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I am submitting herewith a thesis written by Ahsan Ahmad Faruqi entitled "Heteroatom (Sulfur, Nitrogen and Oxygen) Removal from Liquids-Derived from Coal." I 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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HETEROATOM (SULFUR, NITROGEN AND OXYGEN)
REMOVAL FROM LIQUIDS-DERIVED FROM COAL

A Thesis

Presented for the

Master of Science

Degree

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DEDICATION

This thesis is dedicated to my parents Dr. and Mrs. Aulad A. Faruqi, wife Sabiha Faruqi and to my advisor Dr. George C. Frazier of the University of Tennessee-Knoxville, for their helpful comments and suggestions and patient encouragement in all aspects of my graduate work.

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ABSTRACT

Coal-derived liquids require extensive chemical processing in order to produce clean motor fuels and heating oils, which will meet both user and air quality standards. Although the processing technology required to produce such fuels, hydrotreating, hydrocracking and reforming, is standard in the petroleum industry, its utility and applicability to the task of upgrading coal-derived liquids is now only being investigated. This study was therefore conducted in order to consolidate and evaluate the available data in an attempt to assess the current state of the art in this important and newly developing area.

To completely cover all the work done on upgrading coal-derived liquids a comprehensive literature search on the Oak Ridge National Laboratory computer was run. A total of 1679 references were obtained which were thoroughly screened and the references not related were discarded. The main source of data apart from the open literature was the U.S. Department of Energy, Fossil Energy reports of the work conducted under government sponsorship.

Some of the important findings and conclusion after an extensive literature search are as follows:

- Coal-derived liquid distillate products have been hydrotreated, hydrocracked and reformed on commercial catalysts and generally show promise of potential for processing to clean fuels and heating oils.

- The hydroprocessing data are still limited but a few correlations and kinetic models have been developed which relate processing conditions to product properties. In particular, the temperature, pressure, and liquid hourly space velocity relationship to the change in API gravity. Also the heteroatom (sulfur, nitrogen and oxygen) removal correlation with the hydrogen consumption.
- The initial indications are that coal liquids derived from different bituminous coals by different processes may respond to hydroprocessing in similar ways. That is it may be possible to develop a single correlation which will be able to predict the processing results of liquids from different sources. However, additional work, both experimental and analytical, will be required to confirm and quantify the expectation.

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1. INTRODUCTION

At a time when United States is importing more than 40 percent of its crude oil (Braunstein, 1977), and nuclear energy seems to be in trouble (Marshall, 1980), for example, coal appears to be a very logical replacement to fill in the energy "vacuum." However, there are certain problems, both technical and economical associated with the increased use of coal as an energy source in this country. It is the object of this work to review the state of the art in one technological problem area: that is, the technology available, or lack of it, for upgrading liquid fuels derived from coal with respect to their sulfur content.

Coal supplied more than 90 percent of the total energy consumption of United States during the first decade of this century (National Energy Plan II, May 1979). During 1920's petroleum started replacing coal, primarily because of its cost, availability, and ease of handling (Pumpability). By 1950, the U.S. economy was based more on petroleum than coal (Nelson, 1969). The change over from coal to petroleum somewhat restrained the environmental pollution problems, which were beginning to surface on large scale (see page 4) during that time and are more associated with coal than with oil.

Coal and petroleum both contain some quantities of sulfur and nitrogen as an integral part of their molecular structure. When these fuels are burned, these elements sulfur and nitrogen, called heteroatoms, form sulfur oxides and nitrogen oxides. These compounds are poisonous and even in small quantities they are harmful to human health (episodes, as discussed later in this section). Coal contains larger quantities

of these heteroatoms (Table 1.1.1) particularly sulfur than petroleum, so the problem of environmental pollution is more acute with coal than petroleum.

Air pollution by sulfur oxides (and nitrogen oxides), as well as particulates has been of increased and growing concern. Since it has been linked with the human health problems, and in some instances it has even caused deaths (Stern et al., 1973). For example, nine major episodes resulted in human deaths (Stern et al., 1973); minor episodes were probably never reported. Most of the episodes occurred in cities, where too many people and too much industry concentrated in too small an area was probably the main cause.

No single pollutant or group of pollutants responsible for these episodes has been isolated, although sulfur dioxide and particulate matter are most suspect (Stern et al., 1973). Some of the more significant of these events are summarized in Table 1.1.2 in order to show the magnitude of the problem, and to emphasize the need for increased activity in research for methods to control these serious problems.

Two of the major episodes occurred in London, England, and in Donora, Pennsylvania. The London, England episode of December 1952 (Stern et al., 1973), which was responsible of 4000 deaths; and thousands more seriously ill, was thought to have resulted primarily from home heating emissions of coal and wood burning. Sulfur dioxide was suspected to be one of the major pollutants but its concentration did not exceed 1.34 ppm daily average (Stern et al., 1973).

The infamous Donora, Pennsylvania episode during October 1948 which caused 20 deaths and 5910 people ailing (Stern et al., 1973) occurred

Table 1.1.1 Ultimate Analyses of Selected Coal, Coal
Derived Liquids and Petroleum

Elements	Coal weight percent (a)	Coal Liquid weight percent (b)	Petroleum weight percent (c)
Sulfur	0.5 - 7.4	1.6 - 2.0	0.03 - 1.4
Nitrogen	0.47- 1.6	1.1 - 1.47	0.54 - 1.14
Oxygen	3.1 -29.9	4.0 - 6.4	1.0 - 2.5
Hydrogen	2.6 - 5.7	6.2 - 6.7	11.0 -14.2
Carbon	63.3-91.2	84 - 87	83.0 -86.5
Ash	6.0 -20.0	2.0 - 6.0	0.5 - 1.2
H/C	0.7 - 0.9	1.2 - 1.7	1.6 - 1.9

Source: a. Braunstein, H.M. et al, 1977
b. Crynes, B.L. "Chemical reactions as a means of separation, sulfur removal." 1977
c. Nelson, W.L. 1969

Table 1.1.2 Major Air Pollution Episodes

Location	Date	Remark
Meuse Valley	Dec. 1930	6000 ill; 60 deaths; 5 previous episodes
Donora, Pennsylvania	Oct. 1948	5910 ill; 20 deaths; 1 previous episode
Poza Rica, Mexico	Nov. 1950	320 ill; 22 deaths; industrial accident
London, England	Dec. 1952	Unknown number ill; 4000 deaths; 6 previous episodes and 9 subsequent episodes
New York, New York	Nov. 1953	Unknown number ill; 165 deaths; 3 subsequent episodes
New Orleans, Louisiana	Oct. 1953	200 ill; 2 deaths; subsequent episodes
Yokohama, Japan	Dec. 1956	Many ill; patients recovered when removed from area.
World wide episode	Nov. 1962	At least 1000 deaths
Eastern United States seaboard	Nov. 1966	Many ill; data incomplete

Source: Stern, A.C, et al., 1973

due to valley trapping of industrial pollution.

In order to avoid future episodes the Government of the United States formulated the Environmental Protection Agency (EPA) in 1970, and to keep the environment clean several acts dealing with environmental maintenance were legislated. A list of these Acts is given in Table 1.1.3. As a result of these Acts the maximum EPA allowable limit on pollutants is steadily decreasing. A typical example of this trend is the air emission standards for motor vehicles (Table 1.1.4). The emission levels allowed for three major pollutants, hydrocarbon, carbon monoxide and nitrogen oxide in grams per mile travelled by an automobile decreased from 1970 values of 2.2, 23 and 4.0 respectively to 1977 values of 0.41, 3.4 and 0.4 respectively.

In addition to these requirements tighter restrictions on emissions forced oil companies to produce cleaner fuels, which resulted in development of new technological processes for treating crude oils. Hydrotreating, hydrodesulfurization and hydrodenitrogenation are some of the processes developed to decrease the concentrations of pollutants in the product. One of the major operational difficulties in these processes is that of catalyst poisoning, which seems to increase with increased concentration of sulfur and particulates in the feed stream. This problem in some instances is overcome by using fixed bed reactors in parallel to facilitate simultaneous regeneration of catalyst while keeping some of the reactors in operation. Fluidized bed catalytic reactors were also developed which permit continuous removal of catalyst from reactor for regeneration.

All of these technologies developed help in maximizing the output

Table 1.1.3 Environmental Maintenance Acts

1970	Clean Air Act
1972	Federal Water Pollution Control Act Amendments
1974	Safe Drinking Water Act
1976	Toxic Substance Control Act
1976	Resource Conservation and Recovery Act
1977	Endangered Species Act
1977	Surface Mining Reclamation Act
	Federal Mine Safety and Health Act
	Occupational Safety and Health Act
	Coastal Zone Management Act
	National Parks and Recreation Act
	Noise Control Act
	Nuclear Non-Proliferation Act
	Federal Environmental Pesticide Control Act
	National Energy Act

Source: Stern, A.C et al., 1973

Table 1.1.4 Chronology of Standards for Air Emissions from Motor Vehicles

Year	Standard	Emission level (g/mile unless specified otherwise)			
		Hc	CO	NO _x	
Prior to controls	-				4 - 6
1966	California	11 (850 ppm)	80 (3.4 %)		None
1968 ^a	California and United States	275 ppm	1.5 %		
		410 ppm	2.3 %		None
		350 ppm	2.0 %		None
		275 ppm	1.5 %		None
1970	California and United States				
1971	California	2.2	23		None
1972	United States ^b	2.2	23		4.0
	California - old or New	3.4	39		None
	United States	1.5	23		3.0
1973	California	3.2	39		3.2
	United States	3.4	39		3.0
1974	California	3.2	39		3.0
1975	United States	1.5	15		2.0
	California	0.9	9.0		3.0
1977	United States ^c	0.41	3.4		2.0
					0.4

Table 1.1.4 (continued)

- a 1968-1969 standards varied with engine size. The figures given are for 50-100 101-140, and 140 cubic inch displacement respectively.
- b Based on a new test driving cycle used continuously after 1972.
- c This represents a 90 percent reduction from 1970 levels for Hc and CO and the California 1971 standard for NO_x. However, in March 1975, EPA recommended freezing 1975 United States standards on Hc and CO through 1979, adopting 1975 California standards nationwide in 1980 and 1981, and postponing 1977 United States standards to 1982. EPA also recommended a nationwide standard of 2.0 g/mile NO_x for 1977.

of the most desirable products, usually the lighter fuels, from each barrel of crude oil processed. It is very helpful at a time when crude oil prices are increasing very rapidly.

After the 1973 oil embargo our dependence on imported oils became apparent to the general public and to Congress, as well as to the technologists. Combined with the decreasing oil reserves (Figure 1.1.1) and the increasing energy demand the need for replacement of oil has become imperative. Due to the ever growing opposition to nuclear energy coal appears to be the only alternative for oil at least in the near to medium range future.

Because of high demand for lighter liquid fuels, coal has to be converted into liquid form, but due to high ash content and low hydrogen to carbon ratios (Table 1.1.1) the yield of oil from coal is only 0.5 to 4.4 bbl of liquid product per ton of coal (Braunstein, et al., 1977), depending upon the process, which signifies the need for handling large quantities of coal for an industrial scale plant.

Coal contains all the problem producing components found in oil, like sulfur, nitrogen and particulates, but in larger quantities (Table 1.1.1). Upon liquefaction these components are transferred in part to coal liquids and create difficulties in coal liquid processing by the conventional methods. Some of the major problems in coal conversion to liquid fuels are as follows:

a) High Hetroatom Content

High sulfur and nitrogen content of coal (Table 1.1.1) poisons catalysts as well as creates severe corrosion and emission problems.

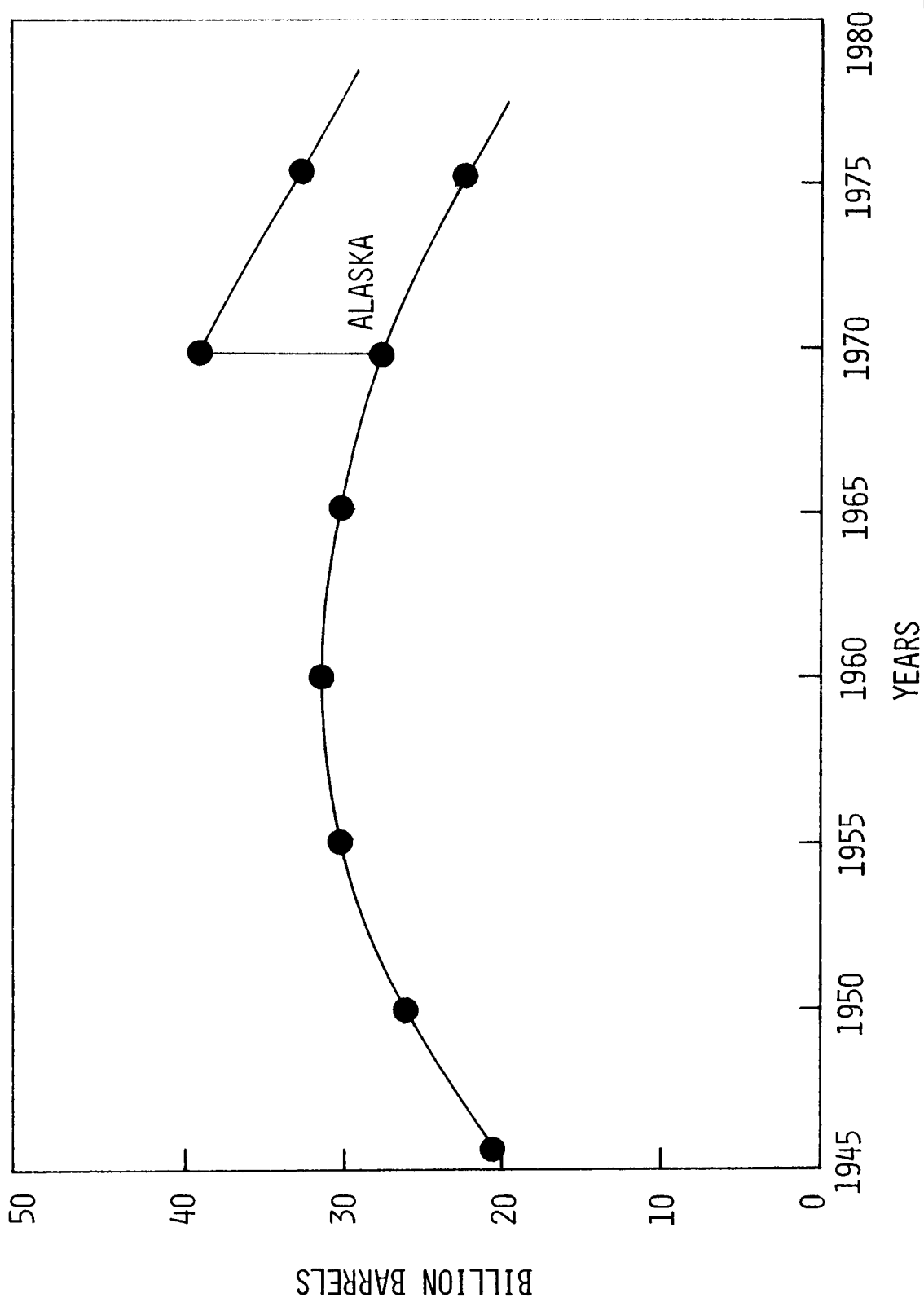


FIGURE 1.1.1 U.S. Oil Reserves (National Energy Plan II, 1977)

Also, requires "high severity" processing conditions, i.e., high temperature and pressure. High oxygen content in coal makes processing more expensive as it consumes hydrogen during coal liquids upgrading.

b) High Ash Content

Large quantities of ash present in coal (Table 1.1.1) poisons the catalyst and creates severe erosion problems during processing.

c) Low Hydrogen to Carbon Ratio

The hydrogen to carbon ratio is in the range of about 0.7-0.9 for coal as compared to 1.6-1.9 for petroleum crudes. This necessitates the need to introduce large quantities of hydrogen in coal processing to produce comparable products, which makes coal processing very expensive.

In addition to these major problems there are some physical problems which contribute to elevate the cost of the final products to such a high level that the coal processing becomes uneconomical. Material handling, waste disposal, stack gas emission and corrosive nature of coal are some of those problems.

In spite of all the problems with coal, the feasibility of the conversion of coal into liquid and gases fuels has been demonstrated on pilot plant scale (Peters, 1977a). Attempts are being made to utilize the existing treating technology, such as hydrodesulfurization, hydrodenitrogenation, etc., which were developed originally for petroleum, to clean liquids (Peters, 1977a; Berg, et al, 1977d, etc). One major problem faced in most of the coal liquid processing is the catalyst deactivation or poisoning and some of the factors for catalyst poisoning are as follows:

a) Coke Deposition

A layer of coke formed over the catalyst pellets deactivated the catalyst, this problem was more severe with the coal liquids than the petroleum crudes due to its lower hydrogen to carbon ratio.

b) Metal and Particulate Deposition

Vanadium and nickel along with other trace metal elements poison the processing catalyst.

c) Nitrogen and Sulfur

Higher concentrations of nitrogen and sulfur seems to deactivate the catalyst.

d) Acid-Base Characteristic of Coal Liquids

The dual acid and base nature of coal liquids can deactivate either acidic or basic catalyst support.

Considerable research and development on coal liquids and their processing to clean fuels is in progress due to the anticipated shortage of petroleum crudes, the increasing cost of petroleum crudes, and the pressure from the Environmental Protection Agency in order to develop economically feasible processes for converting coal liquids to marketable clean fuel products.

This study is considered in order to identify and scope the state of the art, especially in the area of hydrodesulfurization, and to some extent in hydrotreating and hydrocracking of coal liquids, and to identify those additional areas requiring further research and development in this increasingly important technological area. A comprehensive survey of the research results obtained under varied operating conditions, using different catalysts, will point out the

parameters which have not been explored for a particular coal liquid. This will identify the parameters for future experimental studies of coal liquid processing to cleaner fuels.

2. BACKGROUND

The United States Geological survey and the U.S. Bureau of Mines report that the U.S. coal resource base is about 3 trillion tons, or about 80 percent of the total fossil reserves of the country (Braunstein et al., 1977). However, limited past experience with uncontrolled emissions during 1940's indicates a pressing need to examine the possible health and environmental consequences of large-scale industrial applications of coal and coal conversion technologies.

2.1 COAL

During the first half of this century, coal was the predominant fuel in the United States. In the late 1940's however, its dominance began to erode as consumers shifted to cleaner, more convenient, and frequently cheaper energy forms, primarily oil and gas. Figure 2.1.1 shows how the use of coal changed both as a fraction of total energy use and in absolute terms.

For many years, coal was a dominant fuel in all demand sectors, including transportation, in which it supplied the railroads, today its primary utilization is in one major market: utilities. In 1978, 78 percent of the coal used in U.S. was burned by electric utilities (National Energy Plan, 1979).

Even today, however, U.S. coal reserves are still hundreds of times greater than annual production levels, while domestic oil and natural gas use is limited by supply, coal consumption is limited

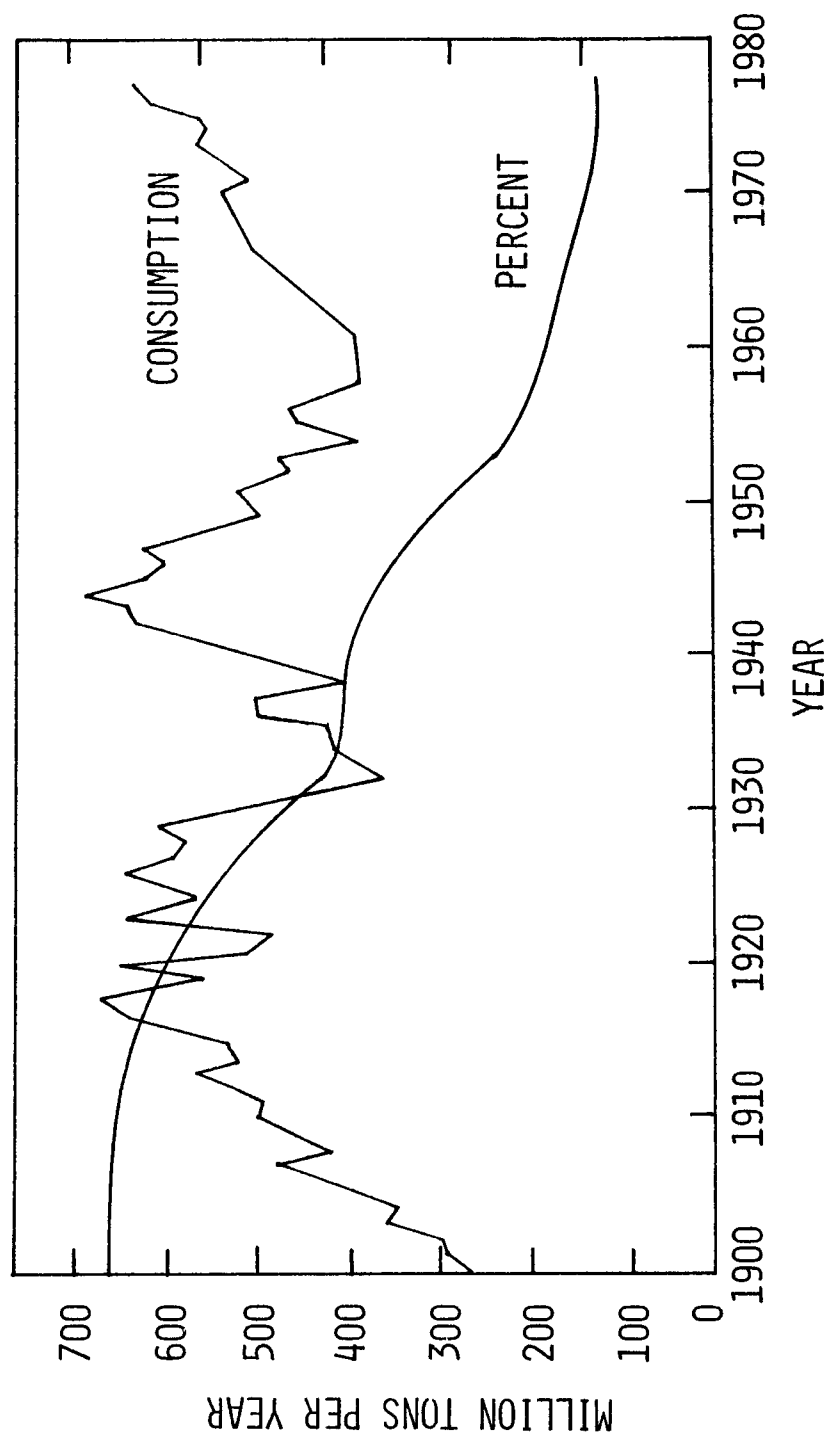


FIGURE 2.1.1.1 U.S. Coal Consumption as a Fraction of Total Energy Consumption
(National Energy Plan II, 1977)

primarily by constraints on demand. Even when the fuel cost economics favor coal, firms have been willing to pay sizable premiums for cleaner, more convenient fuels. Coal's environmental problems have been curbed by Federal and State actions dealing with air and water pollution, underground mine health and safety, and most recently, surface mining and reclamation. However, utilities and industry often find it easier to meet new air emission rules by switching to oil or gas, than by installing pollution control equipment on coal burners.

2.1.1. Environmental Problems of Coal Combustion

Compliance with environmental standards poses the greatest potential constraint on increased direct use of coal. Unless these standards can be met at competitive costs, many firms that might use coal will turn to other fuels instead. The EPA and other agencies are working to develop appropriate control strategies for complying with environmental regulations. The future of coal utilization depends in large measure on the success of these efforts.

Although coal utilization is effected by many environmental standards, air pollution is the major problem. Some of the water pollution and solid wastes problems effecting coal use arise from the techniques used to reduce air emissions from coal combustion.

Coal combustion emits a variety of air pollutants that may damage the environment and public health, including sulfur oxides, nitrogen oxides, particulates, hydrocarbons and carbon monoxide. Compliance with existing sulfur dioxide emission standards is the most expensive.

Closely related and possibly even more difficult to regulate and control are the sulfates formed from sulfur dioxide and particulate matter. Sulfates may have significant effects on human health and ecology. They can be transported several hundred miles in the atmosphere and "washed out" in the form of "acid rains," which adversely affect both plants, animal life and humans. Together, sulfur oxides and sulfates constitute the single most important constraint on direct and indirect coal use.

Nitrogen oxide emissions depend on the amount of nitrogen in coal, and the combustion conditions that can convert nitrogen in the air into nitrogen oxides. Coal generally contains more (Table 1.1.1) nitrogen than either oil or gas, aggravating the general fossil fuel problems. Special combustion techniques can reduce nitrogen oxide emissions slightly. But major new technologies, such as "post-combustion" controls are necessary to completely eliminate nitrogen oxide emissions from stationary sources, such as utilities and industrial plants.

A particulate emission can be effectively reduced with current technologies such as electrostatic precipitators. But current technologies are not as effective for the very small, respirable particulates most closely associated with health and visibility effects. These small particulates act as carriers for trace elements and hydrocarbons, many of which may be toxic or carcinogenic. Alternative controls, such as "bag houses," may be needed to reduce responsible particulate emissions. Such controls have not been used widely by utilities (National Energy Plan, 1979).

2.1.2 Emission Control Methods

Emissions from direct coal combustion can be controlled by applying technology before, during or after the combustion of coal.

Use of low sulfur coal or cleaning of higher sulfur coal, before the combustion, are two common ways to meet current emission standards of EPA, especially for older plants. No matter what the price of low sulfur coal may be, its use costs less than back-end (post-combustion) controls. The solvent refined coal (SRC-1) obtained by cleaning high sulfur coals, an ash free, hydrogenated solid coal product, contains very small fraction of sulfur and can very well be used without post-combustion controls.

Fluidized bed combustion (FBC) is another way to meet air pollution standards of EPA with high sulfur coals. The coal burns in a fluidized bed of coal and limestone. Sulfur dioxide is captured chemically by the limestone and discarded with the ash. Small industrial-scale FBC units are available now, research and development on large-scale utility system is in progress (National Energy Plan, 1979). In the near term, industrial FBC systems should provide energy at about the same cost as does the conventional combustion with flue gas desulfurization. Aside from their environmental advantages, FBC systems could also become more economical and efficient once they have been fully demonstrated and are being built in commercial quantities.

Back-end control systems, particularly flue gas desulfurization (FGD), are now being used to meet sulfur oxide emission standards. Acid gas removal, absorption and catalytic conversion of the flue gases

are some of the processes used to clean up the tail gases. New FGD systems to meet even more stringent standards are being developed.

2.2 COAL CONVERSION

The concept of coal conversion is simple. It involves primarily two basic steps: the cracking of heavy hydrocarbons into lighter ones and the enrichment of the resultant molecules with hydrogen.

Unlike the concept, the application of coal conversion is not simple. It involves the handling of enormous amounts of a highly variable material (upward of 25,000 tons of coal per day) often at high temperatures and pressures (1000°F and 3500 psi) ; it requires containment and control of both highly corrosive process material and those that pose a possible health threat; and it calls for treatment and disposal of a voluminous solid waste and a possible hazardous liquid or gaseous waste.

Nonetheless, coal conversion is a viable technology. Although it is currently practiced in the United States only on a small scale at pilot and demonstration plants, commercially applicable processes, capable of full exploitation of our coal resources, are being developed.

2.2.1 Coal Gasification

Coal can be converted to either a gas (gasification) or a liquid (liquefaction), either underground (in-situ gasification) or by mining the coal and transferring it to a conversion plant.

Converting coal into an environmentally acceptable gaseous fuel

requires nine basic and seven auxiliary steps; these steps include coal preparation and pretreatment, gasification, shift conversion, catalytic methanation, various clean up and disposal procedures, and final compression of the gaseous products into pipeline gas (Haynes and Forney, 1976).

Gasification of coal became a viable process in the early nineteenth century when gas was produced by the destructive distillation of coal in the absence of air. Gasification can be defined as any process for converting solid or liquid fuel to a gaseous product suitable for use as 1) direct source of energy or 2) a feed stock for the synthesis of chemicals, liquid fuels, or other gaseous fuels.

Although highly heterogeneous, a typical bituminous coal contains about 75 percent carbon, 5 percent hydrogen, and 20 percent less desirable constituents (i.e., primarily organic sulfur, pyritic sulfur, and ash). Because natural gas contains 75 percent carbon, 25 percent hydrogen, and only traces of undesirable constituents, converting coal to a usable natural gas substitute requires either the addition of a large amount of hydrogen or the rejection of large amount of carbon. It is most effective to add hydrogen (Linden, et al., 1976).

2.2.1.1 Low and Intermediate Btu Gas

Three ingredients are needed to synthesize gas chemically from coal-carbon, hydrogen and oxygen. Coal provides the carbon; steam most often provides the hydrogen (although hydrogen is sometimes introduced from an external source); and air provides the oxygen (unless oxygen

is needed in the pure form) (University of Oklahoma, 1975). The reactions involved are



Because reaction "3" is highly endothermic and will not occur unless sufficient heat is present (1900°F to 2500°F), some of the coal is usually reacted with oxygen or air to provide a heat source (Reaction "4"). If air is used as a combustor, the raw gas will have a low heating value (roughly 150 to 300 Btu/scf, depending upon design characteristics) and will contain undesirable constituents such as carbon dioxide, hydrogen sulfide, and nitrogen. The use of pure oxygen, although expensive, results in intermediate gas (300 to 400 Btu/scf) with carbon dioxide and hydrogen sulfide as by-product (National Academy of Engineering, 1974). Both carbon dioxide and hydrogen sulfide can be removed from cooled low or intermediate - Btu gas by any of the several available processes.

2.2.1.2 High Btu Gas

In 1965, the Office of Coal Research issued guide lines for coal gas, which may be substituted directly for, or intermingled with, natural gas. The gas should be pumped at 1000 psi and should have the

following desirable characteristics (Strakey, Forney, and Haynes, 1975);

- . Heating value greater than 900 Btu/scf
- . CO less than 0.1 percent
- . H_2S less than 0.25 grains/100 scf
- . Inerts less than 5 percent
- . CO_2 less than 3 percent, etc.

If a high Btu gas of "pipeline" quality (900 to 1000 Btu/scf) is desired, steps must be taken to increase the methane content of the gas. This enrichment requires hydrogen, which is produced by reaction of steam with carbon or carbon monoxide;



Reaction "5," the water-gas shift reaction, is performed to adjust the hydrogen-carbon monoxide ratio to 3:1, the required ratio for carrying out the methanation step (Reaction "6"). At high temperatures the reaction goes to equilibrium, probably catalyzed by ash and reactor surface at temperatures greater than about 1200°F, at lower temperatures the reaction is carried out over a catalyst (Schora, 1974).



Reaction "7" is a combination of reactions "5" and "6."

Normally, after the water-gas shift conversion, the carbon dioxide created during earlier steps and the sulfur pollutants are removed,

leaving a product gas containing only carbon monoxide and hydrogen in the proper ratio for catalytic methanation.

However, Moeller, Roberts, and Britz (1974) have suggested that a product of higher calorific value can be obtained if the synthesis gas contains, instead of a stoichiometric composition, a surplus of carbon dioxide that can be used to reduce the hydrogen content of less than 1 vol. percent by carbon dioxide methanation:



Where as Reaction "5" is only mildly exothermic (heat-producing) Reactions 6,7 and 8 are highly exothermic but are relatively slow, and catalyst are needed to accelerate the reactions to acceptable commercial rates.

The principal advantage of low or intermediate - Btu gasification processes is their lower initial cost. After gasification purification is required only before the synthetic gas is ready for use; no shift conversion is needed, and gas cleanup is relatively simple because no protection of a methanation catalyst is required. Purification of the product gas is less expensive than processes for purification of stack gases (National Academy of Engineering, 1974), However, the ratio of heating value-to-volume makes low and intermediate - Btu gas uneconomical for use in existing city gas system, residences, or present-day pipelines.

High-Btu gas, however, makes use of existing storage, transportation, and utilization facilities made available by the decline in

natural gas. By 1968 the natural gas pipeline system had grown to a total of 862,000 miles in the United States (Erickson and Sherman, 1975). High-Btu gas can be fed into this already existing network and delivered to the point of use without equipment modifications of any kind. Additionally, both industrial and residential consumers are equipped to use a product gas with a high heating value. No expensive retrofitting would be required. High Btu gas also shares with natural gas the advantage of being almost pollutant-free at the point of use.

The most obvious constraint to the development and use of high-Btu gasification facilities is the fact that catalytic methanation, the final processing operation that increases the heating value of the product gas to pipeline quality, is expensive and has not yet been fully proved on a commercial scale.

There are several gasification processes for commercial scale production of low-intermediate and high-Btu gases, Lurgi, Koppers-Totzek, Winkler, HYGAS, Synthane and Bi-Gas are some of them.

2.2.2 Coal Liquefaction

To decrease American dependence on imported crude oil and to conserve our dwindling national reserves increases the urgency for developing coal liquefaction processes. Although liquefaction implies a liquid product, processes considered as coal liquefaction can also give rise to a gaseous or solid product or, in some instances, only to a low melting solid fuel.

Coal is liquefied primarily by either pyrolysis or dissolution.

In pyrolysis, coal is heated in the absence of air to drive off volatile matter so that, in addition to liquid products, by-products gas and char are produced. In dissolution, ground coal is dissolved in a solvent (usually a recycle solvent), the ash is filtered out, and the oil is upgraded by hydrocracking. As with upgrading of gas from coal, coal liquids can be catalytically upgraded with hydrogen to produce a synthetic crude oil. Hydrogenation is needed because natural petroleum contains 11 to 15 percent hydrogen, 83 to 87 percent carbon and up to 4 percent oxygen, nitrogen and sulfur by weight, whereas coal contains only 5 percent hydrogen and 75 percent carbon.

Pyrolysis causes the thermal decomposition of coal by heating it in the absence of oxygen to drive off volatile matter. After separation into gaseous and liquid products, the gases are freed from unwanted substances (sulfur compounds, water, etc), and a usable gas is obtained in addition to the liquids. The gas and char may be used to produce hydrogen for hydrotreating the liquid reaction product to lower its sulfur content and to produce a high-Btu synthetic crude oil. Char may also be burned with air or oxygen to produce the necessary heat for pyrolysis. Because pyrolysis processes yeild low volumes of liquids and require an outlet for the char produced, pyrolysis methods will probably not be a major source of synthetic petroleum (Braunstein et al., 1977). Three current pyrolysis processes under study are the COED (Char Oil Energy Development of FMC Corporation), TOSCOAL (The Oil Shale Company), and Garrett processes (Garrett Research and Development Company, subsidiary of Occidental Petroleum Company).

Dissolution is a more severe method of liquefying coal than is the

pyrolysis method. The crushed or ground coal is dissolved in a selective solvent, the ash is filtered out, and the oil is treated by hydrocracking. Pyritic sulfur, together with the insoluble ash, is removed from the solvent by filtering; however, organic sulfur in the coal is carried along with the liquid fuels. After separation from the solids, the liquids can be catalytically up-graded to produce a synthetic crude oil. The char may be sold as fuel or used for process heat or generation of the hydrogen used in the process. Treatment with hydrogen with or without a catalyst, improves the product quality and removes the organic sulfur.

Three types of dissolution processes can be distinguished:

1) those that use no catalyst and no hydrogen, 2) those that use hydrogen but no catalyst, and 3) those that use both catalyst and hydrogen. A method using neither catalyst nor hydrogen currently under study is the Consol Synthetic Fuel (CSF) process of Consolidation Coal Company, a subsidiary of Continental Oil Company. The Solvent-Refined Coal (SRC) process of Pittsburgh and Midway Coal Company uses hydrogen, but no catalyst. Three processes using both catalyst and hydrogen that are currently under study are the Synthoil (U.S. Bureau of Mines), H-Coal (Hydrocarbon Research Inc.), and Catalytic Coal Liquids (CCL) (Gulf Research and Development) process.

2.2.3 Economic and Environmental Aspects of Coal Conversion

Economic and environmental issues help define the limits to employing coal conversion technology. They demonstrate that while

coal conversion is beginning to be economically competitive for some industries now, it is not an inexpensive energy solution. These issues also identify both the internal and external costs of coal conversion - costs that must be considered when evaluating non-petroleum energy options for industry.

Economic issues associated with coal conversion include the ability to obtain coal and water, and the capital and operating costs of conversion facilities. Environmental issues include the effluents discharged from such systems that must be treated. Necessarily both the economic and environmental issues, when viewed as constraints, are heavily influenced by governmental decisions.

2.2.3.1 Economic Aspects of Coal Conversion

Since the National Energy Plan, 1977 and other Federal policies are mandating a conversion to coal, and since sufficient boiler fabrication capacity to handle an immediate massive conversion to direct firing of coal does not exist at the present time (Analysis of the proposed National Energy Plan, 1977) the extent to which coal conversion to gaseous or liquid fuels is economical must be determined. Questions of obtaining the raw materials, raising the capital, and affording to produce the gas or purchase the liquid are far from moot.

Two raw materials, coal and water, are critical to the development of coal conversion systems. The extent to which they are available or unavailable sets physical-economic limits on coal conversion systems. Coal, presently, is basically demand limited and will remain so for

more than another decade (Kerbs et al., 1977). However, if orders for coal suddenly appeared at unprecedented rates for the next 10 to 15 years coal could be supply limited (Kerbs et al., 1977).

For the past five years coal production grew by 2.24 percent annually - from 595.5 million tons in 1972 to 665 million tons in 1976 (Commodity Data Summaries, 1977). The industry produced approximately 640 million tons in 1977 (a level heavily influenced by the protected coal strike). If the trend of increasing coal mining continues in unchanged forms, coal production will be 812 million tons in 1985 and 906 million tons in 1990 (Bhutani et al., 1975 and National Academy of Sciences, 1977a).

While coal can be made available with reasonable certainty, the water question is less clear. Traditionally water is treated as an environmental issue, however its physical availability is of more than passing economic interest. Water can determine what regions are particularly suited for, or constrained from developing coal conversion plants. Water is both consumed and produced in various stages of coal conversion. Consuming activities of gasification include synthesis gas production, raw gas scrubbing, shift conversion, purification, and all cooling activities. Water is produced as an effluent from scrubbing and cooling, shift conversion, and methanation. The shift conversion, final purification, and methanation phases apply only to SNG production while scrubbing and cooling are related to all gasification systems. In liquefaction water is utilized as a hydrogen source and is also employed for cooling purposes.

The specific water requirements vary by conversion process and

individual plant design. The principal variables are the extent to which water is recycled, and the extent to which water is used for cooling purposes. The U.S. Geological Survey shows minimum water demands for SNG production to be 72 gal/10⁶ Btu produced using water for 90 percent of cooling. The requirement is 37 gal/10⁶ Btu produced using air for 90 percent of cooling requirements (Davis and Wood, 1974). The U.S. Geological Survey estimates of water demand for coal liquefaction suggest a minimum of 31 gal/10⁶ Btu produced as fuel. These water requirements contrast with a rate of 146 gal/10⁶ Btu produced as electricity from fossil fuel based generation stations (Davis and Wood, 1974).

2.2.3.2 Environmental Aspects of Coal Conversion

As has been observed, one reason for utilizing the relatively high cost synthetic fuels is providing the environmental protection. Conversion is substituted for stack gas cleanup. The extent of this substitution can be shown with the following example: combustion of medium Btu gas results in 40 ppm NO₂ and 48 ppm CO released (dry volumetric basis). Similarly, combustion of natural gas produces 60 and 70 ppm, respectively (National Research Council, 1977). Direct combustion of coal causes additional emissions. Conversion is not without its effluent control issues. Thus it is important to consider the production of effluents from selected technologies, for conversion processes, as well as combustion systems, they must meet environmental standards. Effluents causing both air and water pollution, plus solid

wastes, are considered here as a result.

Coal gasification and liquefaction plants typically generate significant quantities of waste that must be controlled. The emissions which must be controlled by air pollution technology include particulates, sulfur oxides, nitrogen oxides, hydrocarbons, carbon monoxide, and aldehydes. Table 2.2.1 summarizes the generation of such effluents by the various processes available.

From Table 2.2.1 one can observe that the production of 0.1×10^{15} Btu causes the release, hence the need to control, some 400 tons of particulates, 2000 to 8000 tons of sulfur oxides, 3500 to 6000 tons of nitrogen oxides, 80 to 130 tons of hydrocarbons, 250 to 450 tons of carbon monoxide, and 1 to 2 tons of aldehydes if the process employed is low Btu gasification. If the Fischer-Tropsch process is employed, up to 1600 tons of particulates, 26,000 tons of sulfur oxides, and correspondingly higher levels of other air pollutants are produced and must be controlled (ERDA, 1975). Air emissions are a function of both process configuration and process efficiency.

Effluents that can cause water pollution include dissolved solids, suspended solids, and organic matter (e.g. phenols). Thermal discharges can also be considered, however these vary with the extent to which water is employed for cooling purposes and whether a once-through water cooling mode is employed or not.

Coal conversion processes generates solid wastes, principally ash, that must be disposed of. This is very much like handling solid wastes from coal combustion.

The generation of solid wastes depends, in large part, on the

Table 2.2.1 Estimated Controlled Air Emissions from
Coal Conversion Facilities (in lbs/10⁶
Btu of fuel produced)

Process/Coal	Products				
	Particu- lates	SO _x	NO _x	Hydro- carbons	CO
Low Btu Gas (eastern coal)	0.008	0.115	0.084	0.002	0.006
Low Btu Gas (western coal)	0.009	0.046	0.135	0.003	0.010
High Btu Gas (eastern coal)	0.011	0.149	0.108	0.002	0.008
High Btu Gas (western coal)	0.036	0.059	0.173	0.004	0.013
Solvent Refined Coal (eastern coal)	0.008	0.044	0.066	0.001	0.006
Solvent Refined Coal (western coal)	0.014	0.014	0.075	0.001	0.007
Light Liquids* (eastern coal)	0.029	0.322	0.270	0.006	0.020
Light Liquids* (western coal)	0.030	0.127	0.415	0.009	0.031

Source: ERDA, 1975

*

Assumes the Fischer-Tropsch Process

specific coal being processed. Low ash bituminous coals result in less solid waste generation than the higher ash subbituminous coals and lignites. Secondly, process efficiency determines the amount of solid waste generated.

2.2.4 Hetero-Atoms in Coal Liquids

Coal conversion processes are dually oriented: to convert coal into scarce liquid and gaseous fuel, and to remove or treat, during processing, environmentally unacceptable or health-endangering compounds. As a result, coal conversion technology is concerned as much with processes for handling the by-product, as with the product itself.

2.2.4.1 Sulfur

Sulfur is one of the main unwanted element in coal and coal liquids, because of the properties of its compounds as being corrosive and poisonous for most of the catalysts. Because organic sulfur is difficult to remove during coal pretreatment and because 90 percent of the organic sulfur is converted to hydrogen sulfide in both gasification and liquefaction, this form of sulfur is estimated to be the major sulfur contaminant in gas streams. Hydrogen sulfide is readily removed from gas streams, as is sulfur dioxide, but carbonyl sulfide and carbon disulfide are more resistant to acid-gas scavenging and can pass through sulfur traps, ending up in gases emitted to the atmosphere. Most of the sulfur in coal is recovered from conversion streams as elemental sulfur. Table 2.2.2 summarizes the sulfur distribution for

Table 2.2.2 Estimated Sulfur Balance in Coal Conversion Processes: Tons/Hours

Process	SRC	COED	COED	CSF	Lurgi	Synthane	Synthane
Coal	Kentucky No.11	Utah A seam	Illinois No.6	Pennsyl- vania coal	Navajo	Illinois	Pittsburgh
Input	12.8	1.89	13.98	38.93	7.36	18.30	8.62
Tar	-	-	-	0.637	0.1	0.25	1.03
Ash	0.14	-	-	-	-	-	-
Char	-	1.312	1.976	-	-	-	-
Sulfur Elemental and sulfates	9.9	0.556	11.757	37.27	7.06	16.99	6.52
SO ₂ Released	0.1	-	-	0.029	0.14	1.13	1.07
Product	2.6	0.019	0.132	0.992	0.06	-	-

Source: Braunstein, H.M. et al., 1977

some of the coal liquefaction and coal gasification processes. The sulfur recovered as elemental sulfur is a by-product of the coal conversion process. Some of the sulfur that reaches the stack gas as sulfur oxides is collected by limestone scrubbing as sulfates, and so very small fraction of sulfur is allowed to disperse in the atmosphere.

2.2.4.2 Nitrogen

Nitrogen is introduced into the conversion process not only from the inherent nitrogen in coal but also from the air used as oxygen source. Thus, nitrogen emissions are primarily elemental nitrogen, although nitrogen oxide levels, which can be environmentally significant, depends upon process designs and the inherent nitrogen content of coal. Nitrogen appears in main process streams in the form of ammonia and hydrogen cyanide gases, which are removed by water scrubbing of the gas streams. Both ammonia and hydrogen cyanide retained in wastewaters are accessible to technologies used for treating industrial wastewaters.

2.2.4.3 Oxygen

Oxygen in coal liquids is present in the form of oxides, phenols and other organic and inorganic compounds. One most significant disadvantage because of large quantities of oxygen presence is that it consumes hydrogen during the upgrading step of coal liquid processing.

2.3 COAL LIQUEFACTION PROCESSES

2.3.1 COED Process

Project COED (Char-Oil-Energy Development sponsored by the Office of Coal Research, Department of the Interior) has been under development by FMC Corporation since 1962. Using pyrolysis the process converts coal into cleaner and more valuable products - synthetic crude oil, gas, and char. The gas can be sold as fuel gas or converted to pipeline gas, and the char can be gasified or used as power plant fuel.

Coal, crushed to 1/8 - in. particles, is dried and heated to successively higher temperatures by stages in a number of fluidized-bed reactors. In each reactor, a fraction of the volatile matter of the coal is released. The maximum temperature of each stage is chosen to be just below the temperature at which the coal will agglomerate or cake, defluidizing the bed. Pressure of the operation is between 6 and 10 psig. Typically, the temperatures and number of stages will depend on the agglomerating characteristics of the coal used. In the final stage char is burned to generate heat for the process, and the hot gas and hot char are transferred from the final stage to the other vessels (Scotti, Jones, Ford, and McMunn, 1975).

Pyrolysis gas is quenched with water to condense the entrained oil, which is separated from the water and filtered. Gas from the oil recovery section is scrubbed to remove ammonia, carbon dioxide and hydrogen sulfide and then steam-reformed to produce hydrogen as:



The filtered crude oil, containing less than 0.1 weight percent solids, is hydrotreated at about 750⁰F in a fixed-bed reactor to produce synthetic crude oil of about 25⁰API gravity.

After filtration, the COED oil is hydrotreated until more than 90 percent of heteroatom impurities (sulfur, nitrogen, oxygen) are removed. Hydrotreatment at pressures of 1750 to 2500 psi and temperatures of 700 to 800⁰F produces a syncrude of 25 to 30⁰ API gravity.

Filtered pyrolysis oil is converted by hydrotreating to COED syncrude which is used as a refinery feedstock and/or a low-sulfur fuel. The COED syncrude can be used as feedstock to a petroleum refinery or fractionated into naptha and low-sulfur fuel oil fractions. A U.S. Navy destroyer using COED syncrude is reported to have operated successfully, giving performance similar to standard Naval distillate fuel (Scotti et al., 1975a).

2.3.2 SRC Process

Solvent-Refined Coal Process was developed by Pittsburgh and Midway Coal Mining Company a subsidiary of Gulf Oil Corporation.

In the SRC process, coal is pulverized and mixed with a solvent, later to be derived from the process, to form a slurry containing 25 to 35 weight percent coal. The slurry is mixed with hydrogen and sent through a slurry-preheater to a "dissolver," or reaction zone, maintained at about 800 to 900⁰F and 1000 to 2000 psi. Here about 90 percent of the organic material in the coal is dissolved in about 20 min. The remaining solids consist of the ash-forming inorganic

material and a small amount of undissolved carbon. The product stream is separated to remove excess hydrogen, and the slurry of liquid and undissolved solids is filtered. The excess hydrogen is freed from hydrogen sulfide by acid gas absorption and then recycled to the system. The undissolved solids are washed with light solvent after filtration and dried to remove adhering wash solvent. The mineral residue is not processed further in the pilot plant.

The liquid filtrate is flash-distilled in vacuum to recover solvent. The overhead from this distillation is fractionated into three fractions: a light liquid by-product, a wash solvent fraction for the filters, and a process solvent for recycle to the slurry preparation. The small amount of solvent converted to light liquids and gases during each pass through the reactor is more than balanced by the amount of coal converted to solvent, with the result being that the process requires solvent only during initial startup.

The bottoms product from the flash distillation is a heavy residual oil called solvent-refined coal that contains less than 0.1 percent ash and less than 0.8 percent sulfur. On cooling, it is a pitch like material having a melting point of 300 to 400⁰F and a heating value of about 16,000 Btu/lb, regardless of the quality of the coal feedstock (Schmid, 1975).

The composition of the recycle solvent is of vital importance because the solvent plays an integral part in the coal dissolution process, which occurs by reaction with about 2 weight percent hydrogen (Anderson, 1975). Much of the hydrogenation occurs through transfer of hydrogen from the solvent to the coal. Thermal decomposition of the

coal is believed to lead to free radicals that may be capable of removing a hydrogen atom from a donor solvent molecule. Known hydrogen donors include hydroaromatic materials, for example, tetralins, hydrophenanthrenes, and hydroanthracenes.

2.3.3 H-Coal Process

The H-Coal Process for catalytic conversion of coal to liquid fuels uses the ebullated bed reactor system, which was originally developed by Hydrocarbon Research, Incorporated, to upgrade petroleum residual oils (Johnson et al., 1973).

Crushed coal is slurried with a heavy recycle oil product, mixed with hydrogen gas, heated to about 850⁰F, and reacted at about 2500 psi in an 8-in-dia reactor handling 200 lb coal per hour. A bed of cobalt molybdate catalyst particles in the reactor is kept in an ebullated state by the upward flow of the coal suspension and rising hydrogen bubbles. Catalyst can be added or removed continuously as required. Because of its high cost, attrited catalyst must be recovered from the unconverted coal or coal ash (Perry, 1974).

Oil used for the slurry donates hydrogen to the coal within the ebullated bed. The oil is recirculated from above the catalyst suspension to the bottom of the reactor and thus keeps the temperature of the reactor uniform. Spent solvent oil is continuously hydrogenated in the reactor to restore its hydrogen-donating capacity (Squires, 1974).

Gas taken off from the top of the reactor is treated for removal and recovery of sulfur and ammonia. Unused hydrogen is also separated

and returned to the dissolution process. Raw oil from the reactor is flashed down to low pressure, the flashed vapors are distilled in an atmospheric distillation unit, whereas the flashed liquids are distilled under vacuum. Products are low-sulfur fuel oils, a heavy recycle oil to the coal slurry preparation, and a residuum slurry that can be coked (Beychok, 1975).

If operated at 3000 psi and 850⁰F, the process can yield a light synthetic crude oil. At 1500 psi and about 800⁰F, a synthetic heavy fuel oil can be made. One of the major problems, however, has been the separation of solids: Hydroclones remove only about two thirds of the solids, centrifuges are too expensive, and magnetic separation results are not good. Filtration is less effective than vacuum distillation of the solid-liquid mixture followed by coking (Perry, 1974). Because a good solids separation techniques is not available, the process is more suited for production of a synthetic crude (Squires, 1974).

2.3.4 Synthoil Process

The Bureau of Mines Synthoil Process produces low-sulfur fuel oil by catalytic hydrodesulfurization of coal in a fixed-bed reactor with turbulent flow of hydrogen through the bed at elevated temperatures and pressures. Hydrogenation conditions are controlled to promote desulfurization of the coal and to minimize additional hydrogenation of products from the primary liquefaction. The liquid fuel can be used as a low-sulfur utility fuel either before or after removal of ash

and unreacted coal.

Akhtar, Friedman, and Yavorsky (1974) of the Pittsburgh Energy Research Center report work with three different feed coals. The coals, ground to 70 percent -200 mesh and slurried initially in a high temperature tar derived from coking metallurgical-grade bituminous coal, were sent with hydrogen through a preheater before entering a 5/16-in-ID by 68 ft tube reactor folded inside a 10 ft-long, 10-in-diameter cylindrical furnace. The reactor was charged with a Co-Mo-SiO₂-Al₂O₃ catalyst. Reactor conditions were 840⁰F and 2000 psi with a short residence time for the feed. The product stream leaving at the top of the reactor was sent through a water-cooled condensor to a high pressure receiver for liquids, whereas the gases were fed through a second high-pressure condensor and receiver, then scrubbed with an alkali solution to remove hydrogen sulfide and ammonia.

By this method Pittsburgh seam coal containing 1.3 percent sulfur was desulfurized to a fuel containing 0.3 percent sulfur, an Indiana No.6 coal containing 3.4 percent sulfur was desulfurized to a fuel containing 0.42 percent sulfur, and a Middle Kittanning No.6 coal containing 3.0 percent sulfur was desulfurized to a fuel containing 0.36 percent sulfur. The heating value of the three fuels was about the same 16,400 Btu/lb.

Yavorsky et al., (1975) have successfully processed five different coals in a 100-lb/day unit and in a 0.5-ton/day unit (reactor unit has a 1-in ID and is 14 ft long). Typically, a Kentucky coal containing 5.5 percent sulfur and 16 percent ash can be converted to oil with 0.2 percent sulfur and 0.2 percent ash. Oil yields of over 3 bbl/ton are

reported for process conditions of 2000 or 4000 psi, 2-min reaction time and 840⁰F. In runs of 500 hr no serious catalyst deactivation was reported.

Hydrocarbon gases can be reformed to supplement the hydrogen needed for the process, and the pyrolyzed residue can be added with the coal to the steam-oxygen gasification to produce the bulk of the hydrogen needed. The product oil has a heating value of 17,400 Btu/lb.

2.3.5 Calcon Process

The Calcon Company of New York was formed in a joint venture by Union Carbide Corporation and Chemical Construction Company in May 1974 to demonstrate the commercial feasibility of Union Carbide's hydrocarbonization technology in converting high-sulfur bituminous coal to clean liquid boiler fuel and gaseous fuels.

The hydrocarbonization process differs from other processes in using a dry, noncatalytic, fluid bed of coal particles suspended in hydrogen gas instead of a fixed-bed or liquid-phase process to produce char, gas, and liquid fuels. The process also converts the organic sulfur compounds in the coal into hydrogen sulfide gas which can be removed and further processed to produce sulfur (Chironis, 1975).

Coal to be used in the hydrocarbonization reactor (hydrogenator) is ground to a size range of 60 to 325 mesh and dried by warm flue gas to about 1 percent moisture. A hot oxygen-free flue gas is used to heat the coal to about 600⁰F and to carry it to a coal feed hopper. The coal is then pressurized with steam in a jacketed lock-hopper system

before being fed by gravity on a 20 to 40-min cycle at 617°F to the coal injection vessel, where the coal is fluidized with hydrogen from the bottom at 260 psi above the reactor pressure.

The reactor operates under the following tentative conditions: temperature, 1040°F ; pressure 555 psi; solids residence time, 25 min; gas residence time in the bed, 25 sec; hydrogen partial pressure in the bed, 419 psi; and superficial velocity, 1.0 fps. Gases leaving the bed surface are charged with solids, which are removed by two cyclones. An initial cyclone returns the solids to the bed, and an external cyclone extracts the final solids from the gas and feeds them to the char surge hopper. The cyclones are designed to remove enough solids to meet specifications for solids content of the heavy oil product.

Most of the char is removed from the bottom of the reactor vessel, quenched with water and steam, depressurized to about 60 psi, cooled in a series of fluid beds by nitrogen, ground in a mill, and fed to a Koppers-Totzek gasifier, where it is reacted with oxygen and steam to produce hydrogen for the hydrogenation process. Oxygen is generated by a conventional cryogenic air separation plant. About 680 tons of oxygen per day are needed for the gasifier.

The gas coming from the external cycle of the hydrogenator is hot (1040°F) and under high pressure (555 psi), and it may contain some entrained solids. A fractionator is used to split the gas into four streams: (1) overhead gas (H_2 , CO , CO_2 , CH_4); (2) light liquid (e.g., No.2 fuel oil); (3) heavy liquid (e.g., No.5 or 6 fuel oil); and (4) wastewater.

The heavy oil is cooled and flashed to atmospheric pressure and sent

to storage. The fractionator overheads are sent to a decanter after cooling against boiler feed water and cooling water. The light fuel, overhead gas, and wastewater are separated. Some of the light fuel oil is used as reflux at the top of the fractionator, and some is pumped to storage.

2.3.6 CSF Process

According to Consolidation Coal Company (1973), the CSF (Consolidation Synthetic Fuel) process consists of a partial conversion of high sulfur caking coal to a solid residue and a synthetic crude oil; the oil is further converted to marketable liquid fuels, such as gasoline by means of commercially available refining procedures. Hydrogen is produced by commercial methods and is not a part of the CSF process.

The process is based on solvent extraction of coal with a "natural" solvent derived from hydrogenation of the extract. By starting initially with synthetic solvents, an inventory of extract is build up in successive cycles and hydrogenated to yield a solvent for the next extraction cycle.

Coal, crushed to 3/8-in. particles and partially dried, is first sent into a preheater, where its temperature is raised to 450⁰F; the coal is then discharged into slurry mixing tanks, where it is mixed with a coal-derived hydrogen donor solvent. Solvent extraction of the coal takes place in a stirred vessel at 765⁰F and 150 to 400 psi. Liquid products and solid residue, consisting of unreacted coal and minerals, are separated in hydroclones. Ash content of the extract is

about 0.9 percent. The ash content is lowered to 0.35 percent by using filters designed to operate at 600⁰F and 150 psi. On the basis of bench-scale results, it was concluded that the additional ash present would not detrimentally affect the catalysts used in hydrogenation of the extract.

Vapors produced in the extractor are sent to fractionation and solvent recovery units, where they are treated with the liquid products. Recycle solvent, distillate, and liquid product for the hydrotreatment are produced here. The solid residue is sent to a low-temperature carbonization reactor, where it is pyrolyzed in a fluid bed of char at about 925⁰ F and 15 psi. Recovered solvent is sent to the slurry system. The char obtained is used in a second carbonization unit to carbonize unconverted residue from the extract hydrogenation operation and to recover additional distillate.

A distillate oil product is taken off the fractionation unit overhead. The bottoms are treated with hydrogen in a catalytic reactor operating at 775 to 850⁰F and 4200 psi. This step converts the heavy liquids to donor solvent and naptha product. A pilot plant was capable of processing 20 tons of coal per day to yield about 60 bbl of oil (C₅ + Synthetic Crude) per day from highly caking Eastern bituminous coal. By-products were high-ash char, light hydrocarbon gases, hydrogen sulfide, ammonia, and water. Hydrogen for the plant was generated from methane by a steam reforming process.

2.3.7 CCL Process

Gulf Research and Development Company has developed a Catalytic Coal Liquid Process bench-scale coal liquefaction unit (0.5 to 5 lb of coal per hour), which can be operated at pressures up to 10,000 psi and at temperatures up to 1000⁰F.

Coal, ground and slurried in a recycle solvent, is sent together with hydrogen through a catalytic, fixed-bed reactor at 900⁰F and 2000 psi. The products from the reactor are flashed to separate gases and liquids; hydrogen, separated from the other gases, is compressed and returned to the process, whereas the liquids, subjected to a low-pressure flash separation, yield water and recycle solvent. The remaining material is filtered; the filtrate is distilled to yield the product, a low-sulfur synthetic crude oil, and the solids are coked to produce gaseous and liquid products, which are combined with the filtrate to be distilled.

A 1-ton/day pilot plant located in Harmarville, Pennsylvania, began operation in January 1975. The plant is designed to produce 3 bbl of oil per ton of moisture-and ash-free coal and to provide design data for a larger demonstration plant (Howard-Smith and Werner, 1975).

2.3.8 TOSCOAL Process

The Oil Shale Corporation has developed a process for retorting oil shale and has applied the technology to the processing of Gillette, Wyoming (Wyodak) sub-bituminous coals in a 25-ton/day pilot plant.

The principal goals were (1) to carbonize the coal to upgrade the heating value of sub-bituminous coal, thus decreasing the transport cost per Btu and (2) to recover liquid hydrocarbons.

Crushed coal is fed to a surge hopper and then preheated by hot flue gas in a fluid bed; from there, the coal is sent to a pyrolysis drum, where it is contacted with heated ceramic pellets. The solid product char leaves the pyrolysis drum and passes through a trommel screen, which separates the ceramic pellets from the char. The char is cooled and sent to storage, and the cooled ceramic pellets are returned to the pellet heater by an elevator. Pyrolysis vapors are condensed and fractionated, whereas uncondensed gas is used as a pellet-heater fuel. The use of heated ceramic pellets to provide the required retorting heat is unique and results in a retort gas not diluted by nitrogen and carbon dioxide.

The handling of solid and liquid products of the TOSCOAL process is similar to that of oil shale except that marketable char replaces the spent shale. Unfortunately, the char product is dustier and more pyrophoric than coal so that conventional coal handling methods are not suitable for this product. An economic evaluation showed that the TOSCOAL process is of considerable interest but that solutions must be found for the problem of char transport before the process is commercially practicable..

In the processing of Wyodak coal over half the coal is converted to char, which has a gross heating value of 11,826 to 12,963 Btu/lb, as compared with the original coal's gross heating value of 8139 Btu/lb. Additionally, the low sulfur content of the char makes it an environ-

mentally acceptable solid fuel.

2.3.9 Garrett Process

In developing its coal pyrolysis process, Garrett Research and Development Company recognized that certain criteria would have to be satisfied for a successful process. There had to be high heat transfer rates to accommodate the endothermic decomposition of the coal, and oxygen had to be excluded to maximize production of the most valuable products - the liquids. In addition, a short residence time in the reactor would provide high liquid yields, prevent further cracking of volatile constituents, and inhibit carbon monoxide formation.

Coal, dried and pulverized is carried by recycled product gas into an entrained-bed carbonizer, where the coal is heated extremely rapidly (5000⁰F/sec) by the recycled char. The product stream flows through cyclones to separate the gases from the char. Part of the char is cooled and stored; the remainder can be upgraded to pipeline gas or used as a hydrogen source in the plant.

Condensed tars are hydrogenated to produce either a low-sulfur fuel oil or a syncrude. Unfortunately, the char produced from most Eastern coals contains sulfur in excess of proposed Environmental Protection Agency standards; however, it has been possible to desulfurize the char experimentally because of its high reactivity and porosity.

Tests conducted with a high-volatile Eastern United States bituminous coal showed a maximum yield of 35 percent conversion of coal to liquids at a temperature of 1075⁰F, a pressure of 25 psi, and

a residence time of 0.03 min (Epperly and Siegel, 1974). A material balance for the process indicated 56.0 percent char, 35.0 percent tar, 6.6 percent gas, and 1.7 percent water. Although the ash content of the char is higher than that of the original coal, the heating value of the char is essentially equal to that of a bituminous coal. The pyrolysis gas has a heating value of about 7000 Btu/ft³ on a dry, hydrogen sulfide-free basis and is high in hydrocarbons. Because the tar undergoes little cracking, its hydrogen content is lower than that of most other low-temperature tars (Sass, 1974), requiring hydrotreatment to produce a synthetic crude oil. By using the product char as heat carrier in the entrained-bed reactor, oxygen could be excluded from the reactor and a rapid rate of heat transfer would be assured in a turbulent solid-gas system.

A pilot plant was constructed at LaVerne, California, and is being operated for further development of the process (Sass, 1974).

2.3.10 Fischer-Tropsch Process

The Fischer-Tropsch process is a method for indirect conversion of coal to liquid products: Coal is gasified to a synthesis gas, which is then converted to a liquid by catalytic liquefaction.

F. Fischer and H. Tropsch at the Kaiser Wilhelm Institute in Germany extensively studied the catalytic reduction of carbon monoxide with hydrogen in the 1920s and developed a normal-pressure process for production of liquid hydrocarbons. In 1934, Ruhrchemie, having purchased rights to the process, erected and successfully operated a semicommercial

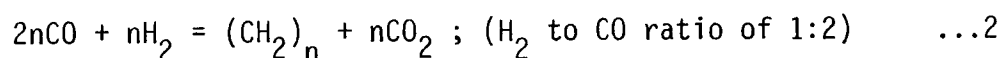
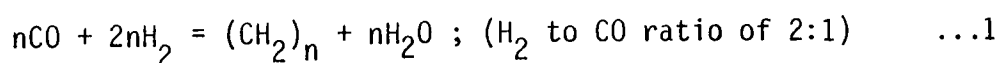
plant. In the following year four full-scale plants were erected. The main steps of the process, as practiced in Germany, were synthesis gas manufacture, gas purification, synthesis of hydrocarbons, condensation of liquid products, and recovery of gasoline from product gas (Pichler and Nector, 1964). In 1936 Fischer and Pichler determined the optimum conditions for carrying out the medium-pressure hydrogenation of carbon monoxide with a cobalt-Kieselguhr catalyst. Yields were 10 to 15 percent higher than with the normal pressure process. Later yields were increased with the use of iron catalysts, but this method was not used commercially until after World War II. Fischer-Tropsch synthesis of hydrocarbons from carbon monoxide contributed greatly to the energy requirements of Germany during the war by producing gasoline, gas oil, and paraffin. The gas oil was excellent diesel fuel; the greater part of German production was used for this purpose. A total of nine plants were put into operation in Germany during 1936-1939, reaching peak production in 1943 at 4,360,000 bbl of synthetic oil per year.

At present there is only one commercial plant, SASOL (Suid-Afrikaanse Steenkool, Olie-en Gaskorporasie), operating in the Republic of South Africa, for production of liquid hydrocarbons from coal by the Fischer-Tropsch process. The following description of the Fischer-Tropsch process is based on this plant.

The coal charged to the SASOL plant is used for two purposes. About 40 percent goes to a boiler house, where steam is produced for power and for production of synthesis gas. The balance of the non-caking coal, crushed to $3/8$ to $1\text{-}1/2$ -in. particles and dried, is

converted in a battery of Lurgi high-pressure, steam-oxygen gasifiers at 350 to 450 psi to produce a gas consisting essentially of carbon monoxide and hydrogen; tar and oil are removed by quenching. To prevent poisoning of the Fischer-Tropsch catalysts, the crude synthesis gas is purified by a low-temperature scrubbing with methanol (Rectisol process), which removes the last traces of tar and oil, as well as 90 percent of the carbon monoxide, all the hydrogen sulfide and organic solids are also removed (Rousseau 1962; Hoogendoorn and Salomon, 1975a).

The two chemical reactions typifying the Fischer-Tropsch formation of hydrocarbons are



These two reactions are connected by the water-gas shift reaction:



The SASOL plant uses two types of reactors to carry out these reactions: One is of German design (ARGE reactor) and works with a fixed bed of iron catalyst in vertical tubes, and the other is of American design (M.W. Kellogg reactor) and operates with a fluidized bed of powdered iron catalyst. The catalyst is highly pyrophoric and is based on a special type of iron ore whose activity is enhanced by a small percentage of metals of group I or III of the Periodic Table of the Elements (Hoogendoorn and Salomon, 1957b).

A major portion of the purified synthesis gas is sent to the

ARGE reactor, where the hydrogen and carbon monoxide (in a 2:1 ratio) are converted at 430 to 490°F and 3550 psi to a mixture of straight chain, high-boiling hydrocarbons, with some medium-boiling oils, diesel oil, liquified petroleum gas, and oxygenated compounds such as alcohols and acids.

The balance of the synthesis gas, together with tail gases from the ARGE and Kellogg reactors, is sent to a methane-reforming unit before being sent to the Kellogg reactor, where a higher ratio of hydrogen to carbon monoxide (3:1) is needed for the reaction occurring at about 600°F and 3270 psi. Product gas and catalyst leaving the reactor are separated by cyclones, and the catalyst is recycled to the reactor. Products of the fluidized-bed synthesis are mainly low-boiling hydrocarbons ($C_1 - C_4$) and gasoline, with substantial amounts of oxygenated products and aromatics.

Hydrocarbon products from the synthesis units are separated in petroleum refinery units especially adapted to handle the Fischer-Tropsch product. Water-soluble oxygenated products from the two reactors are treated together; unsaturated gases (primarily propylene and butylenes) are treated together in a polymerization unit and converted into high-grade gasoline (Hoogendoorn and Salomon, 1957a).

In December 1974, SASOL announced that a second Fischer-Tropsch plant would be constructed and would come onstream in 1979-1981. The SASOL-2 complex will use only a refined Kellogg Synthoil process for synthesis of the Lurgi-produced gas. It will produce mainly gasoline and fuel oil, as well as an estimated 3×10^8 to 4×10^8 lb of ethylene per year, 50×10^4 lb of ammonia per day, 1.84×10^8 lb of

sulfur per year, and 3.8×10^8 lb of tar products per year. The projected plant represents a scale-up, by a factor of 8, of the existing SASOL plant (Howard-Smith and Werner, 1975).

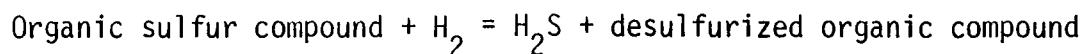
2.4 HYDRODESULFURIZATION

Developments in petroleum refining technology in the last two decades have brought the reactions referred to as hydroprocessing to a level of economic importance matching cracking and reforming. In hydroprocessing applications, petroleum components react catalytically with hydrogen. Hydrocracking, one of the most important examples, involves cracking and hydrogenation of hydrocarbons to give refined fuels with smaller molecules and higher H/C ratios. The most important hydroprocessing application is hydrodesulfurization, which involves reactions leading to removal of sulfur from petroleum compounds by their conversion into H_2S and hydrocarbon products.

The catalyst used in most hydrosulfurization processes are comparable in their complexity to partial-oxidation catalysts, being formed from mixtures of transition-metal compounds. A coherent picture of catalyst structure and surface reaction mechanism has begun to emerge only in the last few years. The kinetics and process-engineering data are almost entirely qualitative since so much of the essential information remains proprietary. Nonetheless, the engineering problems are now clearly defined, and they have a complexity matching that of the catalyst structures: the catalyst age by both chemical and physical processes; the reactors contain gas, liquid, and solid phases

undergoing intricate flow patterns; and the exothermic reactions can sometimes constitute an explosion hazard.

Hydrodesulfurization reactions are those of the following class:



Catalytic processing of light petroleum feedstocks with hydrogen to remove sulfur is carried out with several objectives, among them pre-treatment of catalytic reformer feeds to prevent sulfur poisoning of the platinum-containing catalysts, and treatment of gasoline formed in catalytic cracking to provide sweetened and stabilized products.

Desulfurization of heavy petroleum fractions gives products including diesel and jet fuels, heating oils, and residual fuel oils. The incentive is now strong for removal of sulfur from fuel oils, since combustion of sulfur-containing fuels is the primary cause of SO_2 pollution of the atmosphere; this pollution is most severe in the Eastern United States, Japan, and Western Europe. The need for clean fossil fuels extends to coal, and in the last few years effort has been devoted to development of processes for converting coal into low sulfur liquids to be burned in power plants.

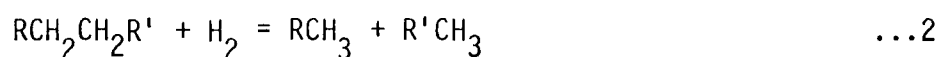
The hydrodesulfurization technology is well established and routinely applied for light petroleum feedstocks. For heavy petroleum feedstocks, like petroleum residua, and coal-derived liquids this technology is relatively new and is undergoing rapid evolution.

2.4.1 Reactions

A summary of the most important classes of reactions occurring in hydrodesulfurization processes is given here (Gates et al., 1979). The desired reactions are hydrogenolyses resulting in cleavage of a C-S bond; e.g.



Under industrial reaction conditions, hydrogenolysis reactions resulting in breaking of C-C bonds also occur, e.g., the hydrocracking reaction



Another kind of hydrogenolysis reaction is hydrodenitrogenation; e.g.



Reactions of this type are effective in removing nitrogen from fuels, is often necessary before refining by hydrocracking, since basic nitrogen-containing compounds are poisonous for the acidic sites of bifunctional hydrocracking catalysts, which have both cracking and hydrogenation activity.

Hydrogenation of unsaturated compounds also occurs during hydrodesulfurization, and the reaction rates are significant compared with

those of hydrodesulfurization.



The last three classes of reactions take on economic importance in the processes by consuming expensive hydrogen without removing sulfur.

Thermal cracking reactions can also take place at relatively high temperatures to produce molecular-weight reduction.

Demetallization reactions are important in accompanying the hydrodesulfurization of residua. The heaviest fractions of some petroleum feedstocks contain significant concentrations of organo-metallic compounds, especially of V and Ni. They react to give solid metal sulfides, which can accumulate in a reactor and ultimately plug the pores of a catalyst or the interstices of a fixed bed of catalyst particles.

Coking reactions, common to virtually all hydrocarbon reaction processes, occur as well in hydrodesulfurization. Coke not only poisons catalyst surfaces but contributes to blocking of catalyst pores and fixed bed interstices. In contrast to inorganic compounds of V and Ni, however, coke can be burned off of catalysts as in catalytic cracking processes, leading to successful regeneration.

The hydrodesulfurization reactions are virtually irreversible at temperatures and pressures ordinarily applied, roughly 570 to 840°F and up to 3000 psi. The reactions are exothermic with heats of reaction of the order of roughly 50 to 100 Btu per standard cubic foot

of hydrogen consumed (Gates et al., 1979).

2.4.2 Catalyst

The catalysts applied in hydrodesulfurization have evolved from those developed in prewar Germany for hydrogenation of coal and coal-derived liquids. They are formed from alumina-supported oxides of Co and Mo, and the surfaces are usually sulfided in operation. Catalysts of this type are often referred to as cobalt molybdate which is a jargon term. Industrial catalysts may contain as much as 10 to 20 percent of Co and Mo. A number of related compositions have been applied, including for example, Ni and W instead of Co and Mo. In contrast to the supported Pt and Pt-alloy catalysts used in reforming, hydrodesulfurization catalysts have hydrogenation activity in the presence of high concentrations of sulfur compounds; their activities, however, are characteristically less than that of Pt by several orders of magnitude.

Hydrodesulfurization catalysts are used as porous particles or extrudates typically having dimensions of 0.059 to 0.118 inch. The particle size and pore geometry significantly influence catalyst performance, especially for the heaviest feeds, since intraparticle mass transport has a significant influence on reaction rates.

In the processing of light petroleum fractions, gas or liquid phase oil is contacted concurrently with hydrogen, flowing downward through solid catalyst particles in a fixed-bed reactor. Unconverted hydrogen from the product stream is scrubbed to remove H_2S and recycled. A

rough guide to the severity of the processing conditions is given in Table 2.4.1, where light and heavy feeds are contrasted.

Temperature is increased gradually during operation to compensate for activity decline caused by coke accumulation. Coke is periodically burned off the catalyst, which may endure several operating cycles and have a lifetime of as much as 10 years. Catalysts costs in light-feed hydrodesulfurization processes account for less than about 10 percent of processing costs, and there is therefore little incentive for developing new catalysts; it seems unlikely that there will soon be significant changes in this well-established processing technology (Gates et al., 1979).

If the reacting petroleum in one of these processes is present as a liquid, such as a gas oil, then the reactor has gas, liquid, and solid phases and is referred to as a trickle-bed reactor. Hydrodesulfurization processes appear to be the most important applications of this reactor type.

Trickle-bed reactors are also used on an industrial scale in hydrodesulfurization of heavy petroleum feeds. Operating conditions are more severe with these less reactive feeds, as summarized in Table 2.4.1. The previously mentioned coking and demetallization reactions are especially important for the petroleum residua. Deposits of coke and inorganic metal compounds are readily formed, and accumulation of the metal-containing deposits prevents regeneration of catalysts.

The catalyst aging has set heavy-feed processes apart from the others, also the problems of obtaining efficient fluid-solid contacting, uniform catalyst-bed temperatures, and efficient catalyst utilization

Table 2.4.1 Approximate Processing Conditions in
Catalytic Hydrodesulfurization

Processing conditions	Feedstock		
	Light petroleum (distillates)	Heavy petroleum (residua)	Coal
Temperature, °F	570 - 750	645 - 790	750 - 860
Pressure range, psi	515 - 1030	810 - 2500	2000 - 3950
LHSV, volume feed/vol.hr	2 - 10	0.2 - 1	1
H ₂ recycle rate. ft ³ /bbl	300 - 2000	2000 - 10,000	25,000
Catalyst life, years	10	1/2 - 1	Undetermined

Processing conditions have been inferred from many literature sources.

in the presence of significant mass-transport resistances make it more difficult to hydrodesulfurize heavy feeds.

Another reactor used commercially in residuum hydrodesulfurization is a fluidized bed. This reactor is distinct from the gas-solid cracking reactor because it also contains liquid. It is alternatively referred to as an ebullating-bed or slurry-bed reactor since the catalyst particles are held in suspension by the upward velocity of the liquid reactant, through which hydrogen flows concurrently. There are several advantages to this reactor design: (1) the deactivating catalyst can be removed and replaced continuously (as in catalytic cracking); (2) small particles of catalyst can be used, and they are more effective than large particles when intraparticle mass-transport resistance is significant (particles with dimensions less than about 0.025 in. are avoided in fixed beds because pressure drops are unacceptably high); and (3) the fluidized-bed reactor contents are expected to be very well mixed, which suggests that uniform temperatures can be maintained.

There are compensating disadvantages to the slurry-bed reactor; (1) the high degree of mixing of reactants in the direction of flow necessitates higher temperatures or lower space velocities than in a fixed bed to achieve the same conversion; (2) corresponding to higher operating temperatures, undesired side reactions such as hydrocracking are more important, leading to higher hydrogen consumptions; and (3) the complex problems of reactor stability and control have not yet been solved for the three-phase fluidized system with exothermic reactions involving hydrogen at high temperatures and pressures.

2.4.3 Coal Liquid Hydrodesulfurization

Synthetic liquid can be produced from coal by liquefaction and solids-removal processes, most of which involve pyrolysis of the polymeric coal matrix and hydrogen transfer to give smaller molecules, many of them polycyclic aromatics. The extensive literature of coal liquefaction processes involving catalysis dating from prewar Germany has been reviewed by Weisser and Landa (1973). In some processes now undergoing development (National Academy of Sciences, 1977b), the coal liquefaction takes place in the same reactor as catalytic hydrodesulfurization of the coal-derived liquids; both slurry-bed and fixed-bed reactors have been used, and the process flow diagrams are similar to those for petroleum residua. The more common processing arrangement, however, allows for liquefaction in one stage, followed by removal of the solids (largely mineral matter) and then catalytic hydrodesulfurization in separate downstream trickle-bed reactors.

Breakup of the organic coal matrix is primarily a pyrolytic (and noncatalytic) process similar to the thermal cracking. It may involve hydrogen transfer to the coal fragments from molecules such as tetralin, after being dehydrogenated, these molecules can be rehydrogenated on a catalyst surface. The coal loses a small amount of its organic sulfur during breakup of the matrix, but most of the sulfur remains organically bound in product molecules such as dibenzothiophene, benzonaphthothiophene, and related compounds (Kilanowski et al., 1980). These compounds are now small enough to diffuse into the pores of a catalyst particle, and on the surface they undergo hydrodesulfurization

reactions like the ones just described.

Since coal-derived liquids are highly aromatic, they may require considerable upgrading by hydrocracking to give suitable fuels; consequently, processing conditions may be more severe than those required for hydrodesulfurization of petroleum residuum (Table 2.4.1), even though hydrodesulfurization of compounds found in coal-derived liquids proceeds more rapidly than hydrodesulfurization of the compounds in petroleum residua, since the latter have more of the highly branched substituent groups which can cause steric hindrance of reaction (Larson, 1974).

3. LITERATURE SEARCH

To conduct a comprehensive study of the research results obtained up to this point for up-grading liquids derived from coal, it was proposed to collect and evaluate the available literature on the subject. To completely cover all the work done on coal-derived-liquids a comprehensive literature search on Oak Ridge National Laboratory computer was run. The main parameter searched were coal, and coal liquids and the search was confined by using secondary parameters as described in Table 3.0.1. A separate search on chemical abstract was also conducted using the same parameters as given in Table 3.0.1. A total number of 1679 references were obtained from both the runs, and were carefully screened. References which were not related to coal liquids were discarded. The articles, books, magazines, and periodicals were gathered, the U.S. patents and theses were ordered.

The literature search is divided into sections based on the coal-liquefaction processes. In each section a brief summary of the process is given, including the properties of products, operating conditions and catalysts used. Each article is then summarized giving objective of the research, feed, product, and catalyst properties, also, operating conditions, results and correlations.

Table 3.0.1 Computer Search Results

Primary Parameter	Secondary Parameter	No of References
Coal	Hydrocracking	64
	Alkylation	16
	Dealkylation	19
	Cracking	125
	Hydrolysis	7
	Depolymerization	14
	Chemical properties	194
	Chemical Reaction Yield	129
Coal Liquid	Hydrocracking	39
	Hydrogenation	220
	Desulfurization	81
	Alkylation	2
	Dealkylation	2
	Hydrolysis	1
	Depolymerization	2
	Carbonization	34
	Dehydrogenation	4
	Denitration	2
	Chemical Properties	9
	Chemical Reaction	18
	Chemical Reaction Yield	27
Total		1009

3.1 COED PROCESS

Pulverized coal is heated to successively higher temperatures in a series of fluidized-bed pyrolysis reactors in which a fraction of the volatile matter in coal is released. Thermal staging prevents agglomeration of the coal, since in each reactor the temperature is kept just below the agglomeration point. Usually four stages are required, operating at 600, 850, 1000 and 1500⁰F; but the staging conditions can be adjusted to fit the type of coal processed. The heat for each of the first three reactors is provided by burning char in the fourth reactor.

The volatile oil released by the pyrolysis process is condensed and filtered to remove char fines and ash. A typical inspection for the pyrolysis oil is given in Table 3.1.1 for Utah and Illinois coals. The pyrolysis oil is then hydrotreated at rather severe conditions (see Table 3.1.2) in a fixed-bed reactor to remove sulfur, nitrogen, and oxygen to produce a 25-30⁰API synthetic crude oil product, the syncrude.

Chemical analysis for COED syncrudes derived from Illinois No.6 seam coal is given in Table 3.1.3. It is apparent that the fixed bed hydrofining of the pyrolysis liquid increases the H/C atom ratio to 1.58, and decreases the sulfur content to 0.068 weight percent, the nitrogen content to 324 ppm, and the oxygen content to 0.64 weight percent.

Typical data for COED syncrudes derived from Western and Eastern coals are given in Table 3.1.4. Some difference in composition of the

Table 3.1.1 Typical Properties of COED Pyrolysis Liquids

	Coal Source	
	Utah A seam	Illinois No.6 seam
Properties of Derived Oil		
Carbon (weight percent)	83.8	79.6
Hydrogen (weight percent)	9.5	7.1
Nitrogen (weight percent)	0.9	1.1
Sulfur (weight percent)	0.4	2.8
Oxygen (weight percent)	5.0	8.5
Ash (weight percent)	0.3	0.9
H/C atom ratio	1.36	1.07
API gravity (60°F)	-3.5	-4
Moisture (weight percent)	0.5	0.8
Pour point (°F)	100	100
Viscosity (SUS 210°F)	390	1333
Solids (weight percent)	3.8	4.0
Gross heating value (Btu/lb)	16,100	15,050

Source: Scotti et al., 1974

Table 3.1.2 Typical Hydrotreating Conditions for
COED Pyrolysis Liquids

Catalyst	NiMo on alumina extrudates
Pressure	1750-2500 psi
Temperature	700-800 ⁰ F
Space velocity	0.3-0.6 lb oil/hr. lb catalyst
Gas recycle rate	40-80 M scf/bbl
Gas recycle concentration	90-95 percent hydrogen
Hydrogen consumption	3500 scf/bbl

Source: Scotti et al., 1974

Table 3.1.3 Analysis of COED Syncrude Derived from
Illinois No.6 Seam Coal

General specifications

Gravity (⁰ API at 60 ⁰ F)	28.6
Flash point (⁰ F)	70
Pour point (⁰ F)	-55
Carbon residue (Ramsbottom) (weight percent)	0.20
Hydrogen (weight percent)	11.30
Carbon (weight percent)	85.65
Sulfur (weight percent)	0.068
Nitrogen (ppm by weight)	324
Oxygen (weight percent)	0.64
H/C (atom ratio)	1.58

Hydrocarbon composition (volume percent)

Paraffins	10.4
Cycloparaffins	41.4
Monoaromatics	34.1
Polynuclear aromatics	14.1

Source: Project COED, 1973

Table 3.1.4 Typical Data for COED Syncrudes Derived from
Western and Eastern Coals

	Coal source	
	Illinois Pea- body mine, No. 6 seam	Utah King mine A seam
Hydrocarbon type analysis (liquid, volume percent)		
Paraffins	10.4	23.7
Olefins	Nil	Nil
Naphthenes	41.4	42.2
Aromatics	48.2	34.1
API gravity (60°F)	28.6	28.5
ASTM distillation (°F)		
Initial boiling point (IBP)	108	260
50 percent distilled	465	562
End point (EP)*	746	868
Fractionation yields (weight percent)		
IBP-180°F	2.5	0
180-390°F	30.2	5.0
390-525°F	26.7	35.0
525-650°F	24.4	30.0
650-EP	16.2	30.0

Source: Project COED, 1973

*

95 percent except for Illinois No.6, which is 98 percent

syncrude are apparent for the two coals. High-volatile bituminous Illinois coal gives a more aromatic syncrude and much less paraffins than Western Utah coal. Both crudes are highly naphthenic in nature. The Western coal have a larger amount of high molecular weight fraction than the Eastern coal as shown by the greater fraction above 650⁰F.

The COED syncrude fraction from IBP-390⁰F is primarily a mixture of light and heavy naphthas and is highly naphthenic, containing 70-79 volume percent mono-and dicycloparaffins. The 390-650⁰F fraction contains 27-30 percent naphthenes and over 50 percent of polynuclear aromatics. The 650⁰F plus fraction contains about the same total weight percent of paraffins as the two previous fractions.

The syncrudes were also found to contain substantial amounts of oxygenates and had a uniform distribution of nitrogen compounds which ranged from pyridine to complex carbazole structures. The sulfur compounds included hetrocyclic aromatic structures.

3.1.1 Peters, B.C.

Peters, B.C.(1976, 1977a, 1977e) working for Dow Chemical Company investigated the possibility of the FMC COED Pyrolysis Process syncrude as a petrochemical feedstock. The syncrude was separated into three fractions; IBP-350⁰F naphtha, 350-650⁰F mid-distillate, 650-850⁰F gas oil. The naphtha was hydrotreated. The mid-distillate and hydrocracate-naphtha was also hydrotreated. Both fractions of hydro-treated naphthas were reformed.

Steam coil cracking experiments were conducted on the straight run

and hydrocrackate mid-distillate naphtha fractions to evaluate their potential as ethylene feedstocks. None of the fractions surveyed was particularly attractive as feedstock for direct olefin production.

The data presented herein was obtained from processing studies on a sample of FMC Corporation COED Western Kentucky syncrude. A sample of the whole crude was distilled into four straight run fractions, whose boiling range and elemental composition are listed in Table 3.1.5. Gas oil had higher sulfur but lower oxygen content of the three lighter fractions.

The straight run mid-distillate was hydrocracked over Harshaw HT-400 E cobalt molybdenum catalyst. This catalyst was chosen for its neutral alumina support and its resistance to deactivation by nitrogen oxygen, and sulfur in the feed. A higher ratio of normal/iso-paraffins was also expected from this catalyst. Operating conditions of 1500-2500 psi and 850-1000°F with LHSV's of 0.3 and 0.7 were surveyed. The naphtha created from hydrocracking the mid-distillate was distilled off and the unconverted mid-distillate was hydrocracked a second time. Nomial requirements for 60 percent conversion to C_1 - C_9 were 2500 psi, 940°F, and 0.7 LHSV.

The straight run gas oil was hydrocracked over the same catalyst. Only two acceptable runs were completed due to solids in the oil which plugged the check valves on the pump and the small amount of material available. Operating conditions of 2500 psi, 850°F, and a LHSV of 1.23 and 2500 psi, 932°F, and a LHSV of 1.45 were surveyed, with 57.2 and 77.9 percent conversion to 650°F-minus respectively.

Both the straight run naphtha and the combined naphtha from two-

Table 3.1.5 Boiling Range and Elemental Composition of
COED Straight Run Fractions

	Naptha IBP-350°F	Mid- distillate 350-650°F	Gas oil 650-850°F	Resid 850°F +
Weight percent of crude	22.4	46.2	27.8	3.6
API Gravity, 60°F	44.5	20.7	12.0	
Elemental Composition				
Carbon weight percent	86.6	88.3	89.0	89.3
Hydrogen weight percent	13.0	11.2	10.7	10.7
Oxygen ppm	3420	3620	2460	
Nitrogen ppm	560	1600	900	
Sulfur ppm	49	55	90	

Source: Peters, B.C. 1976, 1977a, 1977e

pass hydrocracking the straight run mid-distillate were hydrotreated, over Harshaw HT-100 E nickel-molybdenum catalyst. This catalyst was chosen for its resistance to deactivation by heteroatoms in the feed and for its superior activity for denitrogenation. The straight run data is sketchy, due to a large extent to analytical and presulfiding technique difficulties. Sulfur, nitrogen, and oxygen were reduced to 2, 6, and 470 ppm respectively in two passes. The hydrocrackate naphtha was hydrotreated in one pass. Nitrogen in the feed to the hydrotreater was less than 1 ppm due to removal during hydrocracking. Sulfur was reduced from 40 to 1 ppm and oxygen remained at the 450 ppm level, achieved during hydrocracking.

