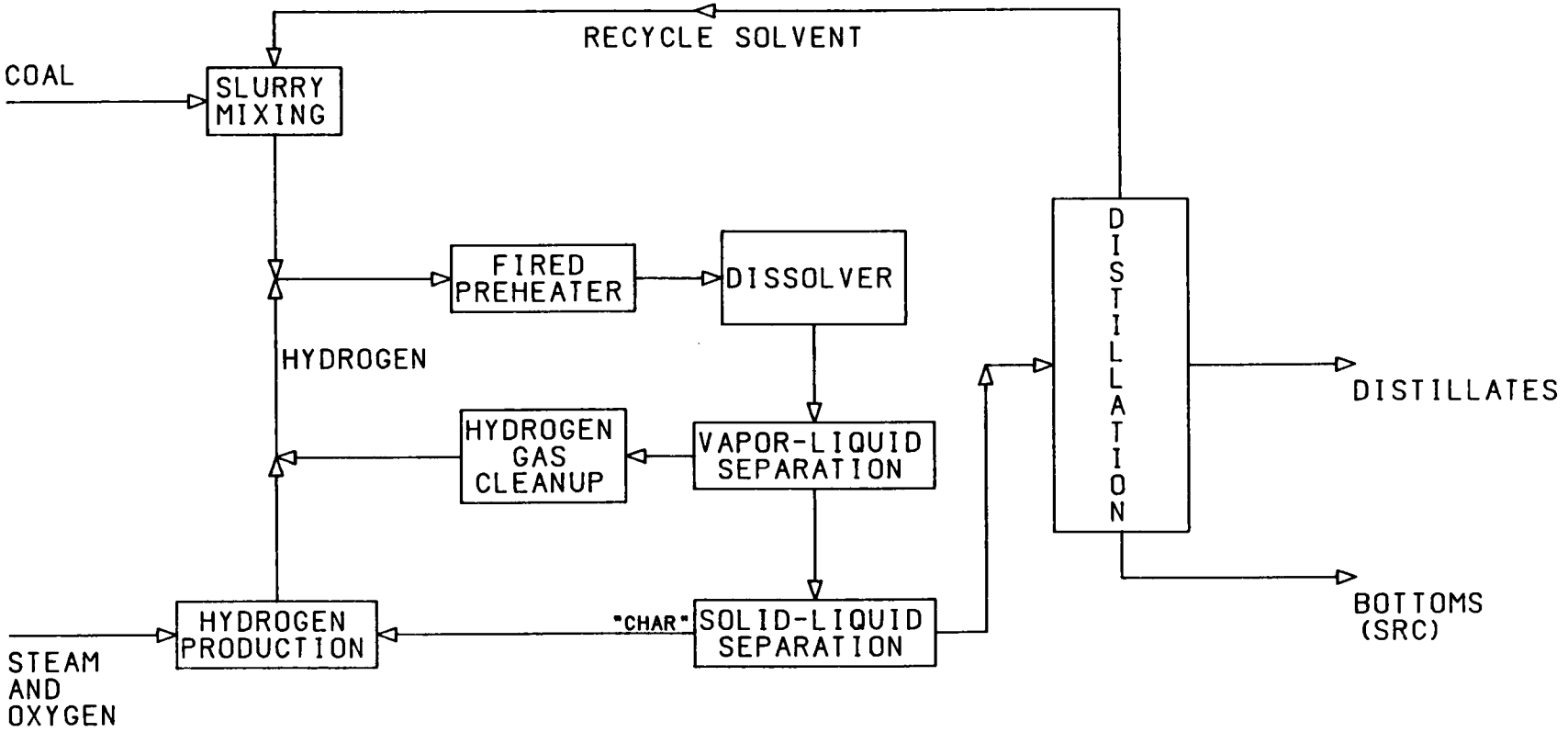

Figure 2.1 Schematic Representation of the SRC-I Direct Coal Liquefaction Process

Source: McNeese, L.E., R. Salmon, H.D. Cochran, Jr., "Recent Developments in Coal Liquefaction in the United States", presented at the 6th Energy Technology Conference, Washington, D.C., Feb. 26, 1979.

Unreacted hydrogen is separated from the product stream in a series of liquid-vapor separation steps, and in turn is freed of hydrogen sulfide by acid gas absorption before being recycled to the system. The resulting product stream goes through a solid-liquid separation step (filtration) which removes any unreacted coal, ash, and mineral matter. The organic portion of these solids is gasified to produce hydrogen for the process. The liquid product stream is vacuum distilled to produce recycle solvent, some distillates, and the bottoms product. The bottoms product, the principle product of the process, is a heavy residual oil called solvent-refined coal. On cooling, this SRC product is a uniform, low-sulfur, low-nitrogen, low-ash, solid material with a melting point between 300-400 ^{o}F and a heating value of about 16,000 Btu/lb (Smith,I.H. and Werner,G.J., 1976).

The net result of the process is the production of a solid material (SRC) with a higher heating value per pound than the feed coal and low enough in sulfur content, nitrogen content, and particulate matter to meet regulatory levels when combusted in commercial boilers. In June 1977, 3000 tons of solid SRC were successfully combusted at Georgia Power Companies plant Mitchell in Albany, Georgia (Hickman,C.E., 1979). Thus, SRC can be burned by utilities to generate electricity, or alternatively it can be used as a starting material to produce liquid fuels, as well as industrial and metallurgical coke.

2.1.2 SRC-II

The SRC-II process, shown schematically in Figure 2.2, is similar to the SRC-I process except that the hydrogenation severity is greater, the separation of solids and liquid is by vacuum distillation instead of filtration, and a slurry of solids (consisting of undissolved coal, ash, and mineral matter) in a process-derived oil is recycled instead of a process-derived solvent alone. Because the hydrogenation severity is greater than the SRC-I process the main products are now naptha and a fuel oil distillate. With lighter hydrocarbons produced a greater amount of hydrogen is required, but, because the products are lighter, the troublesome solid-liquid separation step can be accomplished by distillation, which is a relatively simple operation. Also, the sulfur and nitrogen contents of the fuels are lower than the SRC-I product.

SRC-II products can be further refined to transportation fuels or burned as heavy fuel oil in electric power generating facilities. The successful combustion of an SRC-II liquid was conducted in 1978 at a Consolidated Edison power station in New York City (McNeese,L.E. and others, 1979). Air emissions were within acceptable limits.

2.2 H-COAL Process

The H-Coal process was developed by Hydrocarbon Research Incorporated and utilizes their ebullating bed reactor system shown in Figure 2.3. In this process, shown schematically in Figure 2.4, pulverized coal is slurried with a recycled heavy distillate, combined with a hydrogen rich gas stream, and fed through a fired preheater to

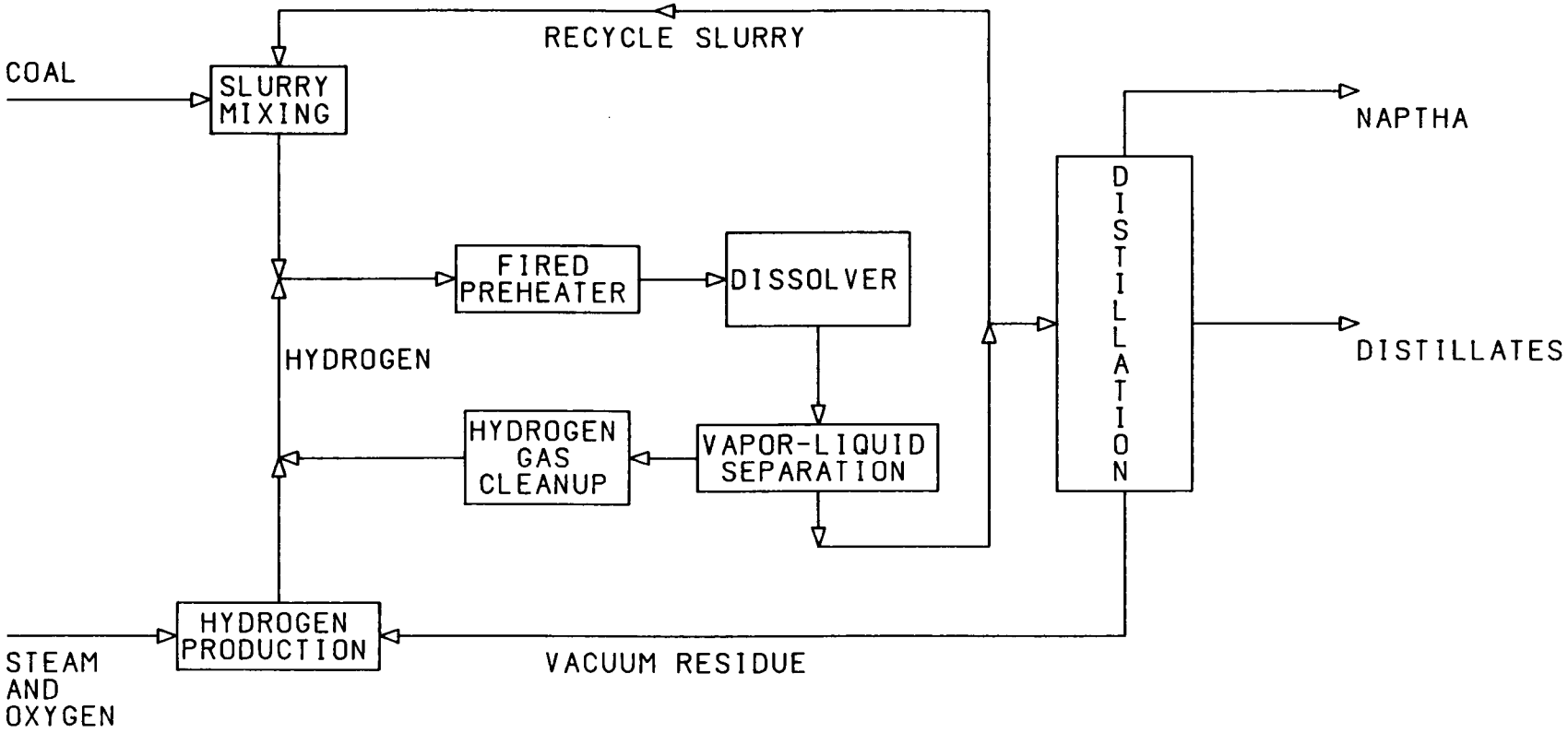

Figure 2.2 Schematic Representation of the SRC-II Direct Coal Liquefaction Process

Source: McNeese, L.E., R. Salmon, H.D. Cochran, Jr., "Recent Developments in Coal Liquefaction in the United States", presented at the 6th Energy Technology Conference, Washington, D.C., Feb. 26, 1979.

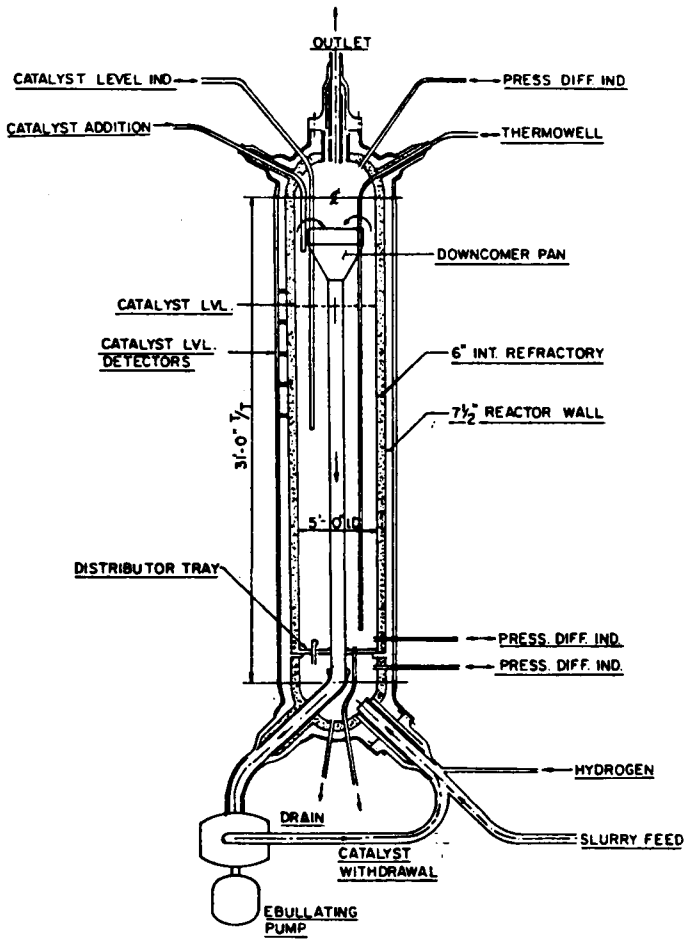

Figure 2.3 H-Coal Ebullating Bed Reactor System

Source: Stotler, H.H. and R.T. Schuttler, "Status and Plans of H-Coal Pilot Plant", in Coal Processing Technology published by AICHE, New York, 1979.

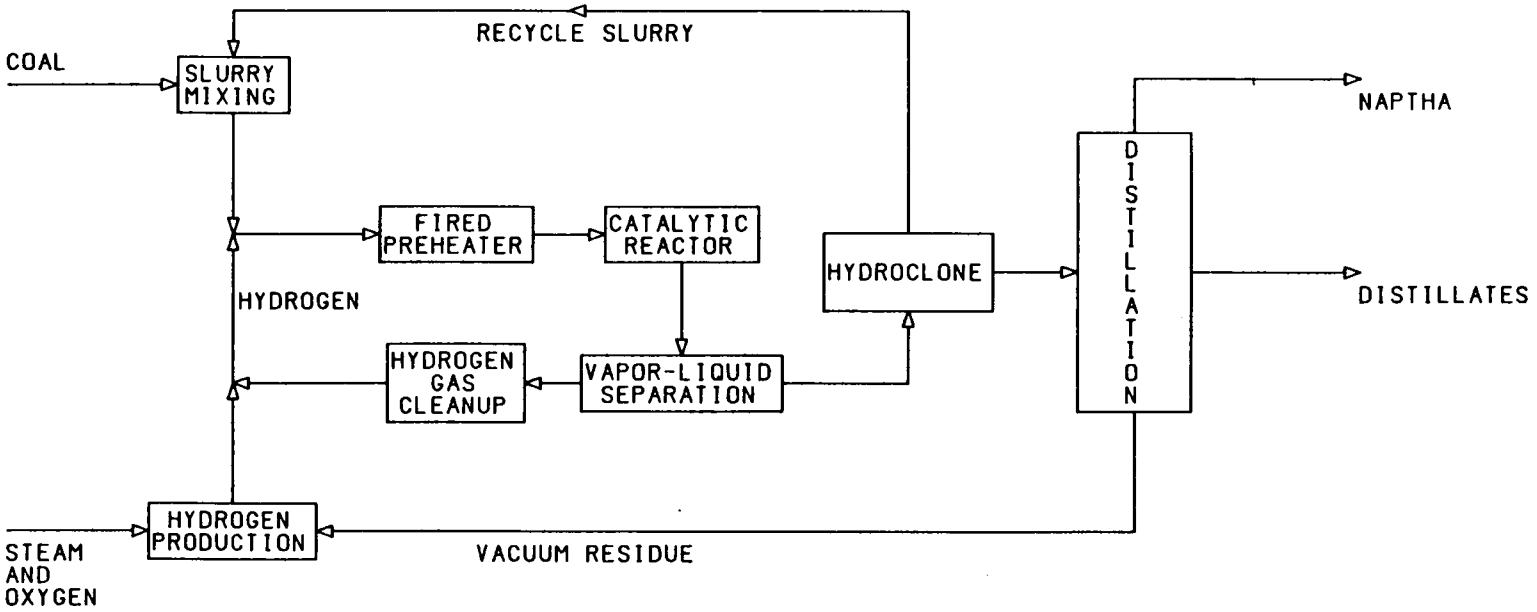

Figure 2.4 Schematic Representation of the H-Coal Direct Liquefaction Process

Source: McNeese, L.E., R. Salmon, H.D. Cochran, Jr., "Recent Developments in Coal Liquefaction in the United States", presented at the 6th Energy Technology Conference, Washington, D.C., Feb. 26, 1979.

the ebullating bed reactor, which typically operates around 200 atm. and 850 ^{o}F. The reactor feed and an internal liquid recycle stream enter the bottom of the reactor and cause the fluidization of the catalyst bed. The catalyst is cobalt-molybdate on alumina pellets and can be added or removed continuously as required. Both a vapor stream (consisting primarily of hydrogen, hydrocarbon gases, hydrogen sulfide, and ammonia) and a liquid stream containing entrained solids are removed from the top of the reactor. After condensation to remove heavier hydrocarbons, hydrogen is recovered from the reactor vapor stream. A portion of the reactor liquid stream is hydrocloned to reduce its solids content and is used as recycle oil to be slurried with fresh coal. The remainder of the liquid product is vacuum distilled to produce naptha, a distillate fuel oil, and a bottoms stream. The bottoms stream, which contains some unreacted carbon, goes to a gasifier for hydrogen production.

2.3 Exxon Donor Solvent Process

In the Exxon Donor Solvent process, shown schematically in Figure 2.5, coal is slurried with a donor solvent which has been catalytically hydrogenated to improve its ability to supply hydrogen during liquefaction reactions. The slurry is preheated, combined with recycle and makeup hydrogen, and fed to a non-catalytic liquefaction reactor which typically operates at 2000 psia and 800-900 ^{o}F. The reactor effluent goes through a vapor-liquid separator to obtain recycle hydrogen. The liquid effluent is vacuum distilled to obtain recyle solvent, naptha, a fuel oil distillate, and a solid residue

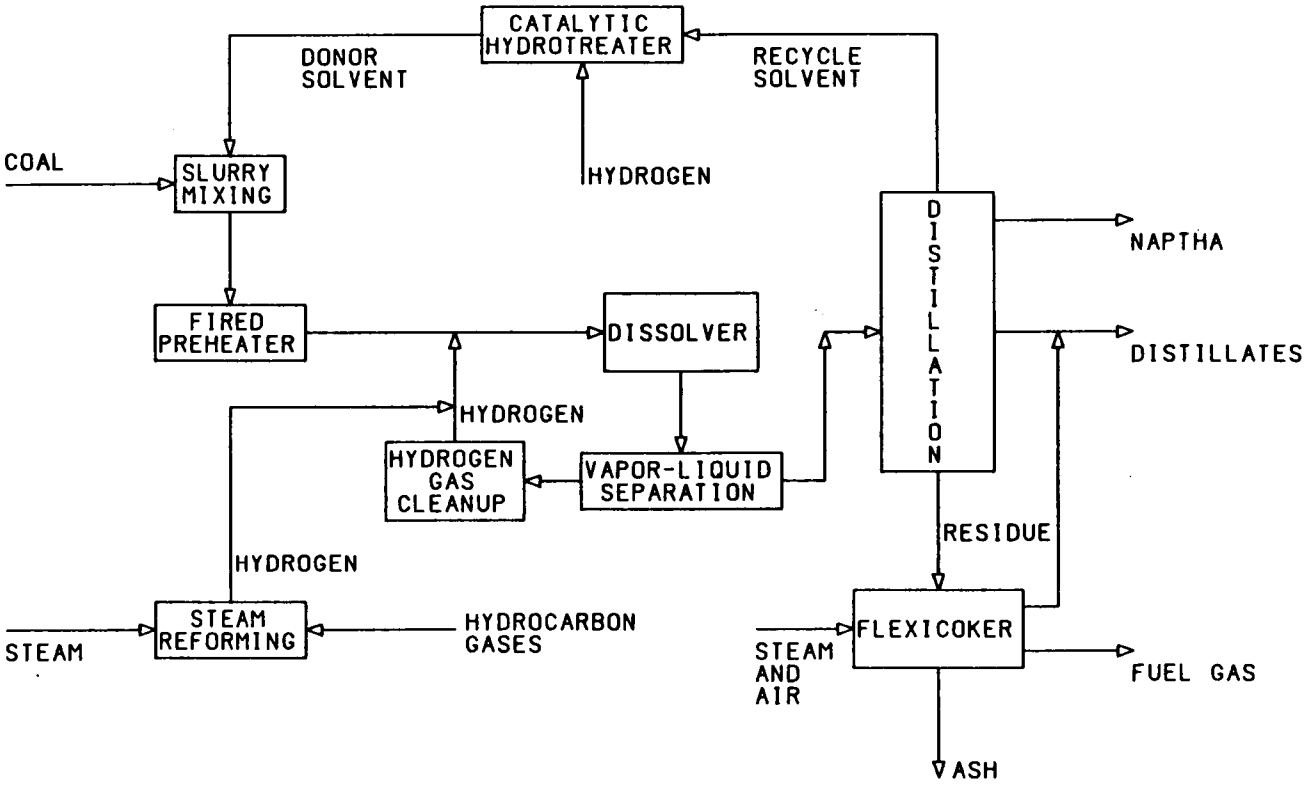

Figure 2.5 Schematic Representation of the Exxon Donor Solvent Direct Coal Liquefacion Process

Source: McNeese, L.E., R. Salmon, H.D. Cochran, Jr., "Recent Developments in Coal Liquefaction in the United States", presented at the 6th Energy Technology Conference, Washington, D.C., Feb. 26, 1979.

consisting of unreacted coal and ash. The recycle solvent is rehydrogenated in a fixed bed catalytic reactor to produce the donor solvent. The solid residue, which is removed as bottoms from the vacuum distillation tower, goes to a Flexicoker/gasifier for recovery of additional liquids and production of a fuel gas. Makeup hydrogen is produced by steam reforming the light hydrocarbon gases produced from the liquefaction reactor and which were previously separated from the recycle hydrogen.

CHAPTER 3

COKING EXPERIENCES IN COAL LIQUEFACTION FIRED PREHEATERS

The fired coal slurry preheaters being used in liquefaction pilot plants are generally gas-fired radiant units with the coal slurry travelling through a helical or serpentine type coil. The preheater at the Wilsonville pilot plant (shown in Figure A.1 of Appendix A), for example, is a gas-fired radiant unit with a single helical coil made of 316 stainless steel 1 1/4 inch diameter schedule 160 tubing, and is 606 feet in length. Typical operating conditions of this preheater are summarized in Table 3.1. One of the two fired preheaters being used at the Fort Lewis pilot plant is also a coil type; the coil, however, is of a " rounded rectangle " configuration. The Fort Lewis preheater can also accommodate either 1 1/2 inch or 2 inch diameter schedule 160 stainless steel tubing. Operating constraints for the Fort Lewis Preheater are summarized in Table 3.2. Both the Wilsonville and the Fort Lewis preheaters are provided with thermocouples for measuring fluid and skin (outer metal surface) temperatures at numerous locations along the coil; pressure taps are also provided at the inlet and outlet of the coil. An unusually high difference between the local skin temperature and the local fluid temperature, combined with a higher than normal pressure drop across the coil, would be indicative of coke buildup in the coil.

TABLE 3.1

Typical ranges of operating conditions for the Wilsonville Fired Preheater

Temperature, ^{o}F	
Inlet	115-155
Outlet	770-885
Inlet Pressure, psia	
Total	1720-2410
Hydrogen Partial Pressure	1460-2050
Coal Type	Kentucky No.9
Wt % Coal in Feed Slurry	33-40
Flow Rates of Feed Streams, lb/hr	
Coal	246-560
Solvent	600-890
Hydrogen Gas (app.85 vol.% Hydrogen)	100-150

Source: Solvent Refined Coal (SRC) Process Operation of Solvent Refined Coal Pilot Plant at Wilsonville, Alabama, Technical Progress Reports FE 2270 -36 -46 -48 -60 -63 -65 -66 -68 -70 , 1979-1980.

Table 3.2

Fort Lewis Preheater Operating Constraints
for Typical SRC-I and SRC-II
Operating Conditions

	SRC-I	SRC-II
Slurry Feedrate to Preheater,lb/hr	6000-13000	5000-8500
Hydrogen Feedrate to Preheater,scf/hr	40-60000	10-64000
Slurry Feed Temperature,^{o}F	150-200	300-370
Hydrogen Feed Temperature,^{o}F	60-360	60-360
Preheater Outlet Temperature,^{o}F	740-760	700-810
Dissolver Temperature,^{o}F	845-855	850-860
Maximum Preheater Pressure Drop,psia	500	500
Dissolver Pressure,psig	1500-2000	2000
Dissolver Residence Time,minutes	22-37	45-80
Coal Feed Concentration in Slurry,wt%	25-45	20-35
Coal Feed Size (Max.-Min.) ,mesh	-30 - 200	-30 - 200

Source: Ackerman,C.D.,"Fort Lewis Pilot PLant Slurry Preheater Experiences and Plans", Proceedings of the DOE Project Review Meeting on Coal Liquefaction Preheater Studies, Oak Ridge, TN, 1979.

A number of occurrences of coking in the Wilsonville preheater have taken place since the initial startup of the pilot plant in 1974. Table 3.3 contains a list of the coking occurrences for which process operating data were available. Operating data are for the period from April 1978 to September 1979 and are presented in Table B.1 (Appendix B). This data consists of material flow rates, inlet and outlet hydrogen partial pressure, selected coal properties, solvent properties, and the preheater temperature profiles. Additional properties of the three coals used during this period are provided in Table B.2 (Appendix B). Also, a similar set of operating data for runs during this same time period for which coking did not occur are presented in Table B.3 (Appendix B). All operational data was compiled from various progress reports issued from the Wilsonville pilot plant through the Department of Energy.

Coking in the Wilsonville preheater does not seem to follow any readily observable trend. As illustrated by inspection of Tables 3.3 and 3.4, coking occurs over fairly wide ranges of operating conditions and for a variety of coals. Also, coking occurred in two consecutive runs (137 and 138) in early June of 1978 and then did not occur until 12 runs (or four months) later. No explanation for this behavior, or for coking problems in general, was given in the Wilsonville progress reports. Also, values for a mean slurry residence time through the coil were not given in the reports. It is proposed in this study, to relate incipient coking with process parameters including the slurry residence time. Thus, the lack of a mean slurry residence time necessitates its calculation. This is discussed in Chapter 4.

Table 3.3

Locations at Which Coking Occurred in the Wilsonville SRC-I Preheater Coil During the Period Spring 1978 — Fall 1979

Run No. and Date	Coal	Location of Coking
137 - May 1978	Indiana 5	Turns 19 to 27
138 - June 1978	Indiana 5	Turns 19 to 27
150 - Oct. 1978	Kentucky 6 and 11	Turns 15 to 27
151 - Nov. 1978	Kentucky 6 and 11	Turns 15 to 27
155 - Jan. 1979	Kentucky 6 and 11	Turns 15 to 27
164MB - June 1979	Kentucky 9 (Lafayette Mine)	Turns 15 to 35
166 - July 1979	Kentucky 9 (Lafayette Mine)	Turn 7

Source: Solvent Refined Coal (SRC) Process Operation of Solvent Refined Coal Pilot Plant at Wilsonville, Alabama, Technical Progress Reports FE 2270 -36 -46 -48 -60 -68 -70 , 1979-1980.

Table 3.4

Range of Wilsonville SRC-I Preheater Operating Conditions Producing Coke

Item	Range	
	Min	Max
Inlet Hydrogen Pressure, psia	1120	2040
Slurry Coal Content, wt%	33.2	40.1
Slurry Flow Rate, lb/hr	697	1465
Inlet Gas Flow Rate, lb/hr	28.9	248.7
Skin Temp. at Location of Coking, ^{o}F	464	854
Solvent Quality Index (Short)	62	74
Slurry Mean Residence Time, minutes	a	a

[a] Not Reported.

Source: Solvent Refined Coal (SRC) Process Operation of Solvent Refined Coal Pilot Plant at Wilsonville, Alabama, Technical Progress Reports FE 2270 -36 -46 -48 -60 -63 -65 -66 -68 -70 , 1979-1980.

After a series of recent slurry preheater test runs at Fort Lewis, visual inspection of the coil revealed irregular deposits of coke towards the coil outlet (See Table 3.5). The deposits ranged from 1/32 to 1/2 of an inch and were produced while testing the 2 inch diameter coil in both the SRC-I and SRC-II modes. Results of the testing also indicated the formation of coking in runs made without coal (solvent and hydrogen only). Very few process parameters were reported by the facility; also, skin temperature measurements during these runs were considered unreliable due to improper installation of the skin thermocouples. Thus, the information provided is insufficient to determine the causes for the somewhat irregular coking behavior. It was speculated, however, that the coke deposition at the outlet region of the coil was caused by stratification of the slurry/hydrogen gas streams combined with a steady increase in the slurry temperature towards the preheater outlet.

Coke deposition in the slurry preheater has also been reported by Exxon (See EDS Process Reports FE 2893-63,-65,-67, 1981). It should be noted, however, that the preheater at the Exxon facility is different than those used by the other pilot plants in that it consists of a serpentine coil of upflow and downflow tubes. During recent high heat flux tests, it was noted that the temperatures of the downflow tubes were consistently higher than those of the upflow tubes. Preheater outlet temperatures of approximately 850 ^{o}F were attained with maximum tube temperatures of approximately 1000 ^{o}F. Hot spots occurred in the preheater tubes presumably due to localized coking, and, in turn, caused the warping of several tubes (See EDS Process Report FE 2893-65, 1981). It was postulated that the coking was

Table 3.5

Recent Fort Lewis Preheater
Coking Experience

Date, 1981	Program	Coke Accumulated
Feb. 5 - May 8	SRC-II Mode; High Heat Flux Tests on 2 inch Coil	3/32 to 1/2 inch in Top Coils; 1/2 inch of Coke Downstream of Top Pressure Tap
May 17 - July 8	SRC-I Mode; 2 inch Coil Tests to Obtain Heat Transfer and Pressure Drop Data	Up to 1/8 inch in Top coils
July 14 - Aug. 18	Continued in SRC-I Mode to test 2 inch Coil	Less than 1/32 inch of coke in Top Coils

Source: Wilson, J.H., ORNL Trip Report of Technical Status Review Meeting held in Denver, Colorado, 1981.

caused by overvaporization of a lighter than normal solvent. Process parameters relevant to coking were not provided in the reports.

No significant coking problem in the slurry preheaters has been reported by the H-Coal facility. The absence of coking may be attributable to a relatively low preheater outlet temperature of approximately 735 ^{o}F (See H-Coal Pilot Plant Report FE 2260-57,1981).

CHAPTER 4

LITERATURE PERTINENT TO COKING

The direct liquefaction of coal involves the combination of three phases (i.e., pulverized coal, a process-derived oil, and gaseous hydrogen) under high pressures and high temperatures and in various flow configurations. The physical properties and chemical constituents of each phase largely determine how liquefaction will proceed under a given set of coal liquefying conditions (Petrakis, L. and others, 1982). The physical properties and the chemical composition of each phase combined with liquefaction process conditions will also determine whether or not coking precursors will be present and if these coking precursors will result in the deposition of coke on liquefaction equipment surfaces. In order to determine the relative importance of individual chemical constituents, physical properties, flow conditions, and liquefaction operating conditions as related to coke deposition, the literature pertinent to coking and these items was examined and is presented in this chapter. The literature dealing with coking, however, is primarily devoted to the production of coke (under conditions appreciably different from coal liquefaction operating conditions), instead of its suppression, from both coal and petroleum by-products and residues. Even so, this literature, combined with the few coking studies conducted on SRC-type liquids, does provide partial insight into the coking process and offers some qualitative guidance in the development of a correlational model for the coking data obtained for the Wilsonville fired preheater.

4.1 Discussion of the Coking Process

In analyzing the coking literature, it seems appropriate to first discuss the process of coking, in relation to coal liquefaction, with the intention of also introducing the nomenclature used in connection with coking. Generally, coke is denoted as being a pyridine-insoluble carbonaceous product which results from the heat treatment of pitches and oils or from the regressive reactions which occur during coal liquefaction. The various types of organic pyridine-insoluble residues which can result during coal liquefaction are listed in Table 4.1.

The production of coke can be either beneficial, as in the case of metallurgical coke manufacture, or it can be detrimental, as has already been mentioned for the case of coal liquefaction. The former case, the production of metallurgical coke, is aimed at the conversion of "coking coal" to a coke which has strong physical properties imparted by the conversion of the coal vitrain to highly ordered carbon, or anisotropic carbon. Electrodes for aluminum and steel manufacture are made from coal tar pitches or petroleum coke having specific properties which yield anisotropic carbon (Whitehurst, D.D. and others, 1979). In contrast to anisotropic carbon, certain coals, oils and pitches produce an amorphous, non-oriented material, or isotropic carbon.