The hydrotreated straight run and hydrocrackate naphthas were reformed over Cyanamid Aeroform PHF-4 platinum chloride catalyst. This catalyst was chosen as a typical example of a readily available bi-functional reforming catalyst. At 250 psi and 950-960°F, the catalyst life was very short, as the straight run naphtha rapidly coked the catalyst. Naphthene conversion dropped from 98 percent to 83 percent in 100 hours. At 500 psi and 968°F, the hydrocrackate naphtha was reformed with a substantial increase in catalyst life. With a first day conversion of 93 percent, after 100 hours, the naphthen conversion was still at 89 percent.

Steam coil cracking experiments were conducted on the straight run and hydrocrackate mid-distillate and naphtha fractions to evaluate their potential as ethylene feedstocks. Due to the high aromatic content of these feedstocks, coke lay down in the reactor was a significant problem. None of the fractions surveyed was particularly

attractive as feedstock for direct olefin production.

In addition to the hydroprocessing studies, each fraction was subjected to mathematical recycle hydrocracking to naphtha, hydrotreating, reforming, and hydrodealkylation (HDA). As a result, each fraction was converted to methane, LPG's, benzene, and liquid fuel and the hydrogen required was also calculated. From this data, presented in Table 3.1.6 the relative value of each fraction was determined.

Based on the yield data calculated for each fraction and the weight percent of each fraction from distillation, a mass balance for a conceptual plant operating on 100.00 lb/hr COED whole crude was calculated. With the flow rates and compositions of key streams known, the preliminary estimate for capital requirements and operating costs could be made. Only the naphtha and mid-distillate fractions were included in this balance, since the gas oil fraction was concluded to be economically unattractive as a petrochemical feedstock. The 46.2 lb/hr methane, 16.48 lb/hr LPG's and 27.6 lb/hr naphtha. The straight run, and hydrocrackate naphthas, 22.4 and 27.6 lb/hr respectively, were hydrotreated mathematically, consuming 0.19 lb/hr hydrogen and producing 3.67 lb/hr gas. The hydrotreated naphtha was then reformed, producing 1.04 lb/hr hydrogen, 5.14 lb/hr gas and 40.34 lb/hr reformate. As in house mathematical model for hydrodealkylation was used to convert the reformate to 8.56 lb/hr methane, 4.30 lb/hr ethane, 26.38 lb/hr benzene, and 2.15 lb/hr liquid fuel, while consuming 1.44 lb/hr hydrogen. With hydrogen needs met by converting part of the methane to hydrogen in an oil fired methane reformer, overall yields from the conceptual plant in pounds per 100 pounds of crude are presented in Table 3.1.7.

Table 3.1.6 Product Patterns and Value for COED
Straight Run Fractions

Processing Sequence	Straight Run Naphtha IBP-350°F	Straight Run Mid-Distillate 350-650°F	Straight Run Gas Oil 650-850°F
	Hydrotreat	Recycle Hydrocrack	Recycle Hydrocrack Gas Oil
	Reform	Hydrotreat	Recycle Hydrocrack Mid-Distillate
	Hydrodealky- lation	Hydrodealky- lation	Hydrodealkylation
Product Pattern, wt %			
Hydrogen	-0.9	-6.3	-7.8
Methane	20.4	20.0	22.9
LPG	20.2	53.3	52.7
Benzene	53.5	31.4	30.8
Liquid Fuel	6.8	1.4	1.3
Value/100 lb Distillate (1980), dollars	10.43	7.29	7.12

Source: Peters, B.C., 1976, 1977a, 1977e

Table 3.1.7 Overall Yield from Conceptual Plant
Using COED Whole Crude as Feedstock

Yield in lb/100 lb Crude	
Methane	7.34
LPG's	28.96
Ethane	34.94 wt %
Propane	26.37 wt %
Butanes	23.05 wt %
Pentanes	15.64 wt %
Benzene	26.38
Fuel (HDA)	2.15
Fuel (Gas Oil)	31.40

Source: Peters, B.C., 1976, 1977a, 1977e

3.1.2 Berg, L. and McCandless, F.P.

Berg, Lloyd and McCandless, F.P. (1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d) of Montana State University hydrocracked and hydrotreated the FMC Corporation COED tar (or Filtered Pyrolysis Oil as called by FMC Corporation) with different catalysts at different operating conditions to find a catalyst which gives best results towards heteroatom removal and hydrogen consumption.

The ultimate analysis of the Pyrolysis Oil used is given in Table 3.1.8 alongwith the analysis of FMC COED syncrude. This syncrude is produced by FMC Corporation by upgrading COED Tar with a cobalt-molybdate catalyst, and was used as a basis for comparing the activity of other catalysts. For comparing the COED tar and COED syncrude quality, their ASTM distillation is plotted in Figure 3.1.1.

For initial catalyst screening a batch type operation was utilized. A 30.5 cubic inch batch autoclave was charged with feed oil and catalyst, and pressurized by hydrogen up to an initial value (about 2200 psi), autoclave was then heated for 1/2 hour at the run temperature (about 840⁰F). The product was tested for sulfur and nitrogen removal. Twenty one commercially available cobalt-molybdate, nickel-tungsten and nickel-molybdate catalysts were batch tested. Sixteen catalysts including six cobalt-molybdate, five nickel-tungsten, and five nickel-molybdate catalysts were selected and then tested for continuous operation.

Table 3.1.8 Ultimate Analysis of
Pyrolysis Oil and
COED Syncrude

	COED Tar or Pyrolysis Oil Wt % (Dry)	Syncrude Wt %
Carbon	82.9	87.27
Hydrogen	7.3	10.59
Nitrogen	0.9	0.20
Sulfur	2.3	0.24
Oxygen	5.9	1.70

Source: Berg, L., and McCandless, F.P., 1975, 1976a, 1976b, 1976c,
1976d, 1977a, 1977b, 1977c, 1977d

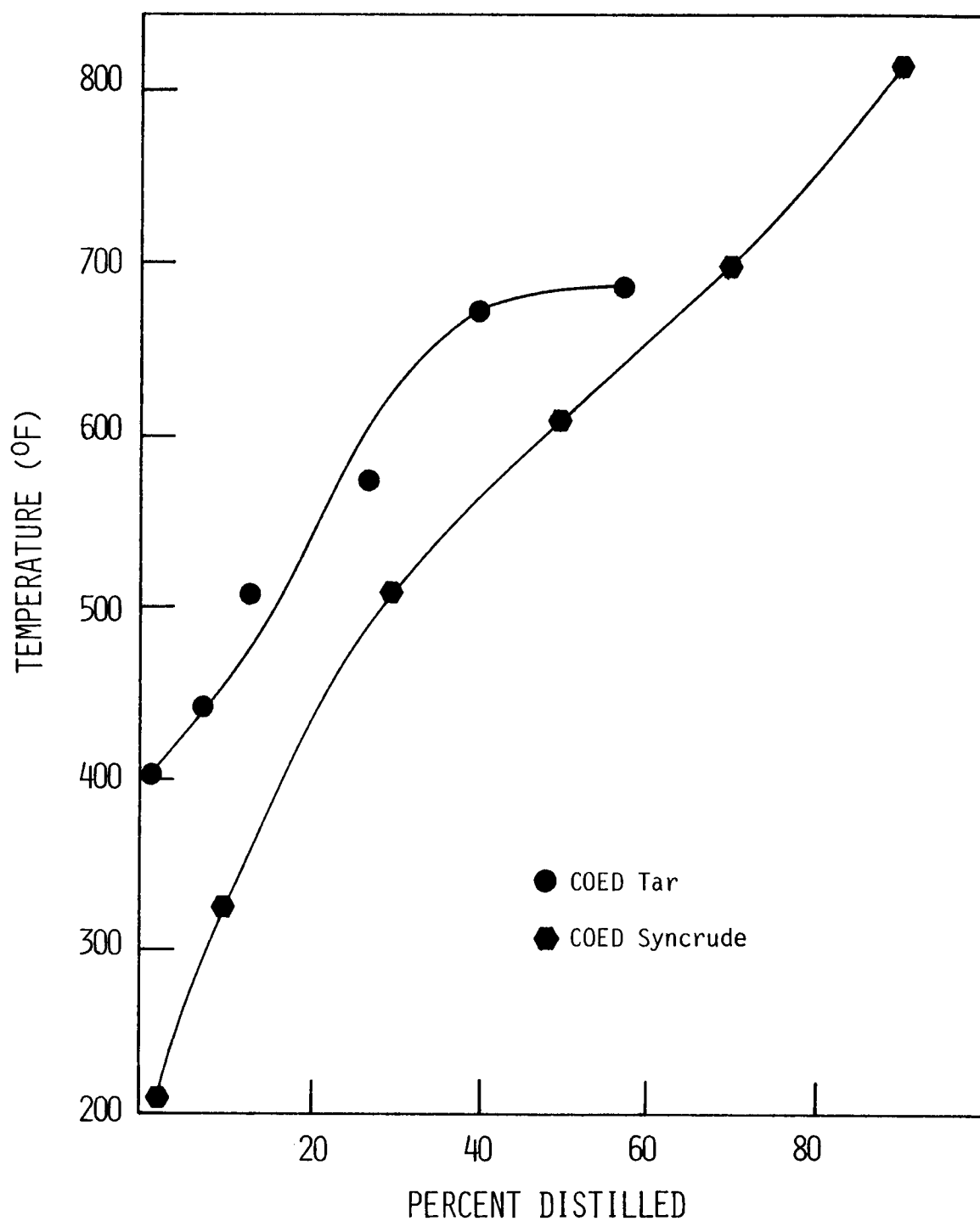


FIGURE 3.1.1 ASTM Distillation of FMC COED Tar and COED Syncrude (Berg, Lloyd and McCandless, F.P., 1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d)

Sulfur removal was best effected with cobalt-molybdate catalyst, little over 90 percent of sulfur in feed was removed with a space velocity of 1.5, nitrogen removal was about 30 percent. Sulfur removal for Shell 344 (2.4 percent CoO, 9.9 percent MoO₃). Harshaw HT 400 (3 percent CoO, 15 percent MoO₃), CCI-C 20-6 (4 percent CoO, 15 percent WO₃) and Houdry HR 801 (3 percent CoO, 15 percent MoO₃), with respect to the space velocity are plotted in Figure 3.1.2 and nitrogen removal is given in Figure 3.1.3. It was observed that the space velocity had a significant effect on sulfur removal while the hydrogen flow rate did not effect very much on sulfur removal as can be seen in Figure 3.1.4.

The nickel-molybdate catalysts yielded larger amounts of product in the range 425-600⁰F with lesser fraction in the upto 425⁰F range, which concluded that the nickel-molybdate catalysts were making less gas. Also these catalyst were the best for nitrogen removal, little more than 50 percent of the nitrogen from the feed was removed, but the sulfur removal was only around 80 percent.

Looking at the sulfur and nitrogen removal of cobalt-molybdate and nickel-molybdate catalysts a possible processing method could be to run the feed over a cobalt-molybdate catalyst to remove sulfur, and then over a nickel-molybdate catalyst to remove nitrogen. This method might bring the hetroatom level down to an acceptable point without increasing the severity of the process.

To determine the effect of external diffusion on catalyst surface, test runs were made using different amounts of catalysts and comparing the conversion obtained plotted against space velocity. The results of this test are plotted in Figure 3.1.5 for sulfur. As can be seen, at

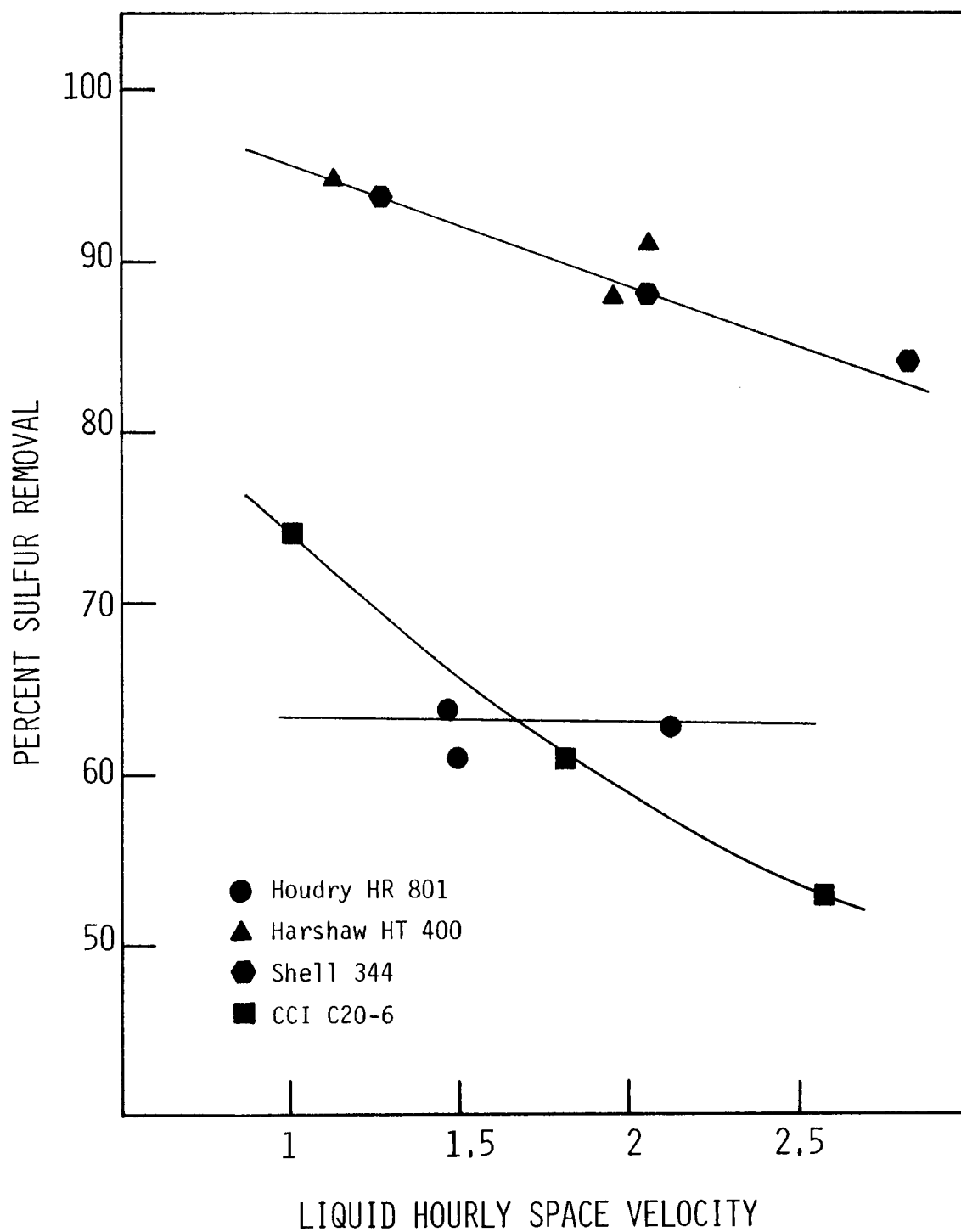


FIGURE 3.1.2 Sulfur Removal from COED Tar (Berg, Lloyd and McCandless, F.P., 1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d)

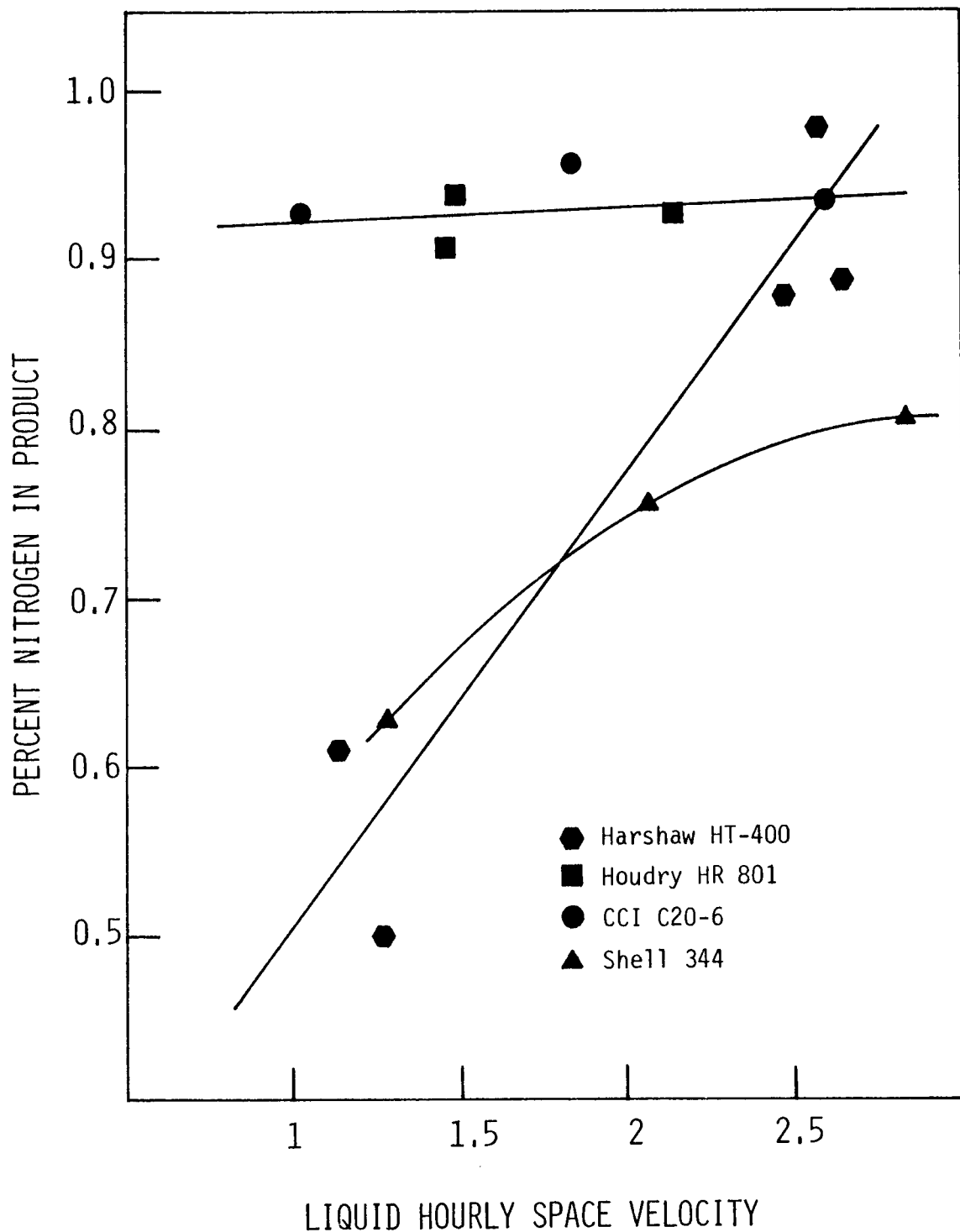


FIGURE 3.1.3 Nitrogen Removal from COED Tar (Berg, Lloyd and McCandless, F.P., 1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d)

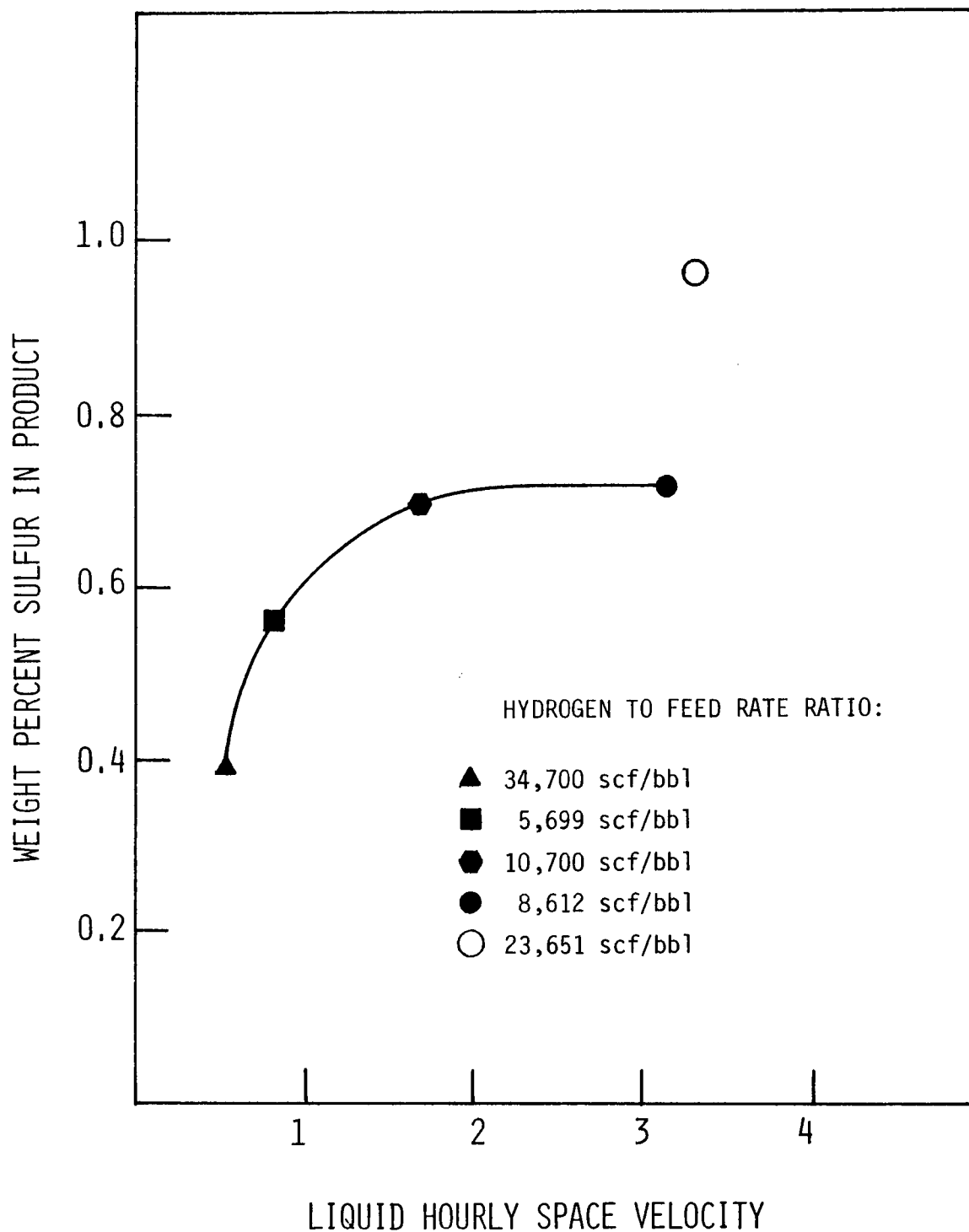


FIGURE 3.1.4 Upgrading COED Tar by Nickel-Tungsten Catalyst
(Berg, Lloyd and McCandless, F.P., 1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d)

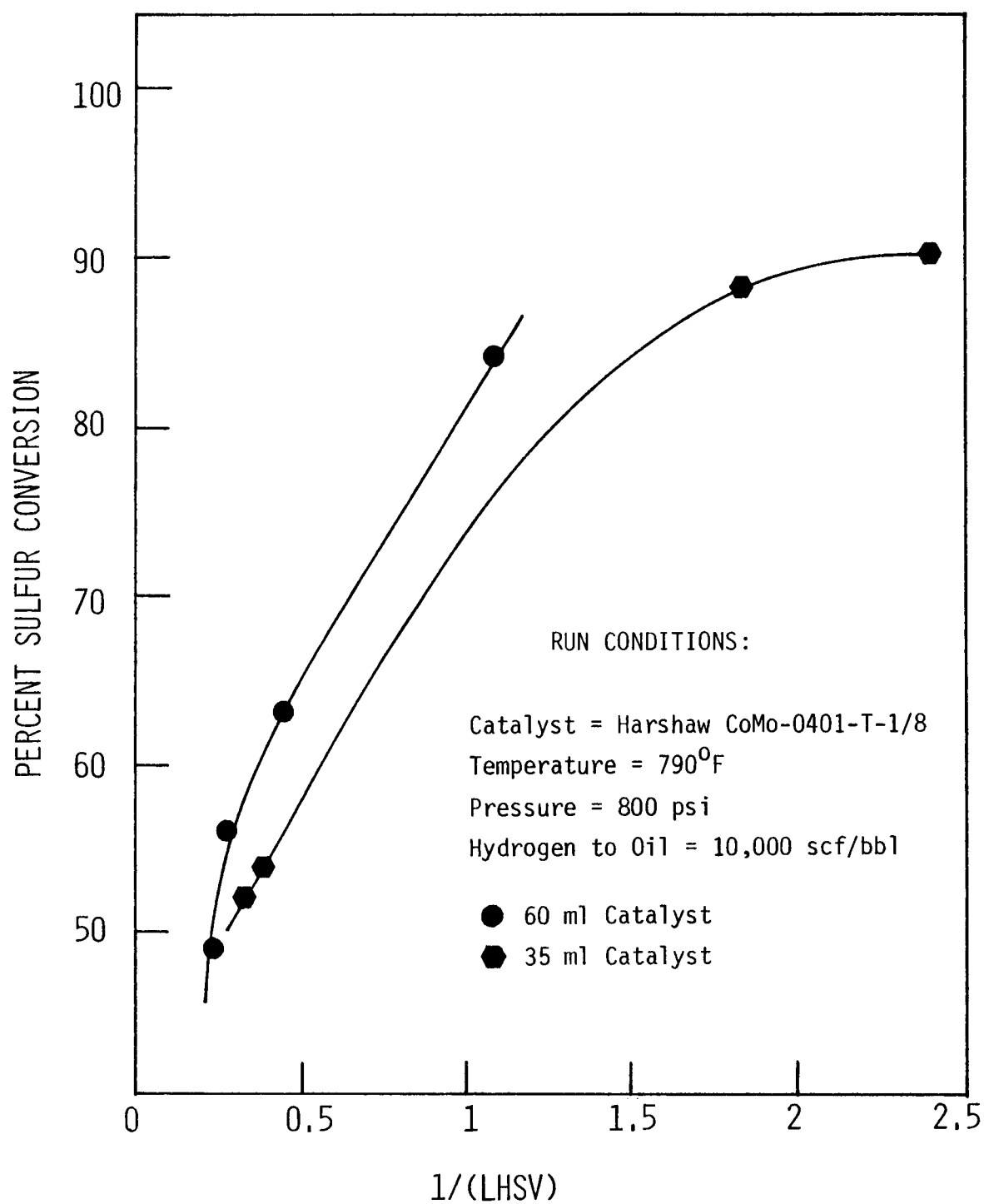


FIGURE 3.1.5 Catalyst Surface Diffusion Test Result
(Berg, Lloyd and McCandless, F.P., 1975,
1976a, 1976b, 1976c, 1976d, 1977a, 1977b,
1977c, 1977d)

space velocity of approximately 2.0, the two curves begin to coincide indicating that the effects of external diffusion on sulfur removal starts to become insignificant at this space velocity and run temperature. But at lower space velocities there is a significant difference in sulfur removal.

It was also observed that:

Nitrogen and to some extent sulfur removal depends on the catalyst support and the pore size of the catalyst.

Increasing hydrogen flow relative to the flow rate of liquid feed increases the yield of lighter products.

Sulfur removal depends on hydrogen flow rate up to a point, then stays level.

No significant increase in cracking or in desulfurization occurs by increasing the run pressure.

3.1.3 Crynes, B.L.

Crynes, B.L.(1975a, 1975b) of Oklahoma State University hydro-treated FMC COED oil to assess the rates of desulfurization, denitrogenation and the catalyst activity decay.

The sulfur and nitrogen levels of the heavy COED oil were 0.35 weight percent and 1.13 weight percent respectively. The catalyst used was Nalco 474 Sphericat (CoO 3.5 weight percent, MoO₃ 12.5 weight percent on alumina) and the operating conditions were: 700°F, 1500 psi at 3.0 volume hourly space time, and the run duration was 150 hours.

The results from product oil sample analyses are plotted in Figure

3.1.6. Sulfur levels in all of the product oil samples were at 0.02 weight percent (94 percent removal). No desulfurization activity decay could be distinguished, because of the low concentration of sulfur in product oil. Figure 3.1.6 reveals appreciable denitrogenation activity decay over the 150 hours of operation. From 60 percent nitrogen removal initially the denitrogenation activity of the catalyst dropped to 40 percent nitrogen removal.

It was also observed that sulfur removal was easy to achieve than the nitrogen removal with this catalyst.

3.1.4 Johns, J.J.

Johns, J.J. et al. (1972) working in collaboration with FMC Corporation, hydrogenated COED oils using Ni-Mo catalyst at different conditions to get synthetic crude oil to fit in with conventional refinery processing. COED oils as produced have a high density of hetroatoms and fines. The fine contents of the raw oil was reduced from 3.0 percent to less than 0.1 percent by weight, by filtration prior to hydrogenation (Analysis of feed oil in Table 3.1.9).

One somewhat unusual design feature was the use of a guard chamber type reactor ahead of the main fixed bed down flow type reactors. This was installed to eliminate plugging of the reactor by residual fine solids or coke formed by cracking of the charge stock.

The hetroatom removal of sulfur, nitrogen and oxygen compounds was essentially complete at the lower space velocity of 0.24 lb/hr/lb catalyst, 700⁰F and 2500 psi (Figure 3.1.7). A removal of up to

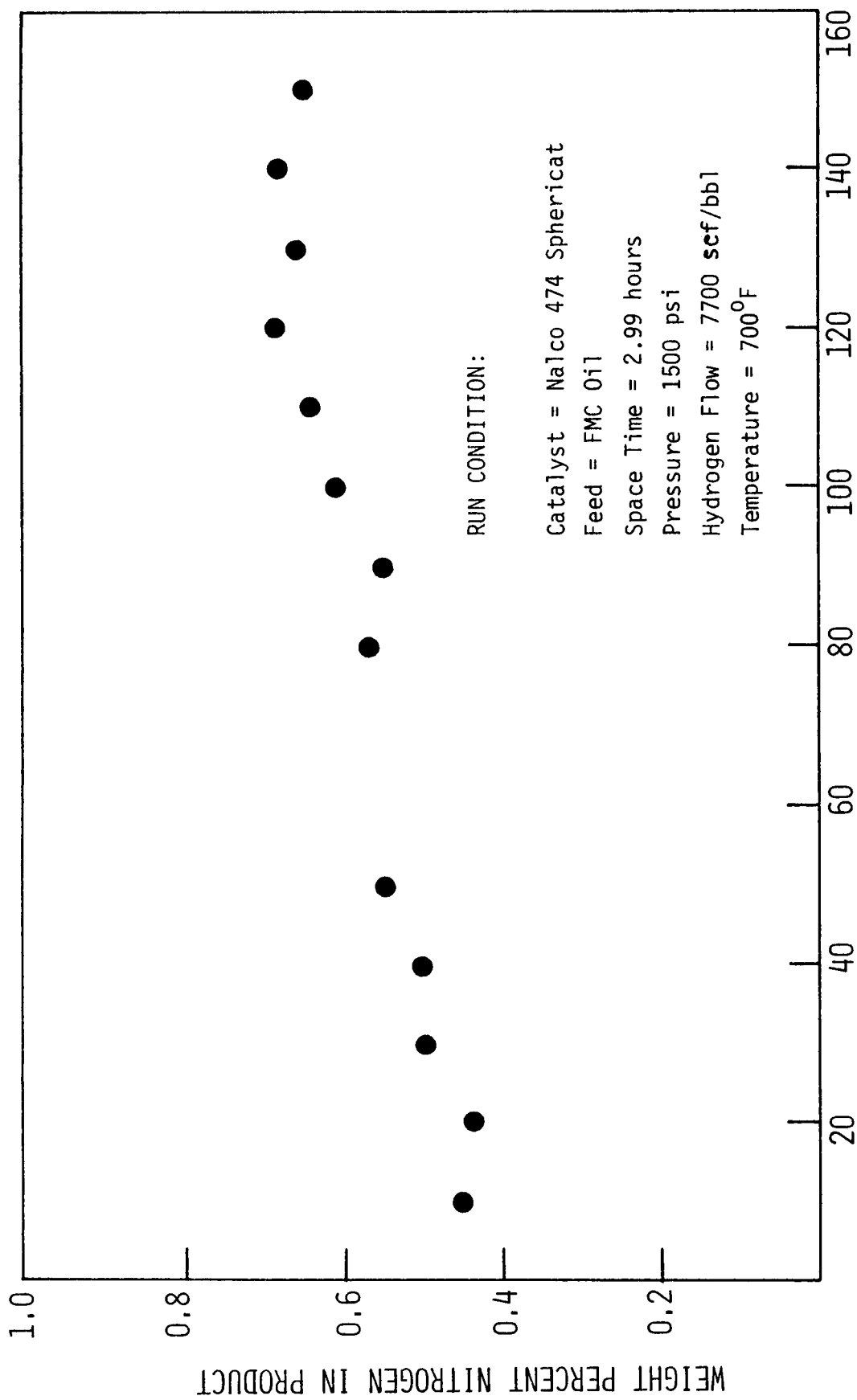


FIGURE 3.1.6 Catalyst Activity Decay (Crynes, B.L., 1975a, 1975b)

Table 3.1.9 Analysis of Feed Oil

Oil Source	Colorado Bear
Moisture wt %	0.20
Ultimate Analysis, wt % dry basis	
Carbon	83.05
Hydrogen	8.35
Nitrogen	1.10
Oxygen	0.35
Sulfur	7.15
Ash	0.0
⁰ API Gravity 60 ⁰ F/60 ⁰ F	-4 to -5
Pour Point ⁰ F	118
Flash Point ⁰ F	350
Viscosity, SUS	1090

Source: Johnson, J.J. et al., 1972

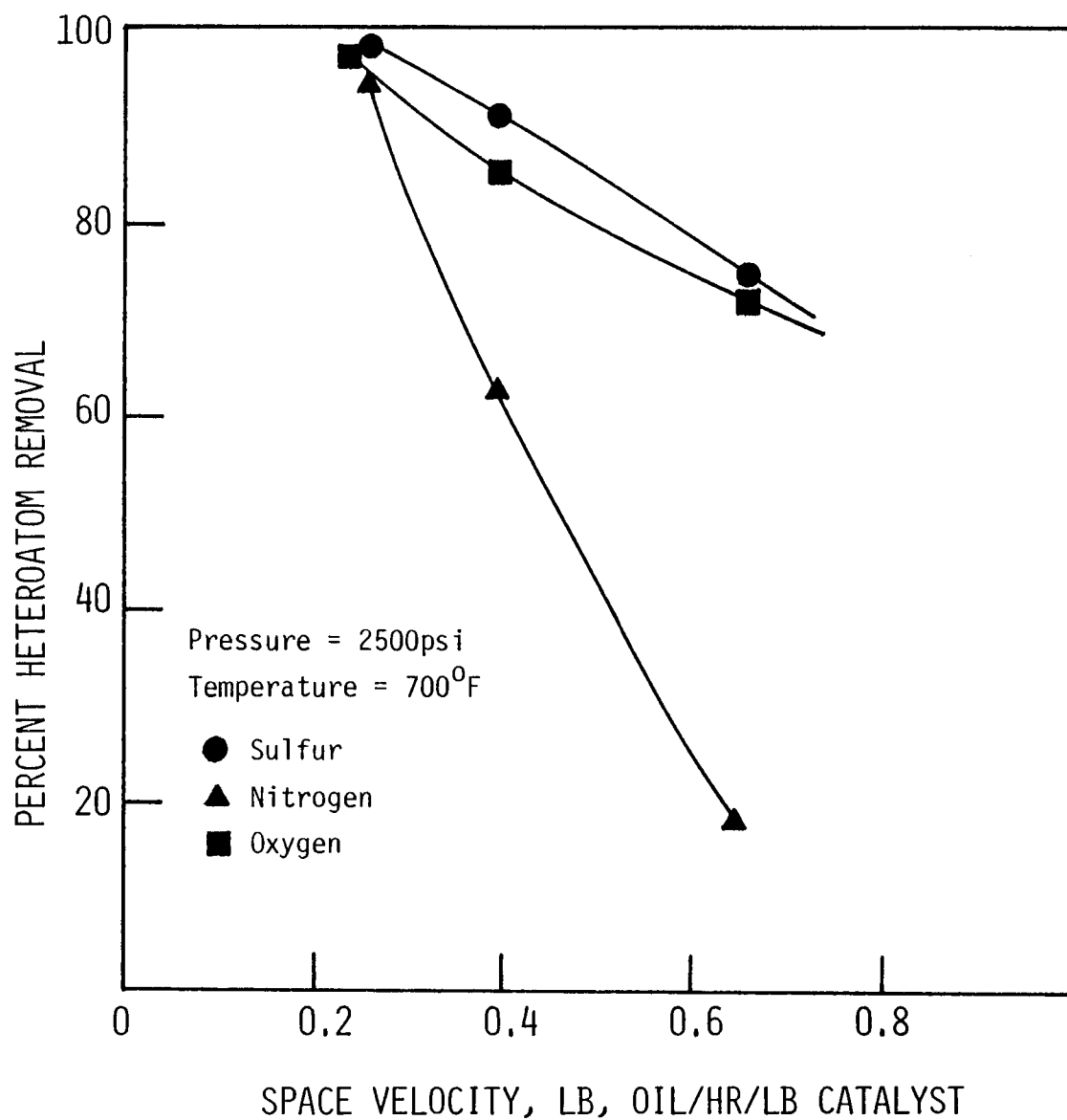


FIGURE 3.1.7 Space Velocity vs Heteroatom Removal for COED Oil (Johns, J.J. et al., 1972)

97 percent sulfur, 99 percent nitrogen and 98 percent oxygen was observed starting with sulfur, nitrogen and oxygen concentration of 7.15 percent, 1.1 percent and 0.35 percent respectively. Sulfur and oxygen were less difficult and almost identical, not only in the relative difficulty of removal, but also in the effect of change in the space velocity.

Unlike most petroleum crudes, there were very few major metallic ingredients in the COED oil. Treatment with hydrogen over a hydrogenation catalyst effectively removed iron, aluminium and silicon. Only minor effect was noted on the boron, sodium and vanadium concentrations.

Hydrotreated COED oil was distilled into several fractions. These fractions represent the conventional distillation ranges for gasoline, middle distillates, gas oil and bottoms products in conventional petroleum refining. From the inspection of these petroleum-type cuts it was obvious that hydrotreated COED oil is a satisfactory crude oil charge to a petroleum refinery and can be adequately blended into conventionally produced refinery streams. The gasoline and middle distillate stocks exhibited a high gum content. This gum can be virtually eliminated by any number of conventional refinery treating processes.

The middle distillates fraction was somewhat low in gravity, as was expected but was very high on a Btu per volume basis. The higher boiling cuts also appeared to be adaptable to conventional refining techniques. The gas oil fraction had a low carbon residue of 0.3 weight percent and metals of less than 0.2 ppm nickel and vanadium,

so it should make excellent feed for either a catalytic-cracking or hydrocracking unit. From the ultimate analysis it appeared that the residue boiling higher than 800⁰F would make excellent feedstock for a carbon black plant.

3.1.5 Jacobs, Harry

Jacobs, Harry et al. (1970) of Atlantic Richfield Company in cooperation with FMC Corporation hydrotreated COED oils obtained from three different coals over a Ni-Mo catalyst to compare the operating conditions for hetroatoms removal. The three oils tested were obtained from Utah coal (0.34 percent sulfur, 6.8 percent oxygen and 1.1 percent nitrogen), Illinois No.6 (2.5 percent sulfur, 9.1 percent oxygen and 1.1 percent nitrogen) and Pittsburgh seam (1.8 percent sulfur, 6.6 percent oxygen and 1.2 percent nitrogen). The major difference between the oils were lower sulfur, lighter density and higher hydrogen content of the Utah oil than the other two. The Illinois No.6 oil was highest in sulfur and oxygen (Table 3.1.10).

All the hydrogenation experiments were conducted at 3000 psi, hydrogen flow rates were generally between 8000 to 12000 scf/bbl. Variation in hydrogen did not have a significant effect on the hydrogenation reactions. The process variables were space velocity and temperature. The temperature ranged from 650⁰ to 850⁰F and space velocities (WHSV) of 0.3 to 3.0 lb/hr of oil per lb of catalyst were used. Hydrogen consumption was between 1500 to 4500 scf/bbl.

Nitrogen was the most difficult of the hetroatoms to be removed.

Table 3.1.10 Properties of Hydrogenation Feeds

Oil Source	% C	% H	% O	% N	% S	Density API
Utah	83.3	8.5	6.8	1.1	0.34	-3.5
Illinois No.6	80.1	7.2	9.1	1.1	2.50	-13.1
Pittsburgh Seam	83.3	7.1	6.6	1.2	1.80	-12.3

Source: Jacobs, Harry, et al., 1970

At 720°F and space velocity of 1.0 WHSV the removals from Illinois No.6 were nitrogen 72 percent, oxygen 91 percent, and sulfur 90 percent.

Comparing the results in terms of severity or space time, for nitrogen removal it was observed that the Utah oil requires only two-third the severity of the Illinois No.6 oil. The Pittsburgh oil requires twice the severity of the Illinois No. 6 oil. For oxygen removal Pittsburgh oil requires 2.5 times the severity of Illinois No.6 oil, and Utah oil needs 80 percent of the Illinois No.6 severity (Table 3.1.11).

Sulfur removal was slightly different. Pittsburgh oil needed 2.3 times the Illinois oil severity. As the sulfur content of the Utah oil feed was only 0.3 percent its removal was indicated to be more difficult than that from Illinois No. 6 oil (Figure 3.1.8).

The effect of temperature above 780°F was so overwhelming that no trends with space velocity could be obtained. Cracking of all three oils fall on a common temperature line at around 780°F. The data indicated the necessity of keeping the catalyst bed temperature below 780°F if oil was the desired product.

The °API gravity of the product varies directly with the hydrogen consumption. For example, the production of a 25°API hydrogenated oil from Utah oil needed only 2700 scf/bbl. A similar product from Illinois No.6 oil would have needed 4050 scf/bbl, and the Pittsburgh seam oil would have used 4550 scf/bbl.

The properties of the product fraction are given in Table 3.1.12. There was little, if any, residuum (material boiling above 1000°F).

Table 3.1.11 Space Velocities for 80 % Removal of Heteroatom
Conditions, 720⁰F, and 3000 psi

	80 % Nitrogen Removal WHSV	80 % Oxygen Removal WHSV	80 % Sulfur Removal WHSV
Utah	1.2	1.8	1.8
Illinois No.6	0.8	1.5	2.6
Pittsburgh	0.4	0.6	1.1

Source: Jacobs, Harry, et al., 1970

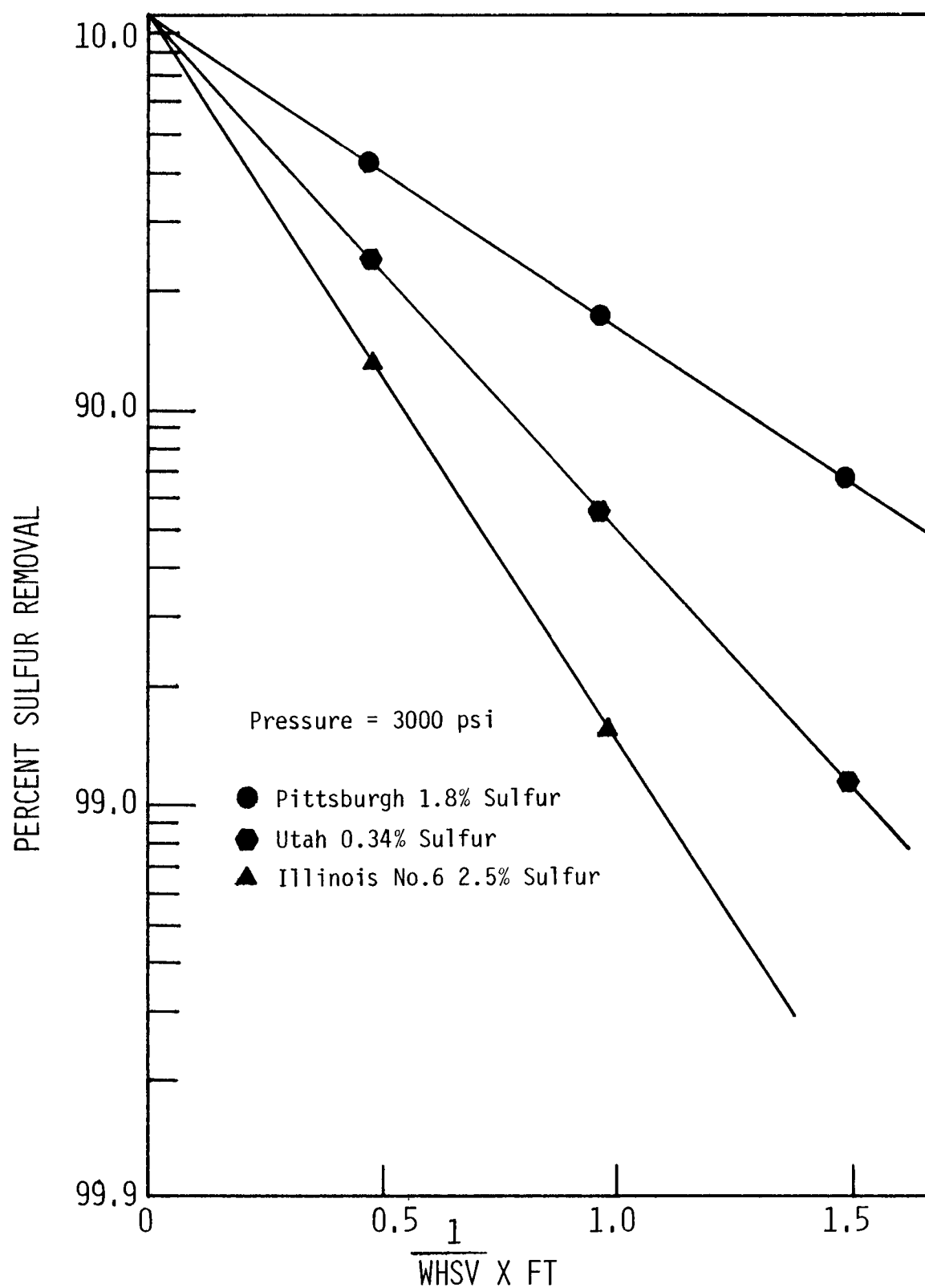


FIGURE 3.1.8 Hydrogenation of COED Coal Oils Sulfur Removal
(Jacobs, Harry, et al., 1970)

Table 3.1.12 Properties of Product COED Fractions

Oil Source	Utah	Pittsburgh
Reformer Stock (C_6 -400°F)		
Yield, Vol %	12.5	9.6
$^{\circ}$ API	38.7	37.6
Paraffins, Vol %	18.0	6.0
Cycloparaffins, Vol %	65.0	74.0
Aromatics, Vol %	17.0	20.0
Oxygen, wt %	0.06	0.47
Nitrogen, wt %	0.10	0.09
Sulfur	Trace	5 ppm
Middle Distillate (400-650°F)		
Yield, Vol %	68.2	38.9
$^{\circ}$ API	30.1	22.5
Paraffins, Vol %	25.0	1.0
Cycloparaffins, Vol %	39.0	55.0
Aromatics, Vol %	36.0	44.0
Oxygen, wt %	0.20	0.48
Nitrogen, wt %	0.06	0.12
Sulfur	Trace	30 ppm

Source: Jacobs, Harry, et al., 1970

3.1.6 Sacks, M.E.

Sacks, M.E. et al. (1969) of FMC Corporation showed that sulfur in COED char can be removed by treatment with hydrogen at 1600°C and 1 atmosphere pressure using calcined dolomite as hydrogen sulfide acceptor. Hydrogen and char from the COED pyrolysis plant plus acceptor were introduced into a heated rotary kiln type reactor, sulfur was transferred from the char to the acceptor via a hydrogen sulfide intermediate. Desulfurized char and spent or sulfided acceptor were then separated. Spent acceptor was regenerated for recycle and sulfur was recovered as by product.

Best results obtained by a calcined dolomite were, 85 percent sulfur removal in 10 minutes from Illinois No.6 seam coal char, with initial concentration of 3 weight percent sulfur.

The rate of desulfurization was found to be independent of acceptor particle size in the range of 6-mesh to minus 325-mesh size.

After desulfurization, spent acceptor was separated from desulfurized char with a fluidized separator utilizing the specific gravity difference of about 2 of acceptor, compared to about 1.0 of the char.

Several routes for the regeneration of spent dolomite acceptor were investigated including carbonation with steam and carbon dioxide and roasting in air or oxygen. The preferred regeneration scheme, however, was found to be the partial oxidation of spent acceptor with carbon dioxide.

The deactivation of dolomite acceptor after repeated cycles of

sulfurization and regeneration was studied at two different regeneration temperatures, 2100°F and 2200°F. At a regeneration temperature of 2200°F, the dolomite was rapidly deactivated. After five cycles the activity was reduced to about 10. At a regeneration temperature of 2100°F, however, the dolomite maintained an average activity of 59 through 10 cycles. It was concluded that dolomite acceptor would remain about 60 percent active through at least 10 cycles if regeneration temperatures below 2100°F were maintained.

Both capital and annual operating cost estimates for the COED char desulfurization process were prepared and it was observed that the annual return on investment, plant-level and before taxes, is highly dependent on the price of by-product sulfur. Also the estimates compare very favorably with both residual oil desulfurization and stack gas clean-up schemes.

The COED Process produces a heavy crude oil compared to the other coal liquefaction processes, also on the average the crude oil produced by this process has more of the aromatic and naphthenic compounds.

3.2 H-COAL

The H-Coal process is based on H-Oil process which was developed several years ago by Hydrocarbon Research, Inc. (HRI) for hydrotreating heavy petroleum feedstocks (Johnson et al., 1974a; Burke, 1974; Johnson et al., 1974b). The key aspect of the process is the ebullient bed reactor into which is fed a slurry of hydrogen, coal, coal liquids and catalyst. The catalyst is promoted cobalt molybdate with appropriate attrition and pore-size characteristics. The coal is hydrogenated and converted to liquid and gaseous products. Careful sizing of the coal and catalyst particles permits unconverted coal, ash, liquids and gases to leave the reactor without loss of catalyst from the reactor. Catalyst is usually added or withdrawn continuously to maintain catalyst activity. An advantage of the ebullient bed is the highly effective contacting of coal, hydrogen, liquids, and catalyst in this multiphase system.

Depending upon process conditions the H-Coal process produces either a syncrude or a low-sulfur fuel oil. Typical compositions of both product types are given in Table 3.2.1 for the liquefaction of Illinois No.6 seam coal. The conversion and product yield are about the same whether a syncrude or fuel oil is produced. However, the latter involves a lower hydrogen consumption and therefore gives a higher molecular weight product. The sulfur and nitrogen levels in the syncrude product (Table 3.2.2) are lower than those in the fuel oil.

The compositions of various fractions distilled from the H-Coal

Table 3.2.1 Product Distribution and Yield for H-Coal Liquids Derived From Illinois No.6 Seam Coal

	Product	
	Synthetic Crude	Low Sulfur Fuel Oil
Normalized product distribution		
C ₁ -C ₃ hydrocarbons	10.7	5.4
C ₄ - 400 ⁰ F distillate	17.2	12.1
400-650 ⁰ F distillate	28.2	19.3
650-975 ⁰ F distillate	18.6	17.3
975 ⁰ F-plus residual oil	10.0	29.5
Unreacted ash free coal	5.2	6.8
H ₂ O, NH ₃ , H ₂ S, CO, CO ₂	15.0	12.8
Total (100.0 + H ₂ reacted)	104.9	103.2
Conversion (%)	94.8	93.2
Hydrogen consumption (scf/ton)	18,600	12,200
Product Yield		
Wt % of M.A.F coal	74.0	78.2
Barrels per ton of M.A.F coal		
C ₄ -400 ⁰ F fraction	1.32	0.90
400-650 ⁰ F fraction	1.64	1.14
650-975 ⁰ F fraction	0.98	0.89
975 ⁰ F ⁺ residue	0.44	1.39
Total	4.38	4.32

Source: Johnson, et al., 1974a, 1974b

Table 3.2.2 Product Inspection of C₄-plus Liquids from H-Coal
Processing of Illinois No. 6 Seam Coal

	Product	
	Synthetic Crude	Low-Sulfur Fuel Oil
°API Gravity	15.0	4.4
Hydrogen, wt %	9.48	8.43
Sulfur, wt %	0.19	0.43
Nitrogen, wt %	0.68	1.05

Source: Johnson et al., 1974a, 1974b

syncrude are given in Table 3.2.3. The C_4 -400°F or naphtha fraction is highly naphthenic and contains 7.03 percent polynuclear aromatics and 0.9 percent phenols. The middle-distillate (400-650°F) fraction contains almost 60 percent aromatics which are predominantly polynuclear in character, 2 percent phenols and 3.1 percent other non-hydrocarbons. The fraction boiling at 650-919°F consists mostly of aromatics (73.3 percent). The nonhydrocarbon portion amounts to about 14 weight percent containing primarily sulfur and nitrogen compounds.

3.2.1 Peters, B.C.

Peters, Bruce C. (1976, 1977b, 1977c) of Dow Chemical Company investigated the suitability of the HRI H-Coal syncrude as a petrochemical feedstock. A sample of the whole crude (produced by Hydrogen Research, Inc from Illinois No.6 bituminous coal) was distilled into three straight run fractions; IBP-350°F naphtha, 350-550°F mid-distillate, 450-800°F vacuum gas oil. The boiling range and elemental compositions of these fractions are listed in Table 3.2.4. The fraction boiling above 800°F was considered as residue and was 56.6 percent of the crude.

The straight run mid-distillate was hydrocracked over Harshaw HT-400 E cobalt molybdenum catalyst. This catalyst was chosen for its neutral alumina support and its resistance to deactivation by nitrogen, oxygen, and sulfur in the feed. A higher ratio of normal/iso paraffins was also expected from this catalyst. Operating conditions of 2500 psi and 870-1010°F with LHSV's of 0.35 to 1.45 were surveyed. The naphtha

Table 3.2.3 Composition of Different Fractions for
H-Coal Liquids from Illinois No.6 Seam
Coal

Components	C ₄ -400 ⁰ F Wt %	400-650 ⁰ F Wt %	650-919 ⁰ F Wt %
Paraffins	11.99	6.5	1.4
Alkylbenzene	17.55	12.6	3.0
Saturated Naphthenes	51.33	24.5	5.4
Unsaturated Naphthenes	11.20	4.3	1.6
Other Aromatics	7.03	47.0	73.3
Non Hydrocarbons			
Phenols	0.90	2.0	0.0
Sulfur and Nitrogen Compounds	0.00	3.10	13.8

Source: Project H-Coal, 1967

Table 3.2.4 Boiling Range and Elemental Composition of
H-Coal Straight Run Fractions

	Naphtha IBP-350°F	Mid-Distillate 350-550°F	Vacuum Gas Oil 450-800°F
Wt % of Crude	19.8	12.1	11.5
API Gravity, 60°F	44.9	25.9	7.9
Elemental Composition			
Carbon, wt %	86.4	88.0	89.6
Hydrogen, wt %	12.9	11.2	10.4
Oxygen, ppm	390	5800	800
Nitrogen, ppm	470	440	83
Sulfur, ppm	2600	1700	1700
Boiling Range °F			
IBP	-50	217	434
10 wt %	170	366	552
20 wt %	188	378	597
30 wt %	217	395	627
40 wt %	229	408	655
50 wt %	256	417	675
60 wt %	282	432	695
70 wt %	306	449	716
80 wt %	330	471	740
90 wt %	353	500	767

Source: Peters, B.C., 1976, 1977b, 1977c

created from hydrocracking the mid-distillate was distilled off and the unconverted mid-distillate was hydrocracked a second time. Nominal requirements for 60 percent conversion to C_1 - C_9 were 2500 psi, 962°F, and 0.75 LHSV.

The straight run gas oil was hydrocracked over the same catalyst. Operating difficulties were encountered due to plugging. Operating conditions of 2500 psi, with temperatures of 840-996°F and LHSV's from 0.69 to 1.68 were surveyed. Conversions of 55.4 to 83.3 percent, 650°F minus were achieved.

Both the straight run naphtha and the combined naphthas from two pass hydrocracking the straight run mid-distillate were hydrotreated over Harshaw HT-100 E nickel molybdenum catalyst, Harshaw HT-400 E cobalt molybdenum catalyst, or Cyanamid HDS-9A nickel molybdenum catalyst. These catalysts were chosen for their resistance to deactivation by hetero-atoms in the feed and for their superior activity for denitrogenation and desulfurization. Sulfur, nitrogen, and oxygen were reduced to 4, 5, and 420 ppm respectively in two passes. The hydrocrackate naphtha was also hydrotreated in two passes. Nitrogen in the feed to the hydrotreater was less than 1 ppm due to removal during hydrocracking. Sulfur was reduced from 100 to 5 ppm and oxygen was reduced to the 50 ppm level.

The hydrotreated straight run and hydrocrackate naphthas were reformed over Cyanamid Aeroform PHF-4 platinum chloride catalyst. This catalyst was chosen as a typical example of a readily available bifunctional reforming catalyst. At 250 psi and 930-980°F, the catalyst life was very short, as the straight run naphtha rapidly coked the

catalyst. Naphthene conversion dropped from 92 percent to 67 percent. At 500 psi and 968⁰F, the hydrocrackate naphtha was reformed with a substantial increase in catalyst life. With a first day conversion of 95 percent, after 50 hours, the naphthene conversion was still at 93.5 percent.

Steam coil cracking experiments were conducted on the straight run mid-distillate and naphtha fractions to evaluate their potential as ethylene feedstocks. Due to the high aromatic content of these feedstocks, coke lay down in the reactor was a significant problem. None of the fractions surveyed was particularly attractive as feedstock for direct olefin production.

In addition to the hydroprocessing studies, each fraction was subjected to mathematical recycle hydrocracking to naphtha, hydro-treating, reforming, and hydroalkylation (HDA). As a result, each fraction was converted to methane, LPG's, benzene, and liquid fuel and the hydrogen required was also calculated. From this data, presented in Table 3.2.5 the relative value of each fraction was determined.

Based on the yield data calculated for each fraction and the weight percent of each fraction from distillation, a mass balance for a conceptual plant operating on 100.00 lb/hr H-Coal whole crude was calculated. With the flow rates and compositions of key streams known, the preliminary estimate for capital requirements and operating costs could be made. Only the naphtha and mid-distillate fractions were included in this balance, since the gas oil fraction was concluded to be economically unattractive as a petrochemical feedstock. The 12.1

Table 3.2.5 Product Patterns and Value for H-Coal
Straight Run Fractions

Processing Sequence	Straight Run		
	Naphtha IBP-350°F	Mid-Distillate 350-550°F	Vacuum Gas Oil 450-800°F
Product Pattern, wt %			
Hydrogen	-1.6	-5.4	-8.9
Methane	19.1	18.6	19.1
LPG	22.6	48.5	55.8
Benzene	51.3	36.3	32.6
Liquid Fuel	8.3	1.4	1.2
Value/100 lb Distillate (1980)	10.06	8.12	6.91
Dollars			
Processing Sequence	Hydrotreat	Recycle Hydrocrack	Recycle Hydrocrack Gas Oil
	Reform	Hydrotreat	Recycle Hydrocrack Mid-Distillate
	HDA	Reform HDA	Hydrotreat Reform HDA

Source: Peters, B.C., 1976, 1977b, 1977c

1b/hr straight run mid-distillate from distillation was recycle hydrocracked mathematically, consuming 0.53 1b/hr hydrogen and producing 0.90 1b/hr methane, 3.70 1b/hr LPG's and 8.1 1b/hr naphtha. The straight run and hydrocrackate naphthas, 19.1 and 7.5 1b/hr respectively, were hydrotreated mathematically, consuming 0.20 1b/hr hydrogen and producing 1.52 1b/hr gas. The hydrotreated naphtha was then reformed, producing 0.58 1b/hr hydrogen, 2.66 1b/hr gas and 23.28 1b/hr reformat. An in house mathematical model for hydrodealkylation was used to convert the reformat to 4.86 1b/hr methane, 2.71 1b/hr ethane, 14.52 1b/hr benzene, and 1.80 1b/hr liquid fuel, while consuming 0.82 1b/hr hydrogen. With hydrogen needs met by converting part of the methane to hydrogen in an oil fired methane reformer, overall yields from the conceptual plant in pounds per 100 pounds of crude are presented in Table 3.2.6.

Besides this conceptual plant studies a preliminary design and economic study for a commercial chemical refinery was carried out. From a chemical refinery sized to process 50,000 barrels per stream day of H-Coal derived syncrude, yields of 653 M lb/yr of ethylene and 245 M gal/year of benzene were calculated. Total annual revenues were estimated at \$447.4M (1980). Total capital investment of \$406.3M and production costs of \$371.5M per year were also calculated. For the base case, H-Coal syncrude was taken at \$16 per barrel. At that feedstock price, a return on total capital (ROI) of greater than 18 percent is realized. The results of this investigation demonstrate both the technical feasibility and economic viability of processing coal derived syncrudes for future production of petrochemical feedstocks.

Table 3.2.6 Overall Yield from Conceptual Plant
Using H-Coal Whole Crude as Feed-
Stock

Components	Yield lb/100 lb crude
Methane	4.02
LPG's	10.33
Ethane	41.98 wt %
Propane	20.76 wt %
Butane	19.04 wt %
Pentanes	18.40 wt %
Benzene	14.52
Fuel (HDA)	1.80
Fuel (Gas Oil)	11.50
Residue	56.6

Source: Peters, B.C., 1976, 1977b, 1977c

3.2.2 Kang, C.C., Johnson, E.S.

Kang, C.C. and Johnson, E.S. (1976) of Hydrocarbon Research Inc (HRI) studied the deactivation pattern of hydrocracking catalysts for H-Coal syncrudes. The H-Coal process uses a commercial Co-Mo catalyst developed originally for desulfurizing the petroleum residua. The Co-Mo selectively hydrocracks the carbon-sulfur bonds to release the sulfur as hydrogen sulfide and to terminate the carbon bond by hydrogenolysis without cracking of the carbon-carbon bond.

Critical examination of the available analytical data on fresh and used catalysts has disclosed three common causes for catalyst deactivation, namely carbon deposition, sintering, and metal deposition contribute to the deactivation of the Co-Mo catalyst. Their relative detrimental effect on the catalyst vary with the rank of coal being processed and the processing conditions.

Catalyst deactivation curves in terms of hydrogen consumption and sulfur content of fuel oil are presented in Figures 3.2.1 and 3.2.2. These curves were derived from HRI's pilot plant operations with Illinois No.6 coal. The deactivation curves are characterized by a steep initial deactivation followed by a gradual decline. The shape of the curve is typical of most catalyst deactivation curves.

The used catalyst contained 10 to 35 percent carbon. The extent of carbon deposition is affected more by process conditions than by either coal feed or catalyst age. Low pressure operations at 1000 psi yielded high carbon deposition of over 22 percent.

The Co-Mo catalysts used in the majority of experiments are

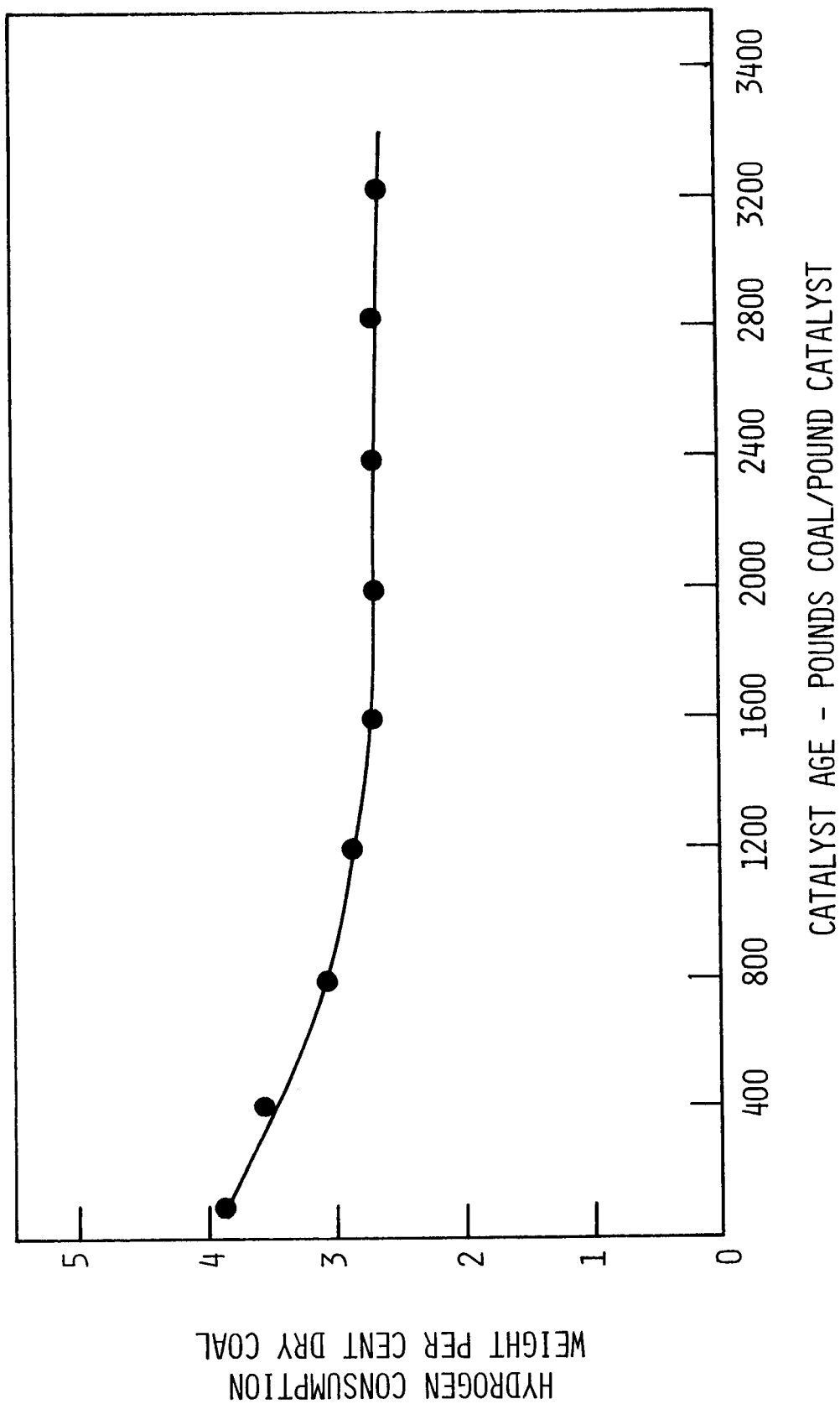


FIGURE 3.2.1 Decline in Hydrogenation Activity of Catalyst
(Kang, C.C. and Johnson, E.S., 1976)

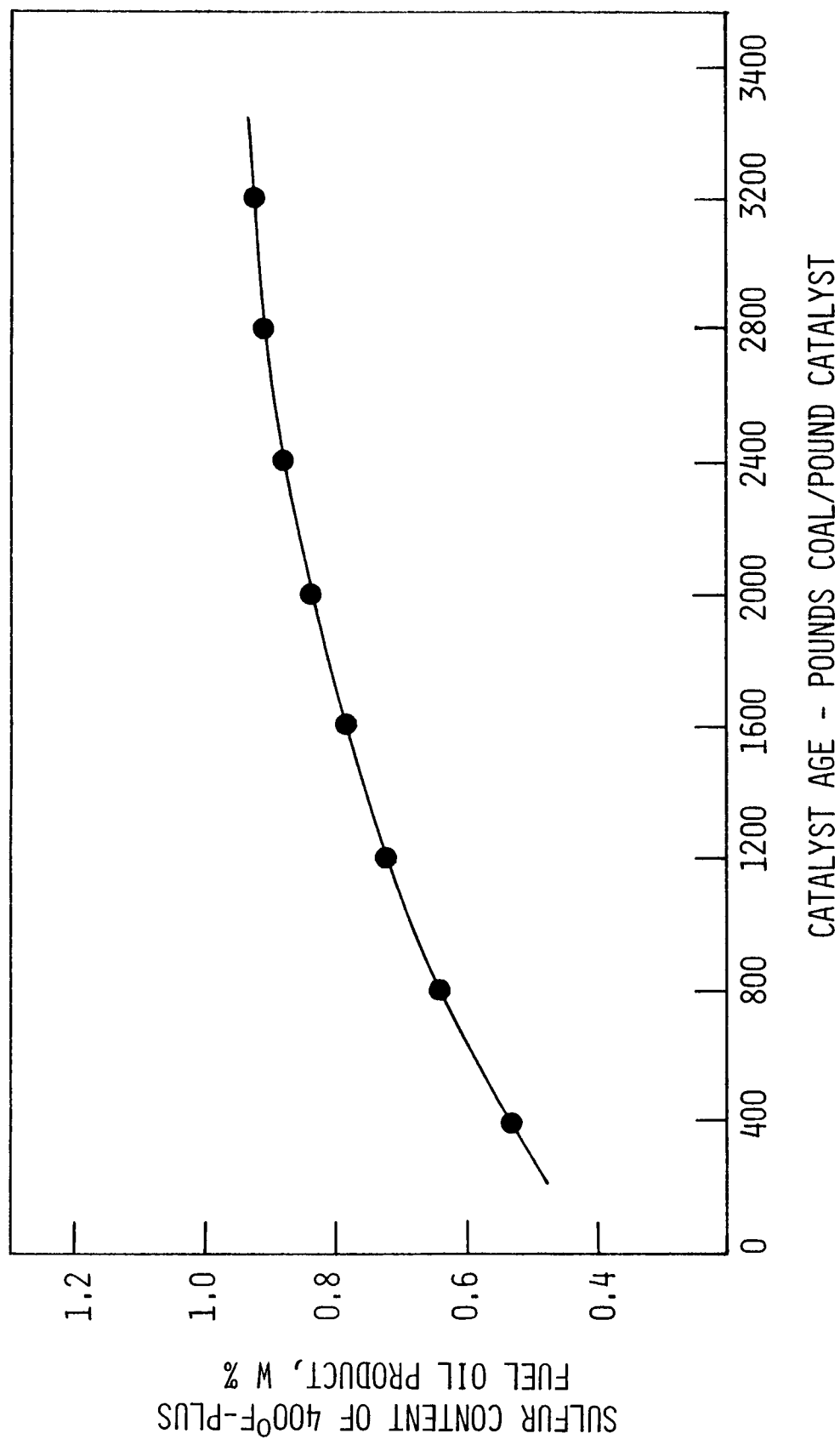


FIGURE 3.2.2 Decline in Desulfurization Activity of Catalyst
(Kang, C.C. and Johnson, E.S., 1976)

supported on gamma alumina. Gamma alumina is thermally unstable, particularly in the presence of steam. For the purpose of illustration, the effect of temperatures and steam on the sintering of a nickel on gamma alumina catalyst presented by Williams, et al. (1972) is shown in Figure 3.2.3. The presence of steam not only causes an initial drop in surface area during the first sixty hours but also enhance the long term slow rate of decline.

Operations with subbituminous coal such as Wyodak coal caused much more pronounced catalyst sintering than those using bituminous coal such as Illinois No.6 coal. The high oxygen and high moisture content of Wyodak coal give rise to a relatively high H_2O/H_2 ratio in the process gas, which caused rapid catalyst deactivation through sintering.

Major metal contaminants found on the catalyst are titanium, iron, calcium, and sodium, and in some cases also aluminium. The magnitude of titanium deposition on catalyst from bituminous coal feed increased with catalyst age. Titanium deposition was concentrated to a depth of approximately 10 percent of the radius of spent 1/16 inch extrudate, whereas iron was found in clusters on the extrudate surface. Some typical analysis of coal ash composition and major catalyst contaminants are listed in Tables 3.2.7 and 3.2.8.

3.2.3 DeRosset, A.J.

DeRosset, A.J. (1977) of UOP, Incorporated investigated the processability of the primary products of H-Coal liquefaction process. The principal process considered for upgrading was fixed bed catalytic

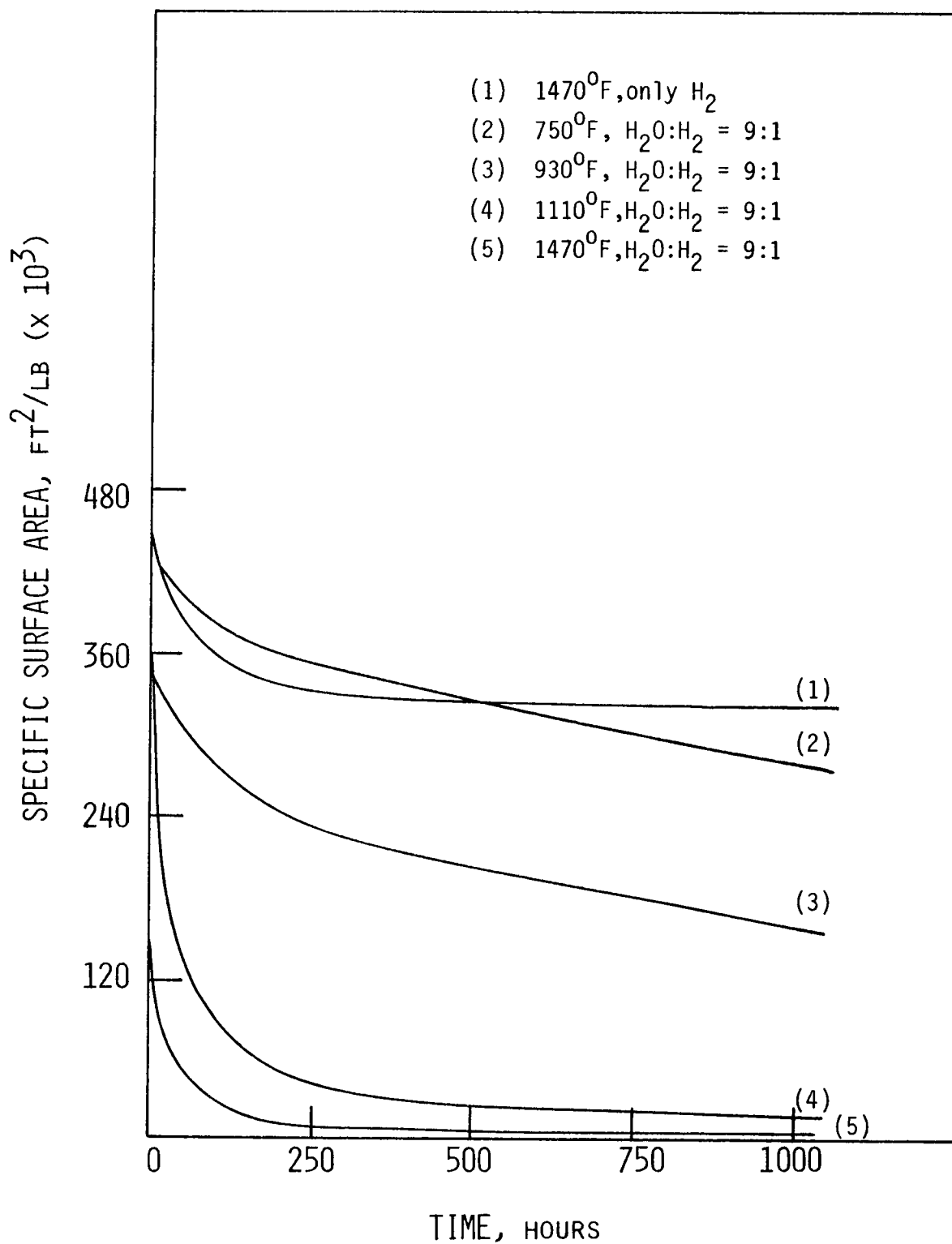


FIGURE 3.2.3 Effect of Temperature and Steam on Sintering of Gamma Alumina Catalyst (Kang, C.C. and Johnson, E.S., 1976)

Table 3.2.7 Composition of Coal Ash

Coal	Wyodak	Illinois No.6
Ash, wt %	9.73	9.95
Phosphorous Pentoxide	0.61	0.06
Silica	33.60	45.74
Ferric Oxide	3.80	16.18
Alumina	17.08	18.95
Titania	1.16	0.95
Calcium Oxide	18.50	9.50
Magnesium Oxide	4.70	0.94
Sulfur Trioxide	18.04	4.52
Potassium Oxide	0.71	1.79
Sodium Oxide	0.80	0.43
Undetermined	0.95	0.94

Source: Kang, C.C., and Johnson, E.S., 1976

Table 3.2.8 Contaminants on Used Catalysts

Coal Feed	Wyodak	Illinois No.6
Catalyst Age, lb Coal/lb Cat	781	2644
Oil Free Catalyst, Analyses, wt %		
Carbon	13.67	10.9
Sulfur	5.13	4.6
Iron	1.73	1.5
Titanium	0.03	5.11
Sodium	1.46	0.42
Calcium	1.04	0.24

Source: Kang, C.C., and Johnson, E.S., 1976

hydrotreating process. Processing was carried out in bench scale pilot plants operated continuously on a 24 hour basis. The catalyst used was a composite of Group VI and Group VII metals dispersed on a high surface area refractory support. The process conditions employed were generally in a range of commercially practiced conditions which may be categorized as "severe" were: Temperature 700-840°F, Pressure 2000-3000 psi, and Space velocity 0.25-1.0 per hour.

The feedstock H-Coal hydroclone underflow, received from Hydrocarbon Research Inc., New Jersey, contained 9.09 percent ash which necessitated filtration prior to processing in fixed bed operation. Inspections of hydroclone underflow and filtrate are given in Table 3.2.9.

One bench scale hydrotreating run was made on the laboratory filtered hydroclone underflow. The run was terminated voluntarily at 178 hours. However, toward the end of the run incipient bed plugging was evidenced by pressure surges. The residual ash in the filtrate was probably to some degree responsible.

Results are given in Table 3.2.10. Following initial periods at base conditions, space velocity was dropped to one-half base, and the heptane insoluble conversion rose to 93 percent. Response to a 18°F temperature increase was minor, and it is evident that by 136 hours catalyst deactivation was appreciable. In the final activity check periods at base conditions, heptane insoluble conversion had dropped to 76.7 percent versus 84.8 percent initial. Also, the benzene insolubles were relatively high (3.24 percent versus 0.93 percent initial).

Table 3.2.9 Inspection of H-Coal Samples

	Hydroclone Underflow	Hydroclone Underflow Filtrate
$^{\circ}\text{API}$ @ 60°F	-16.5	-17.7
Sp. Gr @ 60°F	1.2307	1.2433
Distillation (ASTM) $^{\circ}\text{F}$		
IBP	466	493
5%	533	538
10%	560	567
20%	615	621
30%	690	680
40%	770	752
50%	876	822
% Over	50	60
% Bottoms	50	40
Heptane Insoluble, wt %	49.9	49.0
Benzene Insoluble, wt %	35.0	29.0
Xylene Insoluble, wt %	15.1	0.03
Ash, wt %	9.09	0.12
Conardson Carbon, wt %	39.43	33.20
Molecular weight, average		373
Softening Point, $^{\circ}\text{F}$	172	
Pour Point, $^{\circ}\text{F}$		240
Viscosity, SFS @ 250°F	307.3	161.4
Ultimate Analyses, wt %		
Hydrogen	6.35	6.96
Carbon	79.35	87.07
Sulfur	1.43	0.66
Nitrogen	1.11	1.30
Oxygen	3.92	4.38

Source: DeRosset, A.J., 1977

Table 3.2.10 Hydrotreating Filtered H-Coal Hydroclone Underflow

Hours on Stream	Feed	20-38	54-78	92-128	136-148	166-178
WHSV/WHSV (base)		1.0	0.5	0.5	1.0	1.0
T-T (base) OF		0	0	18.0	16.0	0
P-P (base) psi		0	0	0	0	0
Heptane Insol, wt %	49.0	7.45	3.45	3.25	7.04	11.4
Heptane Insol, Converted, wt %		84.8	93.0	93.4	85.6	76.7
Benzene Insol, wt %	29.0	0.93	0.06	0.25	2.01	3.24
Ash, wt %	0.12	0.003				
Viscosity, Cst, 100°F		484.7	107.4	66.7	406.4	100.4
Sp. Gr @ 60°F	1.2433	1.0420	1.0158	1.0114	1.0486	1.0536
850°F-plus Bottoms, Vol %	46.8	34.0	28.0	25.0	34.0	36.0
Conversion to 850°F-minus, Vol %		27.4	40.2	46.6	27.4	23.1
Ultimate Analyses, wt %						
Hydrogen	6.96	9.33	9.56	9.32	8.84	8.77
Carbon	87.07	89.87	89.48	89.59	90.20	89.70
Sulfur	0.66	0.03	0.02			
Nitrogen	1.30	0.47	0.17	0.22	0.33	0.59
Oxygen	4.38	0.59	0.39			
Nitrogen in 850°F-minus Distillate, wt %		0.17	0.05	0.09	0.22	0.21

Source: DeRosset, A.J., 1977

3.2.4 Stein, T.R.

Stein, T.R. et al. (1977) of Mobil Research and Development Corporation hydrotreated two different fractions of H-Coal liquid over three different catalysts. The objectives of the research were as follows:

- . Evaluation of commercial catalysts and hydroprocessing conditions for decreasing the aromatic, nitrogen, sulfur and oxygen content of coal liquids derived from the H-Coal process.
- . Development of kinetic model for predicting the hydrogen and heteroatom content of processed coal liquids as a function of processing severity. (The kinetic model is presented in Section 4)

Batch hydrogenation studies conducted in a shaker bomb reactor showed that catalytic hydrogenation is an effective means of lowering the heteroatom concentration and increasing the hydrogen content of the coal derived liquids. On the basis of batch test results catalysts were selected for continuous fixed bed hydrotreating operation. The fixed bed reactor used was 7/8 inch ID steel pressure vessel with a capacity of 6.1 to 18.3 cubic inches. The reactor was enclosed in an aluminium heating block for uniform distribution of heat.

The catalysts tested were HDS-1441A (MoO_3 13.8 percent, CoO 2.8 percent, and SiO_2 3.5 percent), Ketjen 153 S (Ni 3.1 percent, MoO_3 15.1 percent, and SiO_2 5.0 percent), and HDS-20 (MoO_3 17 percent, CoO 5.9 percent, and SiO_2 0.21 percent). A mixture of 6.1 cubic inches of catalyst and 2.44 cubic inches of sand were charged to the reactor for every run. The sand dilution was found to give more consistent results. The catalyst was sulfided at 500 psi with a hydrogen stream containing 2 percent H_2S .

A hydrogen flow of 3000-8000 scf/bbl in excess of the consumption was maintained throughout each run. Total hydrogen consumption was determined by making a hydrogen balance around the unit. Hydrogen utilization was calculated for the material balance from the C_1 - C_5 gas make and H_2S , NH_3 and H_2O yields. The hydrogen consumed by the C_6 -plus liquid fractions was calculated by difference.

Four separate distillation fractions were received from the H-Coal Process Development Unit. These consisted of two samples of atmospheric overhead, and two samples of atmospheric bottoms, obtained from Illinois No.6 Burning Star coal. One set of sample (overhead and bottoms) was obtained when the mode of operation of H-Coal plant was to produce fuel oil, and another set of sample (overhead and bottoms) was obtained when the mode of operation for H-Coal plant was to produce syncrude. The analysis of these samples is given in Table 3.2.11. The coal liquid used for hydrotreating was obtained by mixing these samples.

The Fuel Oil H-Coal Distillate material was prepared by blending 60.7 percent by weight Atmospheric Overhead Fuel Oil with 39.3 percent by weight Atmospheric Bottom Fuel Oil. The Syncrude H-Coal Distillate was prepared by blending the $320^{\circ}F$ -plus atmospheric overhead (63.3 percent by weight) with the atmospheric bottoms (36.7 percent by weight) obtained from H-Coal plant operating in syncrude mode.

The Fuel Oil H-Coal Distillate was hydrotreated with HDS-1441A (Co-Mo) catalyst over a range of operating conditions: e.g., Temperature 672 - $786^{\circ}F$; Pressure 800-2500 psi; LHSV 0.44-4.09 per hour. This range of conditions included runs at low severities in terms of

Table 3.2.11 Analysis of H-Coal Fraction

	H-Coal Overhead (Fuel Oil)	H-Coal Bottoms (Fuel Oil)	H-Coal Overhead (Syncrude)	H-Coal Bottoms (Syncrude)
Ultimate Analyses, wt %				
Carbon	87.19	88.67		
Hydrogen	11.99	9.43	11.27	8.64
Oxygen	1.00	1.20	1.40	1.10
Nitrogen	0.20	0.42	0.44	0.41
Sulfur	0.26	0.12	0.24	
ASTM Distillation, °F				
IBP	20	315	71	275
5 %	170	369	159	420
10 %	186	391	192	440
20 %	213	430	251	470
30 %	264	457	300	494
40 %	300	486	332	516
50 %	332	516	361	533
60 %	358	549	381	563
70 %	390	581	402	588
80 %	409	629	432	634
90 %	447	694	469	676
95 %	475	740	507	722
End Point	584	851	808	890

Source: Stein, T.R. et al., 1977

pressure and space velocity, and also runs at high severities in terms of the same variables. The degree of product upgrading can be summarized by comparing the H-Coal feed with the product from the highest and lowest severity runs. This is illustrated in Table 3.2.12.

The total hydrogen consumption ranged from 65 to 1698 scf/bbl of charge. Figure 3.2.4 shows the hydrogen consumed for heteroatom removal, C_1 - C_3 gas make, and C_6 -plus liquid hydrogenation as a function of total hydrogen consumed. Figure 3.2.5 shows the hydrogen consumption for specific heteroatom removal.

Compared to the data reported above for HDS-1441A the results with Ketjen 153 S catalyst showed 100-260 scf/bbl more hydrogen consumption and consistently lower nitrogen level in the liquid product at the same operating severities. However, the oxygen and sulfur levels were equivalent for the two catalysts.

The syncrude H-Coal Distillate was slightly lower in hydrogen and higher in heteroatom content than the Fuel Oil H-Coal Distillate charge. Both distillates, generally, were upgraded proportionately for any given hydroprocessing severity.

Table 3.2.12 H-Coal Distillate Fixed Bed Hydroprocessing

Severity Level	Charge	Low	High
Process Conditions			
Pressure, psi		1200	2500
Temperature, °F		673	770
LHSV, per hour		4.06	0.46
Hydrogen Consumption, scf/bbl		65	1698
Liquid Product Properties			
C ₆ -plus Liquid Yield, wt %	100.0	99.26	97.57
Gravity, °API	18.6	20.0	26.2
Hydrogen, wt %	10.14	10.22	12.36
Sulfur, wt %	0.11	0.04	0.01
Nitrogen, wt %	0.38	0.28	0.005
Oxygen, wt %	1.20	0.90	0.10
Kinematic Viscosity @ 100°F, cs	3.41	2.56	1.82

Source: Stein, T.R. et al., 1977

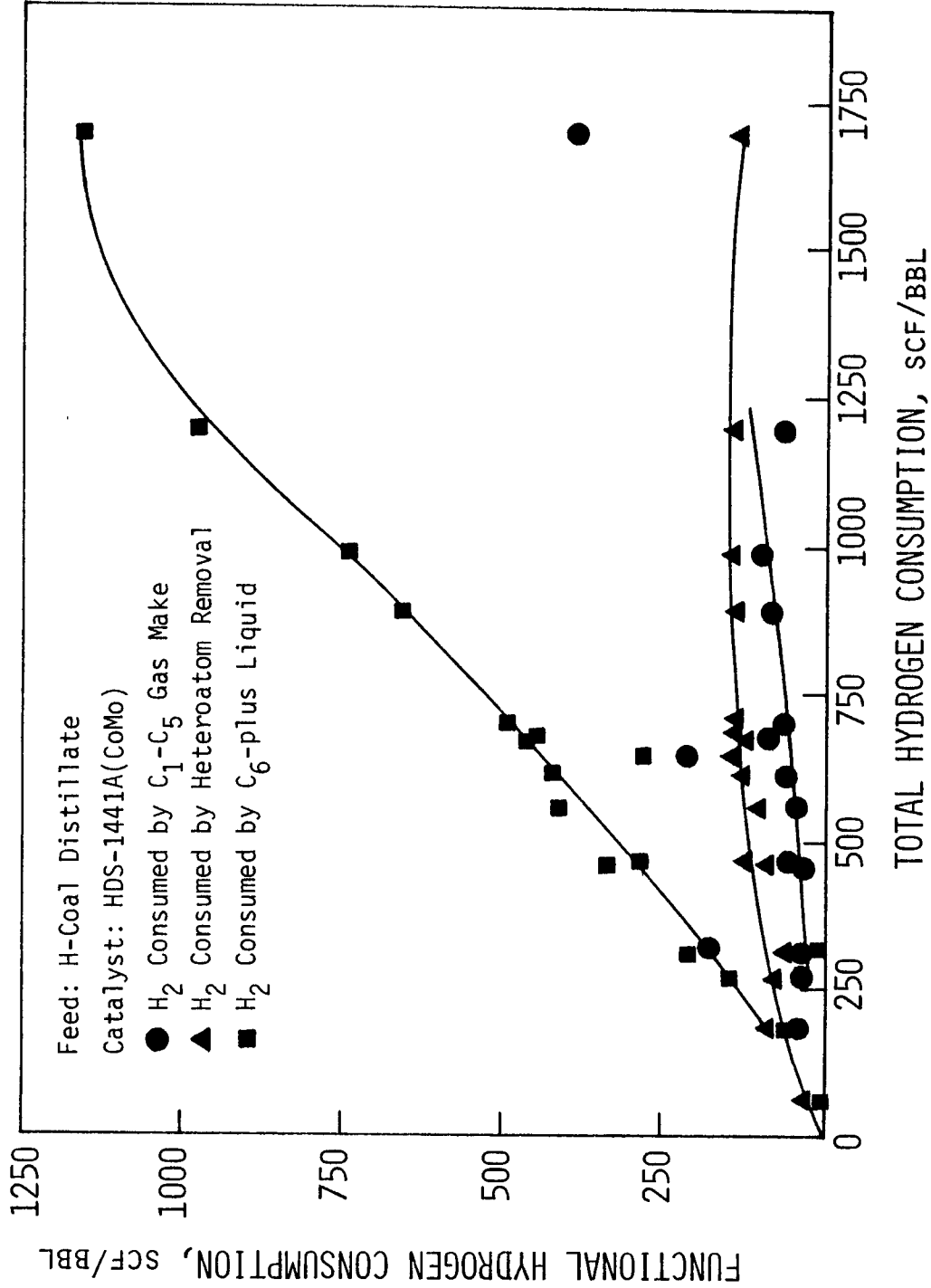


FIGURE 3.2.4 Hydrogen Utilization in Hydroprocessing of H-Coal Distillate
(Stein, T.R. et al., 1977)

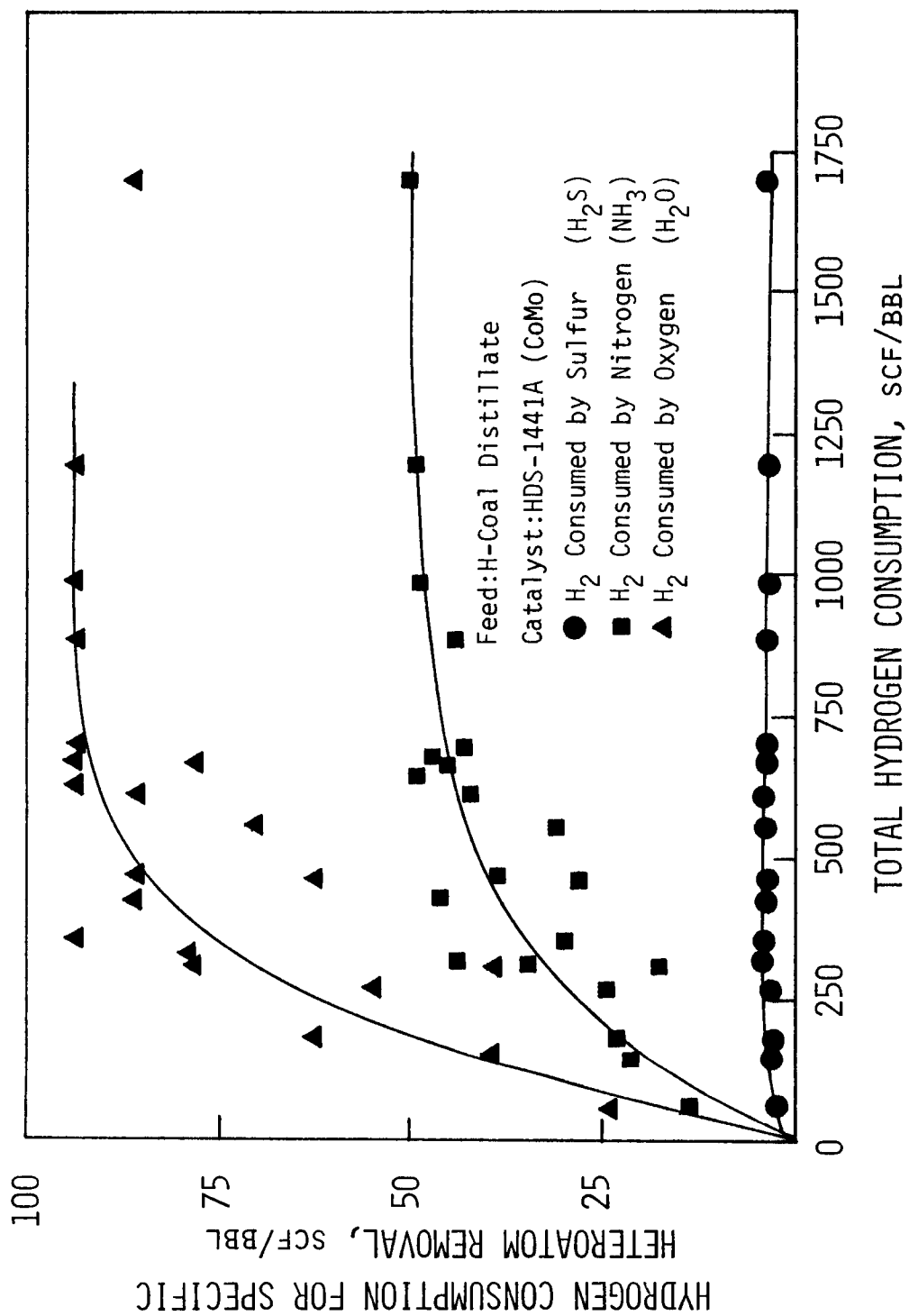


FIGURE 3.2.5 Hydrogen Consumption for Heteroatom Removal from H-Coal Distillate
(Stein, T.R. et al., 1977)

3.3 SYNTHOIL

In the synthoil process coal is slurried in a recycled aromatic oil and flowed, together with hydrogen, at highly turbulent conditions through a fixed bed of cobalt molybdate catalyst (Yavorsky et al., 1975; Friedman et al., 1974; Yavorsky, 1973; Akhtar et al., 1974a; Yavorsky, 1972; Akhtar et al., 1974b). Depending upon the conditions of operation, either a heavy or a light low-sulfur fuel oil is produced. Coal conversion levels of 90-98 percent are common (Yavorsky et al., 1975). As an example, a Kentucky coal with 5.5 percent sulfur and 16 percent ash can be converted to an oil which flows at room temperature and has 0.2 weight percent sulfur, 0.8 weight percent nitrogen, and 0.2 weight percent ash. Process conditions are usually either 2000 or 4000 psi at 840⁰F, depending upon whether the desired product is a light or heavy oil. Usual contact time is 2 min. Oil yields are about 3 bbl/ton of coal with a hydrogen consumption of 4000-5000 scf/bbl of oil, depending upon product quality.

A unique feature of this process is that the ash in the coal causes controlled attrition of the catalyst surface thereby minimizing deposition of mineral matter and carbon. The ash is ultimately separated from the coal liquids by centrifugation.

A study of Woodward et al. (1976) reports on the characteristic constituents of synthoil liquids produced from a West Virginia Pittsburgh seam coal at 4000 psi and 840⁰F by passing hydrogen gas and a 35 weight percent coal slurry in recycle oil at 25 lb/hr through a 14.5-ft-long synthoil reactor containing 1/8 in pellets of cobalt molybdate on

silica-stabilized alumina. The product was a brownish-black liquid with a specific gravity of 1.081, containing 0.79 weight percent of nitrogen and 0.42 weight percent of sulfur. Comparison of the synthoil syncrude with that produced by the COED process from Utah coal (Dooley et al., 1975) and western Kentucky coal (Sturm et al., 1975) showed the synthoil product to be much heavier, and containing a considerably greater amount of carbon residue in both the residuum and total crude oil (Woodward et al., 1976). The synthoil product had higher nitrogen content and substantially more sulfur. The nitrogen and sulfur compounds of the synthoil liquids are concentrated in the heavy ends.

Additional data comparing synthoil coal liquids and COED coal liquids from three different coals are given in Table 3.3.1. Although the starting coals vary in physical and chemical properties, some useful general points can be made. The West Virginia and western Kentucky coals are somewhat similar in overall properties. The concentrations of saturates is lower in the middle and heavy synthoil fractions compared to the corresponding values for the COED liquids. The concentration of monoaromatics in the 685-988⁰F fraction of the synthoil fraction contained 64 percent aromatics with more than one ring while the similar COED fractions contained 43-44 percent. For comparison, it may be noted that the corresponding petroleum distillate fractions contain 17-21 percent polynuclear aromatics (Woodward et al., 1976).

These differences are mentioned to indicate the diversity of composition which can be found among the syncrudes produced from various coals using various coal liquefaction process. It would be of

Table 3.3.1 Comparison of Distillates (wt. percent) of Similar Boiling Range Fractions for Three Syncrudes Produced by the Synthoil and COED Process

Boiling Range (°F)	Synthoil		COED		
	West Virginia Coal	405-685°F	685-988°F	Western Kentucky Coal	Utah Coal
			400-716°F	716°F ⁺	400-716°F
Saturates	30.3	16.0	9.7	25.0	23.8
				27.8	25.8
Monoaromatics	27.6	27.3	4.7	42.0	25.1
				25.1	14.4
Diaromatics	3.2	21.6	22.6	13.0	24.3
				17.5	18.4
Polynuclear Aromatics		7.9	41.1	5.4	20.0
				7.1	25.1
Heteroatomics	35.3	22.2	15.6	4.4	4.5
				15.2	7.4
Distillate wt % of Syncrude		42.6	27.3	54.2	24.2
				45.4	40.3

Source: Woodward, et al., 1976

interest, in this respect, to liquefy a given seam of coal using the various conversion processes to ascertain the exact differences in composition due primarily to processing variations.

The physical properties of three primary fractions boiling below 405⁰F, 405-685⁰F, and 685-988⁰F are summarized in Table 3.3.2.

The 405⁰F minus fraction contained 35.3 weight percent acids which were almost entirely phenols, 27.1 percent paraffins and cycloparaffins, and 30.8 percent aromatics.

3.3.1 DeRosset, A.J

3.3.1.1 DeRosset, A.J. (1976c)

DeRosset, A.J. (1976c) hydrotreated synthoil to characterize the processability of the feed by conventional petroleum refining technology. Hydrotreating was carried out over a range of process conditions. In addition to the process variable study, a preparative run was made to produce 15 gallons of hydrotreated synthoil to be used as feedstock in hydrocracking studies.

The centrifuged synthoil as received contained 1.4 percent ash and was filtered without solvent dilution at 320⁰F. Water washing became necessary after the first run, when the hydrotreating reactor was plugged by ammonium chloride. Water washing decreased the chloride concentration in filtered synthoil from 438 ppm Cl to 10 ppm Cl, also the nitrogen content of synthoil dropped from 1.46 percent to 1.31 percent.

Three bench scale hydrotreating runs were made on pretreated synthoil Commercial hydrotreating conditions, which may be categorized

Table 3.3.2 Physical Property Data for Three Distillates from
West Virginia Coal Liquid

Property	405°F Distillate	405-685°F Distillate	685-988°F Distillate
Specific Gravity at 60/60°F	0.936	0.990	1.109
Gravity (°API)	19.7	11.4	
Pour Point, °F	5	5	
Color (BuMines description)	Brownish black	Brownish black	Greenish black
Kinematic viscosity (100°F, cs)	2.27	9.56	
Saybolt viscosity (SUS, 100°F)	34	57	
Sulfur (bomb), wt %	0.20	0.30	0.44
Nitrogen (Kjeldahl), wt %	0.423	0.724	1.187
Carbon residue (Conardson), wt %	1.29	2.33	7.42

Source: Woodward, et al., 1976

as "severe," were used. At base conditions a conversion of heptane-insolubles of 77.4 percent was observed, which decreased to 67.1 percent with twice the base space velocity and base temperature and pressure. The nitrogen conversion by hydrotreating at base conditions was 66 percent.

A comparison of synthoil and SRC filter feed with respect to response to hydrotreatment at similar operating conditions showed that the heptane insolubles in UOP filtered SRC filter feed was more easily converted than those in synthoil; their removal was first order up to 98 percent conversion; and the effect of pressure was relatively small (Figure 3.3.1).

The heptane-insolubles in synthoil was more refractory; their removal was not first order; and low pressure operation was disadvantageous. These observations extend, for the most part to organic nitrogen, also.

The reason for the difference was not clear. Both feed stocks contained ample solvent to donate hydrogen if needed. Quite possibly the variation in sources of coal used to prepare synthoil and SRC samples, can account for the difference in their response to hydrotreating.

For catalyst deactivation test a run of 436 hours duration was made at a single set of conditions, after an initial set of conditions, after an initial deactivation catalyst showed reasonable stability (Figure 3.3.2).

The operating conditions of temperature pressure and space velocity are reported in a coded form, so it is not possible to derive

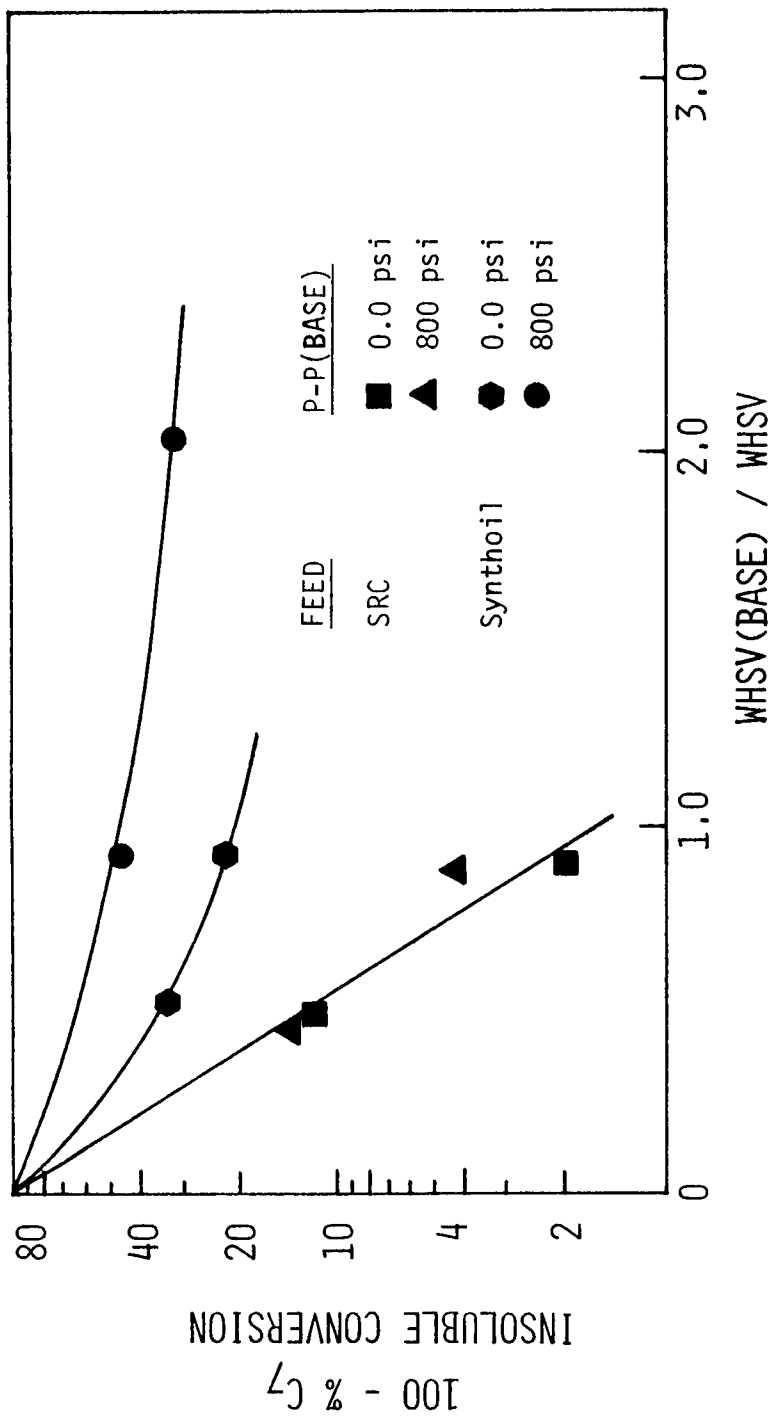


FIGURE 3.3.1 Comparison of Conversion of C₇-insolubles in SRC and Synthoil Derived Stocks (DeRosset,A.J.,1976c)

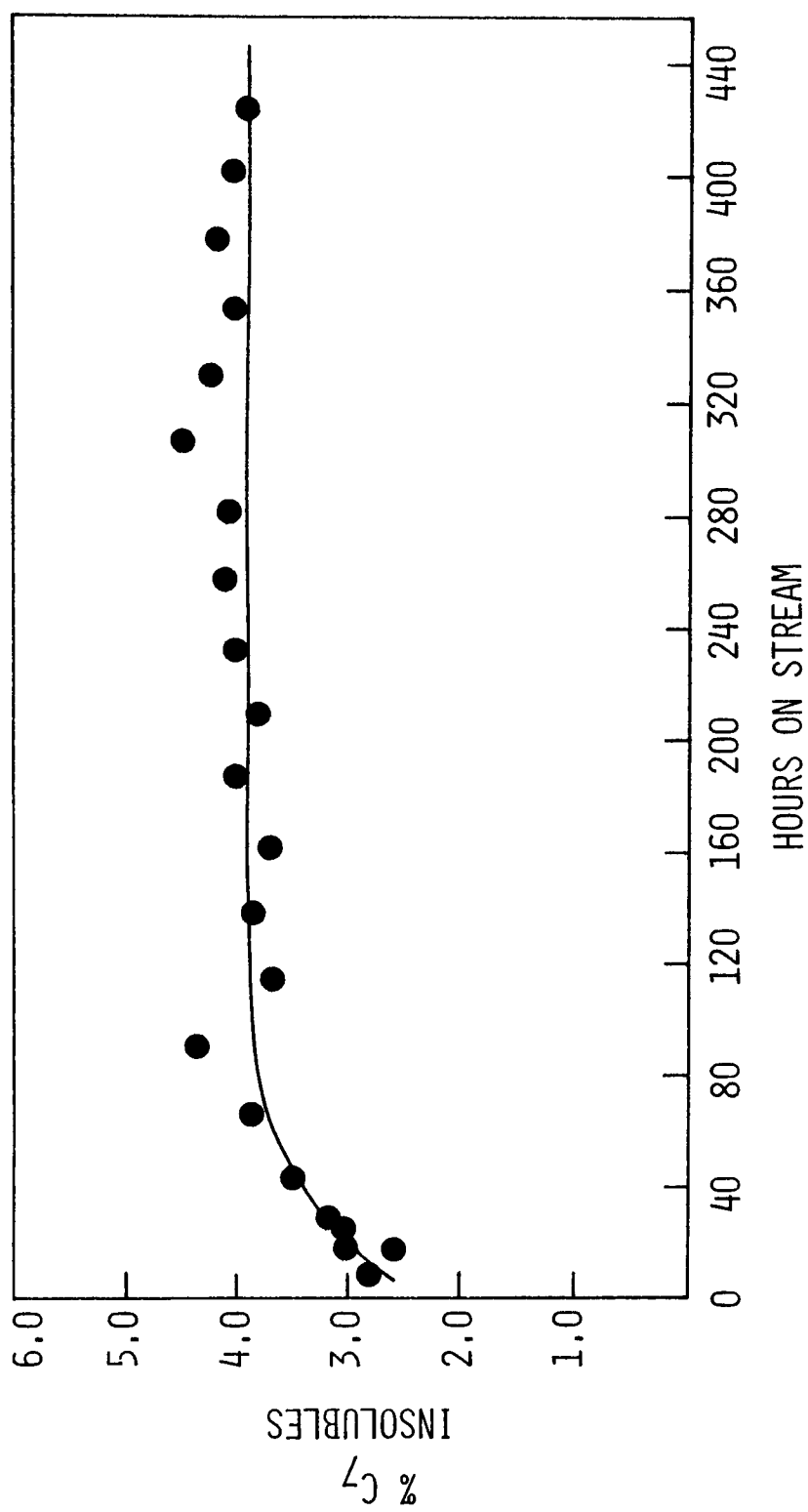


FIGURE 3.3.2 Residual C₇-Insolubles vs Time (DeRosset, A.J., 1976c)

any correlations from the reported data.

3.3.1.2 DeRosset, A.J. (1976e)

DeRosset, A.J. (1976e) also processed the hydrotreated synthoil containing 3.9 percent heptane-insolubles and 59.3 percent 650⁰F plus bottoms, over a commercial hydrocracking catalyst at commercially feasible conditions (DeRosset, A.J., 1976e). Conversion, defined as percentage disappearance of 650⁰F-plus bottoms, was measured as a function of operating variables. At 63⁰F above base temperature, 200 psi above base pressure, and 0.8 times base space velocity, conversion was 35.6 percent. Non-catalytic (thermal) conversion, measured under the same conditions, was 18.9 percent.

Vacuum flashing the hydrotreated synthoil yielded 60 percent of 600-950⁰F distillate containing 66.2 percent of 650⁰F-plus bottoms. This was hydrocracked catalytically. At base space velocity, 18⁰F above base temperature, and 200 psi above base pressure, conversion was initially 59.8 percent, dropping to 50.2 percent after 76 hours of operation. A 18⁰F temperature increase raised conditions at 146 hours gave only 49.7 percent conversion, also the product hydrogen content dropped from an initial value of 11.5 percent to 10.99 percent, and the API gravity of the product decreased from 21.9 to 17.6. It showed a significant loss in catalyst activity. It was also observed that after an initial drop, the catalyst activity lined out.

3.3.2 Peters, B.C.

Peters, Bruce C. (1977d) of Dow Chemical Company investigated the suitability of the USBM Synthoil product as a petrochemical feedstock.

The sample of synthoil subjected to the hydroprocessing experiments was produced in the Pittsburgh Energy Research Center from West Virginia Coal. The source was Pittsburgh seam from the Ireland Mine. The oil was made using the nominal 1000lb/day unit with a 14.5 foot long catalytic reactor. Conditions were 4000 psi, 842⁰F, feeding 35 percent solid slurry in lined-out, coal-derived oil at 25 lb per hour. The catalyst was 1/8" pellets of cobalt molybdenum on silica alumina, Harshaw No. 0402T. The process product yield, based on dry coal, was estimated at 59.3 percent by weight. The material had an API gravity of approximately 0⁰ at 60⁰F, had a viscosity of 30 SSU at 180⁰F, contained about 40 percent asphaltenes, and had a boiling range between 350 and 800⁰F.

An attempt was made to hydrogenate the full range synthoil with a Cobalt-Moly on alumina catalyst. The objective was to reduce molecular weight (boiling range). Little conversion of synthoil was obtained at 2000 psi and 860⁰F. No net mid-distillate was produced. Asphaltene conversion was 37 percent.

In order to parallel existing processing technology for producing petrochemicals from crude oil, the following processing sequence was followed for the USBM Synthoil:

- Distillation into nominally two cuts:

350⁰F-650⁰F (straight run mid-distillate)

650⁰F-plus (residue)

- Hydrocracking of the mid-distillate to produce naphtha with some LPG's.
- Hydrotreating of the hydrocrackate naphtha to remove the hetero-atoms.
- Reforming of the hydrotreated naphtha to produce maximum yields of aromatics.

The yield for mid-distillate by distillation was 34 weight percent while the residue (650⁰-plus) was 66 weight percent. Elemental composition of mid-distillate is listed in Table 3.3.3.

The straight run mid-distillate was hydrocracked over Harshaw HT-400 E cobalt molybdenum catalyst. This catalyst was chosen for its neutral alumina support and its resistance to deactivation by nitrogen, oxygen, and sulfur in the feed. A higher ratio of normal/iso paraffins was also expected from this catalyst. Operating conditions of 1500-2500 psi and 920-950⁰F with LHSV's of 0.62 to 1.47 were surveyed. The naphtha created from hydrocracking the mid-distillate was distilled off and the unconverted mid-distillate was hydrocracked a second time. Nominal requirements for 60 percent conversion to C₁-C₉ were 2500 psi, 941⁰F, and 0.75 LHSV. The boiling range and gravity data for first pass hydrocracked synthoil is given in Table 3.3.4.

The combined naphthas from two-pass hydrocracking the straight run mid-distillate were hydrotreated over Cyanamid Aeroform HDS-9A nickel molybdenum catalyst. This catalyst was chosen for its resistance to deactivation by heteroatoms in the feed and for its superior activity for denitrogenation. Sulfur was reduced from 30 to 1 ppm, oxygen from 5100 to 80 ppm, and nitrogen from 50 to 9 ppm in the hydrotreating step.

Table 3.3.3 Elemental Composition of Synthoil Straight Run Fraction

	Mid-Distillate 350-650°F
Wt % of crude	34.0
API Gravity, 60°F	10.5
Elemental Composition, wt %	
Carbon	86.3
Hydrogen	9.3
Oxygen, ppm	33000
Nitrogen, ppm	7400
Sulfur, ppm	2800

Source: Peters, B.C., 1977d

Table 3.3.4 Boiling Range and Gravity Data for First Pass
Hydrocracked Synthoil Mid-Distillate

	Mid-Distillate 350-650°F	Hydrocracked Mid-Distillate
API Gravity, 60°F	10.5	32.8
Elemental Composition, wt %		
Carbon	86.3	
Hydrogen	9.3	
Oxygen, ppm	33000	
Nitrogen, ppm	7400	
Sulfur, ppm	2800	
Boiling Range from Simulated Distillation, °F		
IBP	359	330
10 wt %	425	365
20 wt %	462	389
30 wt %	489	399
40 wt %	515	412
50 wt %	542	436
60 wt %	569	456
70 wt %	596	484
80 wt %	622	513
90 wt %	653	541

Source: Peters, B.C., 1977d

The hydrotreated hydrocrackate naphtha was reformed over Cyanamid Aeroform PHF-4 platinum chloride catalyst. This catalyst was chosen as a typical example of a readily available bifunctional reforming catalyst. At 500 psi and 964⁰F, the hydrocrackate naphtha was reformed with a first day conversion of 95.3 percent. After 70 hours, the naphthene conversion was still at 92.6 percent.

In addition to the hydroprocessing studies, the mid-distillate was subjected to mathematical recycle hydrocracking to naphtha, hydrotreating, reforming, and hydrodealkylation (HDA). As a result, this fraction was converted to methane, LPG's, benzene, and liquid fuel and the hydrogen required was also calculated. From this data, presented in Table 3.3.5 the value of the fraction was determined.

Based on the yield data calculated for the mid-distillate fraction and the weight percent of the fraction from distillation, a mass balance for a conceptual plant operating on 100.00 lb/hr synthoil whole crude was calculated. With the flow rates and compositions of key streams known, the preliminary estimate for capital requirements and operating costs could be made. The 34.0 lb/hr straight run mid-distillate was recycle hydrocracked mathematically, consuming 2.18 lb/hr hydrogen and producing 2.10 lb/hr methane, 10.06 lb/hr LPG's and 22.35 lb/hr naphtha. The hydrocrackate naphtha, 22.35 lb/hr was hydrotreated mathematically, consuming 0.07 lb/hr hydrogen and producing 1.75 lb/hr gas. The hydrotreated naphtha was then reformed, producing 0.32 lb/hr hydrogen, 0.92 lb/hr gas and 19.39 lb/hr reformate. An in house mathematical model for hydrodealkylation was used to convert the reformate to 4.25 lb/hr liquid fuel, while consuming 0.74 lb/hr

Table 3.3.5 Product Patterns and Value for
Synthoïl Straight Run Fractions

	Straight Run Mid-Distillate 350-650°F
Product Pattern, Wt %	
Hydrogen	-7.9
Methane	19.1
LPG	47.6
Benzene	33.1
Liquid Fuel	3.2
Value/100 lb distillate (1980), dollars	6.89

Source: Peters, B.C., 1977d

hydrogen. With hydrogen needs met by converting part of the methane to hydrogen in an oil fired methane reformer, overall yields from the conceptual plant in pounds per 100 pounds of crude are presented in Table 3.3.6.

3.3.3 Shaw, Henry

Shaw, Henry et al. (1975) of Exxon Research and Engineering company hydroprocessed synthoil fraction boiling below 560°F alongwith shale oil fractions (boiling below 560°F) to compare the results.

Using the background and product characteristics of coal and oil shale liquefaction processes, estimates were made of the type of refining needed to increase present-day specification jet fuel availability. It was found that shale oil, which is chemically similar to petroleum, can contribute directly to fuel availability by being fully integrated into conventional petroleum refinery feed streams. Thus, in about a decade, a fraction of the commercial jet fuel will probably come from shale oil. This shale oil will be transported by pipeline from the mine/retort site to the refinery with a minimum amount of hydro-processing. Coal is not expected to produce jet fuels due to high concentrations of naphthenes. Rather, it will be used selectively to free virgin petroleum stocks for paraffinic-based fuels production. Coal liquids are expected to be used for gasoline production in order to reduce reforming requirements. Some hydroprocessed coal liquids might be used in jet fuel manufacturing to increase the supply by increasing the levels of naphthenes and aromatics. Also, coal liquids lend

Table 3.3.6 Overall Yield from Conceptual Plant Using
Synthoil Whole Crude as Feedstock

Yield, lb/100 lb crude

Methane	0.96
LPG's	16.02
42.13 wt % ethane	
23.42 wt % propane	
22.72 wt % butanes	normal/iso = 5.7
11.73 wt % pentanes	normal/iso = 1.5
Benzene	11.26
Fuel (HDA)	1.12
Residue	66.00

Source: Peters, B.C., 1977d

themselves to the manufacture of new high density fuels which might be used advantageously by advanced aircraft. Coal liquids can therefore provide a potential new aircraft turbine fuel, and in that way increase fuel supplies.

Hydroprocessing runs were made with paraho and synthoil fractions boiling below 560°F as feed materials in Exxon's Coal and Shale Hydrogenation (CASH) unit. These feeds were processed at 700°F, 1500 psi and a liquid hourly space velocity of one using presulfided Cyanamid HDS 3A Ni/Mo catalyst. After hydroprocessing, the products were distilled to recover the heart-cut in the jet fuel range. In general more than 80 percent of the feed material was recovered as jet fuel. The sulfur and nitrogen content of the product was less than 1 percent and 0.5 percent that of the feed respectively. The hydroprocessing results are summarized in Table 3.3.7.

Oil shale is expected to contribute more significantly than coal as a raw material for augmenting supplies of aviation turbine fuels. The refining of raw shale oil will be simpler and cheaper because it starts with a higher hydrogen content and lower specific gravity than raw coal liquids.

Coal provides a potential source of jet fuel components, but is not well suited for making conventional specification jet fuel. Since the starting material is almost all aromatics it needs to be hydrogenated to naphthenes and paraffins. It will be difficult and costly to include the manufacture of paraffinic type components which make up 50 percent or more of conventional jet fuel. However, coal sources can provide a very desirable blending component of naphthenes for jet fuels, so as

Table 3.3.7 Jet-A from Synthetic Oils

LHSV = 1.0, P = 1500 psi. t = 700°F and H ₂ rate = 4000 scf/bbl							
	Jet A		Paraho		Synthoil		
	Specification Max	Feed	Product LHSV=1.0	Feed	Product LHSV=0.8	Product LHSV=0.95	
Aromatics, vol %	20	29.9	7.5	51.9	24.0	31.6	
Sulfur, wt %	0.3	0.82	0.001	0.1	0.0036	0.0022	
Gravity, °API	39-51	31.9	44.2	21.3	34.3	31.8	
Flash Point, °F	105-150 (min)		99	174	75	72	
Freezing Point, °F	-93		-64		-120	-152	
Viscosity @ 100°F, cst	15	2.98	1.80	2.74			
Hydrogen, wt %		12.6	13.9	11.6	12.9	12.5	
Net Heat of Combustion (Btu/lb)	18400	18260	18600	17930	18350	18250	

Source: Shaw, Henry, et al., 1975

to give higher density and thus a higher volumetric heating value (Btu/gal). It would not be advisable to make jet fuel from 100 percent coal sources in order to increase supplies, but if this is to be done, consideration should be given to developing a new grade of jet fuel which would be very high in naphthenes, with a low content of paraffins and aromatics. The suitability of such a fuel would require considerable further evaluation and testing, possibly with engine modifications. The main impact of coal will probably be indirect, by providing clean fuel to utility and industrial users in order to release high value petroleum stocks which can then be easily processed to make jet fuel.

3.3.4 Crynes, B.L.

Crynes, B.L. (1977b, 1977c, 1977d) of Oklahoma State University hydrotreated synthoil and a mixture of synthoil with raw anthracene oil using Co-Mo and Ni-Mo catalyst to assess rate of catalyst activity decay and the removal of heteroatoms.

Two synthoil liquid samples obtained from the same coal and at the same operating conditions had different properties as can be seen in Table 3.3.8. Synthoil II had higher carbon and nitrogen but lower sulfur than Synthoil I.

3.3.4.1 Crynes, B.L. (1977b)

The Synthoil I liquid was rather resistant to sulfur and nitrogen removal, and the trickle bed reactors often became plugged when

Table 3.3.8 Synthoil Liquids Properties

Liquid	Synthoil I	Synthoil II
Carbon, wt %	80.5	84.2
Hydrogen, wt %	7.72	7.73
Sulfur, wt %	1.02	0.62
Nitrogen, wt %	1.19	1.46
Ash, wt %	3.4	2.1

Source: Crynes, B.L., 1977b, 1977c, 1977d

conditions approached 800°F, 3 hours space time. With most of the sulfur in the residue fraction, little desulfurization was achieved with either NiMo or CoMo on alumina catalysts until sufficient hydrocracking had occurred. Very little nitrogen could be removed under all conditions tested. At the most severe conditions assessed (800°F, 3 hr, 1500 psi) only 23-39 percent nitrogen removal was realized. Both catalysts revealed surprisingly little change in hydroremoval when changing reaction temperatures from 700 to 800°F. Figure 3.3.3 shows that up to a space time of 1.0 hours, temperature has no effect on sulfur removal. However, increasing the space time beyond 1.0 hours resulted in an abrupt decrease in product sulfur concentration at a temperature of 800°F. Again, as in desulfurization, there is a sharp drop in product nitrogen concentration when space time was increased beyond 1.0 hours. At 700°F there is little sensitivity to space time. Nalcomo 474 has shown very little ability to remove nitrogen from the Synthoil I liquid. At the most severe conditions tested (1500 psi, 800°F and 1.55 hours), nitrogen removal was only about 33 percent.

The results from product oil analyses are shown in Figure 3.3.4. The entire data set was obtained within one startup and continuous operation of 105.5 hours of oil on catalyst. It presents average sulfur and nitrogen removal data as a function of space time for the two pressures used in this study at a temperature of 700°F. The figure follow the expected pattern except that at a volume hourly space time of 0.62 hours, increasing the pressure from 500 to 1500 psi seems to have no effect on nitrogen removal. Similar results were obtained when Synthoil I liquid was hydrotreated over a monolith catalyst at a

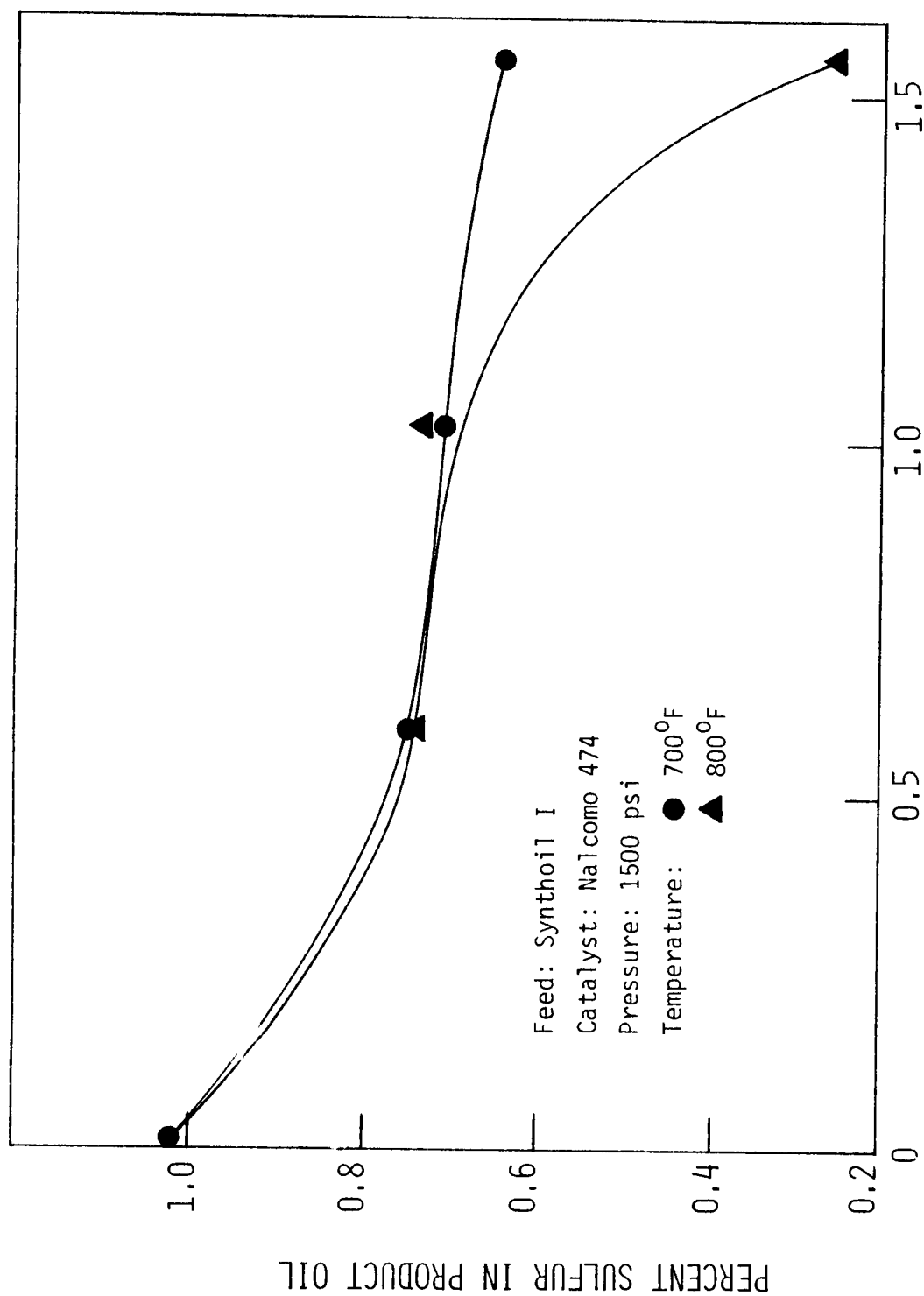


FIGURE 3.3.3 Sulfur Response for Synthoil I (Crynes, B.L., 1977b)

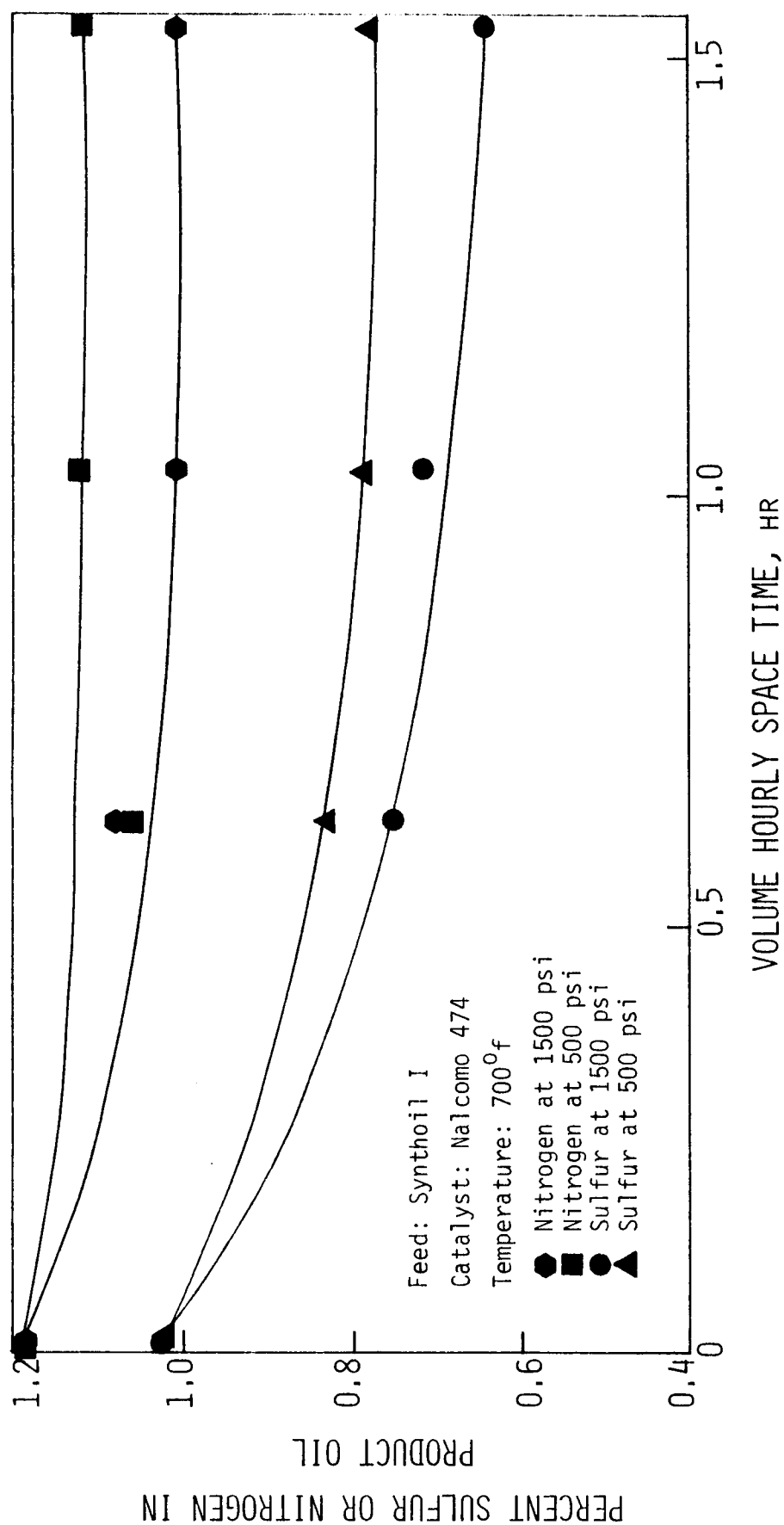


FIGURE 3.3.4 Sulfur and Nitrogen Response for Synthoil I (Crynes, B.L., 1977b)

space time of 1.11 hours at a temperature of 700°F.

The results from several runs on Synthoil I liquid reveal that this feed cannot be successfully hydroprocessed in the reactors at 800°F, 1500 psi and for volume hourly space times greater than 1.5 hours because of plugging of the reactor.

3.3.4.2 Crynes, B.L.(1977c)

Synthoil II obtained from the same coal and operational conditions as was Synthoil I proved to be less resistant to hydroremoval of sulfur and nitrogen. Figure 3.3.5 presents average sulfur and nitrogen removal data as a function of space time at 1500 psi and 700°F. The figure reveals that sulfur removal is relatively linear in space time for this liquid under the conditions tested. Other liquids have shown a much greater rate of removal within the first one hour space time. Nitrogen removal is somewhat easier for the Synthoil II liquid.

Also shown in Figure 3.3.5 are the results from processing Synthoil -I over the same catalyst and at identical conditions. This comparison of two synthoil liquids hydroprocessed under the same condition reveals marked differences. With both liquids having essentially the same nitrogen levels, Synthoil II was significantly easier to denitrogenate. Synthoil I with the greater sulfur content exhibited a somewhat larger removal rate through the first hour space time. These two coal liquids supposedly produced from the same coal source under the same conditions in the 1000 lb per day synthoil pilot plant show significantly different responses to further upgrading by hydrotreatment.

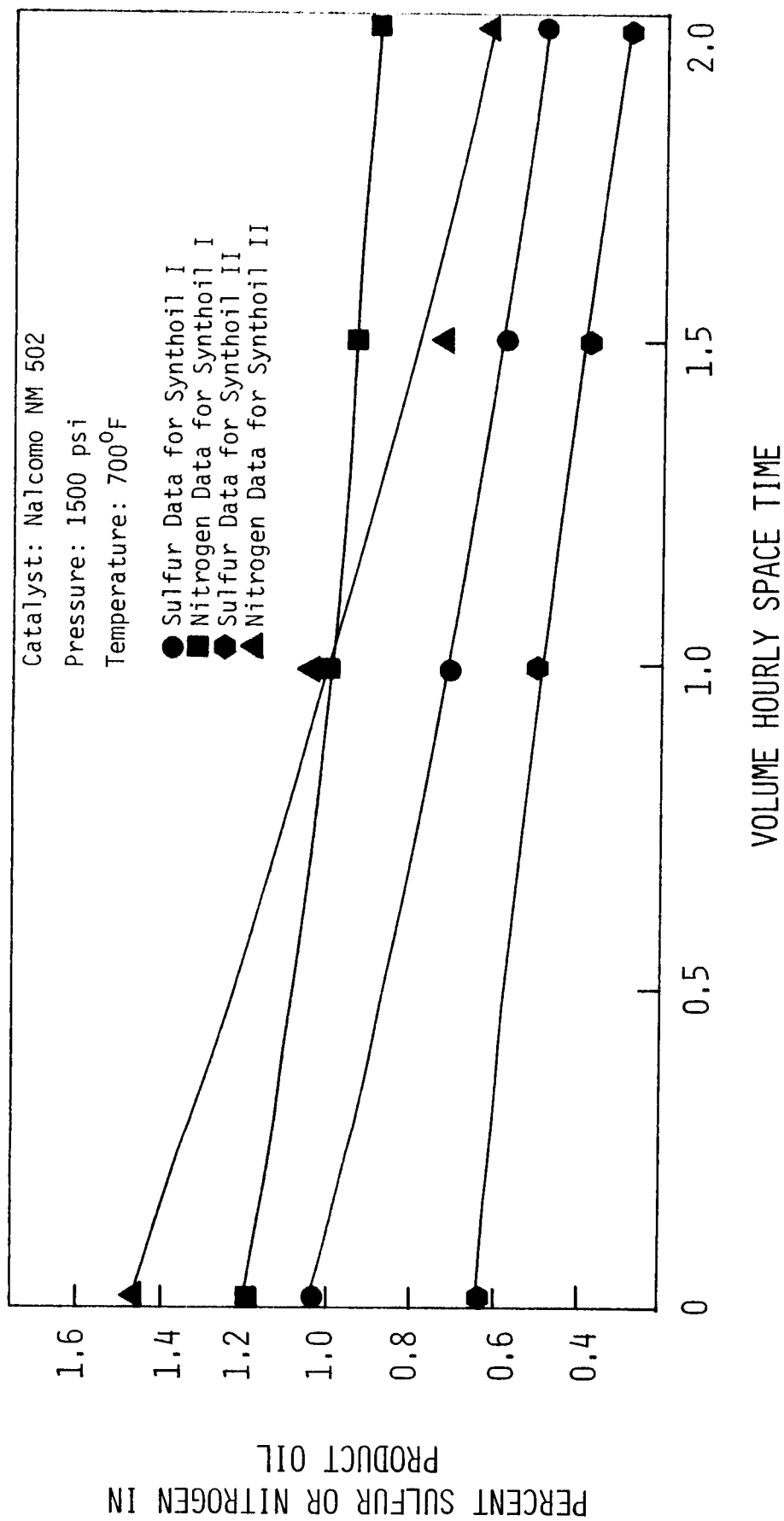


FIGURE 3.3.5 Sulfur and Nitrogen Response for Synthoil I and Synthoil II
 (Crynes, B.L., 1977c)

3.3.4.3 Crynes, B.L. (1977d)

Rasyn oil, a mixture of equal volumes of raw anthracene oil and Synthoil II liquid, was used as a feedstock for catalyst lifetime test runs. Experimental run series at temperature of 750⁰F was resulted in premature shut down due to reactor plugging, but rasyn oil was successfully hydrotreated at 700⁰F, 1500 psi and for volume hourly space times of 1.25 and 2.5 hours for 674 and 501 hours of oil-catalyst contact. As shown in Figure 3.3.6, the weight percent sulfur in the product oil samples seems to increase after 400 hours of operation showing a decay trend in catalyst activity. Sulfur concentration in the product oil seems to level off around 0.3 weight percent. There was appreciable decay in catalyst activity with respect to nitrogen removal also. The nitrogen level in the product oil samples approached that of the feed oil after about 400 hours of oil on catalyst.

3.3.5 Berg, Lloyd

Berg, Lloyd and McCandless, F.P (1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d) of Montana State University converted ERDA's synthoil liquefied coal to clean distillate fuels by hydrogenation at elevated temperatures under hydrogen pressure. ERDA's synthoil liquefied coal is produced in a one-step hydrotreating process using the rapid, turbulent flow of hydrogen to propel a coal slurry through a fixed bed reactor with a catalyst of cobalt molybdate on silica activated alumina. It is tar like substance at room temperature with

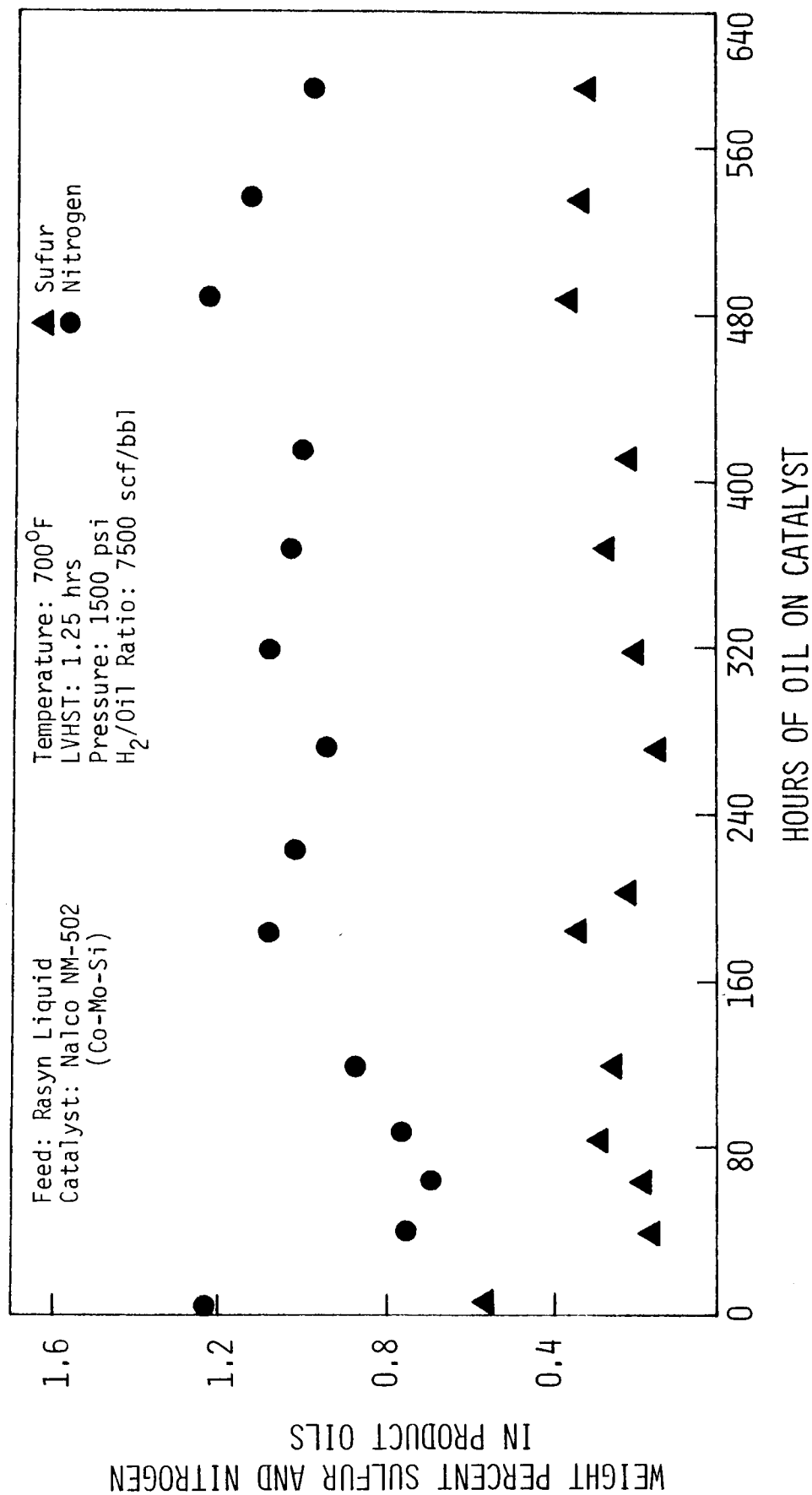


FIGURE 3.3.6 Catalyst Hydrodesulfurization and Hydrodenitrogenation Activity Decay
(Crynes, B.L., 1977d)

flow characteristics like thick molasses. It contains 0.44 percent sulfur and 1.06 percent nitrogen and has a distillate yields of 44 volume percent and 43 weight percent.

Batch and continuous flow catalyst screening tests were made on synthoil feed. In batch tests 9.15 cubic inch of synthoil was charged alongwith 1.52 cubic inch of catalyst in a 30.5 cubic inch Pars rocking autoclave. The autoclave was pressurized with 2000 psi of hydrogen, and was heated to 840⁰F for 1 hour. To determine the amount of cracking and hydration the distillation curve of the product was compared with that of the synthoil feed. Also the amount of heteroatom removal was compared for catalyst screening.

A total of 36 bomb runs were made using 27 commercially prepared catalysts and three catalysts prepared in Montana State University laboratory. The hydrocracking and heteroatom removal results for some of the catalysts are listed in Table 3.3.9. The ASTM distillation results are broken down into four products as follows: (1) Naphtha (IBP-425⁰F), (2) Fuel Oil (425-600⁰F), (3) Gas Oil (600-700⁰F), and (4) Residue (700⁰F-plus). The catalysts are arranged in increasing order of total volume percent distilled. The best desulfurization catalyst was Ni-0104 (60 percent Ni powder). The two best hydrocracking catalysts gave the best denitrogenation results. The catalysts are Harshaw CoMo-0401 (3 percent CoO, 9 percent MoO₃) and Harshaw HT-500 (3 percent NiO, 15.5 percent MoO₃). Denitrogenation was much more difficult than desulfurization.

Twelve catalysts were tested in a fixed bed continuous flow reactor to determine the effect of varying LHSV, temperature, and

Table 3.3.9 Bomb Run Hydrocracking and Heteroatom Removal Results for Synthoil

Catalyst	% Naphtha IBP-425°F	% Fuel Oil 425-600°F	% Gas Oil 600-700°F	% Residue 700°F + Distilled	Total Vol %	% DeS	% DeN
Synthoil							
Harshaw (Ni-W) Ni-4401	4	20	20	56	44	41	18
Harshaw (Ni) Ni-3250	6	23	20	51	49	50	17
Harshaw (Ni-Mo-Si) HT-100	8	20	21	51	49	36	18
Shell (Co-Mo) Shell 344	10	22	18	50	50	48	32
Harshaw (Ni-Cu) Ni-1800	8	21	21	50	50	16	0
Harshaw (W) W-0101	4	23	24	49	51	09	0
Harshaw (Ni-Co-Fe) Ni-1601	6	25	20	49	51	07	06
M.S.U (Sn) SnCl ₂	7	22	22	49	51	20	10
Shell (Ni-Mo) Shell 324	8	24	21	59	51	55	21
Harshaw (Ni-W) Ni 4301	10	21	21	48	52	23	28
Harshaw (Ni-W) Ni-4303	7	22	23	48	52	45	18
Ketjen (Ni-W) 330-3E	12	22	20	46	54	30	12
Harshaw (Ni) Ni-0104	12	22	20	46	54	57	16
Cat & Chem Co (Co-Mo) C-20-6	9	23	22	46	54	18	25
Harshaw (W) W-0101	10	21	25	44	56	25	03
Harshaw (Co-Mo) CoMo-0603	23	25	9	43	57	52	25
Harshaw (Ni-W) Ni-4301	9	25	27	39	61	32	29
Harshaw (Co-Mo) HT-400	9	24	28	39	61	34	13
Harshaw (Co-Mo) CoMo-0401	10	24	30	36	64	16	33
Harshaw (Ni-Mo) HT-500	11	23	31	35	65	32	33
	11	25	29	35	65		

Source: Berg, Lloyd and McCandless, F.P. (1975, 1976a, b, c, d and 1977a, b, c, d)

hydrogen flow. The best catalysts in bomb runs showed an improvement in hydrocracking and desulfurization for the continuous runs. Denitrogenation did not increase and in some cases decreased. The "best" continuous products were usually at LHSV around 1.0.

Figure 3.3.7 shows the effect of LHSV on desulfurization and denitrogenation for three different catalysts. As can be seen the percent desulfurization decreases as the LHSV increases. For denitrogenation the LHSV showed a general trend of increasing with increasing LHSV. However, two data points contradict this statement.

Heteroatom removal vs. hydrogen flow rate (Figure 3.3.8) with constant LHSV reaches a maximum at approximately 10,000 scf/bbl and then decreases. The worst results were at hydrogen flow rates greater than 15,000 scf/bbl.

The heteroatom removal data provide reasonably good correlation with hydrogen consumption, as well as the change in API gravity. The synthoïl whole liquid can be processed by commercial technology up to chemical hydrogen consumption of about 3,100 scf/bbl.

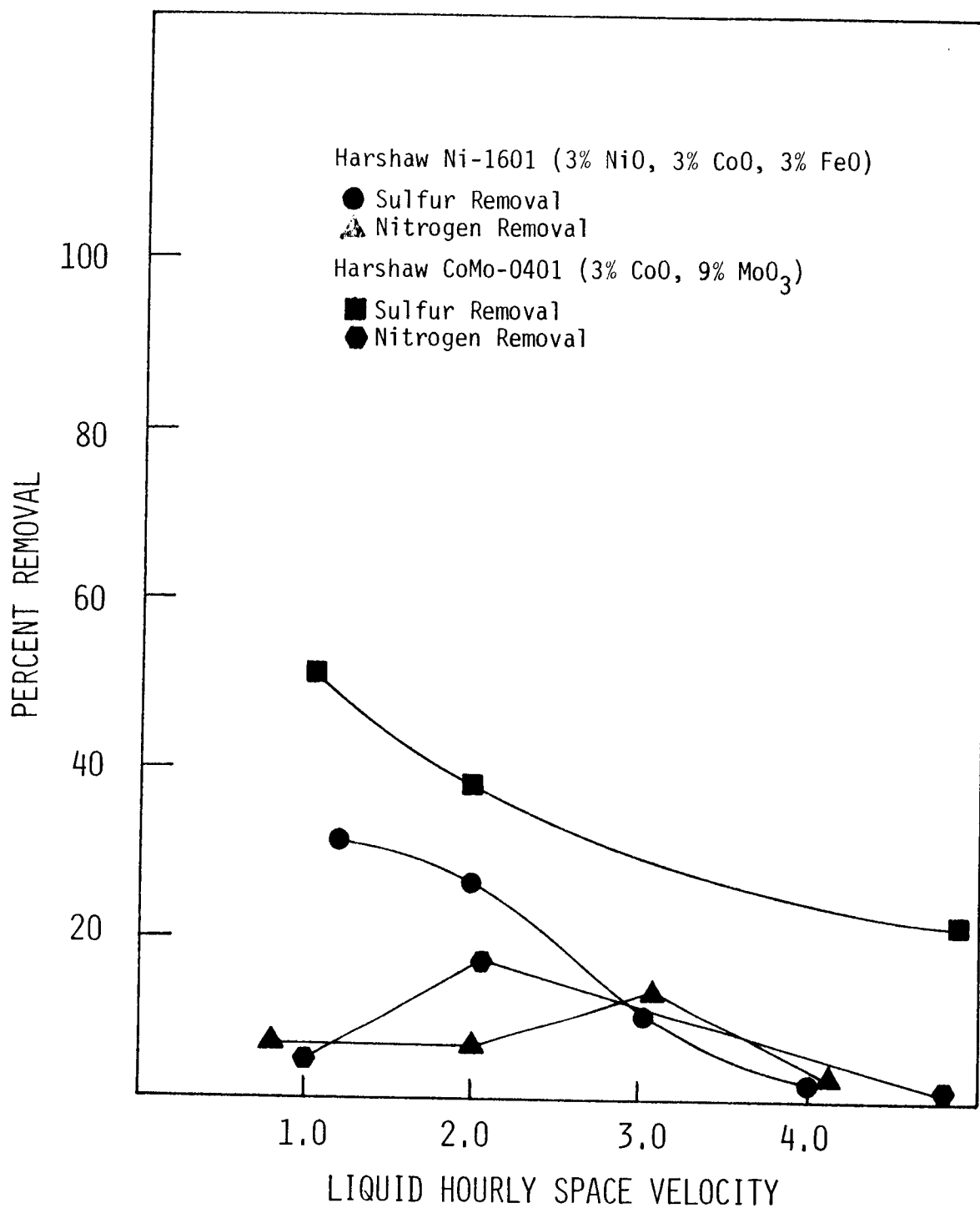


FIGURE 3.3.7 Percent Desulfurization and Denitrogenation vs LHSV for Synthoil (Berg, Lloyd and McCandless, F.P., 1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d)

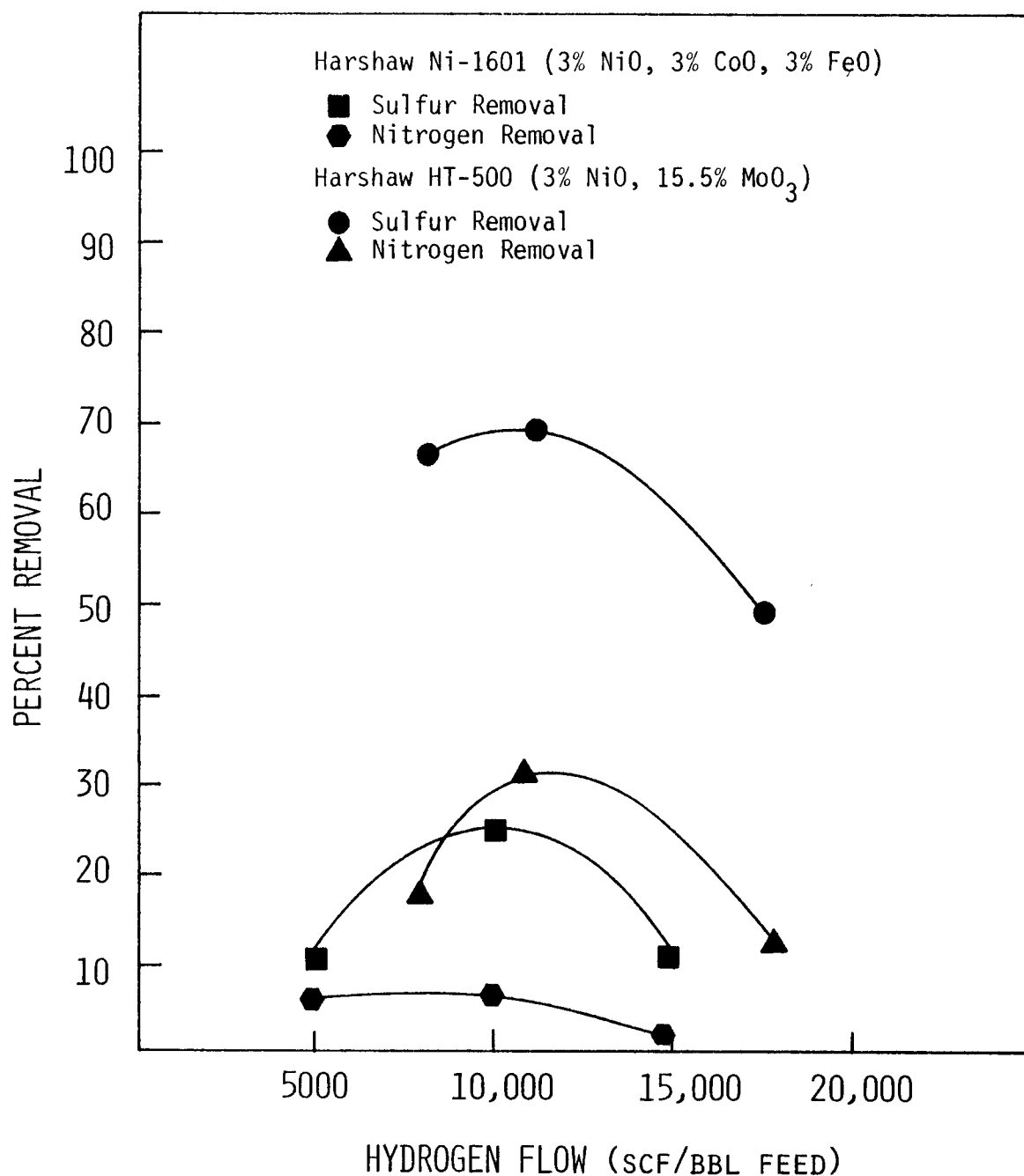


FIGURE 3.3.8 Percent Desulfurization and Denitrogenation vs Hydrogen Flow for Synthoil (Berg, Lloyd and McCandless, F.P., 1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d)

3.4 SOLVENT REFINED COAL (SRC)

Many early experiments were conducted to determine the solubility of coal in various solvents not only to study coal and its reactions, but also as a possible method of separating the valuable fuel portion of coal from its inorganic impurities. The Pott-Broche process was successful in dissolving about 75 percent of the German bituminous coals processed and producing an extract with only 0.5 percent ash (Sternberg, 1951). Plants were operated in Germany in World War II until war damage prevented further processing. Japan also operated such a plant in World War II (Battelle, 1974b). The main use of the German process was to produce a low ash coke for aluminium manufacture.

The restriction of sulfur oxide emissions from stationary combustion sources in the United States has been largely responsible for development of a process for production of a low sulfur, low ash coal. The solvent refined coal (SRC) is obtained by dissolving, suspending or liquefying the coal in a high boiling (550 to 800°F) coal derived solvent in a manner similar to the Pott-Broche process.

In the SRC process coal is ground 0-18 inch, dried to less than 3 percent moisture and slurried with solvent and hydrogen before introduction into the preheater. The mixture is reacted in the dissolver at up to 800°F and 2000 psi where over 90 percent of the organic portion of the coal is dissolved or suspended. Some chemical reactions are involved under such conditions. These may include 1) thermal and catalytic (utilizing minerals in the coal) bond rupture, 2) hydrogenation of reactive fragments, 3) solvent dissociation, dehydro-

genation and isomerization, and 4) removal of oxygen and sulfur from the coal and inorganic materials associated with the coal. This latter step usually reduces the concentration of sulfur to 10 to 15 percent of its original concentration in the coal. Since minerals are not soluble in the organic solvent they may be removed by filtration, centrifugation or other methods. The extract is flash distilled to separate solvent.

The SRC product may be recovered hot as a pumpable liquid or cooled to a low sulfur, low ash solid. The softening point (temperature) of the product SRC depends partially on the degree of solvent removal. SRC produced from a variety of coal feeds has essentially the same physical gross properties. The ash content is low (0.1 to 0.5 percent) and the heating value is about 16,000 Btu/lb, H_2S , CO_2 , and some fuel gases are produced in the process (Braunstein, et al., 1977).

The primary purpose for production of SRC has been to make available a low pollution material suitable for combustion in electric power plants. Other uses may be found for SRC as larger quantities become available from commercial production.

The most difficult problems associated with SRC production concern the liquid-solids separation step. Although pressure filtration, centrifugation, and some other methods have been suggested and studied commercial experience determines the best separation method.

Because of the difficulties in the solid/liquid separation, development of SRC-II was pursued by Gulf. The basic idea behind this development was to produce a distillable liquid product. This would eliminate the need for filters, centrifuges, and other physical

separation methods. The penalty for producing a distillate product is approximately a doubling of the hydrogen required in the process. While SRC production requires about 2 percent hydrogen (based on the feed coal), the SRC-II product can be separated from residue and mineral matter by flash vaporization or distillation.

3.4.1 Berg Lloyd

3.4.1.1 Berg, Lloyd et al. (1975, 1976a, 1976b, 1976c)

Berg, Lloyd and McCandles, F.P (1975, 1976a, 1976b, 1976c) of Montana State University hydrotreated PAMCO (Pittsburgh and Midway Coal Company) solvent-refined liquefied coal to get clean distillate fuels. Variables which were investigated included temperature, pressure, space velocity, hydrogen-to-oil ratio, and chemical nature of the solvent. The catalyst studied included nickel molybdate and sulfide, cobalt molybdate and sulfide, nickel tungstate and metal chlorides.

The PAMCO liquefied coal as received was in solid form from which was dissolved in a synthetic coal oil solvent, different solvent-to-solid feed ratios were tested to get the best results. Order of cracking was determined by two factors:

- . The shape of the distillation curve of the product as compared to that of the feed.
- . Overall conversion of nondistillates (residue) of the feed into distillate.

Catalysts were screened on batch tests in a 30.5 cubic inch rocking bomb. Solvent refined coal and synthetic solvent along with

the catalyst were charged in the bomb, and then the bomb was pressurized with hydrogen upto 2000 psi initial pressure. A one hour heat-up period was sufficient to completely dissolve the solvent refined coal in the solvent. And then the bomb was kept for additional 1/2 hour at the run temperature (approximately 825°F). The product was distilled and tested for sulfur and nitrogen.

Out of 44 catalysts tested in batch runs, the best overall catalyst was Harshaw's HT-400 (Co-Mo) which removed about half of the sulfur and some of the nitrogen from the feed (SRC solution had 0.5 percent sulfur and 1.2 percent nitrogen). Metal chlorides as a group were only fair hydrocracker. Of the group tested, only Aluminium chloride was a little promising. It was observed that sulfur was removed significantly, but nitrogen was more difficult to remove with almost all of the catalyst tested.

For the continuous runs the apparatus consisted of a three foot Inconel reactor, the top one-third of the reactor was a packed preheating section, the middle third holds the catalyst and the bottom third holds filler packing. The reactor was surrounded by an electrically heated aluminium block to maintain the temperature. Four catalysts were tested and the effect of temperature, hydrogen-to-liquid flow ratio, and the liquid hourly space velocity (LHSV) were studied. The catalyst tested included: Harshaw HT-400 (3 percent CoO, 15 percent MoO₃), Ketjen HC-5 (21 percent WO₃, 6.5 percent NiO), MSU STK-7 (17.1 percent MoO₃, 1.5 percent NiO, 1.4 percent Co₃O₄) and MSU STK-5-2-1 (23.9 percent MoO_x, 0.75 percent CoO_x, 0.48 percent NiO_x).

The highest denitrogenation, 64 percent, was achieved by HT-400 catalyst. The highest desulfurization, 88 percent was achieved by Ketjen HC-5 catalyst. Figure 3.4.1 through 3.4.5 summarizes some of the results. Nitrogen removal showed a greater dependency on temperature than did sulfur removal. Figure 3.4.1 shows a gradual effect of temperature on sulfur removal while nitrogen removal has a steep temperature effect between 790 and 835°F. Heteroatom removal decreases with increased space velocity, as displayed in Figure 3.4.2.

The desulfurization peaks or maximizes in the range of 10,000 to 13,000 scf/bbl hydrogen-to-liquid ratio at LHSV equal to 1 and at a temperature of 835°F as shown in Figure 3.4.3. However, denitrogenation results from HC-5 and STK-7 conflicted (Figure 3.4.3).

Figure 3.4.4 displays HT-400 product distillations for three different space velocities. The LHSV equal to 2 has the lowest curve but LHSV equal to 1 had the most overall conversion. The product of LHSV equal to 3 is very much like the reactor feed. The effect of temperature on cracking are shown in Figure 3.4.5. The 790°F product is similar to the feedstock, but the 835°F product is very much improved.

3.4.1.2 Berg, Lloyd et al. (1976d, 1977a, 1977b, 1977c, 1977d)

Berg, Lloyd and McCandles, F.P. (1976d, 1977a, 1977b, 1977c, 1977d) of Montana State University also hydrotreated a SRC Vacuum Flash Feed obtained from PAMCO's SRC pilot plant in Washington. This was a better feedstock because it was direct from PAMCO's dissolver unit and it did not need any remixing in a solvent. This feedstock contained

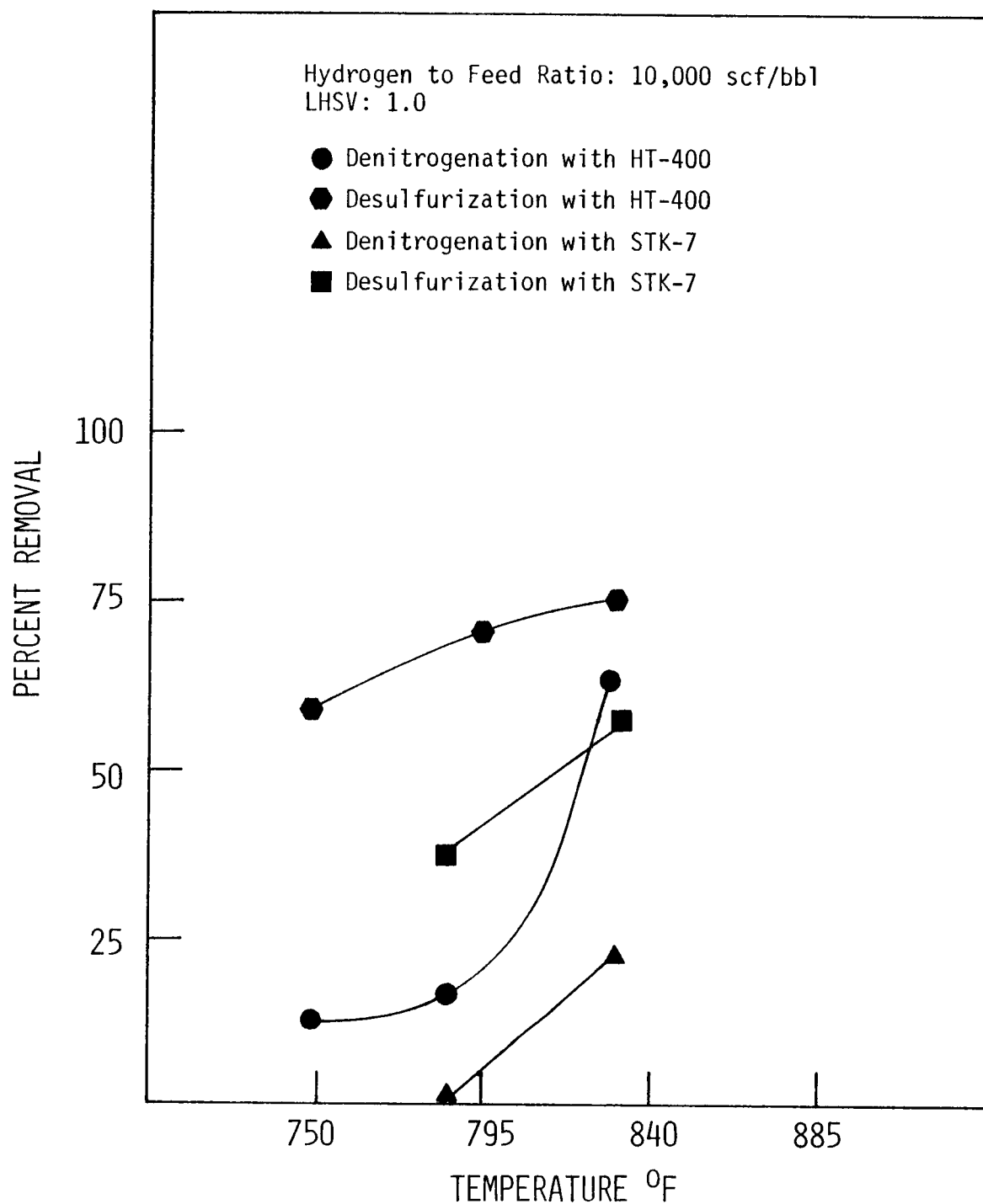


FIGURE 3.4.1 Denitrogenation and Desulfurization of SRC Feedstock with Respect to Temperature (Berg, Lloyd and McCandless, F.P., 1976d, 1977a, 1977b, 1977c, 1977d)

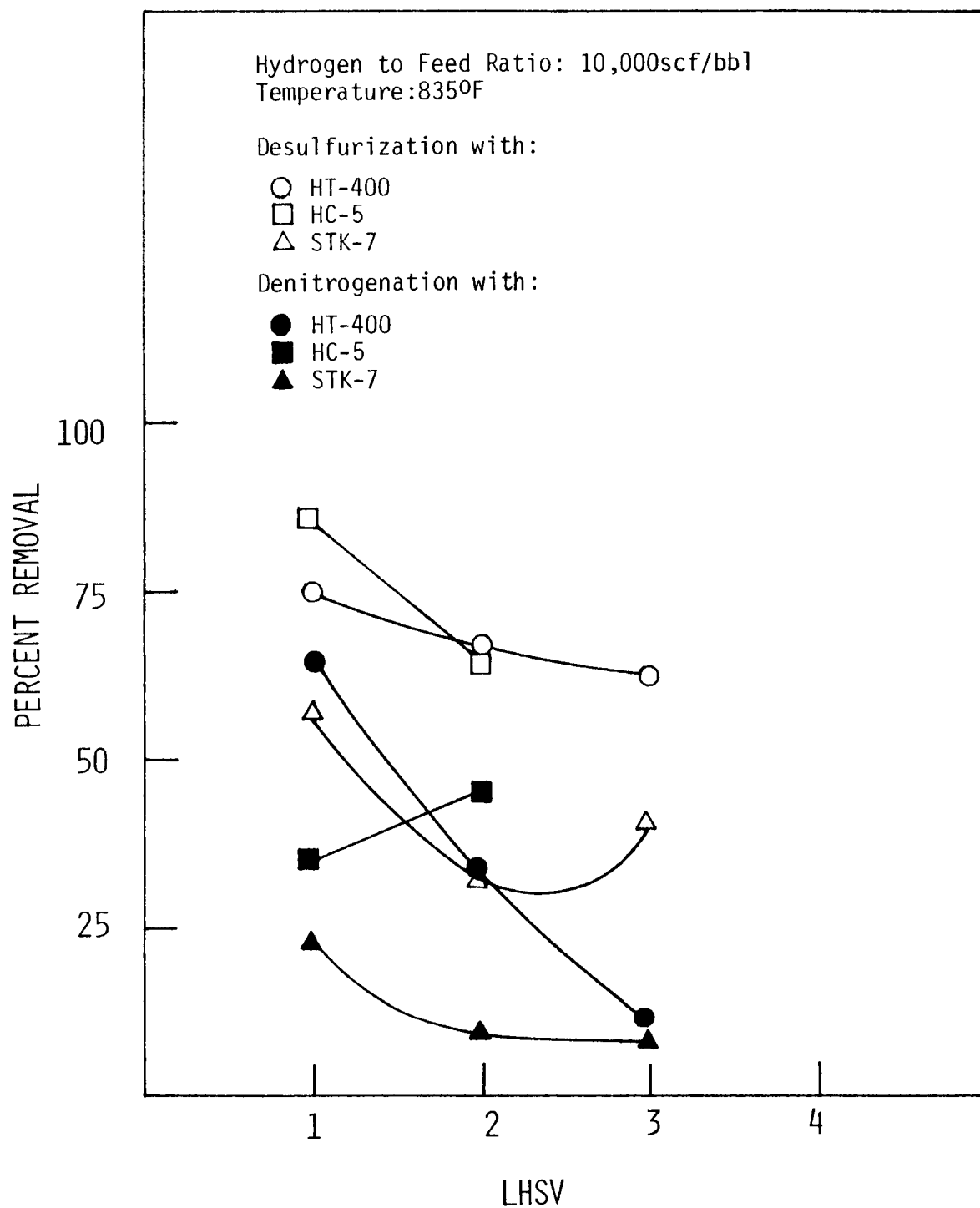


FIGURE 3.4.2 Denitrogenation and Desulfurization of SRC Feedstock with Respect to Liquid Hourly Space Velocity (Berg, Lloyd and McCandless, F.P., 1976d, 1977a, 1977b, 1977c, 1977d)

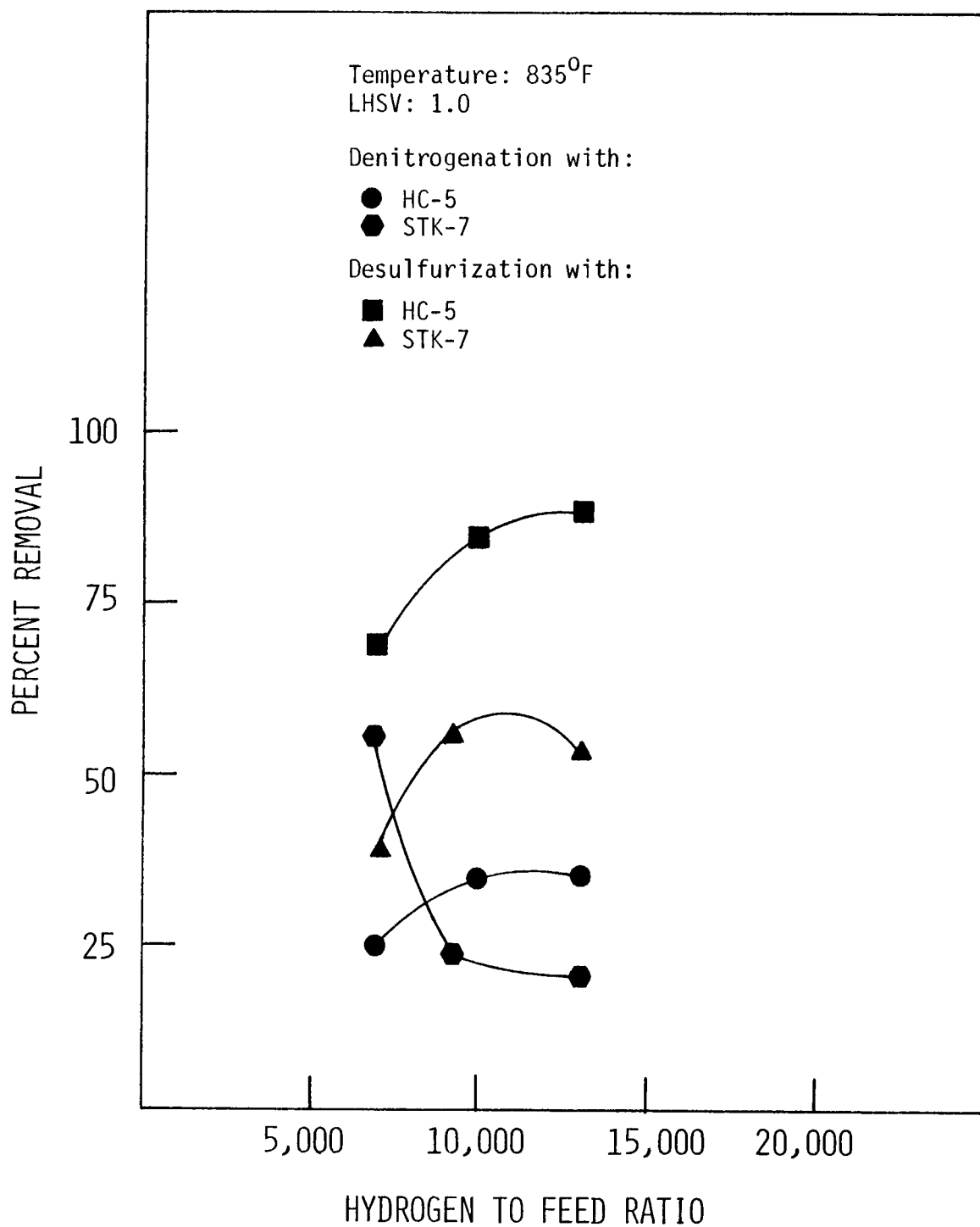


FIGURE 3.4.3 Denitrogenation and Desulfurization of SRC Feedstock with Respect to Hydrogen to Feed Rate Ratio (Berg, Lloyd and McCandless, F.P., 1976d, 1977a, 1977b, 1977c, 1977d)

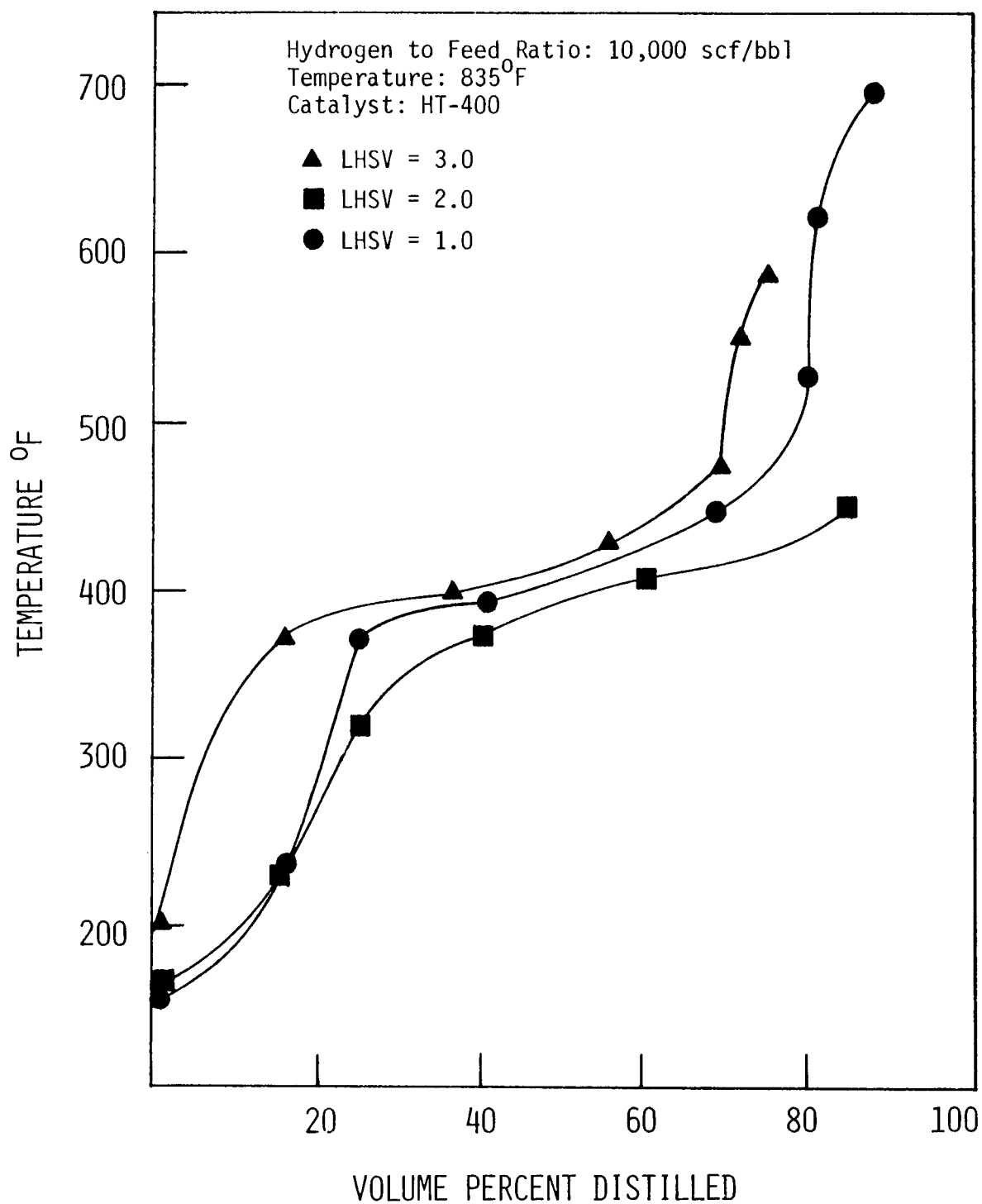


FIGURE 3.4.4 Catalytic Cracking of SRC Feedstock with Respect to Liquid Hourly Space Velocity (Berg, Lloyd and McCandless, F.P., 1976d, 1977a, 1977b, 1977c, 1977d)

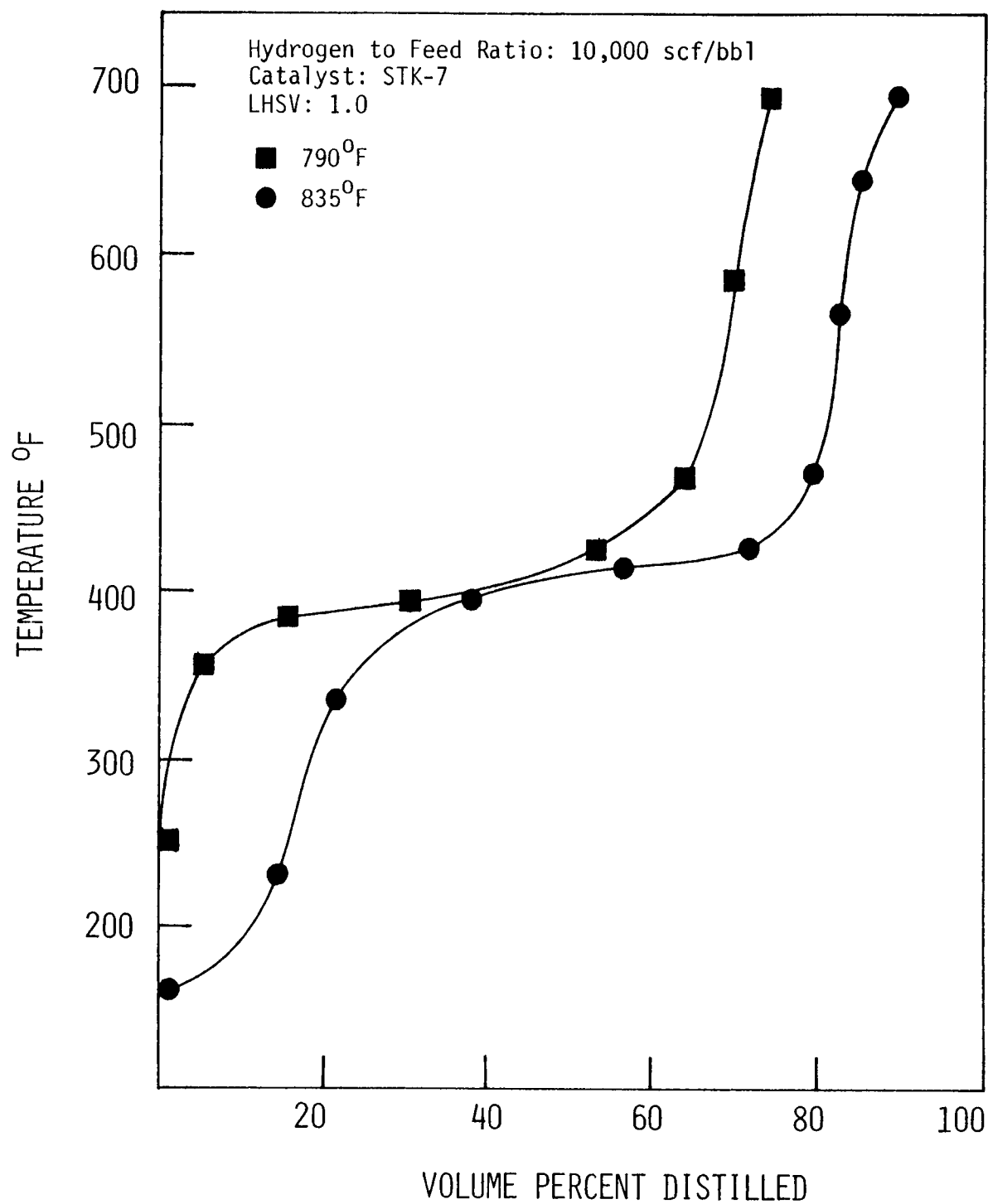


FIGURE 3.4.5 Catalytic Cracking of SRC Feedstock with Respect to Temperature (Berg, Lloyd and McCandless, F.P., 1976d, 1977a, 1977b, 1977c, 1977d)

0.64 percent sulfur and 1.3 percent nitrogen. A comparison of the SRC Vacuum Flash Feed and PAMCO's SRC dissolved in synthetic coal oil solvent is shown in Figure 3.4.6.