An anisotropic carbon of particular interest is mesophase carbon. Mesophase carbon is anisotropic carbon which exhibits the characteristics of a liquid crystal. The work of J. D. Brooks and G. H. Taylor (1968) first described mesophase carbon as flow-type anisotropic carbon which forms through a sequence of conversions,

Table 4.1

Various Types of Pyridine - Insoluble Residues
Which Can Result During Coal
Liquefaction

Item	Definition
Unreacted Coal	- Self explanatory
Altered Coal	- Particles having the shape or other remnant structure of the original coal, usually exhibiting higher reflectance.
Vitroplast	- A plastic or once-plastic and optically isotropic (nonordered) degradation product of vitrinite (also from huminite and semi-fusinite).
Granular Residue	- Particles less than 1 μm which are not identifiable as individual components; includes both maceral and mineral derived materials.
Agglomerate	- Large particles composed of agglomerated smaller particles of coal, altered coal, and/or mineral matter.
Isotropic Carbon	- Amorphous, non-oriented insoluble material.
Anisotropic Carbon	- Insoluble material which exhibits an ordered or layered structure seen via optical microscopy under polarized light.
Mesophase	- Anisotropic carbon which exhibits the characteristics of a liquid crystal. It can occur in several forms such as the following: • Small spheres or domains • Larger or coalesced spheres • Mosaics - Isochromatic areas of <3μm • Flow-type coalescence - the entire mass has oriented into sheets or needles.

Table 4.1 (Continued)

Item	Definition
Glassy Carbon	- Small filaments of ordered carbon intertwined to produce an overall appearance of disordered structure - generally possesses high surface areas.

Source: Whitehurst, D.D., T.D. Mitchell, M. Farcasiu and J.J. Dickert, Jr., The Nature and Origin of Asphaltenes in Processed Coals, Volume 2, Final Report, prepared by Mobil Research and Development Corporation for the Electric Power Research Institute, December 1979, EPRI AF - 1298.

where soluble materials condense to yield first small, spherical anisotropic domains which coalesce to large domains, mosaics, and finally fully-oriented massive flow-type structures. The initial domains which form are internally ordered in a layered structure which consists of large planar aromatic molecules that have combined to form pyridine-insoluble products. In contrast to planar molecules, non-planar molecules undergoing coking form isotropic carbon (Whitehurst, D.D. and others, 1979). Isotropic pitches can be transformed to mesophase, however, by a simple solvent extraction technique (Riggs, D.M. and Diefendorf, R.J., 1979).

During coal liquefaction, coal first undergoes pyrolysis which is the breakdown of the weak bonds of the coal macrostructures by thermal bond rupture. This leads to large molecules which are soluble in pyridine. These molecules can then undergo cracking or hydrocracking reactions in which the large molecules are attacked at weak points including heteroatom linkages. These events result in the formation of free radical fragments (fragments with an unpaired electron) which may then proceed by a number of reaction pathways to an eventual product. Free radicals can be "capped off" by hydrogen, presumably from a donor solvent which acts as a "hydrogen shuttler", thus leading to relatively stable liquids and light gases. On the other hand, free radicals could combine to form larger molecules, possibly coking precursors, and eventually may form either isotropic or anisotropic coke which may or may not precipitate onto process equipment surfaces. In the presence of gaseous hydrogen, free radicals can also generate hydrogen atoms which can attack linkages between aromatic and

aliphatic carbons to further the breakdown of large molecules (McNeese, L.E. and others, 1979).

Clearly, a large number of factors are important in determining the reaction products formed during liquefaction, and in particular whether coking precursors will be present and if they will result in the deposition of coke on process equipment surfaces. The chemical nature of the coal, as indicated by its rank and petrography, will determine the distribution of bond types and structures present in the coal and, hence, will dictate the type and number of free radicals generated at a given temperature, pressure, and reaction time. Also, portions of the coal mineral matter act as catalysts, thus influencing the rate and type of products which are formed during liquefaction. The ability of the solvent to supply hydrogen to cap free radicals and the subsequent rehydrogenation of the solvent at a given temperature and hydrogen partial pressure is also important in determining reaction products. The nature of solvent, however, is not constant but changes as liquefaction results in the production of coal derived liquids and light hydrocarbon gases plus "heteroatom gases". If coking precursors and eventually coke are formed, the solvent's ability to keep the coking precursors and any inital coke formed in solution under a given set of conditions is surely important.

Because of the importance of the role of the solvent in direct liquefaction, the "quality" of the solvent is defined by many of the coal liquefaction pilot plants. For instance, the solvent quality index (short) at the Wilsonville Pilot Plant is defined as being the percent of tetrahydrofuran-soluble organics produced when 14 grams of

a solvent and coal (a specially prepared Indiana V coal of uniform composition) mixture in a ratio of 8 to 1 (solvent-to-coal) are reacted in a 30-cc microautoclave unit shaken in a sand bath at 750 ^{o}F for 10 minutes (FE 2270-46 and FE2270-70). The greater the conversion of the coal to THF soluble products, the better the solvents ability to act as a hydrogen donor.

4.2 Coking Studies of SRC-Type Liquids

A few studies involving the tendency of SRC-Type liquids to form coke or char have been conducted. Of direct interest is the study due to Walker and others (1980) who used a pressurized gold-tube carbonization technique to investigate the propensity of SRC liquids, derived from both short (4 minutes, 800 ^{o}F) and long (10 minutes, 800 ^{o}F) contact time liquefaction conditions, to form coke. In this experiment, the liquid sample to be studied is sealed in a gold tube and heat treated isothermally at 450 ^{o}C (842 ^{o}F) for 1 hour while an external pressure of 5000 psi is applied to the tube. The technique was applied to different SRC samples, their benzene - soluble and insoluble parts, as well as some SESC - chromatographic (Sequential Elution with Specific Solvents Chromatography; designates a fraction isolated from an SRC by liquid chromatography on silica) fractions of two Wilsonville solvent-refined coals produced from Illinois No. 6 (Monterey) coal. Whitehurst and others (1980) summarize the results of these and other related experiments arriving at the following conclusions regarding the formation of mesophase from SRC's:

- Mesophase can be formed from both long and short contact time SRC's; the amount of mesophase increases with the amount of pyridine insolubles and with the coking time. At longer coking times, mesophase from short contact time SRC's changes little but that from long contact time SRC's grows to larger domain sizes.

- The phenol-rich SRC fractions SESC 4, 7, and 8 produce the most mesophase, but surprisingly, fraction SESC 9 does not form any; it forms large quantities of isotropic char.

Whitehurst and others (1980) have also summarized the results of these experiments in terms of the structural features which affect carbonization or charring reactions as follows:

Coke Yields Increase With:

- Increasing functionality (-OH, non-basic N)
- Increasing aromatic content
- Increasing molecular weight
- Decreasing volatility
- Catalysts (Lewis acids or alkali metals)
- Increasing H-scavengers
- Increasing rate of radical generation

Coke Yields Decrease With:

- Increasing H content
- Increasing hydrogen pressure
- Increasing H-donors
- Dilution with inerts

These results are clearly useful in pointing to directions in which one should move in order to minimize coke production in coal processing equipment, but quantitative guidance is lacking. Nor is it suggested, for example, how a solvent quality index or indices might be defined which embodies those factors shown to affect the propensity toward coking or coke suppression such as functionality, aromatic content, and hydrogen donor content. However, these results and others

described herewith will serve as a guide for the development of a preliminary coking correlation based on the SRC-I pilot plant data from Wilsonville.

4.3 Coking Studies of Petroleum and Coal Oils and Pitches

D.M.Riggs and R.J.Diefendorf (1979 and 1980) have extensively studied the coking behavior of a variety of pitches, oils, refinery bottoms and at least one coal tar pitch. In their experiments samples of these materials were heat treated under an argon atmosphere for extended periods of time at a temperature ranging between 350 ^{o}C and 800 ^{o}C. Each material was analyzed with respect to the time-dependent compositional changes taking place as the material was heat treated. These compositional changes were interpreted in terms of the saturates, napthene-aromatics, polar-aromatics, and asphaltene fractions present as well as the amount of coke formed. Their findings from these and related studies are summarized as follows:

- When carbonaceous materials, such as pitches and oils, are heat treated to mesophase forming temperatures (350 - 500 ^{o}C) both distillation and thermal cracking mechanisms tend to operate in such a manner as to remove the lower molecular weight, less aromatic components of the precursor prior to mesophase formation. The removal of these volatile components and cracked products appears to be a key factor controlling both the conversion to mesophase and subsequently, coke, and also the time required for the first appearance of mesophase nuclei.

- The yield of coke is directly related to the asphaltene and polar aromatic content of the precursor material, as illustrated by Figure 4.1. The one point for a coal tar pitch appears to correlate with the petroleum pitch data. Also, results indicate that mesophase primarily forms from the asphaltene fraction of the carbonaceous precursor. This is illustrated by Figure 4.2 which shows the progression of a carbon black oil toward mesophase.

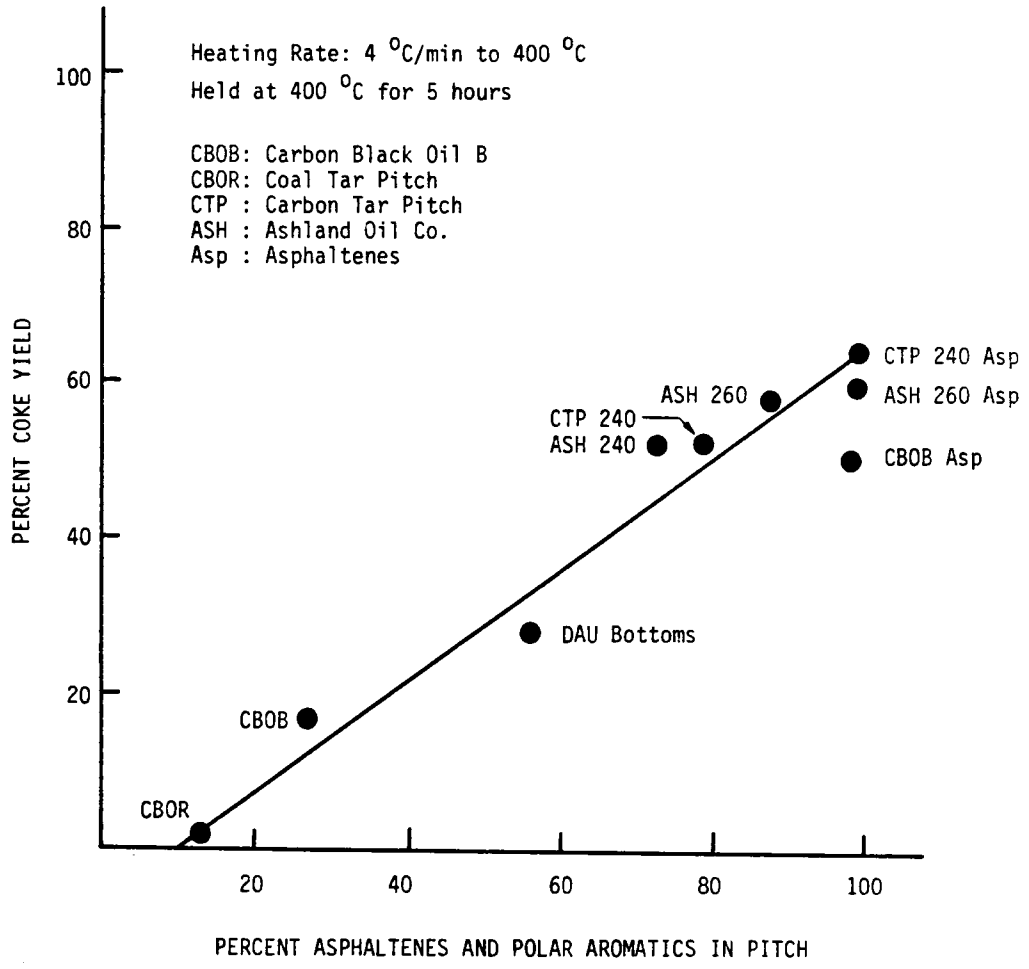

Figure 4.1 Correlation of Coke Yield with the Percent Asphaltenes and Polar Aromatics in some Heat Treated Petroleum Pitches and Coal Tars

Source: Riggs, D.M. and R.J. Diefendorf, "A Phase Diagram for Pitches," Carbon '80, Baden-Baden (June 30 - July 4, 1980), Der Deutschen Keramischen Gesellschaft E.V., Bad Honnef, Germany, pp. 326- 333.

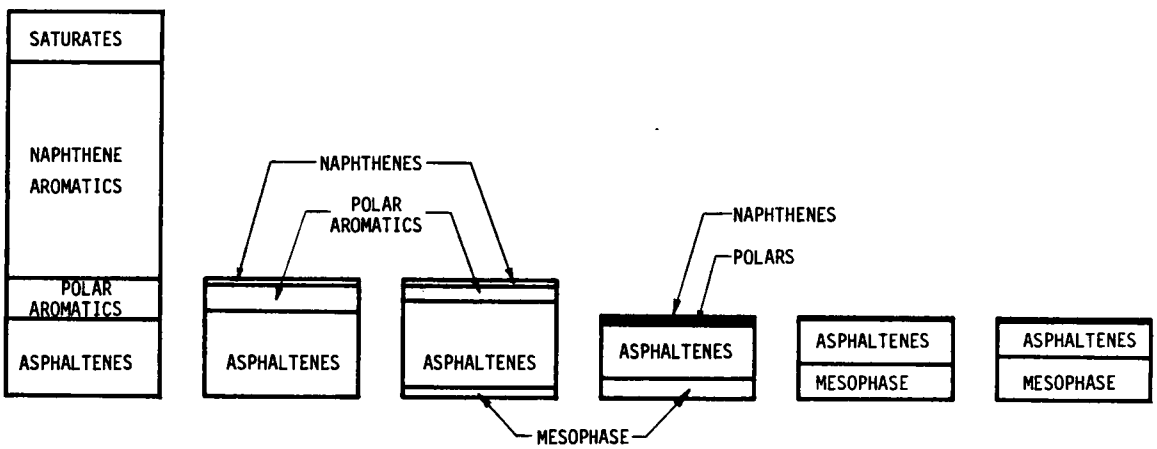

Figure 4.2 Change in the Generic Composition of a Heavy Oil after Heat Treatment at 425 ^{o}C

Source: Riggs, D.M. and R.J. Diefendorf, "A Phase Diagram for Pitches," Carbon '80, Baden-Baden (June 30 - July 4, 1980), Der Deutschen Keramischen Gesellschaft E.V., Bad Honnef, Germany, pp. 326- 333.

- Asphaltenes with small, highly condensed aromatic cores and short attached alkyl groups tend to be more thermally stable, and transform more readily to mesophase than those with long alkyl groups and more "open" aromatic cores.

- The coal tar pitch asphaltenes form mesophase more rapidly than asphaltenes from carbon black oil and refinery bottoms.

- The separation, or "precipitation" of mesophase from an isotropic pitch at elevated temperatures depends on the mesophase solubility parameter which depends upon its C/H ratio. At elevated temperatures, distillation removes much of the isotropic solvent and thermal cracking produces more high C/H mesophase-type material. The isotropic component thus becomes supersaturated and precipitation must occur. A qualitative, three dimensional phase diagram for pitch is suggested which is consistent with their findings. This phase diagram is reproduced as Figure 4.3.

These results supplement the findings of Whitehurst and others (1980) and Walker and others (1980) in certain respects, but differ in others, such as the relative roles the asphaltenes and polar aromatics play in the formation of mesophase. However, it may be that differences such as these can be explained in terms of the difference in the type of experiments used by the various groups of investigators, as well as the differences in starting materials.

Kumura and others (1979) investigated the carbonization characteristics of eleven kinds of heavy oils, including one coal-derived oil, when heat treated at atmospheric pressure in an inert atmosphere at 430 ^{o}C for various residence times ranging from 15 minutes to 30 hours. The heavy oils studied, along with their designations, are listed in Table 4.2. Heat treated samples were split into three fractions (α -fraction, β -fraction, and γ -fraction) according to their solubility in benzene and quinoline. The fraction soluble in benzene was denoted as the γ -fraction, and the

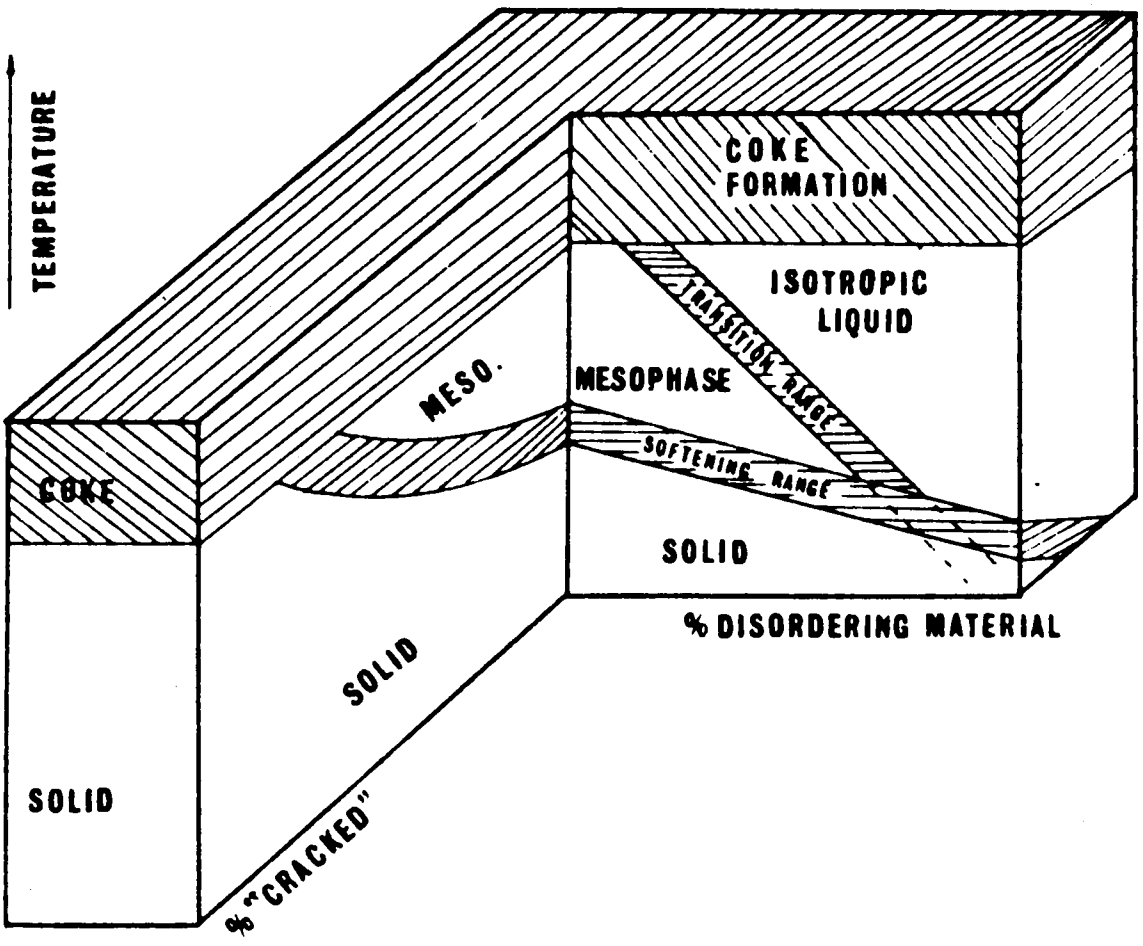

Figure 4.3 A Qualitative Phase Diagram for Pitch

Source: Riggs, D.M. and R.J. Diefendorf, "A Phase Diagram for Pitches," Carbon '80, Baden-Baden (June 30 - July 4, 1980), Der Deutschen Keramischen Gesellschaft E.V., Bad Honnef, Germany, pp. 326- 333.

Table 4.2

Heavy Oils and Their Designations Investigated
by Kumura, Yamasaki, and Sanada

Oil Designation	Source or Type
TS	Tar Sand Oil
KF	Kafji vacuum residue
KW	Kuwait vacuum residue
IH	Iranian heavy vacuum residue
AM	Arabian medium vacuum residue
PDA	Asphaltene derived from propane deasphalting process
SL	Sumatran light vacuum residue
SH	Duri vacuum residue
ET	Ethylene plant tar from naptha cracking plant
DO	Decanted oil from a fluid catalytic cracking process
HCO	Hydrogenated Miike coal oil

Source: Kumura, Y., H.Yamasaki, Y.Sanada, "Carbonization of Heavy Oil - Characteristics of Heavy Oils Heat Treated", Biennial Conference on Carbon, Extended Abstracts Program, Volume 14, p. 421-422, 1979.

benzene-insoluble fraction was split into a quinoline-soluble fraction, denoted as the β -fraction, and a quinoline insoluble fraction denoted as the α-fraction. Since Kumura studied relatively heavy oils, the γ-fraction would primarily contain asphaltenes, the β-fraction would contain asphaltols also known as "preasphaltenes", and the α-fraction would contain any coke or mesophase spherules formed. The aromaticity (f_a values) of the γ-fractions was determined by Nuclear Magnetic Resonance. Also, a scanning electron microscope was used to photograph the α-fraction to determined the average diameter of the mesophase spherules. The results obtained are summarized as follows:

- In the transient state where the α, β, and γ fractions exist together, the β-fraction is affected by the quality of the γ-fraction as measured by its aromaticity (f_a value). As can be seen from Figure 4.4, the amount of β-fraction produced correlates with the aromaticity of the γ-fraction.
- Kumura and others suggest that the β-fraction is a phase change between the γ-fraction (asphaltenes) transformation to the α-fraction (coke).
- The nucleation, growth, and coalescence of mesophase spherules increased progressively with increasing residence time. Also, the size of mesophase spherules correlates with the aromaticity of the γ-fraction, as shown in Figure 4.5. However, the eleven oils investigated appear to fall into one of two distinct groups in Figure 4.5 depending on whether they are cracked residues (ET, DO ,HCO) or straight run residues (TS,KF,KW,IH,AM,PDA,SL,SH).

In addition to these results, Sanada and others (1973), have also pointed out the importance of the quinoline-soluble but benzene-insoluble fraction of pitch ("pre-asphaltenes") upon the development of anisotropy during the carbonization of pitches and coals.

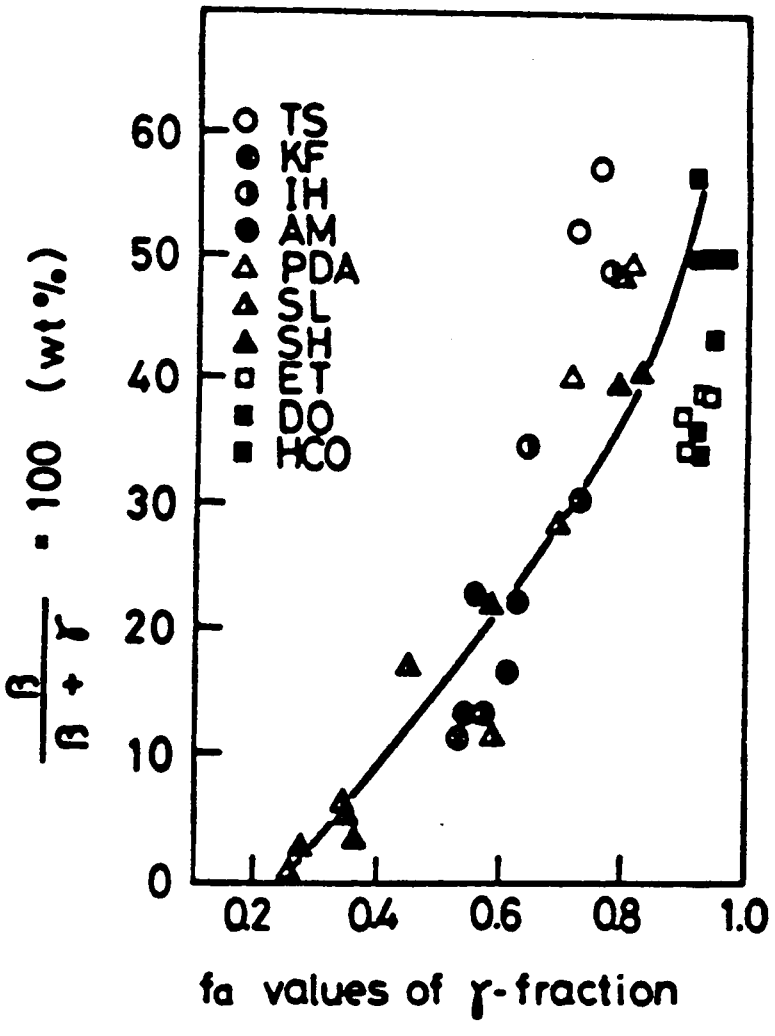

Figure 4.4 Relationship between the β-fraction Concentration and the aromaticity of the γ-fraction, after the Heat Treatment of Selected Heavy Oils

Source: Kumura, Y., H. Yamasaki, Y. Sanada, "Carbonization of Heavy Oil - Characteristics of Heavy Oils Heat Treated," Bienn. Conf. on Carbon, Extended Abstracts program, Vol. 14, p. 421-422, 1979.

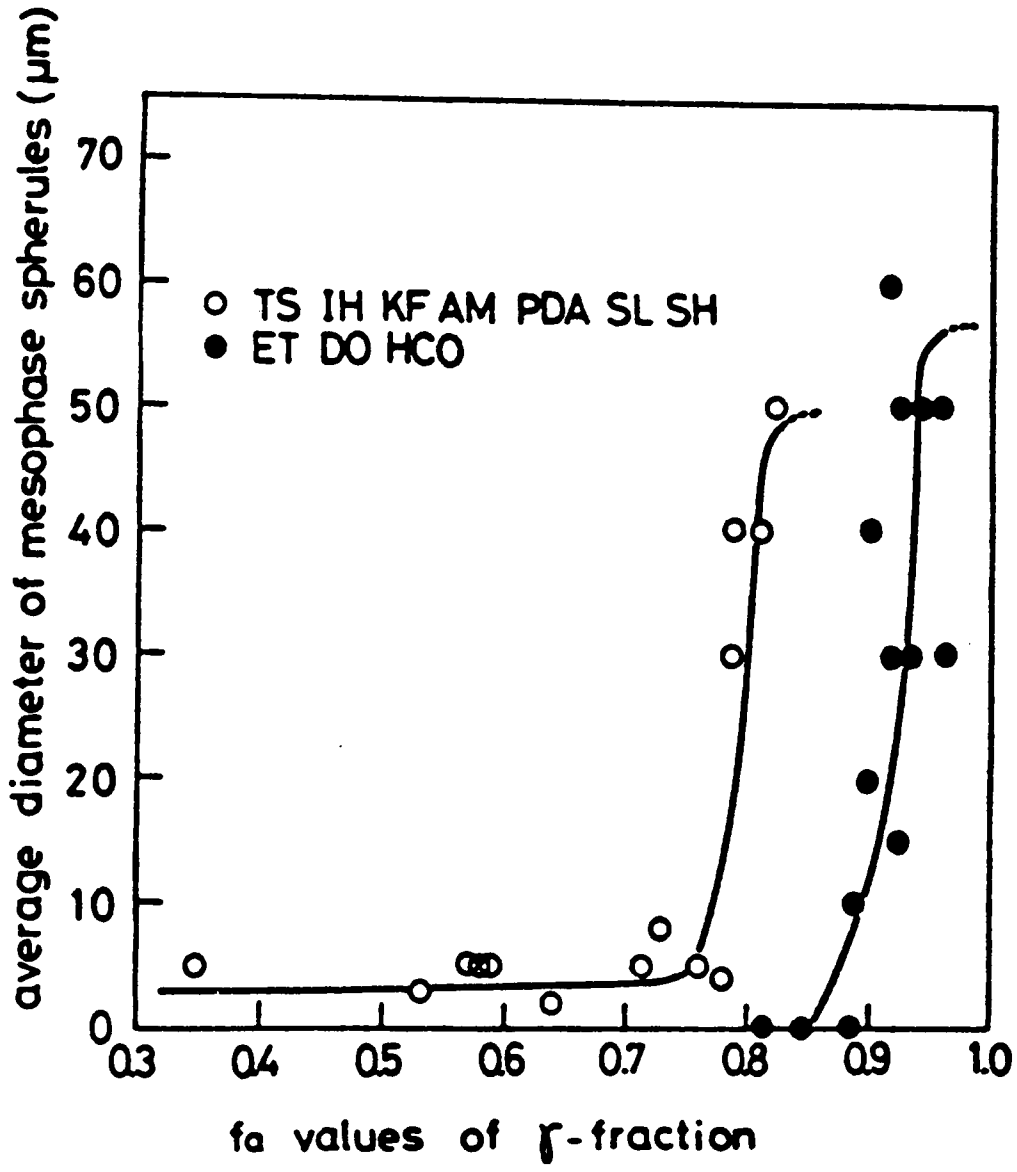

Figure 4.5 Relationship between the Average Diameter of Mesophase Spherules formed and the Aromaticity (f_a values) of the γ-fraction, after the Heat-treatment of selected Heavy Oils

Source: Kumura, Y., H. Yamasaki, Y. Sanada, "Carbonization of Heavy Oil - Characteristics of Heavy Oils Heat Treated," Bienn. Conf. on Carbon, Extended Abstracts Program, Vol. 14, p. 421-422,1979.

4.4 Co-Carbonization of Coals with Model Compounds, Petroleum Pitches, Solvent Refined Coals, and Coal-Tar Pitches

In Western Europe and in Japan there has been a steady decrease in the availability of coals of high rank which are suitable for the production of metallurgical and needle coke (Grint, A. and others, 1978). With this decrease in the reserves of good coking coals, an urgent need has arisen to develop new systems of blended starting materials which are cheaper and available in large quantities (Pacheco,L. and others, 1978). Hence, a number of investigations are underway involving the use of petroleum pitches, coal-tar pitches, solvent refined coals and model organic compounds in co-carbonizations with coal. The results to date, though mostly qualitative in nature, do provide insight into the coking process and are therefore summarized herein.

Grint and others (1978 and 1981) studied vitrains, from a wide range of rank of coals, when carbonized either singly or with 25 weight percent Ashland A200 petroleum pitch. Samples were carbonized to 1273 ^{o}K at a heating rate of 5 ^{o}K per minute while under a nitrogen atmosphere. The resultant products were examined to determine the influence, if any, of one component upon the anisotropic coke, as described by its optical texture, formed from the second component (be it vitrain or pitch). Results obtained for the anthracites, show no modification of either component during co-carbonization; the growth of mesophase from the A200 pitch is not affected. For all other coals tested, either the optical texture of the coke from the vitrain is affected together with that of the coke from the A200 pitch, or the

coke from the pitch alone is affected when co-carbonized with low rank coals.

Pacheco and others (1978) conducted experiments very similar to those of Grint and others (1978). They report that not all pitch substances behave similarily when co-carbonized with the same coal. In addition to both these sets of experiments, Friel and others (1980) studied the characteristics of vitrinite from four different coking coals when carbonized individually. Samples were ion-thinned and subsequently heated on the heating stage of a transmission electron microscope in order to observe the nucleation, growth, and coalescence of the spheres of mesophase within the ultra-thin section of coal as it transforms to semi-coke. Results of this experiment indicate the importance of the coals ability to generate fluidity during the coking process.

Kumai and others (1978) studied the coking properties of five heavy petroleum residual oils when co-carbonized with several coals. Non-coking coals were reported to have little if any compatibility with the oil, in contrast with the coking coals used in the study.

Mochida and co-workers (1978 and 1979) investigated the effects of hydrogenation and alkylation on the carbonization of solvent refined coals and their co-carbonization with coals of several ranks. They report that hydrogenated solvent refined coals provide cokes with an optical texture resembling that of needle-cokes. The hydrogenated solvent refined coals also created an optical texture in the otherwise isotropic cokes from low-rank non-fusing coals in co-carbonization systems. Alkylation of the solvent refined coal, however, reduced the

tendency of this pitch-like material both to form needle-coke structures and to influence the optical textures of cokes from coals in co-carbonization systems.