The batch run screening of the catalyst were made in a Parr rocking autoclave of 30.5 cubic inch internal volume. Batch run conditions were as follows:

- . Vacuum Flash Feed charged = 0.44 lb
- . Catalyst charged = 1.525 cubic inch
- . Initial hydrogen pressure = 2500 psi
- . Run temperature = $790 \pm 10^{\circ}\text{F}$
- . Residence time = 1 hour at run temperature

A total of nineteen catalysts were batch tested. Shell 324 (2.7 percent Ni, 13.2 percent No on alumina) catalyst and MSU STK-14 (17.4 percent MoO_3 , 2.3 percent NiO, 1.8 percent CuO on alumina) gave the best desulfurization (upto to 75 percent) in the batch run. Harshaw Co-Mo-0401-T (3 percent CoO, 9 percent MoO_3 on alumina) gave the best denitrogenation (29 percent) in the batch run.

For the continuous runs the same three foot Inconel reactor was used and the runs were made at the following conditions:

- . Pressure = 1000 psi
- . Temperature = 840°F
- . Hydrogen to oil rate ratio = 10,000 scf/bbl
- . Catalyst bed = 3.66 cubic inch catalyst diuted with 3.66 cubic inch Denstone 1/8 inch support
- . LHSV = 1.0, 1.5, 2.0

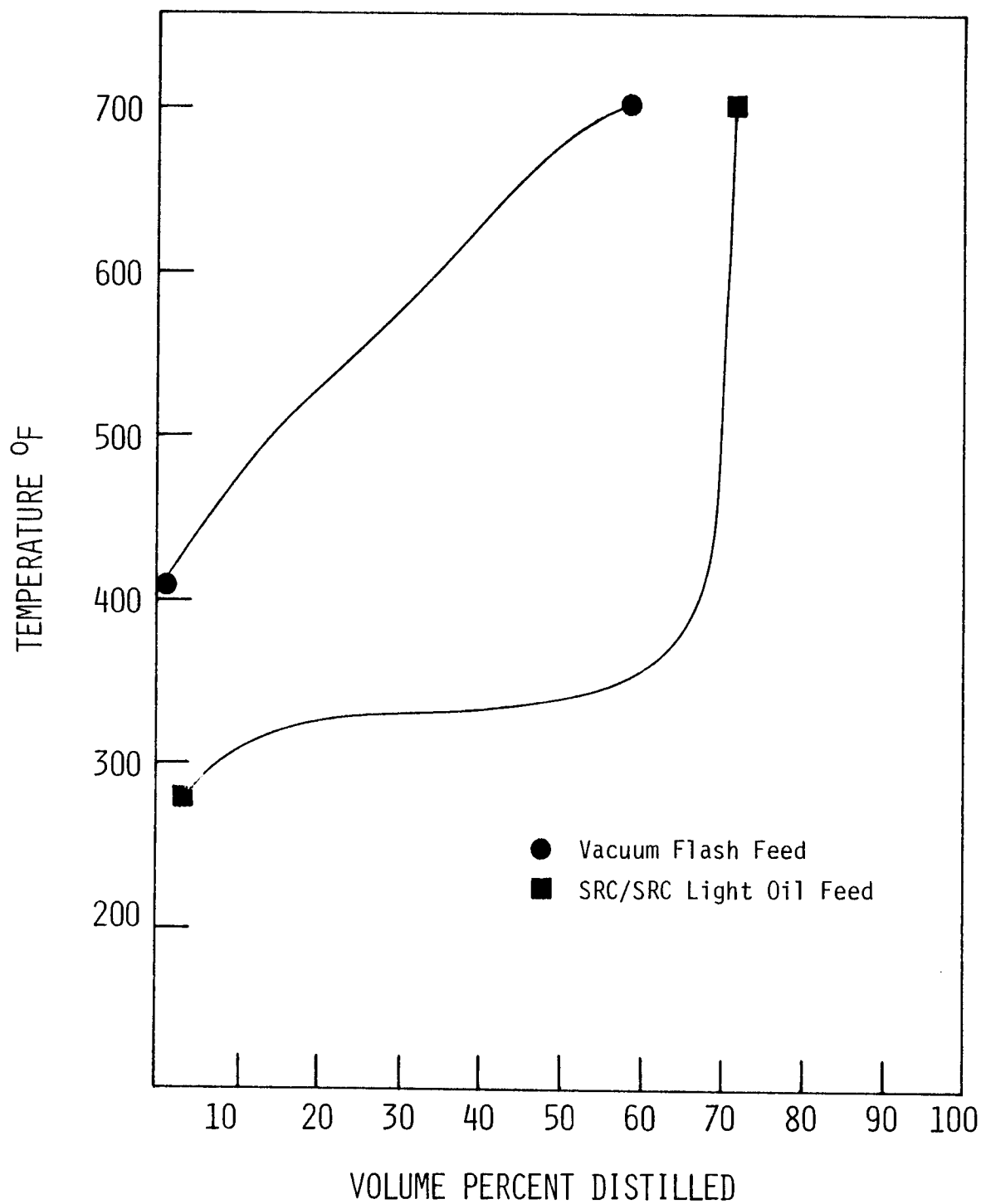


FIGURE 3.4.6 Composition of SRC Feedstocks (Berg, Lloyd and McCandless, F.P., 1976d, 1977a, 1977b, 1977c, 1977d)

Table 3.4.1 summarized heteroatom removal data and ASTM distillation data for continuous fixed bed reactor tests on some of the catalyst tested. It can be seen that the best desulfurization averaged over the three space velocities tested was obtained with MSU-STK 5-2-6. The best denitrogenation, over the space velocities tested was obtained with MSU-STK 5-2-2 catalyst.

3.4.2 Potts, John D.

Potts, John D. et al. (1977a, 1977b, 1978a, 1978b) of Cities Service Company hydrocracked Solvent Refined Coal extract (SRC-I) in an expanded bed hydroprocessing unit using commercially available catalyst. The expanded bed (LC- Finer) reactor maintains the catalyst (typically American Cynamid 1442B cobalt molybdenum 1/32 inch extrudate) in constant motion, suspended by the recirculation of copious volumes of liquid. The recirculation results in a 35-to-50 percent bed expansion and the reactor operates at a uniform temperature with essentially no pressure drop.

The SRC-I is essentially an 850⁰F-plus material obtained from liquefaction of Kentucky 9 and 14 coal with a softening point of 353⁰F, and an ash content of 0.15 weight percent. A coal derived KC-oil (Koppers Heavy Residue Cresosote Oil) was used to dissolve SRC-I. A component analyses of SRC-I and KC-Oil is given in Table 3.4.2.

In a catalyst screening test six catalysts were screened to chose an optimum catalyst. Three Co-Mo, two Ni-Mo, and one Ni-W catalysts were tested. A nickel-molybdenum catalyst (Shell 324) proved superior

Table 3.4.1 Data Summary of Continuous Runs on SRC Vacuum Flash Feed

Catalyst	LHSV	% DeN	% DeS	ASTM Distillation D-86 (Vol %) IBP-425°F 425-600°F 600-700°F Yield	
MSU-STK-5-2-2-E-1/16 inch (CoO=1.15%, MoO ₃ =13.1% NiO=0.26%)	1.0	46.5	56.2	15.4	25.7
	1.5	54.8	65.3	14.8	27.2
	2.0	35.1	53.5	8.1	26.3
MSU-STK-5-2-3-E-1/16 inch (CoO=1.1%, MoO ₃ =16.4% NiO=0.5%)	1.0	32.0	58.3	10.2	23.6
	1.5	36.8	54.9	10.1	14.1
	2.0	30.7	52.1	9.1	25.4
MSU-STK-5-2-5-E-1/16 inch (CoO=0.8%, MoO ₃ =14.0% NiO=0.5%)	1.0	34.2	64.6	10.2	24.0
	1.5	37.7	61.1	10.2	27.6
	2.0	30.3	48.6	10.2	21.3
MSU-STK-5-2-6-E-1/16 inch (CoO=1.1%, MoO ₃ =15.5% NiO=0.2%)	1.0	36.0	72.9	10.1	24.5
	1.5	39.0	74.3	10.2	25.7
	2.0	31.1	70.1	10.3	24.8
Harshaw Ni-1601-T-1/8 inch (CoO=3%, Fe ₂ O ₃ =3% NiO=3%)	1.0	30.3	20.1	5.6	25.3
	1.5	32.9	27.8	6.1	23.9
	2.0	24.1	4.2	7.1	28.5
MSU-STK-5-2-1-E-1/16 inch (CoO=0.75%, MoO ₃ =23.9% NiO=0.48%)	1.0	32.9	47.9	11.8	22.6
	1.5	39.5	47.9	11.9	21.2
	2.0	29.8	39.6	10.0	24.9

Table 3.4.1 (cont) Data Summary of Continuous Runs on SRC Vacuum Flash Feed

Catalyst	LHSV	% DeN	% DeS	ASTM Distillation D-86 (Vol %)		
				IBP-425°F	425-600°F	600-700°F Yield
Shell 324-E-1/16 inch (NiO=3%, MoO ₃ =13%)	1.0	38.8	70.5	13.6	41.2	22.1
	1.5	15.4	61.8	7.3	35.5	31.4
	2.0	8.5	49.5	7.8	33.8	27.3
Shell 344-E-1/16 inch (CoO=2.4%, MoO ₃ =9.9%)	1.0	31.1	73.9	12.4	38.9	23.3
	1.5	37.0	61.2	13.5	39.0	24.2
	2.0	17.7	65.2	8.0	38.3	28.9

Source: Berg, Lloyd and McCandless, F.P., 1976d, 1977a, 1977b, 1977c, 1977d

Table 3.4.2 Component Analyses of SRC-1 and KC-Oil

	KC-Oil	SRC-1
Specific Gravity, 60/60 ^o F	1.1486	1.230
Pour Point, ^o F	10	
Softening Point, ^o F		353
Elemental Content, wt %		
Carbon	91.3	87.0
Hydrogen	5.8	5.7
Oxygen	1.1	4.4
Nitrogen	1.2	2.1
Sulfur	0.6	0.8
Ash, wt %	0.02	0.15
Distillation, ^o F		
IBP	323	620
5%	488	850
30%	607	
50%	650	
95%	845	

Source: Potts, John D. et al. 1977a, 1977b, 1978a, 1978b

to the others tested. This is demonstrated in Figure 3.4.7 by the Shell 324 catalyst showing a higher conversion of 850⁰F-plus based on the heavy oil product. Also Table 3.4.3 presents a comparison on total liquid product (TLP) fractions of the volume percent yield, and weight percent nitrogen content for six of the catalysts tested. Several conclusions may be drawn from the catalyst screening study for nickel-molybdenum catalysts:

- . greater conversion of 850⁰F-plus
- . more selective in production of 500-650⁰F fraction
- . small increase in production of IBP-500⁰F fraction
- . better hydrogenation, oxygen removal, and denitrogenation of all heavy oil fractions

Catalyst activity decay test were run using Shell 324 nickel-molybdenum catalyst and American Cynamid Co-Mo catalyst. Once through operation using KC-Oil solvent and fresh SRC-I was conducted through approximately 12 hours during which time sufficient product was accumulated to provide a recycle solvent. The product from once-through operation was topped to 500⁰F, and the 500⁰F-plus bottoms were analyzed for unconverted 850⁰-plus material. Additional fresh SRC-I was added to the 500⁰F-plus bottoms to provide a 50/50 SRC-I/solvent feed blend for recycle. Thus the 850⁰F-plus fraction of the feed blend recycled contained both fresh and unconverted 850⁰F-plus material. This procedure was repeated for the subsequent recycle passes. The conversion showed a declining trend with time through successive passes as can be seen in Figure 3.4.8. After 38 hours, the feed blend was returned to 50/50 fresh SRC/KC-Oil mixture and the

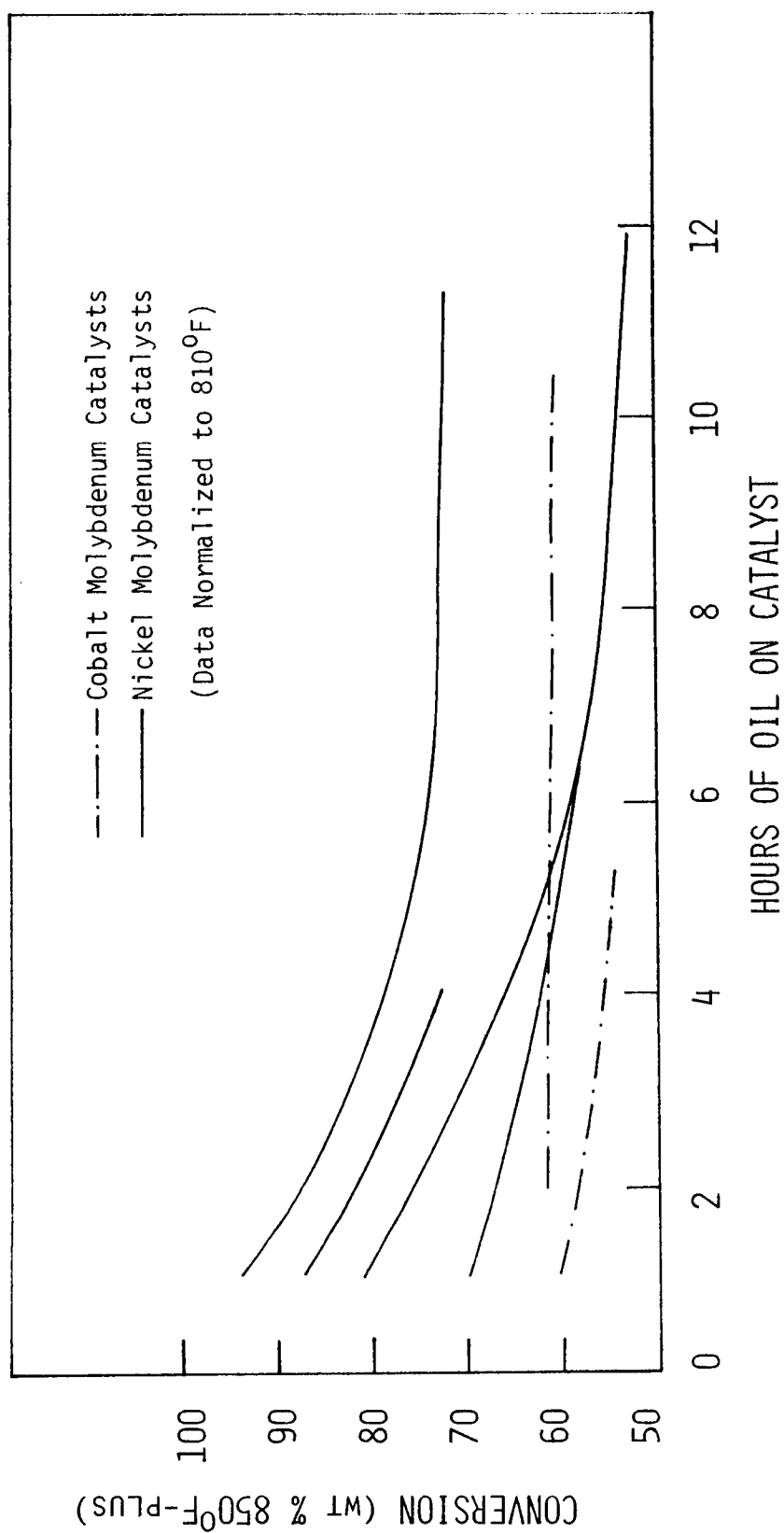


FIGURE 3.4.7 Conversion of 850°F-plus Fraction of SRC Feed (Potts, John D. et al. 1977a, 1977b, 1978a, 1978b)

Table 3.4.3 Co-Mo Versus Ni-Mo Catalysts Liquid Product Fraction Properties

Fraction	IBP-390°F	390-500°F	500-650°F	650-850°F	850°F ⁺	TLP
Volume % on Total Liquid Product						
29/6 (a)	3.2	13.4	34.9	26.6	22.0	
29/12 (a)	2.7	12.7	37.6	27.4	19.6	
32/5 (a)	3.7	12.4	36.2	30.1	17.6	
30/7 (b)	4.4	17.4	40.3	23.4	14.5	
33/6 (b)	5.6	16.5	35.0	25.9	17.0	
31/6 (c)	4.6	14.2	39.0	27.5	14.7	
Nitrogen, wt %						
29/6 (a)	0.88	0.40	0.31	0.53	1.14	0.60
29/12 (a)	0.70	0.50	0.32	0.59	1.28	0.65
32/5 (a)		0.55	0.22	0.45	1.04	0.54
30/7 (b)	0.37	0.07	0.16	0.35	0.97	0.36
33/6 (b)	0.18	0.07	0.15	0.33	1.07	0.40
31/6 (c)	0.19	0.15	0.14	0.41	0.98	0.37

Source: Potts, John, D., et al., 1977a, 1977b, 1978a, 1978b

- (a) Cobalt-Molybdenum on Alumina
- (b) Nickel-Molybdenum on Alumina
- (c) Nickel-Tungsten on Alumina

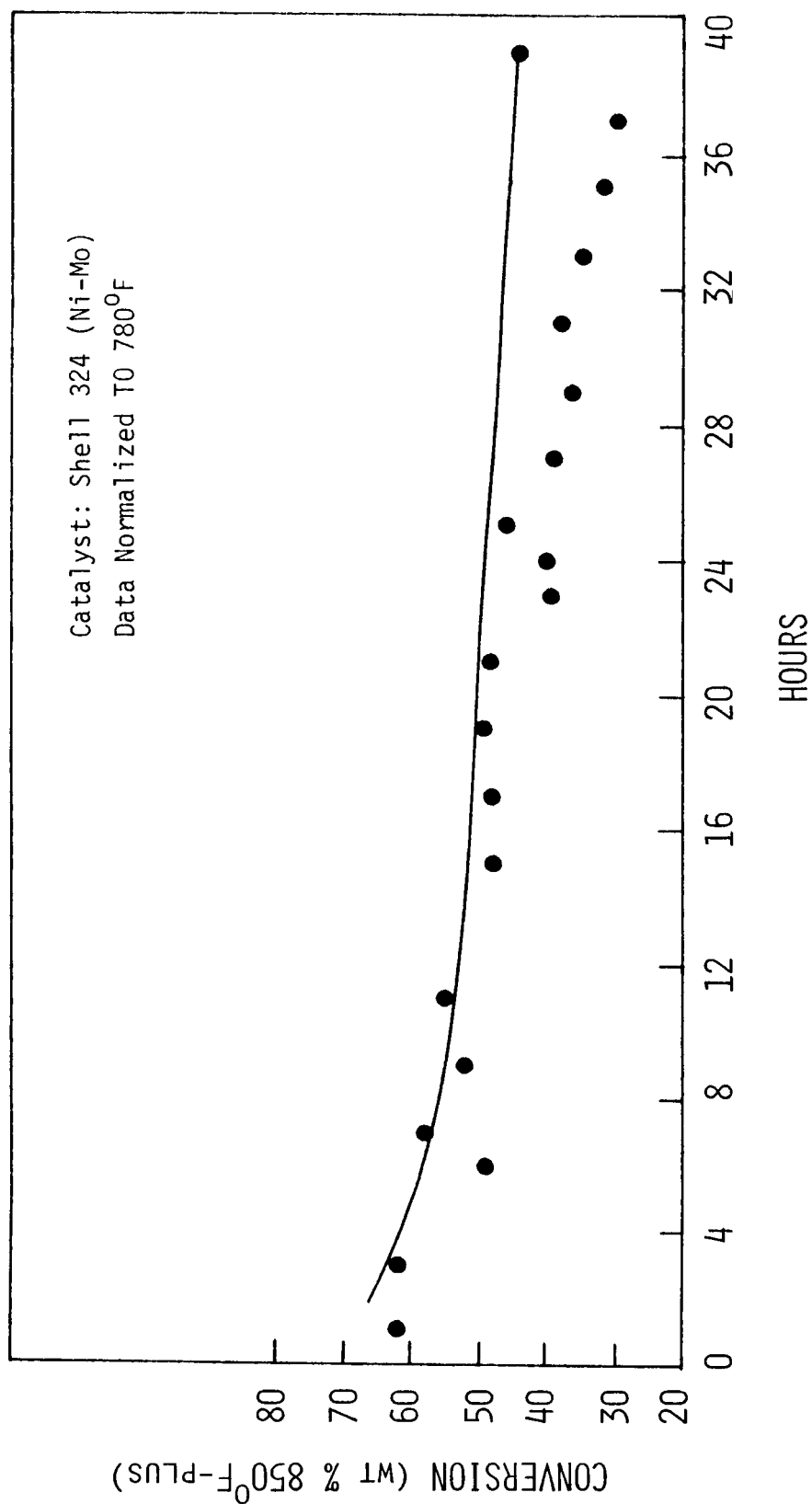


FIGURE 3.4.8 Conversion of 850°F-plus Material in Heavy Oil
(Potts, John D. et al. 1977a, 1977b, 1978a, 1978b)

conversion returned to the normal level. This behavior shows that the catalytic activity of the Ni-Mo catalyst had not decreased by recycle processing other than what would have been expected by once-through processing over the same elapsed time. It also inferred that the decline in conversion was probably due to the buildup of a material in the unconverted 850⁰-plus fraction which was increasingly difficult to convert.

One of the most important criteria for upgrading solvent refined coal is to produce a distillate product with 0.3 weight percent nitrogen. The 390-850⁰F fraction obtained had less than 0.3 weight percent nitrogen for both once-through and recycle operation. The 850⁰F-plus coal liquid feed (SRC-I) had a 2.1 weight percent nitrogen content. This nitrogen removal by two stage liquefaction (SRC-I then LC-Fining) was far superior than by one stage liquefaction represented by SRC-II, Exxon Donor Solvent (EDS), and H-Coal.

3.4.3 Lovertto, D.C.

Lovertto, David C. and Weller, S.W. (1977) of State University of New York at Buffalo compared the effectiveness of SnCl_2 and Co-Mo catalyst for the hydrogenolysis of solvent refined coal in a batch autoclave with tetralin as solvent.

Most of the catalysts studied in coal processing are at least bifunctional, although this aspect has not received much explicit attention. The role of SnCl_2 (or $\text{Sn} + \text{HCl}$, or $\text{Sn} + \text{NH}_4\text{Cl}$) in coal liquefaction is still not understood after some decades of study,

but clearly the catalyst exercises cracking as well as hydrogenative functions. The catalysts consisting of "cobalt molybdate" supported on silica-stabilized alumina are acidic, whatever their detailed action may be in the hydrodesulfurization of coal or coal-derived liquids.

It is an interesting fact that the best catalyst for liquefaction of coal is not best for hydrodesulfurization. The comprehensive catalyst survey of Kawa et al. (1974) provides a recent illustration. Supported SnCl_2 , even in small concentration, was outstanding in its ability to promote both liquefaction and the production of benzene-soluble oil, but not in desulfurization. Supported Co-Mo was equally outstanding in giving products of low sulfur content, but not in liquefaction.

This study was intended to explore the extreme cases of catalytic action, with the use of SRC as feed. The study was a comparison of (1) no catalyst, (2) unsupported SnCl_2 at low concentration, and (3) a commercial Co-Mo catalyst of low concentration.

The SRC feed had the following elemental analysis: 86.77 percent C, 6.0 percent H, 1.3 percent N, 0.7 percent S, and 5.3 percent O, also had 0.2 percent ash. A glass lined stirred autoclave was used. The autoclave was charged with 0.165 lb of SRC and 0.66 lb of tetralin (also 0.0022 lb of catalyst for the catalyst runs). Initial cold hydrogen pressure was 1000 psi and the autoclave was then heated to 840°F for one hour reaction time. Table 3.4.4 summarizes the results of each run, the catalyst used, hydrogen consumed, and the elemental analyses for the oil and asphaltene fraction are reported for

Table 3.4.4 Autoclave Test Results

Run No	Catalyst	Hydrogen Consumed (lb)	Atom Ratio H/C	Product Oil/Asphaltene				
				Wt % Carbon	Wt % Hydrogen	Wt % Nitrogen	Wt % Sulfur	Wt % Oxygen
1	None	0.00249	$\frac{1.20}{0.77}$	$\frac{87.57}{89.62}$	$\frac{8.74}{5.77}$	$\frac{0.05}{1.82}$	$\frac{0.09}{0.38}$	$\frac{3.55}{2.41}$
1A	None	0.00225	$\frac{1.11}{0.87}$	$\frac{88.32}{88.28}$	$\frac{8.20}{6.38}$	$\frac{0.24}{1.82}$	$\frac{0.27}{0.41}$	$\frac{2.97}{3.11}$
2	SnCl ₂	Not det.	$\frac{1.10}{0.87}$	$\frac{88.58}{89.67}$	$\frac{8.10}{6.52}$	$\frac{0.63}{0.73}$	$\frac{0.26}{0.37}$	$\frac{2.43}{2.51}$
2A	SnCl ₂	0.00386	$\frac{1.12}{0.86}$	$\frac{89.22}{89.69}$	$\frac{8.30}{6.46}$	$\frac{0.81}{1.32}$	$\frac{0.24}{0.39}$	$\frac{1.43}{2.14}$
2B	SnCl ₂	0.00401	$\frac{1.08}{0.87}$	$\frac{88.97}{89.35}$	$\frac{8.02}{6.47}$	$\frac{2.38}{1.13}$	$\frac{0.15}{0.37}$	$\frac{0.48}{2.68}$
3	Co-Mo	0.00220	$\frac{1.12}{0.88}$	$\frac{87.49}{88.28}$	$\frac{8.20}{6.49}$	$\frac{0.15}{1.70}$	$\frac{0.15}{0.40}$	$\frac{4.01}{3.13}$
3A	Co-Mo	0.00260	$\frac{1.18}{0.87}$	$\frac{83.70}{87.96}$	$\frac{8.26}{6.38}$	$\frac{0.37}{1.49}$	$\frac{0.23}{0.46}$	$\frac{7.44}{3.71}$
Feed			0.83	86.66	5.99	1.33	0.70	5.32

Source: Loverto, D.C. and Weller, S.W., 1977

the runs. The H/C atom ratios were almost the same for all the asphaltene samples. The average nitrogen elimination for blank runs was 9 percent, for SnCl_2 runs 38 percent, and for Co-Mo runs 1 percent. The average oxygen elimination for blank runs was 57 percent, for SnCl_2 , 69 percent and for Co-Mo runs 42 percent.

Table 3.4.5 summarizes the material balance, total liquefaction, and the oil and asphaltene distribution for the individual runs. It is observed that: although the liquefaction is high in all cases, it is highest in the SnCl_2 runs, and although the material balance are low in all cases, they are consistently lower in SnCl_2 runs. The loses are tentatively attributed to low-boiling liquid products from the SRC which are lost to the overhead during the distillation. The particularly high loses in the SnCl_2 runs are consistent with the higher hydrogen consumption (Table 3.4.4).

3.4.4 Greskovisch, E.J.

Greskovisch, E.J. (1976a, 1976b) of Air Products and Chemicals, Inc. hydrocracked the PAMCO's SRC. The object of the research program was to characterize the inherent physical and chemical properties of solvent refined coal (SRC) and develop optimum methods for the de-sulfurization, denitrogenation, and hydrocracking of SRC using commercially available catalysts.

The chemical and physical characteristics of SRC products from Wilsonville and Ft. Lewis plants are summarized in Table 3.4.6, also the characteristics of Filtrate and Recycle solvent from Wilsonville

Table 3.4.5 Product Distribution

Run No	Catalyst	Total product recovered (1b)	% Liquefaction*	Oil % of total products	Asphaltene % of total products
1	None	0.1360	Not det.	22.1	77.4
1A	None	0.1429	93.7	14.0	77.2
2	SnCl ₂	0.1113	100.0	13.5	86.5
2A	SnCl ₂	0.1241	99.6	21.8	77.5
2B	SnCl ₂	0.1539	99.8	20.5	79.1
3	Co-Mo	0.1490	94.5	2.7	90.1
3A	Co-Mo	0.15412	94.1	5.9	87.2

Source: Loverto, D.C. and Weller, S.W., 1977

* Percent Liquefaction = ((75 - toluene insolubles)/75) x 100

Table 3.4.6 Summary of Analytical Data for Composite
Wilsonville and Ft. Lewis SRC Samples

	SRC	SRC
	Wilsonville	Ft. Lewis
Ultimate Analysis		
Carbon wt%	88.0	87.5
Hydrogen wt%	5.6	5.7
Nitrogen wt%	2.0	2.1
Oxygen wt%	3.6	3.7
Sulfur wt%	0.6	0.61
Ash wt%	0.06	0.19
Density lb/cubic ft	76.47	71.30
Softening Point °F	342	352
Pour Point °F	430	440
Component Class Analysis		
Aromatics wt%	2.4	1.0
Saturates wt%	1.5	0.1
Polars wt%	1.2	0.8
Hexane Insolubles wt%	94.9	98.1
Distillation °F		
IBP	435	563
5 vol%	763	883
9 vol%		915
10 vol%	885	
15 vol%	938	

Source: Greskovisch, E.J., 1976a, 1976b

plant are summarized in Table 3.4.7. The ultimate analyses of composite Wilsonville and Ft. Lewis SRC products and filtrates shows that these materials have very low sulfur and ash content.

Ft. Lewis filtrate was hydrotreated using Harshaw 0402 T Co-Mo catalyst in a long path fixed bed reactor of 2 inch I.D. The filtrate was pumped upflow through a one liter catalyst bed. The catalyst was reduced with hydrogen, but was not presulfided. Reaction temperature was varied between 645⁰F and 805⁰F. Pressure was maintained at 1500 psi. Total time on-stream for the run was 182 hours. The results for percent removal of sulfur and nitrogen as a function of temperature are plotted in Figure 3.4.9, and the percent removal of 590⁰F-plus material (SRC cracking) as a function of temperature is plotted in Figure 3.4.10.

The results, as expected, show increased sulfur and nitrogen removal and increased hydrocracking at higher temperatures. Highest sulfur and nitrogen removal were 94 and 38 percent observed at 800⁰F, 1500 psi and 0.9 LHSV. There was evidence of slight catalyst deactivation when temperature was reduced from 800⁰F to 750⁰F. Raising the pressure to 2000 psi at the end of the run showed a small increase in nitrogen removal but no noticeable effect on sulfur removal.

Based on the data in Figures 3.4.9 and 3.4.10, an Arrhenius plot was prepared in order to better evaluate activation energies. If the conversion of sulfur, nitrogen, and 590⁰F-plus material were assumed to be first order kinetics, a plot of $\ln(1/1-X)$ versus $1/T$ would yield activation energies from the slopes of the respective lines. From Figure 3.4.11, it can be noted that the data correlated reasonably

Table 3.4.7 Summary of Analytical Data for Composite
Wilsonville and Ft. Lewis Filtrate and
Wilsonville Recycle Solvent Samples

	Wilsonville Filtrate	Ft. Lewis Filtrate	Wilsonville Recycle Solvent
Ultimate Analysis			
Carbon wt %	87.8	86.8	87.6
Hydrogen wt %	7.2	7.6	7.5
Nitrogen wt %	0.4	1.0	0.4
Oxygen wt %	3.3	3.8	4.0
Sulfur wt %	0.46	0.55	0.31
Ash wt %	0.001	0.133	0.04
Moisture wt %	0.23	0.21	1.42
Density lb/cubic ft	66.15	66.70	64.64
Flash Point °F	228	215	228
Fire Point °F	235	220	235
Distillation °F			
5 %	340	303	340
10 %	408	409	400
20 %	440	418	417
30 %	457	467	448
40 %	477	495	470
50 %	510	561	492
60 %	555	607	528
70 %	600	668	607
80 %	650	728	607
90 %	745		665
93 %	848		
98 %			730
Percent Over (wt)	90.4	71.6	96.0
Percent Bottoms (wt)	7.0	26.4	2.0
Percent Loss (wt)	2.6	2.0	2.0

Source: Greskovisch, E.J., 1976a, 1976b

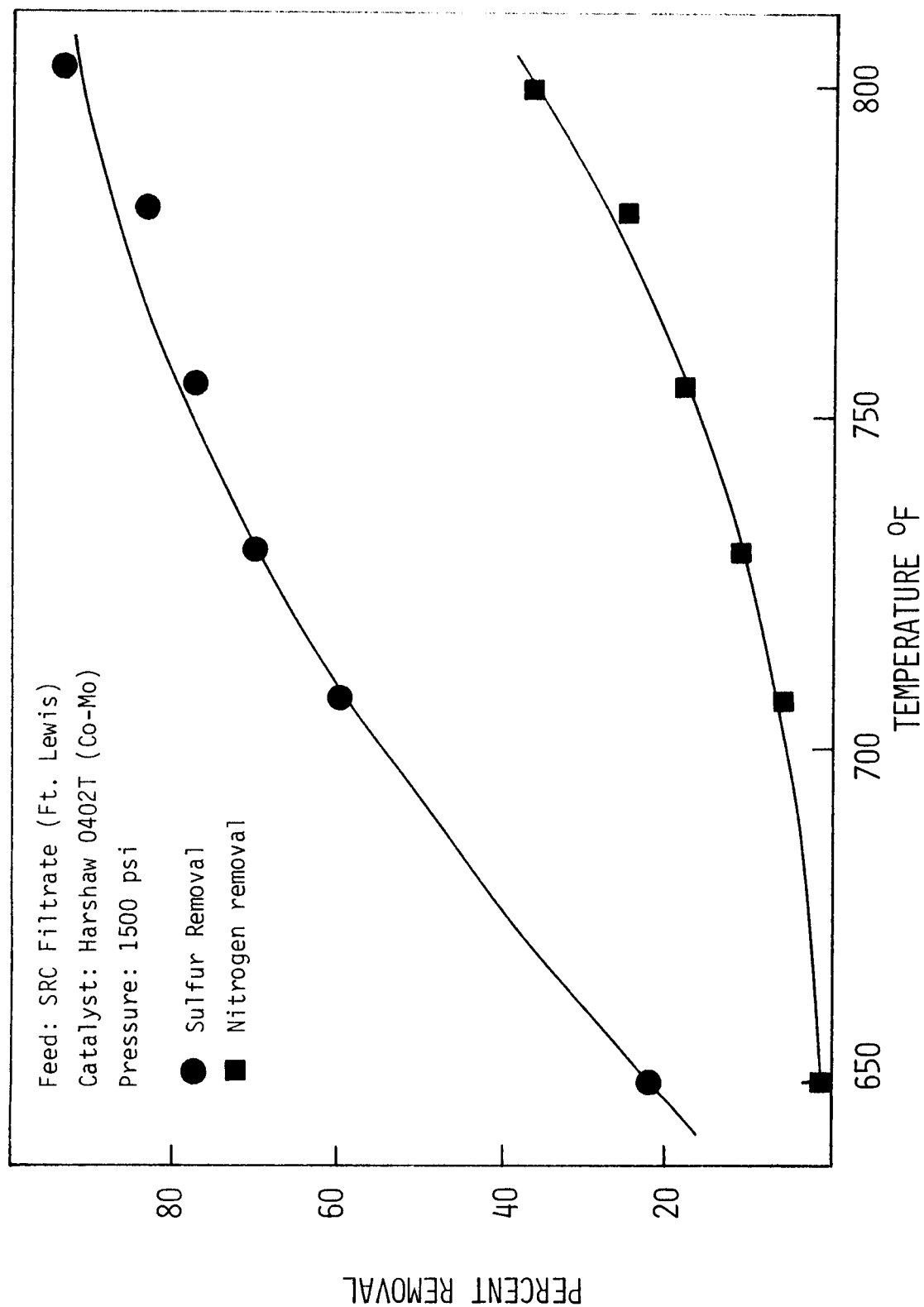


FIGURE 3.4.9 Sulfur and Nitrogen Removal as a Function of Temperature (Greskovisch, E.J., 1976a,1976b)

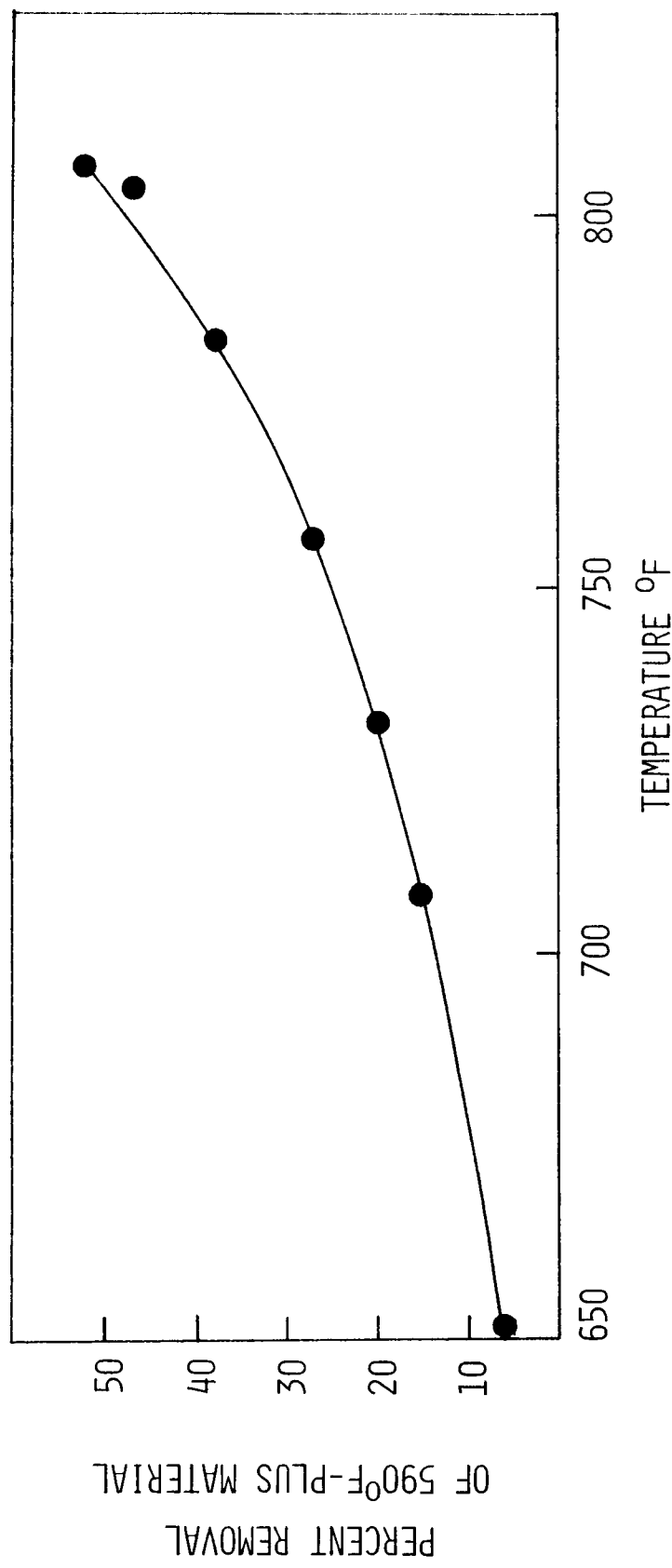


FIGURE 3.4.10 Percent Removal of 590°F-plus Material as a Function of Temperature
(Greskovisch, E.J., 1976a, 1976b)

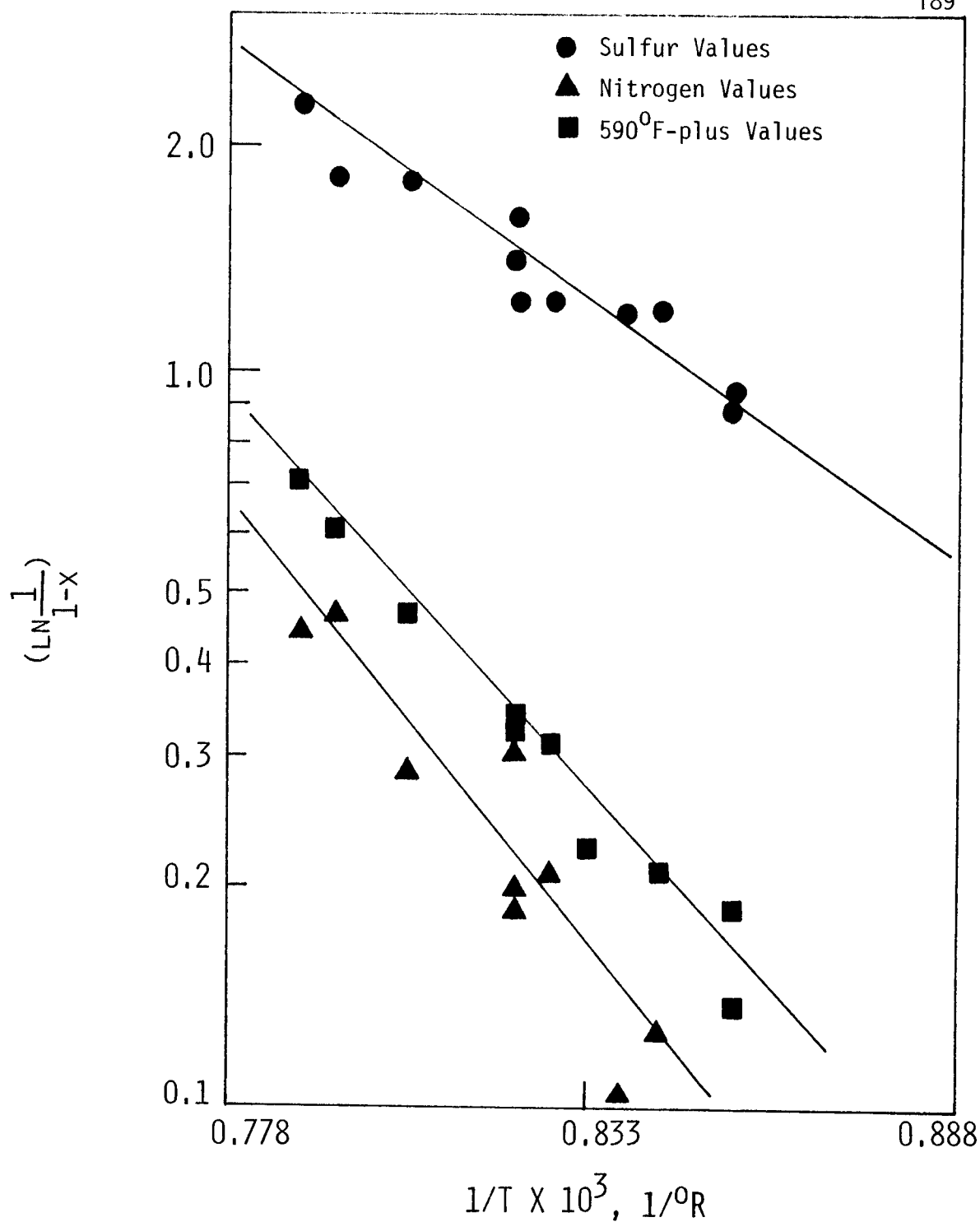


FIGURE 3.4.11 Arrhenius Plot for Activation Energies
(Greskovisch, E.J., 1976a, 1976b)

well. Energies of activations obtained were 28,360; 44,620 and 43,470 Btu/lb mole for sulfur, nitrogen and 590⁰F-plus material, respectively. These data appear to be within the range of typical chemical reaction in the presence of a catalyst. The results obtained here appear to be similar, in nature, to those obtained by DeRosset (1976a) for the hydrofining of coal-derived liquids.

3.4.5 De Rosset, A.J.

3.4.5.1 DeRosset, A.J. (1976a)

DeRosset, A.J. (1976a) of UOP Incorporated hydrofined filter feed from the solvent refined coal (SRC), furnished to UOP Inc., by Pittsburgh and Midway Coal Co. The filter feed as received contained 4 percent ash and 2.7 percent unconverted coal. The solids were removed by filtration at 218⁰F in the presence of 50 percent added toluene to reduce ash to 0.01 percent and to reduce benzene insolubles from 16.7 percent to 7.5 percent. The detailed feed and filtrate inspection is given in Table 3.4.8. It is evident that the filtration, in addition to removing solids, upgraded the liquid.

Hydrorefining studies were carried out in a bench scale continuous unit. Hydrogen and coal liquid were passed concurrently downflow over a fixed bed of 6.0 to 12.0 cubic inches of granular catalyst. The catalyst was a sulfur resistant composite of group VIA and group VIII elements supported on a high surface area refractory. Bed temperature was 775⁰F and pressure was 2800 psi. The products included gas, stripper overhead, and stripper bottoms. The last usually comprised

Table 3.4.8 Feed and Product Inspection of SRC Filtrate

	Filter Feed	Filtrate
$^{\circ}\text{API @ } 60^{\circ}\text{F}$	-11.8	-5.8
Sp. Gr. @ 60°F	1.1813	1.1257
ASTM Distillation, $^{\circ}\text{F}$		
IBP	400	400
5 %	540	520
10 %	579	550
20 %	620	585
30 %	654	620
40 %	699	652
50 %	729	685
60 %	793	740
70 %	925	825
80 %		1020
Percent Over	69.0	80.0
Percent Bottoms	31.0	20.0
Percent 850°F -plus bottoms (SRC)	35.0 33.7	28.0 29.0
Percent Water	0.35	0.0
Percent Heptane Insoluble	34.4	27.5
Percent Benzene Insoluble	22.3	9.6
Percent Xylene Insoluble	6.7	
Percent Ash	4.0	0.01

Source: DeRosset, A.J., 1976a

over 90 percent of the exit stream and was the only portion analyzed in detail, and is referred as "product."

Even a qualitative appraisal of the operating and analytical data from the five hydrorefining runs on SRC liquids indicates that the critical reactions are nitrogen removal, conversion of heptane insolubles, and hydrocracking of SRC to 850°F-minus distillate. The extent of these reactions determines the quantity and quality of the hydrorefined product which is available for further downstream processing into transportation fuels. Hydrogen is consumed in all these reactions, and represents a considerable portion of the price paid for upgrading SRC.

The results of two runs suggested that conversion of heptane-insolubles is a function of the rate at which they are fed to the reaction (heptane-insolubles mass velocity). The reciprocal of this rate is the time parameter with which conversion is correlated: $100 \left[(\text{LHSV}) \times \text{sp. gr. feed} \times (\text{percent heptane-insol. in feed}) \right]^{-1}$. Figure 3.4.12 is a first order (semi-logarithmic) plot of data, with percent heptane-insolubles remaining in the product as ordinate and the above time parameter as abscissa.

The straight line indicates the first order rate constant for conversion of heptane-insolubles.

A similar analysis was made for nitrogen removal. In this case the time parameter was $100/[\text{LHSV} \times \text{sp. gr. feed} \times \text{percent N in feed}]$. First order (semi-logarithmic) plots of percent residual nitrogen vs. the above time parameter are given in Figure 3.4.13.

Chemical hydrogen consumption incurred in hydrorefining can be

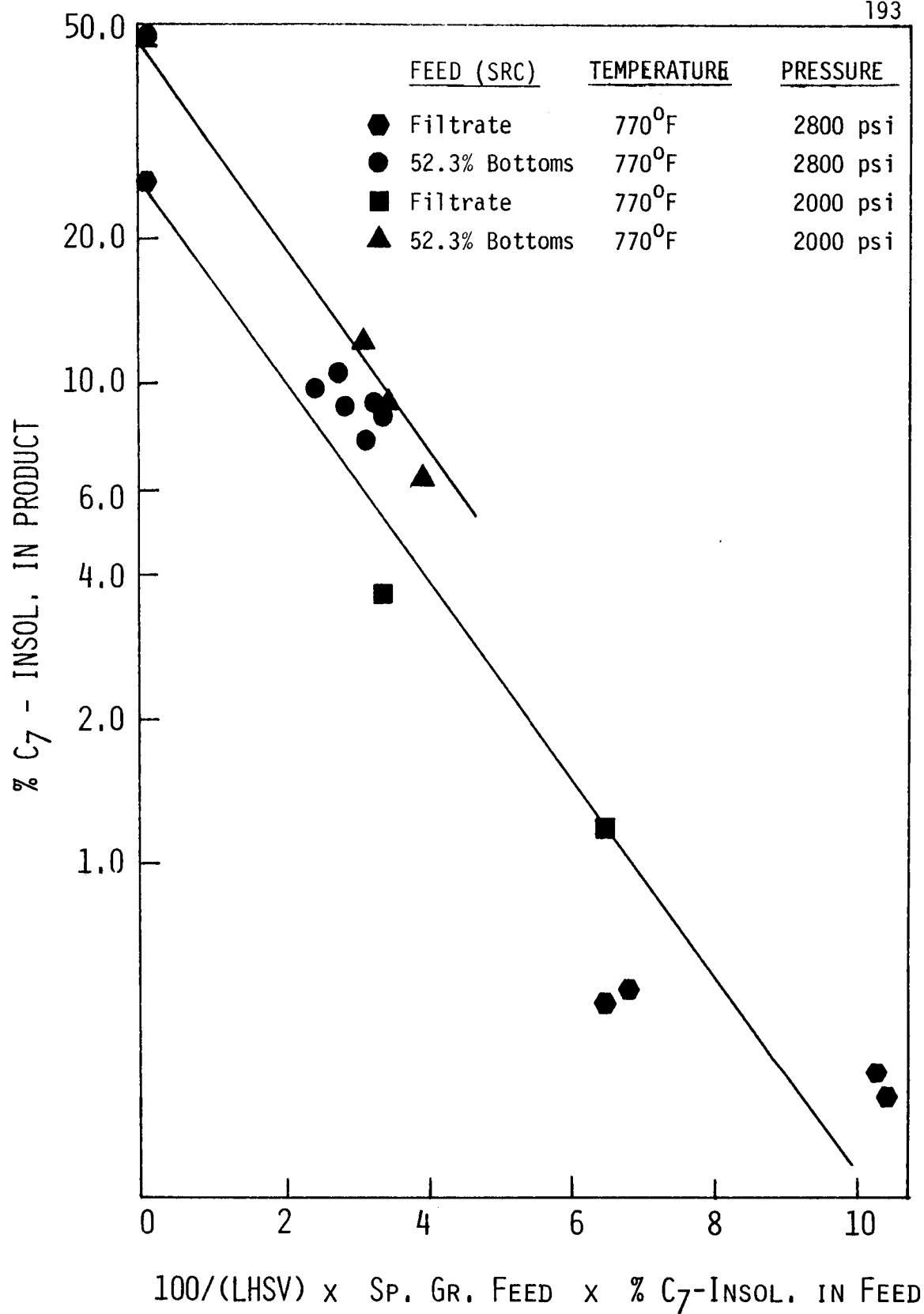
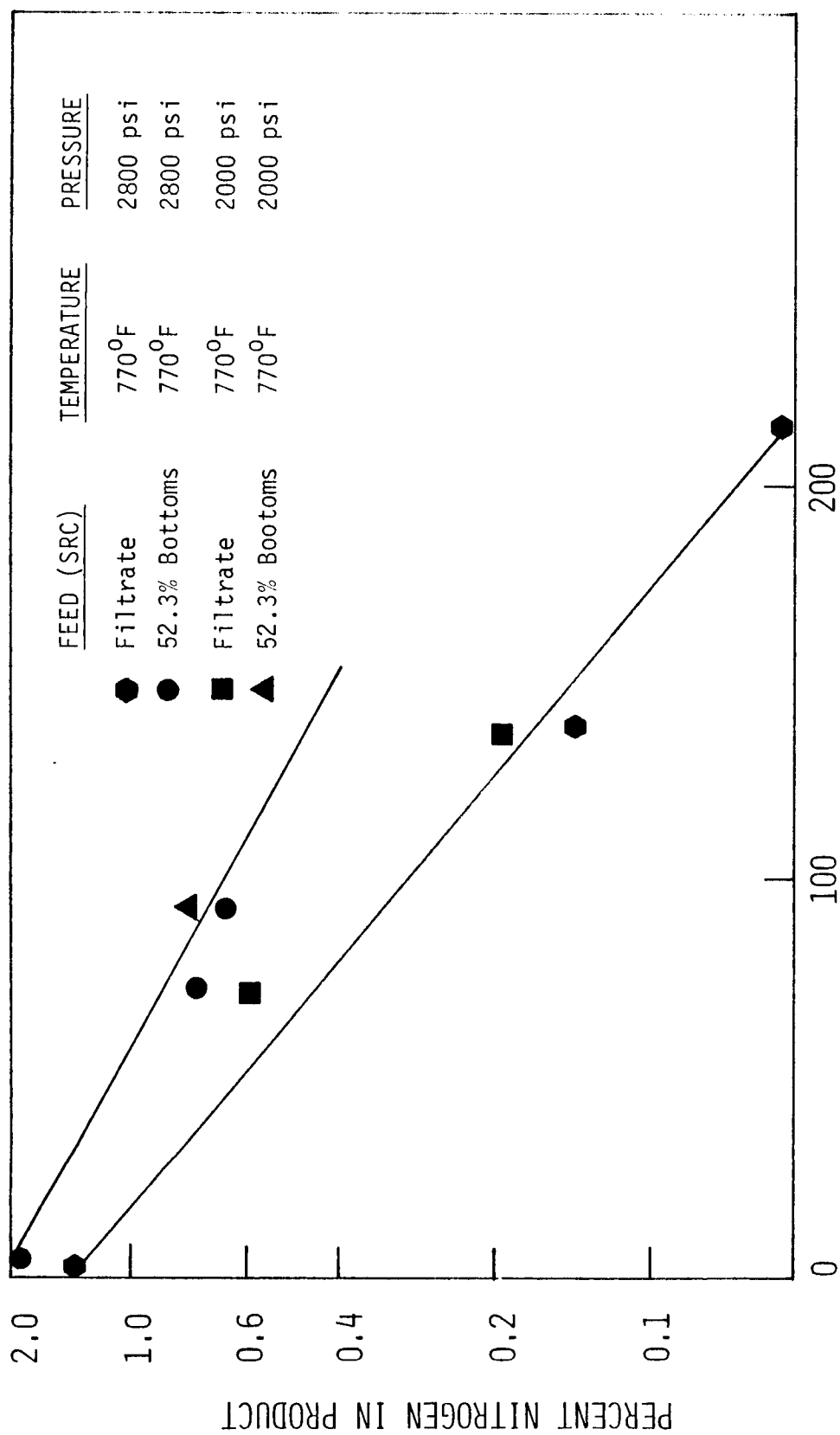


FIGURE 3.4.12 Hydrotreating SRC Liquids-Heptane Insolubles
(DeRosset, A.J., 1976a)



100 / (LHSV x SP. GR. FEED x % NITROGEN IN FEED)

FIGURE 3.4.13 Hydrorefining SRC Liquids-Nitrogen (DeRosset,A.J., 1976a)

calculated from detailed elemental analysis of all product streams. Oxygen removed is assumed to go to water, nitrogen to ammonia, and sulfur to hydrogen sulfide. Light gases are assumed to derive from hydrocracking short side chains. Balance of consumption appears in the increase in hydrogen content of the liquid products. The consumptions range from 1800 to 3300 scf/bbl. These values are in fair agreement with the measured hydrogen feed to the plant, less elemental hydrogen appearing in exit gas streams. About 80 percent of the hydrogen consumed is retained in the liquid product.

3.4.5.2 DeRosset, A.J. (1976b)

DeRosset, A.J. (1976b) of UOP, Incorporated, hydrotreated cutback solvent refined coal (SRC) at four sets of conditions.

The SRC granules were dissolved in a process solvent prepared from SRC filter feed by vacuum distillation (DeRosset, 1976a), a 500-850°F cut was used as solvent. The final mixture contained 82 weight percent SRC. As the SRC granules contained 7 percent solvent so the final feed stock analyzed 73.5 volume percent SRC. Selected properties of feed, SRC and the solvent are given in Table 3.4.9.

Bench scale hydrotreating was carried out under commercial conditions which may be categorized as "severe":

- . Temperature 700-840°F
- . Pressure 2000-3000 psi
- . Space velocity 0.25-1.0 V/v-hr

Catalyst used were of Group VIA and Group VIII elements supported

Table 3.4.9 Properties of Cut Back SRC and Components

	SRC	Solvent	Cut Back SRC
$^{\circ}\text{API @ } 60^{\circ}\text{F}$	-15.6	-0.2	-14.1
Sp. gr. @ 60°F	1.2210	1.0777	1.2052
Softening Point, $^{\circ}\text{F}$	348		
Pour Point, $^{\circ}\text{F}$			285
Chloride, ppm			57
Distillation, $^{\circ}\text{F}$			
IBP	650	475	550
5 %	795	539	610
10 %	896	557	653
20 %	1005	578	749
30 %		593	905
50 %		620	
70 %		660	
90 %		741	
SRC (850-plus) %	92.5	0	73.5

Source: DeRosset, A.J., 1976b

on a high surface area refractory. Four sets of conditions were used.

A preliminary estimate of product slate at base conditions was obtained from measurement and inspection of all effluent streams. It compared closely with the distribution estimated in processing vacuum flash bottoms of UOP filtered SRC filter feed (DeRosset, 1976a).

Rapid catalyst deactivation occurred when processing cut back solvent refined coal which is obvious from the following results:

Hours on stream	69	77	193
Percent heptane insoluble	5.1	7.0	11.5
Percent Nitrogen	0.38	0.43	0.77

This deactivation was unexpected since none was observed when processing the UOP filtered SRC filter feed. The poisons may be either inorganic, arising from the ash, or asphaltenic, generated in the workup of SRC. Ash content of the feed was 0.17 percent. Ash content of the product was, up to 137 hours, less than 0.01 percent.

3.4.5.3 DeRosset, A.J. (1976d)

DeRosset, A.J. (1976d) of UOP, Incorporated hydrotreated vacuum flashed solvent refined coal (SRC) filtrate. The SRC filtrate, furnished by Pittsburgh and Midway Coal Company, was topped in laboratory in vacuum flash equipment to yield a 30 weight percent bottoms containing 0.04 percent ash, and 38.4 percent heptane-insolubles.

Bench scale hydrotreating was carried out under the following conditions:

- . Temperature 700-840⁰F
- . Pressure 2000-3000 psi
- . Space velocity 0.25-1.0 V/v-hr

Best results were achieved at the most severe conditions:

93 percent of heptane-insoluble was converted and 89 percent of nitrogen was removed. A slight decline in catalyst activity was noted. Compared with cut back SRC (DeRosset, 1976b) the yield of distillate gas oil was higher, and the yield of light ends and residuum was lower. This was consistent with the better quality of the SRC filtrate bottoms, which contained only 46 percent SRC, 38.4 percent heptane-insolubles; vs. 73.5 percent SRC and 65.7 percent heptane-insolubles in the cut back SRC.

Table 3.4.10 represents an attempt to compare and correlate change in catalyst activity, measured by change in heptane-insoluble conversion and nitrogen conversion for four coal liquids hydrotreated by DeRosset, A.J: SRC filtrate (1976a), cut back SRC (1976b), synthoil filtrate (1976c) and 30 percent bottoms of SRC filtrate (1976d). The only firm conclusion that can be drawn is that the SRC filtrate, partially deasphalted by filter aid solvent, and reduced to 0.01 percent ash, caused much less deactivation than the other feeds. The cut back SRC contained 0.17 percent ash, synthoil filtrate containing 0.05 percent ash, and the current topped SRC filtrate containing 0.04 percent ash all caused about the same degree of activity loss.

Table 3.4.10 Catalyst Activity Checks

Feedstock	SRC Filtrate (1)	20% Cut- back SRC (2)	Synthoil Filtrate (3)	30% Bottoms of SRC Filtrates (4)
Percent Ash	0.01	0.17	0.05	0.04
Percent Heptane Insolubles	26.94	65.7	18.8	38.4
Percent Nitrogen	1.28	1.92	1.31	1.69
Volume of Catalyst, cubic inch	6.0	12.0	12.0	12.0
Check Periods, hour	1/12	4/16	14/23	1/10
Total Processing Time, hours	114	124	110	128
				3/12
				145
Check Conditions:				
T-T (Base), °F	7	-9	18	0
P-P (Base), psi	0	0	0	0
WHSV/WHSV (Base)	2.0	0.58	2.0	1.0
				0.5
Initial Product Heptane				
Insoluble, percent	2.97	6.95	4.08	5.52
Initial conversion of				2.70
Heptane Insoluble, percent	89.0	89.4	78.3	85.6
Final Product Heptane Insoluble,				93.0
percent	3.40	11.5	5.40	9.81
Final Conversion of Heptane				5.59
Insoluble, percent	87.4	82.5	71.3	74.5
Initial Residual Nitrogen, percent	0.422	0.488	0.414	0.453
Initial Nitrogen Conversion,				85.4
percent	67.0	74.6	68.4	0.235
Final Residual Nitrogen, percent	0.431	0.773	0.544	73.2
Final Nitrogen Conversion, percent	66.3	59.7	58.5	0.684
lb of Oil Charged/lb Catalyst	198.8	77.1	71.6	59.5
				76.8
				87.5

(1) DeRosset, 1976a (2) DeRosset, 1976b (3) DeRosset, 1976c (4) DeRosset, 1976d

3.4.5.4 DeRosset, A.J. (1976f)

DeRosset, A.J. (1976f) of UOP Incorporated, hydrotreated solvent refined coal (SRC) without adding any extraneous solvent. This was accomplished by recycling hydrotreated product as solvent at a combined feed ratio of 2.0 to 2.5. Start-up solvent for continuous bench scale operation was provided by batch hydrotreatment of SRC in an autoclave. In each batch run, charge to the autoclave was 1.1 lb SRC, 0.11 lb catalyst, and 0.011 lb sulfur. The autoclave was sealed and pressured with hydrogen to 1800 psi at ambient temperature. The temperature was raised to 570⁰F and held for two hours to complete liquefaction of the SRC. Temperature was raised to 725⁰F and maintained for 16 hours. Hydrogen pressure was maintained at 2300 psi. After cooling and venting the autoclave, the contents were removed and filtered to separate catalyst. The filtrate was used to absorb SRC for continuous run hydrotreating.

Three bench scale hydrotreating runs were made in recycle mode with SRC. A 456 hours run was made at a single operating conditions to provide a feedstock, for subsequent hydrocracking, containing a minimum amount of heptane-insolubles. The run was scheduled for 480 hours. However, by 456 hours, a pressure drop of 300 psi had built up across the reactor, and the run was terminated. The heptane-insoluble analysis of the product drifted upward with time, as can be seen in Figure 3.4.14 which shows a steady catalyst deactivation with time.

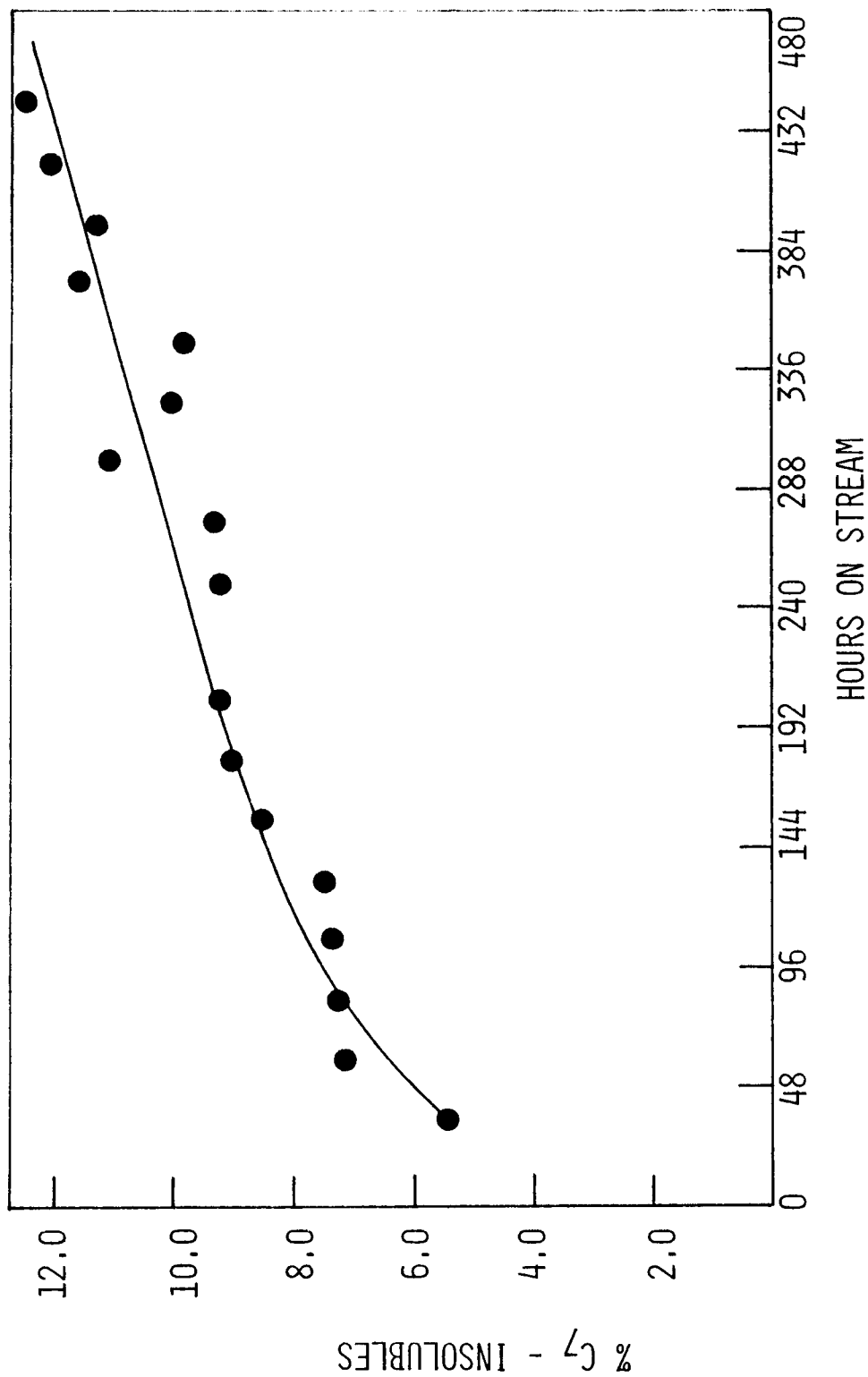


FIGURE 3.4.14 Residual Heptane-Insolubles vs Time (DeRosset,A.J.,1976f)

3.4.5.5 DeRosset, A.J. (1976h)

DeRosset, A.J. and Tang, G. (1976h) of UOP, Incorporated, hydrocracked the hydrotreated SRC (DeRosset, 1976f) to characterize the processability of this feed by conventional petroleum refining technology.

The upgraded SRC, containing 9.8 percent heptane-insolubles and 70.1 percent 650°F-plus bottoms, was processed over commercial hydrocracking catalyst at four sets of conditions, including a catalyst activity check at startup conditions at the conclusion of each run.

Charge stock for hydrocracking was total upgraded SRC. Inspection of the upgraded SRC, as well as the SRC, are given in Table 3.4.11.

Experiments were conducted at four sets of hydrocracking conditions. Results are summarized in Table 3.4.12. At base space velocity, 18°F above the base temperature, and 200 psi above base pressure (period 2) conversion to 650°F-minus distillate was 11.8 volume percent and heptane-insolubles were reduced to 5.36 percent from 9.75 percent in the feed. Raising the temperature 18°F (period 4) at otherwise identical conditions did not improve conversion or lower the heptane-insoluble content in the liquid product. This was first indication of catalyst deactivation. At the latter conditions, lowering the space velocity to 0.66 x base space velocity (period 6) resulted in increasing the conversion to 650°F-minus distillate slightly to 10.9 percent and decreasing the heptane-insolubles to 5.86 percent. When the temperature was lowered to 18°F above base temperature (period 8) while other processing variables remained unchanged, conversion to

Table 3.4.11 Inspection of SRC Samples

	SRC	Upgraded SRC
^o API	-13.7	9.6
Sp.Gr. @ 60 ^o F	1.2012	1.0028
Molecular Weight, avg	622	360
Pour Point, ^o F		+55
Viscosity, 210 ^o F,cst		32.69
Distillation, ^o F		
IBP	648	433
5 %	834	555
10 %	905	600
15 %	915	
20 %		660
30 %		718
40 %		780
50 %		850
60 %		940
65 %		1000
Percent Over	15.0	65.0
Percent Bottoms	85.0	35.0
Heptane Insolubles, percent	89.4	9.76
Benzene Insolubles, percent	34.7	1.68
Conradson Carbon, percent	55.85	16.31
Aromatics, weight percent		91.7
Ash, percent	0.11	0.001
Ultimate Analysis, percent		
Hydrogen	5.63	8.76
Carbon	84.44	90.85
Sulfur	0.78	0.02
Nitrogen	2.12	0.548
Oxygen	3.71	0.20

Source: DeRosset, A.J., 1976h

Table 3.4.12 Hydrocracking Upgraded SRC

Period No.	Feed		Liquid Product			
	2	4	6	8	10	
Hours on Stream	20-28	48-56	85-95	161-131	141-147	
LHSV/LHSV (Base)	1.0	1.0	0.66	0.66	1.0	
T-T (Base) °F	18	36	36	18	18	
P-P (Base), psi	200	200	200	200	200	
Heptane Insoluble, percent	9.79	6.13	5.86	6.47	7.34	
Specific Gravity @ 60°F	1.0028	1.0435	1.0382	1.0505	1.0505	
oAPI @ 60°F	9.6	4.1	4.8	3.2	3.2	
650°F-plus bottoms, vol percent	70.10	65.46	62.43	65.89	68.68	
Conversion to 650°F, vol percent	11.8	6.6	10.9	6.0	2.0	
Ultimate Analysis, percent						
Hydrogen	8.76	9.32	8.99	8.99	8.83	
Carbon	90.85	90.01	89.69	90.77	90.01	
Sulfur	0.02	0.018	0.017	0.016	0.016	
Nitrogen	0.548	0.153	0.269	0.349	0.377	
Oxygen	0.20	0.11	0.10	0.10	0.13	

Source: DeRosset, A.J., 1976h

650⁰F-minus distillate decreased to 6.0 percent while heptane-insoluble content increased to 6.57 percent. The run was then concluded with a catalyst activity check (period 10) at the initial conditions. Results showed that after 119 hours of processing, conversion to 650⁰F-minus distillate decreased from 11.8 volume percent to 2.0 volume percent, the product hydrogen content dropped from 9.32 percent to 8.33 percent, the product nitrogen content increased from 0.153 percent to 0.3777 percent, and the API gravity decreased from 5.0 to 3.2.

Table 3.4.12 also indicate that the API gravity of the liquid products were all lower than that of the feed. This is contrary to experience with catalytic hydrocracking of upgraded synthoil (DeRosset 1976c). The lowering of API gravity in the present case appears to reflect the proportionality greater gas and light ends in the converted SRC which concludes that due to the presence of high molecular weight asphaltic materials, conversion to 650⁰F-minus distillate was very low.

3.4.6 Davis, G.O.

3.4.6.1 Davis, G.O. et al. (1976a)

Davis, G.O. et al. (1976a) hydrogenated 50 percent W/W of solvent refined coal dissolved in oil to produce low boiling liquid hydrocarbons.

Clean coal crushed and dried to pulverized fuel standards was slurried with recycle oil and pumped to a digester where up to 85 percent of the coal was dissolved. The digest was passed through a filter to remove undissolved solid residue. Filtration removed all of

the inorganic sulfur (mainly pyrites), thus the total content of the extract was close to the organic sulfur content of the original coal, just under 1.0 percent for UK coals.

The preliminary studies were carried out in a 122 cubic inch stirred autoclave at 2000 psi, temperatures up to 840⁰F and times of up to 4 hours. The coal feedstock was loaded into the reactor and hydrogen was continuously passed into the bottom of the autoclave through a sintered stainless steel disc, with 0.00039 inch pores. The disc assisted mass transfer of hydrogen to the liquid by creating a large gas-liquid interfacial area.

The catalyst used was cobalt molybdate on alumina, a commercial hydrofining catalyst. The catalyst to feedstock weight ratio was varied from 1:4 to 1:20.

Extracts from a high and low rank coal were hydrogenated. The extract contained 50 percent w/w of coal derived material dissolved in a solvent oil. Since the oil is hydrogenated as well as the coal material, some experiments were performed to investigate the effect of catalytic hydrogenation of the oil alone. The analyses of the solvent oil, coal extract and parent coal are given in Table 3.4.13.

An increase in H/C atomic ratio was observed, as H/C ratio of high rank extract was 0.62 (Table 3.4.13), where as the hydrogenated filtrate ratio was 0.90. Also for solvent oil the H/C ratio increased from 0.77 to 1.06 after 4 hours of hydrogenation.

Heteroatom removal appeared to be increasing in the order of nitrogen, oxygen and sulfur. Non-catalytic hydrogenation of solvent oil showed that the sulfur content was halved in 4 hours.

Table 3.4.13 Analyses of Solvent Oil, Coals and Coal Extracts

	Recycle Oil	Beynon High Rank Coal	Annesley Low Rank Coal	Beynon Coal Extract	Annesley Coal Extract
Carbon, percent	90.8	90.0	84.2	90.5	89.3
Hydrogen, percent	5.8	4.7	5.4	4.7	5.0
Nitrogen, percent	0.95	1.4	1.9	1.6	1.75
Oxygen, percent	1.4	2.9	7.6	2.1	2.9
Sulfur, percent	1.00	1.55	0.65	0.9	0.55
H/C Atomic ratio	0.77	0.62	0.76	0.62	0.67
Softening Point (ring and ball)				444 ⁰ F	435 ⁰ F
Proximate Analysis					
Volatile matter, percent				46.8	48.5
Ash, percent				0.4	0.2
Insolubility in:					
Cyclohexane, percent				66	
Chloroform, percent				52	49
Benzene, percent				50	55
Quinoline				13	2.5
Asphaltene content, percent				12	25
Alcan Coking Value				63.9	66.5

Source: Davis, G.O., et al., 1976a

The low rank coal extract was most altered by hydrogenation; the aromatic nature of the product decreased with increasing severity of hydrogenation. The higher boiling point fractions contained considerable proportions of hydroaromatics, over 85 percent of the carbon being present in ring structure.

The yields of light, middle and heavy oils were found by distilling the liquid products. The majority of the condensate (90 percent or more) was classified as light oil with the remainder middle oil (390-570°F). The filtrate consisted principally of middle oil (75-90 percent) with 1.0 to 4.0 percent residue and the rest heavy oil. A typical distribution with time is shown in Figure 3.4.15. Initially, the decrease in heavy oil corresponds to an increase in medium oil and in light oil production. Later, the rate of decrease in heavy oil yield slows and is accompanied by a fall in the medium oil yield while the rate of light oil production appears to be constant. It seems probable, therefore, that the hydrogenation process is sequential in the series heavy oil to medium oil to light oil and that the medium oil yield reflects a difference between the rate at which it is generated from heavy oil and the rate at which it is lost in light oil production. In addition, very little condensate was produced in the first hour of hydrogenation, there being effectively an induction period, which tends to support this postulate of sequential reaction.

An economic evaluation of a similar process was prepared early in 1974. This study considered a plant processing 1 million tons of coal per annum where the main product was a gas/oil mixture. The plant, to be built at a colliery site, accepted washed coal (moisture 16

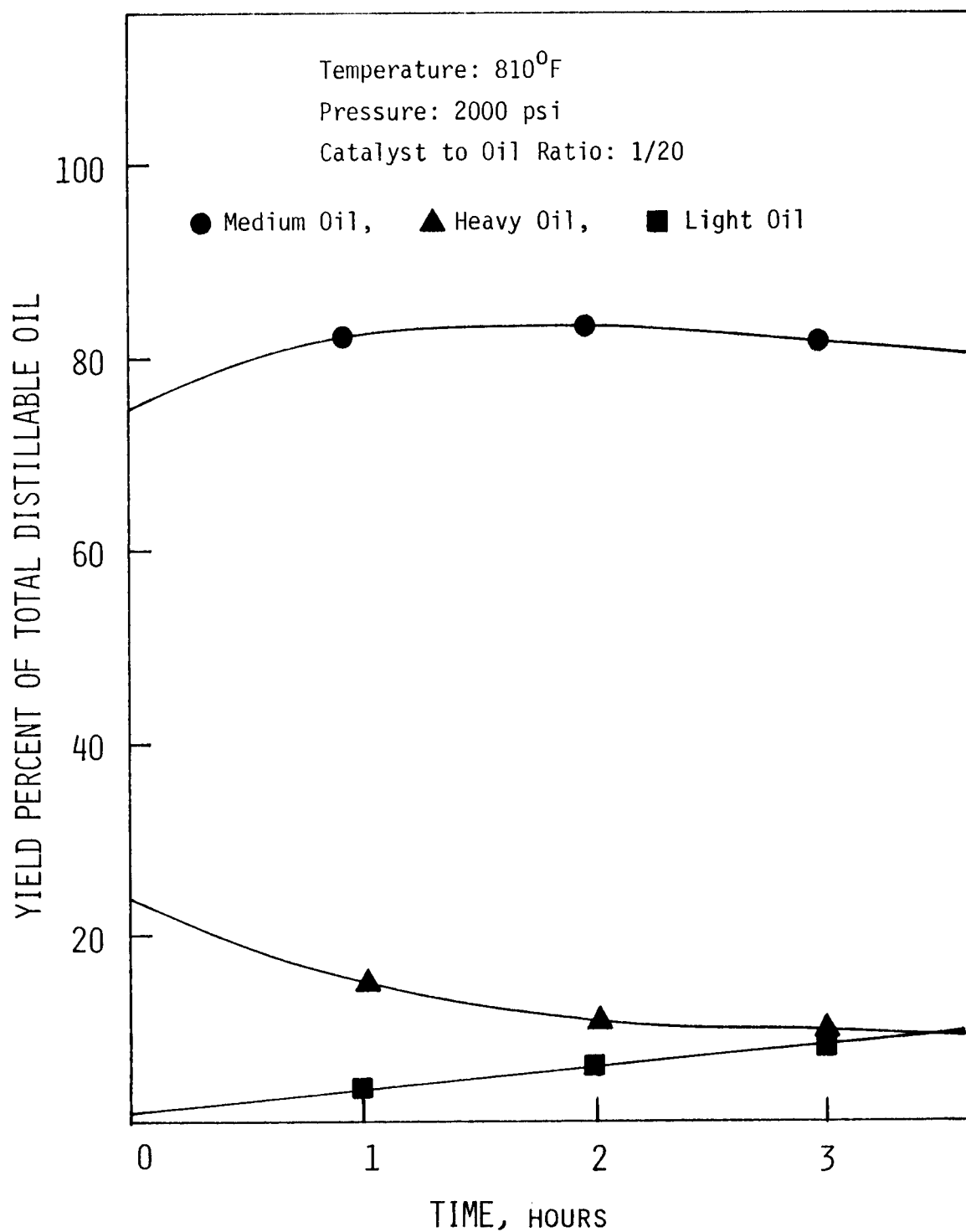


FIGURE 3.4.15 Yields of Oils from Hydrogenation of Solvent Oil
(Davis, G.O. et al., 1976a)

percent, ash 8 percent) for preliminary preparation. A solvent extraction stage was followed by two hydrogenating stages, liquid hydrotreating and vapour phase hydrocracking. The double hydrogenating scheme was chosen for conservative costing as it follows established petroleum practice in producing aliphatic distillates of high hydrogen content. In the event, a coal processing plant would produce aromatic distillates requiring much less (expensive) hydrogen.

The plant would require a total plant investment of \$84,000,000 allocated to the following processing units:

. Coal handling and preparation	9 percent
. Solvent extraction	33 percent
. Hydrogenation	41 percent
. Hydrogen production and gas treatment	15 percent
. Site charges, etc.	2 percent

Product yields were based on laboratory-derived results and can be summarised:

. Gasoline	13 percent coal feed
. Wide range gas oil	27 percent coal feed
. Hydrocracking residue (suitable to make electrode coke)	4 percent coal feed

These yields gave an overall thermal efficiency of 60 percent.

3.4.6.2 Davis, G.O. (1978)

Davis, G.O.(1978) analyzed the economics of a coal liquefaction plant for olefin and aromatics (B.T.X) production.

The kinetic studies were carried out in a stirred autoclave system with powdered catalysts and it was shown that the conversion of coal solutions to light distillates generally follows first order chemical kinetics. The rate data obtained from the experiments at different temperatures and time were used to construct Arrhenius plots and the activation energies (E) obtained from these diagrams (54,000-72,000 Btu/lb mole) were similar to those obtained by other workers when hydrocracking coal derivatives and petroleum residues. The significance of these observations to the prospects for the process lies in the fact that as the conversion of coal to distillates was always directly proportional to the quantity of coal remaining (1st order) then it should be possible to convert most of the coal to distillates by extending the hydrocracking residence time.

The success of the overall liquefaction process depends greatly on the activity and life of the hydrocracking catalyst and to date there are no commercially available catalysts which have been specifically developed for selective coal hydrocracking. The catalysts employed in most experimental coal liquefaction plants are conventional catalysts which are normally used in petroleum refining. It has been reported by Davis, J.C.(1976) that none of the catalysts that he tested remained active for more than 500 hours. Hence, there is an obvious need to develop an active catalyst which is resistant to the

deactivating elements present in coal or alternatively remove all the deactivating elements by refining. In the first selective study by Davis and Derbyshire (1977a) more than fifty catalysts were examined and after successive assessment tests one catalyst was selected for a long-term pilot plant trial.

The results from some of the laboratory assessment tests showed that the best catalyst for producing liquid distillates, at the standard test conditions used, was COMOX 471 (Co-Mo on alumina). This catalyst was subsequently tested in the hydrocracking pilot plant and the results are summarized in Table 3.4.14.

The hydrocracking pilot plant has a trickle-bed reactor with a nominal catalyst capacity of 122 cubic inch. It can operate at high hydrogen pressures and up to a temperature of 930⁰F.

Using the pilot plant, large quantities (1320 lb) of coal extract solutions were hydrocracked in long continuous runs using several different catalysts. The hydrogenated product from these runs were fractionated and the yields and compositions of the various distillate fractions were determined. Characterization of the light, middle and heavy distillate fractions are given in Table 3.4.15.

The coal oil naptha together with a middle oil fraction was assessed by Imperial Chemical Industries, and the results are summarized in Table 3.4.16. It is seen that the olefin yield from the coal oil naptha contains 68 percent naphthenes. This leads to a lower olefin yield compared with a typical petroleum derived naptha which is significantly more paraffinic. The cracking pattern of the middle distillate was poor which is again consistent with its high aromatic

Table 3.4.14 Boiling Point Distribution of Hydrogenated Products from Continuous Hydrocracking of a Coal Extract Solution

Hours on Stream	Cumulative wt %				
	Boiling Point				
	340 ⁰ F	480 ⁰ F	570 ⁰ F	660 ⁰ F	790 ⁰ F
34-42	3.3	12.0	22.6	56.7	72.2
42-50	1.4	10.1	22.1	53.3	
75-83	3.3	9.2	18.0	58.3	
91-99	4.0	7.2	21.6	52.0	60.6
107-115	3.2	5.8	12.6	47.8	75.3
362-370	1.9	5.8	13.5	50.4	

Source: Davis, G.O., 1978

Table 3.4.15 Characterization of Distillates from Pilot
Plant Hydrocracking of Coal Extracts

Light Distillate (IBP-390°F)

H/C Atomic Ratio	1.7
Oxygen wt %	0.07
Nitrogen wt %	0.06
Sulfur wt %	0.1
Paraffins vol %	20.0
Naphthenes vol %	40.0
Aromatics vol %	40.0

Middle Oil (390-480°F)

H/C Atomic Ratio	1.4
Oxygen wt %	0.2
Nitrogen wt %	0.1
Sulfur wt %	0.1
Paraffins vol %	17.0
Naphthenes vol %	11.0
Aromatics vol %	72.0

Heavy Oil (480°F-plus)

H/C Atomic Ratio	1.2
Oxygen wt %	0.2
Nitrogen wt %	0.2
Sulfur wt %	0.1
Mainly Polynuclear Hydroaromatics	

Source: Davis, G.O., 1978

Table 3.4.16 Thermal Cracking Tests on Coal Oil Distillates

Feedstock	Coal Oil Naphtha	Coal Oil Middle Distillate	Petroleum Naphtha	Petroleum Kerosene
CH_4	10.2	7.3	13.9	11.7
C_2H_4	16.9	9.0	23.4	25.0
C_2H_6	2.4	1.6	3.3	2.2
C_3H_6	7.9	3.2	13.2	10.8
C_3H_{10}	0.3	0.2	0.5	0.3
$\text{C}_4\text{H}_{10} + \text{C}_4\text{H}_8$	2.1	0.5	3.5	1.9
C_4H_6	5.6	1.3	3.6	3.8
Benzene	14.4	8.0	8.1	7.6
Toluene	13.7	6.2	5.7	3.9
m- & p-Xylene	2.1	1.7	1.9	0.2
o-Xylene	0.9	0.8	0.8	0.9
Ethyl Benzene	2.3	0.6	0.5	0.3
Cracking Temperature		1500 ⁰ F		
Residence Time		0.5 secs		

Source: Davis, G.O., 1978

content. The coal oil naphtha and middle oils would not therefore be considered primarily as ethylene cracker feedstocks whilst supplies of petroleum naphtha and kerosene are available at a reasonable price.

The coal oil naphtha fraction was catalytically reformed over a Pt-alumina catalyst. High yields of B.T.X aromatics were produced, 81 to 83 percent compared with 40 to 45 percent from petroleum naphtha cuts. The total liquid reformat had an RON (research octane number) value of 108, so it would be an excellent blending component for gasoline as well as a source of aromatics.

These preliminary assessments of the coal oil liquid distillates are very encouraging and no doubt improvements in quality for specific feedstock functions could be achieved by the careful selection of hydrocracking catalyst and conditions. The material flow sheet for the process shows that roughly half of the distillate product boils in the gas oil range and these will have to be further hydrocracked if they are to be used as chemical feedstocks.

3.4.7 Peters, B.C.

Peters, B.C. (1976, 1977b, 1977e) of Dow Chemical Company conducted laboratory studies in metal reactors and performed computer simulations to provide data, from which preliminary capital requirements and operating costs for a commercial plant which uses coal liquefaction products for the production of useful aliphatic and aromatic compounds can be estimated.

The feed was SRC II (slurry recycle mode) produced by Pittsburgh

and Midway Coal Mining Company from Western Kentucky Coal. A 50/50 blend of SRC I (a solid at room temperature) and recycle oil gave a very low conversion when hydrotreated, so it was decided to use an SRC-II liquid containing 25 percent light oil, 29 percent wash liquid and 46 percent process solvent; the same ratio in which they are produced.

The SRC-II was subjected to a processing sequence which parallels existing technology for producing petrochemicals from petroleum crude oil. The SRC-II was distilled into naphtha, mid-distillate and gas oil fractions (mostly the mid-distillate and gas oil fractions). The mid-distillate and gas-oils were hydrocracked to produce more naphtha along with some LPG's. The straight run and hydrocrackate naphthas were hydrotreated to remove the heteroatom (S,N and oxygen). Finally, the hydrotreated naphthas were reformed to maximize the yields of aromatics. These three hydroprocessing experiments were carried out in three similar 1-inch diameter tubular steel reactors in a single phase mode using an excess of hydrogen.