Mochida, Marsh, and Grint (1978) studied several coals of different rank when co-carbonized singly and with acenaphthylene and decacyclene. A caking and a non-caking coal were also co-carbonized with Ashland A200 petroleum pitch. They found that acenaphthylene exerted a smaller influence than decacyclene on the optical texture (anisotropism) of resultant cokes from co-carbonizations. For the caking coal the Ashland A200 petroleum pitch could modify the optical texture more strongly than decacyclene, but the opposite occurred for the non-caking coal.

Mochida and co-workers (1981) also studied the co-carbonization of decacyclene and A240 petroleum pitch with semi-anthracite coals. Their results suggest that during carbonization the preordered structure of the semi-anthracite is slightly rearranged, with the aid of the quinoline-soluble matter ("pre-asphaltene type compounds"), to become more highly ordered giving a domain texture which corresponds to the isochromatic anisotropic regions of its basic anisotropy.

Marsh and co-workers (1973) at the Northern Coke Research Laboratories of the University of Newcastle upon Tyne have conducted numerous investigations involving the co-carbonization of coals with aromatic compounds, heterocyclic compounds, and coal-tar pitches. The pertinent aspects of their findings and interpretations are summarized as follows:

- A qualitative coking model was formulated to explain the coal and coal-blend carbonization processes leading to metallurgical coke. This model is based in part on the assumption that liquid crystal growth processes occur during the carbonization of prime coking coal (Marsh, H., 1973). The most important entity within such a coal is stated to be the reactive vitrain, because it supplies the necessary controlled fluidity. The fusibility of the vitrain of a higher rank coal (than a prime coking coal) is insufficient to provide a coking system as described for a prime coking coal. Lower rank coals differ in two significant respects from a prime coking coal: the first is a decrease in the aromaticity of the coal substance, the second is an increase in the total content of sulfur, nitrogen, and oxygen, perhaps passing through a critical concentration. It is suggested that liquid-crystal-forming systems, such as pure compounds, distilled pitches, and others, appear to be able to accommodate a critical percentage of heterocyclic molecules, probably in the range of 5 to 8 percent, containing sulfur, oxygen, or nitrogen without destroying their (mesophase) growth processes (Marsh, H., 1973). In addition, the chemical nature of the oxygen within the carbonizing system is said to be of importance, in view of the fact that the ability of aromatic compounds to produce anisotropic carbon was actually enhanced by addition of some oxygen-containing molecules.

- "Inert" solids (for example, carbon blacks, graphite or quartz particles) of colloidal size within the plastic phase severly restricts growth processes, but larger surfaces promote coalescence to form anisotropic units such as seen in metallurgical cokes (Marsh, H. and co-workers, 1973).

- Results of experiments in which eighteen oxygen, nitrogen, or sulfur containing compounds were co-carbonized with fluorene, carbazole and acenaphthylene showed that, of the oxygenates, the polycyclics with quinone groupings, or the monocyclic molecules with several functional groupings, assist the growth of anisotropy (Marsh, H. and others, 1973). Phenol was seen to severely retard mesophase growth in these systems. Nitrogen and sulfur containing compounds on co-carbonization with acenaphthylene may cause deterioration of mesophase growth if the nitrogen or sulfur contents are greater than 3 percent by weight.

- Based upon results in which organic compounds were used to simulate coal molecules, Marsh and co-workers (1973) found that factors controlling the size of anisotropic units include the temperature range of fluidity and the mobility of the constituent molecules. It was suggested that the rate of formation of liquid crystals is controlled by both the chemical rate of formation of suitably shaped molecules and the mobility of these molecules in the plastic phase of the carbonization process.

4.5 Kinetics of Carbonization

In order to correlate coking occurrences during the direct liquefaction of coal, it is useful to understand the kinetics of the coking process. Unfortunately, a search of the rather extensive kinetic literature on coke formation yielded nothing on coking and coke suppression under process conditions and in coal-solvent-hydrogen mixtures similar to those experienced in direct liquefaction processes. However, a number of studies have been conducted which involve the kinetics of carbonization of heavy oils and pitches but in the absence of a hydrogen environment. The papers in this area which are of interest to this study are summarized herein.

Rantell and Clark (1978) investigated the kinetics of coke formation from coal solutions under conditions similar to those experienced in a delayed coking preheater coil and at temperatures from 475 to 525 ^{o}C. Coal solutions were prepared from the digestion of a high rank coal with anthracene oil, and consisted of either 80% anthracene oil and 20% dissolved coal or a concentrated mixture of 60% anthracene oil and 40% dissolved coal. Heat treatment tests were also carried out on a sample of anthracene oil and also on a petroleum-based pitch, Ashland A240 pitch, as a comparison with a material known to form an acceptable graphite. Results were interpreted in terms of the solubility of the products in cyclohexane and quinoline. The quinoline-insoluble material indicating the amount of coke formed, and the cyclohexane insoluble material indicating the progressing polymerization of the oil component of the samples. Rantell and Clark found that the polymerization of the dissolved coal

component, as evidenced by the formation of quinoline-insolubles, is basically a second-order reaction with an apparent activation energy of 190 kJ/mole (45.5 kcal/mole). However, the formation of cyclohexane-insolubles from the diluent oil component in isolation from the dissolved coal is a much slower reaction showing first-order kinetics. The polymerization of the petroleum-derived Ashland A240 pitch was found to essentially follow first-order kinetics.

The formation of coke from tars and pitches, as indicated by the formation of pyridine-insolubles, has also been shown to follow first-order kinetics by the investigations of Singer and Lewis (1978) and Honda and others (1970). Singer and Lewis investigated the carbonization of an ethylene tar pitch and a petroleum pitch, with the activation energies determined to be 35 and 53 kcal/mole respectively.

Mukherjee and Mukherjee (1977) compared the coking characteristics of a heavy oil obtained from the hydrogenation of a high sulfur coal with the coking characteristics of an aromatic-rich , heavy petroleum fraction. The sequence of coking reactions was interpreted on the basis of variations in operating conditions and an index defined as the degree of coking. The degree of coking, d, determined after heat treatment of the sample, was defined as the ratio of benzene-soluble matter (BS) plus volatile matter (VM) divided by the residual coke (RC), where the residual coke is the residue left after the solids were washed with benzene. The results, shown in Figures 4.6 and 4.7, indicate that after heating for 30 minutes at 475 ^{o}C coal oil undergoes more coke forming reactions than the petroleum oil, but, at temperatures between 500 and 550 ^{o}C the coal oil and

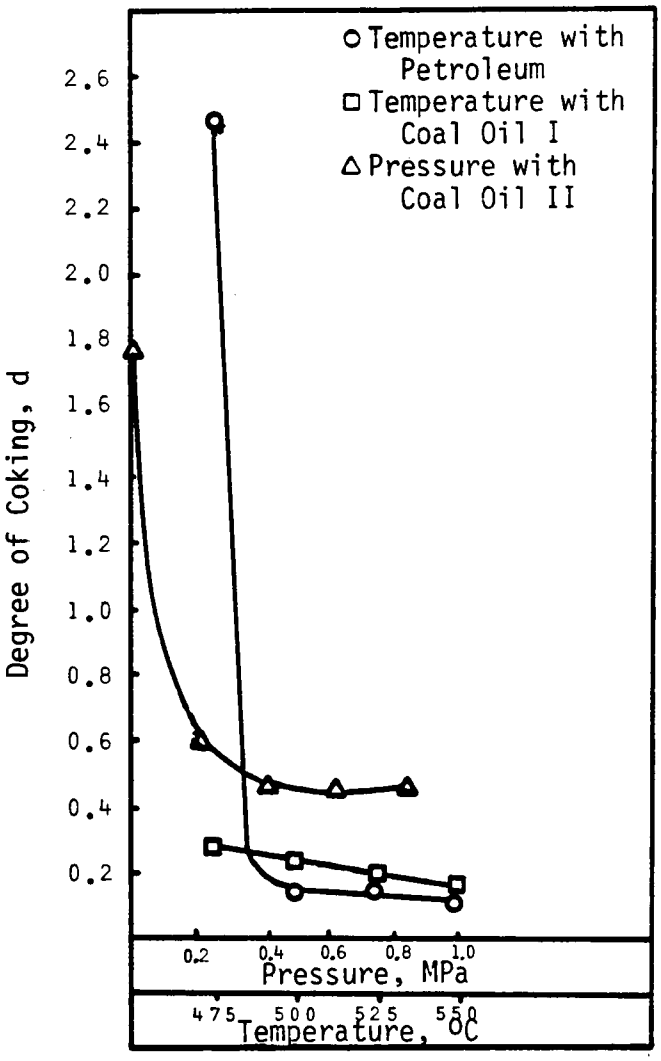

Figure 4.6 The Effect of Heat Treatment Temperature and Pressure on the degree of coking, d, of a Coal Oil and a Petroleum Oil

Source: Mukherjee, S.K. and D.K. Mukherjee, "Coking Characteristics of Heavy Oil from Coal Hydrogenation - Comparison with Petroleum", Indian Journal of Technology, Volume 15, p. 381 - 388, 1977.

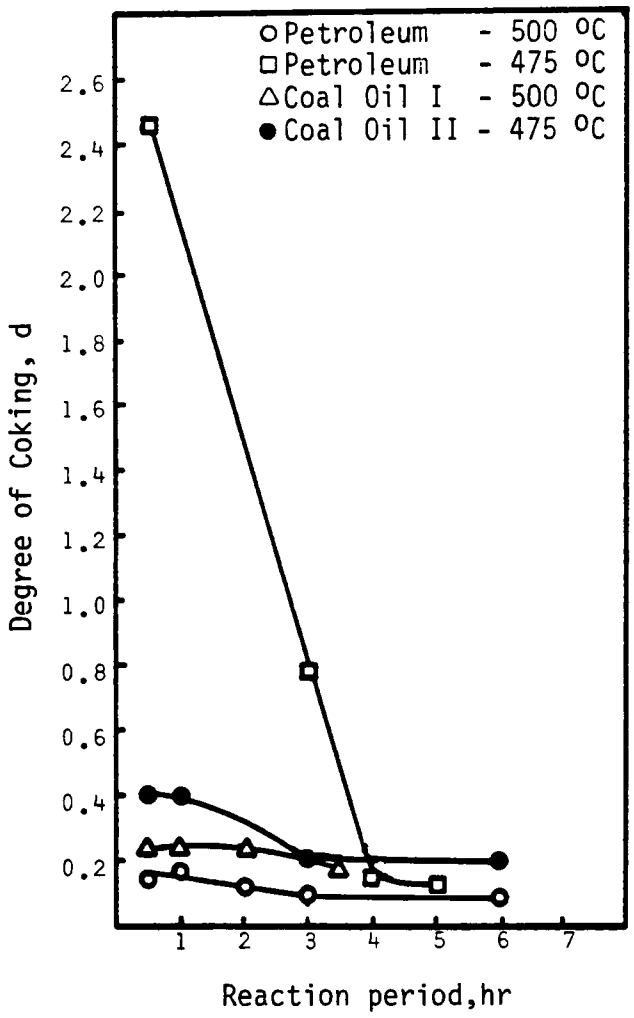

Figure 4.7 The Effect of Heat Treatment Time on the degree of coking, d, of a Coal Oil and a Petroleum Oil

Source: Mukherjee, S.K. and D.K. Mukherjee, Coking Characteristics of Heavy Oil from Coal Hydrogenation - Comparison with Petroleum", Indian Journal of Technology, Volume 15, p. 381 - 388, 1977.

petroleum oil have approximately the same value for the degree of coking. It is suggested that the asphaltene nature of the coal favors the formation of coke in high yield even at a lower temperature, while the influence of the rise in temperature by 25 ^{o}C in the range 475 to 500 ^{o}C was more favorable on the rate of generation of radicals from the paraffic bodies present in the petroleum oil, thus leading to the faster formation of coke to the maximum extent possible. The results also indicate that an increase in pressure, while under a nitrogen atmosphere, at the pressures studied below 0.4 MPa resulted in the formation of more residual coke from the coal oil, but at pressures studied above 0.4 MPa little effect was seen when presure was increased.

Ozaki and others (1978) studied, among other things, the kinetics of the coking of a Kuwait vacuum residual oil. After heat treatment, the gas and oil removed from the reactor were regarded as decomposition products of the feed oil, and the pyridine-insoluble matter was considered to be the product of polymerization-condensation reactions. The total amount of gas, oil, and pyridine-insoluble matter made up the overall product yield of the total coking process, while any pyridine-soluble matter was considered unreacted material. The decomposition segment of the coking process at temperatures of 420, 430, and 440 ^{o}C showed third-order kinetics with an apparent activation energy of 52 kcal/mole and a frequency factor of 2.0 x 10^{16}. The apparent third-order results were suggested as being due to a sequence of first-order reactions, the first of which is relatively fast and the latter of which are relatively slow, yielding a net,

overall third-order appearance. The polymerization-condensation segment of the coking process at temperatures of 420, 430 and 440 ^{o}C showed fourth-order kinetics with an apparent activation energy of 74 kcal/mole and a frequency factor of 3.5×10^{22}. The total coking process, however, showed apparent first-order kinetics with an activation energy of 52 kcal/mole and a frequency factor of 5.4×10^{17}. It is suggested that the first-order behavior of the total coking process resulted from a combination of the third-order decomposition with the fourth-order polymerization-condensation having an induction period. Namely, the decrease of the decomposition reaction rate as coking proceeds is compensated by the reactions producing pyridine-insoluble matter which starts to occur later than decomposition. This compensation makes the reaction rate of the total coking process apparently constant, leading to an apparent first-order reaction rate.

The only work involving hydrogen atmospheres and coke or coke-like substances appears to be that of Blackwood (1959 and 1962) and de Koranyi and others (1978). de Koranyi and others investigated the hydrogen-graphite reaction at temperatures between 1010 ^{o}K and 1473 ^{o}K, and at hydrogen pressures up to one bar (about one atmosphere). Their results yield an activation energy of 148 kJ/mole (35.4 kcal/mole) and a reaction rate of order 1.2 with respect to hydrogen.

4.6 Carbonization Catalyzed by Metals and Metallic Salts

A number of constituents present in the mineral matter of coal have been shown to have a catalytic effect on the hydrogenation of coal (Mukherjee, D.K. and Chowdhury, P.B., 1976) and in coal liquefaction process (McNeese, L.E. and others, 1978). Certain metals and metallic salts have also been investigated, using mainly model aromatic compounds, as to their influence on the reactions leading to coke formation. These metals and metallic salts may be present in the mineral matter of coal or be a component present in the materials of coal processing equipment. If present, a catalyst may control the carbonization reaction because cracking, condensation, isomerization and dehydrogenation reactions which form part of the carbonization process can be accelerated by suitable catalysts (Mochida, I., Masda, K. and Takeshita, K., 1977). Lewis acids (Kovacic, P. and co-workers, 1963, 1964, and 1965) and alkali metals (Beguin, F. and Setton, R., 1972), for example, are known to catalyze the condensation of aromatic hydrocarbons and the cyclization of chain compounds.

Mochida and co-workers (1977) investigated the carbonization of some model compounds as well as an ethylene tar pitch, a petroleum residual pitch, a solvent refined coal, and a gilsonite pitch, as affected by some lewis acids ($FeCl_3$, $CuCl_2$, $ZnCl_2$), aluminum chloride, and potassium. These materials used as catalysts affected the carbonization reaction through the intermediate compounds formed and through the rate of carbonization. Pertinent results of this study are summarized as follows:

- With aluminum chloride as catalyst, needle-shaped cokes were produced from naphthalene and anthracene (which singly did not produce coke), but isotropic carbon was formed from these materials with metallic potassium as the catalyst.

- Heterocyclic compounds (phenazine, diphenylene sulfide, thioxanthene, carbazole, acridine, diphenylene oxide, and xanthene) which contain a heteroatom such as sulfur, nitrogen, or oxygen were also converted into coke with aluminum chloride as catalyst. The tendency for a needle-coke to be produced decreased in the order of heteroatoms: sulfur, nitrogen, and oxygen. The content of heteroatoms in the coke formed showed no relation to the coke's optical features, which suggests that nitrogen and sulfur could be introduced into the planar network of the coke, at least, in small amounts.

- In the case of the carbonization of ethylene tar pitch the carbonization yield increased steeply in proportion to the amount of aluminum chloride added until the amount of the catalyst reached a certain value. This is illustrated in Figure 4.8. In the case of the SRC and the gilsonite pitch the yield did not increase or decrease with the addition of aluminum chloride catalyst.

- The amount of carbon produced paralleled the yield of benzene-insoluble products in the heat treatment residue.

- When some selected pyrenes (pyrene, hexahydropyrene, tetrahydropyrene) were carbonized with aluminum chloride present in a 0.1 mole ratio, the benzene insolubles increased as the temperature was increased over the range of about 240-420 ^{o}C. The pyrenes gave sharply increasing yields of benzene insolubles in the temperature range of 350-420 ^{o}C.

The material of construction for coal liquefaction vessels and process piping is primarily steel containing appreciable amounts of nickel. Although studies of coke formation on steels are not known, a considerable amount of work has been conducted on the formation of coke on nickel. The results from these investigations may not be applicable to the steels of interest, but some insight as to what can be expected on steel surfaces in contact with coal liquids under hydrogen atmospheres can be gained by the review of coke formation on

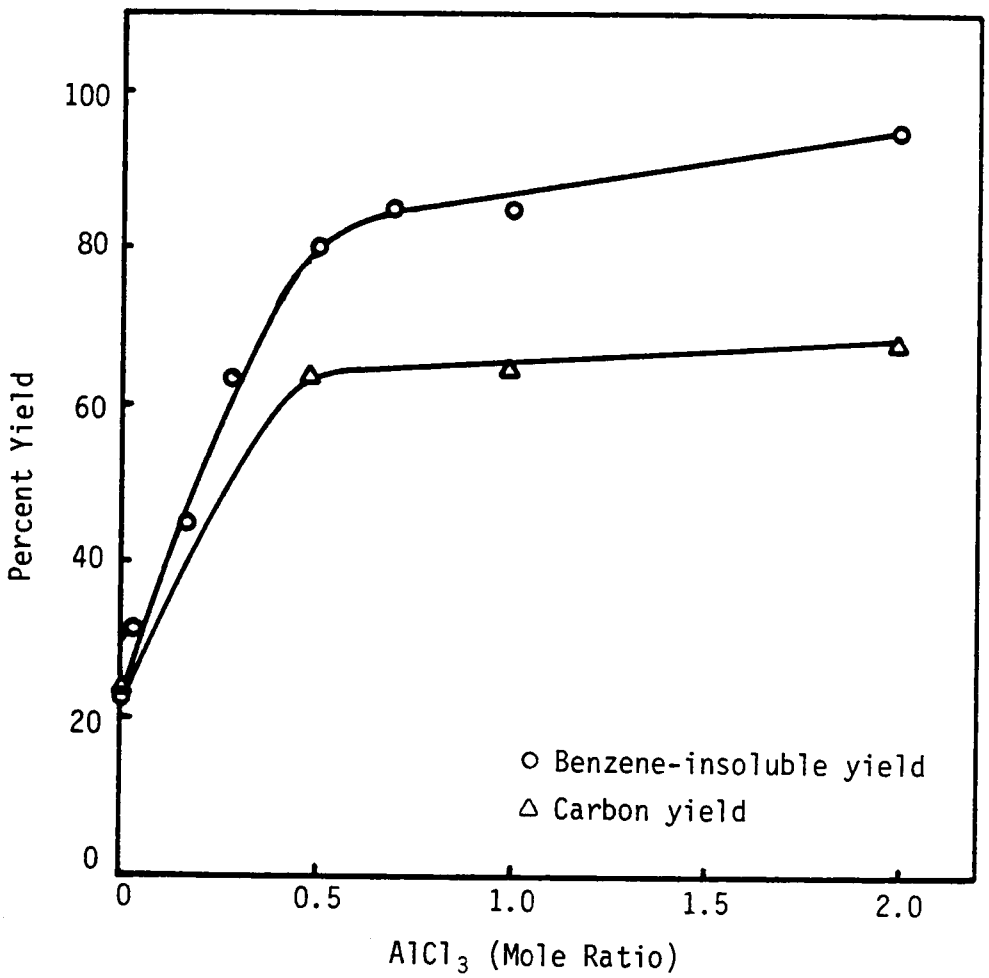

Figure 4.8 Carbonization of an Ethylene Tar Pitch as a function of the Amount of Aluminum Chloride Catalyst Present; Temperature = 600 ^{o}C and Heat Treatment Time = 2 Hours

Source: Mochida, I., K. Maeda, and K. Takeshita, " Catalytic Carbonization of Carbonaceous Compounds ", High Temperatures - High Pressures, Volume 9, p. 123 - 135, 1977.

nickel as presented by Trimm (1977). A summary of the more pertinent aspects of this paper are presented as follows:

- Nickel tends to promote the formation of carbonaceous deposits (from hydrocarbons investigated). Steam, hydrogen, and carbon dioxide may gasify any carbon produced, at least in the temperature range of about 400 to 700 ^{o}C.

- Coke formation on nickel from benzene and toluene has been reported to be some orders of magnitude faster than from carbon monoxide, which gives coke some 10 times faster than methane.

- As seen in Figure 4.9, the coke deposition rate on nickel from light hydrocarbons shows three distinct types of behavior as the temperature is increased. At temperatures less than 500-550 ^{o}C, the rate increases with temperature. In this temperature range, in all cases studied, the addition of a small amount of hydrogen to the feed was found to have a large effect. For example, the deposition of coke from paraffins was found to be negligible below 500-600^{o}C in the absence of hydrogen. In the presence of less than 5 vol % hydrogen, deposition started at 400^{o}C but the rate did not increase as more hydrogen was added. The role of the hydrogen may be in part to keep the metal surface clean by reacting with carbon-forming intermediates rather than by reaction with coke itself, especially in the intermediate temperature range of about 550-650 ^{o}C.

- In attempting to answer the question of whether or not the composition of the metal surface affects the coke forming process, only one alloy seems to have been studied, Ni - Cu alloys. Investigation of the deposition of coke from benzene on Ni - Cu alloys revealed that hydrogen has a significant effect on the reaction, accelerating deposition on a nickel-rich alloy and inhibiting deposition on a copper-rich alloy. As a general trend the maximum rate was found to shift to higher temperatures with increased copper content. However, Trimm suggests that the presence of alloys does seem to affect the kinetics of deposition and that this field would appear to offer fruitful areas for further research.

Bennett and Price (1978) examined a coke formed from a naptha feed stock on a steam cracker tube, and report that this deposit was formed by heterogeneous reactions catalyzed by iron and nickel. The HK40 steel tube operated at 920-930 ^{o}C (wall temperature), in the

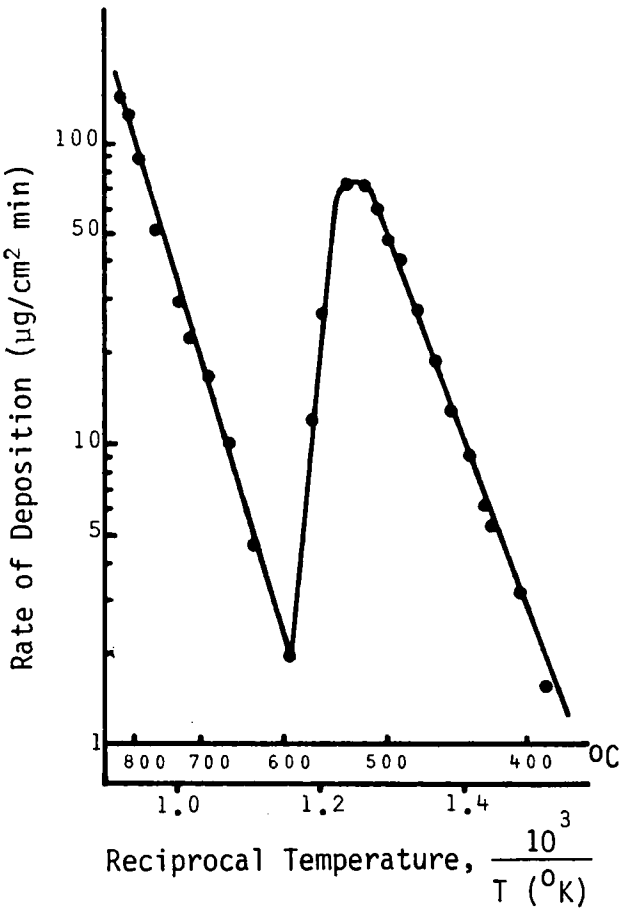

Figure 4.9 The Temperature Dependence of Carbon Deposition on Nickel Foil; Butene-1 pressure of 100 torr, Hydrogen pressure of 25 torr

Source: Trimm, D.L., "The Formation and Removal of Coke from Nickel Catalyst", in Catalysis Reviews, Volume 16, No. 2, 1977, edited by H. Heinemann and J.J. Carberry, Marcel Dekker Inc., New York.

region where the deposits were produced. The deposits occured in spite of the presence of steam in the feed. The partial pressure of steam in the feed was not reported, however.

Although pyrite has been reported as being catalytic to the carbonization of coal liquids (Whitehurst, D.D., 1979), Bennett and others (1973) indicate that sulfur compounds are inhibitors of carbonaceous deposition formed by heterogeneous reactions involving iron and nickel. Additional work is required in order to complete the understanding of sulfur compounds, and their role in coal liquefaction systems.

Menzies and others (1981) indicate that hydrocracking of heavy crude oils or petroleum residue can be achieved without deposition of coke in the reactor and at 66% lower pressure than conventional hydrocracking routes, by the use of an additive consisting of pulverized coal impregnated with iron sulfate or other metallic salts. The reactor operates at temperatures of less than 470^{o}C. The additive represents about 0.5 to 5.0% of the total feed material.

4.7 Estimation of Coal-Oil Slurry Residence Time in Preheaters

As the sequence of reactions leading to coke formation from coal-oil slurries is time-dependent, one expects that coke production, when it occurs, should depend on the residence or contact time, of the liquid-solid mixture in the processing equipment. For the case of the fired preheater used in the coal liquefaction process at Wilsonville, Alabama, one must consider the flow of several phases, including gas, solids and liquids, through the heated helical coil shown in Figure

A.1 (Appendix A). The coal-oil slurry can be considered as a homogeneous mixture, but it exhibits non-Newtonian behavior during certain stages of the coal dissolution process. Methods of estimating liquid holdups, or residence times, in processing equipment, such as preheaters, from first principles are not known, and, experimentally developed holdup correlations, demonstrated to be applicable to coal-oil-gas mixtures, were not found in the literature.

However, the literature does contain a number of empirical holdup correlations for both horizontal and vertical, two phase, isothermal flow in tubes. At the current time, these correlations can be expected to provide no more than a crude estimate of slurry holdup in preheater coils. In the absence of other information, however, even a crude estimate of liquid holdup can be useful as a guide and for exploratory and testing purposes. It is for these reasons that the holdup correlations of Lockhart and Martinelli (1949), Hughmark (1962 and 1965), and Beggs and Brill (1973), were examined.

4.7.1 Holdup Correlations for Two Phase Flow

Lockhart and Martinelli (1949) developed one of the first two phase, gas-liquid, horizontal and near-horizontal flow correlations from a reasonably broad data base. Systems included in their investigation were air with one of the following Newtonian liquids: benzene, kerosene, water, and one of several oils. The flow rates were such that both the viscous and turbulent ranges were covered for both the gas and liquid, yielding four viscous and turbulent flow combinations. Their findings included the following:

- Both pressure drop and liquid holdup (or gas holdup) data could be correlated in all four combinations of flow regime by means of a parameter, X, defined as the square root of the ratio of the pressure drop in the pipe if the liquid flowed alone to the pressure drop if the gas flowed alone:

$$X = \left\{ \frac{(\Delta P/\Delta L)_L}{(\Delta P/\Delta L)_G} \right\}^{\frac{1}{2}} \qquad 4.1$$

- The two phase pressure drop, $(\Delta P/\Delta L)$, defined in terms of a parameter ϕ_G or ϕ_L according to

$$(\Delta P/\Delta L)_{tp} = \phi_G (\Delta P/\Delta L)_G \quad \text{and} \quad (\Delta P/\Delta L)_{tp} = \phi_L (\Delta P/\Delta L)_L \qquad 4.2$$

correlates with X, yielding the curves shown in Figure 4.10, depending on the particular combinations of flow regimes of interest. The liquid or gas holdup fractions, R_L or R_G, is insensitive to the combination of flow regimes existing in the tube, and is also shown in Figure 4.10.

Hughmark (1962) was able to develop a two phase, gas-liquid, upflow holdup correlation using data derived from experiments using air flowing with either water, an oil blend, kerosene, diesel fuel oil, benzene, or an unspecified oil. A flow parameter, K, defined in terms of the gas holdup, R_G, and the gas quality, X_G, according to

$$(1.0/X_G) = 1.0 - (\rho_L/\rho_G)(1.0 - K/R_G) \qquad 4.3$$

was found to correlate with a quantity, Z, defined in terms of the Reynolds Number, Froude Number and the no-slip liquid volume fraction, Y_L :

$$Z = Re^{1/6} \; Fr^{1/8} \; Y_L^{1/4} \qquad 4.4$$

The data along with the best-fit curve is shown in Figure 4.11.

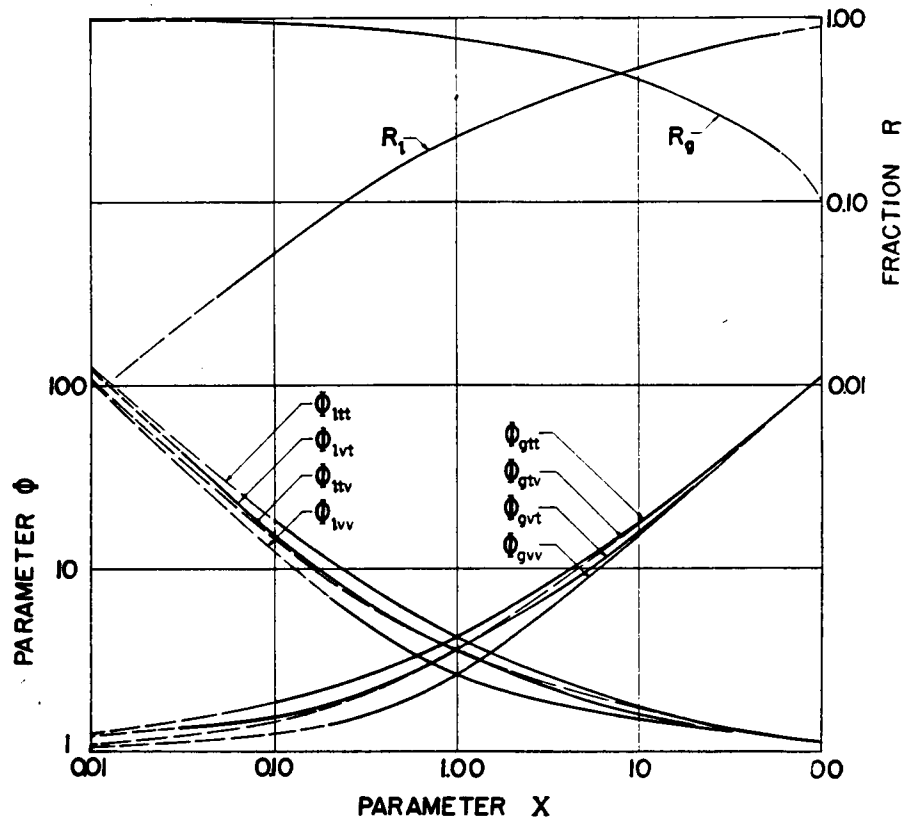

Figure 4.10 Two Phase Flow Pressure Drop and Holdup Correlation Developed by Lockhart and Martinelli

Source: Lockhart, R.W. and R.C. Martinelli, "Proposed Correla- of Data for Isothermal Two-Phase Two-Component Flow in Pipes", Chemical Engineering Progress, Volume 45, No.1, p. 38 - 39, 1949.