Due to high levels of nitrogen and oxygen in the oils, a neutral alumina supported Co-Mo catalyst was used to hydrocrack mid-distillate and gas oils to naphtha and L.P.G's. The catalyst provided a hydrogenation function, while the cracking was largely thermal. The hydrocracked mid distillate was subjected to second pass hydrocracking experiments to determine conversions and selectivities for this material.

In order to successfully reform the naphtha with a conventional bifunctional reforming catalyst, heteroatom levels had to be reduced,

by hydrotreating, to a level such that they would not deactivate the reforming catalyst. Hydrotreating the naphtha proved to be the most difficult step, requiring two passes on most straight-run naphthas to reduce sulfur and nitrogen to less than 5 ppm. Hydrocrackate naphthas were hydrotreated in one step. Neutral alumina supported nickel-molybdenum and cobalt-molybdenum catalysts were used for hydrotreating.

The hydrotreated naphthas were reformed over a conventional platinum reforming catalyst in an attempt to maximize aromatics. By operating at "severe" conditions, the aromatics were purified by selectively cracking away the paraffins. This produced a reformate with a suitably high aromatic content to be fed directly to a hydroalkylator, nominally 80 to 90 percent. Although the initial activity of the catalyst was very encouraging, the activity decline was very rapid.

The data collected from hydrocracking, hydrotreating, and reforming was reduced to mathematical expressions describing conversions and selectivities observed. Aromatic saturation and heteroatom removal data were used to calculate hydrogen consumption. These data were combined to give the calculated results expected from the hydrotreating of the straight run and recycle hydrocracked naphthas as they would exist in a commercial plant.

Based on these results the value of 100 pounds of straight-run-naphtha was \$9.49 and 100 pounds of mid-distillate was \$7.63 (in 1980 dollars). With the added costs for processing gas oils, it would appear that mid-distillate processing would be only marginally

attractive, while the high aromatic yield of naphthas make them very attractive as petrochemical feedstock.

3.4.8 Stein, T.R.

Stein, T.R. et al. (1977) of Mobil Research and Development Corporation hydrotreated three different SRC fractions obtained from two bituminous and one sub-bituminous coals, over five commercial hydrotreating catalysts. The main objectives of the research were as follows:

- . Evaluation of commercial catalysts and hydroprocessing conditions for decreasing the aromatic, nitrogen, sulfur and oxygen content of coal liquids from SRC process.
- . Development of kinetic model for predicting the hydrogen and heteroatom content of processed coal liquids as a function of processing severity. (The kinetic model is presented in Section 4).
- . Determination of the compatibility of raw and processed coal liquids with petroleum derived fuels.

Batch hydrogenation studies conducted in a shaker bomb reactor showed that catalytic hydrogenation is an effective means of lowering the heteroatom concentration and increasing the hydrogen content of the coal derived liquids. On the basis of batch test results catalysts were selected for continuous fixed bed hydrotreating operation. The fixed bed reactor used was 7/8 inch ID steel pressure vessel with a capacity of 6.1 to 18.3 cubic inches. The reactor was enclosed in aluminium heating block for uniform distribution of heat.

The catalysts testes were:

- . HDS-1441A (MoO_3 13.8 percent, CoO 2.8 percent, SiO_2 3.5 percent).
- . Ketjen 153 S (Ni 3.1 percent, MoO_3 15.1 percent, SiO_2 5 percent).
- . HDS-9A (Ni 2.6 percent, MoO_3 12.1 percent).
- . HDS-86 (Ni 7.1 percent, W 17.5 percent, SiO_2 34 percent).
- .HDS-20 (MoO_3 17 percent, CoO 5.96 percent, SiO_2 0.21 percent).

A mixture of 6.1 cubic inches of catalyst and 2.44 cubic inches of sand was charged to the reactor. The sand dilution was found to give more consistent results. The catalyst was sulfided at 500 psi with a hydrogen stream containing 2 percent H_2S .

The three SRC fractions tested were SRC Light Organic Liquid, SRC Recycle Solvent, and 2/1 Blend Recycle Solvent with SRC. The physical properties of these fractions are listed in Table 3.4.17. The results from hydrotreating each of these fractions are summarized separately.

3.4.8.1 Stein, T.R.(Light Organic Liquid)

The light organic liquid from the SRC process was charged as received from Wilsonville. This light stream boils in the naphtha-kerosene range ($100\text{-}500^\circ\text{F}$). Two runs were made utilizing two different startup procedures with a $\text{NiMo/Al}_2\text{O}_3$ catalyst (HDS-9A). The runs were terminated after ten days on-stream due to pressure buildup caused by excessive coking in the preheater spiral.

The operating conditions ranged from $550\text{-}746^\circ\text{F}$, 500-1000 psi, and 0.9-4.0 LHSV. The data showed an overall hydrogen consumption of 82-1441 scf/bbl. Except for a few runs at low severity, the hydrogen

Table 3.4.17 Properties of SRC Fractions

	SRC Light Organic Solvent	SRC Recycle Solvent	2/1 Blend Recycle Solvent and SRC
Carbon wt %	83.70	88.40	86.90
Hydrogen wt%	9.93	7.43	6.93
Oxygen wt %	5.00	3.90	4.10
Nitrogen wt %	0.30	0.60	1.00
Sulfur wt %	0.40	0.37	0.57
Specific Gravity @ 60 ⁰ F	0.8470	1.0333	
Kin. Viscosity, cs @ 100 ⁰ F		5.79	982.34
Heating Value, Btu/lb	181480	16921	
Total Ash, ppm		100	400
Distillation (vol % off) ⁰ F			
IBP	83	306	329
5	149	373	392
10	177	393	405
20	213	409	446
30	250	434	481
40	284	453	529
50	317	483	583
60	339	510	658
70	347	551	
80	384	594	
90	399	669	
End Point	563	902	

Source: Stein, T.R. et al., 1977

utilization was 162-336 scf/bbl for C_1 - C_5 production, 193-282 scf/bbl for water production from the removal of oxygen and 46-57 scf/bbl for the production of ammonia and hydrogen sulfide. The remainder of the hydrogen (251-904 scf/bbl), which represents about 55-65 percent of the hydrogen consumed, went into the C_6 -plus product. This was largely as a result of aromatic saturation.

The heteroatom removal for all runs was high, with the nitrogen content of the product reduced below 0.1 percent by weight. Even some of the high space velocity, low temperature runs gave more than 84 percent sulfur removal. In general for this stock, the order of heteroatom removal was sulfur, nitrogen and then oxygen in the descending order of removal.

The hydrogen and nitrogen content of the liquid products is plotted as a function of total hydrogen consumption in Figures 3.4.16 and 3.4.17, respectively.

3.4.8.2 Stein, T.R. (SRC Recycle Solvent)

SRC recycle solvent was charged to the hydrotreating unit as received. This raw charge stock was a 300-830⁰F boiling range distillate. Compared to virgin petroleum distillates boiling in the same range, the SRC process solvent was high in nitrogen (0.62 percent by weight) and oxygen (3.77 percent by weight) content and low in hydrogen (7.7 percent by weight) content.

Two process variable studies were conducted using $NiMo/Al_2O_3$ (HDS-9A) and $CoMo/Al_2O_3$ (HDS-1441A) catalysts. Each of the catalysts was on-stream for about 20 days, and no operational problems were

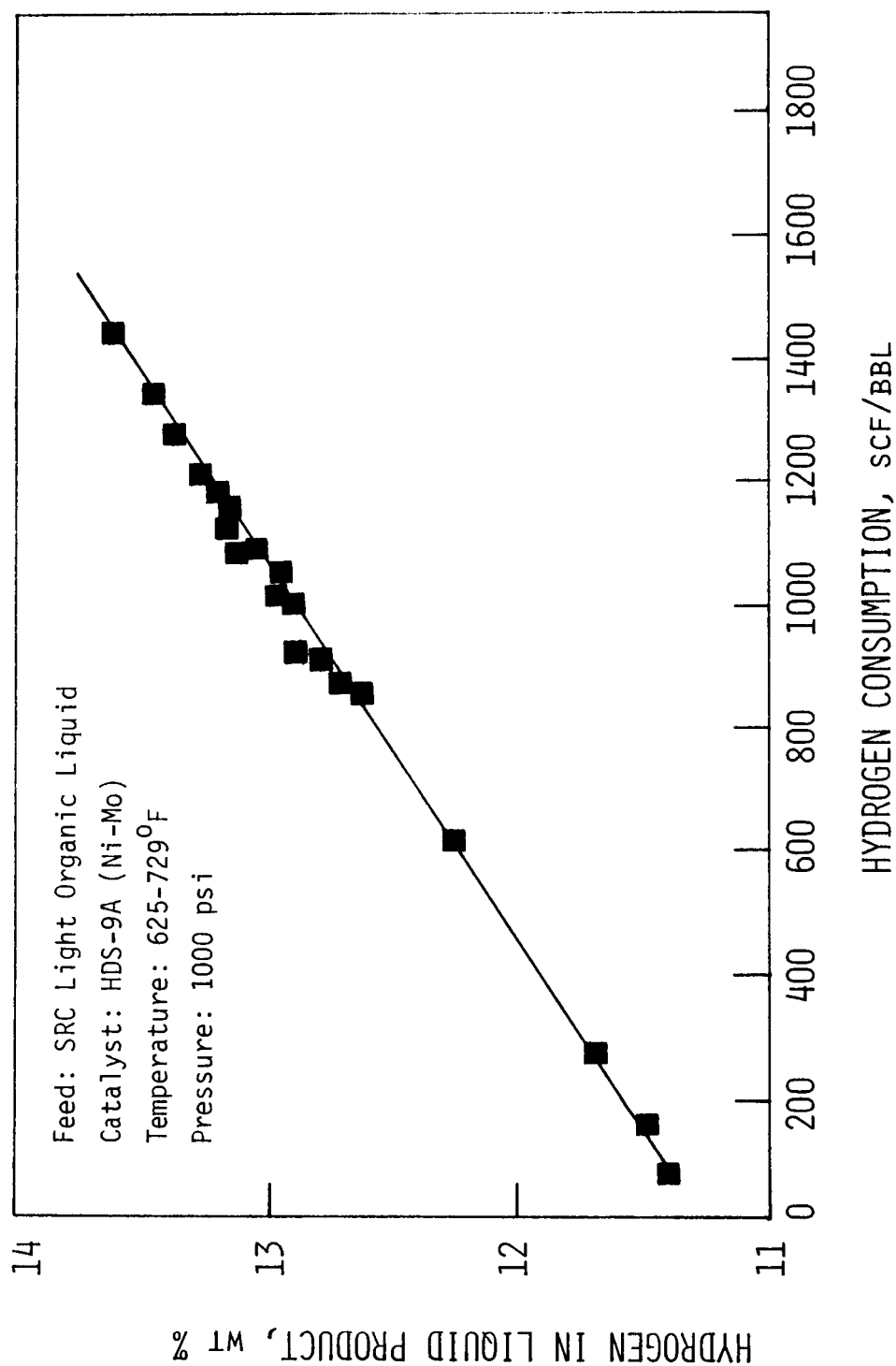


FIGURE 3.4.16 Hydrogen Content of Hydroprocessed SRC Light Organic Liquid as a Function of Total Hydrogen Consumption (Stein, T.R. et al., 1977)

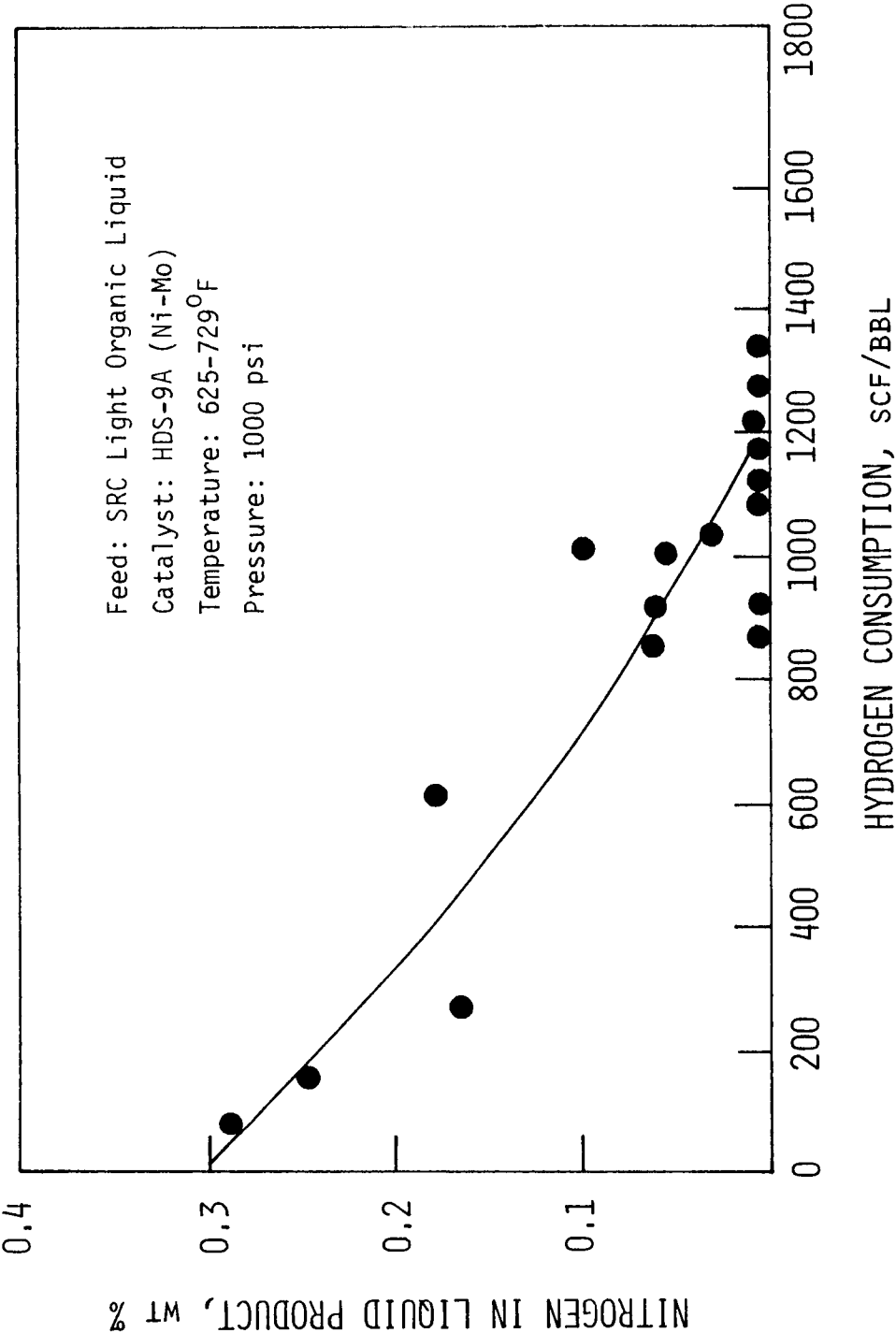


FIGURE 3.4.17 Nitrogen Content of Hydroprocessed SRC Light Organic Liquid as a Function of Total Hydrogen Consumption (Stein, T.R. et al., 1977)

encountered during these runs.

The range of operation conditions for Ni-Mo catalyst (HDS-9A) were:

Temperature	673-798 ⁰ F
Pressure	1200-2500 psi
LHSV	0.45- 2.11 per hour

The yeild of C₆-plus liquid product was 96 to 99 percent by weight on charge. The chemical and physical properties of the hydroprocessed product at all severity levels were significantly improved.

- . Gravity was increased from 5.5 ⁰API in the charge to 12-28 ⁰API in the product.
- . Heteroatom concentrations were uniformly decreased.
 - Sulfur to less than 0.05 weight percent (versus 0.40 weight percent in feed).
 - Nitrogen to 0.03-0.39 weight percent (verus 0.62 weight percent in feed).
 - Oxygen to 0.10 -2.30 weight percent (versus 3.8 weight percent in feed).
- . Hydrogen was increased from 7.7 weight percent in the feed to 9.06-12.03 weight percent in the product.
- . Aromatic carbon content was reduced from 71 percent to as low as 24 percent.
- . Viscosity and boiling range of the liquid products were reduced.

The results of the process variable runs with Co-Mo (HDS-1441A) catalyst were quite similar to those obtained by Ni-Mo (HDS-9A) catalyst.

Figures 3.4.18 and 3.4.19 show the oxygen and nitrogen content of the hydroprocessed product as a function of the total hydrogen consumed. Both oxygen and nitrogen decrease linearly in the hydrogen consumption range of 1000-2000 scf/bbl. Above 2000 scf/bbl, there is very little heteroatom removal for increased hydrogen consumption. The additional hydrogen consumption increases the H/C ratio of liquid product (i.e., decreases the aromatic content).

3.4.8.3 Stein, T.R.(Recycle Solvent/SRC Blend)

Two parts of recycle solvent and one part of SRC were mixed for hydrotreating studies. This was the maximum amount of SRC that could be blended into the recycle solvent and still produce a liquid of low enough viscosity which could be processed in the standard hydro-processing unit. These heavy viscous liquids periodically plugged the filters and control valves downstream of the reactor, even though these lines were maintained at 200⁰F.

Continuous, fixed bed pilot unit runs were made on two catalysts which had previously been evaluated in exploratory shaker bomb experiments. The catalysts used were HDS-1441A (Co-Mo) and HDS-86 (Ni-W). In batch tests HDS-1441A showed the highest activity for nitrogen and oxygen removal, while HDS-86 showed a considerably lower activity for removal of these heteroatoms.

The operating conditions tested were:

Temperature 674-788⁰F

Pressure 2000 psi

LHSV 0.21-1.05 per hour

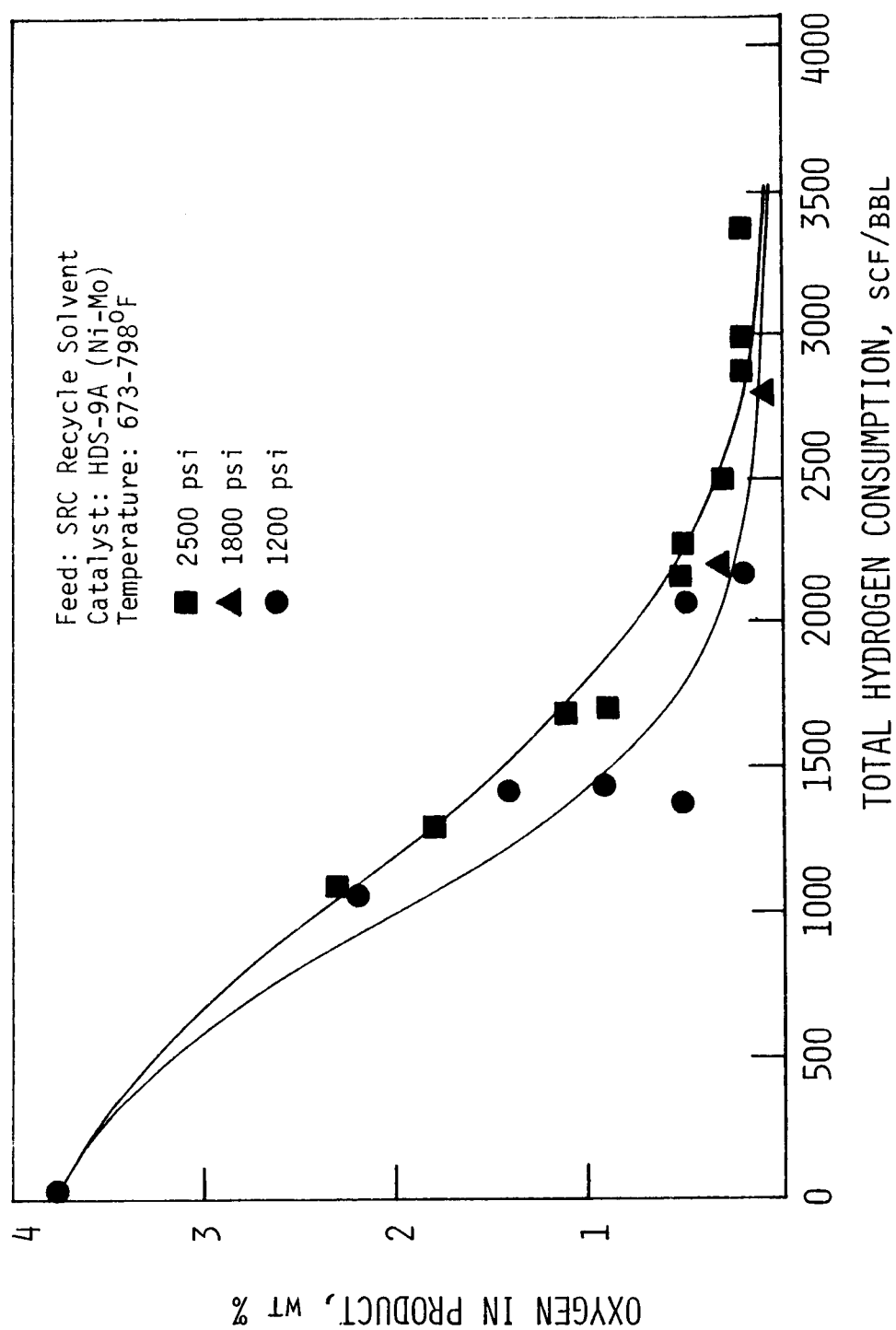


FIGURE 3.4.18 Oxygen Content of Hydroprocessed SRC Recycle Solvent as a Function of Total Hydrogen Consumption (Stein, T.R. et al., 1977)

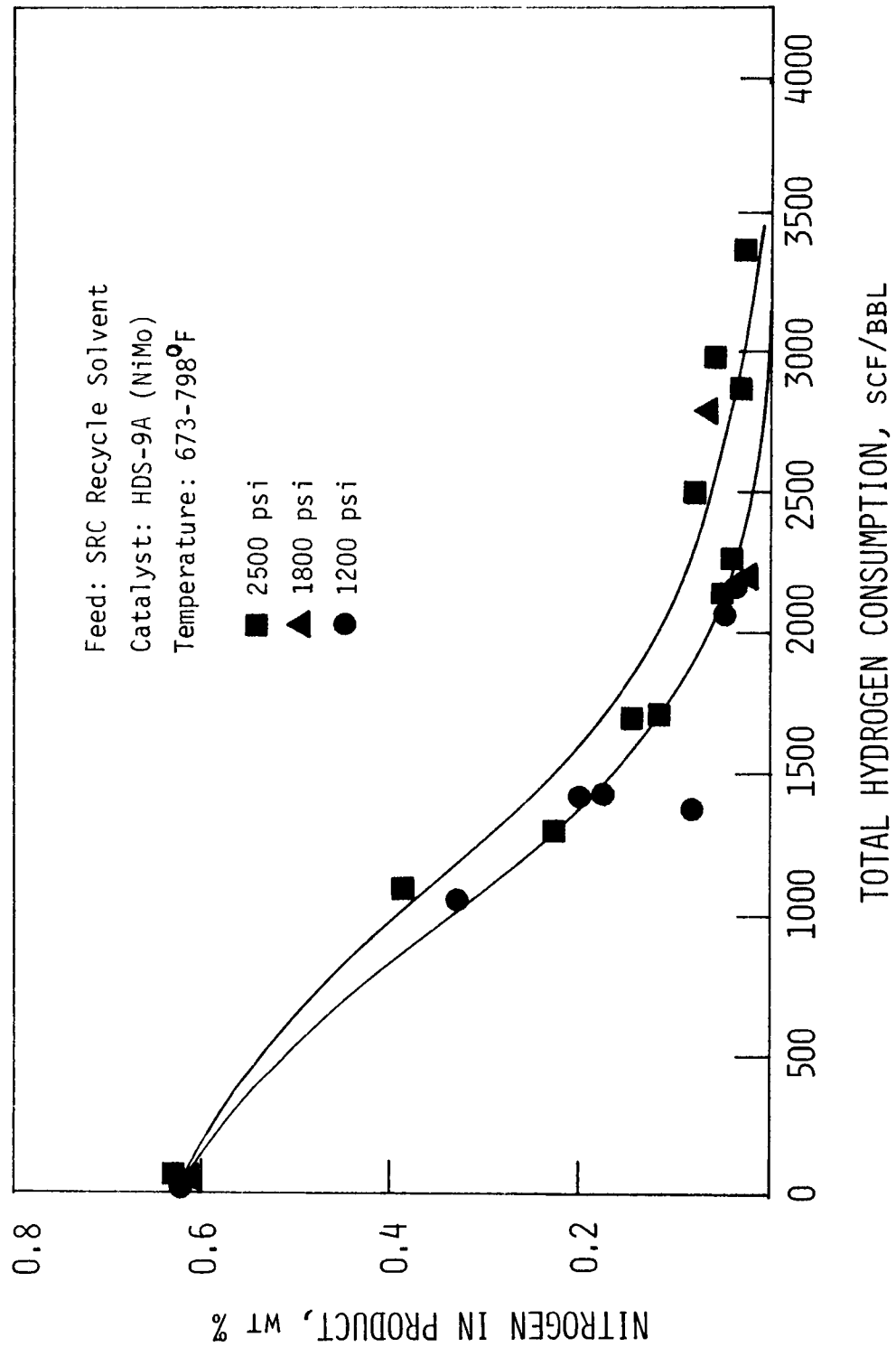


FIGURE 3.4.19 Nitrogen Content of Hydroprocessed SRC Recycle Solvent as a Function of Total Hydrogen Consumption (Stein, T.R. et al., 1977)

By distilling the raw and hydroprocessed blends it is possible to look at the composition, conversion, and heteroatom removal as a function of boiling range (Table 3.4.18). The hydrogen content increases and the nitrogen content decreases with increasing boiling range for both the raw and hydrotreated samples. The oxygen content is highest in the IBP-400⁰F fraction for the raw sample, but is lowest for this fraction on the hydroprocessed product. For this run, which consumed 2136 scf/bbl of hydrogen, 44 weight percent of the 750⁰F-plus material (SRC) is converted to lighter material. The 750⁰F-plus material which remains is upgraded, but not nearly to the extent of the lighter fractions. The 650-750⁰F fraction also shows a net conversion of about 29 weight percent to lighter products and the material remaining in this boiling range is significantly higher in hydrogen and somewhat lower in heteroatoms than the same fraction in the feed. The 400-650⁰F fraction shows 37 weight percent net make and has 60 weight percent lower nitrogen and 73 weight percent lower oxygen than this fraction in the feed. The IBP-400⁰F fraction also shows a 37 weight percent net make with 64 weight percent lower nitrogen and 96 weight percent lower oxygen content. In general the data show the heavier portion of the recycle solvent/SRC blend is converted to lighter material with a lower nitrogen and oxygen content. The unconverted heavy material has higher hydrogen and lower heteroatom than the feed, but it is not upgraded to the extent of the lighter fractions.

Table 3.4.18 Analysis of Raw and Hydroprocessed
2/1 Blend of Recycle Solvent/SRC

	Feed	Hydroprocessed Product	Percent Heteroatom Reduction
Total Sample			
Hydrogen wt %	6.84	9.04	
Oxygen wt %	3.91	0.70	82
Nitrogen wt %	1.03	0.58	53
Distillation Fractions			
IBP-400 ⁰ F wt % (Total)	12.0	16.4	
Hydrogen wt %	8.62	12.64	
Oxygen wt %	7.1	0.3	94
Nitrogen wt %	0.25	0.09	51
400-650 ⁰ F wt % (Total)	40.6	55.6	
Hydrogen wt %	7.20	9.01	
Oxygen wt %	3.0	0.8	63
Nitrogen wt %	0.48	0.19	46
650-750 ⁰ F wt % (Total)	10.1	7.2	
Hydrogen wt %	6.35	8.21	
Oxygen wt %	2.5	0.8	77
Nitrogen wt %	1.04	0.75	51
750 ⁰ F-plus wt % (Total)	37.3	20.8	
Hydrogen wt %	6.0	7.05	
Oxygen wt %	4.3	1.8	77
Nitrogen wt %	1.88	1.40	58

Source: Stein, T.R. et al., 1977

3.5. COAL EXTRACTS

3.5.1. Brynes, B.L.

Brynes, B.L. (1975a, 1975b, 1975c, 1976a, 1976b, 1976c, 1977) of Oklahoma State University hydrotreated a petroleum oil using Co-Mo catalysts at different temperatures, pressures and space time, to investigate catalysts for upgrading liquids from coal to oil processes and to remove sulfur, nitrogen and other heteroatoms. Also to determine the life of catalysts, prolonged experimental runs at different conditions were made.

Under the most severe conditions tested (700°F, 1500 psi, 1.6 hours space time), maximum sulfur and nitrogen removal were 94 and 41 percent respectively, using Nalco 474 Co-Mo catalyst. Other Co-Mo catalysts tested did not give as good results as Nalco 474. The change in sulfur and nitrogen removal with respect to temperature and space time is shown in Figure 3.5.1 and 3.5.2.

Two experimental runs were made using support material only, without metal deposited. No difference was noted between a pure sulfided and a pure sulfided support. However, the supports alone gave better desulfurization but poorer denitrogenation than an "inert", porous, nonporous solid used in place of a catalyst or a support (Table 3.5.1).

A three run series was made using a feedstock of raw anthracene oil deoiled with quinoline to significantly increase the nitrogen level. The increase in nitrogen content had a slightly adverse effect on the sulfur removal. The catalyst made from a pure, treated support, lower surface area, greater pore radius, gave a lower desulfurization than

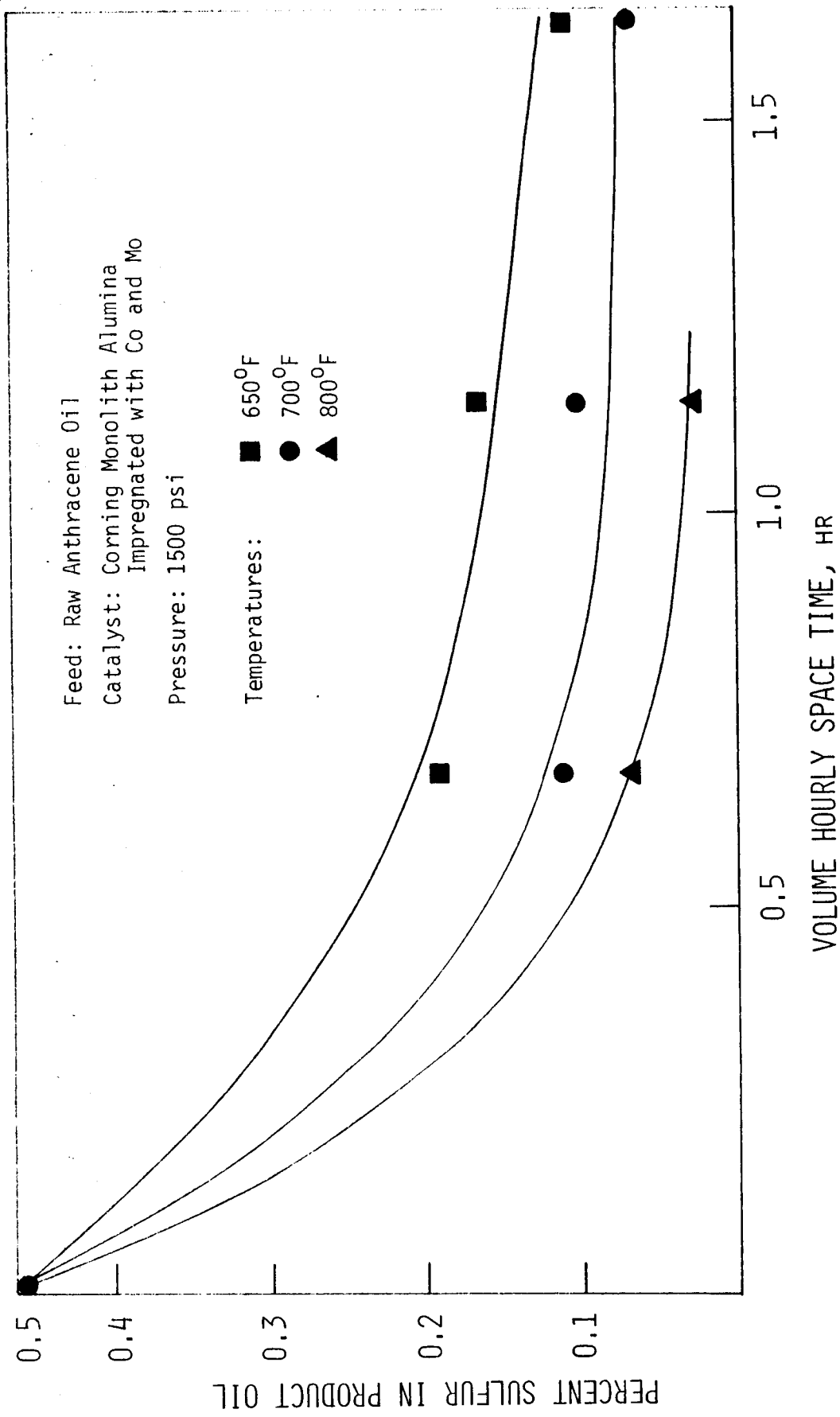


FIGURE 3.5.1 Sulfur Response of Anthracene Oil (Crynes, B.L., 1975a,1975b,1976a,1976b, 1976c,1977c)

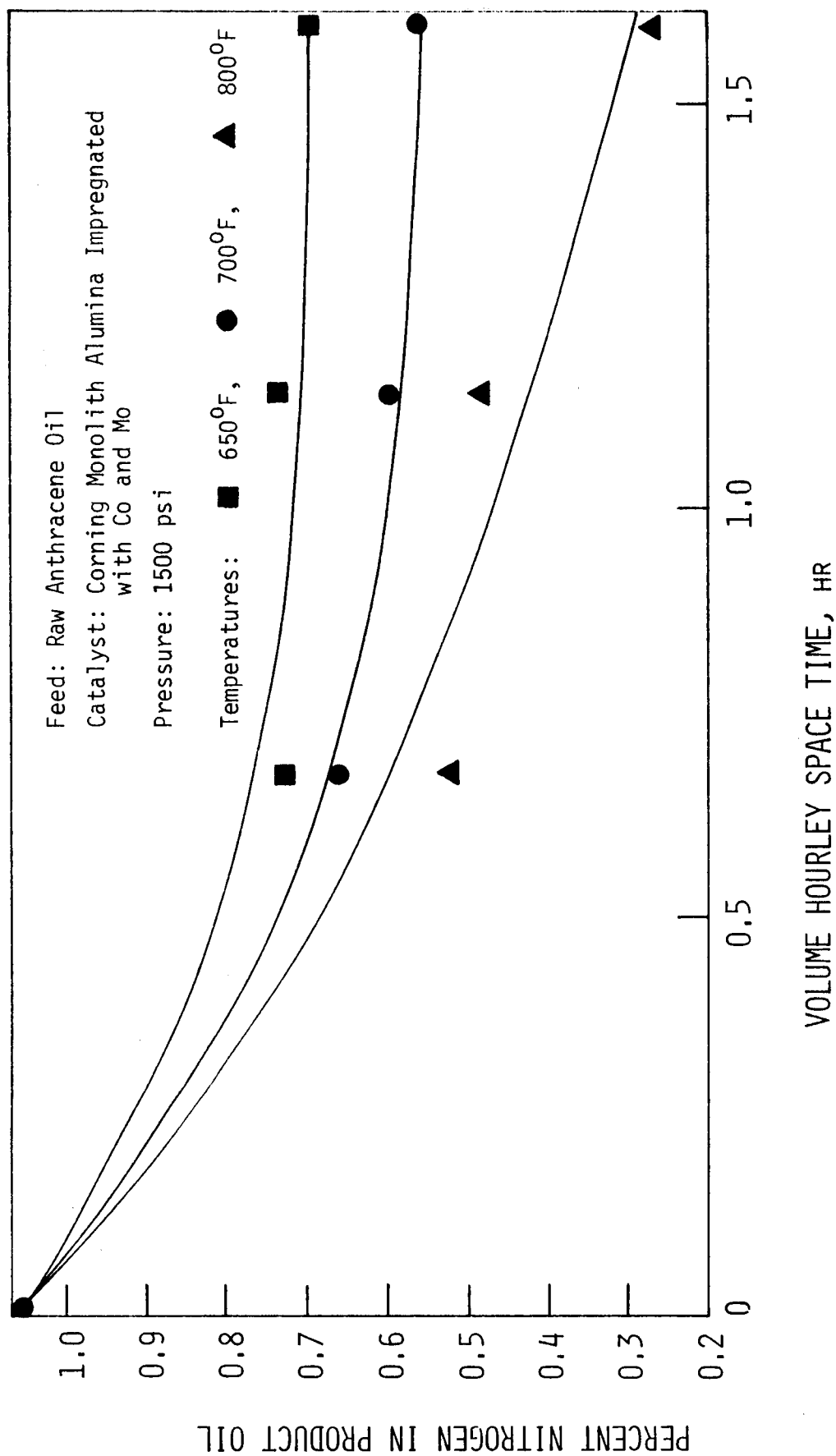


FIGURE 3.5.2 Nitrogen Response of Anthracene Oil (Crynes, B.L., 1975a,1975b,1976a,1976b, 1976c,1977c)

Table 3.5.1 Hydrotreating Raw Anthracene Oil

	0.46 hrs % Removal		0.92 hrs % Removal		1.84 hrs % Removal	
	<u>S</u>	<u>N</u>	<u>S</u>	<u>N</u>	<u>S</u>	<u>N</u>
Support Only	16	17	32	22	46	27
Support + 3.5% CoO and 12.5% MoO ₃	95	74	95	87	93	93
Inert Ceramic (Porcelain Berl Saddles)	33	8	44	11	58	17

Feed Properties: Sulfur = 0.47 wt %, Nitrogen = 1.06 wt %

Operating Conditions: Temperature = 750°F, Pressure = 1500 psi

Source: Crynes, B.L., 1975a,1975b,1976a,1976b,1976c,1977c

that obtained from a non-treated support.

Under the maximum conditions tested (750°F, 1500 psi, 1.65 hours space time) the raw anthracene oil over an alumina support which had not received active metal species (Co and Mo) resulted with a sulfur and nitrogen removal of 47-54 percent and 30-39 percent respectively. In a similar experimental series, but without hydrogen present, nitrogen removal was only 4-6 percent and the sulfur concentration of the product oils increased over that of the feedstock as shown in Figure 3.5.3.

A Norton support catalyst prepared from extrudate material was used for hydrotreating the anthracene oil, the results from the product oil samples analyses are shown in Figure 3.5.4. The figure presents the percent removal of sulfur and nitrogen in the product samples as a function of oil-catalyst contact. The entire data set was obtained within one startup and continuous operation of 115 hours. The history plot reveals the catalyst and equipment response as operational conditions are varied throughout the run. After catalyst lineout during the first 50 hours at 650°F, 1000 psi and 0.82 hours space time, the run conditions were changed to obtain data at other conditions. Before shutdown, the original lineout conditions were assessed to determine catalyst activity decay. Over the interval from 50 to 115 hours, no measurable decay was noted. Maximum nitrogen and sulfur removal at the most severe operational conditions tested were 53 and 87 percent respectively.

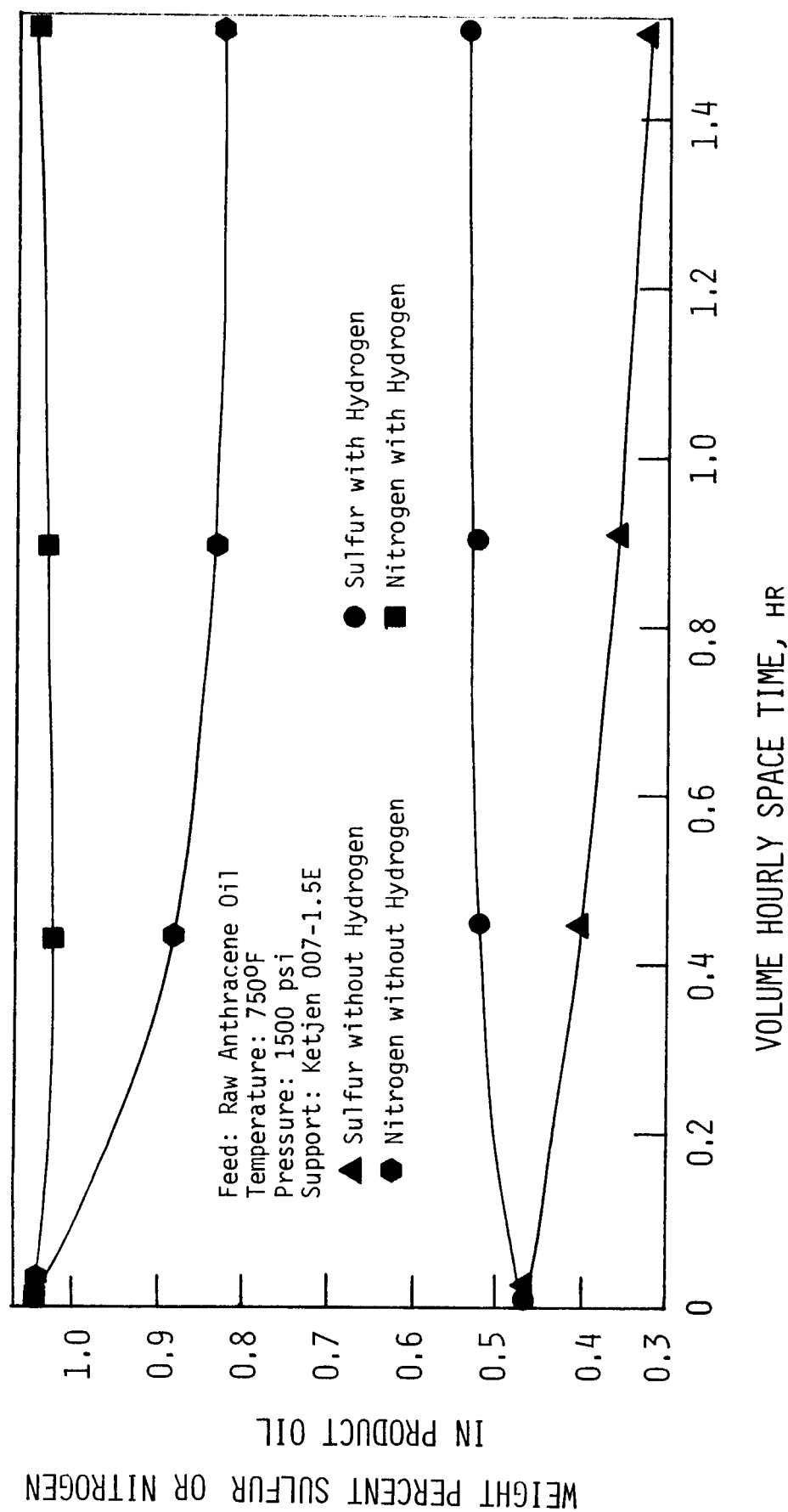


FIGURE 3.5.3 Sulfur and Nitrogen Response of Anthracene Oil with and without Hydrogen over Support Only (Crynes, B.L., 1975a,1975b,1976a,1976b,1976c,1977c)

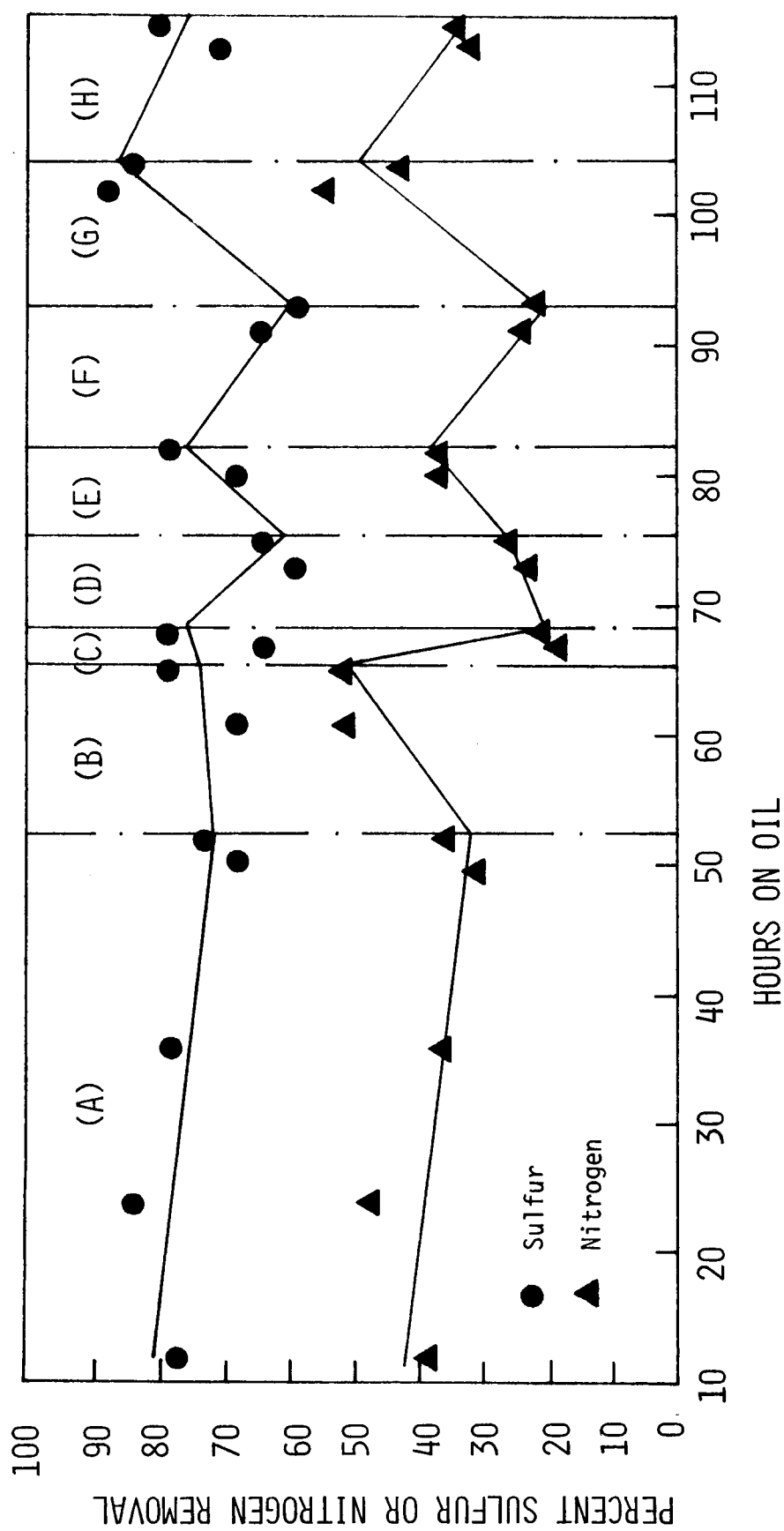


FIGURE 3.5.4 Run History of Anthracene Oil (Crynes, B.L., 1975a,1975b,1976a, 1976b,1976c,1977c)

Feed: Anthracene Oil

Catalyst: Norton SA6175
3.5% CoO, 12.5% MoO₃

Pressure: 500, 1000, 1500 Psi

Temperature: 600, 650, 700°F

	A	B	C	D	E	F	G	H
Temperature °F	650	600	650	650	650	600	700	650
Pressure, Psi	1000	1000	1000	500	1500	1000	1000	1000
Volume Hourly Space Time, hr	0.82	1.63	0.41	0.82	0.82	0.82	0.82	0.82

FIGURE 3.5.4 (cont.) Run History of Anthracene Oil (Crynes, B.L., 1975a, 1975b, 1976a, 1976b, 1976c, 1977c)

3.5.2 Qader, S.A. and Hill, G.R.

Qader, S.A. and Hill, G.R. (1971) of the University of Utah hydro-cracked coal oil, shale oil and tar sand oil in a continuous fixed bed reactor to compare the results of the three feedstocks. The coal oil was obtained by the hydrogenation of a high volatile bituminous coal from Utah. The shale oil was obtained by in situ retorting, and the tar sand oil was prepared by solvent extraction of tar sands found in Utah. A dual functional catalyst was used for hydrocracking the synthetic oils.

Synthetic oils differ significantly in composition from petroleum crudes. The coal oils contain large amounts of oxygenated compounds and aromatic hydrocarbons and the shale oils contain large quantities of nitrogen compounds. Because of the difference in composition the synthetic oils pose new problems in their processing as compared to the conventional processing of petroleum oils.

The product distribution and the severities of hydrocracking mainly depends upon the composition of the feed-stocks and the processing conditions. The data in Table 3.5.2 indicates that the coal oil is more aromatic in nature when compared to the shale and tar sand oils as shown by the hydrogen to carbon atomic ratios. The coal oil also contains more heterocompounds and asphaltenes.

The product distribution from hydrocracker as reported in Table 3.5.3 indicates that the coal oil is a more refractory feed-stock when compared to the shale and tar sand oils. This appears to be due to the higher aromatic and asphaltene contents of the coal oil. The hydro-

Table 3.5.2 Properties of Feed Stocks

	Coal Oil	Shale Oil	Tar Sand Oil
Gravity, $^{\circ}\text{API}$	0.75	20.2	17.3
Viscosity, SUS, 175°F	205.0	180.0	220.0
Sulfur, wt%	0.43	0.85	0.34
Nitrogen and Oxygen, wt%	3.84	2.14	1.84
H/C, Atomic Ratio	1.06	1.81	1.62
Asphaltene, vol%	30.0	2.0	2.5
Distillation, $^{\circ}\text{F}$			
IBP	390	390	390
50%	660	635	600

Source: Qader, S.A. and Hill, G.R., 1971

Table 3.5.3 Hydrocracking Product Distribution

	Coal Oil	Shale Oil	Tar Sand Oil
Yield of Products, vol %			
Naphtha	60.0	68.0	66.0
Gas	9.5	14.0	12.0
Coke	5.1	4.0	6.0
Recycle Oil	27.0	14.5	17.5
Severity	0.7	0.82	0.78

Temperature : 895⁰F

Pressure : 2000 psi

Space Velocity : 0.96

Source: Qader, S.A. and Hill, G.R., 1971

cracking severities seem to be somewhat related to the aromaticity of the feed-stocks. The data in Table 3.5.4 indicates that the yield of naphtha depends upon the total conversion irrespective of the type of feed-stock used. The three feed-stocks yielded almost the same quantities of naphtha at equal conversion levels. However, the gas yield was high in case of shale oil while the coal oil yielded relatively more coke.

The composition of naphtha and gas depend upon the nature of the feed-stock as indicated by data in Table 3.5.5. The coal oil naphtha is more aromatic and will have a higher octane rating when compared to the naphthas from shale and tar sand oils. It is evident that the aromatic feed-stocks need more severe process conditions but they produce better quality naphthas.

The data in Table 3.5.6 indicates that hydrogen consumption varies with the nature of the feed-stock and is directly proportional to the conversion in all the three cases. The consumption of hydrogen in coal oil hydrocracking is higher than the consumption in tar sand oil processing which in turn is more when compared to shale oil processing. This again seems to be related to the aromaticity of the feed-stocks. The hydrocracking reactions are exothermic and the heat of the reaction varies with the nature of the feed-stock and conversion as shown by the data in Table 3.5.6. Coal oil hydrocracking produces more exothermic heat when compared to tar sand oil which in turn gives more heat when compared to shale oil. The reaction heat seems to be also related to the aromaticity of the feed-stock.

Table 3.5.4 Hydrocracked Products

Conversion, Vol %	20	40	60	80
Naphtha Yield				
Coal Oil	15	32	48	65
Shale Oil	16.5	35	48	63.5
Tar Sand Oil	15.5	32	47.5	64.0
Gas Yield				
Coal Oil	2.5	5.0	8.0	10.5
Shale Oil	2.0	6.0	9.0	13.0
Tar Sand Oil	3.5	6.0	8.5	11.0
Coke Yield				
Coal Oil	0.5	2.0	4.0	5.6
Shale Oil	0.5	1.6	2.7	4.0
Tar Sand Oil	0.5	2.0	3.6	5.0

Source: Qader, S.A., and Hill, G.R., 1971

Table 3.5.5 Composition of Naphtha and Gas

	Coal Oil	Shale Oil	Tar Sand Oil
Composition of Naphtha, Vol %			
Saturates	75.2	40.2	49.5
Olefins	2.8	3.1	2.5
Aromatics	22.0	56.7	48.0
 Composition of Gas, Vol %			
CH ₄	16.0	13.0	12.0
C ₂ H ₆	28.0	27.0	28.0
C ₃ H ₈	42.0	40.0	37.0
C ₄ H ₁₀	14.0	20.0	22.0

Temperature : 895⁰F

Pressure : 2000 psi

Space Velocity : 0.96

Source: Qader, S.A. and Hill, G.R., 1971

Table 3.5.6 Hydrogen Consumption and Reaction Heat in Hydrocracking

Conversion, Vol %	30	50	60	80
H ₂ Consumption, scf/bbl				
Coal Oil	600	1020	1240	1660
Shale Oil	380	720	900	1230
Tar Sand Oil	350	720	910	1290
$\Delta H \times 10^3$, Btu/bbl				
Coal Oil	47	30	96	130
Shale Oil	34	58	70	96
Tar Sand Oil	32	60	75	104

Source: Qader, S.A. and Hill, G.R., 1971

3.5.3 Wan, K.T. and Crynes, B.L.

Wan, K.T. and Crynes, B.L. (1972) compared two catalysts for hydrocracking raw anthracene oil. The feedstock used contained 0.45 weight percent sulfur and 0.8 weight percent nitrogen, the properties of the feed are given in Table 3.5.7.

The two Nalco catalysts which were tested were Nalcomo 474 and Sphericat 474. These were both compounded with 3.5 weight percent of cobalt oxide and 12.5 weight percent molybdenum oxide on alumina support. Pore volume was 12.82 cubic inch per pound for Nalcomo 474 and 27.17 cubic inch per pound for the Sphericat 474.

The fixed bed reactor used was 1/2 inch diameter packed with 0.030-0.034 lb of catalyst. Experiments were made over a temperature range of 600 to 800°F, a total pressure range of 500 to 2000 psi, and space times (based on reciprocal liquid hourly space velocities) of 1/4 to 2 hours. Most of the experiments were made on Nalcomo 474 over these variable ranges, and the comparison of the two catalysts was made with data taken at a fixed set of conditions. These conditions were 700°F, 1000 psi pressure, and about one hour space time. These two comparative runs each covered a total of over 40 hours oil-catalyst contact. For ease of comparison, the experiments on these two 40-hour runs were performed at identical weight hourly space velocities. This means that the volume hourly space velocities were different because of a difference in the catalyst pellet density.

The temperature and space time effects for desulfurization of the Nalcomo 474 catalyst are shown in Figure 3.5.5. The rate of

Table 3.5.7 Feed Oil Properties

Carbon, wt %	90.65
Hydrogen, wt %	5.76
Sulfur, wt %	0.45
Nitrogen, wt %	0.8
Ash, wt %	Nil
API Gravity @ 60 ⁰ F	-7
Distillation, ⁰ F	
IBP	380
10 vol %	450
30 vol %	570
50 vol %	650
70 vol %	700
90 vol %	815

Source: Wan, K.T. and Crynes, B.L., 1972

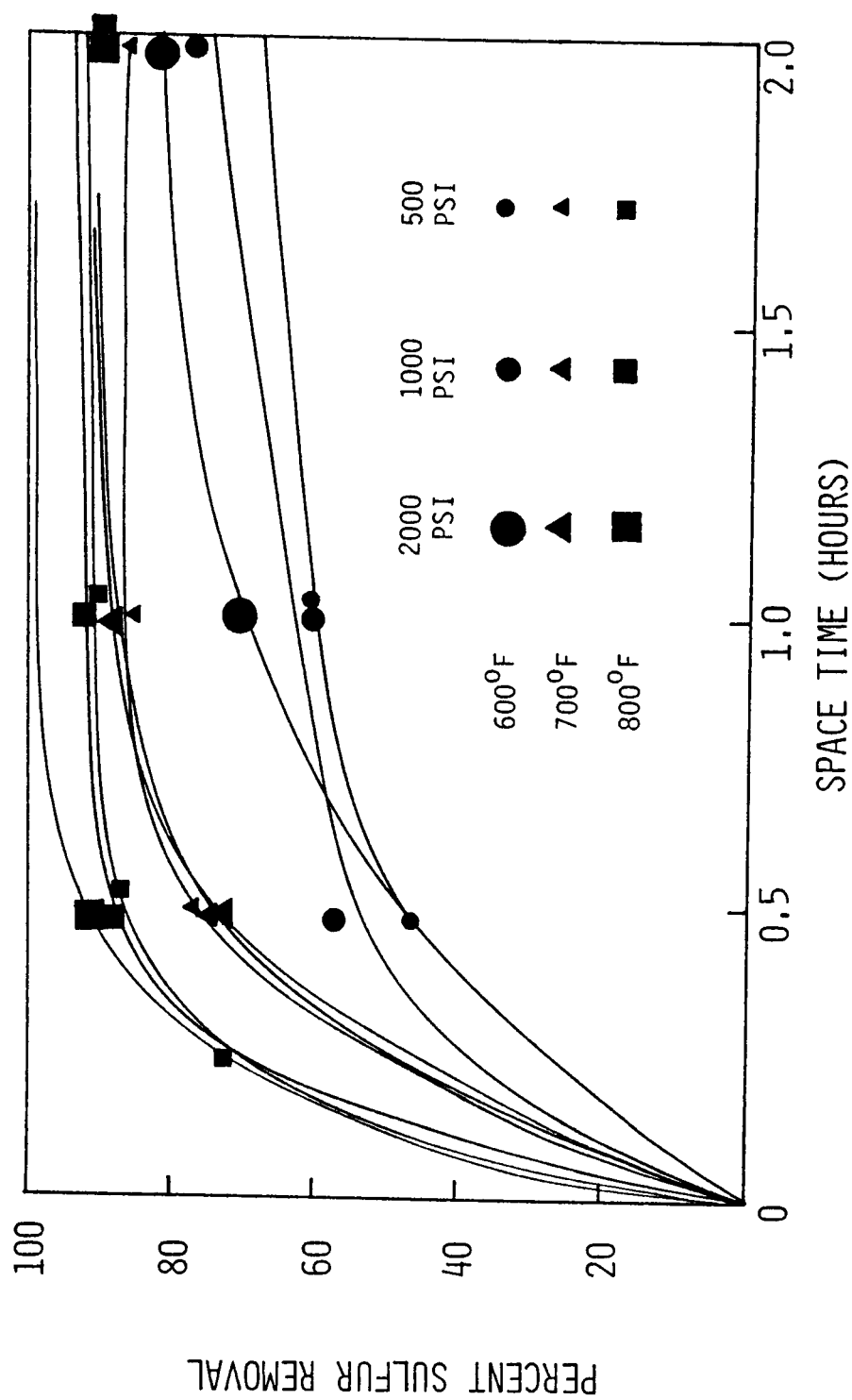


FIGURE 3.5.5 Sulfur Removal for Anthracene Oil
(Wan, K.T. and Crynes, B.L., 1972)

desulfurization is rapid within the first 0.5 to 1.0 hours space time, and becomes quite slow thereafter. The maximum desulfurization appears to be fixed at around 90-95 percent removal. However, at 90 percent removal of sulfur from the feed oil, the product sulfur level is in the range of 400 parts per million. The effect of pressure between 500 to 2000 psi on desulfurization was the greatest at 600°F operation; whereas, there was little pressure response noted at 700 and 800°F.

There was negligible loss of catalyst desulfurization activity during the 70 plus hours total oil-catalyst contact. Shown in Figure 3.5.6 is a comparison of the desulfurization levels for both the Nalcomo 474 and the Sphericat 474 catalysts. The desulfurization activity of the Nalcomo catalyst achieved a level of about 92 percent removal after 10 hours on oil, and remained relatively steady between 88 to 90 percent for over 50 hours. The Sphericat 474 showed almost identical desulfurization characteristics from ten through 42 hours on oil. For both catalysts, there is no noticeable loss in desulfurization over 40-50 hours.

Figure 3.5.7 presents a comparison of the two catalysts for denitrogenation for over 40-50 hours oil-catalyst contact. Although the Nalcomo 474 catalyst maintained a stable denitrogenation activity, the Sphericat 474 denitrogenation activity dropped rather quickly. Further, the ability of the Sphericat 474 to remove nitrogen was always lower than that of the Nalcomo catalyst. In both cases the ability to remove nitrogen was limited. For Nalcomo this was no more than 60 percent at best; and for the Sphericat, no more than about 50 percent. The cause of the difference in denitrogenation behavior of the two

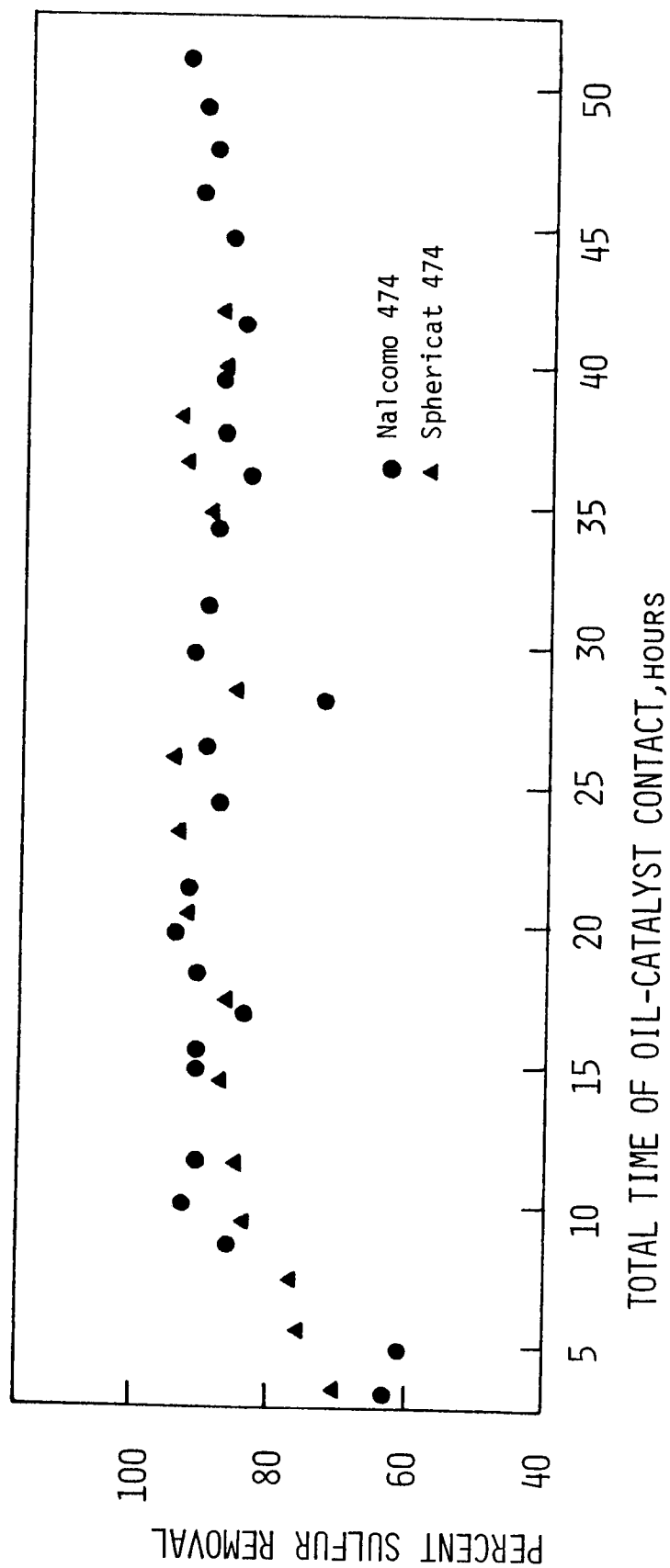


FIGURE 3.5.6 Sulfur Removal as a Function of Catalyst Age
(Wan, K.T. and Crynes, B.L., 1972)

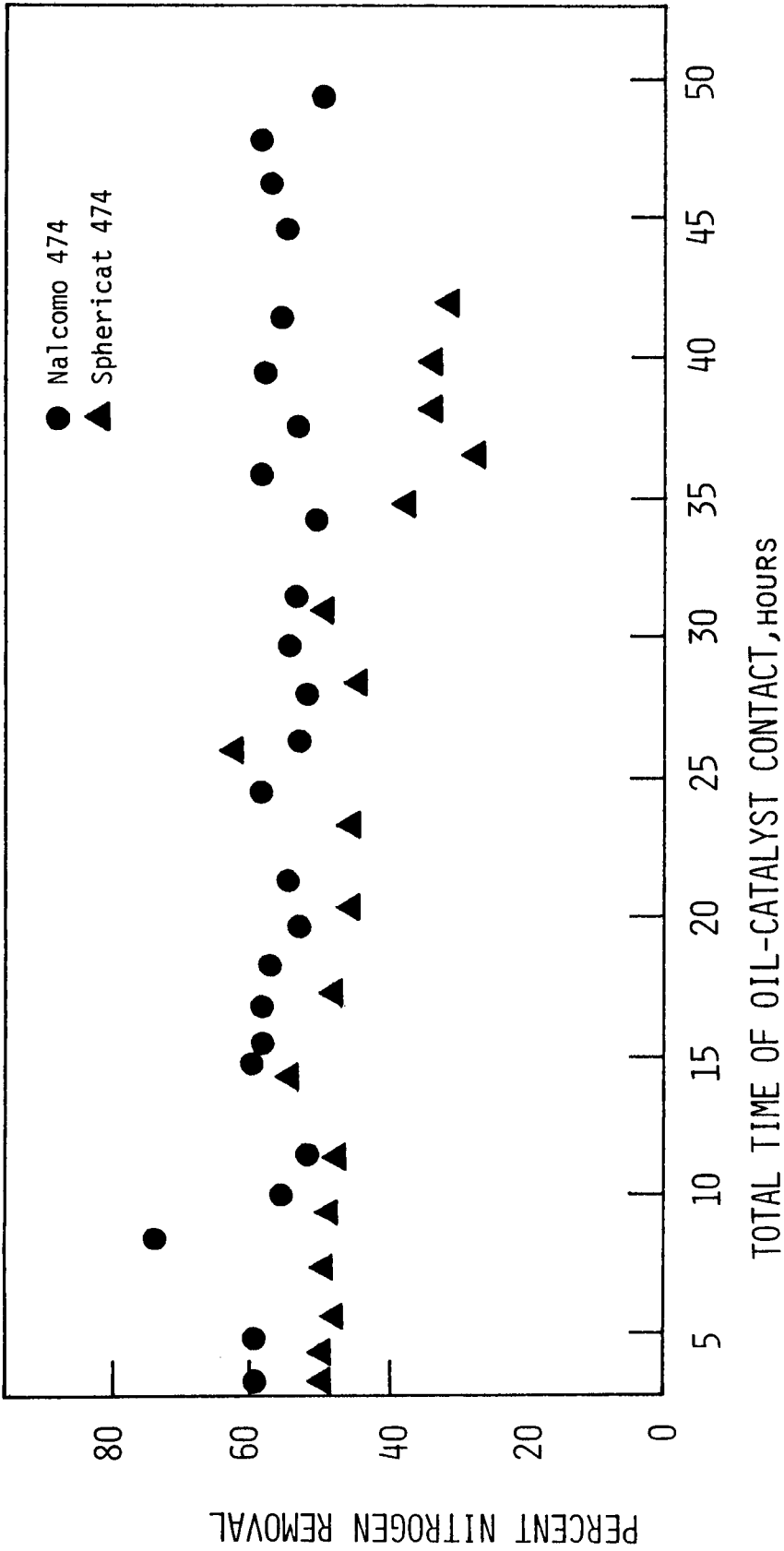


FIGURE 3.5.7 Nitrogen Removal as a Function of Catalyst Age
(Wan, K.T. and Crynes, B.L., 1972)

catalysts is difficult to resolve. The initially lower nitrogen removal of the Sphericat suggests that the pretreatment might have been sufficiently different to affect nitrogen but not sulfur removal. In any case, there is a loss in activity which indicates a greater carbon formation by the Sphericat.

In general, satisfactory nitrogen removal is more difficult to obtain than that for sulfur, and it was very much the same for both the catalysts tested.

3.6 COALCON

In 1975, Coalcon Co., an affiliate of Union Carbide and Chemico, received a contract from Energy Research and Development Administration (ERDA) to build a coal-to-clean-liquid-fuel demonstration plant. The project concerned the design, construction and operation of a 2600 ton of coal/day demonstration plant to produce 3990 bbl/day of liquid products and 22 million cubic feet per day of pipeline gas.

The process involves pyrolysis of coal at a hydrogen pressure of 550 psi. The coal is heated in the hydrocarbonization reactor producing liquid, gaseous, and solid products. The gas is separated from the liquid to produce synthetic natural gas (SNG) and liquified petroleum gas (LPG). The liquid is segregated into a light and heavy fraction with characteristics similar to those of a light to heavy petroleum naphtha and a light to medium gas oil, respectively. The solid char is used for fuel for hydrogen generation.

Coal containing 10 percent or less ash and 2.9 percent sulfur is dried and sized to 50 percent through 100 mesh. While the Coalcon

process was originally developed for low-rank western coals of low sulfur but high moisture, oxygen, and ash content, recent emphasis has been on the use of high volatility, high sulfur, and medium ash coals. Pittsburgh No.8, Illinois No.6 and Western Kentucky No.11 are considered particularly attractive coals.

After preheating to 617°F , the coal is fed to the hydrocarbonization reactor as a dense fluid phase from lock hoppers which operate at 900 psi.

Hydrogen from the hydrogen plant is mixed with recycled hydrogen, preheated, and fed into the hydrocarbonization reactor to fluidize the coal. The hydrocarbonization reaction takes place at 1040°F and 550 psi. Hydrocarbon vapors and gas leave the top of the reactor, and char is discharged at the bottom.

The char exits through lock hoppers after being cooled to 600°F and stripped of hydrocarbons. It is ultimately cooled to about 200°F , pulverized and fed either to the steam boilers or to the hydrogen plant where hydrogen is produced via partial oxidative gasification of the char.

The vapors which leave the top of the hydrocarbonization reactor are cooled and condensed into heavy fuel oil and light hydrocarbons. The residual gases are treated by conventional technology to remove ammonia, hydrogen sulfide, and carbon dioxide. The dried process gases are then separated cryogenically. Hydrogen is recycled to the reactor, and a $\text{CO-H}_2\text{-CH}_4$ stream is fed to a methanation plant to make high-Btu pipeline gas (SNG).

The heavy oil fraction from the hydrocarbonization reactor has an approximate initial boiling point of 400°F and a final boiling point of 840°F which corresponds to the boiling range of a light and medium gas oil petroleum fraction with some contribution from the heavy gas oil fraction. The constituents may be conveniently divided into two broad groups, the paraffin-naphthenic-aromatic (PNA) fraction and the heteroatom fraction as shown in Table 3.6.1. The hydrocarbon fraction, representing 75.8 percent of the heavy oil product, contains 98.5 percent aromatics consisting primarily of condensed two-to four-ring compounds and a very small amount of benzene and its homologs.

The heavy oil product also contains 17.7 percent of phenols and naphthols, 6.4 percent of pyridine, and 0.03 percent of thiophene, containing the heteroatoms oxygen, nitrogen and sulfur, respectively. Although this distribution may be correct, it is likely that other oxygen, nitrogen, and sulfur compounds are also present. It is to be noted that the presence of 0.09 weight percent ash in the heavy oil fraction could cause processing problems by deposition on the catalyst.

The light oil fraction boils in the 97-377°F range which corresponds to the boiling range of a light to heavy petroleum naphtha. Its composition is summarized in Table 3.6.2.

Compared to the heavy oil product, the light oil is less aromatic. The PNA hydrocarbon fraction makes up 84.9 weight percent of the total light oil product and of this 40.7 weight percent is paraffinic, 9.7 weight percent naphthenic, and 49.6 percent weight percent aromatic. The major component of the paraffins is decane. The only naphthene identified is cyclopentane and this is present at a relatively low level

Table 3.6.1 Composition of the Heavy Oil Product from the Coalcon Process

Compound	Amount in Liquid Product	
	Weight Percent	Mole Percent
PNA Fraction		
Paraffins		
Decane	0.5	0.06
Others	0.03	0.111
Total Paraffins	0.53	0.171
Naphthenes		
Cyclopentane	0.6	0.144
Aromatics		
Benzenes	0.06	0.118
Toluene	0.20	0.401
p-Xylene	0.10	0.149
Propylbenzene	0.10	0.152
Mesitylene	0.70	0.973
Naphthalene	8.6	10.89
Methylnaphthalene	2.9	3.28
Methylphenanthrene	6.2	5.22
1,2-Benzoflourene	15.4	11.52
Chrysene	40.4	28.70
Total	74.66	61.40
Heteroatom Fraction		
Oxygenated Compounds		
Phenol	1.8	3.16
o-Cresol	7.1	10.66
3,5-Xylenol	2.8	3.67
2-Naphthol	6.0	6.79
Total Oxygenated Compounds	17.7	24.28
Sulfur Compounds		
Thiophene	0.03	0.06
Nitrogen Compounds		
Pyridine	6.4	18.0
Miscellaneous		
Ash	0.9	
Water	0.03	0.20

Source: Coals and Creton, 1977

Table 3.6.2 Composition of the Light Oil Products from the Coalcon Process

Compound	Amount in Liquid Product	
	Weight Percent	Mole Percent
PNA Fraction		
Paraffins		
Methan	0.009	0.05
Ethane	0.067	0.22
Propane	0.080	1.93
n-Butane	0.890	1.53
n-Pentane	1.150	1.60
Decane	32.360	22.66
Total Paraffins	34.556	27.99
Naphthenes		
Cyclopentane	8.22	11.68
Aromatics		
Benzene	6.11	7.78
Toluene	18.27	19.76
p-Xylene	4.03	3.78
Propylbenzene	2.78	2.30
Mesitylene	10.80	8.95
Total Aromatics	41.99	42.58
Heteroatom Fraction		
Phenol	3.35	3.55
o-Cresol	0.56	0.52
3,5-Xylenol	0.33	0.27
Thiophene	1.69	2.00
Pyridine	7.74	9.74
Total Heteroatom Fractions	13.47	16.08

Source: Coal and Cretons, 1977

(8 weight percent) compared to most petroleum naphtha fractions.

The nonhydrocarbon portion accounts for 13.7 weight percent of the total light oil with 31 weight percent of this fraction being phenols, 12 weight percent thiphenes, and 57 weight percent pyridine.

4. DISCUSSION

Coal derived liquids differ from each other because of the different processes utilized to produce these liquids, and also because of different kinds of coals used to produce these liquids. Therefore the problems in refining these liquids vary with the process of coal liquefaction and the kind of coal used. A summary of overall problems faced in refining coal derived liquids is presented giving the problems for refining each type of syncrude separately.

The products obtained from refining different types of syncrudes are at least qualitatively similar with respect to various molecular constituents. Therefore, the technical difficulties in converting these syncrudes to high-octane gasoline, jet fuel, and diesel fuel are expected to be similar and to vary primarily in degree. The products obtained from refining different types of syncrudes are compared with each other to give a general idea of the final products from each syncrude.

Finally correlations are developed from the pilot plant results for hydrotreating and hydrocracking of these refinery products obtained from various syncrudes.

4.1 REFINING PROBLEMS

4.1.1 COED Process

The refining problems of COED syncrude derived from Illinois No.6 seam coal were studied by Atlantic Richfield Co. (ARCO) in a subcontract

from FMC Corporation (Project COED, 1973) and covered hydrogen pre-treatment and reforming of naphtha fractions; evaluation of middle-distillate oils as jet, diesel, and home heating fuels; fluidized bed catalytic cracking of the atmospheric bottoms fraction; and hydrocracking of the atmospheric bottoms fraction.

4.1.1.1 COED Gasoline

The COED naphtha (180-390°F) containing 70 percent naphthenes, 10 percent paraffins, and 20 percent aromatics is easy to process since the naphthenes readily isomerize and/or dehydrogenate over conventional reforming catalysts (e.g. Pt/Alumina) to high-octane aromatics. However, because of the presence of sulfur (100 ppm) and nitrogen (100 ppm), the naphtha must be hydrotreated to reduce each of these catalyst poisons to less than 2 ppm.

The highly naphthenic nature of these naphthas ensures good activity maintenance during reforming, even for conventional Pt/Alumina catalysts. The ARCO study (Project COED, 1973) indicates that catalyst aging for COED naphthas occurs half as fast as for petroleum naphthas if measured by the decline of the research octane number of the reformat. Also, the yield of reformat gasoline blending stock is substantially higher than from conventional petroleum naphthas. For example, operating at conditions which yield a 100 RONC product, a typical petroleum naphtha gave 75.5 vol. percent yield of C₅ - plus fraction, compared to 91 vol. percent for the COED naphtha (Project COED, 1973).

The major problems are encountered in the refining of the 650°F plus fraction to high octane gasoline. Prior to fluid cracking or hydrocracking this fraction, it is necessary to lower its polyaromatics and nitrogen content to avoid catalyst deactivation by excessive coke deposition and poisoning by nitrogen bases. This is done by rather severe hydrotreatment at 0.6 weight hourly space velocity (WHSV), 700°F, 2000 psi and a hydrogen rate of 6000 scf/bbl. The gasoline yield from fluid catalytic cracking of the hydrotreated COED atmospheric residuum is 51 percent, which compares favorably with a 54 percent yield from a midcontinent petroleum gas oil (Project COED, 1973).

The difficulty in hydrocracking this 650°F-plus fraction to gasoline and middle distillates arises from two sources. The reduction of the nitrogen content from 800 ppm to less than 10-20 ppm required to prevent catalyst poisoning cannot be accomplished even with very severe HDN (0.33 WHSV, 750°F, 2000 psi, and 6000 scf/bbl hydrogen flow rates) because of the presence of very refractory N-heterocycles. The second source of processing problems is the presence of four and five ring aromatics, which adsorb very strongly on the catalyst surface and cause carbon deposition and decrease catalyst life. The only way the 650°F-plus fraction could be processed by ARCO was to fractionate it into a 650-800°F cut (84 percent) and an 800°F-plus cut (16 percent). The latter is reportedly a reasonable blending stock for No.6 fuel oil because of its low sulfur level and reasonable Conradson carbon and polynuclear aromatics level (Project COED, 1973). Hydrocracking the 650-800°F fraction gives a normal product yield distribution, but requires twice as much hydrogen as needed by a corresponding petroleum

feedstock and involves excessive catalyst deactivation. Therefore it appears that conventional hydrocracking technology would not be practical for COED heavy liquids.

4.1.1.2 COED Jet Fuel

The COED middle distillate can be processed to both jet and diesel blending stocks. However a highly aromatic product such as derived from Illinois No.6 seam coal needs hydrotreating before it can be used for this purpose.

As shown by Table 4.1.1 the "as-distilled" 390-525°F fraction does not meet the primary jet fuel specifications for a number of parameters including gravity, aromatics content, smoke point, luminosity, and net heating value (Project COED, 1973). In an attempt to overcome some of these limitations the fraction was hydrotreated at 600-700°F, 1000-2000 psi, 1.0 WHSV, and 5000 scf/bbl hydrogen flow rate. However, even at these conditions the product could not meet all specification, including smoke point, probably because of the very high cycloparaffin content. The only way in which the smoke point specification could be met was by using a second stage noble metal Pt, hydrogenation at 700°F, 2000 psi, 5000 scf/bbl hydrogen flow rate, and 2 WHSV to reduce the aromatic level to zero. It is expected that all specifications will only be met by selective cracking of the cycloparaffins to branched and linear paraffins at low temperatures and high hydrogen pressure to prevent the formation of aromatics. It is questionable whether this would be a cost-effective process because with less

Table 4.1.1.1 Comparison of COED Jet Fuel Fraction with JP-5 Jet Fuel Specifications

COED jet fuel (390-525°F)			
Properties	JP-5	As distilled	2-Stage HDS
ASTM 10 % distillation point (°F)	400 max	436	412
ASTM distillation end point (°F)	550 max	530	526
Gravity (°API, 60°F)	36-48	25.7	33.2
Sulfur (wt %)	0.4 max	0.007	0.001
Freezing point (°F)	-51 max	-70 ^c	-80 ^c
Net heating value (Btu/lb)	18,300 max	18,070 ^c	18,390 ^c
Aniline gravity product ^d	4500 min	1490	4501
Aromatics (liquid vol %)	25 max	60.7	0-5
Olefins (liquid vol %)	5 max	0	0
Smoke point ^e	19 min	10	22
Luminometer number ^f	50 min	20.4 ^c	43.6 ^c
Flash point	140 min	186	156
Copper corrosion test ^g	1	1	-

^aSource Project COED

^bAfter hydroprocessing of 390-525°F syncrude fraction

^cCalculate

^dA measure of the aromaticity of an oil

^eA measure of the smoke and soot-producing characteristics of jet fuels

^fA measure of the flame temperature of jet fuels

^gA measure of the corrosiveness of oil to copper

a "1" designation indicates slight tarnish

difficulty it is possible to convert this fraction into an aromatic feedstock for gasoline blending.

4.1.1.3 COED Diesel Fuel

The 525-650⁰F COED fraction is highly aromatic and therefore does not meet diesel specification because of high density (19⁰API versus 33-37⁰API) and low cetane number (Project COED, 1973).

A 390-650⁰F fraction can be distilled from the middle-distillate cut which meets diesel fuel specifications for flash point, distillation and pour point, but the high aromaticity still gives an unacceptably low gravity and cetane number. On hydrotreatment the gravity specification is met, but the distillation end point is low. These data are presented for comparison in Table 4.1.2.

The problems in converting COED syncrude to a diesel fuel are, therefore, similar to those for producing a jet fuel. It might be possible to hydrotreat the middle-distillate fraction to a paraffinic-cycloparaffinic fuel which would just meet product specifications, but the most desirable normal and branched paraffins can be made by selective hydrogenation and hydrocracking requiring substantially greater amounts of hydrogen.

4.1.2 H-Coal Process

Few data have been published concerning the refining H-Coal liquids on a large scale, but the key catalytic problems can be anticipated from the product composition data.

Table 4.1.2 Comparison of a COED Diesel Fuel Fraction with ASTM Specifications

Properties	Specifications	As distilled				390-525°F Fraction 2-stage HDS*
		390-650°F	525-650°F	390-525°F	390-525°F	
Pour point (°F)	0 max	-70	-20	-80	-80	-80
Flash point (°F)	130 min	215	300	186	156	156
Sulfur (wt %)	Legal	.001	.001	.007	.001	.001
ASTM distillation (°F)						
10 % distilled	460 max	459	562	436	412	412
50 % distilled			588	455	437	437
90 % distilled	620 max	586	626	494	483	483
100 % distilled	660 max	613		530		
Gravity (°API, 60°F)	33-37	22.5	19	25.7	33.2	33.2
Cetane number	30 min	18	24	23.0	30	30
Aromatics (liquid vol %)				58.3	5.2	5.2

Source: Project COED, 1973

*After hydroprocessing of 390-525°F fraction of syncrude

4.1.2.1 H-Coal Gasoline

The composition of the naphtha fraction given on page 102 indicates that the conversion of this product to high-octane gasoline will involve dehydrogenation and hydroisomerization to aromatics. Both reactions occur readily over conventional reforming catalysts. Activity maintenance would not normally be expected to be a problem for such a highly naphthenic naphtha. However the bicyclic aromatics, 7 percent of indans and naphthalenes, could, because of their strong adsorption by acidic sites, cause carbon deposition with time unless the reforming is carried out under hydrogen pressures higher than used normally.

The 400-650⁰F fraction should be convertible to a naphthenic-aromatic naphtha by a moderate hydrotreating operation in which oxygen, sulfur, and nitrogen compounds are removed to sufficiently low levels to allow further processing either by reforming or by mixing with catalytic cracker feedstock.

Processing the 650-919⁰F fraction presents more serious problems because of the presence of 73 percent of refractory polynuclear aromatics and of 13.8 percent of high molecular weight nonhydrocarbons which are difficult to desulfurize and denitrogenate. One possible option would be to distill off a 650-800⁰F fraction for processing with the 400-650⁰F fraction. The remaining heavy residuum could then be used as a blending stock for heavy fuel oils if the sulfur, nitrogen, and polynuclear aromatic constraints are met (Project H-Coal, 1967).

4.1.2.2 H-Coal Jet Fuel

The middle and heavy H-Coal liquids are highly aromatic and therefore do not yield a good jet fuel. It is likely that severe hydrotreating would improve the product quality for certain specifications sufficiently to allow the product to be used as a jet fuel blending stock.

4.1.2.3 H-Coal Diesel Fuel

The 400-650°F fraction from the H-Coal process is highly aromatic and therefore is not expected to meet diesel specifications, particularly for density, cetane number, and oxidation stability. Severe hydrotreating and more effective hydrocracking will be needed to upgrade H-Coal liquids to a diesel fuel.

4.1.3 Synthoil Process

Four potential problems areas are expected to affect the required processing steps of synthoil liquids: high Conradson carbon in all fractions; high concentrations of large polynuclear aromatic molecules; the presence of heterocyclic sulfur, nitrogen, and oxygen compounds; and the ash content.

4.1.3.1 Synthoil Gasoline

Before the synthoil 405°F-minus fraction can be used as a naphtha feedstock it requires severe hydrotreating to convert the high

concentration of phenols (35.3 percent) to single-ring aromatics, to reduce the nitrogen (0.423 percent) and sulfur (0.2 percent) levels to less than 2 ppm, and to minimize the high level of Conradson carbon (1.29 percent).

The 405-685°F fraction contains almost 30 percent di- and polynuclear aromatics(see page 128) which are basic in nature and adsorb strongly on metals and oxides and lead to excessive catalyst deactivation by blocking active sites, as well as by acting as coke precursors. This middle-distillate fraction could be hydrocracked or catalytically cracked, but would also require hydrotreatment to lower the sulfur (0.30 percent) and nitrogen (0.724 percent) levels and to reduce the Conradson carbon (2.33 percent). An alternate possibility would be to distill off a lighter fraction and blend the heavy residuum with fuel oil.

The heavy fraction, 685-988°F, is even more difficult to process than the middle distillate because of the higher sulfur, nitrogen, and Conradson carbon levels. The di- and polynuclear aromatics content is 63 percent, most of the constituents containing large condensed structures highly substituted with naphthenes. Unless this fraction is subjected to a very severe hydrotreatment, it is likely that it would have to be vacuum distilled and the residuum coked.

4.1.3.2 Synthoil Jet Fuel

The middle distillate can potentially be converted to jet fuel, or at least to jet fuel blending stock, but would require pretreatment. The primary problem is likely to be the high level of aromatics. The

synthoil fraction contains 27 percent monoaromatics, 21 percent diaromatics, and 8 percent polynuclear aromatics (see page 128), substantially more than the level of 25 vol percent allowed for jet fuel. High-pressure hydrotreating could saturate many of these aromatic structures to naphthenic materials and thus improve smoke point and energy density. However, in the presence of substantial amounts of naphthenes it may be necessary to reduce the aromatics level to practically zero, as their smoking properties are enhanced in the presence of naphthenes. Ultimately, the most effective processing for converting this fraction to jet fuel would be hydrogenation to naphthenic structures followed by selective cracking of these saturates to branched paraffins and paraffin-substituted single-ring aromatics.

4.1.3.3 Synthoil Diesel Fuel

Because of its highly aromatic nature, the synthoil middle-distillate fraction would not meet the cetane number and specific gravity requirements for diesel fuels (Woodward et al., 1976).

High-pressure hydrotreating and selective cracking to a paraffinic-naphthenic fuel is expected to be necessary to reduce aromaticity and produce a fuel which meets the specifications.

4.1.4 SRC Process

Mobil (1966) has shown that SRC contains a large fraction of asphaltenes, and has the highest aromatic level of a number of coal liquids tested. These constituents raise problems of the activity,

selectivity, and activity maintenance in processing SRC.

In the hydrotreatment of petroleum residuum, one of the main catalyst problems is the fast initial deactivation by the deposition of carbonaceous materials (Yakabayashi, 1973) which is aggravated by the deposition of mineral matter throughout the reaction. In view of the composition of the residuum, the initial carbon deposition is believed to be due to the large asphaltene molecules (Schuit and Gates, 1973) which are very small in size, and plug the similarly sized micropores of the alumina support which represents a large fraction of the total catalyst surface area.

In upgrading SRC the carbon deposition problem is likely to be at least as severe as observed for petroleum processing due to the high asphaltenic content of the coal. The ash content of SRC is also expected to have an adverse effect on catalyst stability because even a content of 0.1 percent represents a relatively large quantity of ash. In a pilot plant processing 200,000 lb of SRC per day, such a level would amount to 200 lb of ash per day, which could cause serious deactivation.

The presence of asphaltenes leads to additional problems in coal and residuum hydrotreatment processes by limiting diffusion in the catalyst pores and in the main fluid stream of the three-phase reaction. The choice of reactor systems used in catalyst testing is therefore particularly important for SRC as well as for other coal conversion studies.

In the upgrading of SRC to boiler fuels, the objective of primary importance is the minimization of hydrogen consumption necessary to

adjust the H/C ratio and to remove the nitrogen compounds from SRC. The acidity of the catalyst plays an important part in these processes. Both surface acidity and the nature of the catalyst are therefore important parameters in efforts to maximize selectivity. Most currently used liquefaction catalysts are designed for optimum HDS but they are not necessarily the best for SRC upgrading.

In spite of the efforts to minimize HDS, some sulfur removal is likely to occur during SRC upgrading, yielding some H_2S , the presence of which will have to be considered in selecting catalysts and assessing their stability in a sulfiding environment.

The regeneration of SRC-upgrading catalysts may create some serious thermal stability and sintering problems because of the presence of sodium in SRC ash. This is based on the belief that sodium is the cause of irreversible surface area loss during the regeneration of hydrotreating catalysts used for petroleum residua (McColgan and Parsons, 1974).

4.1.5 Coalcon Process

Since few data have been reported for Coalcon liquid upgrading, anticipated problems must be extrapolated from the reported chemical and physical properties of Coalcon liquids, and by analogy to processing of similar coal liquids or petroleum fractions.

4.1.5.1 Coalcon Heavy Oil Product

The heavy liquid fraction (400-840°F) is similar in physical and

chemical characteristics to No.6 fuel oil. In terms of the common refined fuels, one can consider upgrading this feed to gasoline, stationary turbine fuel, and refined (low sulfur and nitrogen) heating oils. Because of the high aromatic character of this feedstock, its conversion into jet and diesel fuels requiring substantial amounts of paraffinic components is not practical. However, a more severe treatment could convert it into a light aromatic blending stock for use in jet and diesel fuels. Upgrading to gasoline, turbine fuel, and refined heating oils presents two basic problems: selective cracking of the high molecular weight polynuclear aromatic constituents to lighter aromatics, and reduction of the heteroatom content to an acceptable level (Coals and Crellons, 1977).

The highly condensed aromatic nature of the preponderant portion of this liquid product is a particular problem since the condensed ring compounds must be selectively cracked to one- and two-ring compounds to reduce molecular weight and thereby give improved burning characteristics. For a gasoline fraction, selective cracking would lead to high-octane constituents (BTX). In any cracking process, high levels of polycyclic aromatics promote carbon deposition and consequent catalyst deactivation. This is less of a problem for hydrocracking than for catalytic cracking because the catalysts used in the former process contain a hydrogenation function which improves activity maintenance by hydrogenating coke precursors. Selective cracking is also important to minimize light gas production and maximize the liquid yield.

The presence of nitrogenous compounds at a high concentration in

the heavy oil product is another problem. The nitrogen content must be reduced not only to assure an environmentally acceptable NO_x emission upon combustion but also to prevent the basic pyridine from poisoning the acidic function of the catalysts used in the upgrading of these liquids to gasoline or lighter aromatics.

The high oxygen content of the heavy liquids is also a potential problem. The presence of phenols can affect the stability, in particular during storage. However, these oxygenated compounds are likely to be removed in any hydrodenitrogenation operation.

The ash content reported to be around 0.1 weight percent is definitely a problem for a fixed-bed process in which all of the ash can be deposited on the catalyst. It could also affect the use as turbine fuel. It may be necessary to reduce the ash level by about one order of magnitude for a continuous catalytic upgrading step.

The requirements for upgrading the heavy oil fraction to turbine fuel can be deduced from the specifications. The constraint of 1.0 weight percent maximum sulfur is easily met by the heavy oil product since it contains only 0.01 percent sulfur (0.03 percent thiophene). The hydrogen content of the oil, around 6 percent, is low and will have to be increased to reach 11.3 percent, the specification for stationary turbine fuel. It is expected that some hydrocracking would be necessary to meet the hydrogen specification and to give the appropriate specific gravity, viscosity, and Conradson carbon residue.

4.1.5.2 Coalcon Light Oil Product

The light liquid fraction has a boiling range similar to that of motor gasoline. The only upgrading which need be considered for this fraction is desulfurization (1.69 weight percent thiophene) and denitrogenation (7.74 weight percent pyridine), which should be easier for this oil than for the heavy oil product. After hydrotreating to remove the sulfur and nitrogen to adequate levels, this fraction could be blended to give high octane gasoline.

4.1.6 Fischer-Tropsch Process

The Fischer-Tropsch products are well suited for diesel fuel, jet fuel and LPG. Liquefied petroleum gas consists essentially of C_3 and C_4 hydrocarbons. It is, in fact, sold in many cases as butane or propane with minimum concentrations of the major component specified. This composition gives LPG a very high energy content compared to methane, 2500 Btu/cu ft for propane and 3200 Btu/cu ft for butane, making this material very useful as an exceptionally clean fuel in mobile equipment (octane number of 100) as well as a storable replacement for natural gas. The sulfur content depends on use, but is generally low.

For diesel and jet fuels the preferred components are paraffinic hydrocarbons, mainly normal paraffins with some branched chain components desirable to control physical properties. These are just the materials produced by the low-temperature Fischer-Tropsch synthesis as practiced over promoted iron and cobalt catalysts. The product

distribution for a typical cobalt catalyst shows a broad maximum from C_5 to C_{16} . This is somewhat low for diesel fuel where the distillation range of 325-800°F specifies a hydrocarbon composition extending from approximately C_9 to C_{25} . Thus, much of the synthesis products is below the desired range. A lighter distillation fraction such as kerosene for use as a jet fuel has a distillation range of 300-500°F and corresponding composition in the vicinity of C_9 to C_{16} . This more closely corresponds to that found on the Co-catalyst. The important point is that appropriate fractions of the synthesis products formed under certain operating conditions can be used for this class of fuels with minimum subsequent treatment. The broad range of paraffinic hydrocarbons together with a small fraction of branched chain hydrocarbon may only require a simple hydrogenation step and distillation. If the heavier diesel fuel fraction is wanted, a shift in the product distribution to higher molecular weights would be required.

4.2 PRODUCT COMPARISON

Although the syncrudes produced from a given coal may vary for the COED, H-Coal, and Synthoil processes, it is apparent that the compositions are at least qualitatively similar with respect to various molecular constituents. Therefore, the technical difficulties in converting these syncrudes to high-octane gasoline, jet fuels, and diesel fuel are expected to be similar and to vary primarily in degree.

A summary of the characteristics and the processes used to obtain the end products is presented before comparing the products obtained

from different syncrudes.

4.2.1 Products

4.2.1.1 Motor Gasoline

Motor gasoline is a blend of paraffins, naphthenes and aromatics. It contains a substantial fraction of branched paraffins, benzene, toluene, and xylene (BTX), the typical high-octane components.

4.2.1.2 Jet Fuel

Jet fuel is a highly paraffinic kerosene fraction with an aromatic content limited to less than about 20 volume percent. This gives better control of smoke emissions and optimum energy density. The latter property is important for aircraft range and is set at a minimum of 18,400 Btu/lb. The energy density increases with an increasing H/C ratio and is therefore favored by paraffins and naphthenes. Polycyclic aromatics increase smoking, lead to excessive carbon deposition in the engine, and are therefore kept below 3 volume percent. Some monocyclic aromatic content is desirable to improve the rich mixture performance of the jet aircraft during takeoff. Olefins must be held below 5 volume percent because they decrease thermal stability and form polymeric gums. Sulfur and mineral constituents present potential problems because they form deposits and facilitate corrosion in the hot section of the jet engine. Mercaptans are generally limited to a maximum of 0.003 weight percent.

4.2.1.3 Diesel Fuel

Diesel fuel uses range from low-speed engines such as marine diesels to medium-speed railroad diesels as well as high-speed applications for buses, trucks, and tractors. The boiling range of the fuel varies from 325-550°F to 350-800°F, depending on the application. The sulfur constraint ranges from 1.2 weight percent for low-speed use to 0.12 weight percent for high-speed use. Nitrogen content varies with the local requirements for total NO_x emissions.

4.2.1.4 Heating Oil

Heating oil most frequently used is called No.2 oil. It has an API gravity of 34, a viscosity (Saybolt Seconds Universal @ 100°F) of 35, and a boiling range of 325-645°F. Other specifications require a maximum carbon residue of 0.10 weight percent, a pour point of -5°F, a flash point of 150°F, and a maximum sulfur content of 1 weight percent. The oil should have proper viscosity to give optimum atomization and burning characteristics and minimum carbon deposition. The sulfur level is controlled for environmental reasons and to minimize burner corrosion.

4.2.1.5 Residue

Residual fuels are classified into several grades because of a variety of commercial applications, each having different requirements. Properties of primary importance for residual oils are viscosity and

sulfur content, the latter being limited by local SO_x emission standards.

4.2.2 Processes

Of the catalytic processes used, the most important ones for upgrading coal liquids are catalytic cracking, hydrocracking, naphtha reforming, and hydrofining. The latter process encompasses removal of sulfur, nitrogen, and oxygen compounds.

In catalytic cracking, a heavy feed, usually virgin gas oil, boiling point 600-1050°F, containing aromatics, naphthenes, and paraffins, is contacted with an acidic catalyst at 800-980°F and near atmospheric pressures in a fluidized bed which allows the withdrawal of the catalyst for oxidative regeneration. The objective is to produce gasoline, heating oil, and some diesel and jet fuel from heavy feedstocks with the formation of the minimum amount of light gases and of the optimum amount of coke. The coke is needed to provide heat on its oxidative removal from the catalyst during regeneration to balance the endothermicity of the cracking step. In addition to cracking, isomerization, alkylation, and dehydrogenation also occur.

Hydrocracking accomplishes the same function as catalytic cracking with higher molecular weight feedstocks and better control of product distribution. It is carried out at hydrogen pressures of a few thousand psi, using a bifunctional catalyst which contains both acid and hydrogenation sites.

Catalytic reforming converts a naphtha containing paraffins, naphthenes, and aromatics to high-octane gasoline over a bifunctional

catalyst such as Pt/Alumina by maximizing the production of branched paraffins and single-ring aromatics. The process usually operates at 200-600 psi, 800-980°F, and at hydrogen flow rates of 5000-8000 scf/bbl of naphtha.

Hydrofining operation involves hydrodesulfurization (HDS) or hydrodenitrogenation (HDN) of the various streams in a refinery. It is carried out at pressures of up to 1500 psi at 600-800°F with hydrogen feed rates up to 5000 scf/bbl. Typical catalysts are cobalt molybdate on alumina and nickel-tungsten on alumina for HDS and HDN, respectively, HDN requiring more severe conditions.

4.2.3 Syncrude Comparison

A comparison of syncrudes obtained from different coals by different processes is given in Table 4.2.1 (FMC, 1974; DOE, 1979a; DOE, 1979b). The composition of the syncrudes vary with the coal used, processing conditions and many other variables, the syncrudes reported in Table 4.2.1 are not obtained from either the same coal or at the same process conditions, but still it provides rough idea of how the different syncrudes compare with each other.

DeRosset et al., (1977) also reported a comparison of SRC, Synthoil and H-Coal syncrudes which is given in Table 4.2.2. These syncrudes were hydrotreated at different processing conditions, and the properties of hydrotreated crudes are presented alongwith the syncrude. The hydrotreating conditions were reported in a coded form, so the exact value of temperature, pressure and WHSV were unavailable.

Table 4.2.1 Syncrude Comparison

	COED III.#6	H-COAL III.#6	SRC II	EDS
API Gravity	28.6	17.1	18.6	33
IBPOF	108	270	150	64
Mid BP OF	465	433	440	
End BP OF	746	942	850	1000
MW		174	132	
Con. Carbon wt %		0.17		3.44
Rams Carbon wt %	0.2		0.7	
Analysis				
C wt %	85.65		82.82	86
H wt %	11.30	9.8	9.24	11.2
S wt %	0.068	0.13	0.29	0.1
N wt % (ppm)	(325)	0.38	0.85	0.2
O wt %	0.64	1.5	3.79	2.5
Cl - ppm			50	
Ash wt %		0.01	0.0004	
Inspection wt %				
Paraffins	10.4			
Cycloparaffins	41.4			
Polycycloparaffins				
Aromatics	34.1	55 %		
Polynuclear aromatics	14.1			

Table 4.2.1 (cont)

	COED Ill.#6	H-COAL Ill.#6	SRC II	EDS
Fractional Yields				
65-180°F	2.5	0	1.5	20
180-390°F	36.2	30	24.5	
390-650°F	51.1	60	65.0	20
950-plus °F				

Source: FMC, 1974; DOE, 1979a; DOE, 1979b

Table 4.2.2 Inspection of Coal Oils

SRC/UOP		Filtrate	Cutback SRC		Synthoil		H-Coal Filtrate	
Feedstock	Product	Product	Feedstock	Product	Feedstock	Product	Feedstock	Product
Hydrotreating Conditions								
WHSV/WHSV (base)		2.30		0.58		0.98		1.0
T-T (base), °F		0		-9		16.0		0
P-P (base), psi		-800		0		0		0
Properties of Sample								
API @ 60°F	-5.8	5.5	-14.1	3.7	-4.3	4.2	-17.7	4.3
Sp Gr @ 60°F	1.1257	1.0328	1.2052	1.0466	1.1124	1.0427	1.2433	1.0420
Distillation (°F)								
IBP	400	400	550		455	388	493	425
5%	520	482	610		519	480	538	508
10%	550	503	653		552	510	567	535
20%	585	540	749		606	565	621	587
30%	652	593			730	660	752	677
40%	685	619			795	705	822	733
50%	740	650			865	750	910	797
60%	825	710			970	809		850
70%	1020	805				900		
80%		985				982		
90%								
% Over	80.0	88.0	30.0		70.0	87.0	60.0	66.0
% Bottoms	20.0	12.0	70.0		30.0	13.0	40.0	34.0
Heptane Insoluble, wt %	27.5	3.73	67.5	5.45	18.8	6.14	49.0	7.90
Benzene Insoluble, wt %	9.6	0.10	29.1	0.01	4.4	0.81	29.0	0.93
Xylene Insoluble, wt %	0.01			0.02	0.16	0.17	0.03	0.01
Ash (ASTM), wt %	0.01	0.001	0.17	0.001	0.015	0.001	0.12	0.003

Table 4.2.2

	SRC/UOP Filtrate		Cutback SRC		Synthoil		H-Coal Filtrate	
	Feedstock	Product	Feedstock	Product	Feedstock	Product	Feedstock	Product
Molecular Weight, average	273				308	282	373	320
Ultimate Analysis								
Wt %								
Hydrogen	6.90	8.93	6.06	9.18	7.42	8.96	6.96	9.33
Carbon	86.77	89.51	87.65	91.01	88.28	90.16	87.07	89.87
Sulfur	0.72	0.04	0.59	0.02	0.56	0.02	0.66	0.03
Nitrogen	1.28	0.60	1.92	0.38	1.31	0.54	1.30	0.47
Oxygen	3.80	1.01	4.80	0.22	2.27	0.42	4.38	0.59

Source: DeRosset et al. (1977)

Table 4.2.3 gives a product distribution of a syncrude (H-Coal) fractions obtained by atmospheric and vacuum distillation similar to the petroleum refinery crude fractions. Straight run gasoline, naphtha, gas oil and atmospheric bottoms were obtained by distillation of the syncrude under atmospheric pressure. The vacuum gas oil and vacuum bottoms were obtained by vacuum distillation of atmospheric bottoms (FMC, 1974; DOE, 1979a; DOE, 1979b). The composition and quantities of these fractions vary depending on coal source, method of liquefaction and degree of pre-hydrotreatment.

4.2.4 Naphtha Comparison

A comparison of straight run naphtha fractions obtained by atmospheric distillation of different syncrudes is given in Table 4.2.4 (FMC, 1974; DOE, 1979a; DOE, 1979b). Peters (1977e) also reported a comparison of straight run naphthas obtained from different syncrudes by a computer simulated conceptual plant (Table 4.2.5). A 1980 value for 100 pound of naphtha obtained from COED syncrude was \$10.43, for H-Coal syncrude \$10.06, and for SRC II syncrude \$9.49.

4.2.4.1 Hydrotreated Naphtha Comparison

Straight run naphtha is hydrotreated to remove heteroatoms, to upgrade the product by saturating the aromatic compounds, and also to reduce polynuclear aromatics to some degree.

The systems for hydrotreatment of naphtha and gas oil are similar. Feed is mixed with hydrogen and pumped to reaction pressure, and then

Table 4.2.3 Syncrude Fractions

	Straight run gasoline	Naphtha	Gas Oil	Atmospheric Bottoms	Vacuum Gas Oil	Vacuum Bottoms
API	60	37	14.3	-7.6	-0.6	-10.2
Boiling Range ^o F		180-390	390-659	650-1000	650-800	800-1000
Mid BP ^o F		280	520	850	700	900
Analysis wt %						
C	87.0	87.5	90.8	93.0	91.5	93.6
H	13.0	12.5	9.2	7.0	8.5	6.4
N ppm		5000	6000	10,000	7000	10,800
S ppm		2500	2500	3500	2800	11,300
O ppm		28,000	36,000	53,500	42,200	57,500
Inspections wt %						
Paraffins	39	7	11	11		
Napthenes	37	66	27	19		
Aromatics	24	22	27	236		
Polynuclear aromatics		0	35	44	40	45.3
Olefins wt %	2.3	26.4	50.9	20.4		

Source: FMC, 1974; DOE, 1979a; DOE, 1979b

Table 4.2.4 Straight Run Naphtha Comparison

	COED I11.#6	SRC II Kentucky 9&14	H-COAL	EDS
API	43.8	36.2	43.7	38.4
Boiling Range ^o F	200-390	180-400	170-375	180-380
Mid BP ^o F	284	290	260	302
Octane (RON)	70.1		80.3	83.2
MW		118		
Gum mg/100 ml			40	44
Analysis				
C wt %		84.22	85.90	86.24
H wt %		12.23	12.80	11.80
S ppm	93.2	2600	12.89	9,998
N ppm	128	4200	1930	2097
O ppm		35,100	5,444	13,700
Cl ppm		18-20	23	18
Inspection Vol %				
Paraffins	7.1	23	16.2	13.2
Cycloparaffins	58.9	38	53.9	44.5
Polycycloparaffins	12.5			7.1
Aromatics	21.5	34	24.7	25.3

Source: FMC, 1974; D0E, 1979a; D0E, 1979b

Table 4.2.5 Straight Run Naphthas

	COED	H-COAL	SRC II
Hydrogen	-0.90	-1.58	-1.90
Methane	20.40	19.08	19.36
Ethane	10.32	11.45	15.01
Propane	3.18	2.52	3.11
Butanes	2.85	3.11	4.24
Pentanes	3.89	5.53	7.46
Benzene	53.50	51.28	44.74
Other liquid fuel	6.75	8.25	5.74
Value/100 lb Distillate (1980)	\$10.43	\$10.06	\$9.49

Source: Peters, B.C. 1977e

Basis: 100 lb Distillate of Coal-Derived Liquid

heated to reaction temperature before entering a set of ebullated bed reactors. The product from the reactor is fractionated.

A comparison of hydrotreated naphthas from different syncrudes is reported in Table 4.2.6 (DOE, 1979a; DOE, 1979b; FMC, 1974).

Severe hydrotreatment is required to upgrade coal-derived naphthas to a suitable reformer feed because the reformer cannot tolerate more than 2 ppm nitrogen.

4.2.4.2 Hydrocracked Naphtha Comparison

Hydrotreated naphtha fractions were hydrocracked to increase the output for lower molecular weight products. Table 4.2.7 summarizes the hydrocracked naphtha fractions for COED, H-Coal and EDS syncrudes (FMC, 1974; DOE, 1979a; DOE 1979b).

Table 4.2.8 gives a comparison of straight run, hydrotreated and hydrocracked naphthas obtained from H-Coal syncrude.

Hydrotreated and hydrocracked naphthas of different syncrudes are reformed. Table 4.2.9 gives a comparison of different naphthas (DOE, 1979a; FMC, 1974).

4.2.5 Gasoline Comparison

A comparison of straight run gasoline from COED process (Illinois No.6 coal) with hydrocracked straight run gasoline, gasoline from hydrotreating light gas oil and the regular gasoline from petroleum crudes is reported in Table 4.2.10.

Table 4.2.6 Hydrotreated Naphtha Comparison

	COED I11.#6	SRC II	H-Coal	EDS
API	43.9	45.8	46.8	44.1
Boiling Range ^{OF}	200-390	180-390	185-370	215-375
Mid BPOF	284	261	263	287
Octane (RON)	70.1	69.2	66.8	64.5
Analysis				
C wt %	86.73		86.45	86.18
N wt %	13.27		13.58	13.93
S ppm	1.0	11	3.9	0.1
N ppm	2.0	0.1	0.63	0.2
O ppm		90	34	98
Cl ppm		0.6	4	1.0
Inspection Vol %				
Paraffins	7.1	16.8	19.0	12.9
Cycloparaffins	61.0	61.3	62.1	50.2
Dicycloparaffins	11.7			15.3
Aromatics	20.2	21.9	18.9	21.6
Hydrogen Consumption scf/bbl	80	1121	480	850

Source: FMC, 1974; DOE, 1977a; DOE, 1979b

Table 4.2.7 Hydrocracked Naphtha Comparison

	COED	EDS	H-Coal
API	47.8	50.0	49.7
Boiling Range °F	180-385	160-390	150-400
Mid BP °F	249	236	233
Octane (RON)		83.2	84.2
MW		100	NA
Analysis			
C wt %		86.70	86.52
H wt %		12.84	13.09
S. ppm		1.3	0.1
N ppm		0.3	0.1
O ppm		237	40.9
Cl ppm		NA	1.0
Inspection Vol %			
Paraffins	16.5	16.2	13.22
Cycloparaffins	71.3	45.5	52.35
Polycycloparaffins		6.6	
Aromatics	12.2	29.7	34.43

Source: FMC, 1974; DOE, 1979a; DOE, 1979b

Table 4.2.8 Naphtha Inspection and Analysis

	Straight Run Naphtha	Hydrotreated Naphtha	Hydrocracked Naphtha
API	37	44	50
Boiling range °F	180-390	180-390	180-390
Mid BP °F	280	280	240
UOP "K"	10.8	11.2	11.4
Octane (RON)	80	65	84
Analysis			
C wt %	87.5	86.7	87
H wt %	12.5	13.3	13
S ppm	5000	0.1	0.3
N ppm	2500	0.2	0.3
O ppm	28,000	100	400
Inspection Vol %			
Paraffins	7-13	7	15
Cycloparaffins	59-44	61	70
Polycycloparaffins	12-18	11	
Aromatic	22-75	21	15

Source: FMC, 1974; DOE, 1979a; DOE, 1979b

Table 4.2.9 Reformer Products Comparison

	Hydrotreated Naphtha Reformate			Hydrocracked Naphtha Reformate		
	H-Coal	EDS	COED	EDS	H-Coal	
API	33.7	32.6	33.5	42.7	41.7	
Mid BP °F	276	303		250	245	
Boiling Range °F	188-394	219-409		164-352	150-390	
Octane (RON)	102.6	101.5	102.5	98.2	99.6	
H ₂ Generation scf/bbl	1816	1816	1858	939	994	
LPG Generation wt %	1.8	0.6	2.11	2.3	1.5	
Gasoline Yield wt %	94.8	96.0	94.81	97.7	96.7	
Analysis						
C wt %	88.96	90		87.86	88.65	
H wt %	90.11	10.18		11.77	10.89	
S ppm		0.1 ppm		0.1	0.1	
N ppm		1 ppm		0.3	0.1	
O ppm		100		272		
Inspection Vol %						
Paraffins		14.98	11.5	16.4		
Cycloparaffins		5.26	5	13.43		
Dicycloparaffins		0.38		0.73		
Aromatics		76.55	82.7	69.39		
Naphthalenes		2.85		0.03		

Table 4.2.10 Gasoline Analysis

	COED III # 6 SR Gasoline	Gasoline from Gas oil Hydrotreating	Hydrocracked Straight Run Gasoline	Petroleum Straight Run Gasoline
API	60	66	77	78.6/79
Boiling Range °F IBP	180			
Reid VP psi				13.5/12.9
Octane (RON)		80	(71-82)	
Analysis				
Carbon wt %	13	14.3	15.5	
Hydrogen wt %	87	85.7	84.5	
Product Inspection Vol %				
Paraffin	38.9	30		
Cycloparaffin	36.3	63		
Polycycloparaffins	0.8			
Aromatics	24.0	7		

Source: FMC, 1974; DOE, 1979a; DOE, 1979b

4.2.6 Gas Oil Comparison

Table 4.2.11 gives a comparison between straight run, hydrotreated and hydrocracked gas oils for H-Coal syncrude. Severe hydrotreatment is required to upgrade gas oil suitable hydrocracker feed or to make specification comparable to jet or diesel fuel.

Hydrocracking is used to reduce the molecular weight and to a limited extent nitrogen content, of the gas oil from coal liquids. The hydrocracking operation in presence of hydrogen give maximum naphtha yield. These naphtha products are usually suitable for re-forming without additional hydrotreatment.

Hydrocracking is highly exothermic and occurs at elevated temperatures in the presence of special selective cracking catalysts. This catalyst is sensitive to nitrogen, coke, metals and asphaltenes. Therefore, severe pretreatment of feedstocks is required to assure adequate catalyst life and activity.

4.2.7 Coal Liquid and Petroleum Comparison

A comparison between the products obtained from syncrude and petroleum crude in a very general terms is given in Table 4.2.12 (DOE, 1979a; DOE, 1979b; FMC, 1974). The properties of products obtained from different syncrudes depends very much on the type of coal, process conditions and other factors.

Table 4.2.11 Gas Oil Analysis

	Straight Run Gas Oil	Final Hydrotreated Gas Oil	Hydrocracked Gas Oil
API Gravity	11-25	30	20
Boiling range °F	390-650	340-650	390-650
Mid BP°F	520	470	520
Cetane No	18	44	
Smoke Point	160-200	20-24	
MW			
Analysis			
Carbon wt %	88.50-92.2	86.5	88.50
Hydrogen wt %	11.50-8.8	13.5	11.50
Sulfur ppm	40-2,500	10	0.1-1.0
Nitrogen ppm	240-10,000	20-0.1	0.2-2.0
Oxygen ppm	1900-36,000	300	30
Metals ppm	5		
Cl-ppm	50-100		
Inspection Vol %			
Paraffins	11	1.0	8
Cycloparaffins	11		
Polycyclic Paraffins	16	97	50
Aromatics	27		36
Polynuclear Aromatics	35	2.0	6

Source: FMC, 1974; DOE, 1979a; DOE, 1979b

Table 4.2.12 Coal Liquid vs. Petroleum Products

	ASTM Octane No (RON)	API Gravity	Vol % Aromatics						
Coal Liquid Reformate	102-100	33-42	70-80						
Petroleum Reformate	100	44	65-75						
				ASTM Cetane No	API Gravity	Vol % Aromatics	Mid BP ^o F		
Coal Liquid Diesel Fuel		36	6-8				390		
Coal Liquid Diesel Fuel	44	31	2				470		
Petroleum Diesel Fuel	40 min	33-37	25				440-500		
				ASTM Smoke Pt	API Gravity	Vol % Aromatics	Mid BP ^o F/End pTF	Freeze Pt ^o F	
Coal Liquid Jet Fuel		36	6-8				390/650		
Coal Liquid Jet Fuel	24	39	6				376/530	-81	
Petroleum Jet Fuel	20 min	39 min	20 % max				460max/550max	-40 max	

4.3 CORRELATIONS

Refinery design is a complicated and approximate activity due to the complex structure of petroleum (or syncrude) feed-stocks, the variety of products produced, and the large number of operations used in their production. Refinery design is both a science and an art, employing both first principles (e.g., material balance), and experimentally derived correlations (e.g., change in API gravity with hydrogen consumption, during hydrotreating). An attempt is made in this section to:

- . Bring together the pertinent correlations which appear in the literature, for coal liquid processing.
- . Extend or develop, these additional correlations where basic data can be found.
- . Compare where possible the coal liquid results with similar results for petroleum.

Data are available in the literature to develop correlations for: heteroatom removal, API improvement, hydrogen consumption, aromatic content, conversion or yield, and catalyst deactivation. Some of these correlations will be presented and discussed in this section.

4.3.1 Heteroatom Removal

Berg, Lloyd and McCandles, F.P (1975, 1976a,b,c,d and 1977a,b,c,d) compared different catalysts for the removal of sulfur and nitrogen from

Synthoil, SRC, and COED liquids.

Synthoil liquid was a tar like substance with flow characteristics of thick molasses. It contained 0.44 percent sulfur and 1.06 percent nitrogen. Table 4.3.1 presents a comparison of different catalysts for removing heteroatom and hydrocracking of the synthoil liquid in bomb runs. A 30.5 cub inch Parr rocking autoclave was used for the tests, the autoclave was charged with synthoil and catalyst, and was pressurized with 2000 psi of hydrogen before heating it to 840° F for one hour. To determine the amount of cracking the distillation curve of the products is compared with that of the synthoil feed in Table 4.3.1, along with the percent removal of sulfur and nitrogen with each catalyst. Figure 4.3.1 shows the effect of LHSV on desulfurization and denitrogenation of synthoil liquid by two different catalysts, in a fixed bed continuous flow reactor. The operating temperature was 835° F with hydrogen to feed ratio of 10,000 scf/bbl.

A similar correlation is presented in Figure 4.3.2 for PAMCO's solvent refined coal. SRC as received was in solid form and was dissolved in synthetic solvent. SRC solution had 0.5 percent sulfur and 1.2 percent nitrogen. The reactor used was a three foot Inconel reactor operating at 835° F with hydrogen to feed ratio of 10,000 scf/bbl.

Figures 4.3.3 and 4.3.4 present correlations for heteroatom removal for different catalysts with respect to liquid hourly space velocity for COED tar. The operating temperature was 835° F with hydrogen to feed ratio of 10,000 scf/bbl.

Table 4.3.1 Bomb Run Hydrocracking and Heteroatom Removal Results for Synthoil

Catalyst	% Naphtha IBP-425°F	% Fuel Oil 425-600°F	% Gas Oil 600-700°F	% Residue 700°F + Distilled	Total Vol %	% DeS	% DeN
Synthoil	4	20	20	56	44	41	18
Harshaw (Ni-W) Ni-4401	6	23	20	51	49	50	17
Harshaw (Ni) Ni-3250	8	20	21	51	49	36	18
Harshaw (Ni-Mo-Si) HT-100	10	22	18	50	50	48	32
Shell (Co-Mo) Shell 344	8	21	21	50	51	16	0
Harshaw (Ni-Cu) Ni-1800	4	23	24	49	51	09	0
Harshaw (W) W-0101	6	25	20	49	51	07	06
Harshaw (Ni-Co-Fe) Ni-1601	7	22	22	49	51	20	10
M.S.U (Sn) SnCl ₂	8	24	21	59	51	55	21
Shell (Ni-Mo) Shell 324	10	21	21	48	52	23	28
Harshaw (Ni-W) Ni 4301	7	22	23	48	54	45	18
Harshaw (Ni-W) Ni-4303	12	22	20	46	54	30	12
Ketjen (Ni-W) 330-3E	12	22	20	46	54	57	16
Harshaw(Ni) Ni-0104	9	23	22	46	56	18	25
Cat & Chem Co (Co-Mo) C-20-6	10	21	25	44	57	25	03
Harshaw (W) W-0101	23	25	9	43	61	52	25
Harsahw (Co-Mo) CoMo-0603	9	25	27	39	61	32	29
Harshaw (Ni-W) Ni-4301	9	24	28	39	64	34	13
Harshaw (Co-Mo) HT-400	10	24	30	36	65	16	33
Harshaw (Co-Mo) CoMo-0401	11	23	31	35	65	32	33
Harshaw (Ni-Mo) HT-500	11	25	29	35			

Source: Berg, Lloyd and McCandles, F.P (1975, 1976a, b, c, d and 1977a, b, c, d)

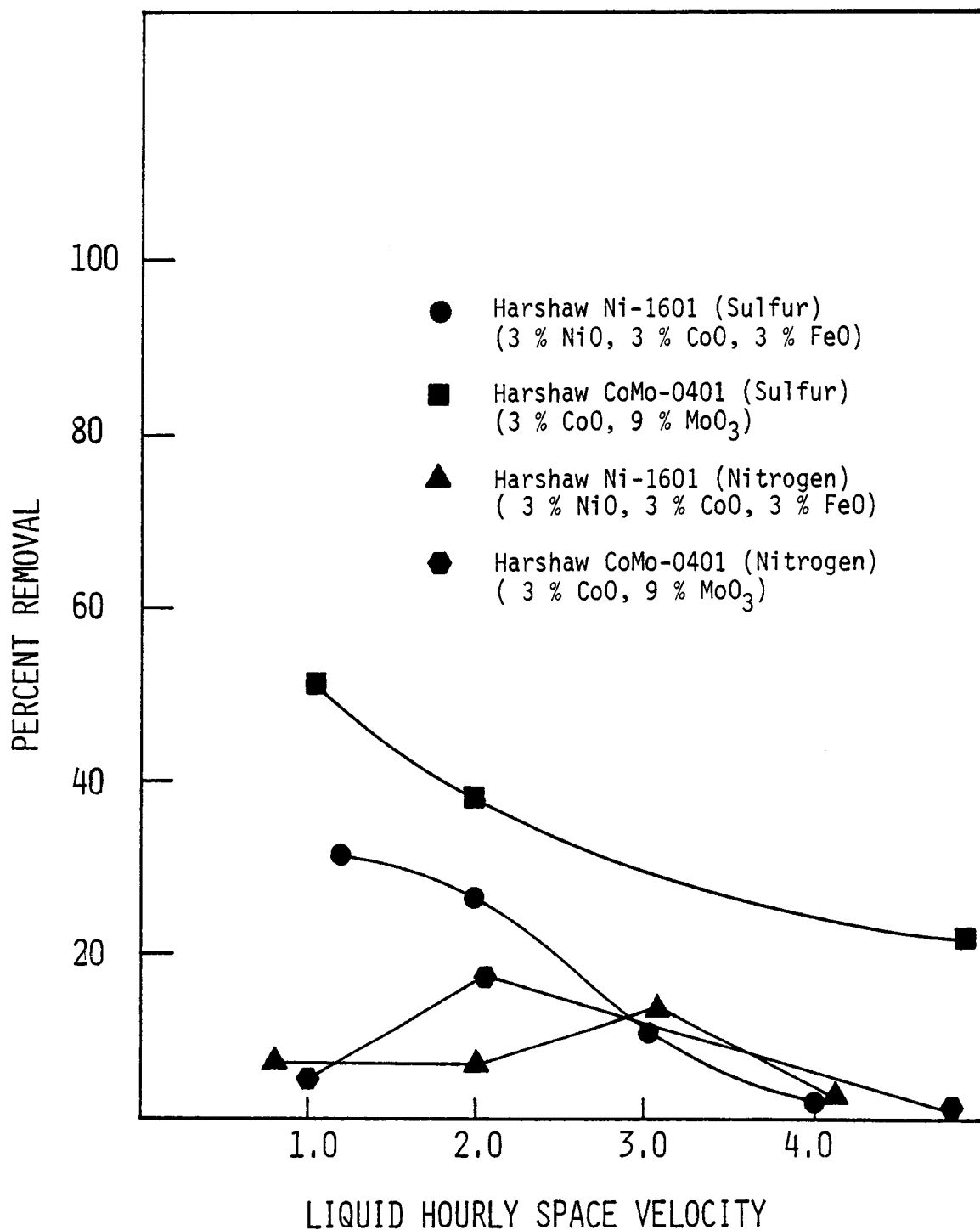


FIGURE 4.3.1 Percent Desulfurization and Denitrogenation versus LHSV for Synthoil (Berg, Lloyd and McCandless, F.P., 1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d)

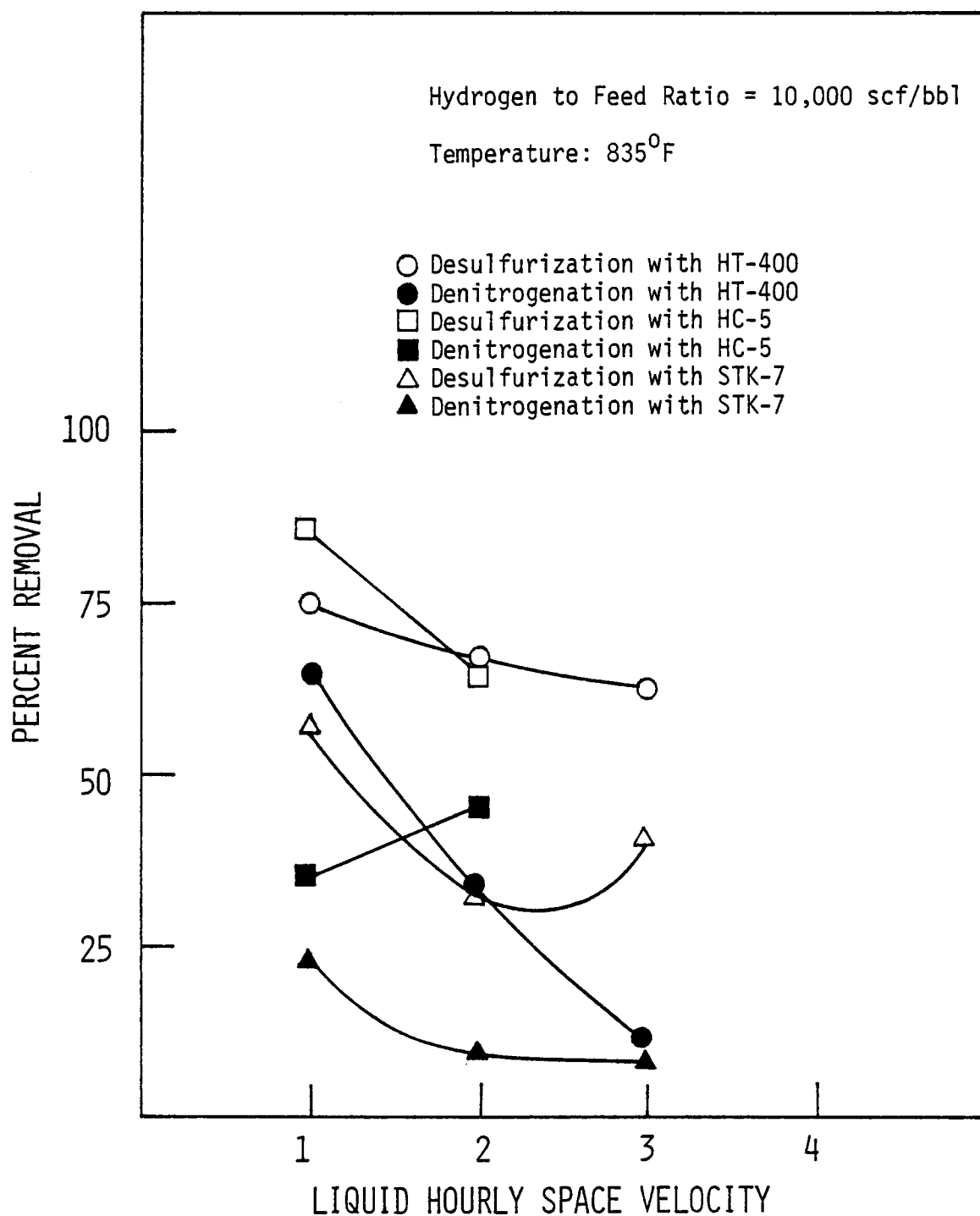


FIGURE 4.3.2 Denitrogenation and Desulfurization of SRC Feedstock with Respect to Liquid Hourly Space Velocity (Berg, Lloyd, and McCandless, F.P., 1975a, 1976a, 1976b, 1976c)

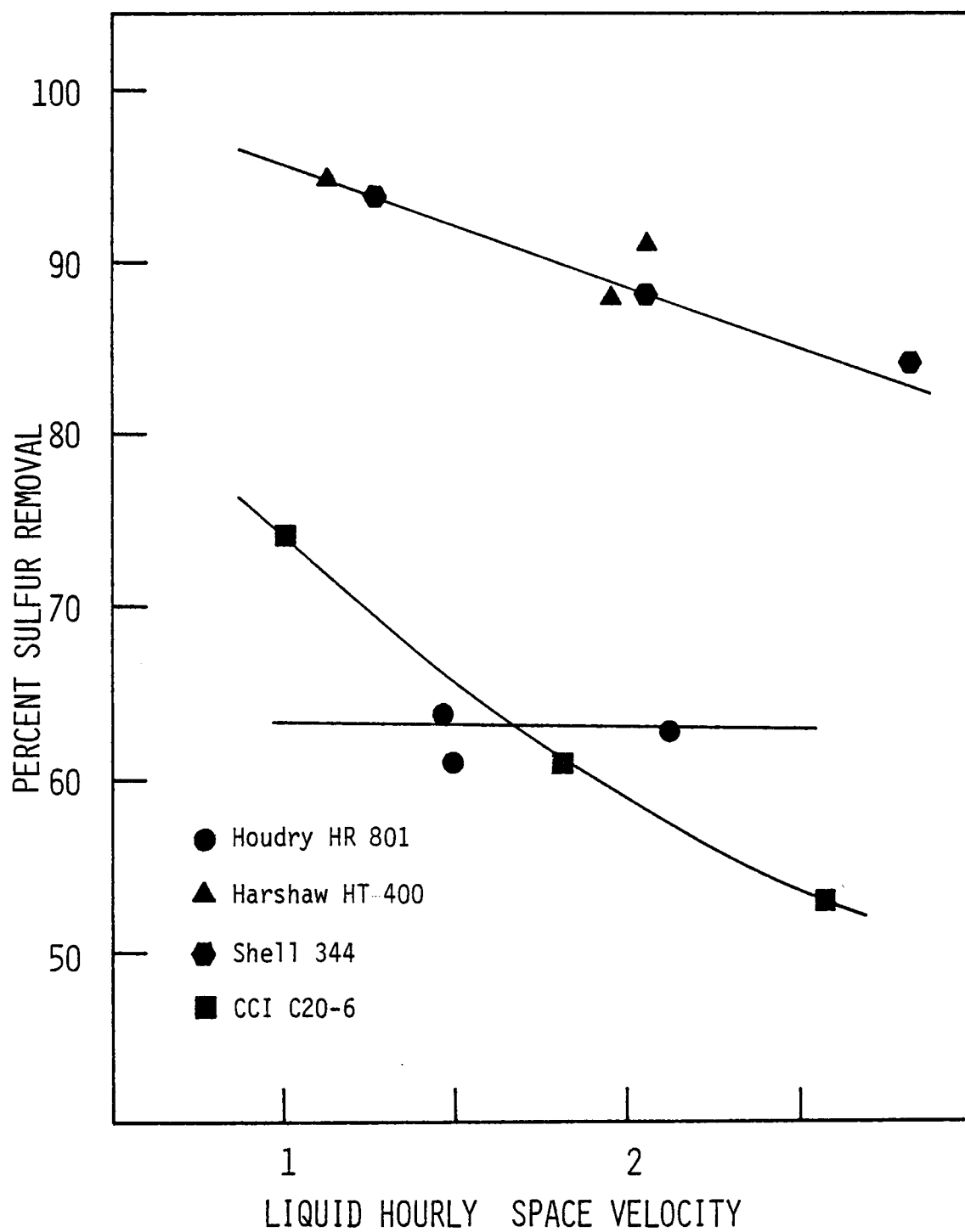


FIGURE 4.3.3 Sulfur Removal from COED Tar (Berg, Lloyd, and McCandless, F.P., 1975, 1976a, 1976b, 1976c, 1976d, 1977a, 1977b, 1977c, 1977d)

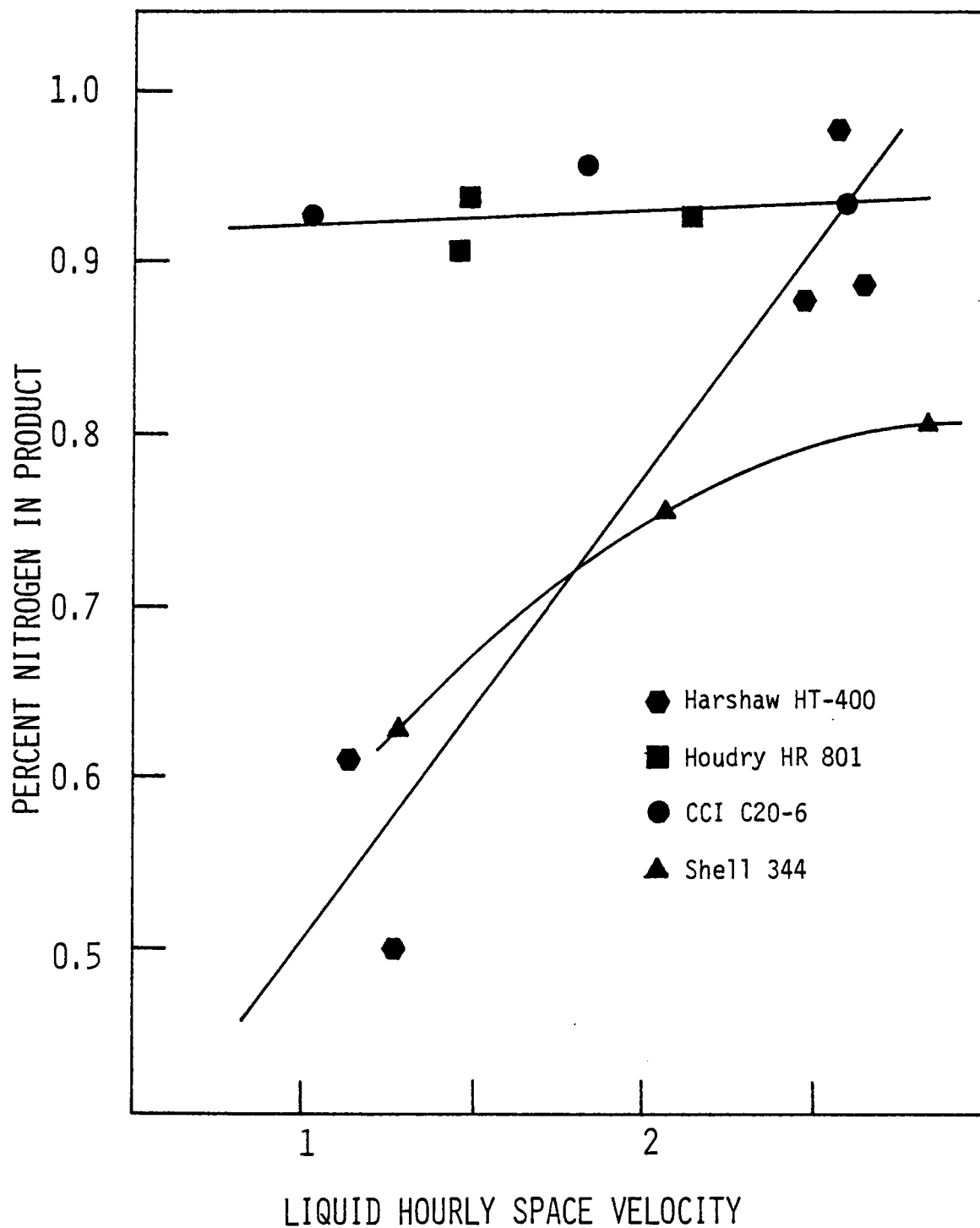


FIGURE 4.3.4 Nitrogen Removal from COED Tar
(Berg, Lloyd, and McCandless, F.P.,
1975,1976a,1976b,1976c,1976d,1977a
1977b,1977c,1977d)

The effect of different hydrogen to liquid feed rate ratio for removing sulfur from COED tar is given in Figure 4.3.5 for different liquid hourly space velocities. The operating temperature was 835° F.

B.L. Crynes (1977b, 1977c, 1977d) hydrotreated synthoil and anthracene oil in a fixed bed reactor using different catalysts and operating conditions. Figure 4.3.6 gives a relationship between nitrogen removal with respect to volume hourly space time of Nalcomo-474 catalyst for Synthoil I. The catalyst Nalcomo 474 (14.0 percent MoO_3 and 2.8 percent NiO) were tested at two different temperatures for nitrogen removal. At both the temperatures the Co-Mo catalyst showed very little ability to remove nitrogen from the synthoil feed (nitrogen content of the feed was 1.19 percent).

The sulfur response of Nalcomo 474 is presented in Figure 4.3.7. At 800° F the removal of sulfur at a volume hourly space time of 1.5 hours has drastically increased.

A relationship between heteroatom (sulfur and nitrogen) removal with respect to pressure is given in Figure 4.3.8 for Synthoil I liquid over Corning Monolith Alumina impregnated with Co and Mo. The operating temperature was 700° F at a volume hourly space time of 1.11 hours.

A similar relationship for raw anthracene oil is given in Figure 4.3.9 for the same catalyst, and operating conditions of 700° F temperature and 1.118 hour space time.

Wan and Crynes (1972) hydrocracked raw anthracene oil over two different catalysts. A relationship obtained from his data for sulfur

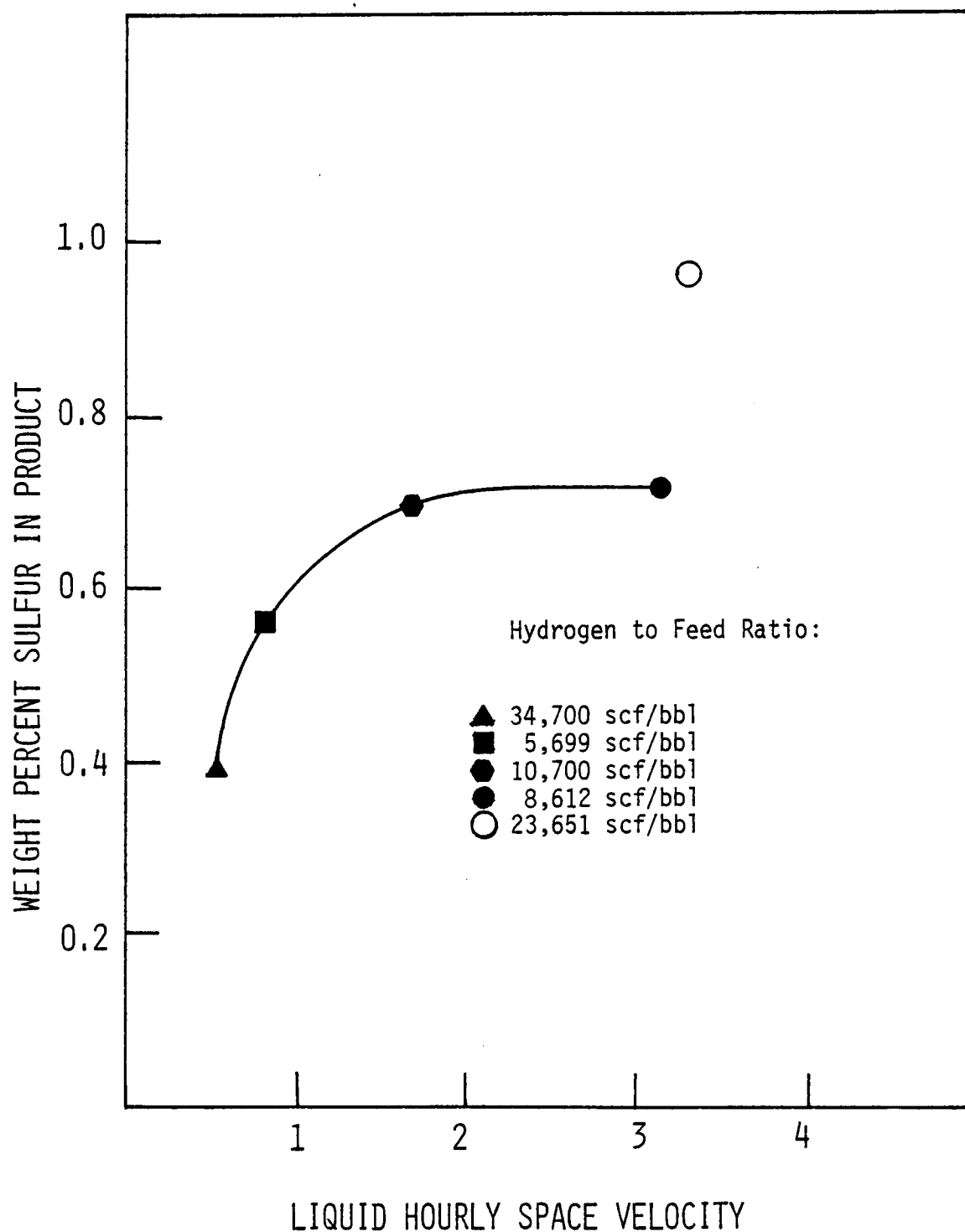


FIGURE 4.3.5 Upgrading COED Tar by Nickel- Tungsten
(Berg, Lloyd, and McCandless, F.P., 1975,1976a
1976b,1976c,1976d,1977a,1977b,1977c,1977d)

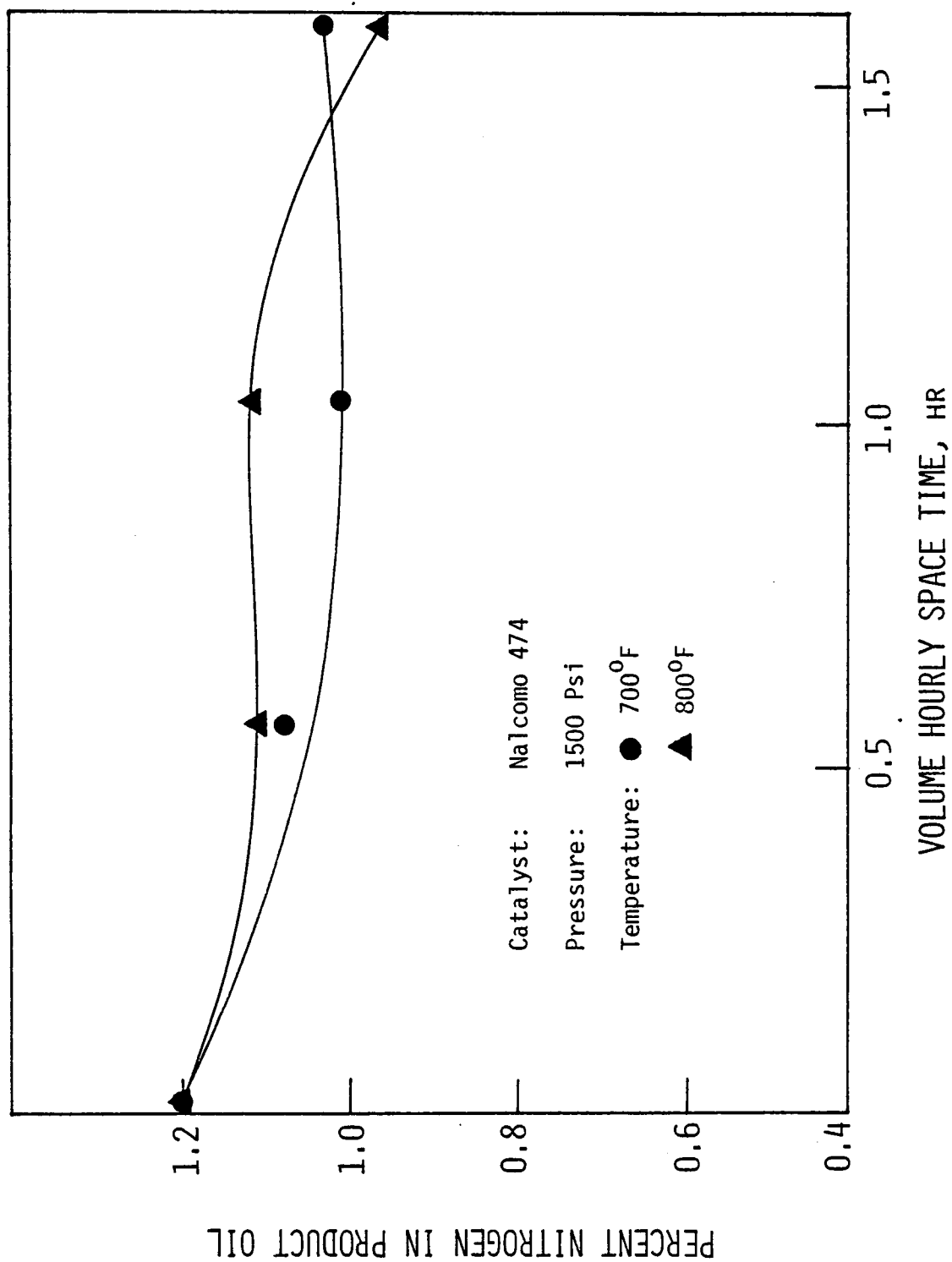


FIGURE 4.3.6 Nitrogen Response for Synthoil I (Crynes, B.L., 1977b, 1977c, 1977d)

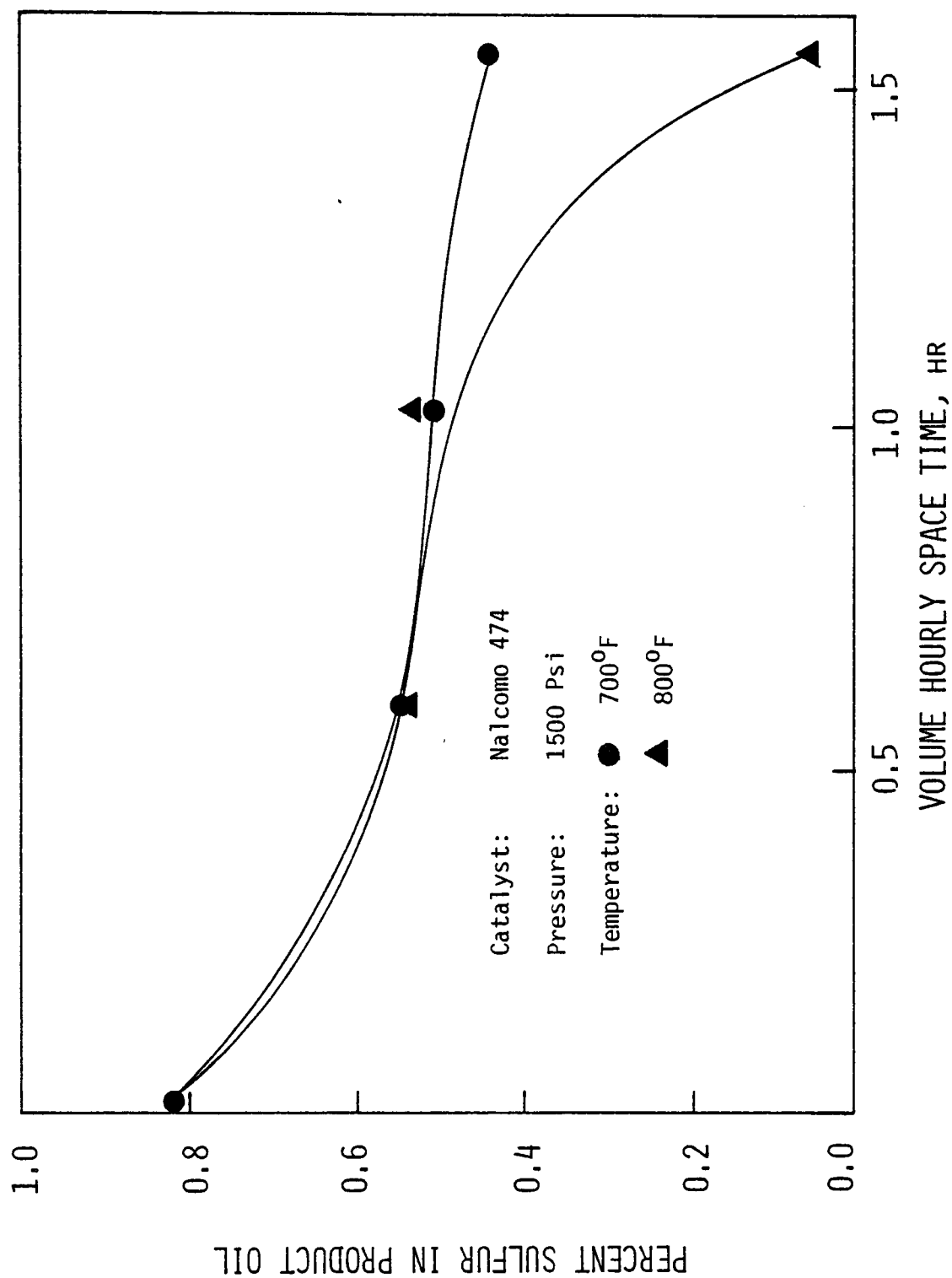


FIGURE 4.3.7 Sulfur Response for Synthoil I (Crynes, B.L., 1977b)

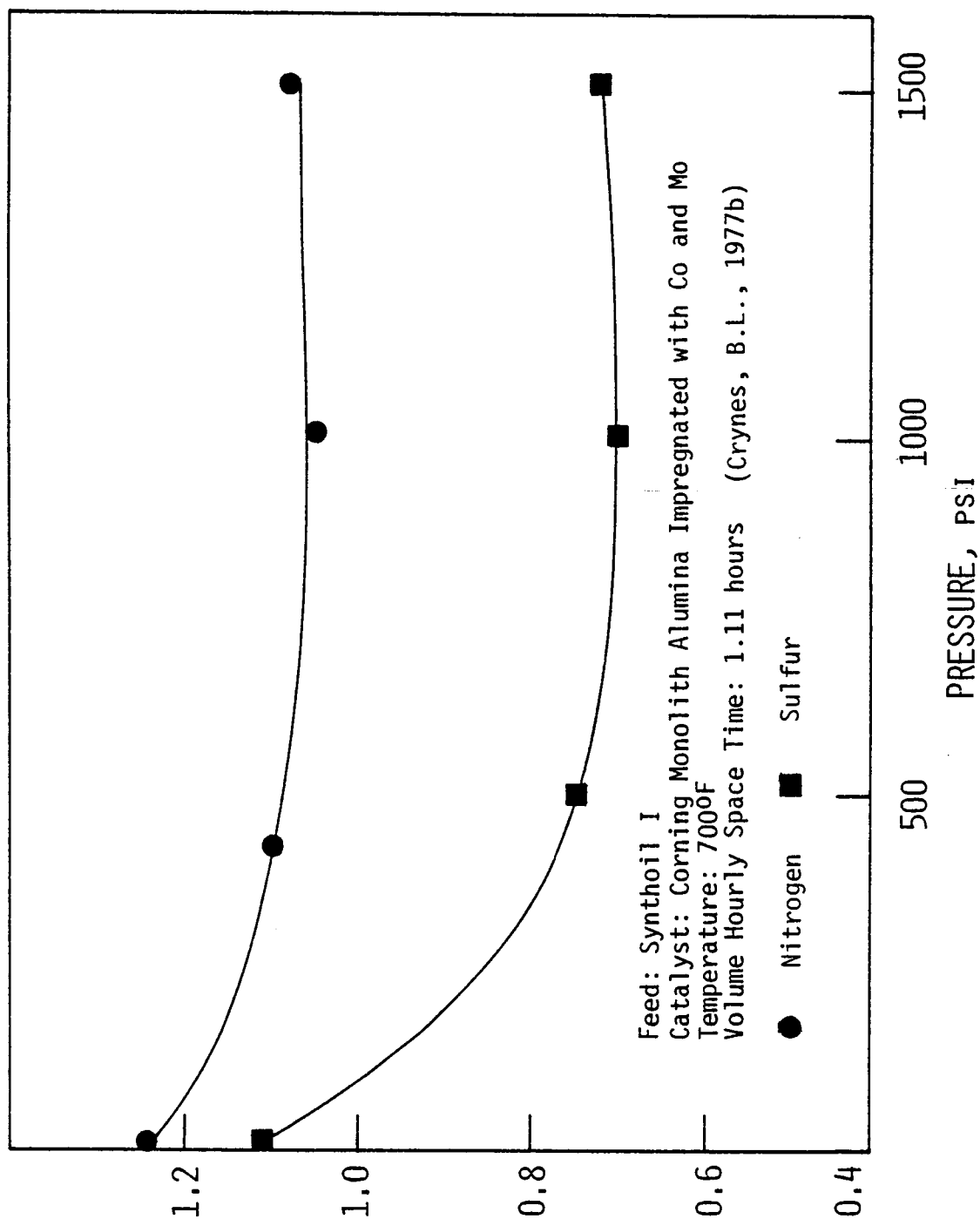


FIGURE 4.3.8 Sulfur and Nitrogen Response to Change in Pressure for Synthoil I

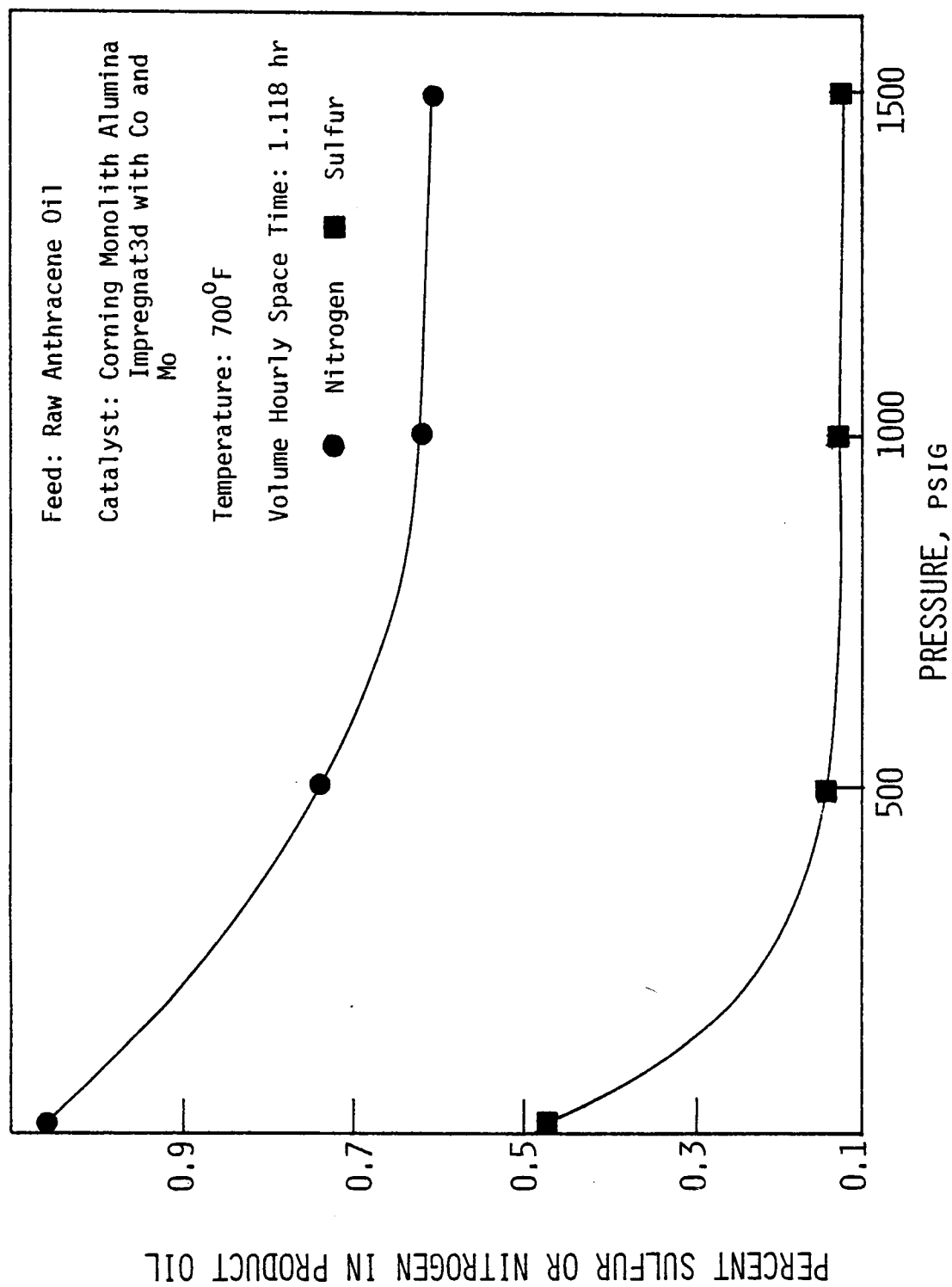


FIGURE 4.3.9 Sulfur and Nitrogen Response to Change in Pressure (Crynes, B.L., 1977b)

removal with respect to space time at different temperatures and pressures is presented in Figure 4.3.10. The Anthracene oil which was used as feed stock had 0.45 weight sulfur and 0.8 weight percent nitrogen. The fixed bed reactor used was 1/2 inch in diameter packed with 0.034 lb of Nalco 474 (Co-Mo) catalyst.

Jacobs Harry (1970) presented a relationship between sulfur removal and weight hourly space velocity for three different COED tars obtained from three different coal sources (Figure 4.3.11). The sulfur content of the feed stocks were 0.34 percent, 2.50 percent and 1.80 percent for Utah, Illinois No. 6 and Pittsburgh seam coal feeds respectively. The operating pressure was 3000 psi. The temperature ranged from 650° F to 850° F and the space velocity (WHSV) ranged from 0.3 to 3.0 lbs/hr of oil per lb of catalyst.

Another relationship between heteroatom removal and space velocity for COED oil presented by Johns, J.J. et al. (1972) is given in Figure 4.3.12. The sulfur, nitrogen and oxygen contents of the feed oil were 7.15 percent, 1.1 percent and 0.35 percent respectively. Sulfur and oxygen were less difficult and almost identical, not only in the relative difficulty of removal, but also in the effect of change in the space velocity.

Greskovisch, E.J. (1976a, 1976b) hydrocracked SRC filtrate (Ft. Lewis) over Harshaw 0402T (Co-Mo) catalyst in a long path fixed bed reactor of 2 inch ID. The operating pressure was 1500 psi at a temperature range from 645° F to 805° F. A relationship between percent removal of sulfur and nitrogen to the operating temperature is shown

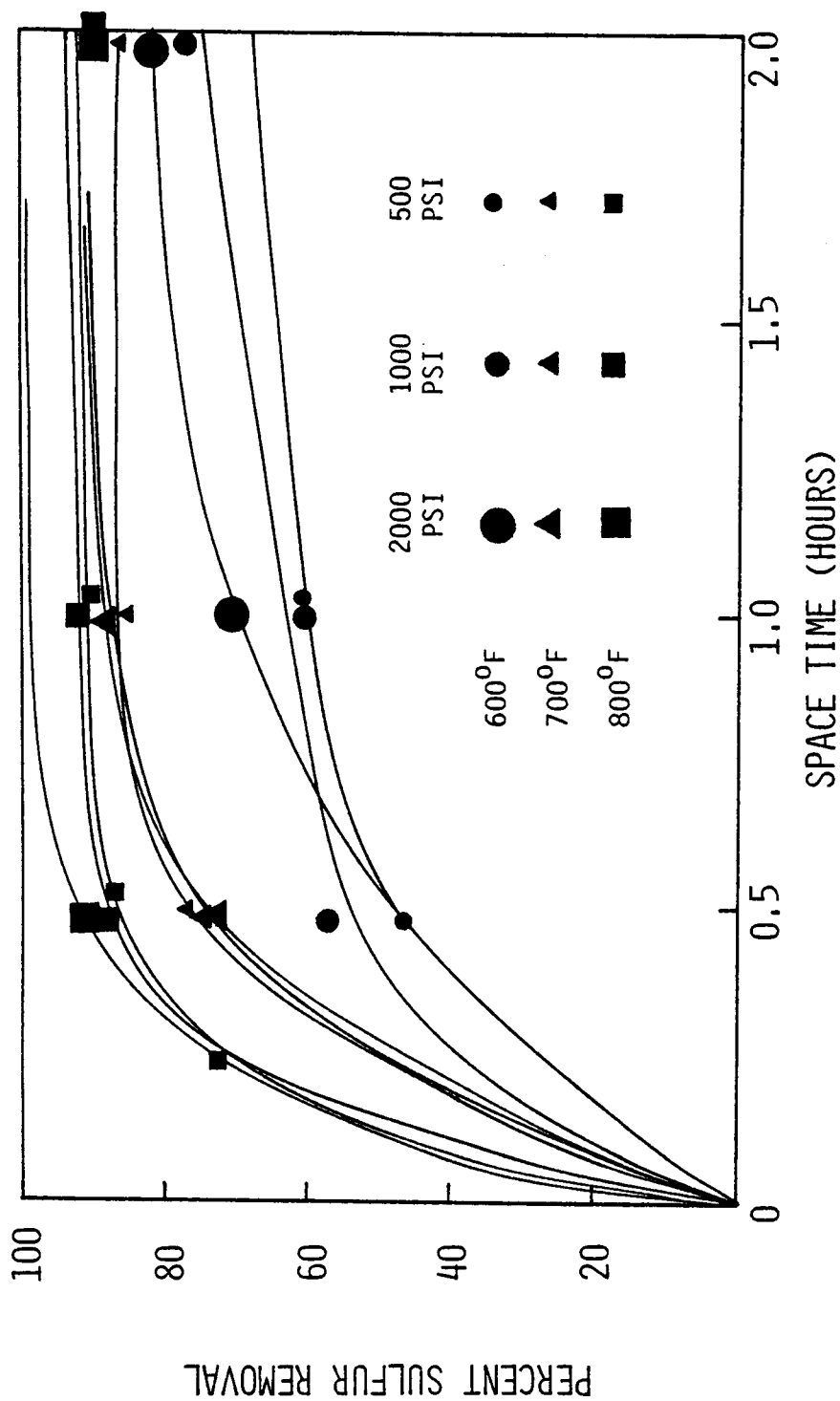


FIGURE 4.3.10 Sulfur Removal for Anthracene Oil
(Wan, K.T. and Crynes, B.L., 1972)

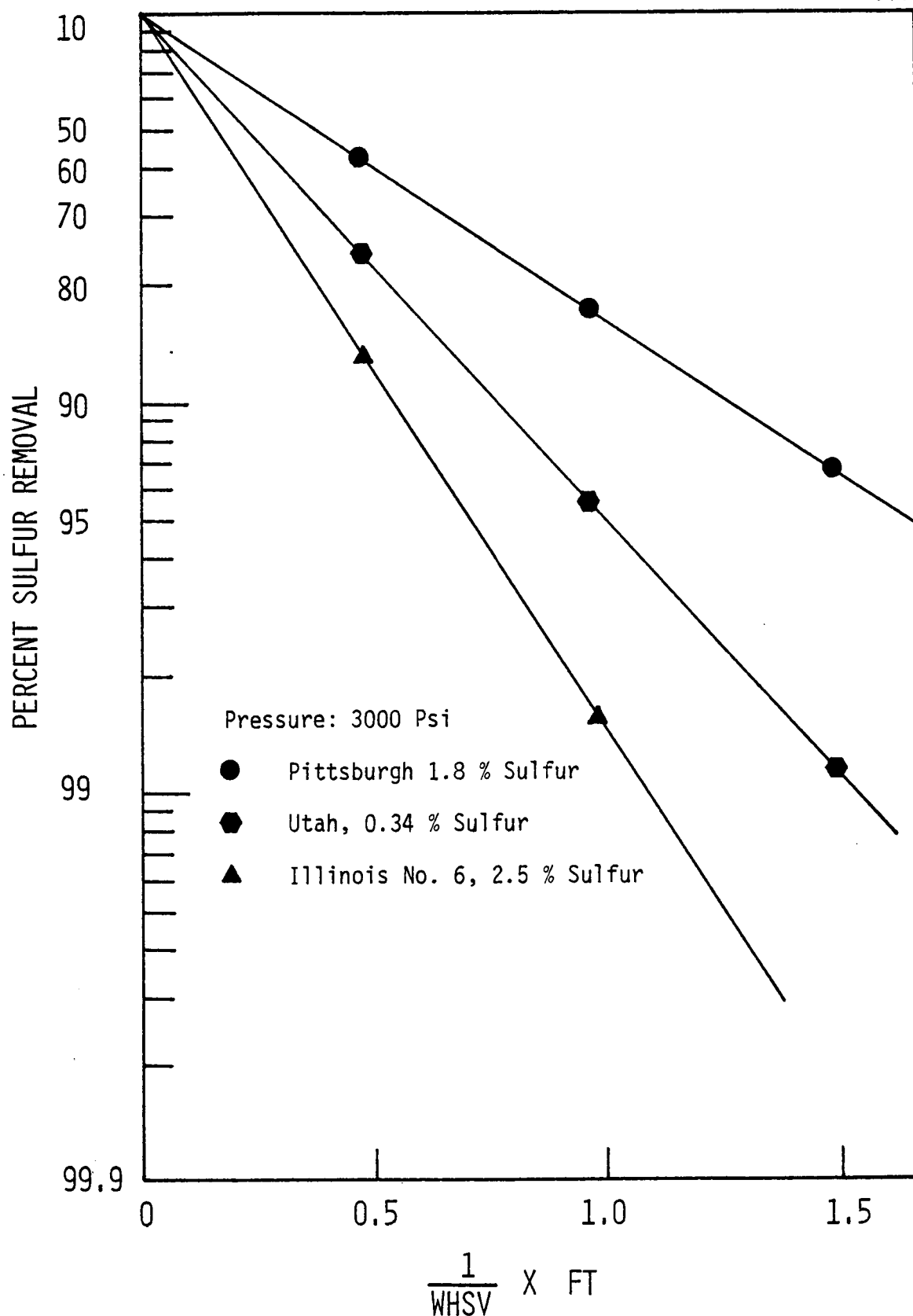


FIGURE 4.3.11 Hydrogenation of COED Coal Oils, Sulfur Removal (Jacobs, Harry, 1970)

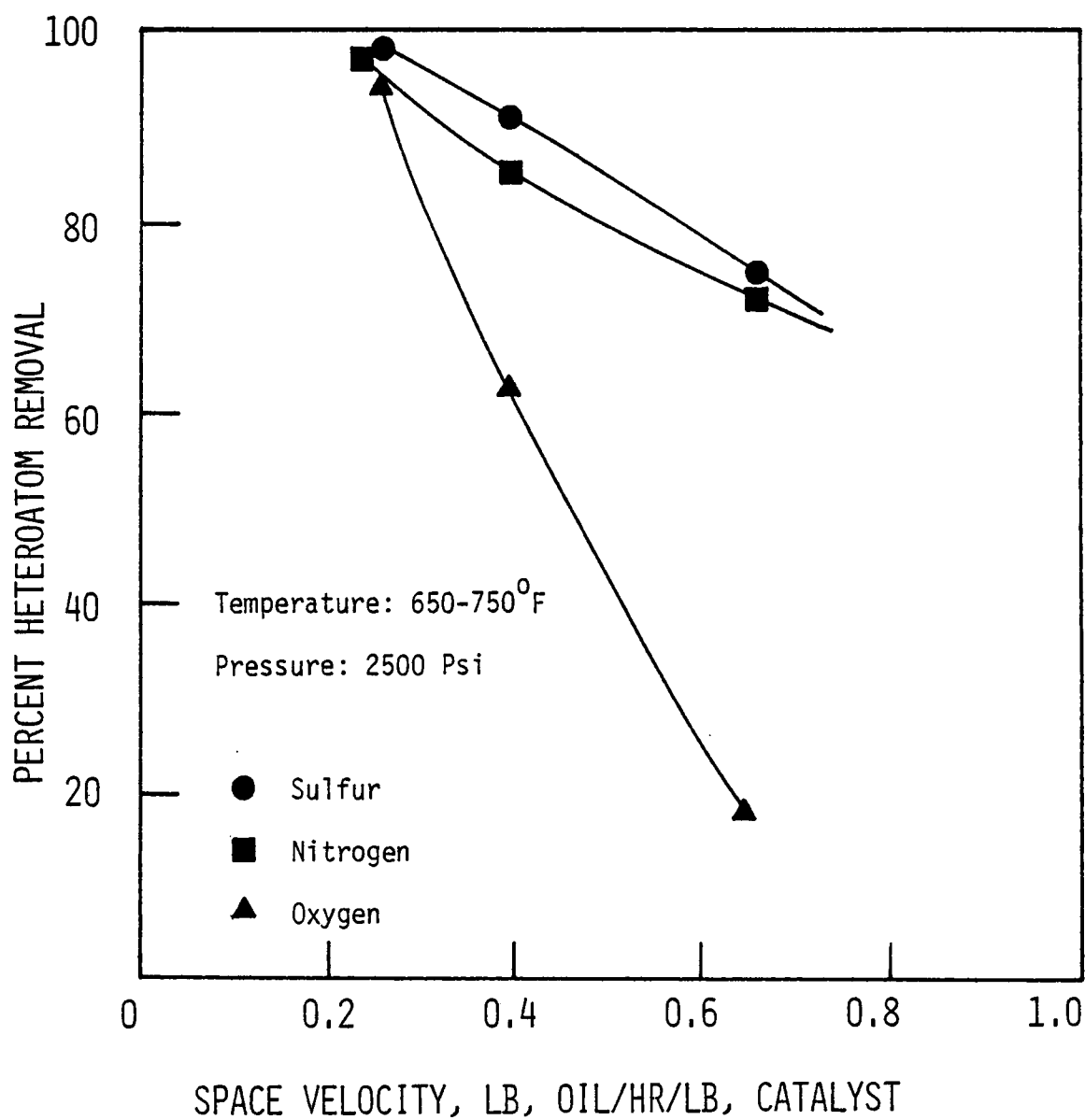


FIGURE 4.3.12 Space Velocity versus Heteroatom Removal for COED Oil (Johns, J.J. et al., 1972)

in Figure 4.3.13. The results, as expected, show increased sulfur and nitrogen removal with the increase in temperature.

Stein, T.R. et al. (1977) hydrotreated one H-coal fraction and three SRC fractions to obtain fuels of lower heteroatom content. A relationship between the amount of hydrogen required to produce fuels of varying nitrogen content for these four fractions is give in Figure 4.3.14. The H-coal distillate does not need very much hydrogen as it has already been hydroprocessed at the H-coal plant. The SRC light organic liquid is a very light fraction (naphtha-kerosene range, 100-500° F) and had a very little nitrogen (0.3 percent to start with.

This relationship between nitrogen content of the product and hydrogen consumed is somewhat dependent on operating conditions and catalyst. However the data show that for an 0.1 weight percent nitrogen in the fuel, the hydrogen consumption requirement is about 600 scf/bbl for H-coal distillate, 800 scf/bbl for SRC light organic liquid, 2000 scf/bbl for SRC recycle solvent, and 3000 scf/bbl for a 2/1 recycle solvent/SRC liquid.

4.3.2 Hydrogen Consumption

Stein, T.R. et al. hydrotreated SRC recycle solvent (300-830° F boiling range) over HDS-9A (Ni-Mo) catalyst in the range of 673-798° F temperature and 1200-1500 psi pressure. The total chemical hydrogen consumption ranged from 1065 to 3370 scf/bbl of charge. The breakdown of total hydrogen consumption for heteroatom removal, C₁-C₅ gas make, and C₆-plus liquid hydrogenation at each condition of operation

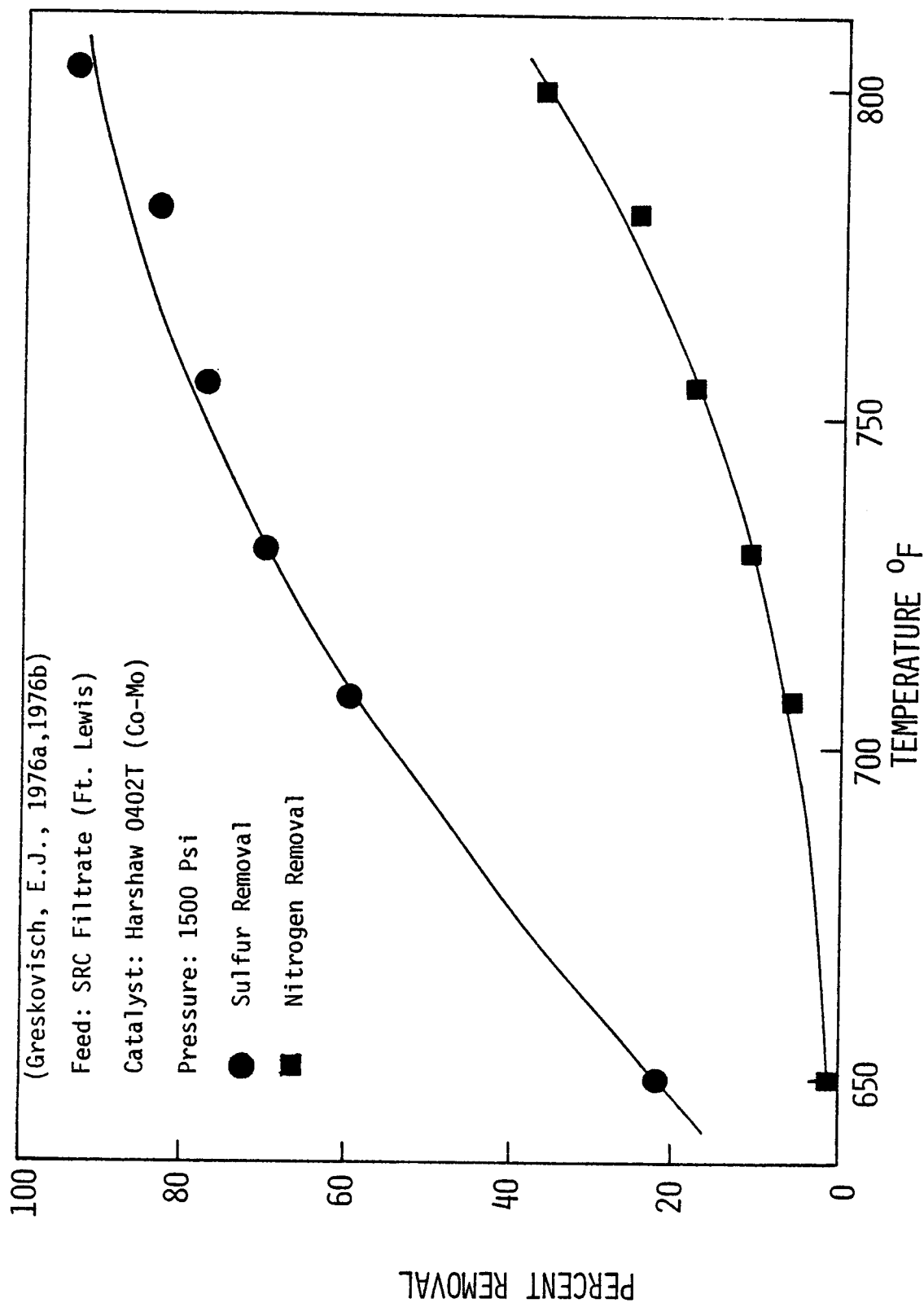


FIGURE 4.3.13 Sulfur and Nitrogen Removal as a Function of Temperature

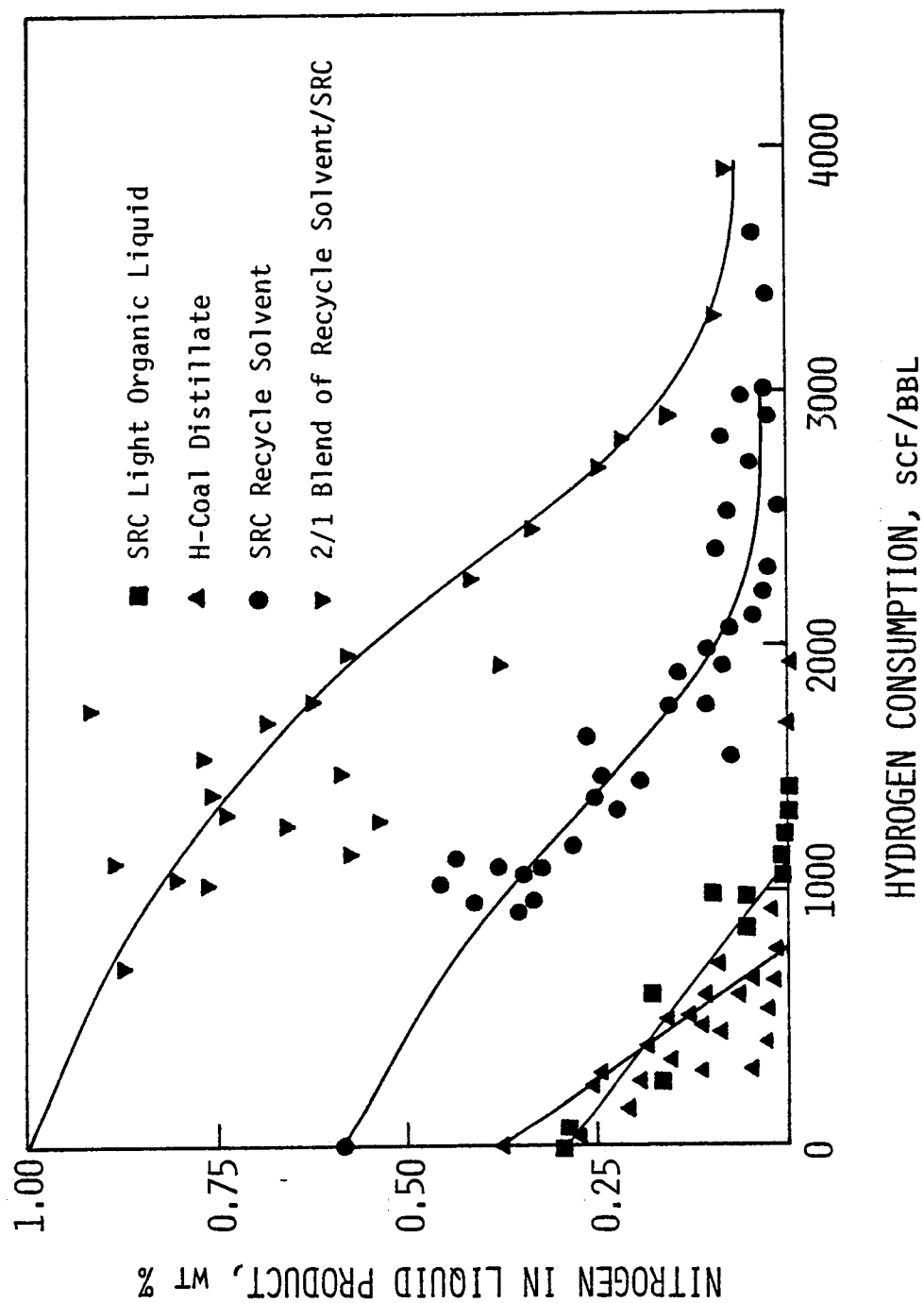


FIGURE 4.3.14 Chemical Hydrogen Consumption Required to Hydroprocess Coal Liquids to Fuels of Varying Nitrogen Content
(Stein, T.R. et al., 1977)

was calculated, and is plotted in Figure 4.3.15 as a function of total hydrogen consumption. From Figure 4.3.15 it is apparent that most of the consumed hydrogen goes into hydrogenation of the C_6 -plus material with lesser amounts into the heteroatom removal and gas make.