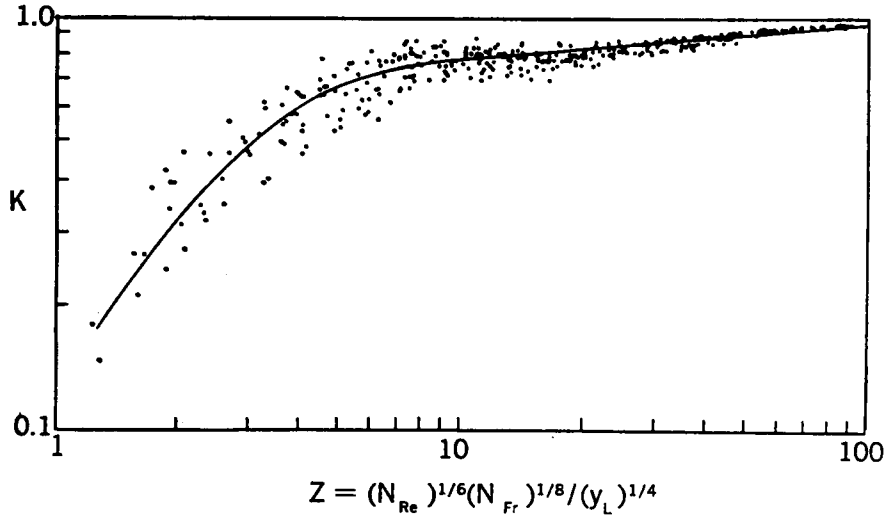

Figure 4.11 Correlation for Flow Parameter K for Two-Phase, Gas-Liquid Flow

Source: Hughmark, G.A., "Holdup in Gas-Liquid Flow", Chemical Engineering Progress, Volume 58, p. 62 - 65, 1962.

Hughmark notes that the proposed correlation appears to be applicable to horizontal as well as to vertical upward flow. The reynolds Number used in this correlation is defined in terms of a averaged mixture viscosity as follows:

$$Re = DG/(R_L\mu_L + R_G\mu_G) \qquad 4.5$$

In a later paper, Hughmark (1965) provides a correlation for calculation of the gas "bubble" velocity, and hence, holdup, in horizontal slug gas-liquid flow. The correlation is based on the data of a number of previous workers and includes systems of air flowing with either water, SAE 10 oil, an unspecified oil, diethylene glycol, or spindle oil. The bubble velocity, V_b, is computed by the equation,

$$V_b = K_2(Q_L + Q_G)/A \qquad 4.6$$

where the coefficient, K_2, is a function of the "liquid slug Reynolds Number" which is defined as:

$$Re_{LS} = \rho_L(Q_L + Q_G)/(A\mu_L) \qquad 4.7$$

Hughmark's correlation for K_2 is shown in Figure 4.12.

Beggs and Brill (1973) investigated holdup and pressure drop in tubes using air-water mixtures, at various angles of inclination ranging from -90 to +90 with the horizon. The liquid holdup in horizontal flow, $H_L(0)$, was found to correlate with the input liquid

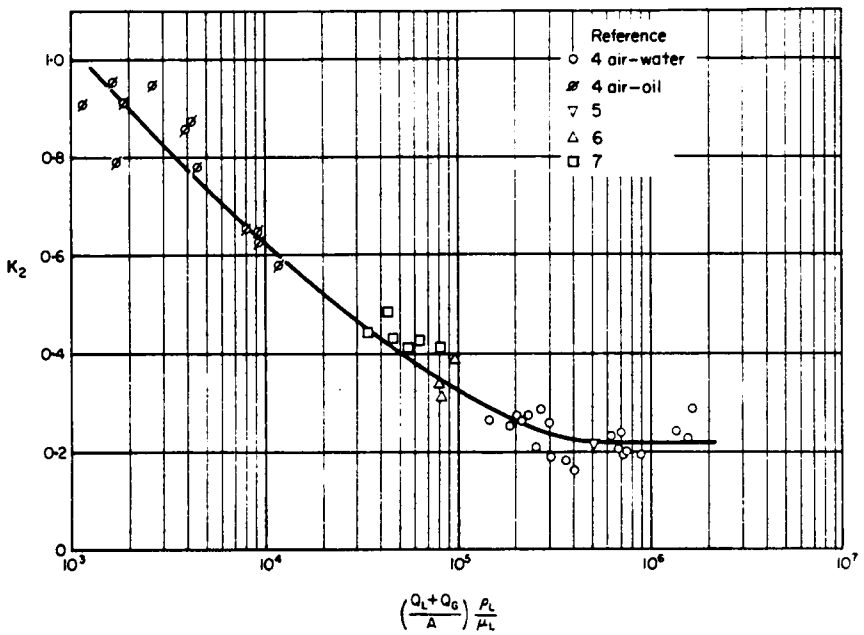

Figure 4.12 Dependence of the Parameter K_2 on the Liquid Slug Reynolds Number

Source: Hughmark, G.S., "Holdup and Heat Transfer in Horizontal Slug Gas-Liquid Flow," Chemical Engineering Science, Volume 20, p. 1007 - 1010, 1965.

volumetric fraction, λ, and the Froude Number, Fr, in the form:

$$H_L = A\,\lambda^a\,Fr^b \qquad 4.8$$

The holdup at an angle, θ, with the horizon is computed according to:

$$H_L(\theta) = H_L(0) \cdot \psi \qquad 4.9$$

where ψ is the inclination correction factor computed according to:

$$\psi = 1.0 + C\{\sin(1.8\theta) - (1/3)\sin^3(1.8\theta)\} \qquad 4.10$$

The coefficient, C, in the above equation depends on whether the liquid is flowing up (C+) or down (C-). The forms of the coefficient C for both up and down flow are given in Table 4.3, along with the horizontal holdup correlation, $H_L(0)$, for three flow patterns: segregated,intermittent , and distributed flow. The flow patterns are determined by the relative values of the input liquid volumetric fraction, λ, and the Froude Number , Fr. The holdup as computed by these correlations does not depend on Reynolds Number or pressure drop, as one might expect, based on the correlations of Lockhart and Martinelli and of Hughmark. Beggs and Brill suggest that this may be due to the fact that both the liquid and the gas phases were in turbulent flow in all their tests, so that viscous effects were presumably negligible. Furthermore, the use of only two fluids, air and water, was also suggested as tending to mask viscous effects.

Table 4.3

Correlations for Predicting Liquid Holdup for Two Phase Flow Through Tubes

Horizontal Flow Pattern	Horizontal Holdup	C^+	C^-
Segregated	$H_L(0) = \frac{0.98\,\lambda^{0.4846}}{Fr^{0.0868}}$	$C^+ = (1-\lambda)\mathrm{Ln}\,\frac{0.011\,N_{LV}^{3.539}}{\lambda^{3.768}\,Fr^{1.614}}$	$C^- = (1-\lambda)\mathrm{Ln}\,\frac{4.7\,N_{LV}^{0.1244}}{\lambda^{0.3692}\,Fr^{0.5056}}$
Intermittant	$H_L(0) = \frac{0.845\,\lambda^{0.5351}}{Fr^{0.0173}}$	$C^+ = (1-\lambda)\mathrm{Ln}\,\frac{2.96\,\lambda^{0.305}\,Fr^{0.0978}}{N_{LV}^{0.4473}}$	$C^- = (1-\lambda)\mathrm{Ln}\,\frac{4.7\,N_{LV}^{0.1244}}{\lambda^{0.3692}\,Fr^{0.5056}}$
Distributed	$H_L(0) = \frac{1.065\,\lambda^{0.5824}}{Fr^{0.0609}}$	$C^+ = 0$	$C^- = (1-\lambda)\mathrm{Ln}\,\frac{4.7\,N_{LV}^{0.1244}}{\lambda^{0.3692}\,Fr^{0.5056}}$

Source: Beggs, H.D. and J.P. Brill, "A Study of Two - Phase Flow in Inclined Pipes", Journal of Petroleum Technology, Volume XXV, p.607 - 617, 1973.

4.7.2 Comparison of Holdup Correlations with Experimentally Measured Preheater Residence Time

There appears to be no data in the literature which can be used to establish the accuracy to which the above mentioned holdup correlations can predict the holdup of gas-coal-oil slurry mixtures in equipment such as preheaters. However, the mean residence time of slurries in the Fort Lewis pilot plant preheater B coil were determined using a radioactive tracer technique (Cassidy, 1981), and are shown in Table 4.4. These values are compared with calculated values in Figures 4.13 - 4.16, where the calculated values of mean residence time, $\bar{\Theta}$, were determined from the previously mentioned holdup correlations according to:

$$\bar{\Theta} = R_L(\text{or } H_L(0))\ V_C \div (W_S/\rho_L) \qquad 4.11$$

Values of the properties used in the calculations are shown in Table 4.5. The average slurry viscosity existing during the Fort Lewis mean residence time tests is unknown. It was therefore necessary to use estimates based on the viscosity versus temperature relationship previously reported for the Wilsonville preheater as shown in Figure 4.17. The average viscosity range of 40 to 60 cp shown in Table 4.5 was obtained as integrated averages under the empirical fit curve of Figure 4.17, for the temperature ranges of 175 to 400 ^{o}C and of 150 to 425 ^{o}C, respectively.

According to the results displayed in Figures 4.13 - 4.16, the Lockhart-Martinelli and the Beggs-Brill correlations provide the best agreement with the experimental data. Also, the mean residence time

Table 4.4

Results of Radioactive Tracer Tests with
Fort Lewis Pilot Plant Preheater B

Test Number	Gas Rate (lb/hr)	Slurry Rate (lb/hr)	Type of Injection	Mean Residence Time (minutes)
RT-1	227	9,080	Gas	0.88
RT-2	224	9,070	Liquid	1.83
RT-3	574	9,050	Gas Liquid	0.57 1.23
RT-4	569	9,070	Liquid	1.24
RT-5	537	10,960	Gas Liquid	0.57 1.20
RT-6	539	10,960	Liquid	1.19
RT-7	269	10,970	Gas Liquid	0.77 1.49
RT-8	270	10,960	Liquid	1.50
RT-9	264	5,600	Liquid	2.18
RT-10	266	5,550	Gas	0.79
RT-11	532	5,490	Gas	0.51
RT-12	534	5,530	Liquid	1.62

Source: Cassidy, Personal Communication, 1981.

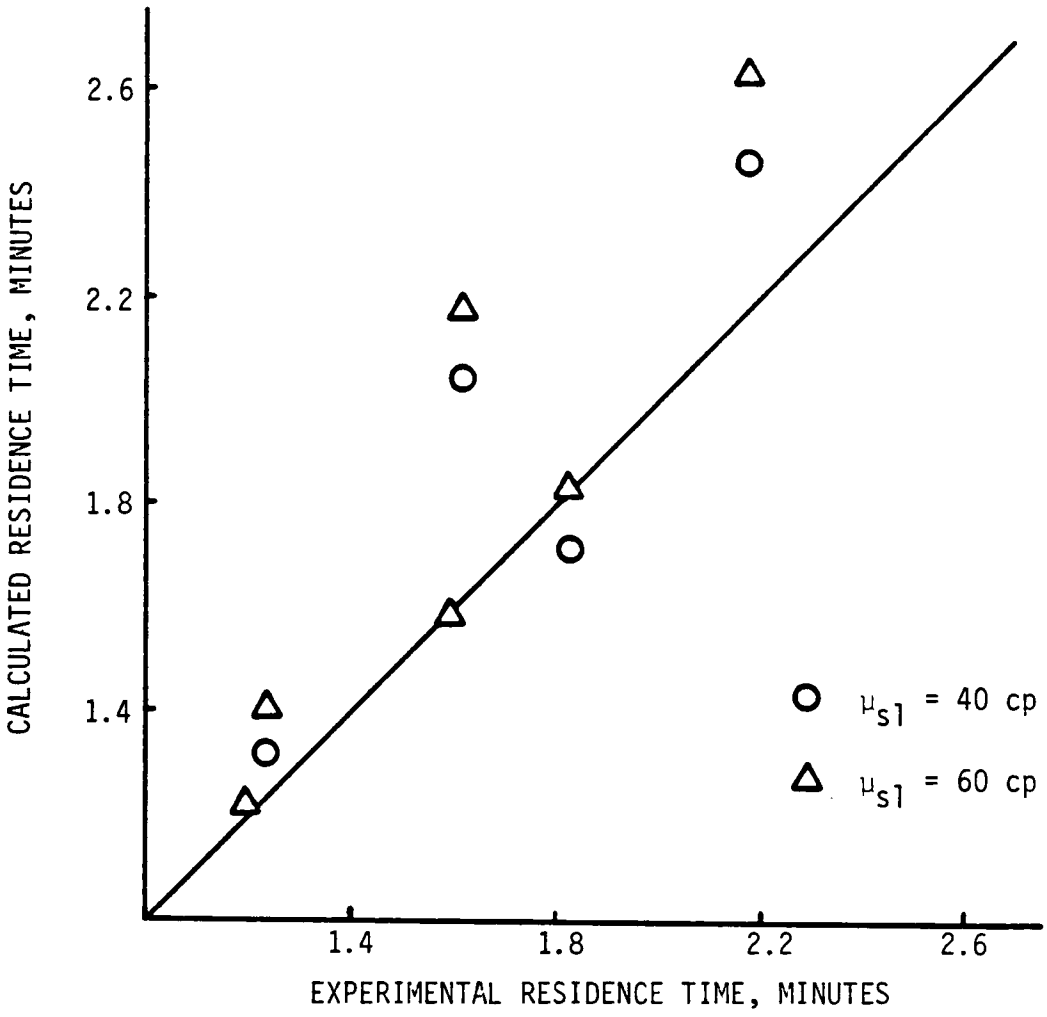

Figure 4.13 Comparison of Slurry Mean Residence Times in the Fort Lewis Preheater Coil: Calculated Values by use of the Lockhart-Martinelli Holdup Correlation versus Experimental Values as listed in Table 4.4

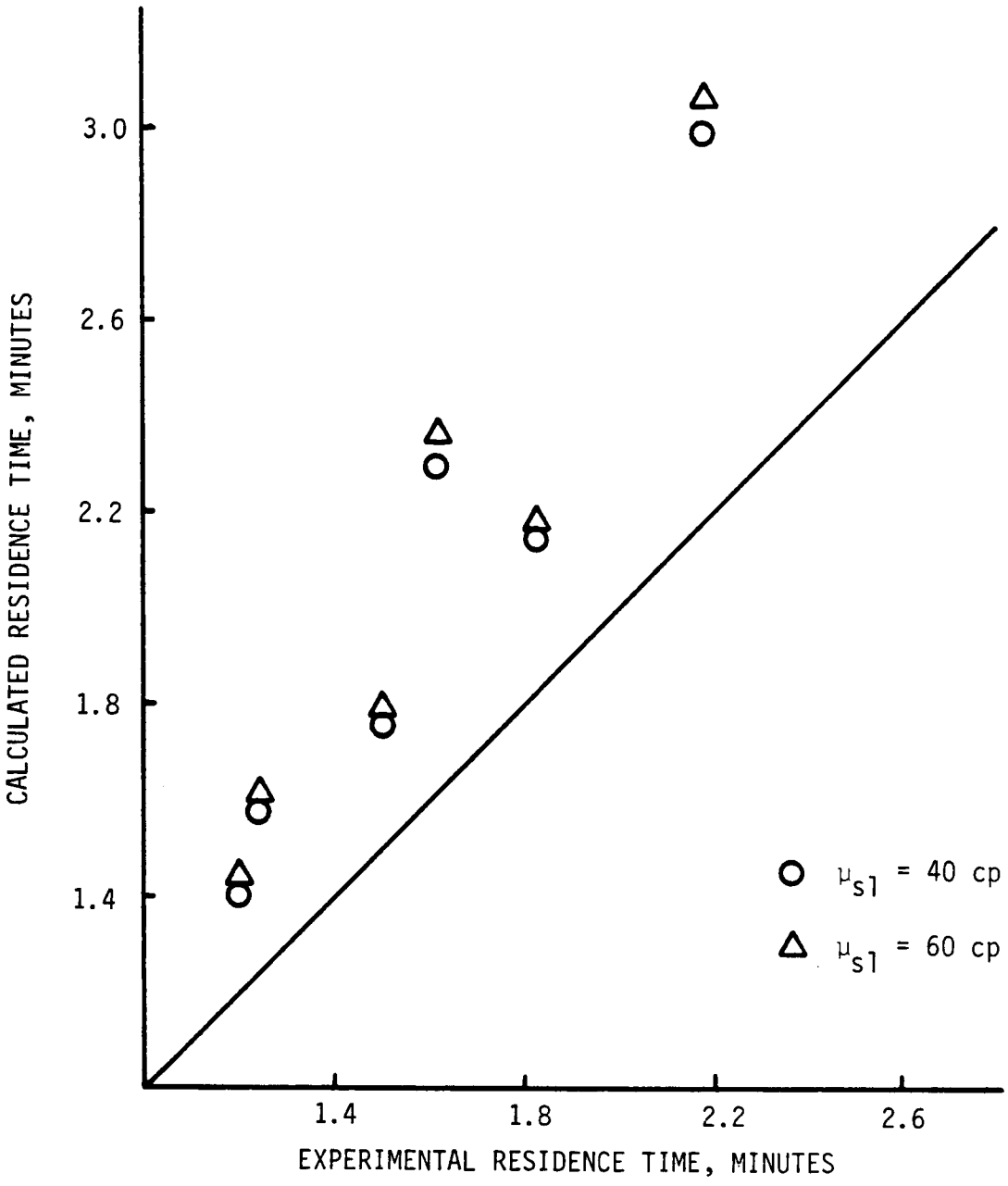

Figure 4.14 Comparison of Slurry Mean Residence Times in the Fort Lewis Preheater Coil: Calculated Values by use of the Hughmark Upflow Correlation versus Experimental Values as listed in Table 4.4

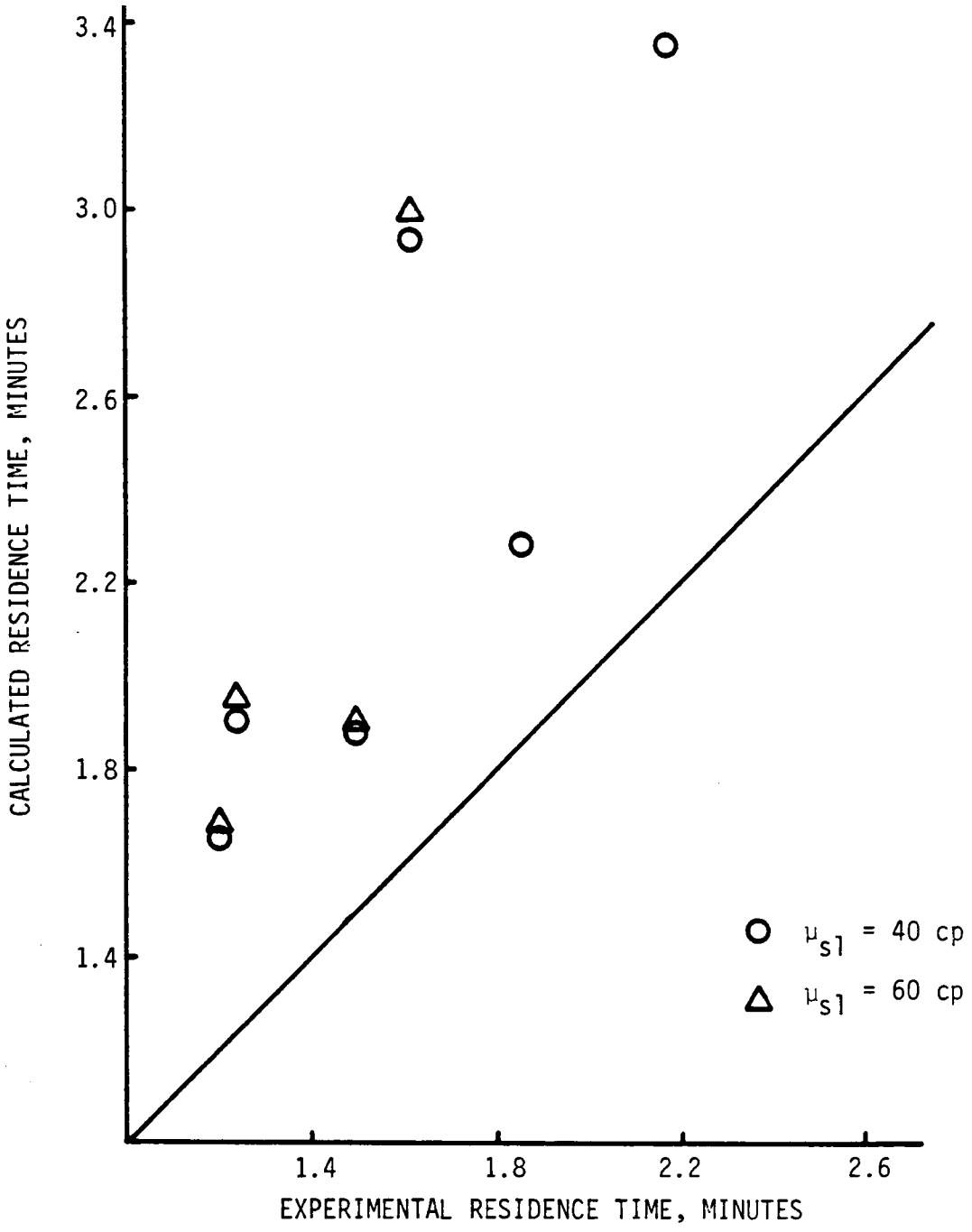

Figure 4.15 Comparison of Slurry Mean Residence Times in the Fort Lewis Preheater Coil: Calculated Values by use of the Hughmark Horizontal Slug Flow Correlation versus Experimental Values as listed in Table 4.4

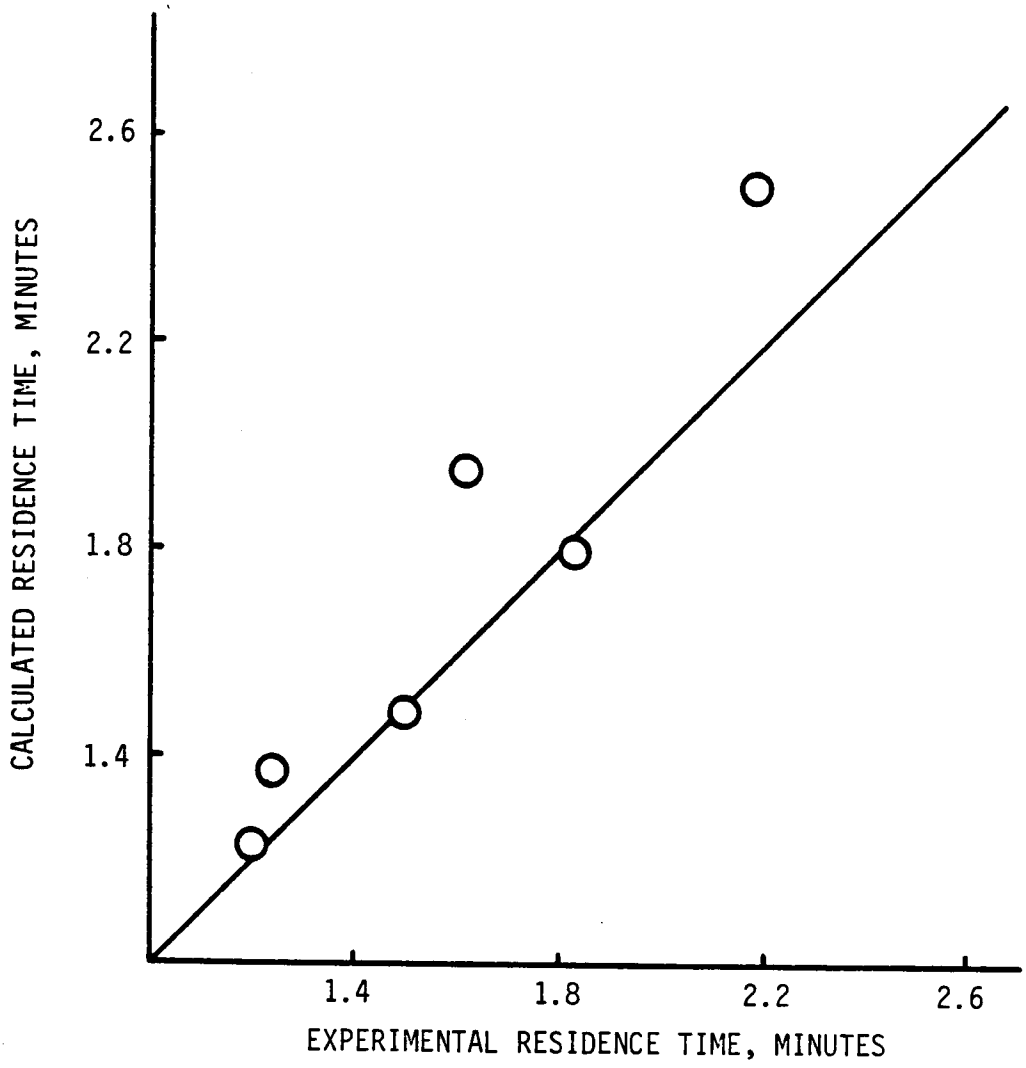

Figure 4.16 Comparison of Slurry Mean Residence Times in the Fort Lewis Preheater Coil: Calculated Values by use of the Beggs and Brill Horizontal, Intermittent Flow Correlation versus Experimental Values as listed in Table 4.4

Table 4.5

Property and Parameter Values used in Estimating Slurry Mean Residence Times in the Fort Lewis Pilot Plant Preheater B Coil

Property/Parameter	Value	Reference/Comments
Average Slurry Viscosity, cp	40 - 60	Integrated average obtained from the viscosity model shown in Figure 4.17 using SRC-II operating conditions
Gas Viscosity, cp	0.02	Based on SRC-I information[a]
Gas Molecular Weight		
Inlet	5.0 - 6.0	Based on SRC-I information[a]
Outlet	20.0	
Average Slurry Density	60.0	See Figure 4.18
Gas Flow Rate, lb/hr	224 - 574	Listed in Table 4.4
Slurry Flow Rate, lb/hr	5530 - 10970	Listed in Table 4.4
Tube Inside Dia., inches	1.687	a
Tube Length, feet	467	a

[a] Proceedings of the Department of Energy Project Review Meeting, Coal Liquefaction Preheater Studies, March 21, 1979, Oak Ridge, TN, published by the Department of Energy.

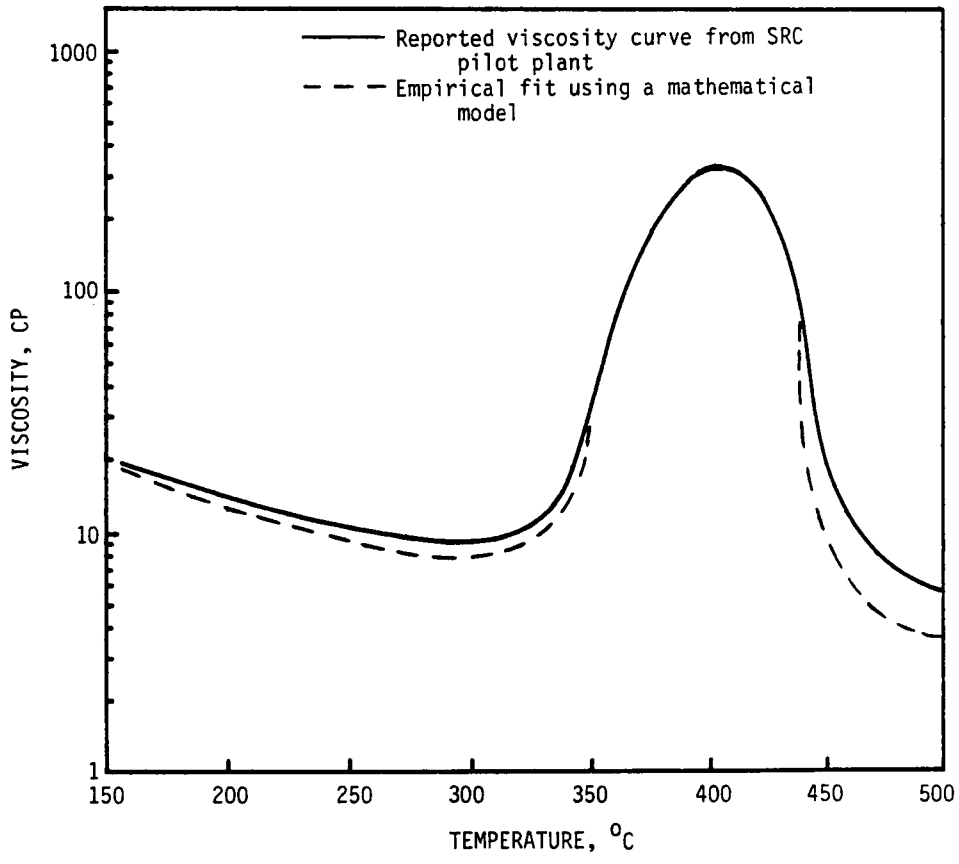

Figure 4.17 Comparison of the Empirical Fit from a Mathematical Viscosity Model with the Slurry Viscosity Data Reported from the Solvent Refined Coal Process Development Facility at Wilsonville, Alabama

Source: "Preparation of a Coal Conversion Systems Technical Data Book," Project 8979 Annual Report for the Period May 1, 1976 - April 30, 1977, prepared by the Institute of Gas Technology, FE 2286-16, January 1978.

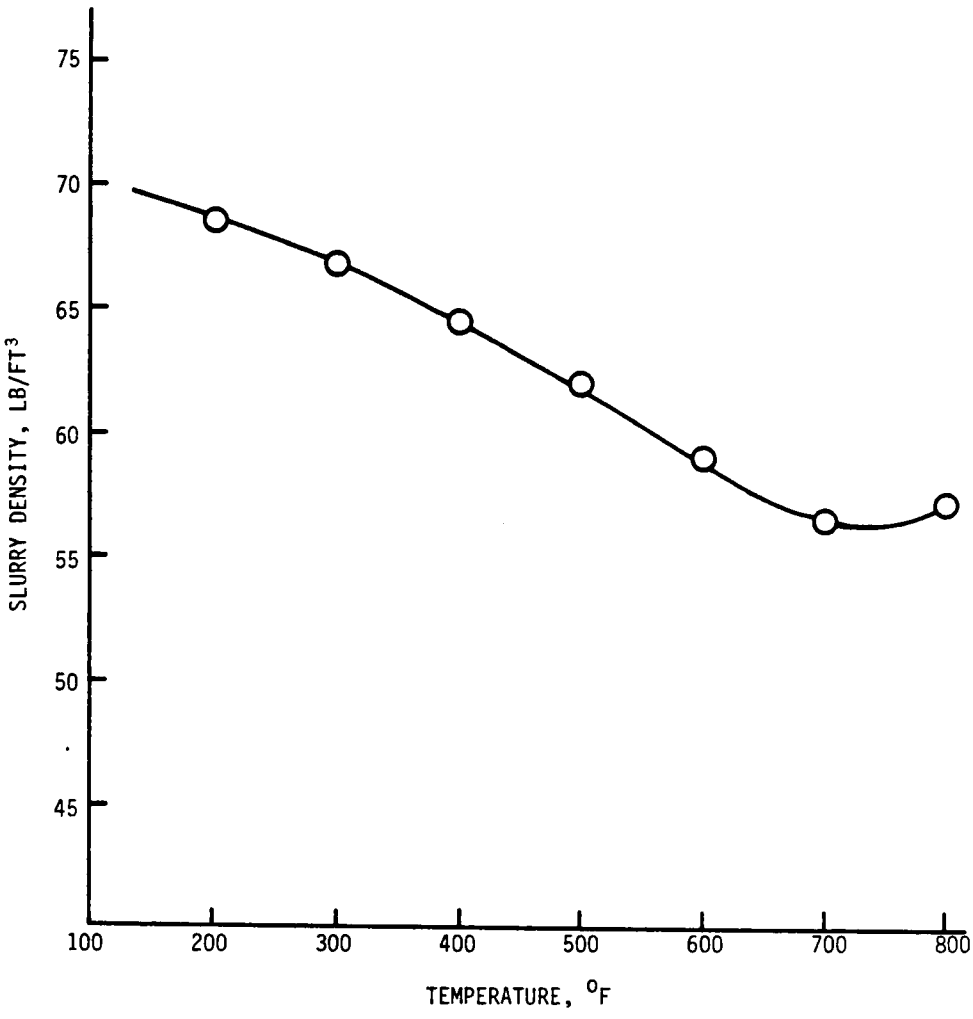

Figure 4.18 SRC-I Slurry Density Based on Fort Lewis Runs for July and August 1980.

Source: Catalytic Inc., Fired Heater Data Sheet, SRC-I, Phase 0, September 26, 1980.

values computed by the Lockhart-Martinelli correlation, Figure 4.13, suggest the correlation is not particularly sensitive to mean slurry viscosity in the range of 40 - 60 cp. The Beggs-Brill intermittent flow correlation does not require the liquid phase viscosity. However, this correlation provides results which are in surprisingly good agreement with the Fort Lewis preheater B test results, as illustrated by Figure 4.16.

CHAPTER 5

DATA ANALYSIS AND CORRELATION

The coking data from the Wilsonville SRC-I pilot plant preheater (see Appendix B), although limited in quantity, is sufficiently complete to serve as a basis for the development of a coking correlation. Undoubtedly the formation of coke is a complicated process, but a simple model can be tested which embodies those factors, as listed in Table 5.1, which the literature indicates can affect the formation or suppression of coke. This simple mechanism of coking and the proposed correlational model resulting from it are presented hereafter.

5.1 Mechanism of Coke Formation and Proposed Correlational Model

The formation of coke during the heat treatment of petroleum pitches, coal-oil mixtures, and other suitable starting materials is a relatively complicated process involving a number of chemical reactions and physical changes. The analysis of the formation of coke in coal liquefaction preheaters is even more complicated. In this case, a three phase mixture, consisting of coal (a notably inhomogeneous substance containing many components), a multicomponent recycled oil, and a hydrogen rich gas stream, is travelling through a radiantly heated coil during which time each phase is undergoing continuous changes due to the devolatilization and dissolution of the coal, the evaporation of the solvent, and the exothermic chemical reactions which occur as these materials are heated under high

Table 5.1

Factors Affecting the Propensity of
Coal-Solvent Systems to Coke[a]

A. Process Conditions

- Hydrogen Partial Pressure
- Temperature
- Percent Coal in Slurry
- Slurry Mean Residence Time

B. Coal - Solvent Properties

- Functionality, especially hydroxylic oxygen and non-basic nitrogen
- Aromatic Content and/or Polar Aromatic Content
- Asphaltene and Pre-Asphaltene Content
- Hydrogen Content
- Hydrogen Donating and Shuttling Capacity
- Sulfur Compounds, such as iron sulfides and, possibly, sulfates
- Certain other Factors in the Coal Mineral Matter, such as chlorides
- Vitrinite Content of the Coal

[a]Refer to Chapter 4 for the sources of these results.

pressures. It is under these conditions that it is desirable to predict the occurrence of coking. To accomplish this task, a simple model of the coking process can be formulated and put forth for testing.

This simple representation of coking, as first proposed by Frazier and others (1982), is based on the following postulates and assumptions:

1. Coking occurs as key coking precursors are formed and subsequently precipitate from the oil phase. This postulate is consistent with aspects of the coking mechanism as discussed by Riggs and Diefendorf (1980) and also by Kang and others (1977). It is of interest to know the concentration of these coking precursors, C_c , as they travel through the preheater coil. In such a multicomponent mixture this concentration should be related to process factors as well as properties of the solvent and coal, for instance,

$$C_c = \Phi(P_{H_2}, f_c, \bar{\Theta}, T, Q_s, w_s, \ldots) \qquad 5.1$$

where P_{H_2} is the hydrogen partial pressure, f_c is the weight fraction coal in the feed slurry, $\bar{\Theta}$ is the slurry residence time, T is the temperature, Q_s represents the solvent quality, and w_s is the weight fraction sulfur.

2. The precipitation or deposition of coke takes place when the concentration of key coking precursors reaches its solubility limit, C_c^s . Thus, the incipient coking condition is given by

$$C_c = C_c^s \qquad 5.2$$

3. The buildup of coke which occurs in coal liquefaction preheaters, occurs slowly enough that the conditions which exist are just beyond the incipient coking condition. This is representative of conditions during which coking occurred in the Wilsonville preheater.

With the conditions for incipient coking given by Equation 5.2, it becomes necessary to suggest functional forms for the concentration of key precursors, C_c , and for the solubility limit of key precursors, C_c^s . The form chosen for C_c is a truncated power series. This form was selected because the manufacture of coke in petroleum processing equipment has been shown to correlate with a simple truncated power series. Also, such forms have been successfully used to correlate heat and mass transfer data over moderate ranges in the independent variables. Thus, C_c is expressed by

$$C_c = K P_{H_2}^{a} f_c^{b} \bar{\Theta}^{c} Q_s^{d} \Phi'(T) \qquad 5.3$$

where k, a,b,c, and d are empirical constants. For simplicity, the

temperature dependent function $\Phi'(T)$ is assumed to be of the Arrhenius form as follows:

$$\Phi'(T) = K' \exp(-E_0/RT) \qquad 5.4$$

The quantity, E_0 , is considered to be the apparent activation energy for the formation of a key coking precursor which is assumed to be chemical reaction controlled.

In considering a functional form for the solubility limit, C_c^s , the following candidate was selected:

$$C_c^s = K'' \exp(-E_1/RT) \qquad 5.5$$

Hildebrand and Scott (1950) have compiled considerable data for binary liquid-liquid and binary solid-liquid, non-electrolyte systems which can be fit over wide temperature ranges by an equation of this form. This equation follows the "regular" solution theory and holds for many binary solid-liquid solutions provided the temperature does not approach the critical solution temperature. The quantity, E_1 , is directly related to the heat of fusion of the solute for ideal, binary solid-liquid solutions.

Inserting the forms for C_c and C_c^s as listed in Equations 5.3, 5.4, and 5.5 into the condition for incipient coking, Equation 5.2, yields, after rearranging and taking logarithms,

$$\text{Ln} \{ P_{H_2}^{a} f_c^{b} \bar{\Theta}^{c} Q_s^{d} \ldots \} = C_1 + C_2/T \qquad 5.6$$

where $C_1 = \text{Ln}(K''/K'K)$ and $C_2 = (E_0-E_1)/R$. Equation 5.6 is the proposed correlational equation to represent incipient coking conditions.

The proposed correlational incipient coking equation (Eq. 5.6) is used to analyze the coking data from the Wilsonville preheater. This analysis consists of the multiple linear regression of the logarithms of four to five process parameters [for example, Ln (P_{H_2}), Ln (Q_s), Ln (f_c), Ln ($\bar{\theta}$)] versus the reciprocal of the coking temperature. The multiple regression is performed using the canned statistical package STATPACK (Houchard, 1974). Results are interpreted in terms of the " goodness of fit " as measured by the square of the correlation coefficient (R^2 - value) and by the statistical significance of each process parameter as measured by it's F-level. Also, since the correlational equation represents incipient coking conditions, results are interpreted on the basis of the non-coking data lying in a region bounded by the incipient coking curve.

A number of regression cases are analyzed in which different combinations of process operating parameters, coal heteroatom measures, and petrographic measures are chosen four and five at a time. The process operating conditions and coal and solvent properties selected for investigation due to their possible ability to enhance or suppress coking are listed in Table 5.2. The regression cases are discussed in Section 5.3 which is first preceded by a discussion of the basic considerations that are necessary in order to analyze the Wilsonville SRC-I preheater coking data.

Table 5.2

Coking Variables Investigated

- Slurry Residence Time
- Solvent Quality
- Hydrogen Partial Pressure
- Fraction Coal in Slurry
- Coal Sulfur, Nitrogen, and Oxygen Contents
- Coal Organic and Pyritic Sulfur Contents
- Coal Vitrinite Content

5.2 Basic Considerations Regarding the Correlation of the Wilsonville Preheater Coking Data

A number of assumptions must be made in regards to the treatment of the Wilsonville preheater coking data in order that it may be analyzed by use of Equation 5.6, the proposed correlational incipient coking equation. For instance, it is necessary to make decisions regarding the estimation of values for missing data, such as slurry mean residence time, and to make decisions with respect to the use of such factors as the hydrogen partial pressure and the coil skin temperature or the slurry bulk temperature at the point of coke formation. The approach taken and the assumptions used in the treatment of the data are itemized as follows:

1. A complete time-temperature history of the slurry in the coil to the point of initial coking would be desirable. However, since this is not possible, the slurry mean residence time in the complete coil was estimated by either the Beggs and Brill correlation or the Lockhart and Martinelli holdup correlation. Based on the results from the Fort Lewis radioactive tracer tests one correlation appears to be as good as the other. The correlations developed here make use of the estimated slurry mean residence time, $\bar{\Theta}$, in the entire coil. Also, attempts were made to incorporate the mean slurry residence time to that section of the coil between the inlet and the point at which coking occurred.

2. It is assumed that coking, when it occurs, is initiated by elements of the slurry in closest contact with the tube wall, and that the outer wall skin temperature is a better approximation to the state of these fluid elements than the bulk fluid temperature. The skin temperature, T_s, at the initial location of the coke deposits was therefore used as the correlating variable in this work.

3. One would expect the onset of coking should be more dependent on the local hydrogen partial pressure in the coil than, say, that at the coil inlet. However in the absence of such data, the coil inlet hydrogen partial pressure was used. Correction of this pressure to obtain the local hydrogen partial pressure in the coil requires knowledge of factors such as the amount of solvent vaporized and the amount of hydrogen consumed, both as a function of position in the tube.

4. Data such as the coal and solvent functionality (especially hydroxyl and non-basic nitrogen contents) were not reported. It is therefore assumed that these factors are present in the three coals of interest (Ind.V, Ky 6 & 11, Ky 9) in the same proportions, and that they are in proportion to the total organic oxygen and nitrogen content in the coal. As the coal organic oxygen and nitrogen analyses, as well as the other heteroatom contents, were not reported for all runs, the available data for each coal were averaged and the average

values for each coal were used, when attempts were made to establish the importance of heteroatom content in coking tendency.

5. The aromatic and asphaltene contents of the dissolved coal and solvent mixture were not reported in the data. Thus, consideration of these factors was not possible in this study.

6. The role of the solvent quality, Q_S, as measured and reported by the Wilsonville pilot plant, in the suppression or promotion of coking is unclear. However, this factor was included in this study in an effort to determine the sensitivity of incipient coking to the reported solvent quality as determined by the short method. The definition of solvent quality (short) as measured by the Wilsonville pilot plant is given in Section 4.1.

7. Factors in the coal mineral matter other than pyrite were not tested as potential correlating variables. Factors such as chloride content were not always reported, and in view of the limited quantity of data in the data base it appears that combinations of no more than four or five factors at a time can be expected to show statistical significance.

The values of the Wilsonville SRC-I preheater operational conditions and of the coal properties used in the attempts to correlate the coking data are summarized in Tables 5.3 and 5.4. Aside from the two runs which coked with Indiana V coal, the bulk of the coking data are for the two Kentucky coals, No. 6 & 11 and No. 9. Kentucky 6 & 11 is a blend of these two coals. The proportion of each in the blend was not reported.

5.3 Development of Incipient Coking Correlations

The combinations of process operating conditions and coal and solvent properties chosen for the regression analysis of the Wilsonville preheater coking data are listed in Table 5.5. An individual discussion of the results from each of these regression cases follows.

5.3.1 Case A

This case involved the combination of the slurry mean residence time through the coil as estimated by the Beggs and Brill method, $\bar{\Theta}_{BB}$, the weight fraction of coal in the slurry, f_c, the solvent quality, Q_s, and the inlet hydrogen partial pressure, P_{H_2}. The resultant correlation of the nineteen data points of Table 5.3 is shown in Figure 5.1 and the values of the F-factors for each parameter are listed in Table 5.6. The value obtained for the correlation coefficient (R^2-value) for this correlation is 0.68, and although this is not outstanding, it does indicate a fairly good fit of the data while using only process condition factors in the incipient coking model. The F-factors, which are an indication of the significance of

Table 5.3

Summary of Wilsonville SRC-I Preheater Coking Data

Point No.	Run No.	Coal Type	Inlet H_2 Partial Pres., P_{H_2}, psia	Skin Temp. T_s, °F	Estimated Residence Time, $\bar{\theta}_{RR}$, Min.	Solvent Quality Index, Q_s	Wt. % Coal f_c	Source
1	137.0	Ind V	1161.	660.0	4.16	71.90	37.80	FE2270-36
2	138.0	Ind V	1119.	667.0	4.18	73.80	37.25	FE2270-36
3	150.0	Ky 6 & 11	1538.	602.0	5.12	70.60	38.00	FE2270-46
4	150.0	Ky 6 & 11	1542.	603.0	5.10	64.00	38.70	FE2270-46
5	150.0	Ky 6 & 11	1543.	625.0	5.13	63.50	38.80	FE2270-46
6	151.0	Ky 6 & 11	1870.	600.0	5.54	63.00	38.40	FE2270-46
7	151.0	Ky 6 & 11	1859.	613.0	5.55	63.90	37.50	FE2270-46
8	151.0	Ky 6 & 11	1876.	619.0	5.66	63.90	37.90	FE2270-46
9	155.0	Ky 6 & 11	1549.	623.0	6.82	62.60	36.50	FE2270-48
10	155.0	Ky 6 & 11	1571.	625.0	7.26	62.60	37.80	FE2270-48
11	155.0	Ky 6 & 11	1556.	647.0	6.28	62.60	37.10	FE2270-48
12	155.0	Ky 6 & 11	1491.	693.0	6.80	62.60	33.20	FE2270-48
13	164.0	Ky 9	2040.	854.0	13.6	66.40	35.30	FE2270-60
14	166.0	Ky 9	1860.	473.0	4.91	71.40	40.10	FE2270-68
15	166.0	Ky 9	1860.	516.0	4.86	71.80	38.40	FE2270-68
16	166.0	Ky 9	1511.	469.0	4.48	68.80	38.80	FE2270-68
17	166.0	Ky 9	1520.	488.0	4.30	67.30	38.30	FE2270-68
18	166.0	Ky 9	1534.	504.0	4.37	68.70	38.70	FE2270-68
19	166.0	Ky 9	1483.	464.0	4.40	67.00	37.60	FE2270-68

Table 5.4

Average Values of the Coal Property Data[a]

Component, wgt %	Coal		
	Ind. V	Ky. 6 & 11	Ky 9
Nitrogen	1.24	1.57	1.19
Oxygen	12.16	9.92	8.55
Organic Sulfur	2.02	1.60	1.86
Pyritic Sulfur	1.20	1.04	1.11
Sulfates	0.35	0.18	0.09
Total Sulfur	3.59	2.83	3.06
Carbon	68.39	71.21	72.96
Hydrogen	4.81	5.17	4.89
C/H, Atomic Basis	1.18	1.15	1.24

[a]See Table B.2 (Appendix B) for the reported coal analyses from the Wilsonville Solvent Refined Coal pilot plant.

Table 5.5

Combinations of Factors Used in the Regression Analysis
of the Wilsonville Preheater Coking Data

Case	Factors								
	$\bar{\Theta}_{BB}$	$\bar{\Theta}_{LM}$	$\bar{\Theta}_{BBPC}$	P_{H_2}	Q_s	f_c	$(w_n f_c + w_o f_c)$	$(w_s f_c)$	$(w_v f_c)$
A	✓			✓	✓	✓			
B		✓		✓	✓	✓			
C			✓	✓	✓	✓			
D	✓			✓	✓		✓	✓	
E			✓	✓	✓		✓	✓	
F	✓			✓	✓			✓	✓

Note: $\bar{\Theta}_{BB}$ is the mean slurry residence time in the entire coil as estimated by the Beggs and Brill holdup correlation.

$\bar{\Theta}_{LM}$ is the mean slurry residence time in the entire coil as estimated by the Lockhart and Martinelli holdup correlation.

$\bar{\Theta}_{BBPC}$ is the mean slurry residence time from the coil inlet to the point of coking as estimated by the Beggs and Brill holdup correlation.

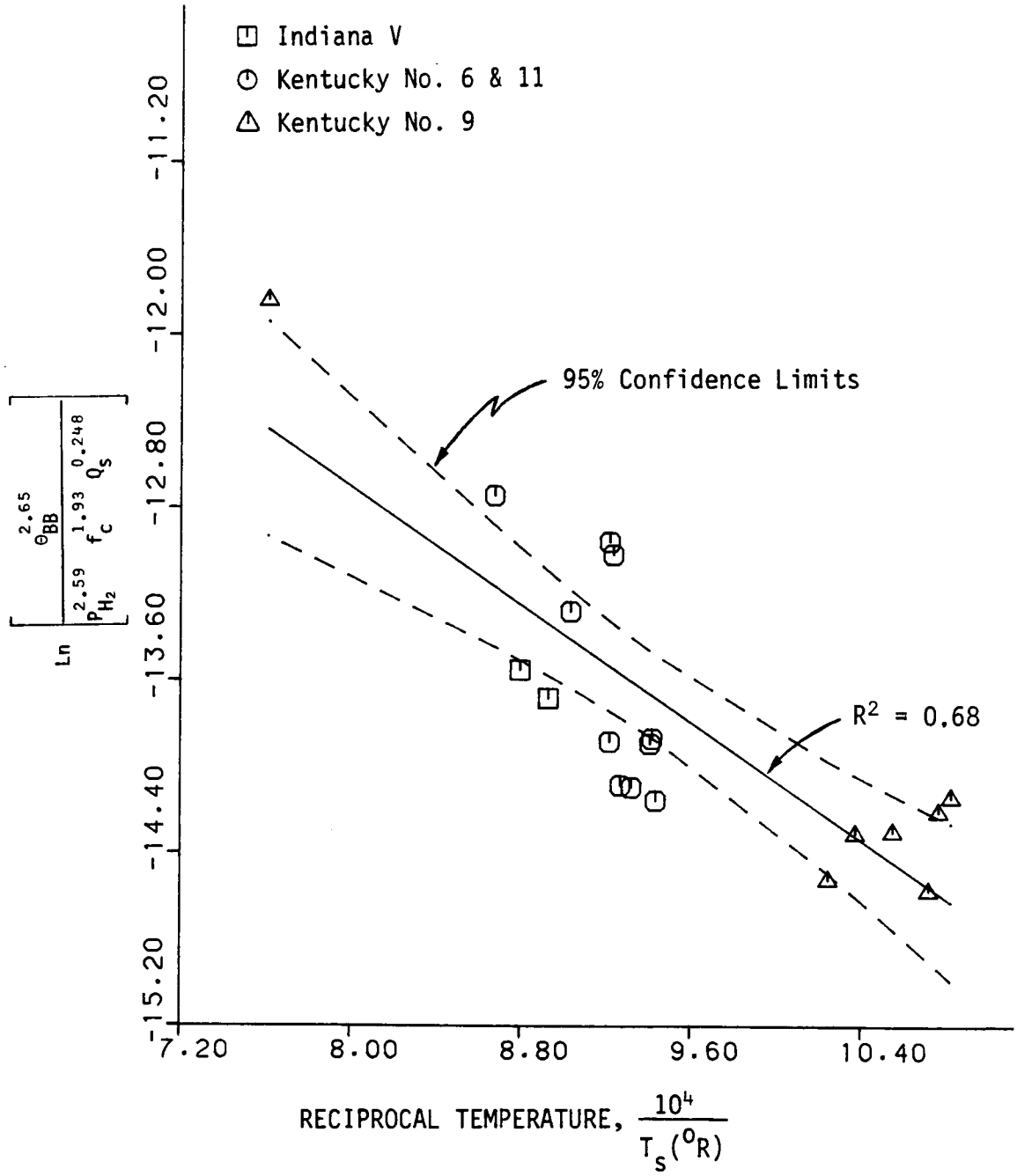

Figure 5.1 Case A: Correlation of the Wilsonville Fired Preheater Coking Data, using Four Process Condition Factors. Mean Slurry Residence Time Estimated by the Beggs and Brill Holdup Correlation.

Table 5.6

Values of F-Factors for Cases Investigated

Case	Factors								
	$\bar{\Theta}_{BB}$	$\bar{\Theta}_{LM}$	$\bar{\Theta}_{BBPC}$	P_{H_2}	Q_s	f_c	$(w_n f_c + w_o f_c)$	$(w_s f_c)$	$(w_v f_c)$
A	15.7			9.71	0.009	0.204			
B		22.1		10.3	0.0009	0.172			
C			155.2	11.4	0.292	0.740			
D	15.7			4.38	0.604		32.5	1.03	
E			155.2	11.4	0.184		1.50	1.39	
F	15.7			9.71	0.281			0.228	2.69

each variable, show that mean slurry residence time is the most significant factor and solvent quality is the least significant factor in the regression equation. The regression equation, shown in Figure 5.1 is given by:

$$\text{Ln}\left[\frac{\theta_{BB}^{2.65}}{P_{H_2}^{2.59}\, f_c^{1.93}\, Q_s^{0.248}}\right] = -7.25 - 6820/T_s \qquad 5.7$$

These results encourage one to believe that the approach taken in analyzing the preheater coking process by way of the model, Eq. 5.6, though rough, is reasonably promising. In testing this approach and the correlation developed for this case, it is interesting to note where the data for the non-coking runs, Table B.3 (Appendix B), fall in relation to the incipient coking correlation, Eq. 5.7. This comparison is shown in Figure 5.2, where the non-coking data use skin temperatures in the coil at various turns, provided the temperature is within the range of the developed coking correlation. With the exception of two of the non-coking points, all of the data fall below the incipient coking curve. It is therefore indicated that the area below the curve in Figure 5.2 represents non-coking conditions and the area above the curve represents coking conditions, for a given skin temperature. Thus, for a given skin temperature, the coking correlation indicates that increasing the slurry mean residence time in the coil moves the argument toward the coking region, or enhances coking. It also suggests that increasing inlet hydrogen partial pressure, solvent quality, or the fraction coal in the slurry, moves the argument toward the non-coking region, or suppresses coking. The

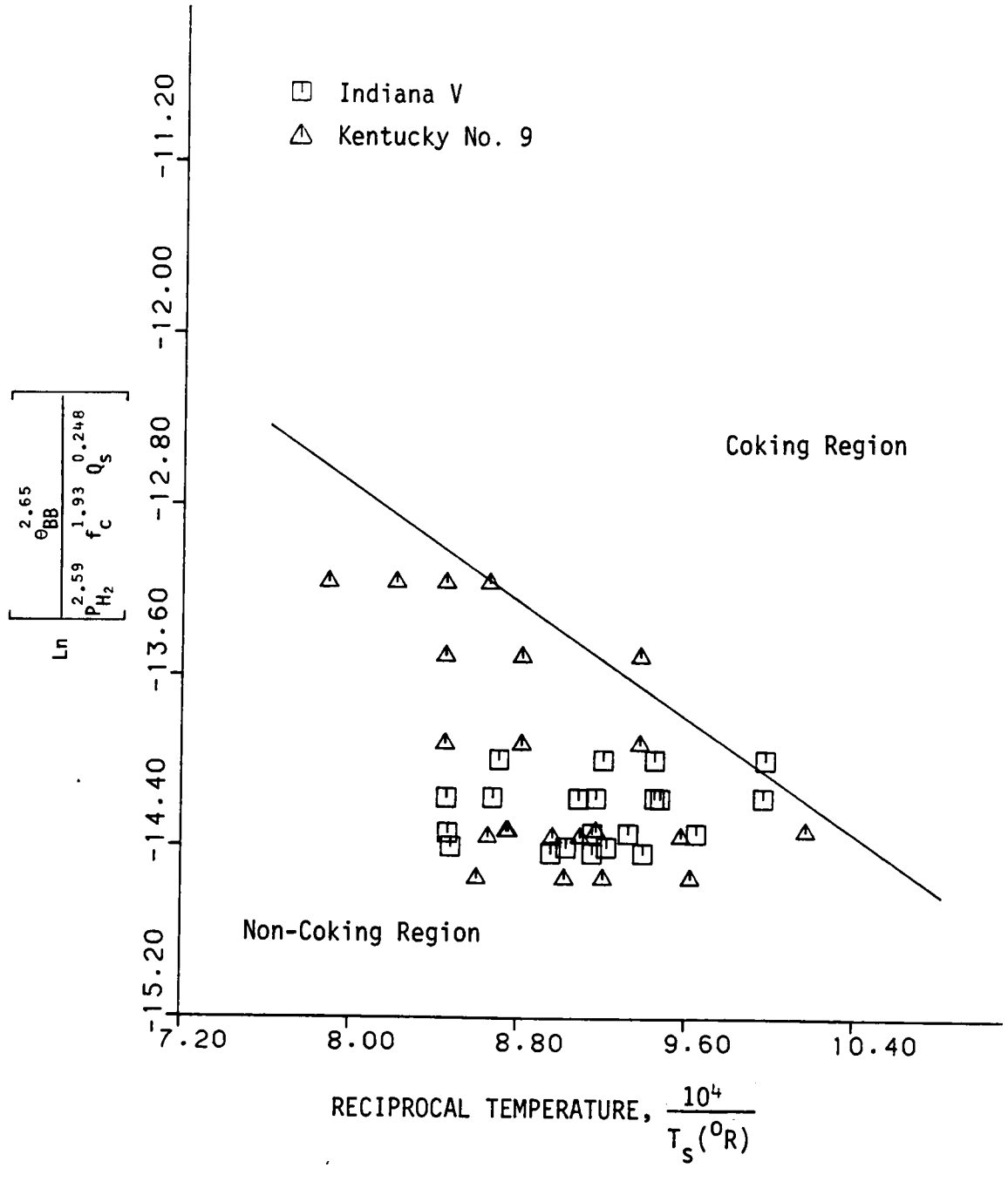

Figure 5.2 Comparison of the Wilsonville Preheater Non-Coking Data with the Proposed Incipient Coking Correlation of Case A.

increase in coal fraction in order to suppress coking seems to contradict both intuition and past experience. However, the range of values of this parameter is observed to be small when inspecting the coking data, and this could be of some influence. Additional investigations of this factor and others, including coal heteroatom contents, appear warranted.

5.3.2 Case B

This regression case is essentially the same as the previous one (Case A), but this time the Lockhart and Martinelli holdup correlation (See Section 4.7.1) has been used to estimate the mean slurry residence time. Thus, any difference in the use of either the Beggs and Brill holdup correlation or the Lockhart and Martinelli holdup correlation can be ascertained. In order to use the Lockhart and Martinelli correlation it is necessary to know the mean slurry viscosity. A value of 50 cp was obtained for the Wilsonville preheater by numerical integration of the viscosity curve, shown in Figure 4.17, between the average inlet and outlet slurry temperatures (125 ^{o}F - 800 ^{o}F). Previous results had indicated that the calculation of residence time by the Lockhart and Martinelli correlation was not very sensitive to viscosity in this range (Frazier and others, 1982).

The resultant correlation for this regression case is shown in Figure 5.3 and the values for the F-factors for each parameter in the correlation are listed in Table 5.6. The correlation, given by the equation

$$\text{Ln}\left[\frac{\theta_{LM}^{2.96}}{P_{H_2}^{2.37}\, f_c^{1.59}\, Q_s^{0.0713}}\right] = -3.51 - 7390/T_s \qquad 5.8$$

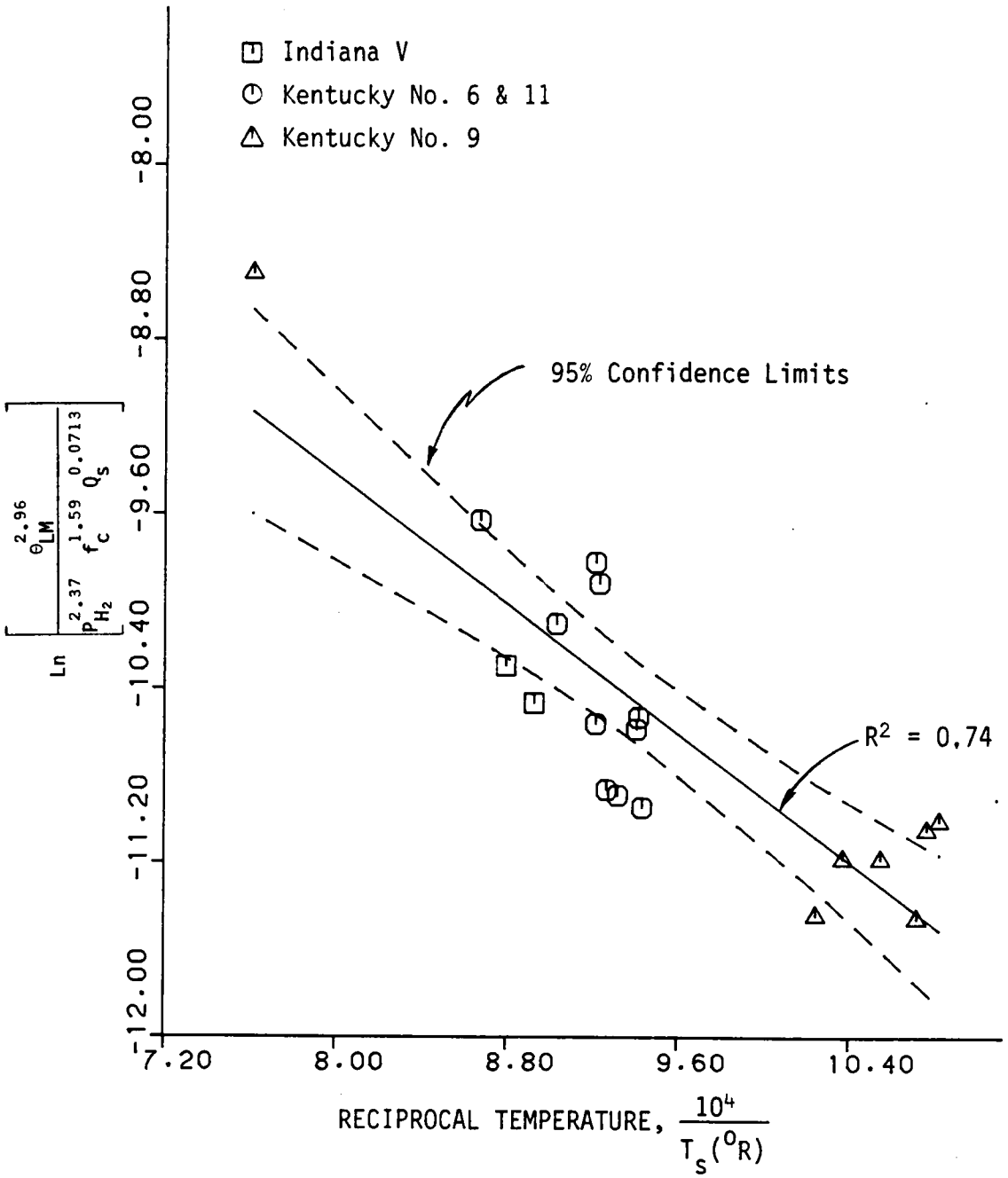

Figure 5.3 Case B: Correlation of the Wilsonville Fired Preheater Coking Data, using Four Process Condition Factors. Mean Slurry Residence Time Estimated by the Lockhart and Martinelli Holdup Correlation.

yields a correlation coeficient (R^2 value) of 0.74, which is somewhat better than that obtained using the Beggs and Brill holdup correlation. In addition, using the Lockhart and Martinelli correlation yields results which give greater significance to the mean slurry residence time and less significance to the solvent quality (see Table 5.6). The comparison of the non-coking data with the correlation obtained for this case is shown in Figure 5.4. It exhibits the same characteristics as that of the previous case, that is all but two of the points lie below the incipient coking curve, suggesting that the coking domain does indeed lie above the curve of Figure 5.4.