Figure 4.3.16 shows a more detailed breakdown of the hydrogen consumption for the production of H_2O , H_2S , and NH_3 as a function of the total hydrogen consumed. Oxygen consumes the greatest amount of hydrogen. Extrapolation back to zero heteroatom removal shows that the first 500-600 scf/bbl of hydrogen is consumed with very little removal of heteroatom

Stein, T.R. et al. (1977) hydroprocessed four different coal derived liquid fractions at different operating conditions. The range of hydrogen content of all the four coal derived liquids was from 6.84-11.33 percent by weight. Roughly 70 percent of the hydrogen consumed in the processing went into increasing the hydrogen content of the liquid product. Figure 4.3.17 gives the hydrogen content of the liquid product versus total hydrogen consumption for the coal liquids processed. The slope of the lines on this plot depends on the efficiency of adding hydrogen to the liquid product and the density of the charge. The higher density stocks would be expected to have a smaller slope than the lower density stocks.

The hydrogen consumption comes largely as a result of aromatic saturation. Figure 4.3.18 gives the percent aromatic carbon (percent C_A) as a function of hydrogen content of the hydroprocessed coal liquids. The data shows one curve for the H-Coal distillate and SRC recycle solvent. The light organic liquid data lie above this curve,

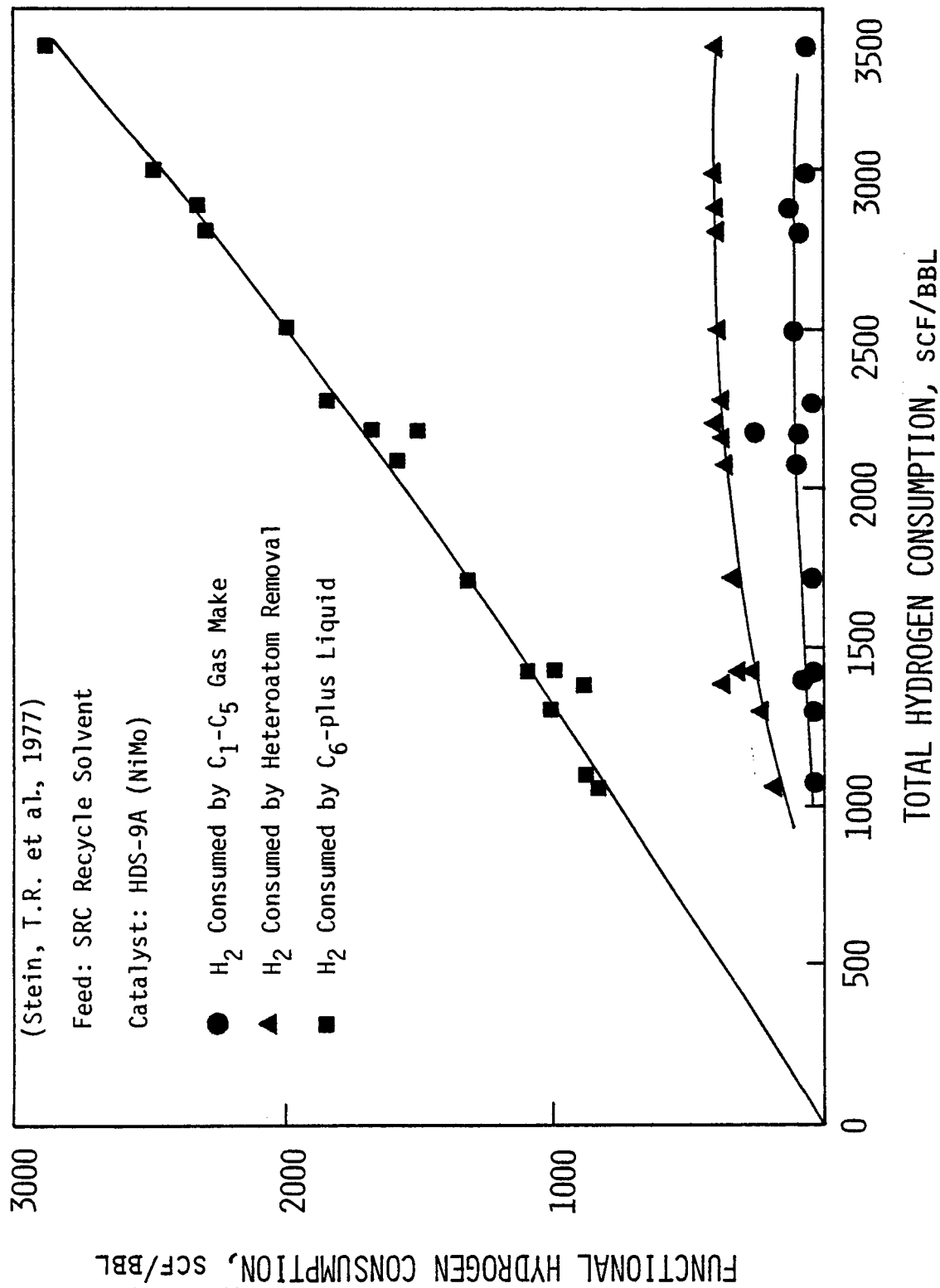


FIGURE 4.3.15 Hydrogen Utilization in Hydroprocessing of SRC Recycle Solvent

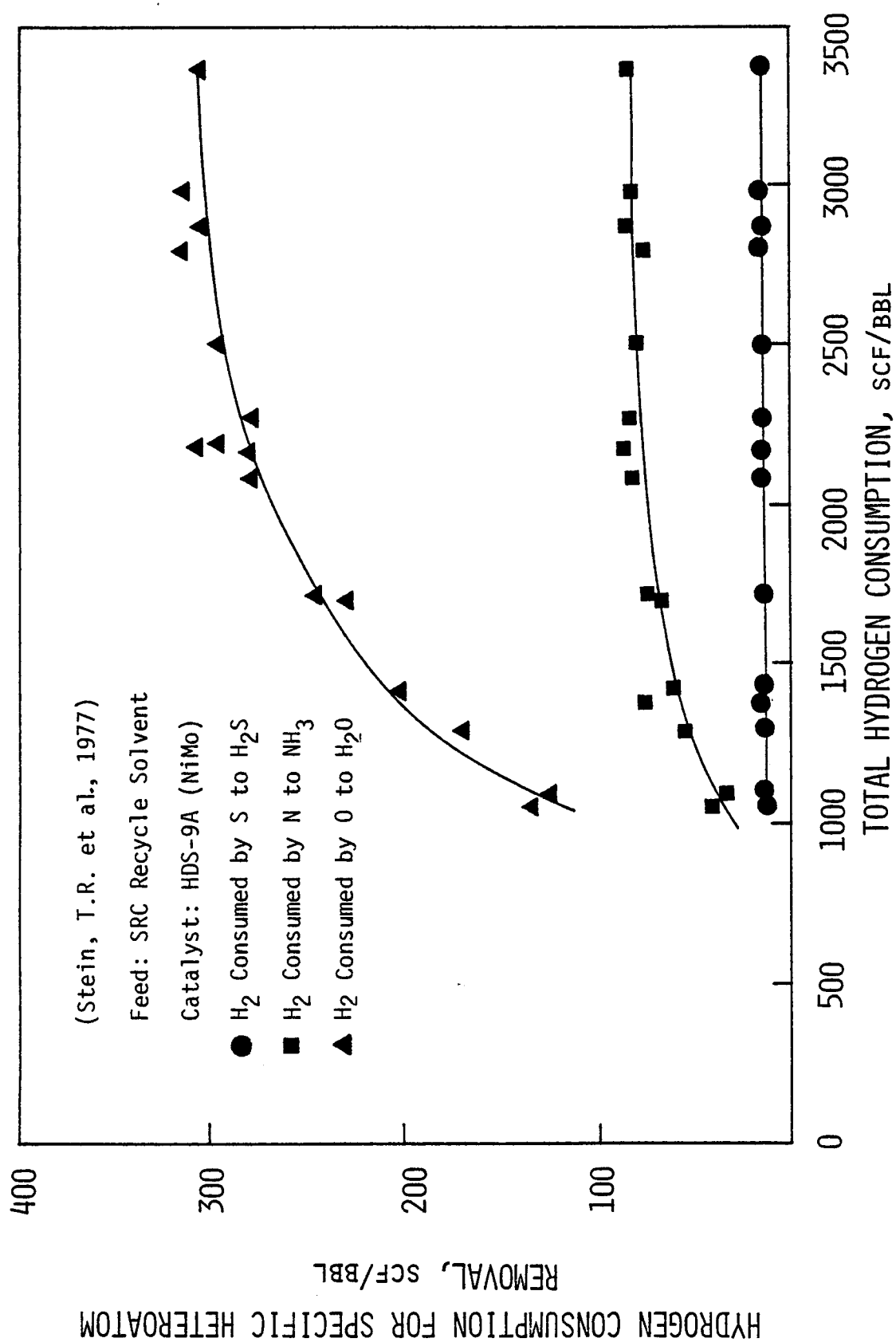


FIGURE 4.3.16 Hydrogen Consumption for Heteroatom Removal from SRC Recycle Solvent

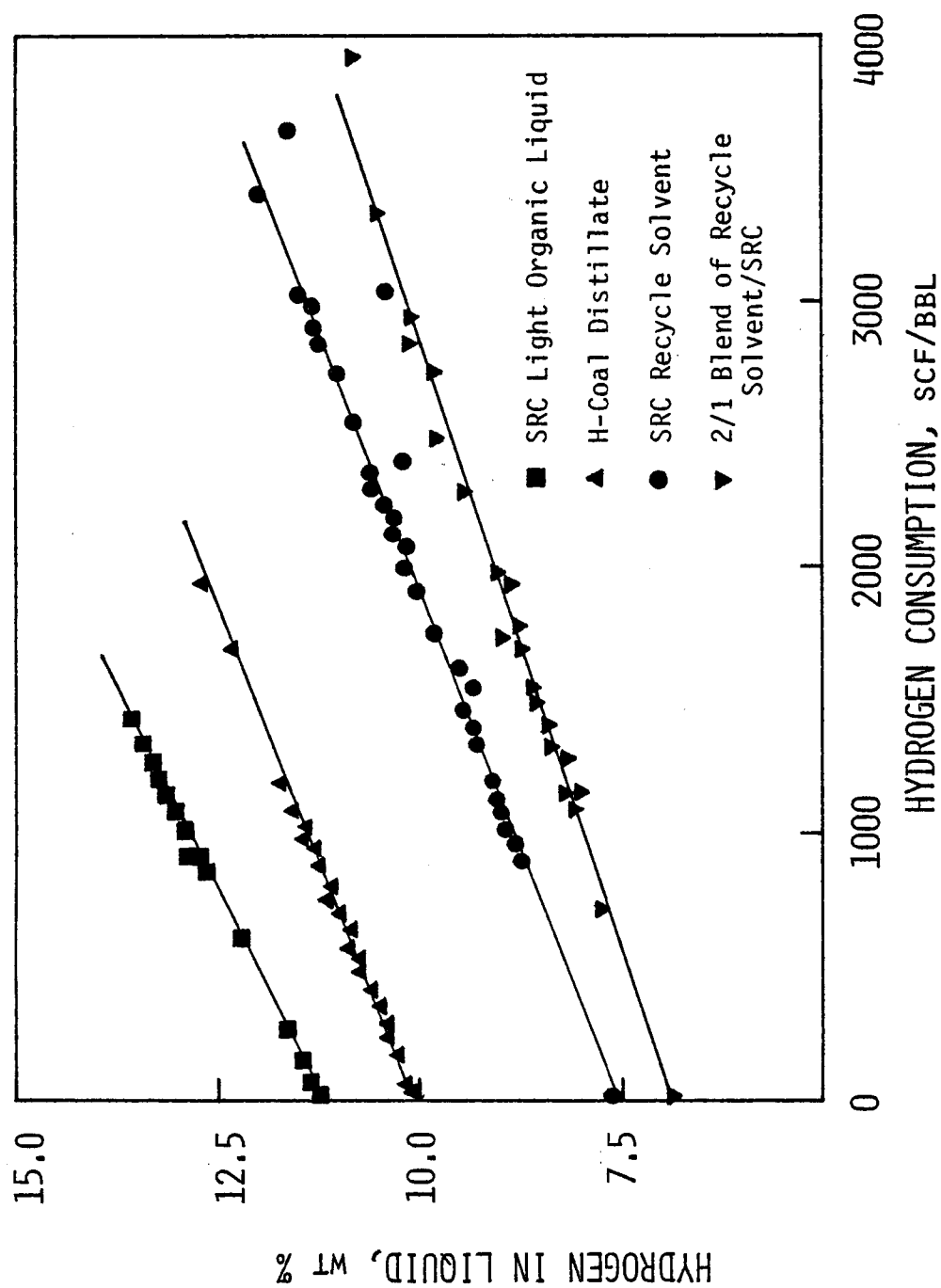


FIGURE 4.3.17 Chemical Hydrogen Consumption Required to Hydroprocess Coal Liquids to Fuels of Varying Hydrogen Content
(Stein, T.R. et al., 1977)

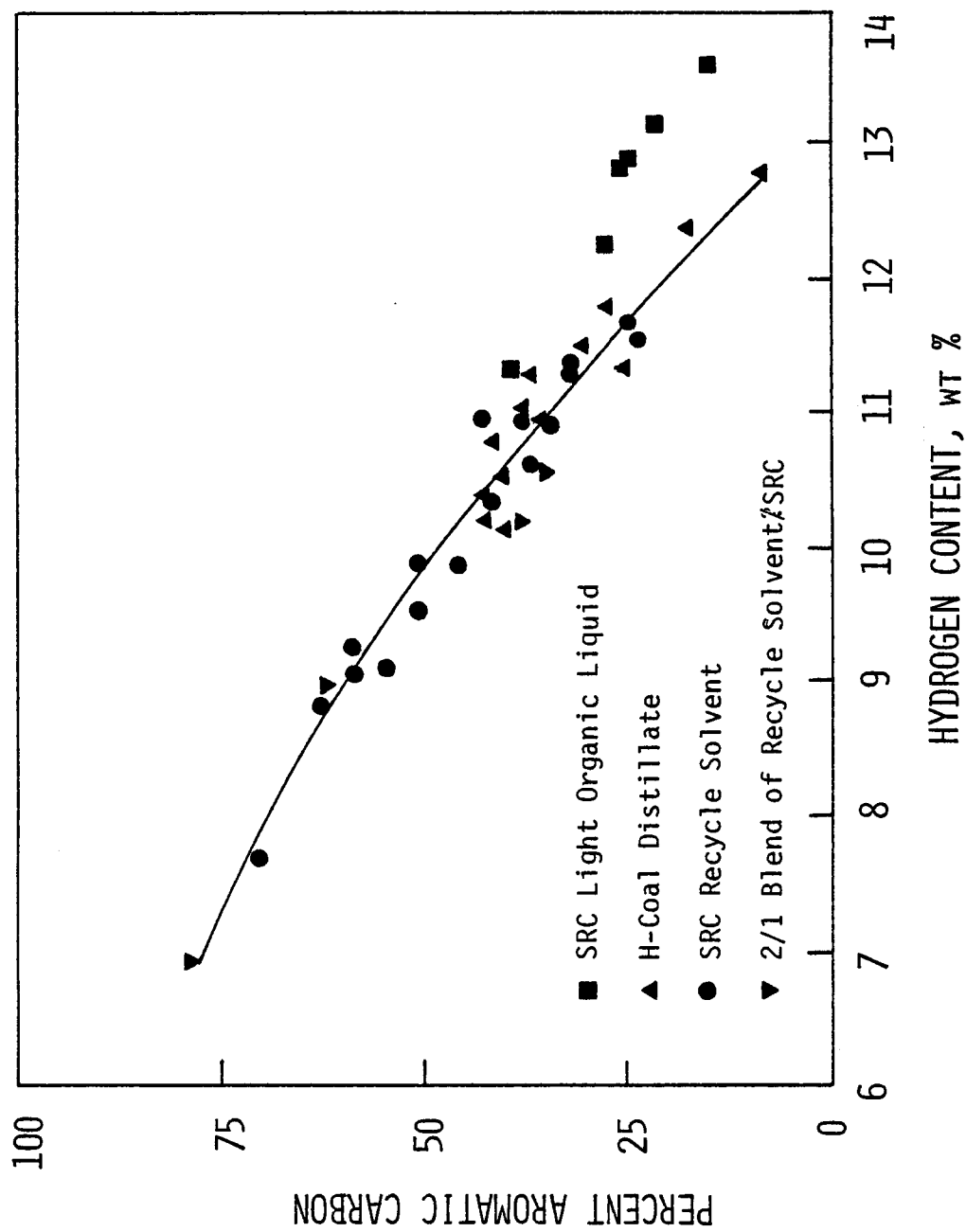


FIGURE 4.3.18 Percent Aromatic Carbon as a Function of Hydrogen Content for Hydroprocessed Coal Liquids
(Stein, T.R. et al., 1977)

indicating a higher percentage of aromatic carbon at the same hydrogen content, while the limited data on the 2/1 recycle solvent/SRC blend lie below the curve.

A comparison of hydrogen consumption for hydrotreating different coal liquid naphtha fractions to that of petroleum naphthas is presented by Econergy Associates (1980) in their report (Figure 4.3.19). The data presented for coal liquids is actual data obtained from several reports for hydrotreating several different coal derived liquid naphthas. Because of the confidential nature of the reports the actual data was unavailable. The curve for petroleum naphthas was calculated from procedures described for petroleum stock by Nelson (1973).

4.3.3 Catalyst Deactivation

Catalyst deactivation has been reported by several researchers, but the catalyst life estimates and the factors for catalyst poisoning have been searched by very few researchers.

Crynes, B.L. (1975a, 1975b) reported an increase in nitrogen content of the product as a measure of catalyst deactivation with respect to time (Figure 4.3.20). The FMC oil used as feed stock had 1.13 percent by weight nitrogen, and was hydrotreated at 700° F, 1500 psi and 2.99 hour space time. The catalyst used (Nalco 474-Sphercat) had CoO (3.5 percent) and MoO₃ (12.5 percent) on alumina.

Figure 4.3.20 reveals appreciable denitrogenation activity decay over the 150 hours of operation. From 60 percent nitrogen removal initially the denitrogenation activity of the catalyst dropped to 40 percent nitrogen removal.

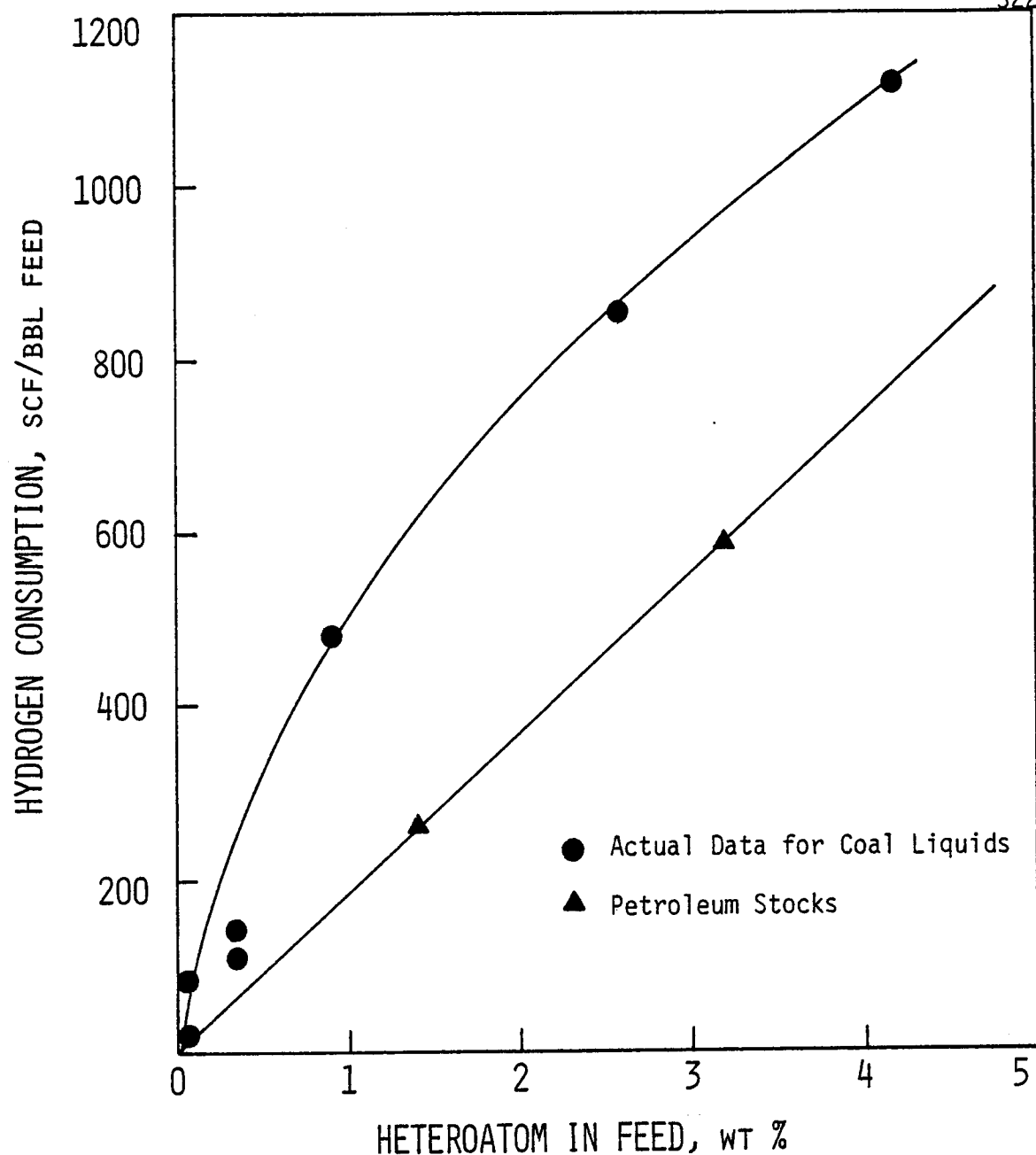


FIGURE 4.3.19 Naphtha Hydrotreating, Hydrogen Requirement versus Heteroatom in Feed

(Econergy Associates, 1980)

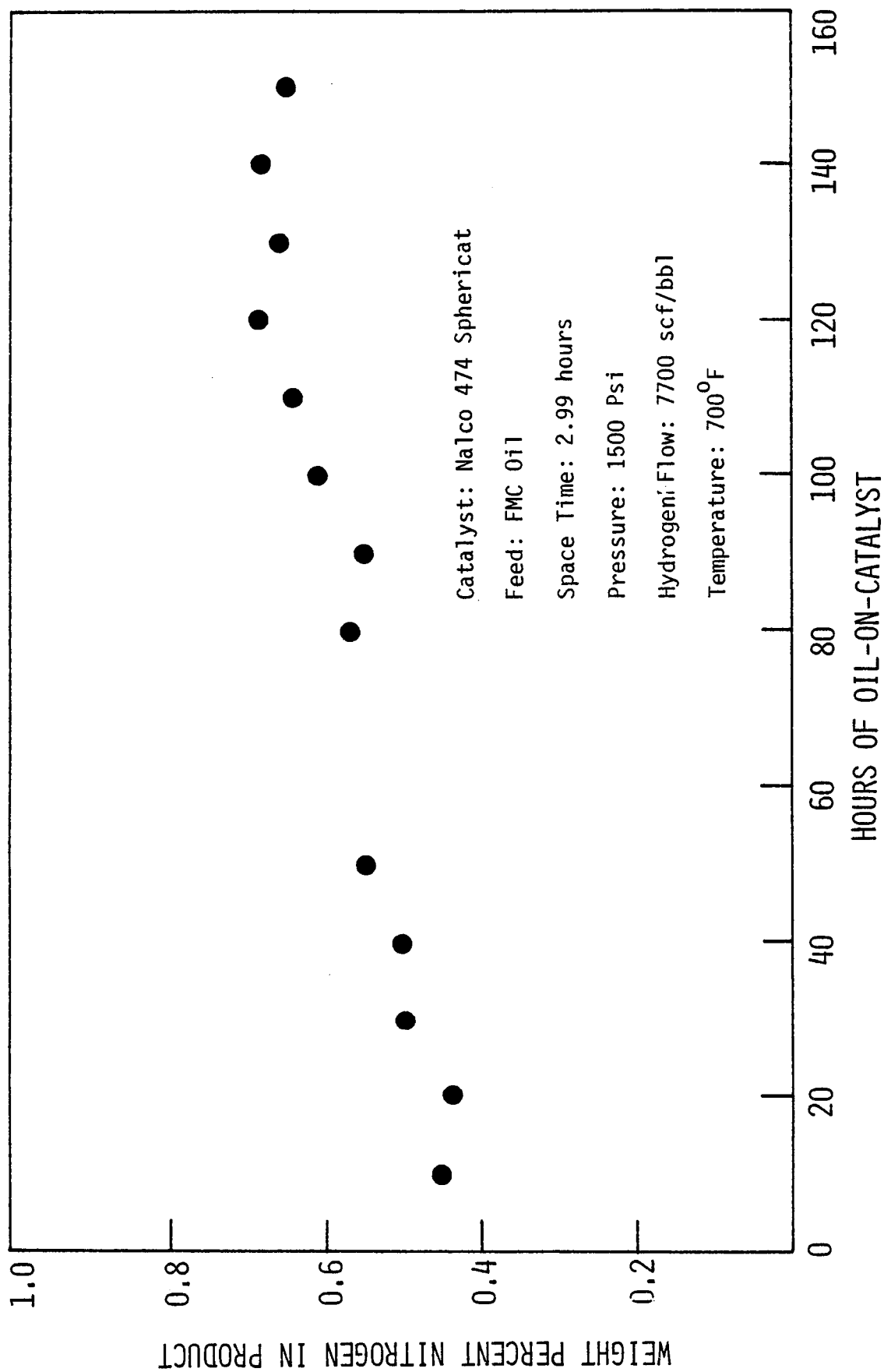


FIGURE 4.3.20 Catalyst Activity Decay for COED Oil (Crynes, B.L., 1975a, 1975b)

Potts, J.D. et al. (1977a, 1977b, 1978a, 1978b) hydrocracked SRC-1 and KC-oil in an expanded bed hydroprocessing unit using Shell-324 (Ni-Mo) catalyst. For catalyst activity decay test a mixture of KC-Oil and SRC-1 was fed for 12 hours during which time sufficient product was accumulated to provide a recycle solvent. The product from once-through operation was topped to 500° F, and the 500° F-plus bottoms were analyzed for unconverted 850° F-plus material. Additional fresh SRC-1 was added to the 500° F-plus bottoms to provide a 50/50 SRC-1/solvent feed blend for recycle. Thus the 850° F-plus fraction of the feed blend recycled contained both fresh and unconverted 850° F-plus material. This procedure was repeated for subsequent recycle passes. The conversion showed a decline trend with time through successive passes as can be seen in Figure 4.3.21. After 38 hours, the feed blend was returned to 50/50 fresh SRC-1/KC-oil mixture and the conversion returned to the normal level. This behavior shows that the catalytic activity of the Ni-Mo catalyst had not decreased by once-through processing over the same elapsed time. It also inferred that the decline in conversion was probably due to the build up of a material in the unconverted 850° F-plus fraction which was increasingly difficult to convert.

The catalyst deactivation in terms of percent sulfur removal was reported by Wan and Crynes (1972) for hydrocracking raw anthracene oil. The feed stock used contained 0.45 percent sulfur. The fixed bed reactor used for testing was operating at a pressure of 1000 psi, and at a temperature of 700° F with liquid hourly space time of 1 hour. The two catalyst tested were Nalcomo 474 and Sphercat 474 and both had

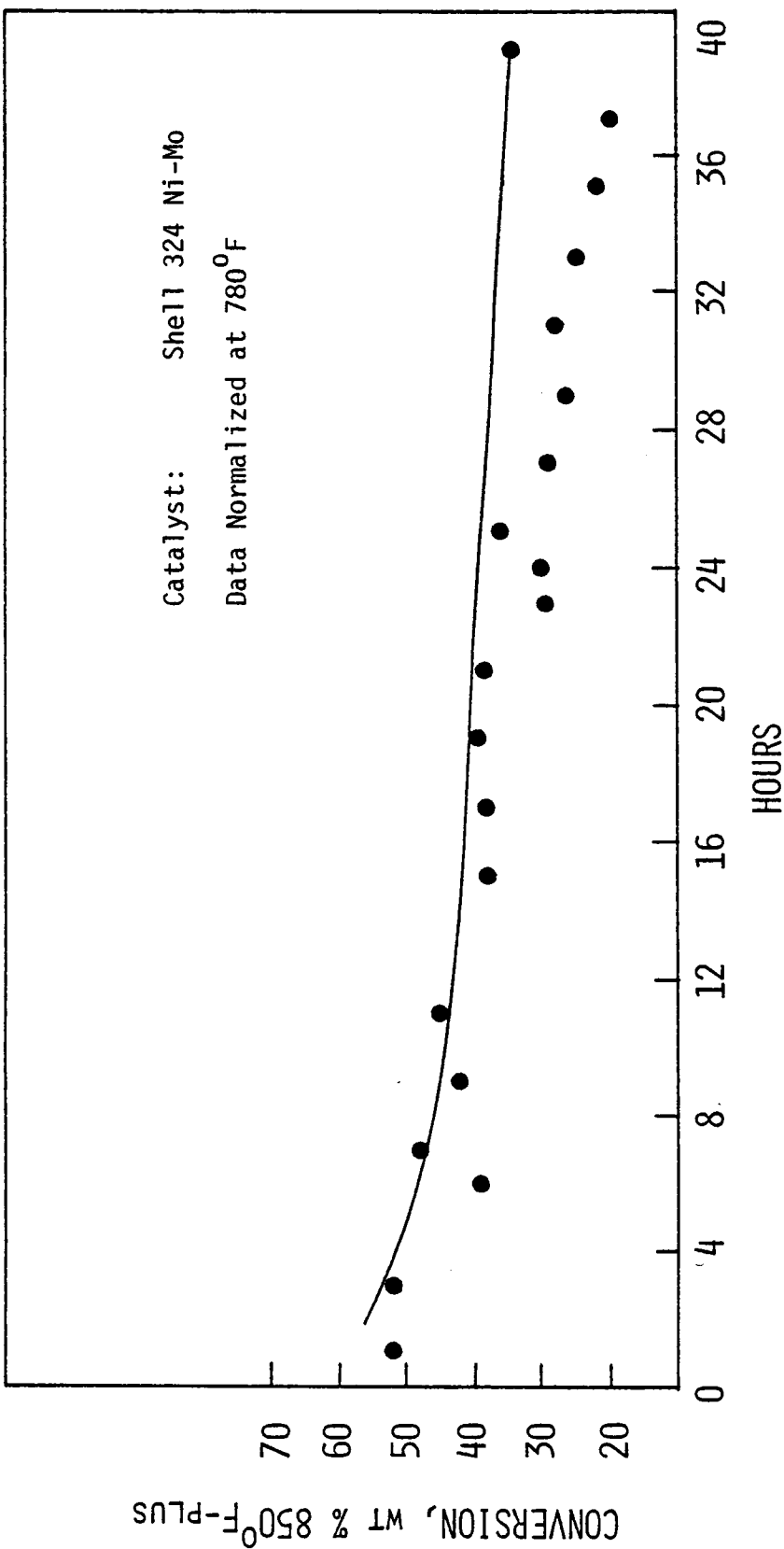


FIGURE 4.3.21 Conversion of 850°F-plus in Heavy Oil

(Potts, J.D. et al., 1977a,1977b,
1978a,1978b)

3.5 percent cobalt oxide and 12.5 percent molybdenum oxide on alumina. The difference between these two catalysts was in the pore volume. Pore volume for Nalco 474 was 12.82 cubic in/lb while for Sphercat 474 was 27.17 cubic in/lb. Figure 4.3.22 shows that there was a negligible loss of catalyst activity during the 50 hours of oil-catalyst contact. The desulfurization activity of Nalco catalyst achieved a level of about 92 percent sulfur removal after 10 hours on oil, and remained relatively steady between 88 to 90 percent over 50 hours. The Sphercat 474 showed almost identical desulfurization characteristics from ten through 42 hours on oil.

Crynes, B.L. (1975a, 1975b, 1976c, 1977c) hydrotreated anthracene oil using Co-Mo catalyst. The anthracene oil tested had 0.47 percent sulfur and 1.06 percent nitrogen. Figure 4.3.23 presents the percent removal of sulfur and nitrogen in the product samples as a function of oil-catalyst contact. The entire data set was obtained within one start up and continuous operation of 115 hours. This history plot reveals the catalyst and equipment response as operational conditions are varied throughout the run. After catalyst lineout during the first 50 hours at 650° F, 100 psi and 0.82 hours space time, the run conditions were assessed to determine catalyst deactivation. Over the interval from 50 to 115 hours, no measurable decay, in catalyst activity to remove sulfur, was noted.

Crynes, B.L. (1977d) also hydrotreated rasyn oil, which is mixture of equal volumes of raw anthracene oil and Synthoil II. A catalyst activity decay test was run in trickle bed reactor using

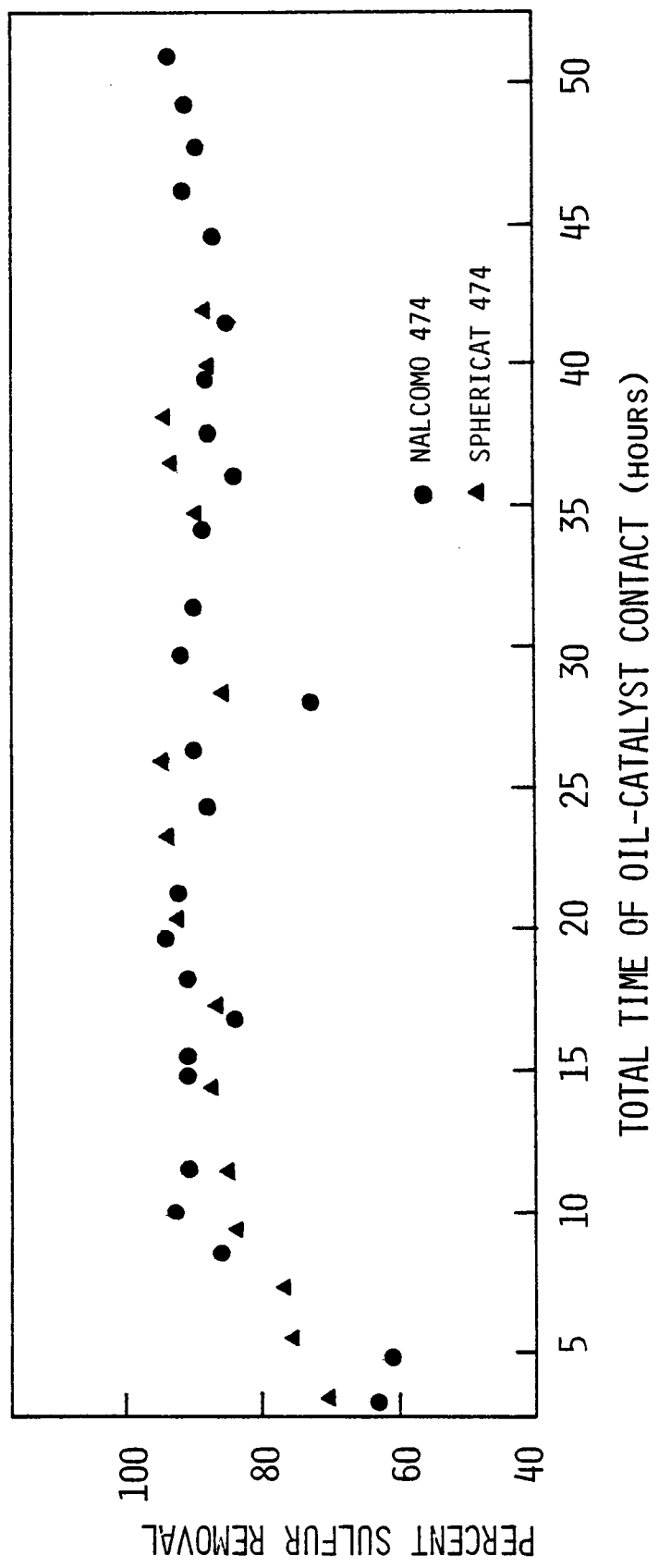


FIGURE 4.3.22 Sulfur Removal as a Function of Catalyst Age
(Wan, K.T. and Crynes, B.L., 1972)

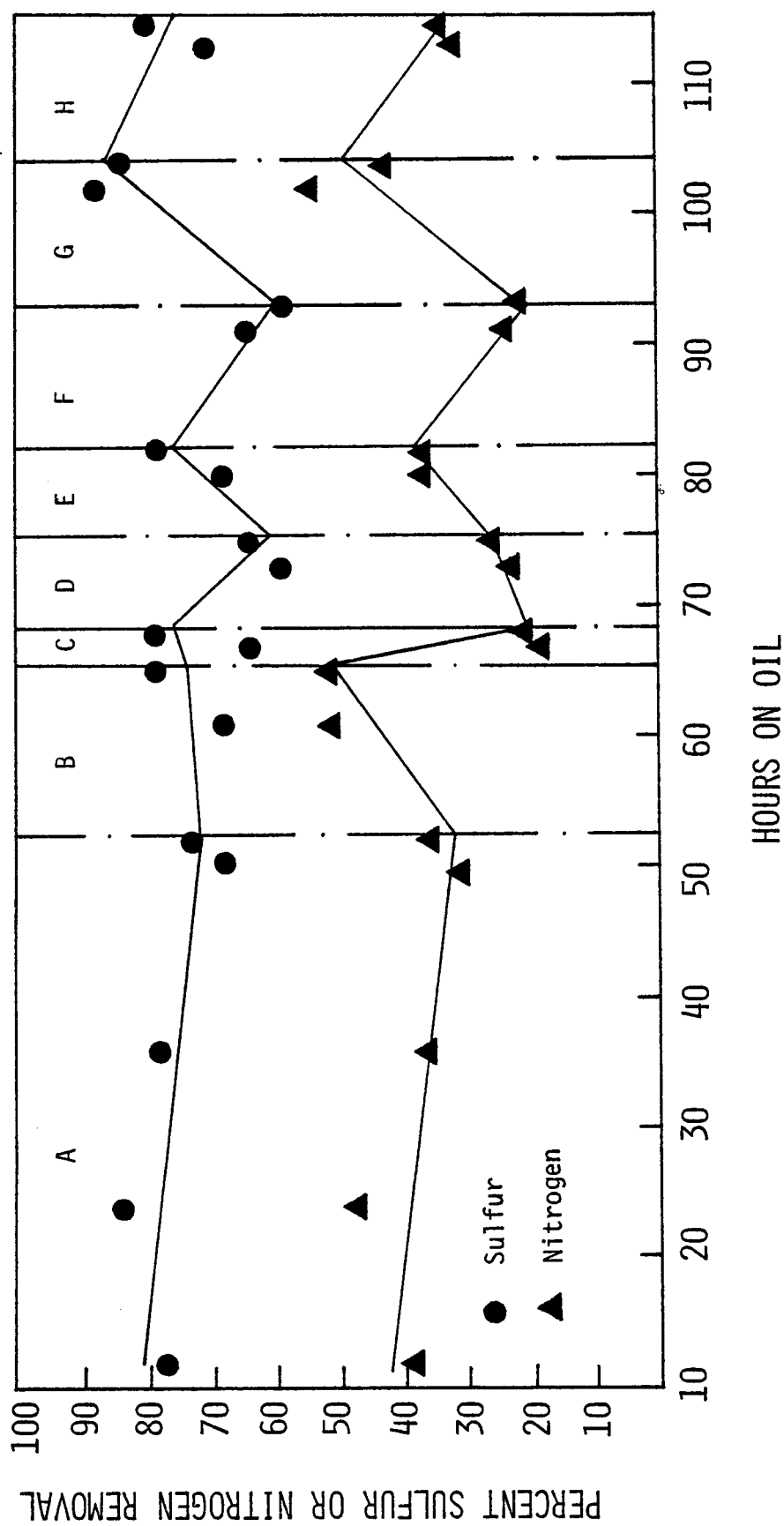


FIGURE 4.3.23 Run History of Anthracene Oil

(Crynes, B.L., 1975a, 1975b,
1976a, 1976b, 1976c)

Feed: Anthracene Oil

Catalyst: Norton SA6175
3.5% CoO, 12.5% MoO₃

Pressure: 500, 1000, 1500 Psi

Temperature: 600, 650, 700°F

	A	B	C	D	E	F	G	H
Temperature °F	650	600	650	650	650	600	700	650
Pressure, Psi	1000	1000	1000	500	1500	1000	1000	1000
Volume Hourly Space Time, hr	0.82	1.63	0.41	0.82	0.82	0.82	0.82	0.82

FIGURE 4.3.23 (cont)

Nalco NM-502 (14.0 percent MoO_3 , 2.8 percent NiO , 1.5 percent SiO_2 over alumina). At 700° F, 1500 psi and 1.25 hour volume hourly space time, the sulfur and nitrogen in the product oil samples seems to increase after 400 hours, as shown in Figure 4.3.24.

4.4 KINETIC MODEL

A simple kinetic model relating the properties of the hydroprocessed coal liquids to the charge stock composition and the hydroprocessing conditions is developed by Stein (1977) based on the research data by Stein (1977) for H-coal and SRC liquid hydrotreating to turbine fuels (for the properties of feed, composition of catalyst, and operating variables refer to sections 3.2.4 and 3.4.8).

This model can be used to predict processing conditions in economic scoping studies for developing costs to upgrade various coal liquids to projected turbine fuel specifications. This model relates processing condition to product yields, quality, and hydrogen consumption. The principle quality parameters for coal distillates are the oxygen, nitrogen, sulfur, and hydrogen content.

4.4.1 Heteroatom Removal

Both a first and second order rate expression in terms of heteroatom concentration were investigated. The second order rate expression gave a better fit to the data over the range of operating

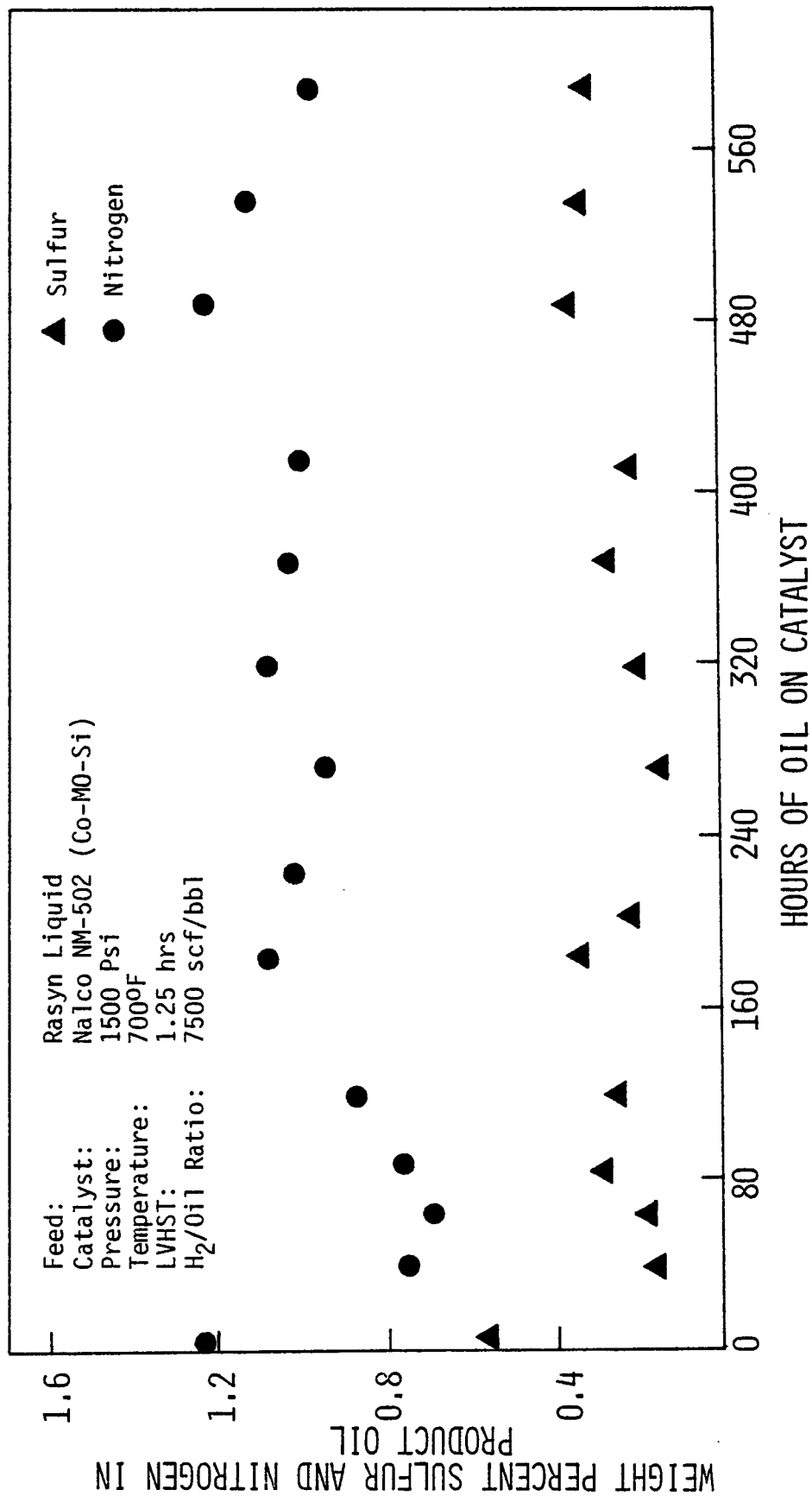


FIGURE 4.3.24 Catalyst Hydrodesulfurization and Hydrodenitrogenation Activity Decay

(Crynes, B.L., 1977d)

conditions. This higher than first order dependence is a necessary result of the lumping of heteroatom compounds of different reactivities (Beuther et al., 1963). This phenomenon is also observed when modelling heteroatom removal from petroleum streams. The second order rate equation used to model all heteroatom removal rates was

$$-\frac{dC_i}{dt} = k_i \exp(-E_i/RT) C_i^2 P^N \quad \dots 1$$

This equation assumes an Arrhenius temperature dependence and an Nth order pressure dependence. Integrating equation 1 gives the following expression for heteroatom conversion

$$F_i = \frac{K_i}{1 + K_i} \quad \dots 2$$

$$\text{where } F_i = \text{fractional conversion} = 1 - \frac{C_i}{C_i^0} \quad \dots 3$$

$$K_i = \frac{C_i^0 k_i \exp(-E_i/RT) P^N}{LHSV} \quad \dots 4$$

The kinetic constants in Equation 2 were determined using a modified Marquardt fitting routine. These constants along with the average deviation of the model from the data are given in Table 4.4.1 for the H-coal distillate and Table 4.4.2 for the SRC recycle solvent.

The sulfur data were obtained over a limited range of conversion and the sulfur concentration in the product was low (less than .05 weight percent). Therefore, the kinetic constants for sulfur are probably less reliable than those for nitrogen or oxygen.

The activation energies are in the range of 56,750-68,550 Btu/lb-mole for nitrogen and oxygen removal for both catalysts and both charge stocks with the activation energy for denitrogenation slightly lower in each case. The activation energies for sulfur removal are 28,380-55,830 Btu/lb mole and are in general smaller than for the other heteroatoms. The reaction rate depends on the 0.7-1.5 power of the total pressure with most of the values falling very close to 1.0.

The relative activity of the catalysts and charge stocks for heteroatom removal can be compared by evaluating the fraction of sulfur, nitrogen, and oxygen converted from the two charge stocks at a given reactor condition. This is shown in Table 4.4.3 for a reactor pressure of 2000 psi, temperature of 725⁰F, and a liquid hourly space velocity (LHSV) of 1.0.

The removal of sulfur at the conditions prescribed in Table 4.4.3 is 96-97 percent for both stocks and both catalysts. The percent removal of oxygen and nitrogen is lower than that of sulfur. Oxygen removal is higher than nitrogen removal for both stocks over CoMo/Al₂O₃

Table 4.4.1 Kinetic Constants from Reaction Model
 H-Coal Distillate
 Catalyst - HDS-1441A (CoMo/Al₂O₃)

	k_i	E_i Btu/lb Mole	N	Mean Deviation
Sulfur	8.52E7	45,630	0.84	0.008
Nitrogen	1.90E7	56,750	1.30	0.18
Oxygen	6.00E7	64,030	1.49	0.074

Source: Stein, T.R. et al., 1977

Table 4.4.2 Kinetic Constants from Reaction Model SRC Recycle Solvent

Catalyst - HDS-1441A (CoMo/Al ₂ O ₃)				
	k _i	E _i Btu/lb ¹ Mole	N	Mean Deviation
Sulfur	1.25E9	55,830	0.96	0.007
Nitrogen	1.23E9	63,980	1.04	0.033
Oxygen	2.63E10	68,550	0.71	0.091
Catalyst - HDS-9A (NiMo/Al ₂ O ₃)				
Sulfur	3.76E2	28,380	1.36	0.005
Nitrogen	3.58E9	64,150	0.96	0.024
Oxygen	2.46E9	65,840	0.85	0.086

Source: Stein, T.R. et al., 1977

Table 4.4.3 Fraction of Sulfur, Nitrogen and Oxygen Converted from H-Coal Distillate and SRC Recycle Solvent at 2000 psi, 725°F, 1.0 LHSV Using HDS-1441A and HDS-9A Catalysts

		H-Coal Distillate	SRC Recycle Solvent
Catalyst		HDS-1441A	HDS-1441A HDS-9A
Fraction Converted			
Sulfur	0.96	0.97	0.97
Nitrogen	0.83	0.77	0.83
Oxygen	0.90	0.83	0.81

Source: Stein, T.R. et al., 1977

(HDS-1441A), while nitrogen removal is slightly higher than oxygen removal on NiMo/Al₂O₃ (HDS-9A).

4.4.2 Dry Gas Production

In the hydroprocessing of coal liquids to liquid turbine fuels, the dry gas (C₁-C₃) make is a byproduct which contains large amounts of hydrogen relative to the liquid product. The amount of the C₁-C₃ gas make can be minimized in a hydrotreating operation by the proper choice of catalyst and operating conditions to limit the amount of cracking. The yield of C₁-C₃ gas for the hydroprocessing of H-Coal distillate and SRC recycle solvent varied from 0-2 weight percent on charge.

The production of dry gas was found to fit the zero order kinetic expression:

$$\frac{dC}{dt} = k e^{-E/RT} \quad \dots 5$$

where C = C₁-C₃ yield, weight percent

k = rate constant, per hour

E = activation energy, Btu/lb mole

The rate constants listed in Table 4.4.4 were determined using a modified Marquardt fitting routine.

The model predicts a higher gas yield with increasing residence

Table 4.4.4 Constants for Kinetic Model of Dry Gas Production

	k, HR ⁻¹	E, Btu/lb mole	Mean Deviation wt %
H-Coal (HDS-1441A)	1.04×10^{10}	57,610	0.20
SRC Recycle Solvent (HDS-9A)	3.20×10^{11}	66,220	0.12

Source: Stein, T.R. et al., 1977

time (i.e., lower LHSV) and increasing temperature. An Nth order pressure dependence term was also evaluated in the rate Equation 5. The fit of the data was found to be approximately zeroth order in pressure so no pressure dependence is included in the final rate expression.

4.4.3 Aromatics

Aromatic saturation is important in hydroprocessing of coal liquids as that most of the hydrogen consumed goes into the liquid product. This increase in hydrogen content is reflected in a less aromatic product compared to the charge.

The aromaticity of the H-Coal distillate and SRC recycle solvent are defined as the percentage of aromatic carbon (percent C_A). The aromatic saturation model assumes the following simple reaction scheme:



where f_A = percent $C_A/100$ is the fraction of the carbon atoms which are aromatic. The rate expression for this reversible reaction is

$$\frac{df_A}{dt} = -k_f f_A p^N + k_r (1-f_A) \quad \dots 7$$

This expression assumes that the rate of conversion of aromatic carbon atoms is first order in aromatic carbon concentration and Nth order in pressure. The back reaction is assumed first order in non-aromatic carbon concentration. Integrating, and substituting $(1/LHSV)$ for t yields,

$$f_A = \frac{k_r}{k_r + k_f p^N} + \left[f_0 - \frac{k_r}{k_r + k_f p^N} \right] \exp \left[- \frac{(k_f p^N + k_r)}{LHSV} \right] \dots 8$$

where f_0 is the fraction of aromatic carbons in the charge. For $K_r=0$ this equation reduces to the simple first order rate expression

$$f_A = f_0 \exp \left(\frac{-k}{LHSV} \right) \dots 9$$

where $k = k_f p^N$

The rate constants are assumed to follow an Arrhenius equation.

$$k_f = k_{f_0} \exp \left(\frac{-E_f}{RT} \right) \dots 10$$

$$k_r = k_{r_0} \exp \left(\frac{-E_r}{RT} \right) \dots 11$$

The difference between the activation energies of the forward and reverse reaction is equal to the heat of reaction, ΔH . The value of ΔH is on the order of 27,920 Btu/lb mole of hydrogen consumed for 2-4 ring aromatics (Jaffe, 1974). Thus

$$E_r = E_f + \Delta H = E_f + 27,920 \quad \dots 12$$

Using this value for H , there are four unknowns in Equation 8: k_f , k_r , E_f and N . With this number of constants to fit, a large number of data points are required to cover the temperature, pressure and space velocity range used in the hydroprocessing runs. The model was fit to all the data from hydroprocessing runs using HDS-1441A, a CoMo on alumina catalyst. Since the H-Coal distillate and SRC recycle solvent are approximately the same boiling range they were modelled together, changing only the fraction of aromatic carbons in the charge. Figure 4.4.1 shows the least squares fit of the experimentally determined percent C_A as a function of the hydrogen content for the H-Coal distillate and SRC recycle solvent, it was obtained at pressures from 800-2500 psi, temperatures from 670-793⁰F, and space velocities from 0.32-4.09 per hour. This correlation was then used to calculate percent C_A of some of the runs based on the hydrogen to check the model for accuracy.

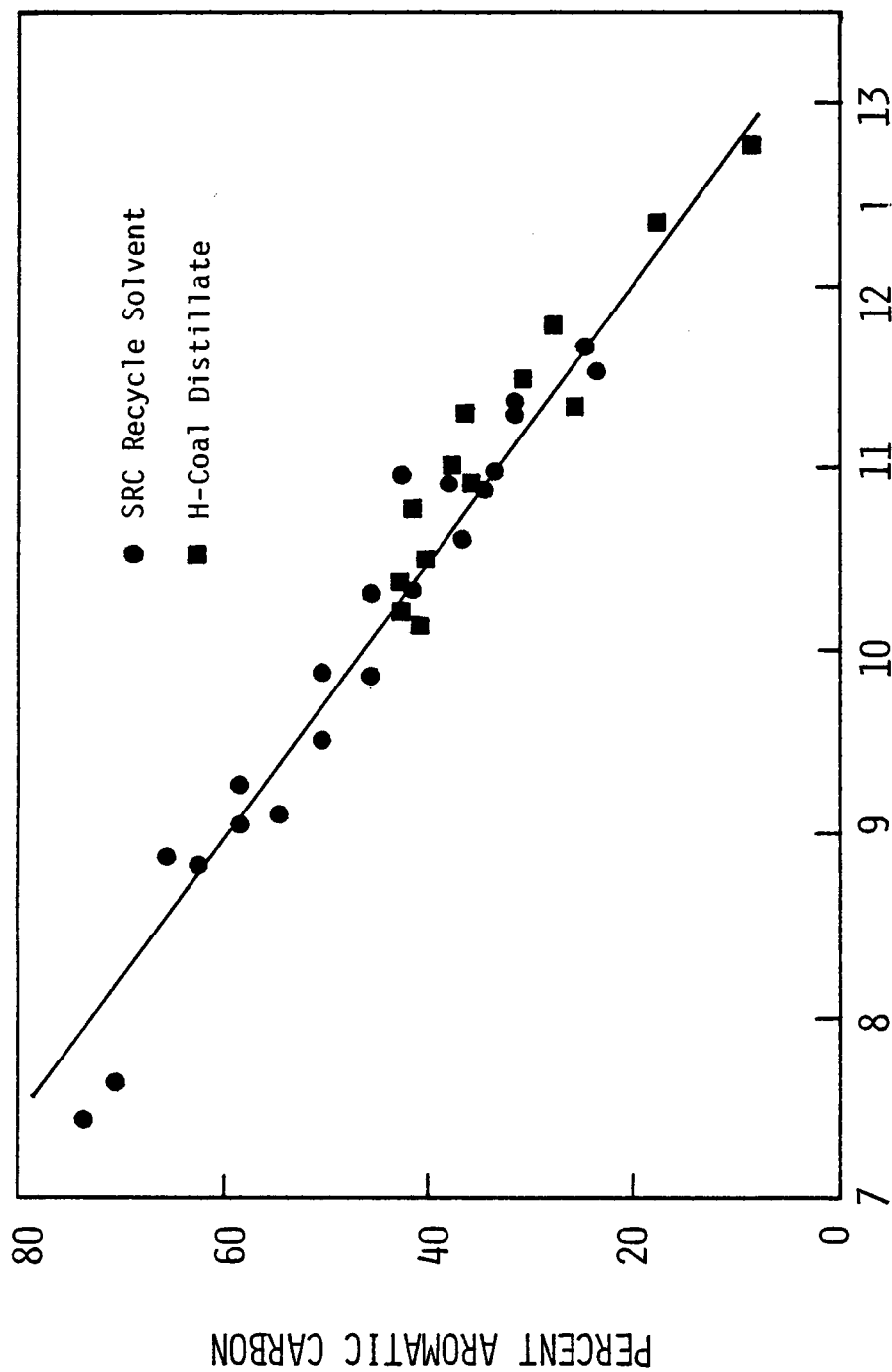


FIGURE 4.4.1 Aromatic Carbon Content as a Function of Hydrogen Content for H-Coal Distillate and SRC Recycle Solvent

(Stein, T.R. et al., 1977)

4.4.3.1 Fit of Model to Data

The integrated rate equation was fit to the data using the modified Marquardt routine to determine the constants which minimize the average error. The difference in the activation energies was fixed, leaving four constants to be determined. The numerical value of these constants together with the standard deviation (σ) are given in Table 4.4.5.

The fit of the data to the model is given in Figure 4.4.2. The model gives an excellent fit of the data (standard deviation = 2.9 percent C_A) over a range of aromatic carbon contents of 20-65 percent. Using the model one can predict the aromatic content and hence the hydrogen content for these two stocks over this catalyst at a wide range of processing conditions. The equilibrium aromatic saturation can also be determined at any temperature and pressure.

4.4.3.2 Predicted Percent C_A

Figure 4.4.3 shows the predicted dependence of aromatic content on temperature for three different pressures at 1.0 LHSV with SRC recycle solvent. The figure shows that the percent C_A decreases monotonically with temperature; however, at high temperatures (greater than 750°F) there is very little increase in saturation with increasing temperature. This figure also shows that at this LHSV, high pressure operation is necessary to achieve a significant decrease in the percent C_A .

Figure 4.4.4 shows the predicted effect of temperature on aromatic carbon content for a number of LHSV's at 1500 psig. At LHSV's below about 1.0, there is a minimum in the curve indicating that increased

Table 4.4.5 Kinetic Constants for Aromatic Saturation Model

$$K_{f_o} = 2.31 \times 10^{-4} \text{ hr}^{-1} \text{ PSIA}^{-N}$$

$$K_{r_o} = 9.26 \times 10^{-2} \text{ hr}^{-1}$$

$$E_f = 49,320 \text{ Btu/lb mole}$$

$$E_r = 77,240 \text{ Btu/lb mole}$$

$$N^* = 0.9763$$

$$\sigma = 2.9 \% C_A$$

*The pressure dependence is very nearly first order (0.98) and could have been set equal to 1.0 with little change in the fit

Source: Stein, T.R. et al., 1977

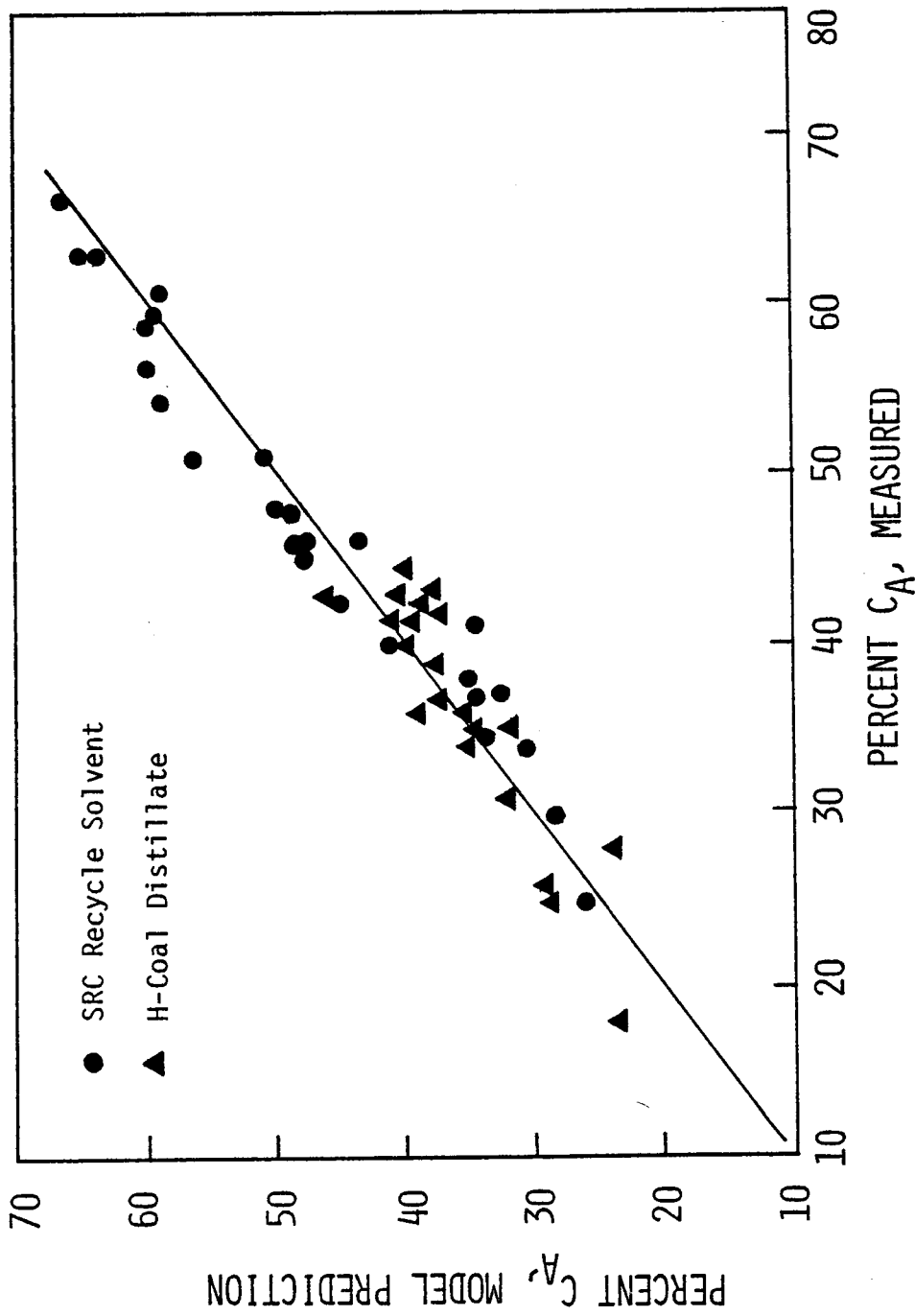


FIGURE 4.4.2 Fit of Aromatic Saturation Model to Measured Percent C_A Values

(Stein, T.R. et al., 1977)

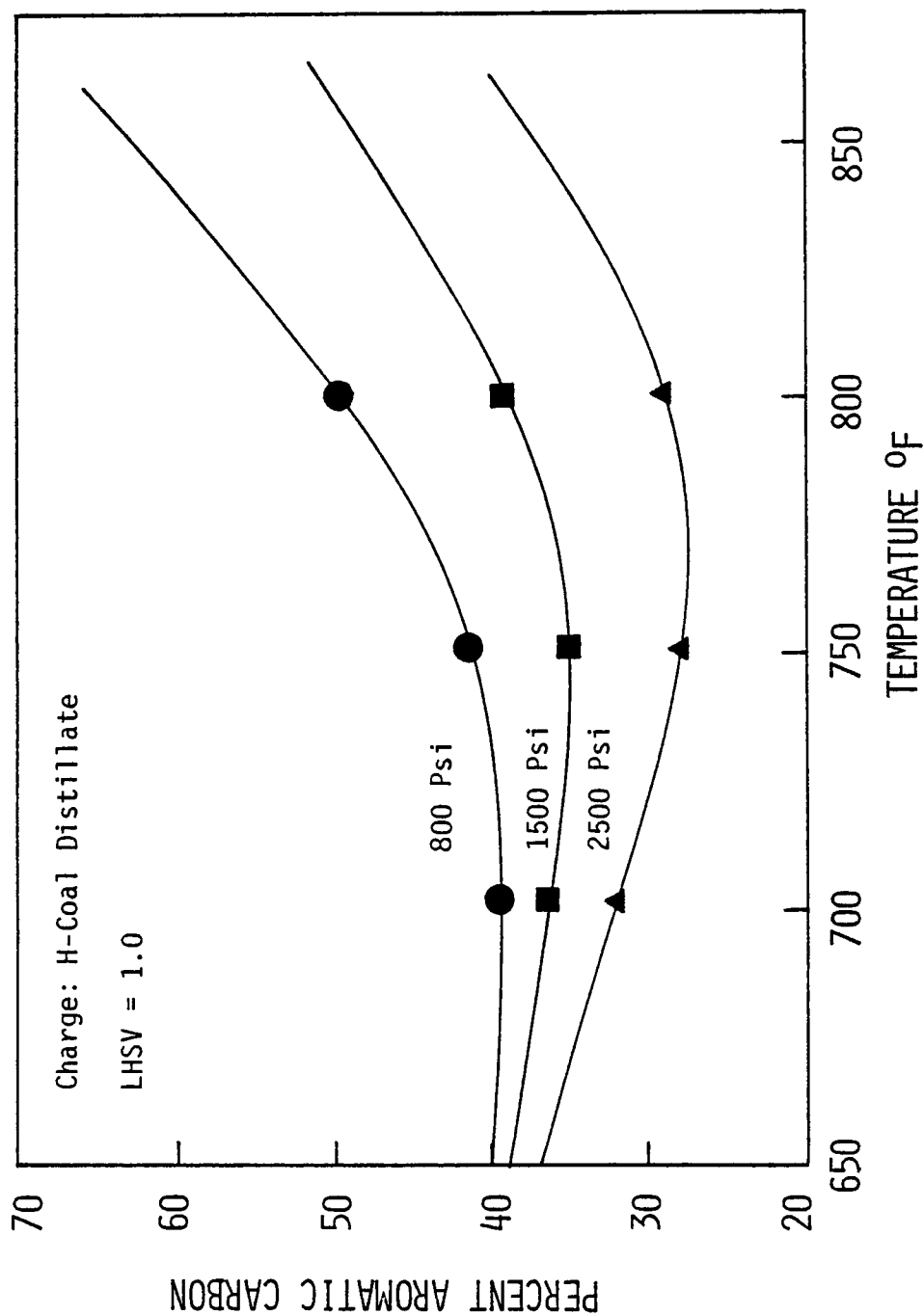


FIGURE 4.4.3 Predicted Effect of Pressure on Aromatic Saturation for H-Coal Distillate
(Stein, T.R. et al., 1977)

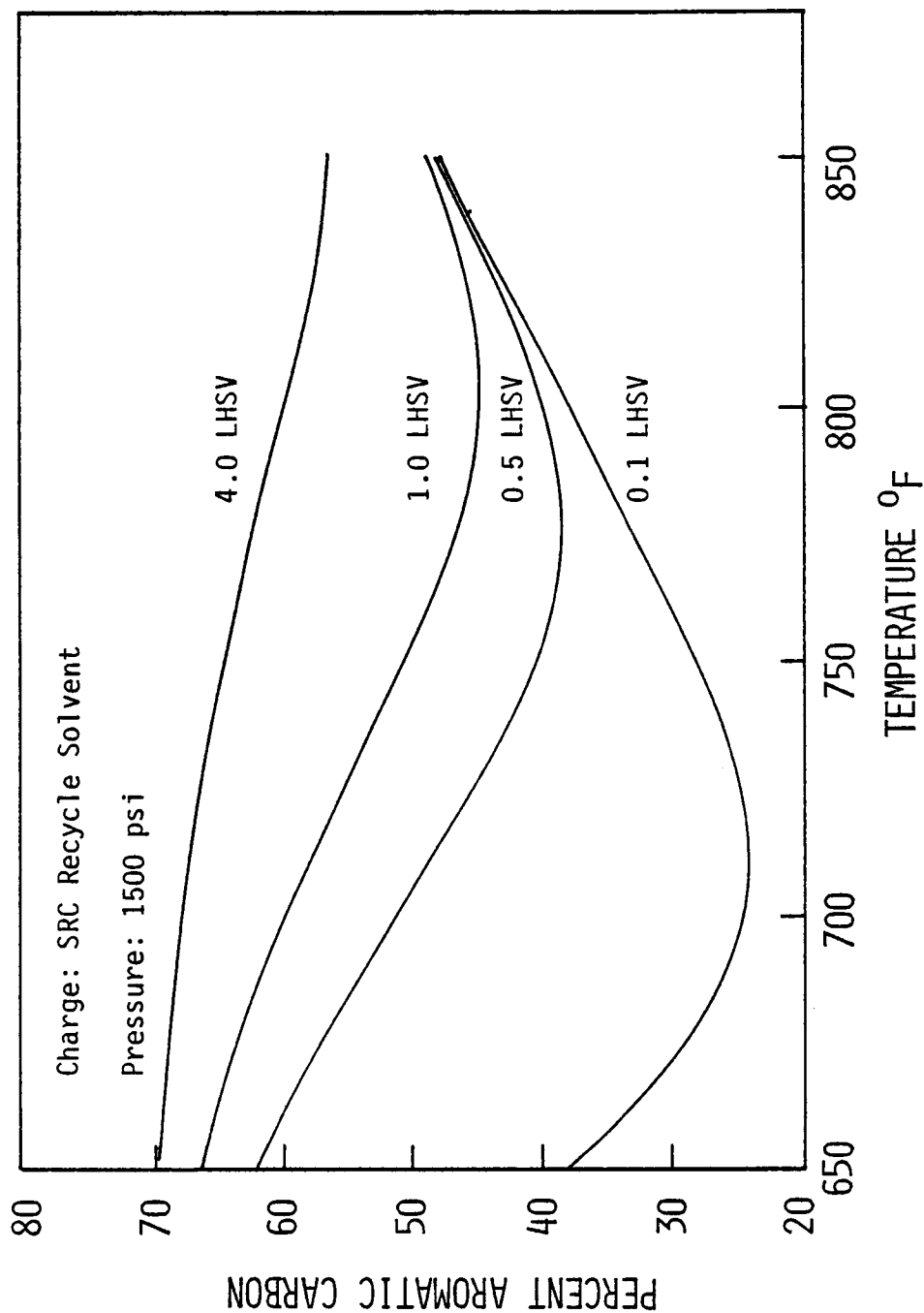


FIGURE 4.4.4 Predicted Effect of LHSV on Aromatic Saturation for SRC Recycle Solvent
(Stein, T.R. et al., 1977)

temperature can lead to less saturation at these conditions. By going to even lower space velocities it is possible to determine the equilibrium aromatic saturation for this stock (Figure 4.4.5). The model predicts that at space velocities below about 0.01, we are essentially at equilibrium for temperatures greater than 675°F. The pressure dependence for aromatic saturation equilibrium can be calculated by predicting the percent C_A at very low space velocity for different pressures. This is shown in Figure 4.4.6. As should be expected, lower pressures result in a higher equilibrium percent C_A . These calculated equilibria are catalyst independent and apply equally well for H-Coal distillate and SRC Recycle Solvent. They represent the minimum percent C_A (i.e., maximum hydrogen content) at a given temperature and pressure. It should be pointed out that these equilibrium calculations represent a considerable extrapolation of the data to very low space velocity (i.e., infinite residence time). Additional data at very low space velocity or in a batch reactor is needed to confirm these predictions.

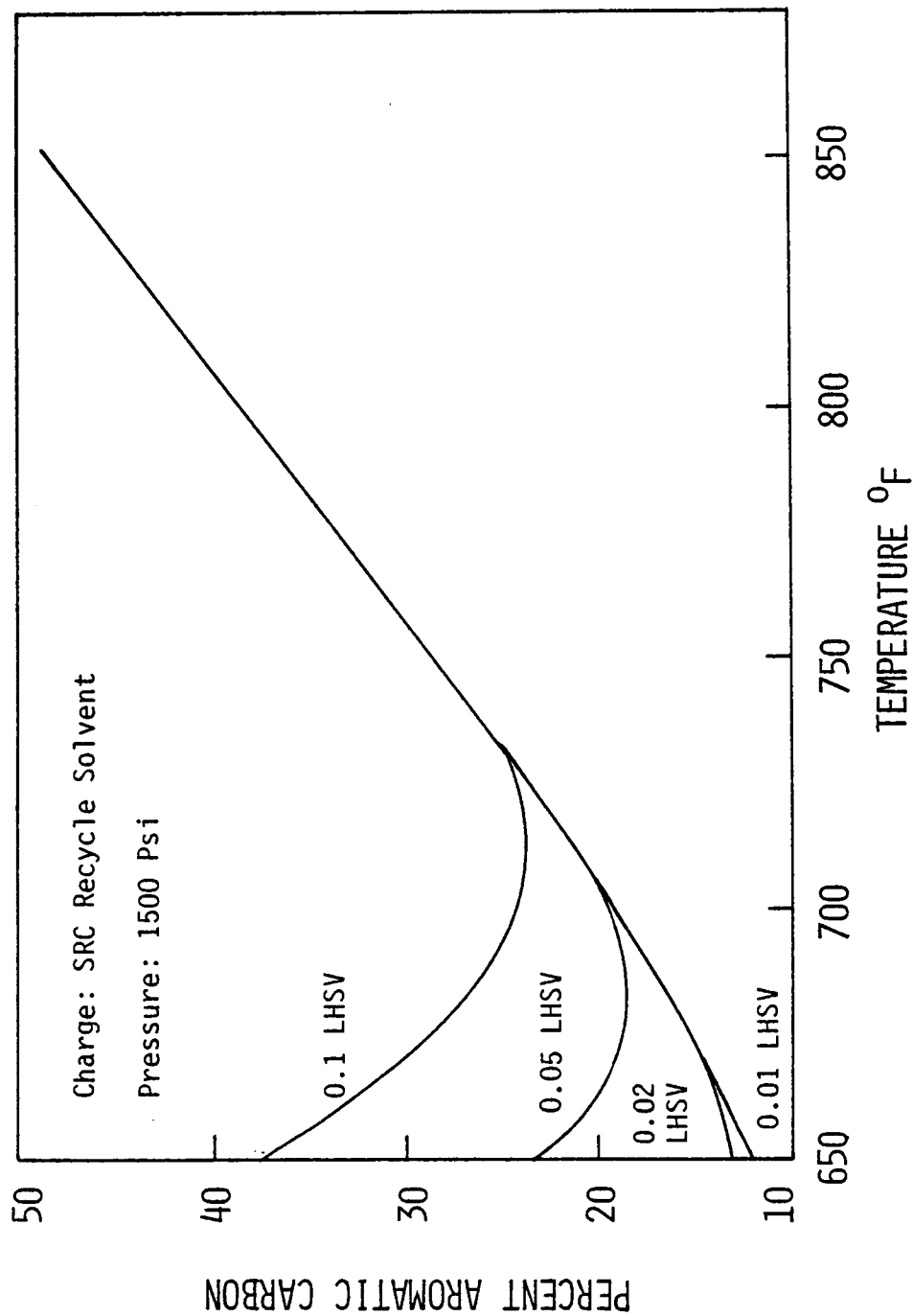


FIGURE 4.4.5 Predicted Equilibrium Aromatic Saturation for SRC Recycle Solvent at 1500 Psi
(Stein, T.R. et al., 1977)

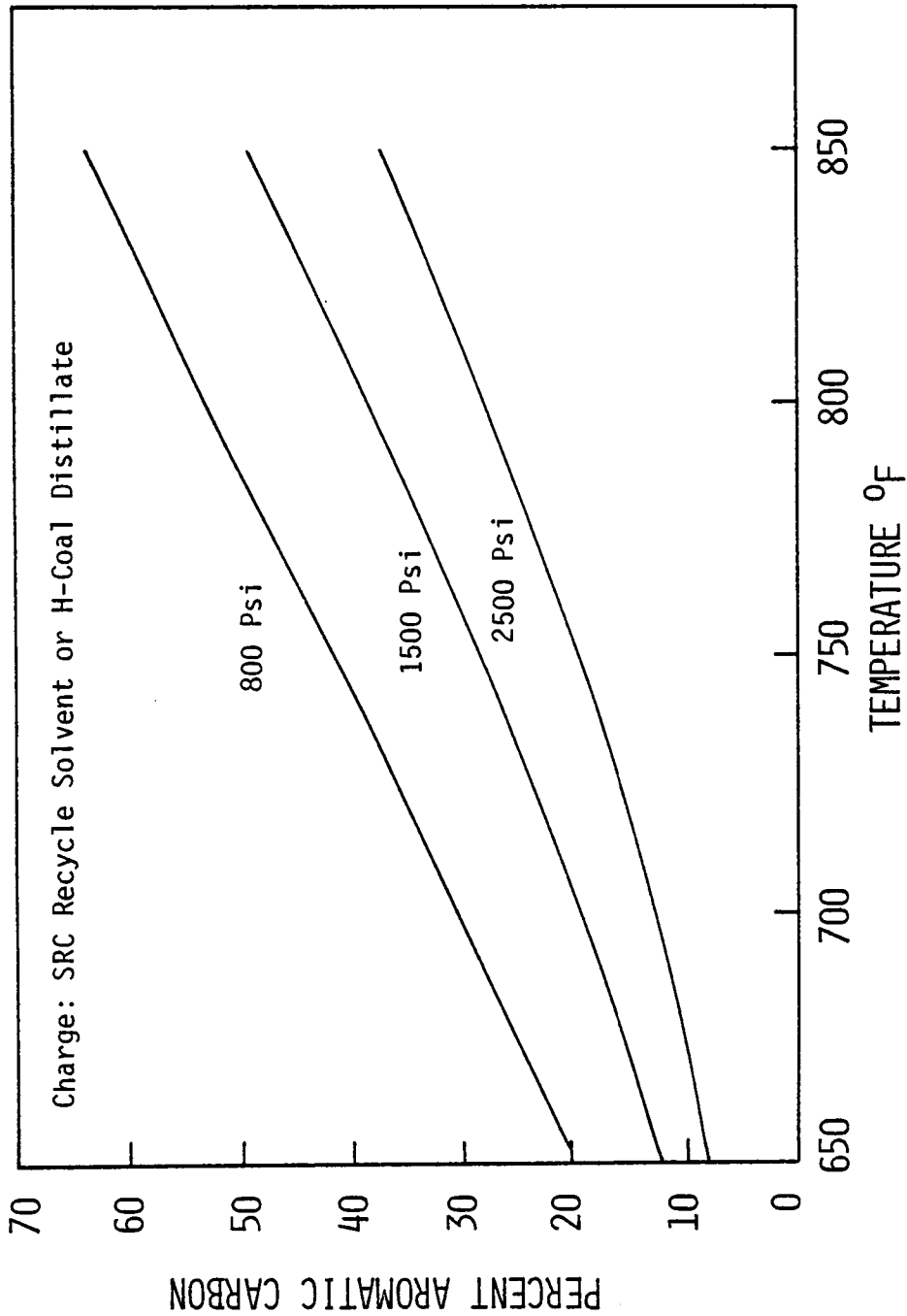


FIGURE 4.4.6 Effect of Pressure on Aromatic Saturation Equilibrium for Distillate Coal Liquids
(Stein, T.R. et al., 1977)

5. HYDROTREATING DATA BASE

The study reported on here was undertaken with the objective of reviewing the coal derived liquid hydrotreating data base in order to determine whether or not there are sufficient data on those areas such as hydrogen requirements, gas yields, heteroatom removal, product stability, and others, to provide a sound basis for design. Particular attention was also given to determining whether or not there are gaps in the data and if so, how they might be bridged.

The hydrotreating data used for this study is taken from the work by Chevron Research on SRC-II syncrude (Sullivan and Frumpkin, 1980) and by UOP on H-Coal (Tan and DeRosset, 1978a, 1978b), SRC-II (Riedl and DeRosset, 1979a, 1979c) and EDS (Tan and DeRosset, 1979b). These groups hydrotreated both the naphtha and the gas oil, and in the case of Chevron, the whole liquid product.

The assembled data were reviewed both for applicability to the task of hydrotreating the product liquid and its naphtha and gas oil fractions, and for completeness with respect to:

- Hydrogen consumption as a function of degree of hydrotreating severity (temperature, pressure, and liquid hourly space velocity).
- Heteroatom removal, especially nitrogen and sulfur, and a function of processing conditions and hydrogen consumption.
- Yields, especially gas yields, as a function hydrotreating conditions.

- Reduction in aromatic content, as a function of processing conditions and hydrogen consumption.
- Hydrotreated product storage stability, as a function of extent of hydrotreatment.

5.1 NAPHTHA HYDROTREATING

The data on SRC-II hydrotreating was available from Chevron and UOP, but for H-Coal and EDS naphtha the data from Chevron is not yet published. The complete processing data are available from Chevron, but the processing temperature, pressures and LHSV (liquid hourly space velocity) ranges used by UOP are available only in coded form.

The inspections of SRC-II naphtha, gas oil and whole crude is given in Table 5.1.1. The EDS process naphthas hydrotreated by UOP is reported in Table 5.1.2, and the H-Coal naphtha inspections is given in Table 5.1.3.

The ranges in process conditions used by Chevron and UOP for hydrotreating SRC-II naphtha is shown in Table 5.1.4. This data indicates that the nitrogen content of the SRC-II naphtha can be reduced sufficiently for reformer feed-stock (less than 1 ppm) by the use of commercial technology and process condition ranges. However, there are only a few data points available at this time for SRC-II naphtha, so a designer would likely be unable to optimize a hydrotreating process for this feed by consideration of these data alone. This constraint is relaxed somewhat, however, by the inclusion of the data for coal-derived naphtha produced by the EDS and the H-Coal process, as can be seen in Figures 5.1.1 through 5.1.8.