5.3.3 Case C

This case was developed to evaluate the combination of solvent quality, coal fraction, inlet hydrogen partial pressure, and the slurry mean residence time as estimated by the Beggs and Brill method. However this latter factor, slurry mean residence time, was scaled to the point at which coking occurred in the coil and is denoted as $\bar{\Theta}_{BBPC}$. The resultant correlation, given by the equation

$$\text{Ln}\left[\frac{\theta_{BBPC}^{1.22}\; Q_s^{0.587}}{P_{H_2}^{0.991}\; f_c^{1.60}}\right] = 6.46 - 9460/T_s \qquad 5.9$$

has a correlation coefficient (R^2 value) of 0.94, which is quite respectable. This correlation is shown in Figure 5.5 and the F-factors are listed in Table 5.6. The results of this correlation indicate that the residence time to the point of coking is a very significant factor but that solvent quality and coal fraction are not very significant

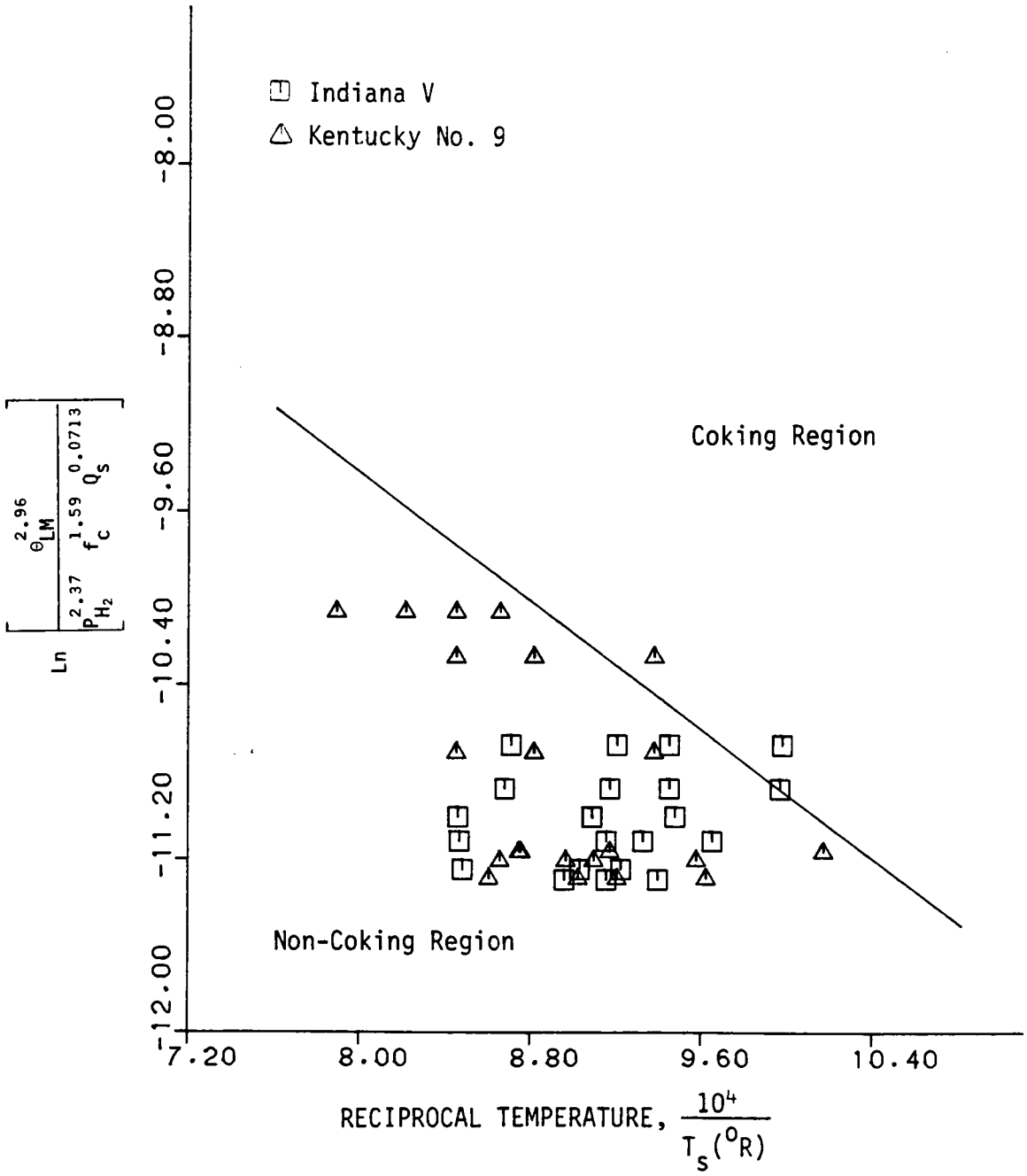

Figure 5.4 Comparison of the Wilsonville Preheater Non-Coking Data with the Proposed Incipient Coking Correlation of Case B.

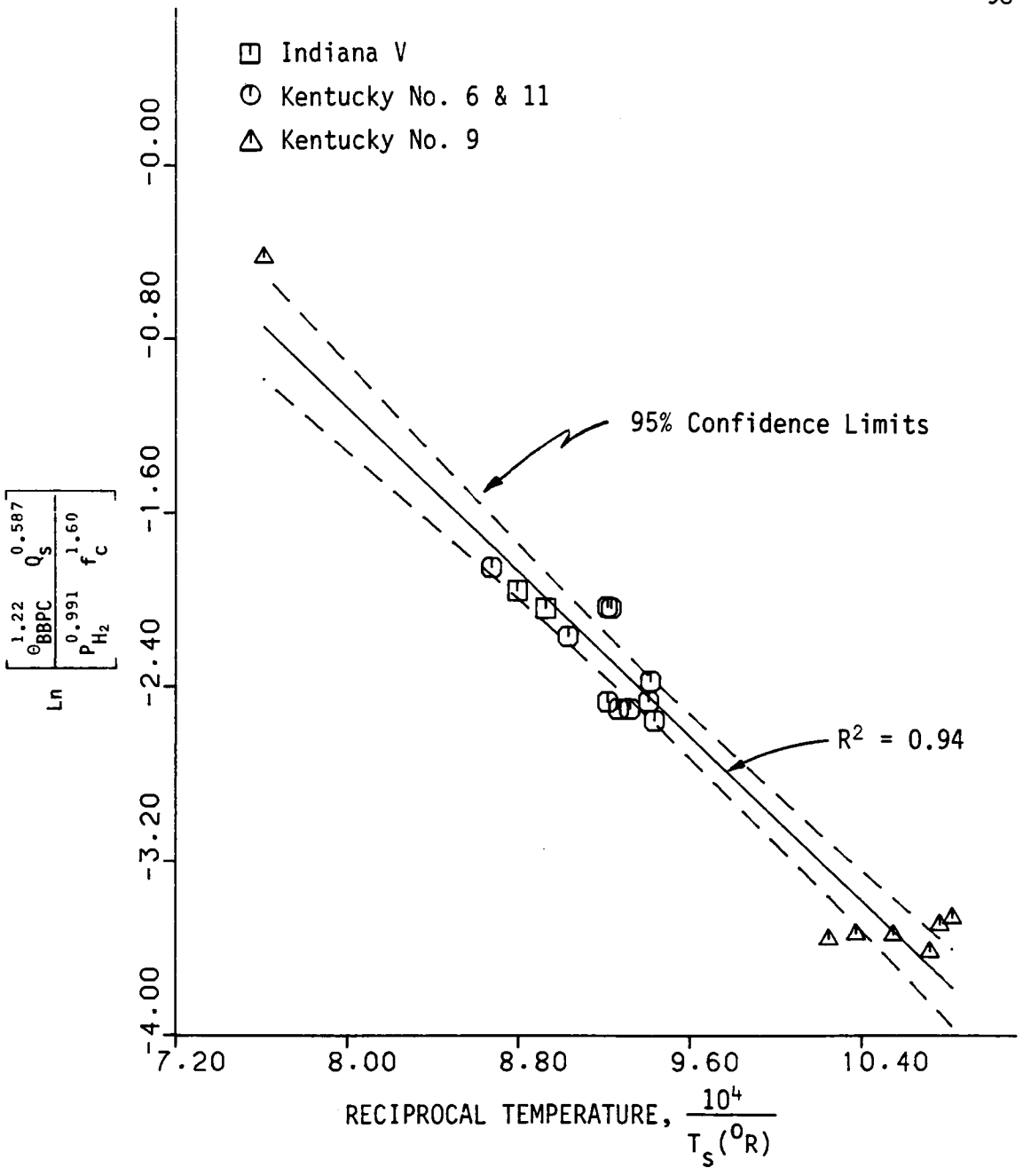

Figure 5.5 Case C: Correlation of the Wilsonville Fired Preheater Coking Data, using Four Process Condition Factors. Mean Slurry Residence Time to the Point of Coking Estimated by the Beggs and Brill Holdup Correlation.

factors and could probably be omitted from the correlation. The comparison of this correlation with the non-coking data is shown in Figure 5.6. In this case, the non-coking data, as presented in Table 5.7, are those data points with exit coil conditions, that is skin temperature at the coil exit and residence time at the coil exit. This is presumably the highest attained temperature at the longest residence time of the slurry in the coil. As illustrated by Figure 5.6, the non-coking data generally fall below this proposed incipient coking curve with only one data point out of twelve clearly above the coking curve. The use of the Lockhart and Martinelli correlation to calculate the residence time to the point of coking yields results which are similar to these. It should be noted that when using the mean slurry residence time from the coil inlet to the point of coking it would be much better to incorporate the local hydrogen partial pressure at the point of coking. However, the inability to estimate, even roughly, the local hydrogen partial pressure prevents this consideration at this time. This is due to the lack of properties for the recycle coal oils, such as vapor-liquid equilibrium data.

5.3.4 Case D

With previous attempts being made (Cases A,B, and C above) to ascertain the influence of process conditions ($\bar{\theta}$, f_c, Q_s, P_{H_2}) on coking tendencies, and with satisfactory results obtained, it was now desired to determine the influence of the coal properties, especially heteroatom contents, on coking tendencies. Because of the limited amount of coking data available, attempts to correlate more than five

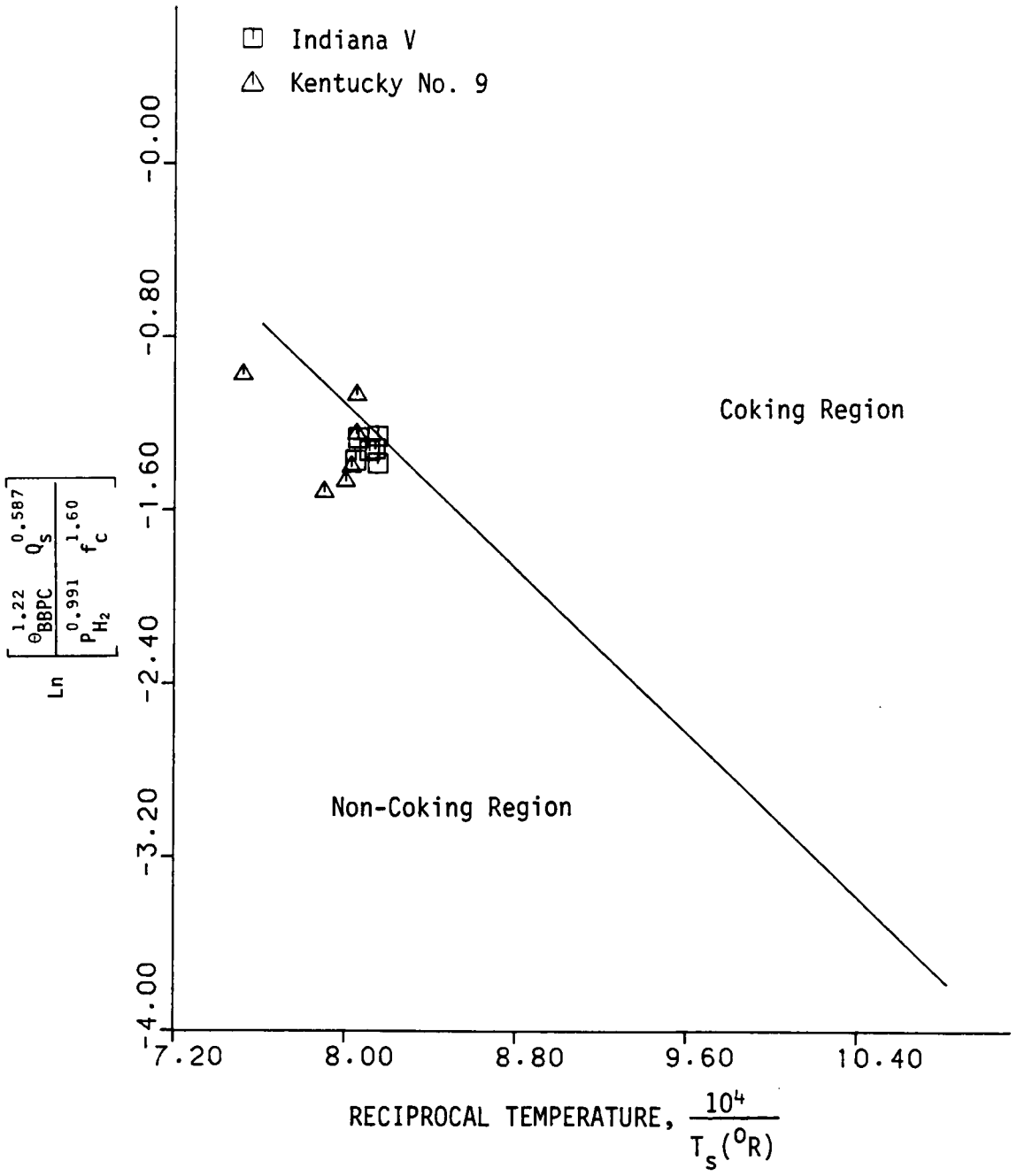

Figure 5.6 Comparison of the Wilsonville Preheater Non-Coking Data with the Proposed Incipient Coking Correlation of Case C.

Table 5.7

Summary of Wilsonville SRC-I Preheater Non-Coking Data at Exit Coil Conditions[a]

Run Number	Coal Type	Inlet H Partial Pressure P_{H_2}, psia	Skin Temp. T_s, °F	Estimated Residence Time, $\bar{\theta}_{BB}$, min	Solvent Quality Index, Q_s	Weight Percent Coal in Slurry $f_c \times 100$
135	Ind V	2033.	781.0	5.976	76.0	37.5
136	Ind V	1933.	783.0	5.532	77.4	39.2
140	Ind V	2103.	767.0	5.590	75.2	37.4
140	Ind V	2133.	773.0	5.647	77.9	36.5
143	Ind V	1593.	769.0	4.782	77.0	38.2
147	Ind V	1553.	767.0	4.956	74.6	38.0
159	Ky 9	1428.	782.0	5,357	71.0	37.0
160	Ky 9	1430.	782.0	4.679	73.6	37.8
161	Ky 9	1834.	806.0	4.760	71.9	38.5
162	Ky 9	1834.	786.0	5.129	74.7	38.4
163	Ky 9	1436.	870.0	6.306	67.9	38.7
167	Ky 9	1840.	790.0	5.134	66.4	38.3

[a] Skin temperature at the exit of the coil and slurry mean residence time to the exit of the coil.

variables at a time were unsuccessful. Thus, in order to limit the number of variables to five or less and to include heteroatom contents, it is necessary to omit one or two of the previous variables. For the inclusion of heteroatoms, it seems reasonable to replace, f_c, a measure of the total coal in the inlet slurry, with factors such as $w_o f_c$, $w_n f_c$, or $w_s f_c$, which are measures of the heteroatom contents in the inlet slurry. Also, since the effects of oxygen and nitrogen increase the tendency towards coking, as illustrated by the literature (Whitehurst, D.D., 1979 and Marsh, H., 1973) and by regression analysis of the coking data incorporating the factors $w_n f_c$ and $w_o f_c$ (Frazier, Lin, and Edwards, 1982), the factor $w_n f_c + w_o f_c$ was introduced as a means of limiting the number of factors to five.

This regression case, then, includes the mean slurry residence time for the entire coil as estimated by the Beggs and Brill method, the inlet hydrogen partial pressure, the solvent quality, the sulfur content of the inlet slurry, and the combined oxygen and nitrogen contents of the slurry. The resulting correlation, as shown in Figure 5.7, is given by:

$$\text{Ln}\left[\frac{\Theta_{BB}^{3.03}\, Q_s^{3.50}\, (w_n f_c + w_o f_c)^{4.62}}{P_{H_2}^{1.37}\, (w_s f_c)^{1.94}}\right] = 12.1 - 8820/T_s \qquad 5.10$$

Because coal analyses for a particular run were not always available, for instance run 155, it was necessary to use average values, as listed in Table 5.4, for the coal heteroatom contents.

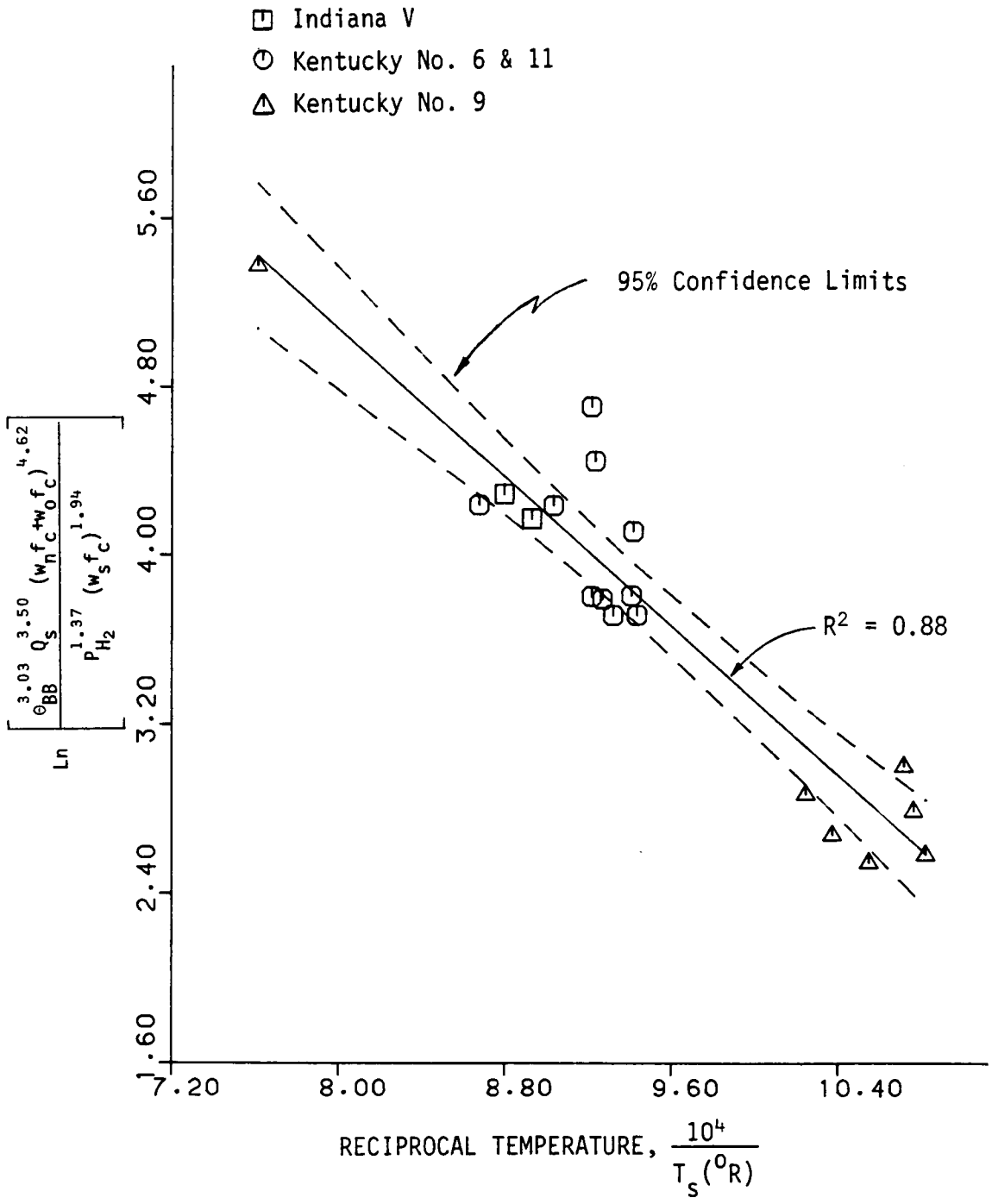

Figure 5.7 Case D: Correlation of the Wilsonville Fired Preheater Coking Data, using Process Condition Factors and Coal Heteroatom Contents. Mean Slurry Residence Time Estimated by the Beggs and Brill Holdup Correlation.

The correlation coefficient (R^2 - value)for this case is a respectable 0.88 and inspection of the F-factors, as listed in Table 5.6, shows the most significant factor to be the combined nitrogen and oxygen content in the slurry, $w_n f_c + w_o f_c$. This parameter is followed in significance by the slurry residence time, the inlet hydrogen partial pressure, the sulfur content in the inlet slurry, and lastly the solvent quality. The comparison of the correlation equation for this case with the non-coking data is shown in Figure 5.8. This comparison indicates a problem with the correlation equation, Eq. 5.10. The non-coking data points for the Indiana V coal lie above the proposed incipient coking curve, while those for the Kentucky No. 9 coal lie well below the curve. This apparent split in the data is indeed troublesome and efforts to resolve this problem have been extensive. The use of pyritic sulfur and organic sulfur in this case, instead of total sulfur, also produced similar results. However, both pyritic sulfur and organic sulfur were indicated to be more significant factors than the total sulfur. Part of the reason for the smaller significance of total sulfur may be due to the presence of the sulfur in sulfate and sulfide forms. Table B.2 (Appendix B) shows that some of the coal analyses ran as high as 0.63% sulfate (Indiana V).

Some reasons for the split behavior pattern of the Indiana V and Kentucky No. 9 coals, as illustrated by Figure 5.8, have been postulated as follows:

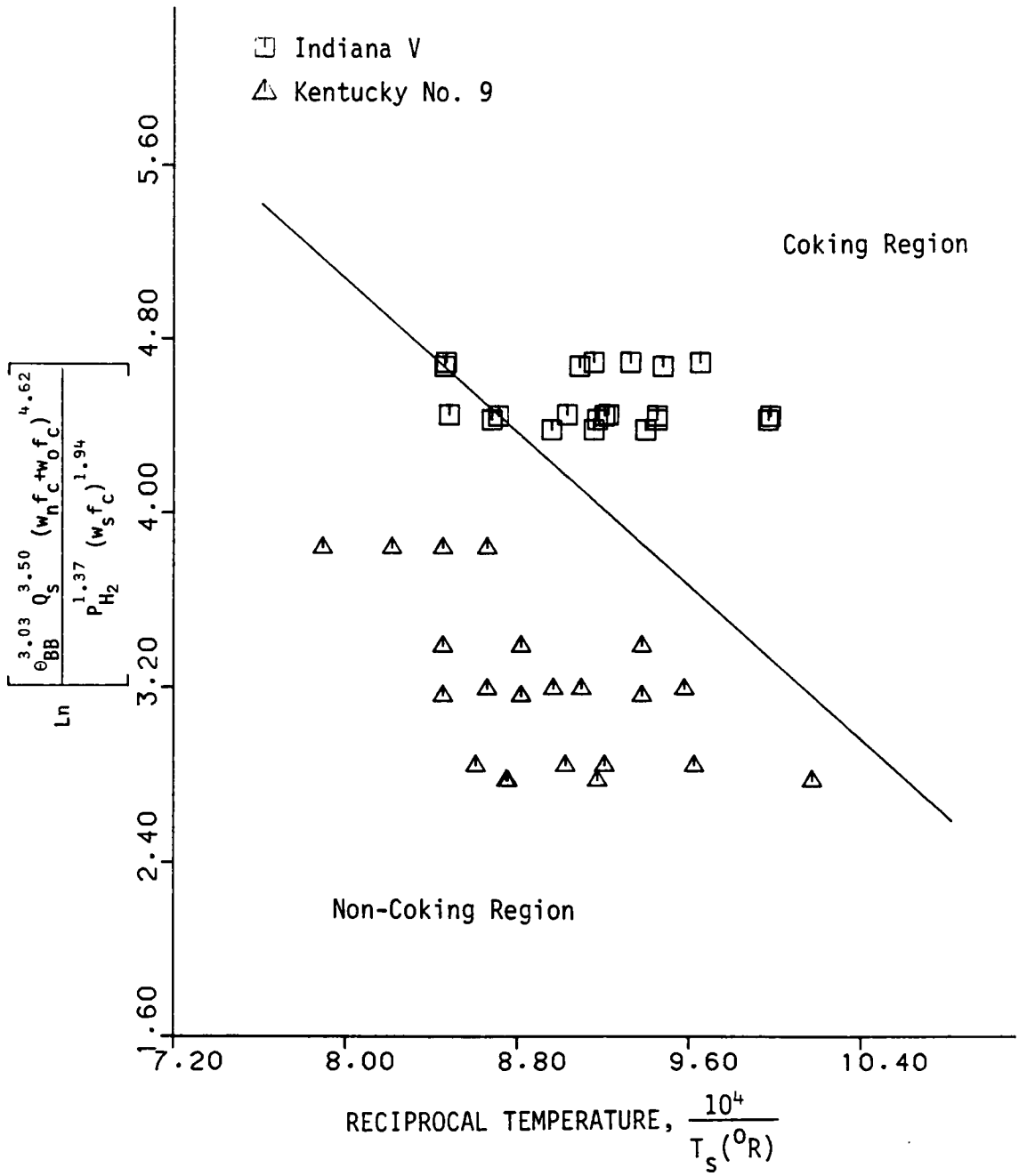

Figure 5.8 Comparison of the Wilsonville Preheater Non-Coking Data with the Proposed Incipient Coking Correlation of Case D.

1. The coking data base is not large enough or too much scatter exists in the data to properly determine the influence of heteroatom contents.

2. The total organic oxygen and nitrogen contents of the coals may not be representative of the heteroatom factors responsible for the coking tendency.

3. An additional factor, such as coal vitrinite content, may be responsible for the apparent different coking characteristics of of these two coals.

The second of the above mentioned points is probably the most intriguing, in view of the fact that the work of Whitehurst (1979) and of Walker (1980) suggest that it is the hydroxylic oxygen and the non-basic nitrogen which appear to be the heteroatoms most responsible for promoting coking. It is possible that the hydroxylic oxygen and non-basic nitrogen heteroatoms are present in differing ratios in the Indiana V and Kentucky No. 9 coals. This point is further supported by the fact that the split in the data always seem to occur when the oxygen and nitrogen contents, either combined or taken as separate terms, are introduced into the correlation. Unfortunately, the reported coal analyses from Wilsonville do not include the necessary analytical data to resolve this problem.

5.3.5 Case E

This case incorporates the same factors as Case D but now the mean slurry residence time to the point of coking as estimated by the Beggs and Brill method is used instead of the residence time throughout the entire coil. The resultant correlation is shown in Figure 5.9 and the values of the F-factors for each parameter are listed in Table 5.6. The correlation coefficient (R^2 - value) is a high 0.95 and the resultant correlation is given by:

$$\text{Ln}\left[\frac{\theta_{BBPC}^{1.21}\, Q_s^{2.07}\, (w_n f_c + w_o f_c)^{1.03}}{P_{H_2}^{0.848}\, (w_s f_c)^{1.42}}\right] = 15.4 - 9530/T_s \qquad 5.11$$

The results indicate a high significance being given to the residence time and the inlet hydrogen partial pressure. The combined nitrogen and oxygen term and the sulfur term are also significant. As for all previous cases (A-D), solvent quality is the least significant term.

The comparison of this correlation, Eq. 5.11, with the non-coking data at the exit of the coil is presented in Figure 5.10. The data appear to split into two groups although the distinction is not as pronounced as in Case D. Note that the two non-coking data points for Indiana V coal, although slightly above the incipient coking correlation, are within the 95% confidence limits of the correlation.

5.3.6 Case F

Marsh (1973) indicates that the reactive vitrain content of a coal is important in providing the necessary fluidity to produce an isotropic coke. Thus, to determine the effect of the coal vitrinite content on coking in the Wilsonville preheater, and to possibly

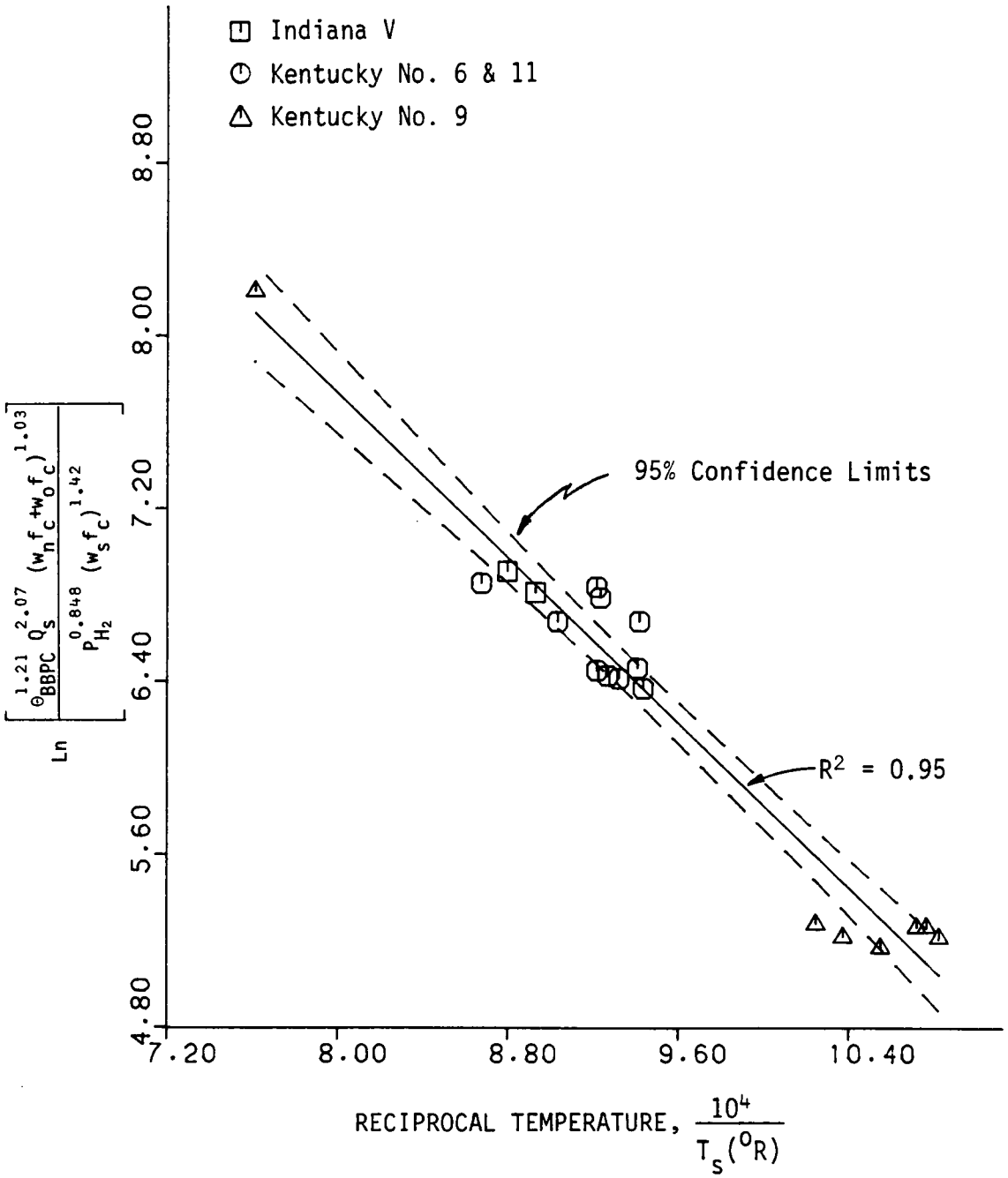

Figure 5.9 Case E: Correlation of the Wilsonville Fired Preheater Coking Data, using Process Condition Factors and Coal Heteroatom Contents. Mean Slurry Residence Time to the Point of Coking Estimated by the Beggs and Brill Holdup Correlation.

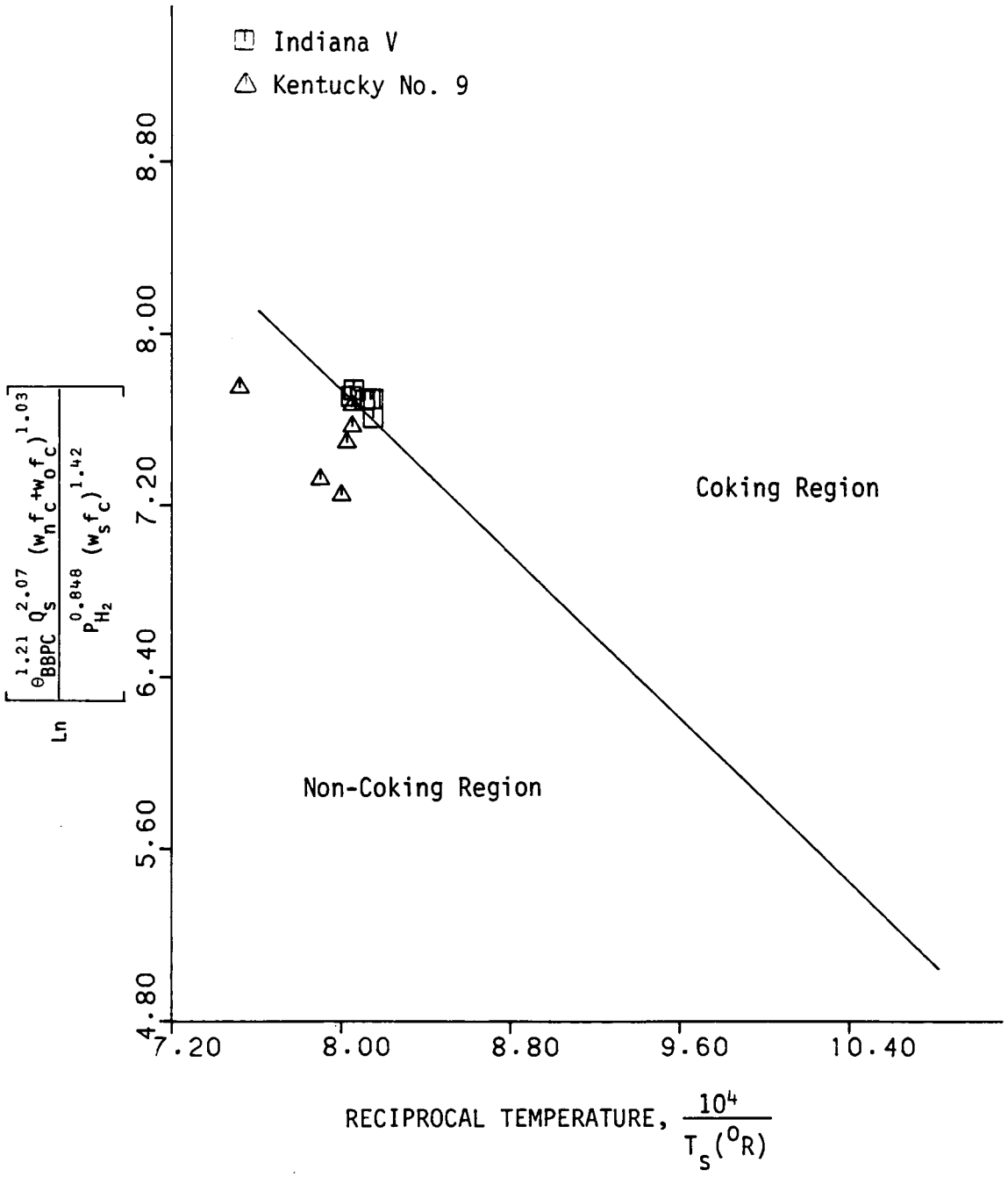

Figure 5.10 Comparison of the Wilsonville Preheater Non-Coking Data with the Proposed Incipient Coking Correlation of Case E.

resolve the split between the Indiana V and the Kentucky No. 9 non-coking data points, this parameter was investigated. The values for the vitrinite content of the coals were not available from the Wilsonville pilot plant, but representative values for the coals of interest were obtained through the Pennsylvania State Office of Coal Research. These values are presented in Table 5.8 and are intended for exploratory purposes.

This case involves the correlation of mean slurry residence time for the entire coil as estimated by the Beggs and Brill method, inlet hydrogen partial pressure, solvent quality, fraction total sulfur in the slurry, and fraction vitrinite in the slurry. The resultant correlation, as shown in Figure 5.11, has a correlation coefficient (R^2 - value)of 0.74. The regression equation is given by:

$$\text{Ln}\left[\frac{\Theta_{BB}^{3.48}\, Q_s^{2.29}\, (w_v f_c)^{7.08}}{P_{H_2}^{3.29}\, (w_s f_c)^{2.25}}\right] = -0.869 - 7360/T_s \qquad 5.12$$

This indicates that increasing coal vitrinite content increases the tendency for coking to occur, as one might have anticipated from Marsh's findings. Also, the vitrinite content is a fairly significant term in the correlation as illustrated by inspection of Table 5.6. The comparison of this correlation with the non-coking data, as shown in Figure 5.12, reveals that the majority of the non-coking data points fall below the coking curve and that no distinct split between the Kentucky No. 9 and the Indiana V points occur.

Table 5.8

Vitrinite Content of Coals

Coal	Weight Percent Vitrinite	Source
Indiana V (Old Ben Mine No. 1)	74.3	PSOC - 585 PSOC - 590
Kentucky 6 & 11 (Pyro Mine)	72.3	Average of other Ky 6 & 11 Coals (PSOC - 223, 640, 746, 166, 220, 273, and 1082)
Kentucky 9 (Pyro Mine)	69.4	Average of other Ky 9 Coals (PSOC - 165, 213, 215, 217, and 272)
Kentucky 9 (LaFayette Mine)	71.4	PSOC - 215

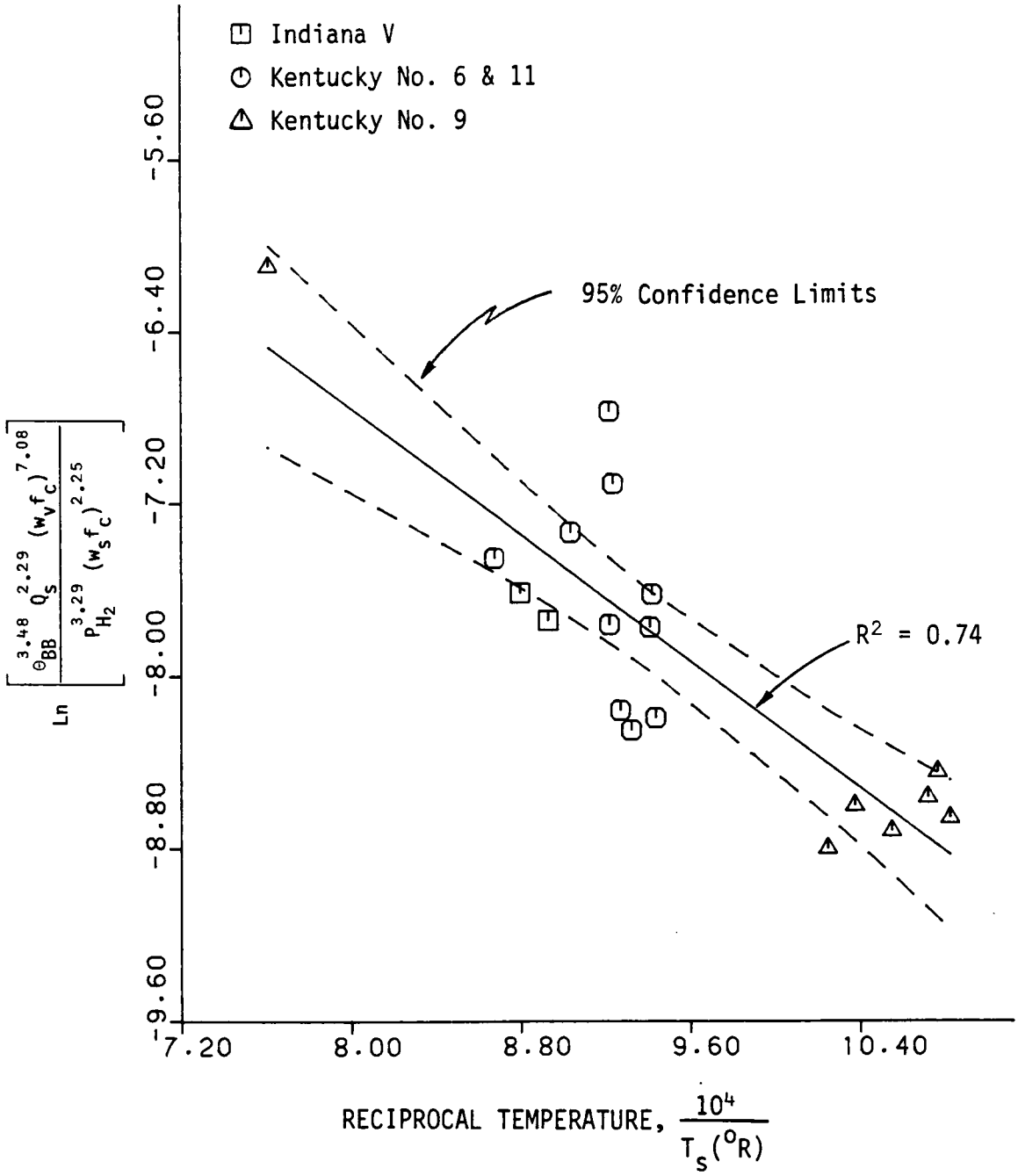

Figure 5.11 Case F: Correlation of the Wilsonville Fired Preheater Coking Data, using Process Condition Factors, Coal Sulfur Content, and Coal Vitrinite Content. Mean Slurry Residence Time Estimated by the Beggs and Brill Holdup Correlation.

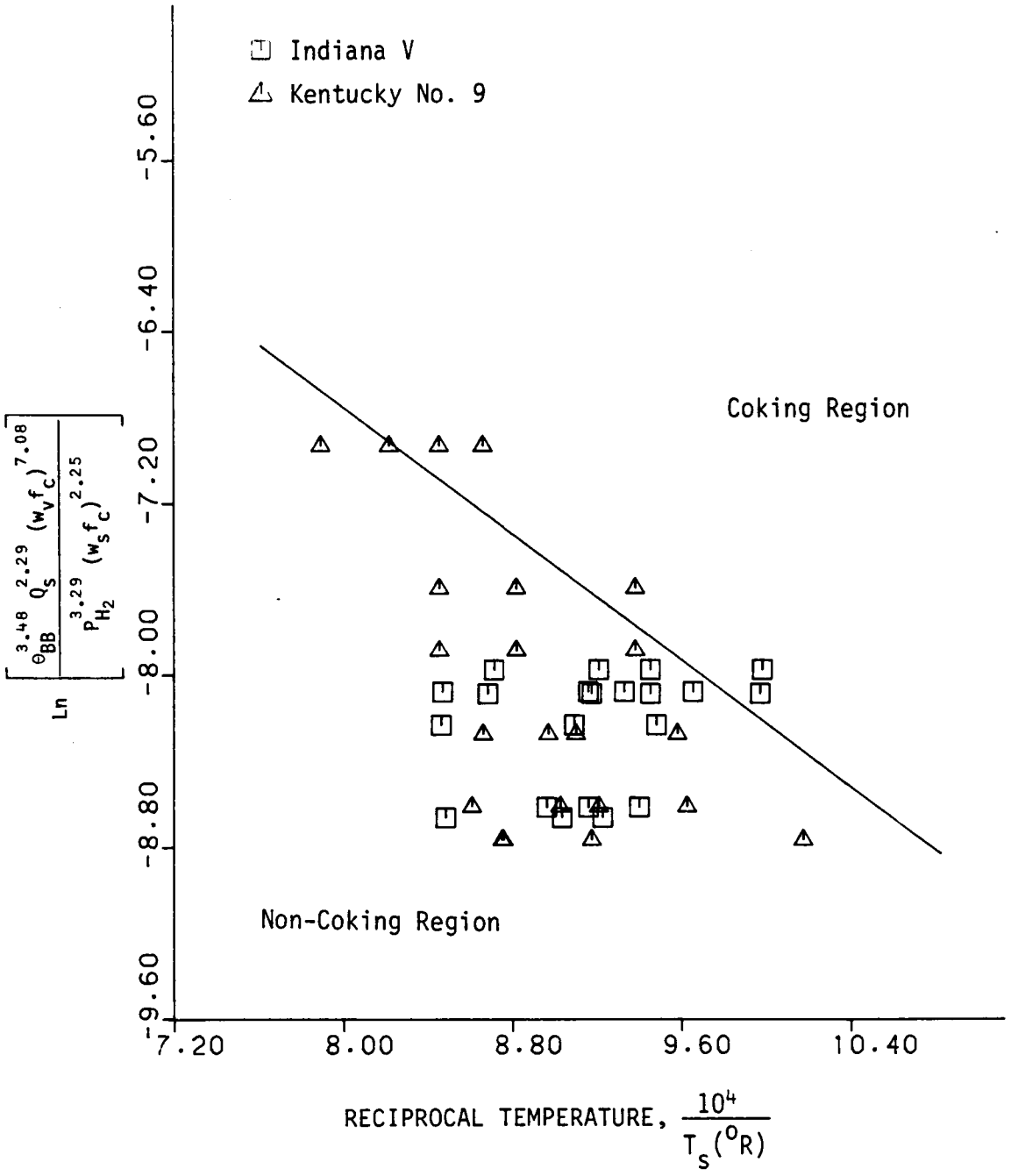

Figure 5.12 Comparison of the Wilsonville Preheater Non-Coking Data with the Proposed Incipient Coking Correlation of Case F.

CHAPTER 6

SUMMARY AND CONCLUSIONS

The formation of coke in coal liquefaction fired preheaters is a problem which is common to the major coal liquefaction processes of interest, including the SRC-I, SRC-II, H-Coal, and EDS process designs. This study was conducted to evaluate and analyze this problem by compiling the operating data relating to the specific occurrence of coking in fired preheaters, reviewing the literature pertinent to coke formation or suppression under similar or related conditions in coal processing plants, and using the available data to test a simple incipient coking model in terms of process operating conditions and coal-solvent properties.

The largest source of information in regards to the formation of coke in coal liquefaction fired preheaters is from the operation of the Solvent Refined Coal (SRC-I) pilot plant at Wilsonville, Alabama. Process operational data and coal analyses from this facility have been reasonably well documented for both runs in which coking occurred as well as runs during which coking did not occur. This data base, however, is limited with respect to the quality of data as well as to the completeness of the data. For instance, the hydrogen partial pressure at the coil outlet was not always reported, also neither measurements nor estimates were provided for the slurry mean residence time in the coil. Coal analyses for a particular run were also not always reported. However, the Wilsonville data is adequate enough to test a simple proposed incipient coking correlational model applicable to coking occurrences in coal liquefaction preheaters.

The review of the literature pertinent to coke formation or suppression produced little quantitative information on coking under conditions similar to those experienced in coal liquefaction preheaters. However, results of one study, for example, show that the yield of coke from the heat treatment of some petroleum pitches and coal tar pitches correlates with the amount of asphaltenes and polar aromatics present in the starting material. It has also been shown that the amount of anisotropic coke (mesophase) produced from the heat treatment of heavy petroleum oils and a hydrogenated coal oil correlates with the aromaticity (f_a value) of that fraction of the starting material which is soluble in benzene (primarily asphaltenes). In studies using SRC-type liquids those items shown to promote carbonization or charring reactions are increasing functionality (especially hydroxylic oxygen and non-basic nitrogen), increasing aromatic content, increasing molecular weight, decreasing volatility, certain catalysts, increasing hydrogen scavengers, and increasing rate of radical generation. Those items indicated to suppress coking tendencies are hydrogen pressure, increasing hydrogen donors, and dilution with inerts.

The Wilsonville SRC-I fired preheater coking data, although limited in quantity, was adequate enough to serve as a data base for the preliminary correlation of coking occurrences using process operating conditions and coal-solvent properties. The multiple regression analysis of these data was conducted in terms of a proposed incipient coking correlational model. The conclusions resulting from this analysis are itemized as follows:

1. A simple incipient coking model form has been proposed which shows promise in being able to correlate coking data for multiphase flow of coal-oil slurries through fired preheater coils in direct coal liquefaction processing plants. Based on 19 data points this model form yielded correlation coefficients (R^2 values) as high as 0.95, depending on the combination of process condition factors and coal-solvent properties used in the multiple regression analysis. The proposed incipient coking model is based on coking occurring when the concentration of a key coking precursor reaches its solubility limit and as a consequence developed incipient coking curves should serve as a boundary between the non-coking and the coking domains.

2. Although one might anticipate from first principles that a complete time-temperature history of the coal-oil slurry during a run which produced coke would be necessary to predict or correlate coking occurrences, the choice of the local skin temperature at the location of the initial deposition of coke in the preheater coil appears to be adequate based on the correlational results of this study.

3. Because the residence time of the coal-oil slurry in the preheater was not reported by the Wilsonville pilot plant and due to the importance of this factor towards coking tendencies, it became necessary to estimate the residence

time of the slurry in the coil during a particular run. This was accomplished by means of either the Beggs and Brill holdup correlation or the Lockhart and Martinelli holdup correlation, and although these correlations are based on two phase gas-Newtonian liquid flow in tubes, they gave surprisingly good results when compared with the experimentally determined residence times at the Fort Lewis pilot plant. Thus these correlations appear applicable for use as a means to provide estimates of the mean slurry residence time in preheaters, and, indeed they provide reasonable estimates for use in the proposed incipient coking model, at least, based on the results of this study.

4. Correlation of the Wilsonville coking data using the proposed incipient coking model and process operational variables only (estimated mean slurry residence time to the point of coke deposition, Θ_{BBPC}, inlet hydrogen partial pressure, P_{H_2}, coal fraction in the slurry, f_c, and solvent quality, Q_s) yielded a correlation coefficient (R^2 value) of 0.94 and an incipient coking curve given by:

$$\text{Ln}\left[\frac{\Theta_{BBPC}^{1.22}\ Q_s^{0.587}}{P_{H_2}^{0.991}\ f_c^{1.60}}\right] = 6.46 - 9460/T_s \qquad 6.1$$

This incipient coking curve successfully bounds the Wilsonville non-coking data at coil exit conditions (highest coil skin temperature and longest slurry residence time in

the coil). The analysis indicates that the relative significance of the process factors decreases in the order: a) residence time, b) inlet coil hydrogen partial pressure, c) coal fraction in the slurry, and d) solvent quality. This correlation (Equation 6.1) suggests, as one would anticipate, that increasing slurry residence time promotes coking tendencies, while increasing hydrogen partial pressure suppresses coking tendencies.

5. Correlation of the Wilsonville coking data in terms of process operational variables and coal properties (coal total sulfur content, w_s, and combined coal total oxygen and nitrogen content, w_n+w_o) yielded a correlation coefficient (R^2 value) of 0.95 and an incipient coking curve given by:

$$\text{Ln}\left[\frac{\theta_{BBPC}^{1.21}\, Q_s^{2.07}\, (w_n f_c + w_o f_c)^{1.03}}{P_{H_2}^{0.848}\, (w_s f_c)^{1.42}}\right] = 15.4 - 9530/T_s \qquad 6.2$$

This incipient coking curve successfully bounds the non-coking run data for which Kentucky No. 9 coal was used, and, although the non-coking data for runs using Indiana V coal overlap the proposed incipient coking curve slightly, it nonetheless falls within the 95% confidence limits of the correlation. The relative significance of the factors affecting coking tendencies is indicated by this correlation to decrease in the order: a) residence time, b) inlet hydrogen partial pressure, c)combined coal oxygen and

nitrogen contents, d) coal sulfur content, and, lastly, e) solvent quality. In addition to the previous result (Equation 6.1) this correlation suggests that increasing coal nitrogen and oxygen content tends to promote coking tendencies, while increasing coal sulfur content tends to suppress coking tendencies.

6. Analytical data for additional factors suggested in the literature to affect coking behavior, such as hydroxylic oxygen content and non-basic nitrogen content, were not found in the literature for the coals of interest (Indiana V, Kentucky 6 and 11, and Kentucky 9). When such properties become available it is anticipated that further improvement in the proposed correlations may be achieved.

7. The exploratory testing of coal vitrinite as having a possible influence in the promotion of coking tendencies indicates that it is indeed a significant factor. More complete petrographic data should provide improvement in the proposed incipient coking correlations.

8. While the proposed correlational model appears promising as a form for coal-oil slurry preheaters, the two correlations presented (Equations 6.1 and 6.2) are not recommended for use as a tool in the final design of these process units, in view of the limited data set upon which they are based. Instead,

it is suggested they be used only to guide development of a design at this time.

For future studies aimed at providing an incipient coking correlation suitable for design purposes or for future studies involving coking in coal liquefaction preheaters, the following recommendations are made:

1. Obtain a larger coking/non-coking data base in order to test candidate correlational forms which contain the relatively large number of factors known to influence coking in coal liquefaction preheaters.

2. Improved methods should be developed to calculate the mean slurry residence time in coal liquefaction fired preheaters.

3. Coal analytical data must include such factors as the distribution of the organic oxygen and nitrogen among their functional forms. Complete petrographic data should also be available for the coals of interest.

4. Methods must be developed to calculate the hydrogen partial pressure locally in coal liquefaction preheaters. Vapor-liquid equilibria data must be obtained for multi-component process-derived solvents.

5. Solubility studies of the solubility of coking precursors in multi-component coal-derived liquids should be conducted.

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APPENDICES

APPENDIX A

WILSONVILLE FLOWSHEET AND PREHEATER COIL

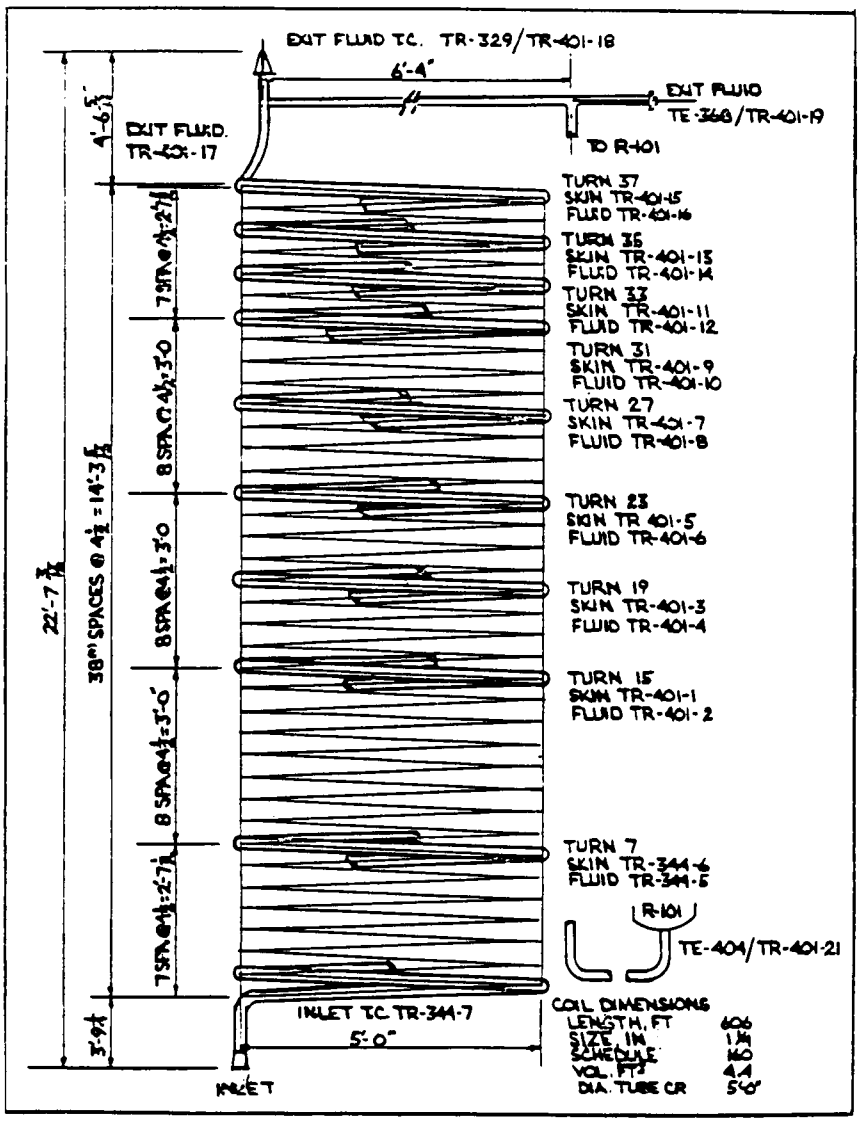

Figure A.1 Wilsonville Fired Preheater Coil Configuration

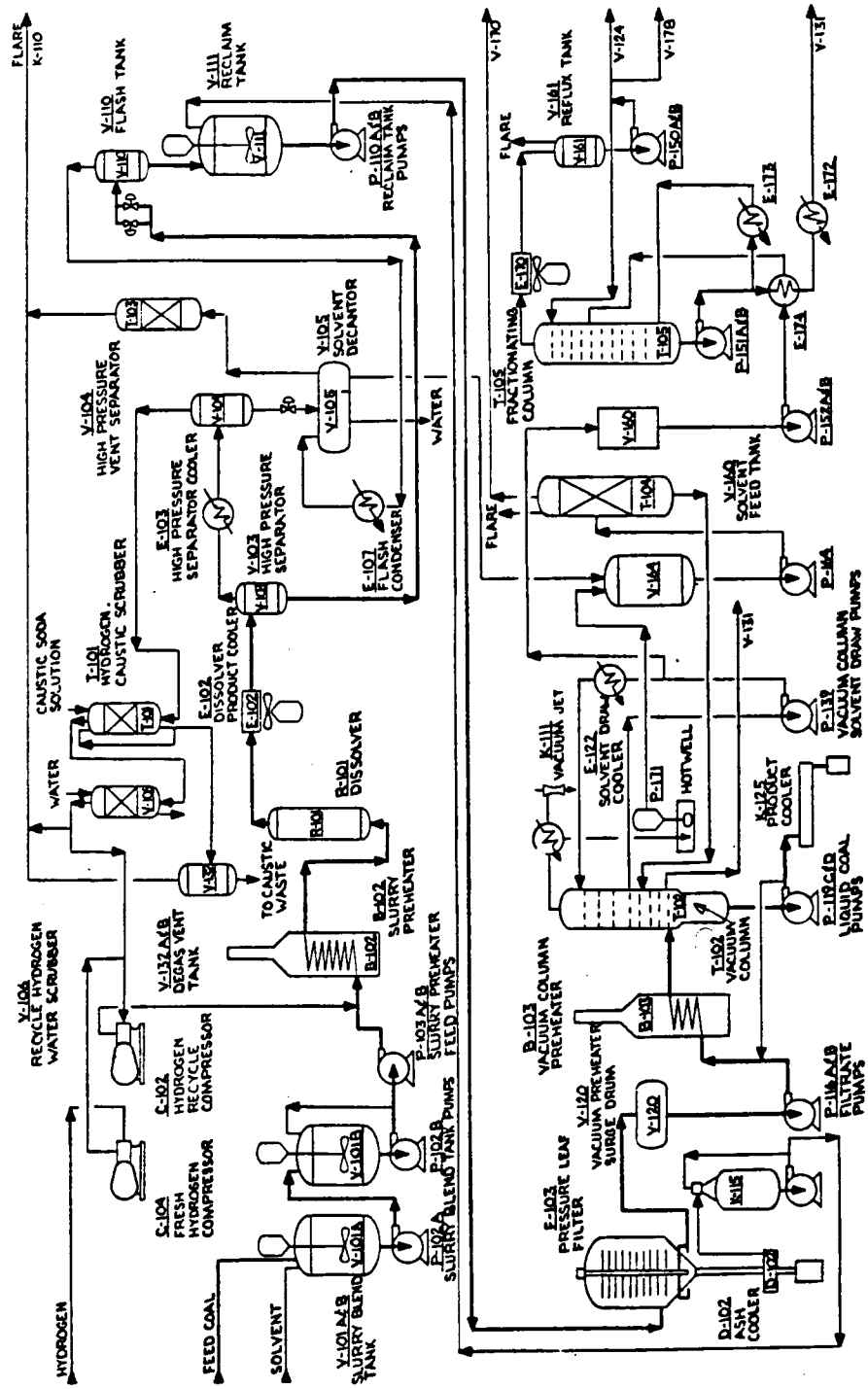

Figure A.2 Wilsonville SRC-I Pilot Plant Process Flowsheet

APPENDIX B

WILSONVILLE PREHEATER COKING DATA

Table B.1

Wilsonville SRC-I Preheater Operating Data for Runs during which Coking was Reported

RUN NO. & DATE	** PREHEATER OPERATING CONDITIONS ** COAL FEED LB/HR	SOLVENT FEED LB/HR	GAS FEED LB/HR	SLURRY % COAL	INLET PRESS. (PSIA)	PH2 IN (PSIA)	PH2 OUT (PSIA)	TEMP. IN (F)	TEMP. OUT (F)
137 5/31 TO 6/2/78	479.0	788.2	235.6	37.80	1760.	1161.0	990.0	126.0	781.0
138 6/10 TO 6/12/78	454.5	765.6	248.7	37.25	1763.	1119.0	960.0	126.0	774.0
150 10/4/78	432.0	704.8	136.0	38.00	1810.	1538.0	0.0	125.0	800.0
150 10/24/78	446.0	706.5	135.3	38.70	1815.	1542.0	0.0	130.0	785.0
150 10/26/78	441.0	695.6	136.0	38.80	1816.	1543.0	0.0	130.0	788.0
151 10/28/78	443.0	710.6	136.7	38.40	2200.	1870.0	0.0	125.0	775.0
151 11/4/78	431.0	718.3	138.0	37.50	2202.	1859.0	1705.0	115.0	773.0
151 11/5/78	427.0	699.6	135.8	37.90	2207.	1876.0	1705.0	115.0	772.0
155 1/8/79	442.0	769.0	59.5	36.50	1801.	1549.0	900.0	0.0	780.0
155 1/9/79	439.0	722.4	53.5	37.80	1785.	1571.0	900.0	0.0	781.0

Note: A value of zero indicates missing data.

Table B.1 (continued)

RUN NO. & DATE	COAL FEED LB/HR	SOLVENT FEED LB/HR	GAS FEED LB/HR	SLURRY % COAL	INLET PRESS. (PSIA)	PH2 IN (PSIA)	PH2 OUT (PSIA)	TEMP. IN (F)	TEMP. OUT (F)
				** PREHEATER OPERATING CONDITIONS **					
155 1/10/79	430.0	729.0	79.2	37.10	1787.	1556.0	900.0	0.0	812.0
155 1/11/79	382.0	768.6	64.0	33.20	1755.	1491.0	900.0	0.0	799.0
164 6/4 TO 6/5/79	246.0	450.9	28.9	35.30	2411.	2040.0	0.0	149.0	885.0
166 7/3/79	545.0	814.0	142.0	40.10	2188.	1860.0	0.0	126.0	775.0
166 7/7 TO 7/9/79	536.0	859.0	140.0	38.40	2189.	1860.0	0.0	121.0	785.0
166 7/16 TO 7/18/79	541.0	854.0	139.0	38.80	1799.	1511.0	0.0	128.0	787.0
166 7/23 TO 7/25/79	561.0	904.0	142.0	38.30	1799.	1520.0	1335.0	123.0	789.0
166 7/27/79	560.0	887.0	141.0	38.70	1805.	1534.0	1335.0	127.0	783.0
166 8/2 TO 8/3/79	538.0	891.0	136.0	37.60	1766.	1483.0	1315.0	146.0	790.0

Table B.1 (continued)

RUN NO. & DATE	TYPE& MINE	VOLATILE FRACTION	** COAL PROPERTIES ** HETEROATOM CONTENT(WGT%) OXYGEN	SULFUR	NITROGEN	MINERAL CONTENT(WGT%) SODIUM OXIDE	POTASSIUM OXIDE	CHLORIDE
137 5/31 TO 6/2/78	IND.5	42.58	12.17	3.55	1.29	0.32	2.51	.00
138 6/10 TO 6/12/78	IND.5	34.52	12.06	3.62	1.17	0.25	2.60	.00
150 10/4/78	KEN#6&11 PYRO	0.00	0.00	0.00	0.00	0.00	.00	.00
150 10/24/78	KEN#6&11 PYRO	30.56	11.37	2.84	1.60	0.00	.00	.00
150 10/26/78	KEN#6&11 PYRO	30.56	11.37	2.84	1.60	0.00	.00	.00
151 10/28/78	KEN#6&11 PYRO	0.00	0.00	0.00	0.00	0.00	.00	.00
151 11/4/78	KEN#6&11 PYRO	34.70	8.47	2.81	1.54	1.90	1.88	.00
151 11/5/78	KEN#6&11 PYRO	34.20	8.47	2.81	1.54	1.90	1.88	.00
155 1/8/79	KEN#6&11 PYRO	0.00	0.00	0.00	0.00	0.00	.00	.00
155 1/9/79	KEN#6&11 PYRO	0.00	0.00	0.00	0.00	0.00	.00	.00

Table B.1 (continued)

RUN NO. & DATE	TYPE& MINE	** COAL PROPERTIES ** VOLATILE FRACTION	HETERCATOM CONTENT(WGT%) OXYGEN	SULFUR	NITROGEN	MINERAL CONTENT(WGT%) SODIUM OXIDE	POTASSIUM OXIDE	CHLORIDE
155 1/10/79	KEN#6&11 PYRC	0.00	0.00	0.00	0.CC	0.00	.00	.00
155 1/11/79	KEN#6&11 PYRC	0.00	0.00	0.00	0.0C	0.00	.00	.00
164 6/4 TO 6/5/79	KEN#9 LAF.	27.33	9.57	2.88	0.95	0.46	2.80	.00
166 7/3/79	KEN#9 LAF.	0.00	0.00	0.00	0.0C	0.00	.00	.00
166 7/7 TO 7/9/79	KEN#9 LAF.	0.00	0.00	0.00	0.0C	0.00	.00	.00
166 7/16 TO 7/18/79	KEN#9 LAF.	0.00	0.00	0.00	0.00	0.00	.00	.27
166 7/23 TO 7/25/79	KEN#9 LAF.	0.00	0.00	0.00	0.00	0.00	.00	.00
166 7/27/79	KEN#9 LAF.	0.00	0.00	0.00	0.00	0.00	.00	.00
166 8/2 TO 8/3/79	KEN#9 LAF.	32.80	9.42	2.88	0.93	0.44	2.11	.00

Table B.1 (continued)

RUN NO. & DATE	QUALITY (SHORT)	** SOLVENT PROPERTIES ** BOILING POINT FRACTIONS (WT%) IBP	<450F	<550F	<650F	>650F	EP
137 5/31 TO 6/2/78	71.9	424.0	1.0	44.0	30.0	25.0	823.0
138 6/10 TO 6/12/78	73.8	414.0	5.0	53.0	27.0	15.0	815.0
150 10/4/78	70.6	0.0	0.0	0.0	0.0	0.0	0.0
150 10/24/78	64.0	0.0	0.0	0.0	0.0	0.0	0.0
150 10/26/78	63.5	0.0	0.0	0.0	0.0	0.0	0.0
151 10/28/78	63.0	0.0	0.0	0.0	0.0	0.0	0.0
151 11/4/78	63.9	318.0	8.1	39.5	28.8	23.6	906.0
151 11/5/78	63.9	318.0	8.1	39.5	28.8	23.6	906.0
155 1/8/79	0.0	0.0	0.0	0.0	0.0	0.0	0.0
155 1/9/79	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table B.1 (continued)

RUN NO. & DATE	QUALITY (SHORT)	** SOLVENT PROPERTIES ** BOILING POINT FRACTIONS (WGT%) IBP	<450F	<550F	<650F	>650F	EP
155 1/10/79	0.0	0.0	0.0	0.0	0.0	0.0	0.0
155 1/11/79	62.6	0.0	0.0	0.0	0.0	0.0	0.0
164 6/4 TO 6/5/79	66.4	335.0	31.1	35.3	16.8	16.8	838.0
166 7/3/79	71.4	0.0	0.0	0.0	0.0	0.0	0.0
166 7/7 TO 7/9/79	71.8	0.0	0.0	0.0	0.0	0.0	0.0
166 7/16 TO 7/18/79	68.8	0.0	0.0	0.0	0.0	0.0	0.0
166 7/23 TO 7/25/79	67.3	0.0	0.0	0.0	0.0	0.0	0.0
166 7/27/79	68.7	0.0	0.0	0.0	0.0	0.0	0.0
166 8/2 TO 8/3/79	67.0	444.0	3.2	48.0	29.9	19.0	838.0

Table B.1 (continued)

PREHEATER TEMPERATURE PROFILES

RUN NO. & DATE	TEMPERATURE (SKIN,BULK,DELTAT;ALL IN DEG.F) TURN7	TURN15	TURN19	TURN23	TURN27	TURN31	TURN33	TURN35
137	468.0	588.0	660.0	668.0	757.0	751.0	770.0	831.0
5/31 TO 6/2/78	405.0	506.0	573.0	515.0	616.0	727.0	706.0	742.0
	63.0	82.0	87.0	153.0	141.0	24.0	64.0	88.0
138	480.0	601.0	677.0	657.0	745.0	741.0	807.0	821.0
6/10 TO 6/12/78	402.0	500.0	573.0	503.0	607.0	717.0	778.0	733.0
	72.0	101.0	104.0	154.0	138.0	24.0	62.0	88.0
150	465.0	602.0	650.0	674.0	726.0	751.0	765.0	797.0
10/4/78	395.0	552.0	592.0	564.0	646.0	736.0	719.0	733.0
	70.0	50.0	58.0	110.0	80.0	15.0	46.0	64.0
150	470.0	603.0	649.0	675.0	715.0	741.0	757.0	787.0
10/24/78	390.0	566.0	586.0	560.0	622.0	726.0	723.0	715.0
	80.0	37.0	63.0	115.0	93.0	15.0	34.0	72.0
150	485.0	625.0	704.0	673.0	713.0	742.0	760.0	794.0
10/26/78	405.0	586.0	590.0	521.0	585.0	727.0	721.0	725.0
	80.0	39.0	114.0	152.0	128.0	15.0	39.0	69.0
151	480.0	600.0	686.0	663.0	701.0	730.0	748.0	782.0
10/28/78	400.0	570.0	583.0	524.0	624.0	715.0	712.0	719.0
	80.0	30.0	103.0	139.0	77.0	15.0	36.0	63.0
151	470.0	613.0	688.0	672.0	702.0	731.0	750.0	784.0
11/4/78	395.0	580.0	585.0	533.0	619.0	716.0	715.0	717.0
	75.0	33.0	103.0	139.0	83.0	15.0	35.0	67.0
151	475.0	619.0	697.0	668.0	701.0	731.0	750.0	783.0
11/5/78	400.0	582.0	584.0	517.0	586.0	715.0	716.0	712.0
	75.0	37.0	113.0	151.0	115.0	16.0	34.0	71.0
155	0.0	623.0	667.0	686.0	731.0	0.0	0.0	0.0
1/8/79	0.0	527.0	583.0	546.0	649.0	0.0	0.0	0.0
	0.0	96.0	84.0	140.0	82.0	0.0	0.0	0.0
155	0.0	625.0	670.0	690.0	741.0	0.0	0.0	0.0
1/9/79	0.0	536.0	599.0	545.0	658.0	0.0	0.0	0.0
	0.0	89.0	71.0	145.0	83.0	0.0	0.0	0.0

Table B.1 (continued)

PREHEATER TEMPERATURE PROFILES

RUN NO. & DATE	TEMPERATURE (SKIN,BULK,DELTAT;ALL IN DEG.F) TURN7	TURN15	TURN19	TURN23	TURN27	TURN31	TURN33	TURN35
155	0.0	647.0	686.0	704.0	750.0	0.0	0.0	0.0
1/10/79	0.0	535.0	605.0	576.0	668.0	0.0	0.0	0.0
	0.0	112.0	81.0	128.0	82.0	0.0	0.0	0.0
155	0.0	693.0	706.0	711.0	735.0	0.0	0.0	0.0
1/11/79	0.0	561.0	626.0	583.0	637.0	0.0	0.0	0.0
	0.0	132.0	80.0	128.0	98.0	0.0	0.0	0.0
164	542.0	713.0	770.0	806.0	862.0	856.0	854.0	878.0
6/4 TO 6/5/79	437.0	640.0	716.0	751.0	767.0	839.0	790.0	769.0
	105.0	73.0	54.0	55.0	98.0	17.0	64.0	109.0
166	473.0	626.0	693.0	690.0	708.0	733.0	764.0	783.0
7/3/79	375.0	563.0	587.0	647.0	648.0	675.0	715.0	751.0
	98.0	63.0	106.0	43.0	60.0	58.0	49.0	32.0
166	516.0	700.0	696.0	694.0	725.0	748.0	778.0	788.0
7/7 TO 7/9/79	400.0	647.0	610.0	649.0	662.0	701.0	723.0	772.0
	116.0	53.0	86.0	45.0	63.0	47.0	55.0	16.0
166	469.0	635.0	692.0	692.0	716.0	740.0	779.0	800.0
7/16 TO 7/18/79	350.0	563.0	580.0	659.0	667.0	690.0	720.0	775.0
	119.0	72.0	112.0	33.0	49.0	50.0	59.0	25.0
166	488.0	615.0	685.0	696.0	716.0	741.0	781.0	806.0
7/23 TO 7/25/79	351.0	546.0	573.0	663.0	647.0	683.0	715.0	774.0
	137.0	69.0	112.0	33.0	69.0	58.0	66.0	32.0
166	504.0	647.0	706.0	701.0	719.0	740.0	778.0	799.0
7/27/79	366.0	570.0	589.0	674.0	652.0	680.0	714.0	771.0
	137.0	77.0	117.0	27.0	67.0	60.0	64.0	28.0
166	464.0	586.0	683.0	721.0	716.0	735.0	775.0	801.0
8/2 TO 8/3/79	331.0	505.0	562.0	690.0	628.0	672.0	710.0	768.0
	133.0	81.0	121.0	30.0	87.0	63.0	65.0	33.0

Table B.2

Analyses of the Coals used in the Wilsonville SRC-I Pilot Plant during the Period Spring 1978 – Fall 1979

	Feed Coal Analyses Indiana V Coal					
Date, 1978	8-10 April	3-5 May	31-2 May/June	10-12 June	22-24 June	1-3 July
Run	135	136	137	138	140A	140B
Dry heating value, Btu/lb	12,264	12,396	12,662	12,604	12,570	11,870
Dry Composition, wt %						
Carbon	66.83	69.49	68.17	68.61	67.56	67.32
Hydrogen	4.55	4.99	4.88	4.74	4.58	4.33
Nitrogen	1.16	1.57	1.29	1.17	1.14	1.18
Sulfur	3.72	3.39	3.55	3.62	3.74	3.36
Ash	10.44	10.11	9.94	9.80	10.50	10.70
Oxygen, by difference	13.30	10.45	12.17	12.06	12.48	13.11
Sulfur forms, wt %						
Pyritic	1.09	1.02	1.14	1.15	1.23	0.85
Sulfate	0.63	0.51	0.47	0.28	0.50	0.04
Sulfide	<0.01	0.03	<0.01	0.02	<0.01	0.01
Organic	2.00	1.83	1.94	2.17	2.01	2.46
Proximate analysis, wt %						
Moisture	2.86	4.09	3.29	3.38	3.81	3.76
Ash	9.64	9.89	8.86	9.44	9.93	10.16
Volatile matter	38.65	33.60	42.58	34.52	32.11	33.10
Fixed carbon	48.85	52.42	45.27	52.66	54.15	52.98
Mineral analysis, wt %						
Phosphorus pentoxide, P_2O_5	0.07	0.08	0.09	0.08	0.07	0.07
Silica, SiO_2	43.54	46.13	45.74	46.09	44.91	47.47
Ferric oxide, Fe_2O_3	22.45	21.06	20.25	22.37	21.26	19.94
Alumina, Al_2O_3	18.69	19.34	19.98	19.82	20.92	20.58
Titania, TiO_2	2.34	3.22	1.80	1.45	1.18	1.14
Lime, CaO	3.97	3.70	3.64	2.64	3.05	3.36
Magnesia, MgO	0.80	0.75	0.03	0.60	0.75	0.77
Sulfur trioxide, SO_3	4.27	1.51	4.92	3.50	3.77	4.32
Potassium oxide, K_2O	2.56	2.37	2.51	2.60	1.90	1.94
Sodium oxide, Na_2O	0.14	0.43	0.32	0.25	0.32	0.41
Undetermined	1.17	1.41	0.72	0.60	1.87	-

Table B.2 (continued)

Feed Coal Analyses
Kentucky 6 and 11 Coal

Date, 1978	25-27 October	3-5 November
Run	150	151
Proximate Analyses, wt %		
Moisture	1.45	1.33
Ash	9.28	9.24
Volatile Matter	30.56	34.20
Fixed Carbon	58.71	55.23
Ultimate Analysis, wt %		
Carbon	69.84	72.57
Hydrogen	5.09	5.25
Nitrogen	1.60	1.54
Sulfur	2.84	2.81
Ash	9.28	9.36
Oxygen (by difference)	11.37	8.47
Dry Heating Value, Btu/lb	13,112	13,161
Sulfur Forms, wt %		
Pyritic	0.95	1.12
Sulfate	0.22	0.14
Sulfide	<0.01	<0.01
Organic	1.65	1.54
Mineral Analysis, wt %		
Phos. pentoxide, P_2O_5	0.07	0.08
Silica, SiO_2	52.49	53.96
Ferric Oxide, Fe_2O_3	18.37	18.07
Alumina, Al_2O_3	19.34	18.88
Titania, TiO_2	2.07	1.07
Lime, CaO	1.85	1.83
Magnesia, MgO	0.83	0.80
Sulfur Trioxide, SO_3	2.05	1.09
Potassium Oxide, K_2O	1.68	1.88
Sodium Oxide, Na_2O	0.52	1.90
Undetermined	0.73	0.44

Table B.2 (continued)

Feed Coal Analyses

Coal Date Run	Ky 6 and 11 3-5 Nov 1978 151 MB	Ky 9 9-11 Mar 1979 159 MB	Ky 9 25-26 Mar 1979 160 MB
Proximate Analysis, wt %			
Moisture	1.33	1.11	1.02
Ash	9.24	11.18	10.40
Volatile Matter	34.20	31.00	29.74
Fixed Carbon	55.23	56.71	58.84
Ultimate Analysis, wt %			
Carbon	72.57	71.95	71.65
Hydrogen	5.23	4.78	5.10
Nitrogen	1.54	1.50	1.46
Chlorine		0.28	0.20
Sulfur	2.81	2.79	3.61
Ash	9.26	12.10	10.51
Oxygen (by difference)	8.59	6.60	7.47
Dry Heating Value, Btu/lb	13,161	13,106	12,976
Sulfur Forms, wt %			
Pyritic	1.12	1.32	1.11
Sulfate	0.14	0.03	0.04
Sulfide	<0.01	<0.01	0.03
Organic	1.54	1.45	2.43
Mineral Analysis, wt %			
Phos. pentoxide, P_2O_5	0.08	0.13	0.16
Silica, SiO_2	53.96	49.68	55.90
Ferric Oxide, Fe_2O_3	18.07	18.93	13.26
Alumina, Al_2O_3	18.88	22.46	20.93
Titania, TiO_2	1.07	1.25	1.56
Lime, CaO	1.83	1.64	1.97
Magnesia, MgO	0.80	0.85	0.98
Sulfur Trioxide, SO_3	1.09	0.95	1.55
Potassium Oxide, K_2O	1.88	1.87	2.37
Sodium Oxide, Na_2O	1.90	0.69	0.37
Undetermined	0.44	1.55	0.95

Table B.2 (continued)

Coal Date Run	Feed Coal Analyses Kentucky 9 25-26 March 160 MB	Kentucky 9 9-10 April 161 MB	Kentucky 9 26-27 April 162 MB	Kentucky 9 11-12 May 163 MB	Kentucky 9 4-5 June 164 MB
Proximate Analysis, wt %					
Moisture	1.02	0.84	0.24	0.84	0.92
Ash	10.51	12.60	13.44	12.90	8.77
Volatile Matter	29.74	27.83	29.56	28.11	27.33
Fixed Carbon	58.73	58.73	56.76	58.15	62.98
Ultimate Analysis, wt %					
Carbon	71.65	70.16	68.70	69.60	72.66
Hydrogen	5.10	4.67	4.54	4.80	4.91
Nitrogen	1.46	1.67	1.45	0.88	0.95
Chlorine	0.20	0.45	0.28	0.28	0.26
Sulfur	3.61	2.86	3.27	3.30	2.88
Ash	10.51	12.60	13.4	12.9	8.77
Oxygen (by difference)	7.47	7.59	8.36	8.24	9.57
Dry Heating Value, Btu/lb	12,976	12,530	12,677	13,930	13,665
Sulfur Forms, wt %					
Pyritic	1.11	1.39	1.17	1.58	1.11
Sulfate	0.04	0.03	0.02	<0.01	0.14
Sulfide	0.03	0.02	0.01	<0.01	0.02
Organic	2.43	1.51	2.07	1.72	1.61
Mineral Analysis, wt %					
Phos. pentoxide, P_2O_5	0.16	0.14	0.14	0.15	0.08
Silica, SiO_2	55.90	54.42	50.66	54.13	53.54
Ferric Oxide, Fe_2O_3	13.26	17.65	18.75	18.18	18.06
Alumina, Al_2O_3	20.93	19.79	20.57	19.03	21.43
Titania, TiO_2	1.56	1.12	1.05	1.03	0.90
Lime, CaO	1.97	1.86	1.57	1.62	0.92
Magnesia, MgO	0.98	1.21	1.08	1.23	0.80
Sulfur Trioxide, SO_3	1.59	0.47	0.52	0.99	0.57
Potassium Oxide, K_2O	2.37	2.66	4.89	3.01	2.80
Sodium Oxide, Na_2O	0.37	0.51	0.49	0.35	0.46
Undetermined	0.91	0.17	0.28	0.28	0.44

Table B.2 (continued)

Feed Coal Analyses
Kentucky 9, Lafayette Mine Coal

Date Run	21 July 166A-B MB	2-3 August 166A-C MB	9 September 167C MB	12 September 168A MB
Proximate Analysis, wt %				
Moisture	0.61	0.99	1.77	0.65
Ash	8.50	8.38	8.65	8.84
Volatile Matter	32.27	32.79	31.92	38.40
Fixed Carbon	58.62	57.84	57.66	52.11
Ultimate Analysis, wt %				
Carbon	72.01	73.26	73.11	73.44
Hydrogen	4.66	4.86	4.83	4.77
Nitrogen	0.86	0.93	1.25	0.92
Chlorine	0.27	0.19	0.22	0.18
Sulfur	3.07	2.88	2.81	3.11
Ash	8.55	8.46	8.80	8.90
Oxygen (by difference)	10.58	9.42	8.98	8.68
Dry Heating Value, Btu/lb	13,168	13,314	13,402	13,418
Sulfur Forms, wt %				
Pyritic	0.85	0.76	0.75	1.15
Sulfate	0.20	0.12	0.09	0.04
Sulfide	<0.01	0.09	0.01	<0.01
Organic	2.02	1.91	1.96	1.92
Mineral Analysis, wt %				
Phos. pentoxide, P_2O_5	0.08	0.05	0.07	0.06
Silica, SiO_2	57.01	54.52	56.24	54.51
Ferric Oxide, Fe_2O_3	15.04	16.96	17.10	18.41
Alumina, Al_2O_3	20.70	20.25	19.51	11.96
Titania, TiO_2	1.48	1.44	1.04	1.15
Lime, CaO	0.76	0.84	0.95	0.90
Magnesia, MgO	0.66	0.73	0.78	0.79
Sulfur Trioxide, SO_3	0.37	0.22	0.37	0.94
Potassium Oxide, K_2O	2.69	2.11	2.31	3.20
Sodium Oxide, Na_2O	0.39	0.44	0.28	0.35
Undetermined	0.82	2.44	1.35	7.73

Table B.3

Wilsonville SRC-I Preheater Operating Data for Runs during which no Coking Occurred

RUN NO. & DATE	TYPE & MINE	** COAL PROPERTIES ** VOLATILE FRACTION	HETEROATOM CONTENT(WGT%) OXYGEN	SULFUR	NITROGEN	MINERAL CONTENT(WGT%) SODIUM OXIDE	POTASSIUM OXIDE	CHLORIDE
135 4/8 TO 4/10/78	IND 5	38.65	13.30	3.72	1.16	0.14	2.56	.00
136 5/3 TO 5/5/78	IND 5	33.60	10.45	3.39	1.57	0.43	2.37	.00
140 6/22 TO 6/24/78	IND 5	32.11	12.48	3.74	1.14	0.32	1.90	.00
140 7/1 TO 7/3/78	IND 5	33.10	13.11	3.36	1.18	0.41	1.94	.00
143 8/20 TO 8/22/78	IND 5	36.00	10.78	3.58	1.22	0.63	1.36	.00
147 9/7 TO 9/9/78	IND 5	34.70	12.95	3.73	1.15	0.43	1.61	.00
159 3/9 TO 3/11/79	KEN#9	31.40	6.60	2.79	1.50	0.69	1.87	.28
160 3/25 TO 3/26/79	KEN#9 PYRC	29.74	7.47	3.61	1.46	0.37	2.37	.20
161 4/9 TO 4/10/79	KEN#9 PYRO	28.10	7.59	2.86	1.67	0.51	2.66	.45
162 4/26 TO 4/27/79	KEN#9 PYRC	29.60	8.36	3.27	1.45	0.49	4.89	.28
163 5/11 TO 5/12/79	KEN#9 PYROLAF	28.30	8.24	3.30	0.88	0.35	3.01	.28
167 9/9/79	KEN#9 LAF	31.90	8.98	2.81	1.25	0.28	2.31	.22

Note: A value of zero indicates missing data.

Table B.3 (continued)

RUN NO. & DATE	COAL FEED LB/HR	SOLVENT FEED LB/HR	GAS FEED LB/HR	SLURRY % COAL	INLET PRESS. (PSIA)	PH2 IN (PSIA)	PH2 OUT (PSIA)	TEMP. IN (F)	TEMP. OUT (F)
			** PREHEATER OPERATING CONDITIONS **						
135 4/8 TO 4/10/78	431.0	718.3	126.4	37.50	2445.	2032.5	1805.0	135.0	776.0
136 5/3 TO 5/5/78	460.0	713.5	138.0	39.20	2255.	1932.5	1705.0	120.0	768.0
140 6/22 TO 6/24/78	456.0	763.3	138.0	37.40	2458.	2102.5	1825.0	130.0	763.0
140 7/1 TO 7/3/78	436.0	758.5	138.7	36.50	2459.	2132.5	1835.0	144.0	753.0
143 8/20 TO 8/22/78	468.0	757.1	145.8	38.20	1818.	1592.7	1375.0	140.0	762.0
147 9/7 TO 9/9/78	447.0	729.3	140.4	38.00	1802.	1552.7	1365.0	140.0	766.0
159 3/9 TO 3/11/79	440.0	749.2	108.9	37.00	1714.	1427.7	1240.0	122.0	802.0
160 3/25 TO 3/26/79	488.5	814.2	135.5	37.80	1748.	1430.0	1307.0	120.0	782.0
161 4/9 TO 4/10/79	498.0	795.5	133.3	38.50	1795.	1834.0	1674.0	130.0	796.0
162 4/26 TO 4/27/79	494.0	792.5	137.2	38.40	2168.	1834.0	1674.0	133.0	776.0
163 5/11 TO 5/12/79	498.0	788.8	62.0	38.70	1749.	1436.0	1252.0	126.0	848.0
167 9/9/79	479.0	772.0	143.0	38.30	2190.	1840.0	0.0	142.0	782.0

Table B.3 (continued)

RUN NO. & DATE	QUALITY (SHORT)	** SOLVENT PROPERTIES ** BOILING POINT FRACTIONS (WGT%) IBP	<450F	<550F	<650F	>650F	EP
135 4/8 TO 4/10/78	76.0	405.0	6.0	41.0	28.0	25.0	893.0
136 5/3 TO 5/5/78	77.4	401.0	5.0	37.0	23.0	35.0	937.0
140 6/22 TO 6/24/78	75.2	460.0	0.0	45.0	37.0	18.0	813.0
140 7/1 TO 7/3/78	77.9	424.0	1.0	52.0	30.0	17.0	815.0
143 8/20 TO 8/22/78	77.0	376.0	7.0	55.0	25.0	13.0	789.0
147 9/7 TO 9/9/78	74.6	400.0	5.0	48.0	26.0	21.0	814.0
159 3/9 TO 3/11/79	71.0	433.0	1.7	37.0	37.8	23.5	859.0
160 3/25 TO 3/26/79	73.6	405.0	3.4	25.0	29.8	41.8	918.0
161 4/9 TO 4/10/79	71.9	405.0	4.1	30.7	29.1	36.1	937.0
162 4/26 TO 4/27/79	74.7	401.0	8.2	37.2	27.5	27.2	909.0
163 5/11 TO 5/12/79	67.9	383.0	6.3	35.8	27.2	26.7	892.0
167 9/9/79	66.4	394.0	5.3	45.1	25.1	24.5	891.0

Table B.3 (continued)

PREHEATER TEMPERATURE PROFILES

RUN NO. & DATE	TEMPERATURE (SKIN,BULK,DELTAT;ALL IN DEG.F) TURN7	TURN15	TURN19	TURN23	TURN27	TURN31	TURN33	TURN35
135	415.0	595.0	640.0	640.0	722.0	722.0	736.0	781.0
4/8 TO 4/10/78	373.0	515.0	556.0	511.0	608.0	703.0	686.0	733.0
	45.0	80.0	84.0	129.0	114.0	19.0	50.0	48.0
136	415.0	576.0	612.0	632.0	721.0	713.0	734.0	783.0
5/3 TO 5/5/78	361.0	476.0	545.0	505.0	595.0	694.0	681.0	726.0
	55.0	91.0	67.0	127.0	126.0	19.0	53.0	57.0
140	0.0	0.0	604.0	632.0	656.0	716.0	738.0	767.0
6/22 TO 6/24/78	326.0	487.0	546.0	531.0	592.0	700.0	700.0	723.0
	0.0	0.0	58.0	101.0	64.0	16.0	38.0	44.0
140	0.0	0.0	624.0	647.0	719.0	723.0	752.0	773.0
7/1 TO 7/3/78	345.0	508.0	563.0	545.0	597.0	708.0	707.0	725.0
	0.0	0.0	61.0	102.0	122.0	15.0	50.0	48.0
143	390.0	543.0	598.0	630.0	692.0	713.0	730.0	769.0
8/20 TO 8/22/78	340.0	505.0	541.0	515.0	588.0	696.0	691.0	710.0
	50.0	38.0	57.0	115.0	104.0	17.0	39.0	59.0
147	390.0	542.0	598.0	626.0	688.0	711.0	729.0	767.0
9/7 TO 9/9/78	350.0	513.0	540.0	514.0	586.0	693.0	683.0	702.0
	43.0	29.0	58.0	112.0	102.0	18.0	46.0	65.0
159	400.0	606.0	674.0	674.0	723.0	743.0	762.0	782.0
3/9 TO 3/11/79	360.0	524.0	584.0	543.0	651.0	723.0	703.0	701.0
	40.0	82.0	90.0	131.0	72.0	20.0	59.0	81.0
160	400.0	606.0	674.0	674.0	723.0	743.0	762.0	782.0
3/25 TO 3/26/79	360.0	52.0	584.0	543.0	651.0	723.0	703.0	701.0
	40.0	82.0	90.0	131.0	72.0	20.0	59.0	81.0
161	421.0	579.0	626.0	648.0	702.0	730.0	758.0	806.0
4/9 TO 4/10/79	385.0	512.0	564.0	521.0	620.0	710.0	712.0	711.0
	36.0	67.0	62.0	127.0	82.0	20.0	46.0	95.0
162	420.0	584.0	639.0	655.0	695.0	723.0	745.0	786.0
4/26 TO 4/27/79	348.0	530.0	572.0	532.0	615.0	703.0	702.0	703.0
	22.0	54.0	67.0	123.0	80.0	20.0	43.0	83.0
163	511.0	695.0	723.0	757.0	807.0	807.0	838.0	870.0
5/11 TO 5/12/79	446.0	609.0	672.0	709.0	666.0	767.0	771.0	791.0
	65.0	86.0	51.0	48.0	141.0	40.0	67.0	79.0
167	359.0	523.0	630.0	683.0	682.0	738.0	763.0	790.0
9/9/79	343.0	477.0	553.0	597.0	604.0	708.0	735.0	765.0
	16.0	46.0	77.0	86.0	58.0	30.0	28.0	25.0

APPENDIX C

LIST OF SYMBOLS

LIST OF SYMBOLS

a	-	Exponent
A	-	Flow Cross-Sectional Area, ft^2
b	-	Exponent
BS	-	Benzene Soluble Matter
c	-	Exponent
C	-	Coefficient for Computing ψ
C_c	-	Concentration of Key Coking Precursors
C_c^s	-	Solubility Limit of Key Coking Precursors
d	-	Exponent
D	-	Inside Pipe Diameter, ft
E	-	Apparent Activation Energy
f_a	-	Fraction of a Mixture Which is Aromatics
f_c	-	Weight fraction of coal in Coal-Oil Slurry
Fr	-	Froude Number, V^2/gD
g	-	Gravitational Acceleration
G	-	Mass Velocity, lb_m/ft^2 sec
$H_L(0)$	-	Horizontal Liquid Holdup
$H_L(\theta)$	-	Liquid Holdup at an angle
k	-	Proportionality Constant
N_{LV}	-	Liquid Velocity Number, $(Q_L/A_p)(\rho_L/g\tau)^{0.25}$
P_{H_2}	-	Partial Pressure of Hydrogen, psia
$\Delta P/\Delta L$	-	Pressure Drop per Unit Length of Pipe
Q	-	Volumetric Flow Rate, ft^3/min
Q_s	-	Solvent Quality Index (Short)
R	-	Liquid Holdup

Re_{LS} - Liquid Slug Reynolds Number

Re - Reynolds Number, $\rho VD/\mu$

RC - Residual Coke

T - Temperature

T_s - Preheater Coil Skin Temperature, ^oR

V - Velocity, ft/sec

V_b - Bubble Velocity

V_c - Preheater Coil Volume, ft^3

VM - Volatile Matter Content

w - Weight Fraction Associated with Coal

W_s - Slurry Mass Flow Rate, lb_m/min

X - Lockhart and Martinelli Holdup Correlation Flow Modulus

X_g - Gas Quality

y - Volume Fraction of a Phase in Two-Phase Flow that would exist if there were no Slip between the Phases

Greek Symbols

α - Fraction of Benzene Insolubles which are also Insoluble in Quinoline

β - Fraction of Benzene Insolubles which are soluble in Quinoline

γ - Fraction which is Soluble in Benzene

λ - Input Liquid Volumetric Fraction

μ - Viscosity, $lb_m/ft\ sec$

ϕ - Function of X Utilized in Calculating Two-Phase Flow Pressure Drop

ψ - Inclination Correction Factor

θ - Angle of Inclination

$\bar{\Theta}$ - Mean Slurry Residence Time, minutes

ρ - Density, lb_m/ft^3

τ - Liquid Surface Tension

General Subscripts

BB - Indicates Beggs and Brill Holdup Correlation

G - Gas

L - Liquid

LM - Indicates Lockhart and Martinelle Correlation

n - Nitrogen

o - Oxygen

p - Pipe

PC - Indicates Residence Time to the Point of Coking

s - Sulfur

tp - Two-Phase Flow

tt - Turbulent Liquid, Turbulent Gas

tv - Turbulent Liquid, Viscous Gas

v - Vitrinite

vt - Viscous Liquid, Turbulent Gas

vv - Viscous Liquid, Viscous Gas

VITA

Richard E. Edwards, Jr. was born in Wilmington, Delaware on May 24,1957. He attended elementary school in that city until the age of ten, after which time he resided in Waverly, Tennessee until he graduated from Waverly Central High School in June of 1975. The following September he entered the Georgia Institute of Technology, where he participated in the co-operative plan under the employment of E.I.DuPont in Aiken, South Carolina. In June of 1980 he received the Bachelor of Chemical Engineering degree from Georgia Tech. He was subsequently employed by E.I.DuPont in New Johnsonville, Tennessee during the summer of 1980, and in September of that year he married Nancy V. Busbee of Aiken, South Carolina. In late September of 1980 he enrolled in the chemical engineering graduate program at The University of Tennessee, Knoxville. While attending this university he co-authored a report entitled "Evaluation and Analysis of Coke Formation and Deposition in Coal Liquefaction Process Equipment" in a project funded by Oak Ridge National Laboratory through the Department of Energy. He shall receive the Master of Science degree in Chemical Engineering in August of 1982.