Table 5.1.1 Properties of SRC-II Process Products
Received by Chevron

Inspections	Whole Crude	Naphtha	400°F ⁺ Gas Oil
Weight Percent of Whole SRC-II	100	29	71
Gravity, °API	18.6	36.2	10.7
Sulfur, Weight Percent	0.29	0.2	0.25
Nitrogen, Weight Percent	0.85	0.42	0.99
Oxygen, Weight Percent	3.79	3.51	3.63
Carbon, Weight Percent	84.61	83.66	86.86
Hydrogen, Weight Percent	10.46	12.15	9.27
Hydrogen/Carbon Ratio	1.47	1.73	1.29
Ash, Weight Percent	0.004	-	0.01
Viscosity, cSt, @100°F	2.196	0.8933	4.213
ASTM Distillation, °F (D-86)			
St	154	151	393
5%	217	179	413
10%	281	197	427
30%	382	249	448
50%	438	290	471
70%	484	332	506
90%	597	366	590
95%	699	380	662
EP	850	393	847
Percent Overhead	98	98	99

Source: Sullivan and Frumpkin, 1980

Table 5.1.2 Inspection Data of EDS Process Naphthas

	Raw Naphtha	Upgraded Naphtha
Gravity, °API , @ 60°F	38.4	44.1
Hydrogen, Weight Percent	11.8	13.13
Carbon, Weight Percent	86.24	86.18
Sulfur, ppm	9,978	0.1
Nitrogen, ppm	2,097	0.2
Oxygen, ppm	13,700	98.0
Chloride, ppm	18	1.0
Research Octane Number, Clear	83.2	64.5
Distillation, ASTM, (D-86), °F		
IBP	142	202
5%	178	215
10%	208	226
20%	244	237
30%	268	250
40%	286	264
50%	302	287
60%	316	305
70%	319	322
80%	339	336
90%	348	351
95%	-	360
EP	380	374
Percent Over	-	98.6

Source: Tan and DeRosset, 1979

Table 5.1.3 Inspection Data of H-Coal Naphthas

	Raw Naphtha	Upgraded Naphtha
Gravity, °API, @ 60°F	43.7	46.8
Hydrogen, Weight Percent	12.8	13.59
Carbon, Weight Percent	85.9	86.45
Sulfur, ppm	1,289	3.9
Nitrogen, ppm	1,930	0.63
Oxygen, ppm	5,944	34.0
Chloride, ppm	23	4.0
Research Octane Number, Clear	80.3	66.8
Distillation, ASTM (D-86), °F		
IBP	132	153
5%	170	185
10%	189	199
20%	215	217
30%	233	231
40%	251	246
50%	260	263
60%	292	284
70%	312	306
80%	328	329
90%	351	352
95%	373	367
EP	396	393
Percent Over	99.0	99.0

Source: Tan and DeRosset, 1978a

Table 5.1.4 SRC-II Process Naptha
Hydrotreating Conditions

Processing Condition or Property	Chevron	UOP
Temperature Range, °F T-T (base), °C	692-699	24
Pressure Range, psig P-P (base), psi	793	450
Hydrogen Pressure Range, psig	642-645	Not Reported
LHSV Range LHSV/LHSV (base)	0.95-1.03	0.125
Recycle Gas Rate Range, SCF/bbl	3,282-3,449	Not Reported
Hydrogen Consumption Range, SCF/bbl	1,056-1,121	560
Boiling Range of Feed, °F	393-590	107-367
Nitrogen Content Range of Product, ppm	0.1-0.21	0.8
Catalyst	ICR-113 (Ni, W, Si, Al)	DCB (Groups VI B and VIII Elements)

Source: Sullivan and Frumpkin, 1980; Riedl and DeRosset, 1979a

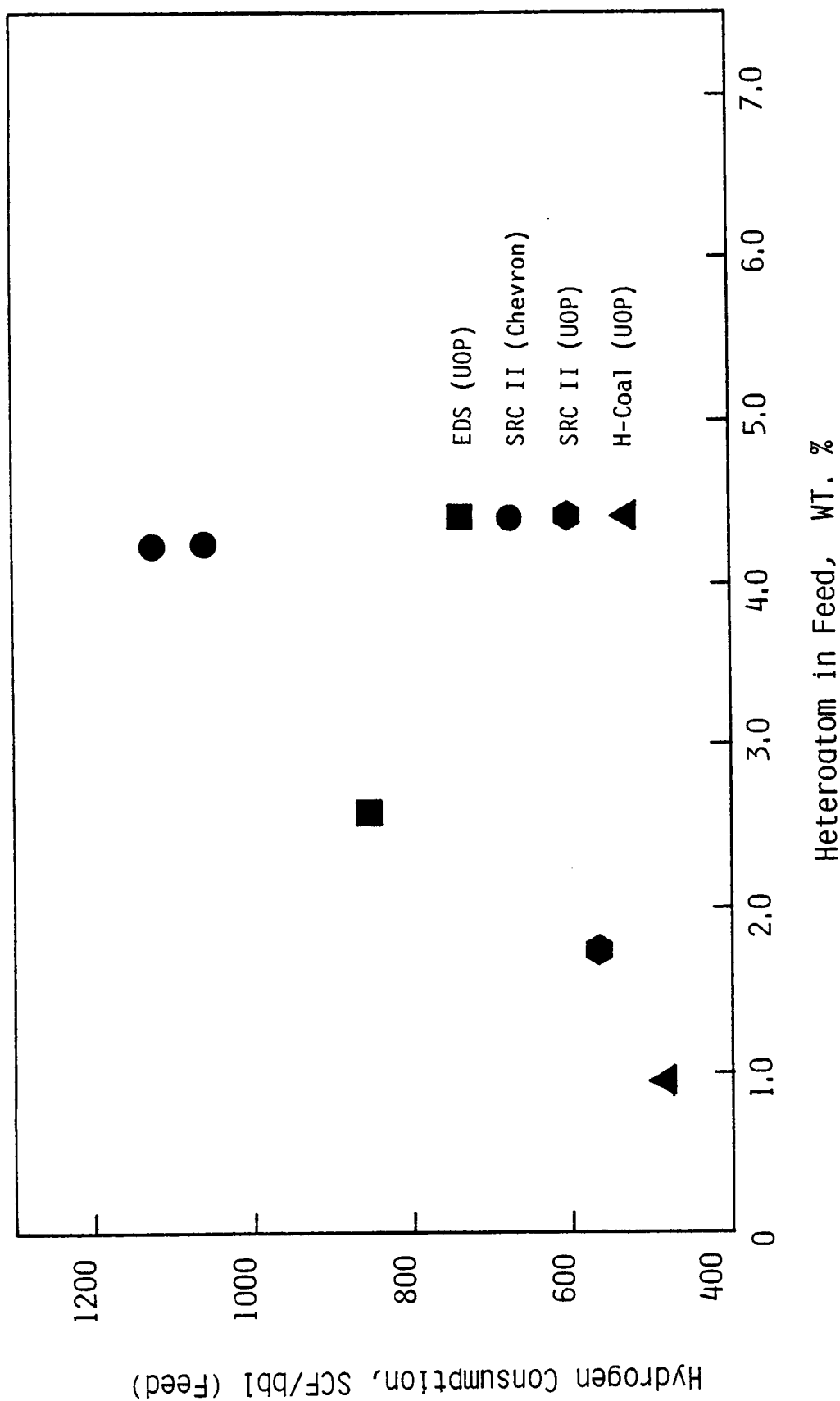


FIGURE 5.1.1.1 Hydrotreating of Coal-Derived Naphthas for the Production of Reformer Feed-stocks: Hydrogen Requirements as a Function of the Heteroatom Content of Feed (Sullivan and Frumpkin, 1980; Tan and DeRosset, 1978a, 1979; Riedl and DeRosset, 1979)

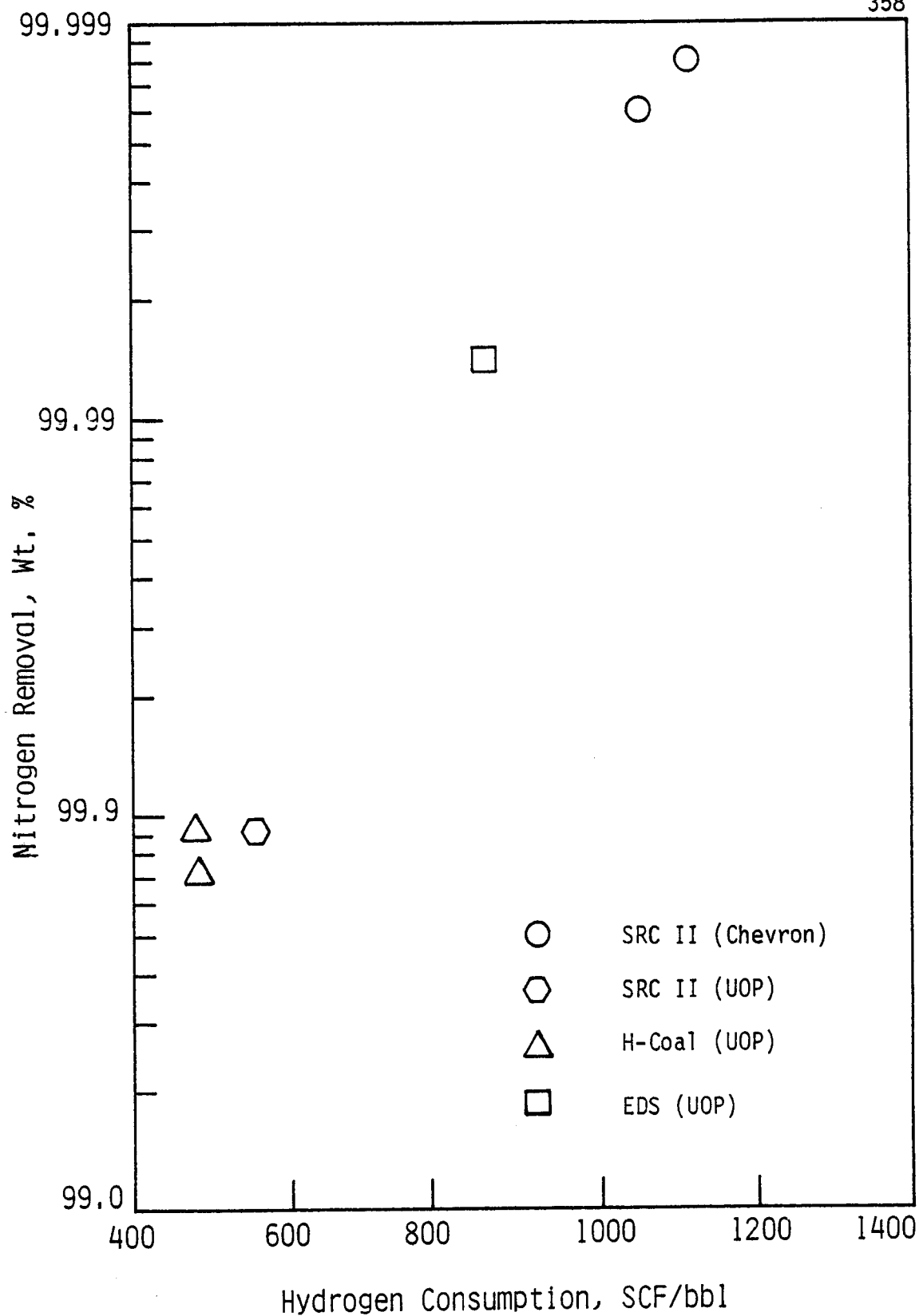


FIGURE 5.1.2 Nitrogen Removal from Coal-Derived Naphthas During Hydrotreating (Sullivan and Frumpkin, 1980; Tan and DeRosset, 1978a, 1979; Riedl and DeRosset, 1979a)

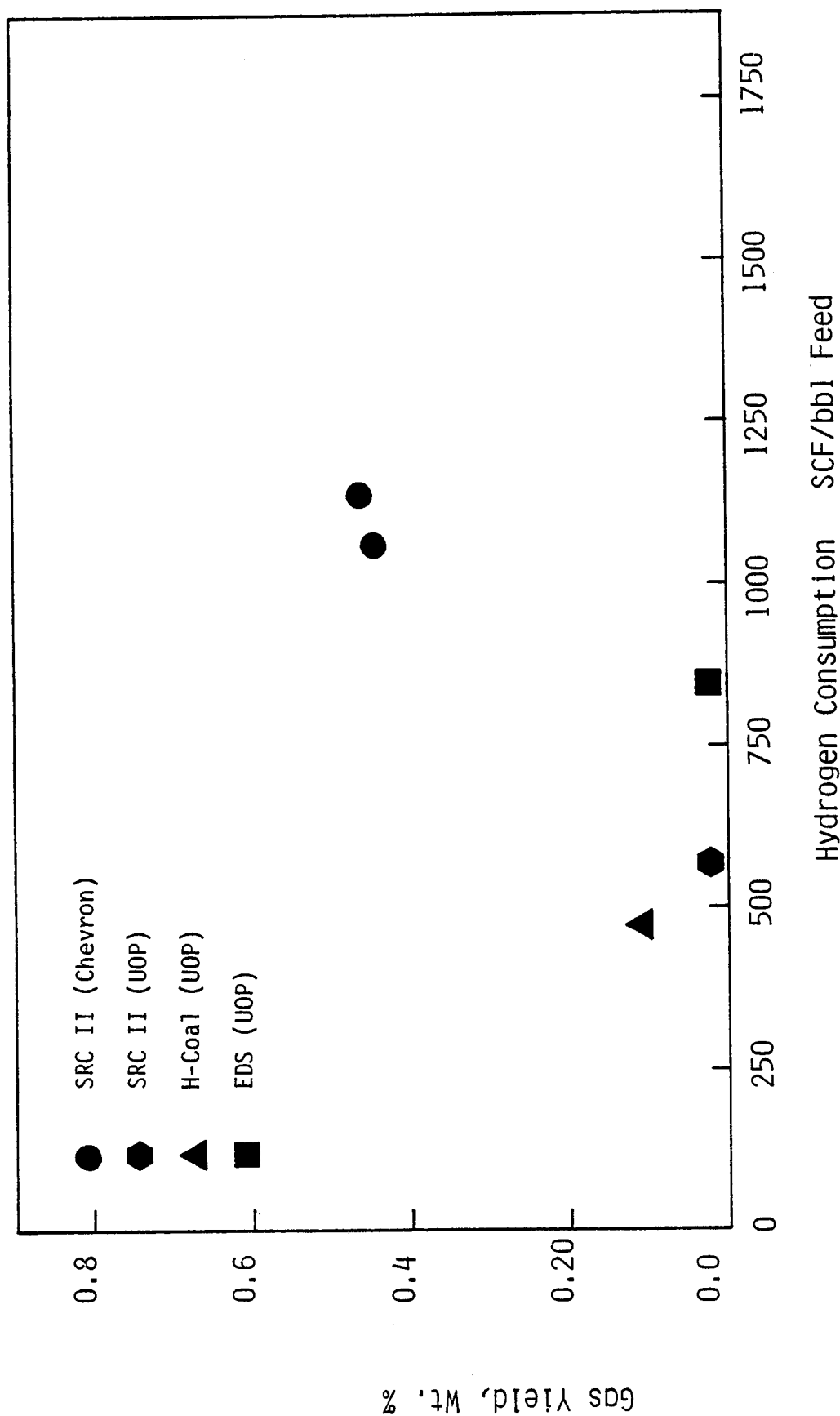


FIGURE 5.1.3 Gas Yield from Coal-Derived Naphthas During Hydrotreatment
(Sullivan and Frumpkin, 1980; Tan and DeRosset, 1978a, 1979;
Riedl and DeRosset 1979a)

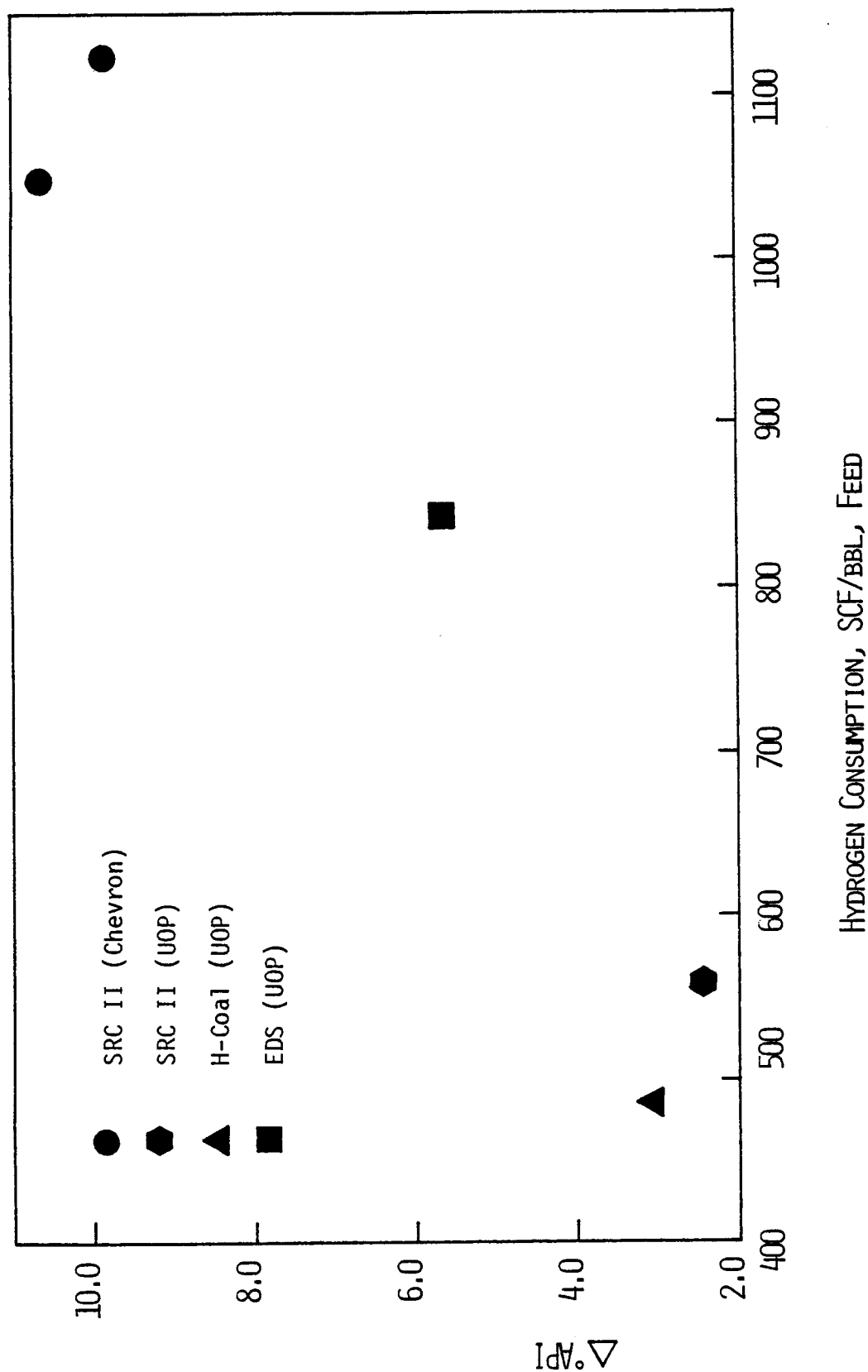


FIGURE 5.1.4 Effect of Hydrotreatment on the API Gravity of Some Coal-Derived Naphthas (Sullivan and Frumpkin, 1980; Tan and DeRosset, 1978a,1979; Riedl and DeRosset, 1979a)

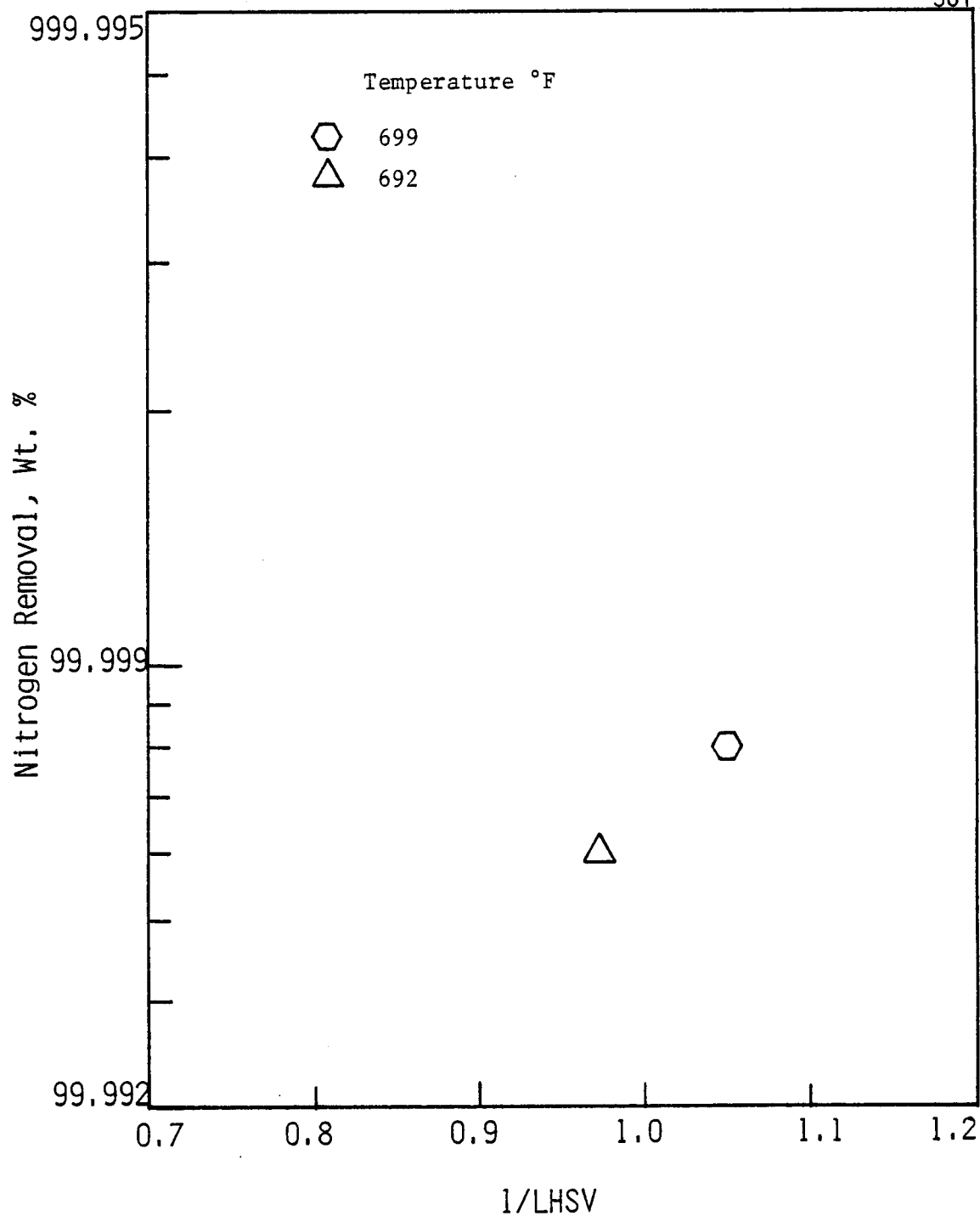


FIGURE 5.1.5 Nitrogen Removal from Raw SRC-II Naphtha as affected by LHSV During Hydrotreating (Sullivan and Frumpkin, 1980)

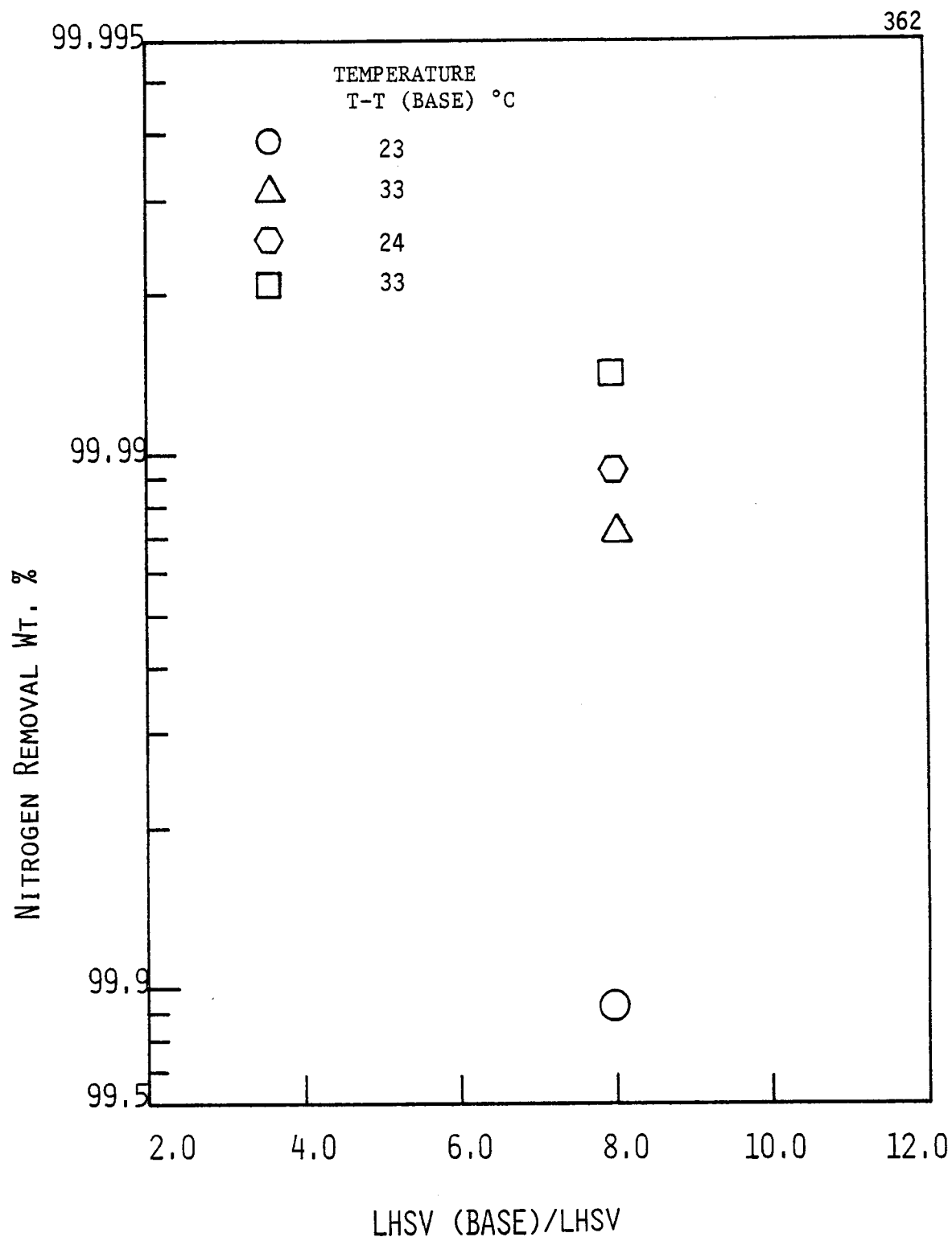


FIGURE 5.1.6 Nitrogen Removal from Some Coal-Derived Naphthas, as Affected by LHSV
(Tan and DeRosset, 1978a, 1979;
Riedl and DeRosset, 1979a)

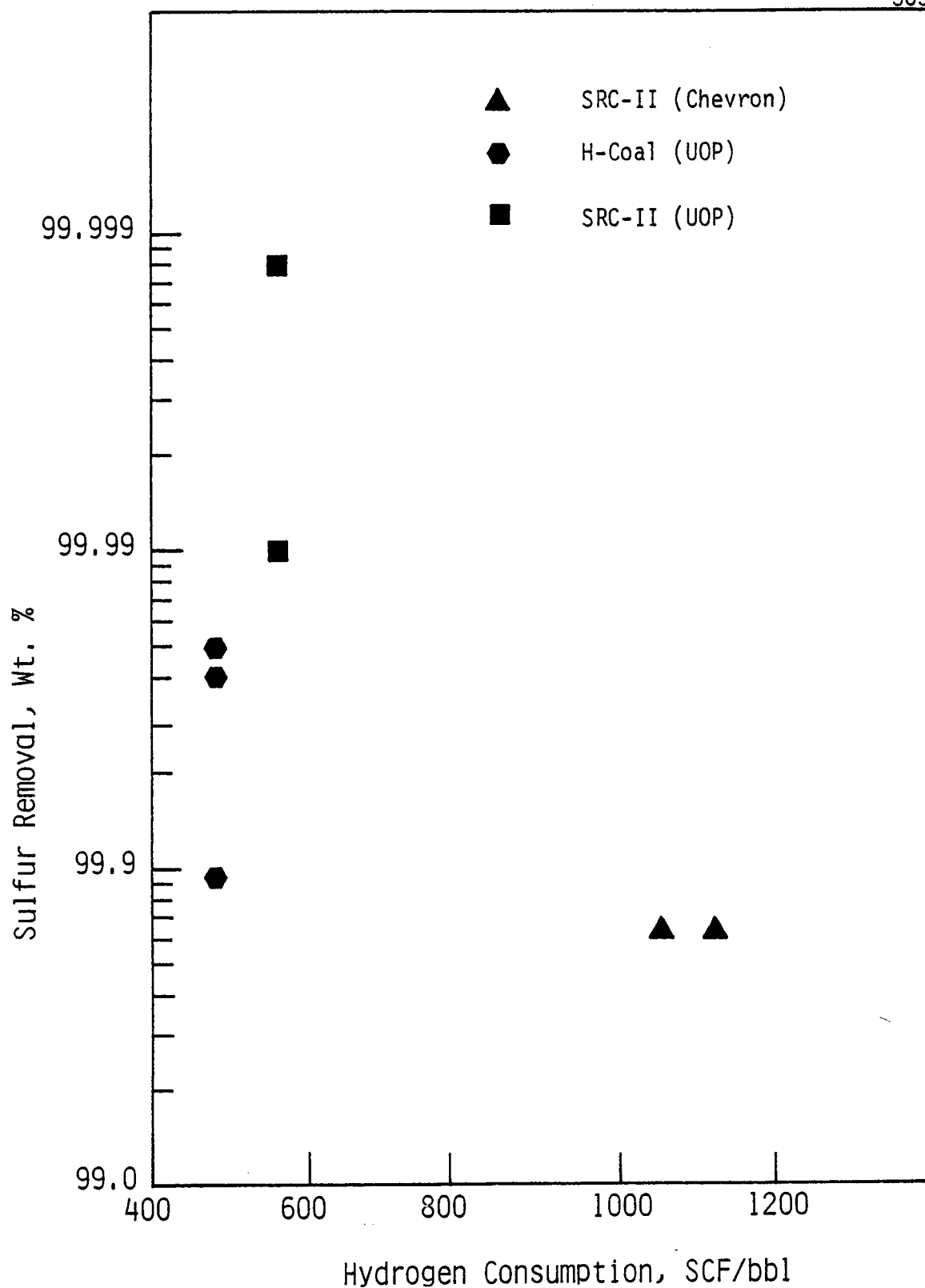


FIGURE 5.1.7 Sulfur Removal from Some Coal-Derived Naphthas During Hydrotreating (Sullivan and Frumarkin, 1980; Tan and DeRosset, 1978a; Riedl and DeRosset, 1979a)

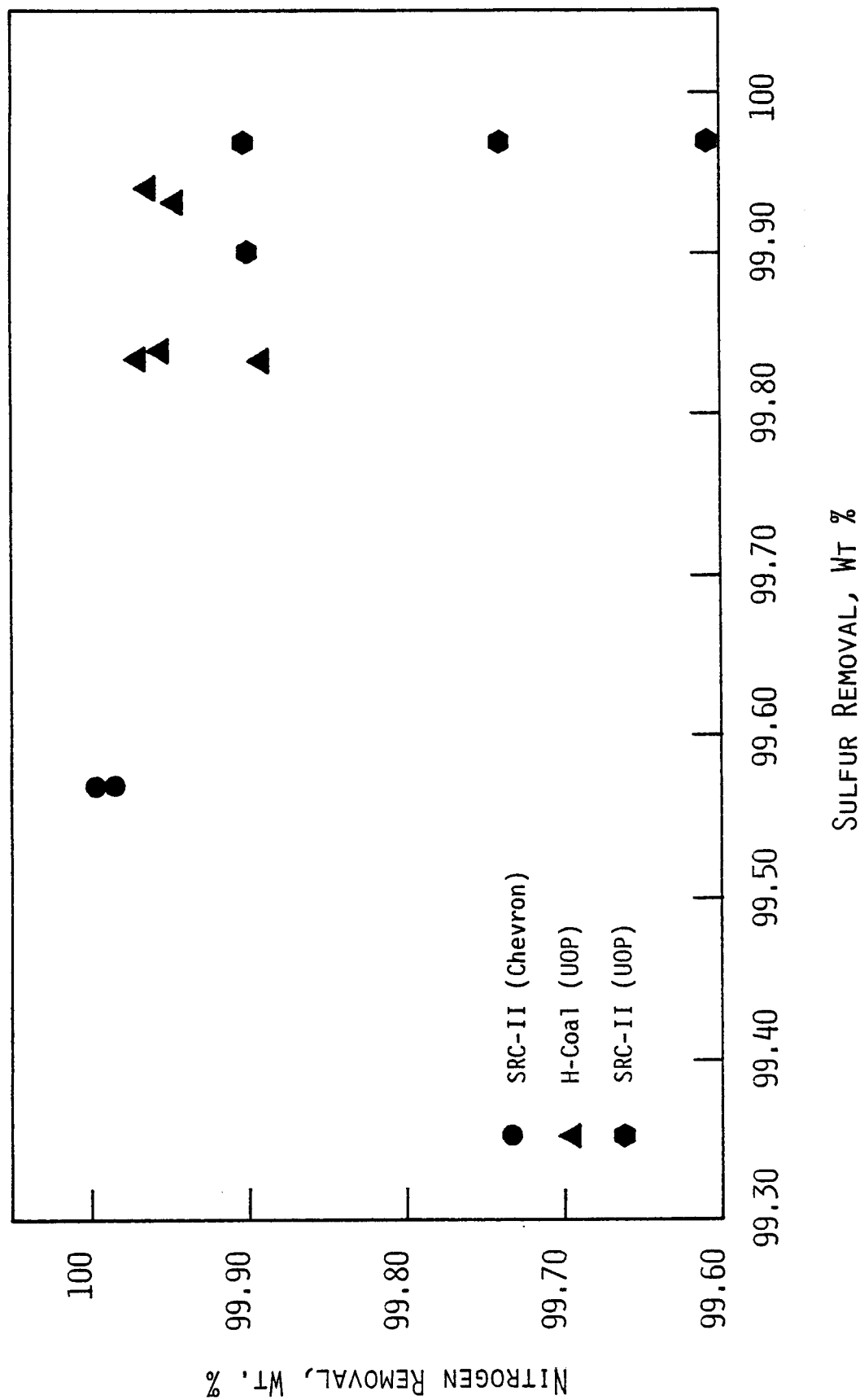


FIGURE 5.1.8 Nitrogen and Sulfur Removal from Some Coal-Derived Naphthas During Hydrotreating
(Sullivan and Frumpkin, 1980; Tan and DeRosset, 1978a; Riedl and DeRosset, 1979a)

Keep in mind that the data shown in these figures were generated with the primary objective of showing that these naphthas could be reduced in nitrogen content sufficiently for reformer feedstock. This means that the nitrogen of the SRC-II Naphtha would have to be reduced by about 99+ wt percent, more or less, depending on the nitrogen content of the coal from which naphtha is derived.

The chemical hydrogen consumption required to reduce the nitrogen content to reformer feedstock levels is shown as a function of heteroatom content of the raw naphtha feed in Figure 5.1.1, for three coal-derived naphthas: SRC-II, H-Coal, and EDS. Though limited, these data appear to correlate over the range of about .95 to 4.2 wt percent feed heteroatom content. This suggests that the hydrogen consumption may be independent of the process used to generate the naphtha. One could therefore interpolate to predict the required hydrogen consumption for intermediate heteroatom contents, with some confidence. For example, for a naphtha of these types with a heteroatom content of 3.5 wt percent, a hydrogen consumption of about 960 SCF/bbl of feed is indicated. However, the data should be extrapolated outside the data range with caution, if at all.

The extent of the data correlation between nitrogen removal and hydrogen consumption is shown in Figure 5.1.2. These data suggest an essentially linear relationship between log nitrogen removal and hydrogen consumption, in the range of about 480 to 1120 SCF/bbl. Again one should be able to interpolate with some confidence to hydrogen consumption levels within this range.

The data of Figures 5.1.1 and 5.1.2 exhibit surprisingly little

scatter in view of the fact that they were produced from three different naphthas and in different laboratories under somewhat different conditions. However, the gas yield data for naphtha hydrotreating, Figure 5.1.3, is somewhat more widely scattered. These data, when extrapolated to a hydrogen consumption of 350 SCF/bbl of naphtha feed, suggest the gas yield should be in the range of about 0.5-0.1 weight percent of the feed.

The change in the naphtha API gravity with hydrogen consumption is shown in Figure 5.1.4, for three naphthas: SRC-II, EDS, and H-Coal.

The task of establishing precisely the hydrotreating processing conditions (temperature, pressure, LHSV) required to effect a naphtha hydrogen consumption in the range of, say, 350 SCF/bbl is difficult at this time, given only the published data, as these data have been generated for somewhat more severe conditions. For example, a hydrogen consumption of about 350 SCF/bbl by SRC-II naphtha should reduce the naphtha nitrogen content by about 99.2 weight percent. This value is outside the range of the processing condition parameters, as shown in Figures 5.1.5 and 5.1.6, but on the "safe" side. Hence one could use the available data to "over design" the hydrotreater, and then back off on the operating temperature or pressure, or both, after plant startup, until the design hydrogen consumption is reached.

Finally the question arises as to what fraction of the sulfur would be removed by hydrotreatment, given a particular hydrogen consumption level or nitrogen removal percent. The available data are shown in Figures 5.1.7 and 5.1.8. There appears to be no particular pattern or correlation in the data. However, it seems safe to say that naphtha

hydrotreating conditions which would consume 350 SCF/bbl of feed and reduce the range of 99.2 percent, as discussed above, would certainly remove 99+ weight percent of the sulfur.

5.1.1 Physical and Thermal Property Data

Data such as liquid heat capacities and latent heats of vaporization are required for precise firm-up of the design of a SRC-II naphtha hydrotreating process. Little if any thermal property data appear to be available for liquids of this type.

An approach to the design of a hydrotreating process, in the absence of such data, is to use the petroleum data and correlations. This was the approach taken by Econenergy Associates (1980) in their preliminary design of a complete coal liquid upgrading facility. According to their results, the overall plant heat balance closed to within 31 percent, with a maximum deviation of 7.0 for light gas oil hydrotreating. It is therefore concluded here that a SRC-II naphtha hydrotreating process designed on the basis of thermal property data taken from petroleum correlations should not be in serious error. However, the implementation of an experimental program designed to obtain these data for coal-derived liquids is recommended.

5.1.2 SRC Naphtha Hydrotreating Assessment

The naphtha hydrotreating data are somewhat spotty and in some instances, non-existent. However, based upon these data we make the following assessment:

- There are sufficient experimental data for the design of a naphtha hydrotreating unit which will remove an

estimated 99.2 weight percent of the nitrogen if the hydrogen consumption is 350 SCF/bbl, but factors may have to be introduced into the design to account for the sparsity of the data, its scatter, and certain extrapolations which will be necessary. As much as 1000-1100 SCF/bbl of hydrogen have been consumed during the hydrotreating of SRC-II naphtha, so additional hydrogen beyond that could be added to the naphtha without exceeding the range of the available data. Major data weaknesses are in the areas of the limited range of process conditions (temperature, pressure, LHSV), and the scatter in the gas yield data. Insufficient data are available for process optimization, but the SRC-II data are supplemented considerably by the use of the EDS and the H-Coal naphtha hydrotreating data, particularly in the area of nitrogen removal as affected by hydrogen consumption.

- There appear to be no data on the bioactivity of SRC-II naphtha particularly as affected by hydrotreatment, so a study in this area would appear warranted.
- Similarly, there appear to be no data showing the extent to which SRC-II naphtha is stabilized by level of hydro-treatment, so, unless data are forthcoming, the extent to which the naphtha should be hydrotreated on site will be a matter of the designer's judgment.
- Thermal property data from petroleum correlations can be used to estimate the energy requirements of a naphtha

hydrotreating process, but data for coal-derived naphthas, particularly heat capacity and latent heat of vaporization data, would allow better estimate of process fuel requirements.

5.2 GAS OIL HYDROTREATING DATA

The gas oil hydrotreating data used was for SRC-II from Chevron and UOP, and for EDS and H-Coal was from UOP only. The inspection of EDS and H-Coal gas oil fractions is reported in Table 5.2.1 and 5.2.2.

The hydrotreating processing conditions employed by Chevron and UOP in the hydrotreating of some coal-derived gas oils are shown in Table 5.2.3. The Chevron experiments were at a nominal temperature of 750° F and a nominal total pressure of 2500 psig. The liquid hourly space velocity range was 0.43 to 1.01. The UOP processing conditions are reported in coded form.

A collection of pertinent gas oil hydrotreating results are shown in Figures 5.2.1 through 5.2.12.

Figure 5.2.1 shows the response of the SRC-II and H-Coal gas oils to heteroatom removal, as a function of hydrogen consumption. These data suggest the SRC-II gas oil product may be a somewhat more difficult feed than the H-Coal product, so far as heteroatom removal is concerned. The nitrogen removal data are shown in Figures 5.2.2 and 5.2.3. Figure 5.2.3 shows that nitrogen removals in the range of 99.99 percent can be achieved, but with a hydrogen consumption of about 2600 SCF/bbl. Nitrogen removal as a function of reciprocal LHSV is shown in Figures 5.2.4 and 5.2.5. A pseudo first-order reaction model result would plot as a straight line on these graphs. Even though there is considerable scatter in the data, these results suggest such a simple

Table 5.2.1 Inspection of EDS Product Used for Hydrating
by UOP

°API @ 60° F	3.5
Sp. Gr. @ 60° F	1.0481
Distillation, ASTM D-1160	
IBP, °F	403
5%	447
10%	454
20%	471
30%	511
40%	563
50%	620
60%	690
70%	778
80%	878
90%	930 (85%)
95%	
EP	
% Over	85.0
% Bottoms	15.0
Hydrogen, Wt-%	8.66
Carbon, Wt-%	89.22
Sulfur, Wt-ppm	4900
Nitrogen	7130
Oxyben, Wt-ppm	19300

Source: Riedl and DeRosset, 1979b

Table 5.2.2 Inspection of H-Coal Atmospheric Still Bottom
Used for Hydrotreating by UOP

	As Received	After Flash Distillation
°API @ 60° F	7.4	12.9
Sp. Gr. @ 60° F	1.0187	0.9799
Distillation, ASTM D-1160		
IBP, °F	412	418
5%	462	467
10%	485	480
20%	509	499
30%	530	517
40%	558	536
50%	580	557
60%	603	578
70%	631	603
80%	661	639
90%	715	690
EP	857	770
% Over	99.0	99.0
% Bottoms	1.0	1.0
Hydrogen, Wt-%		9.57
Carbon, Wt-%		89.28
Sulfur, Wt-ppm	951	500
Nitrogen, Wt-ppm	3534	4180
Oxygen, Wt-ppm	5006	5200
Con. Carbon, Wt-%	0.41	0.01
Heptane Insoluble, Wt-%	0.37	0.11

Source: Tan and DeRosset, 1978b

Table 5.2.3 Coal-Derived Gas Oil Hydrotreating Process Conditions

	Chevron	UOP
Temperature, °F	746-752	
T-T (base), °C		- 59 to 33
Total Pressure, psig	2945-2501	
P-P (base), psig		750 to 1050
LHSV Range	0.43-1.01	
LHSV/LHSV (base)		0.36 to 1.22
Recycle Gas Rate, SCF/bbl	12,776-16,368	Not reported
Hydrogen Consumption, SCF/bbl	2949-4061	
Wt. %		1.26-3.94
Nitrogen Content of Product, ppm	0.22-0.21	0.1-5970
Catalyst	ICR-106 (Ni, W, Si, Al)	DCB (Group VIB and Group VIII elements)
Oils Processed to Date	SRC-II	SRC-II, H-Coal, EDS

Source: Sullivan and Frumpkin, 1980; Tan and DeRosset, 1978b; Riedl and DeRosset, 1979b, 1979c.

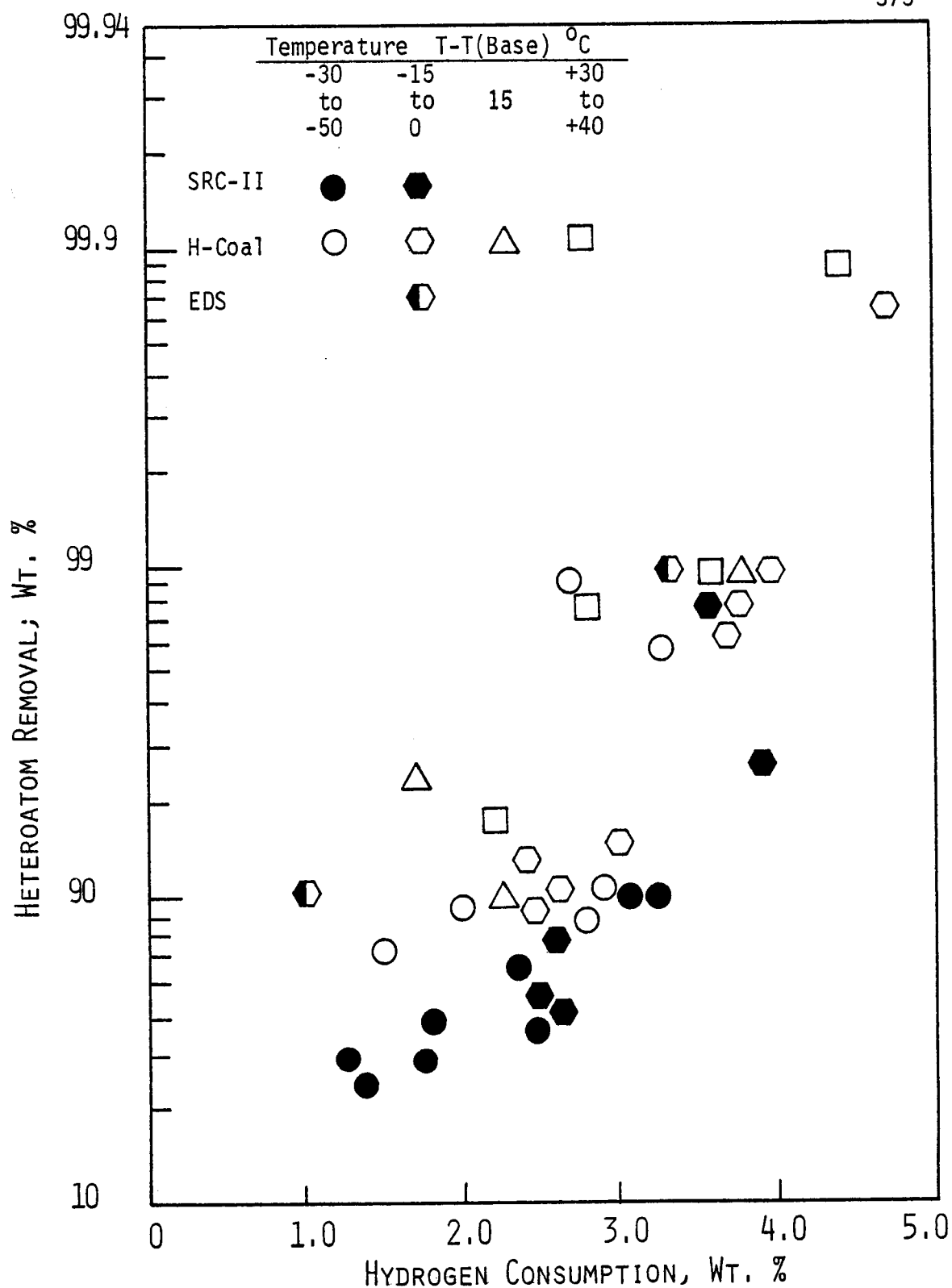


FIGURE 5.2.1 Heteroatom Removal by Hydrotreating of Some Coal-Derived Gas Oils; UOP Results (Tan and DeRosset, 1978b, 1979; Riedl and DeRosset, 1979c)

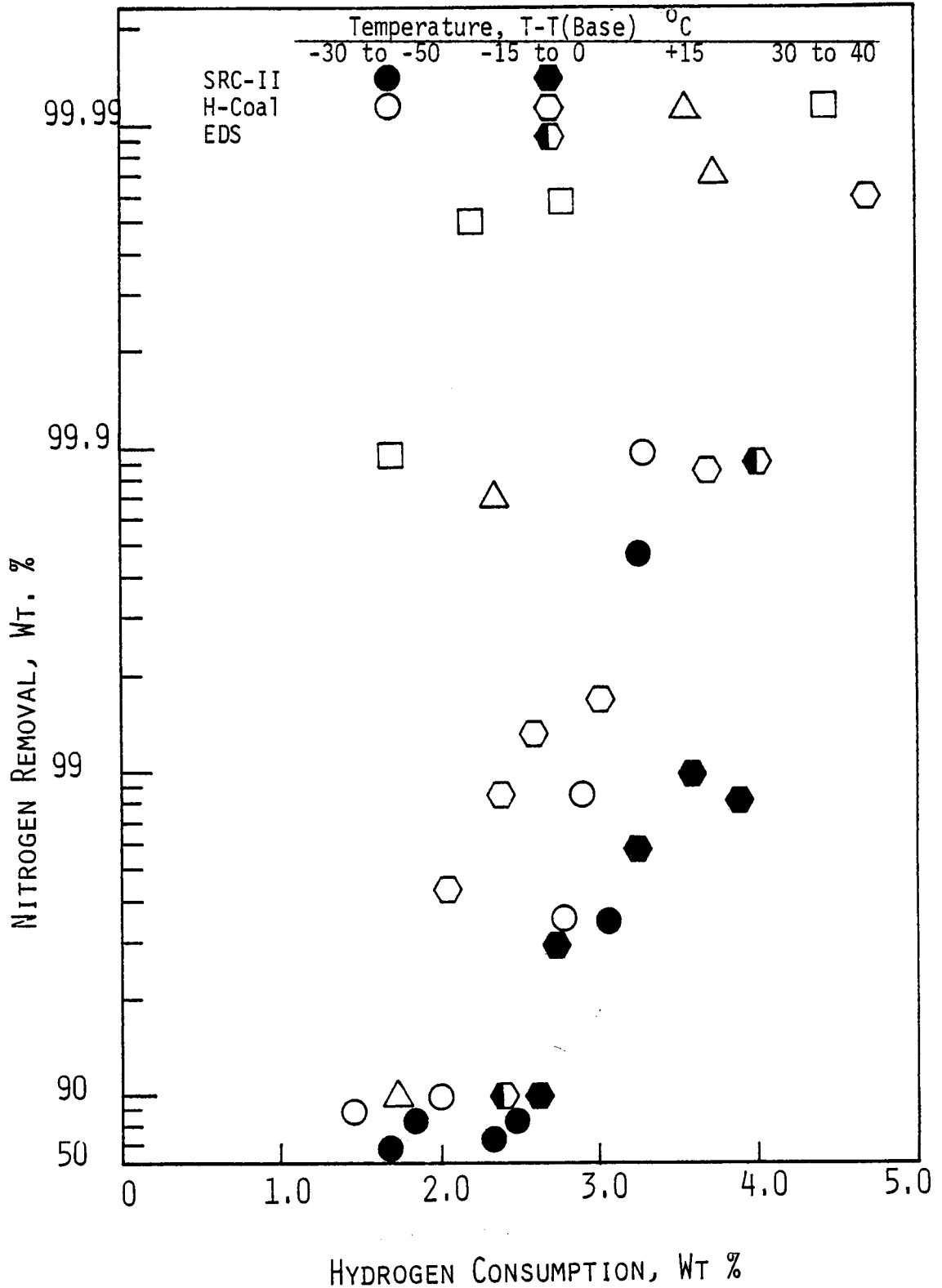


FIGURE 5.2.2 Nitrogen Removal by Hydrotreating of Some Coal-Derived Gas Oils; UOP Results (Tan and DeRosset, 1978b; Riedl and DeRosset, 1979b, 1979c)

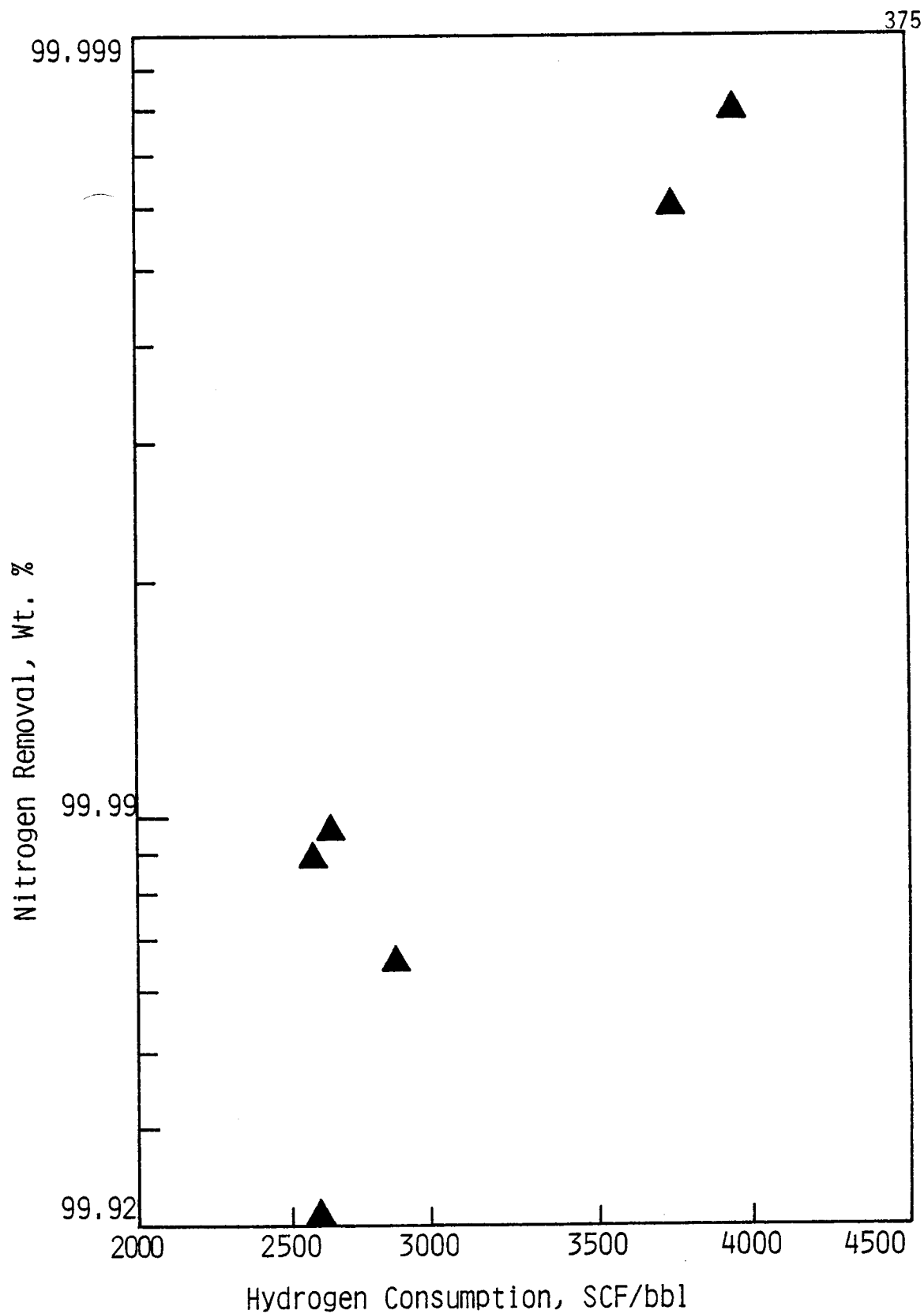


FIGURE 5.2.3 Nitrogen Removal by Hydrotreating of SRC-II Gas Oil
(Sullivan and Frumpkin, 1980)

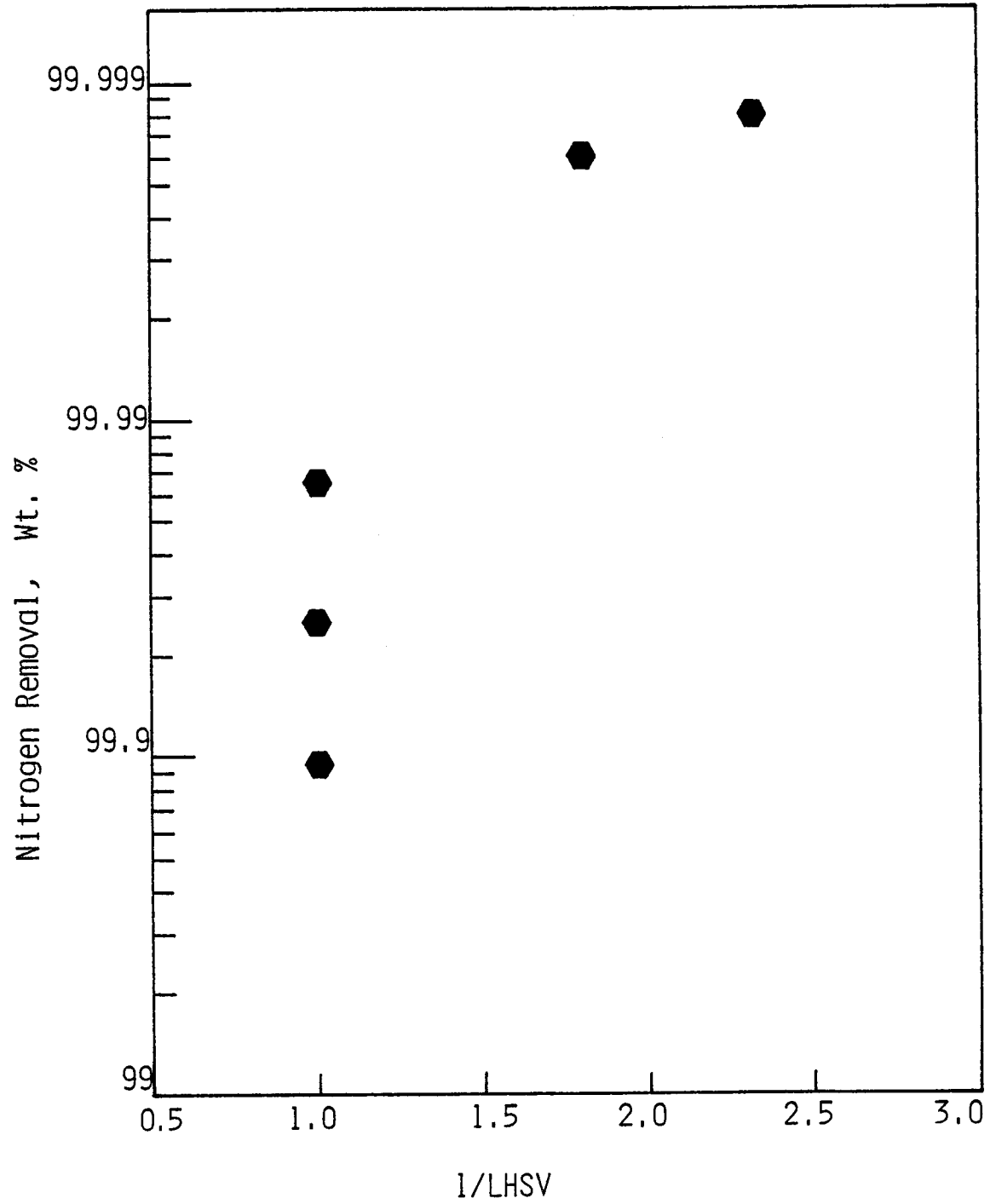


FIGURE 5.2.4 Nitrogen Removal from SRC-II Gas Oil as a Function of Processing Conditions During Hydrotreating; Chevron Results (Sullivan and Frumpkin, 1980)

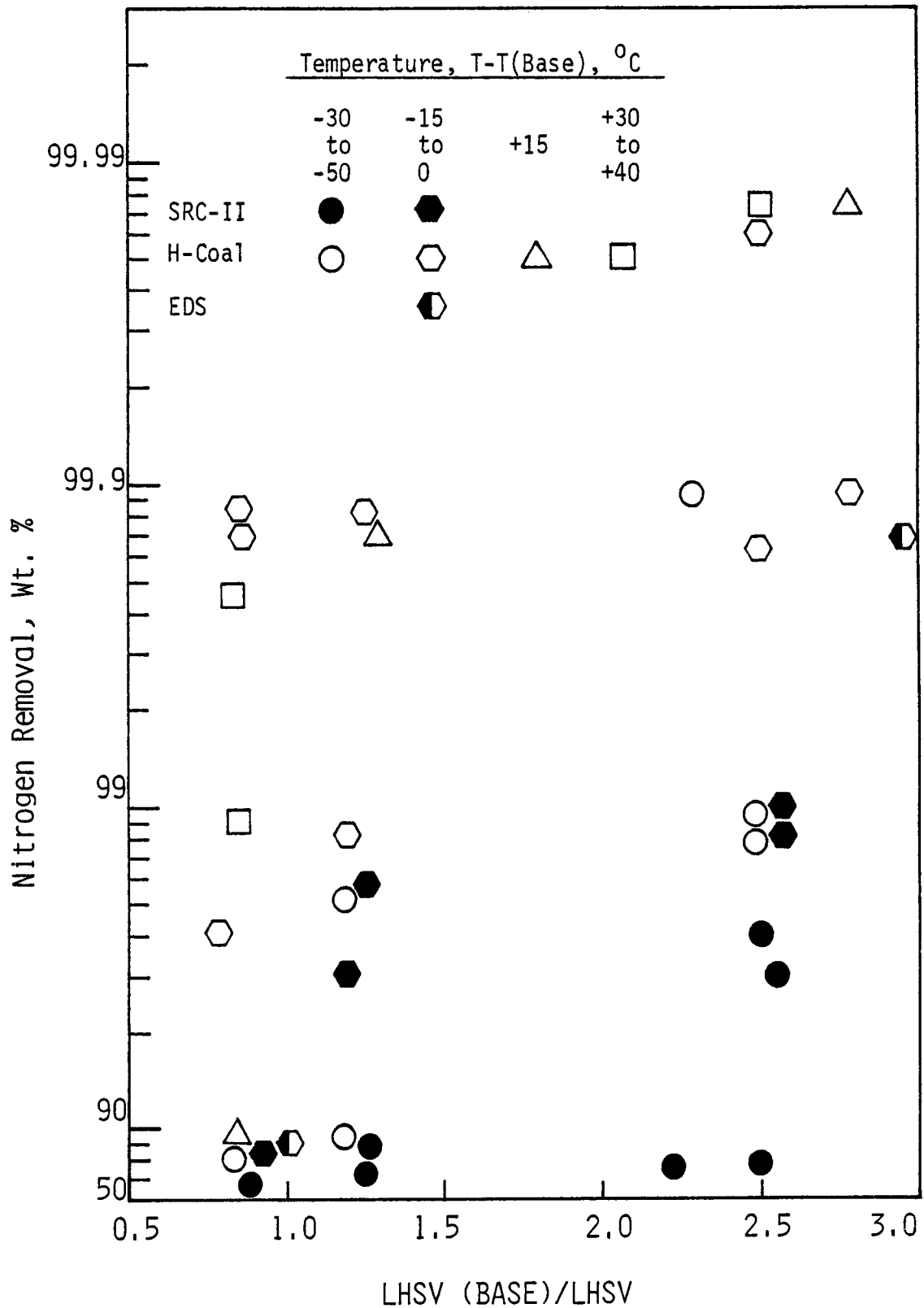


FIGURE 5.2.5 Nitrogen Removal from Some Coal-Derived Gas Oils as a Function of Processing Conditions During Hydrotreating; UOP Results (Tan and DeRosset, 1978b; Riedl and DeRosset, 1979b, 1979c)

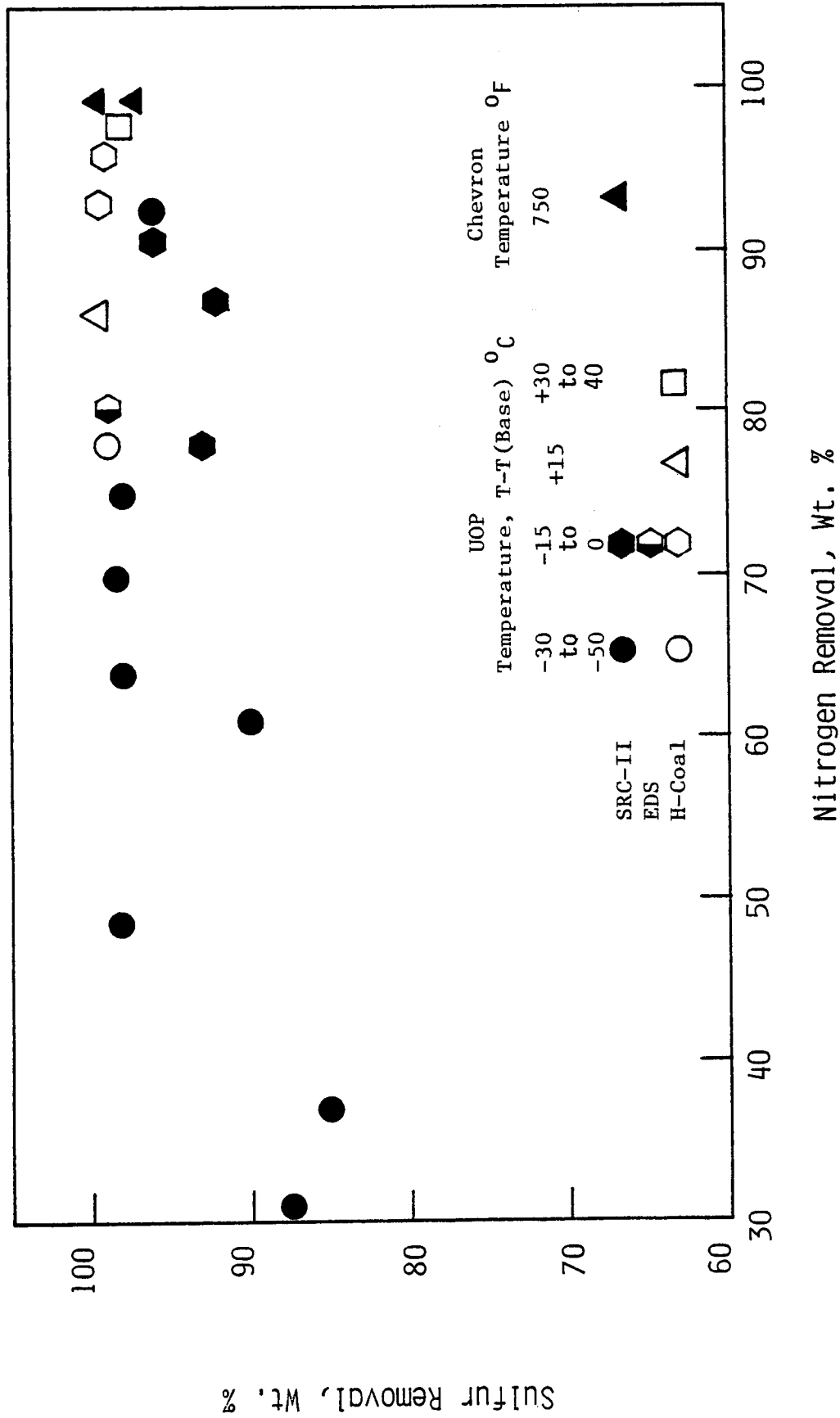


FIGURE 5.2.6 Nitrogen-Sulfur Removal Correlation for Hydrotreating of Some Coal-Derived Gas Oils
(Sullivan and Frumppkin, 1980; Tan and DeRosset, 1978b; Riedl and DeRosset, 1979b,1979c)

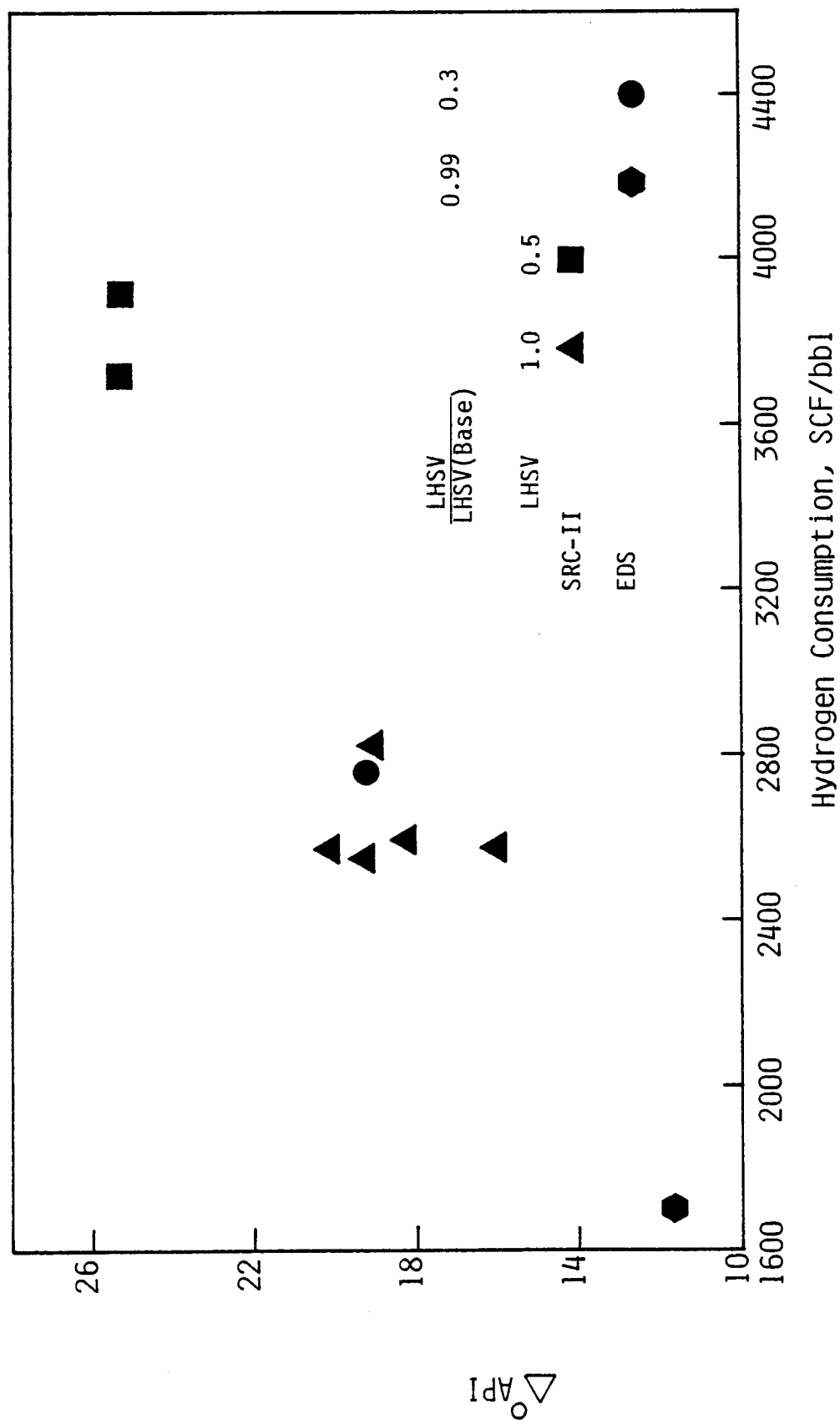


FIGURE 5.2.7 Effect of Hydrogen Consumption on Change of API Gravity of Some Coal-Derived Gas Oils During Hydrotreating (Sullivan and Frumppkin, 1980; Riedl and DeRosset, 1979b)

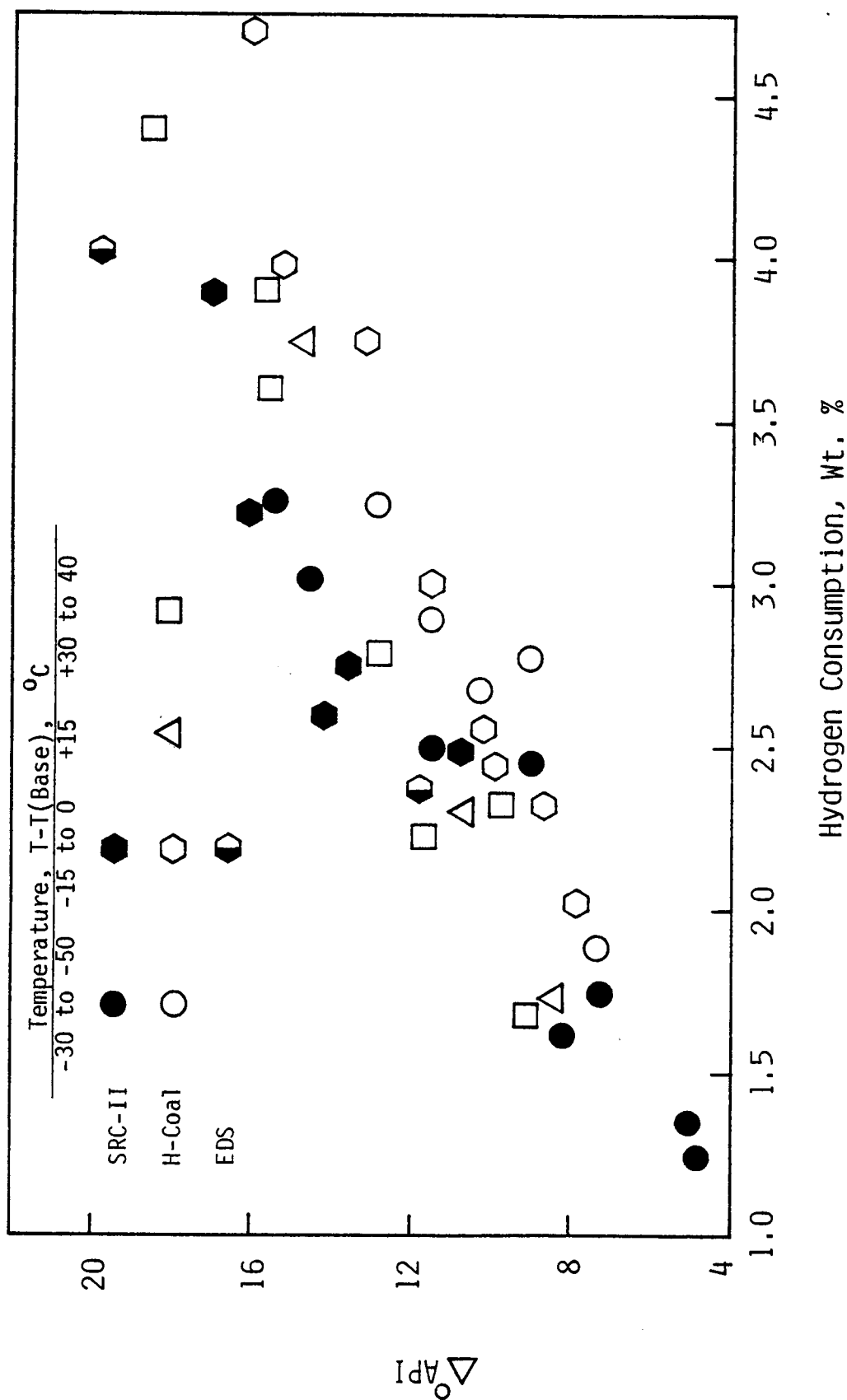


FIGURE 5.2.8 Effect of Weight Percent Hydrogen Consumption on Change in API Gravity of Some Coal-Derived Gas Oils During Hydrotreating (Sullivan and Frumpkin, 1980)

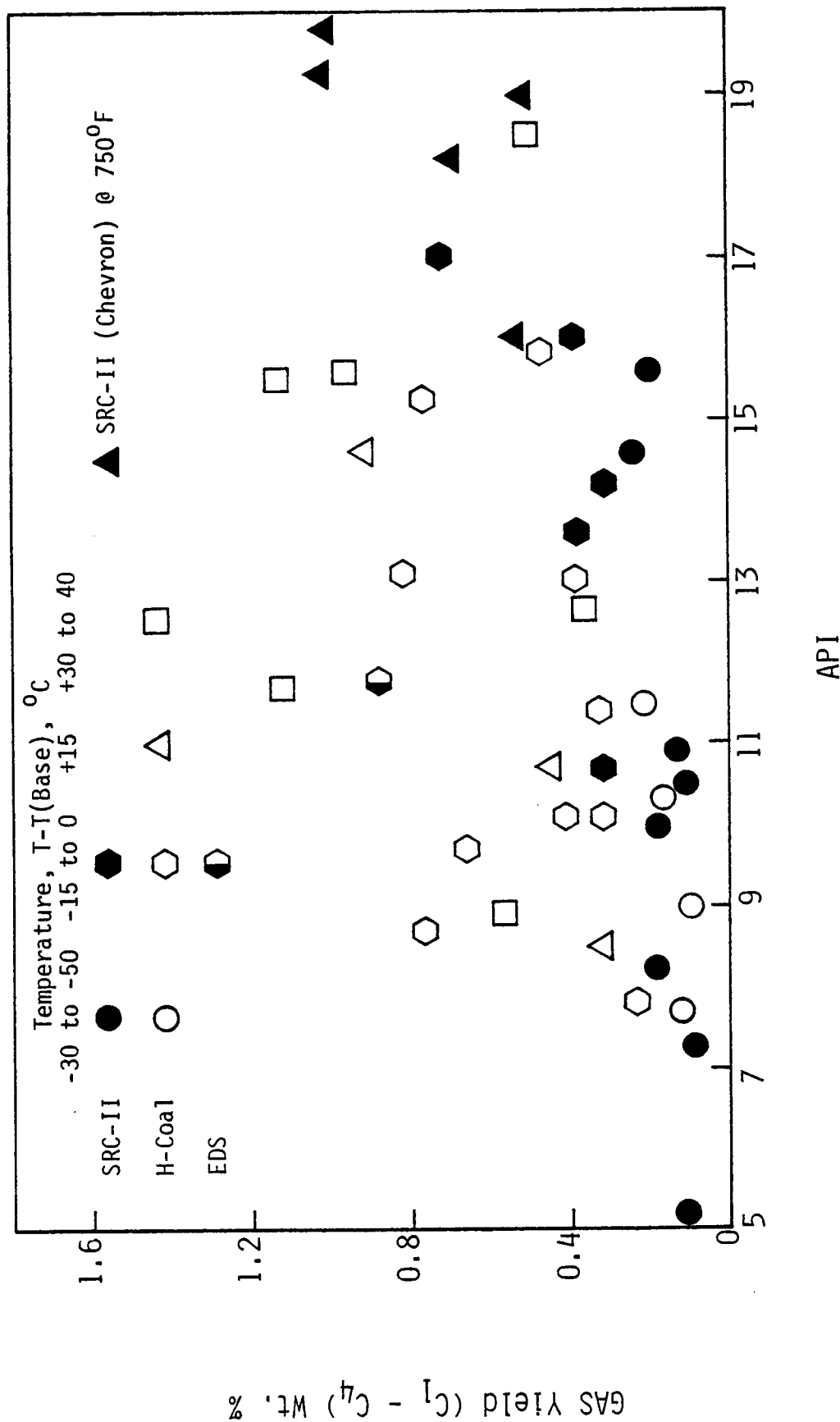


FIGURE 5.2.9 Gas yield From Some Coal-Derived Gas Oil Hydrotreating (Sullivan and Frumppkin, 1980; Tan and DeRosset, 1978b, Riedl and DeRosset, 1979b, 1979c)

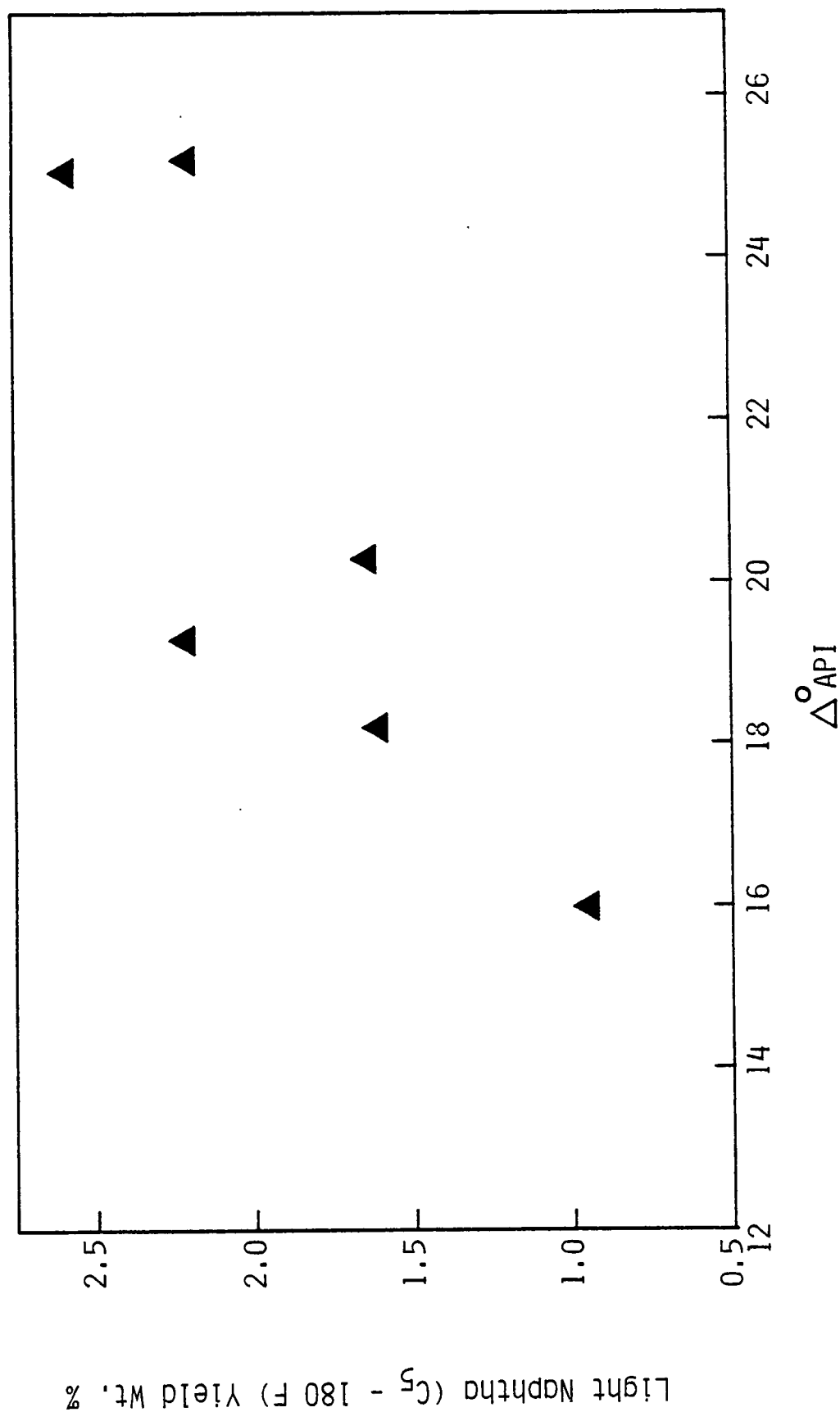


FIGURE 5.2.10 Light Naphtha Yield From Hydrotreating of SRC-II Gas Oil
(Sullivan and Frumkin, 1980)

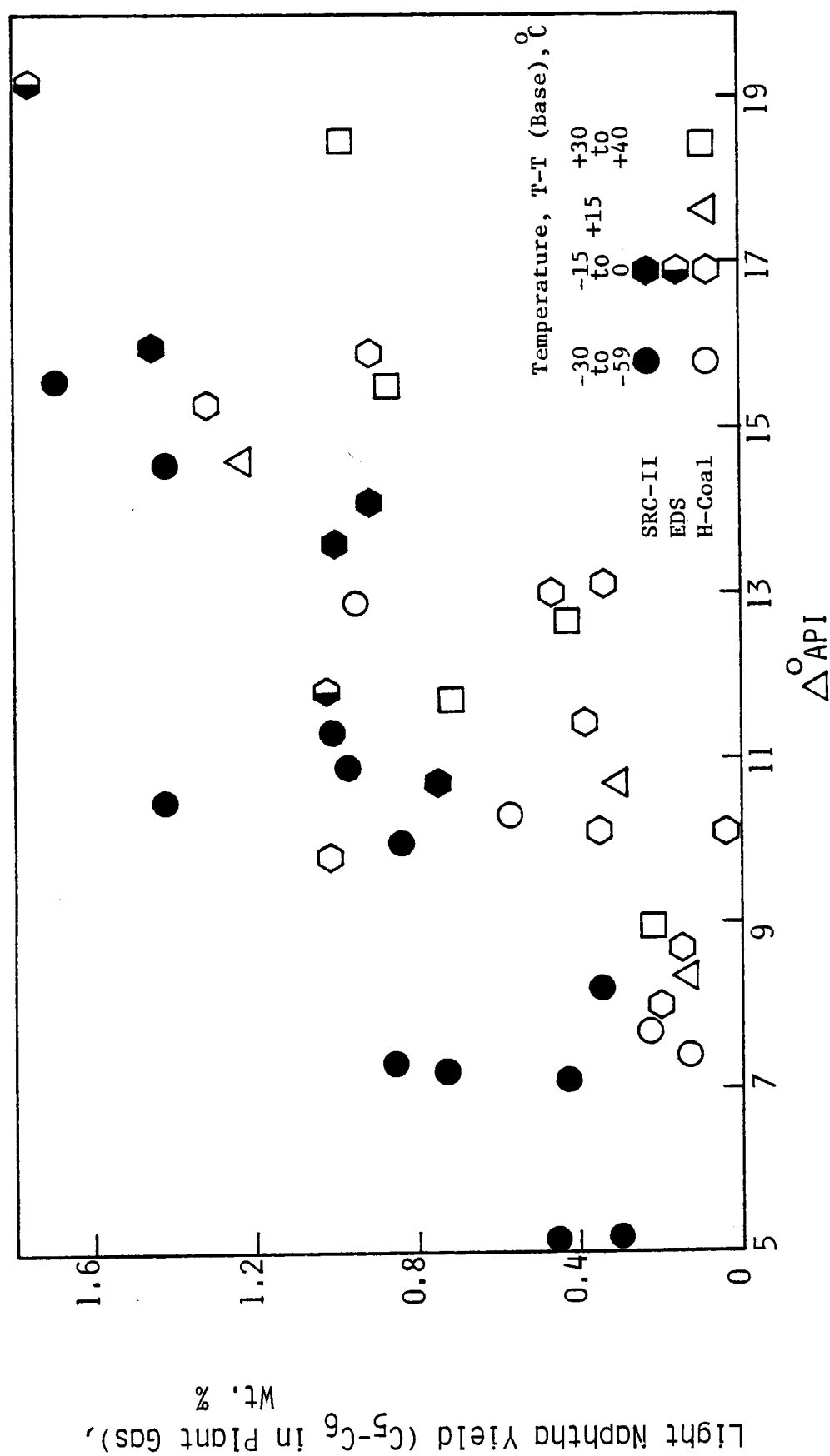


FIGURE 5.2.11 Light Naphtha Yield From Some Coal-Derived Gas Oils During Hydrotreating (Tan and DeRosset, 1978b; Riedl and DeRosset, 1979b, 1979c)

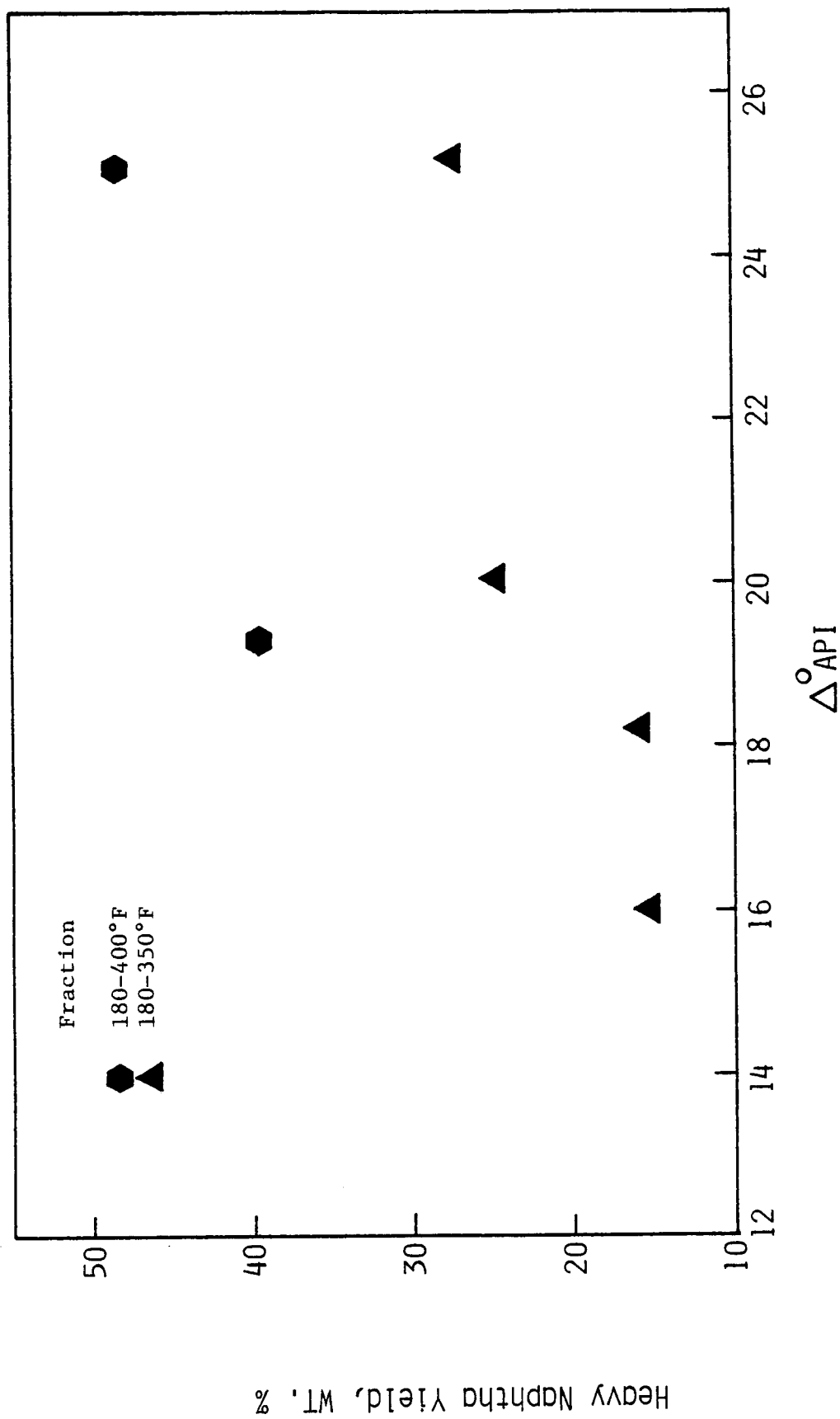


FIGURE 5.2.12 Heavy Naphtha Yield From SRC-II Gas Oil During Hydrotreating (Sullivan and Frumpkin, 1980)

model is not appropriate for this class of reactions (nitrogen removal).

A correlation between the nitrogen removal and sulfur removal data is shown in Figure 5.2.6. These results indicate that 85+ percent of the sulfur has been removed from these liquids by the time only 30 percent of the nitrogen has been removed.

The change in the gas oil API gravity with hydrogen consumption is shown in Figures 5.2.7 and 5.2.8. The UOP data, Figure 5.2.8, suggests the SRC-II liquid may be more responsive to °API change than the H-Coal product for a given value of hydrogen consumption, which may be due to the fact that the SRC-II sample was lighter at the outset.

The gas, light, and heavy naphtha yields due to gas oil hydro-testing are shown in Figures 5.2.9 through 5.2.12. The gas yield, Figure 5.2.9, tends to suggest a lower gas yield from SRC-II gas oil than the H-Coal product for a given change in API gravity, but this may be misleading, due to the fact that the SRC-II sample is of higher gravity than the H-Coal sample. Additional data or further analysis of these results would be useful for clarification of this point.

5.2.1 Physical and Thermal Property Data

Among the findings of the Econergy Associates study (1980) was the result that the heat balance of a coal-derived light gas oil, such as the SRC-II product, hydrotreating process might not close within 7 percent if designed by the use of thermal property correlations developed in the petroleum industry. Hence additional experimental data on the thermal properties of coal-derived gas oils will be required before designers can proceed with confidence in the prediction of the fuel requirements for coal derived gas oil hydrotreating plants.

5.2.2 Gas Oil Hydrotreating Assessment

The SRC-II gas oil samples which were hydrotreated by Chevron and UOP were lighter than the gas oil samples from H-Coal and EDS processes. However, the data obtained from EDS and H-Coal samples can be used to supplement the SRC-II data, especially with respect to gas yields and hydrogen consumption.

Missing are the thermal data required for reasonably precise closure of the process heat balance, although data from the petroleum industry can be used for an approximate heat balance design.

There appears to be little guidance in the literature to assist the designer to establish the extent, if any, to which the gas oil should be hydrotreated on site. The Wimen, Pelroy and Wilson (1980) results indicate that the mutagenicity of SRC-II gas oil can be reduced by 99+ percent by severe hydrotreating, but do not suggest the extent to which the mutagenicity should be reduced.

No data could be found which would allow a quantitative estimate of the degree of hydrotreating required to provide a given level of storage stability to the product.

The available hydrotreating data show that these coal-derived gas oils can be upgraded by the use of commercial technology. However, the extent to which it is useful to hydrotreat the SRC-II gas oil on site, if any, will be determined by the judgment of the designer unless additional data, particularly with respect to storage stability and allowable mutagenicity levels in these products, are forthcoming.

5.3 SRC-II WHOLE LIQUID HYDROTREATING

In addition to the hydrotreatment of the SRC-II napgtha and gas oil fractions, Chevron (Sullivan and Frumpkin, (1980) hyrdotreated

the SRC-II whole liquid product. In contrast to gas oil hydrotreating, summarized in the preceeding section, no comparable whole liquid product hydrotreating data could be found for heavier liquids, such as the Chevron SRC-II whole liquid product data.

The range in the hydrotreating processing conditions used by Chevron are shown in Table 5.3.1. These data show that hydrotreating nominal temperatures and pressures in the range of 750-775° F and 2000-2500 psi, respectively, can remove up to 99.999% of the nitrogen and up to 99.89% of the sulfur from the liquid. Space velocities required are in the range of 0.5-1.50.

The whole liquid hydrotreating data of Chevron are shown in Figures 5.3.1 through 5.3.11. The heteroatom removal data correlate well with chemical hydrogen consumptions, as can be seen in Figures 5.3.1 through 5.3.11. The heteroatom removal data correlate well with chemical hydrogen consumptions, as can be seen in Figures 5.3.1 through 5.3.3. Oxygen removal can be predicted within limits from nitrogen removal requirements, Figure 5.3.4 Figure 5.3.5 shows that 99.9+ percent of the sulfur has been removed from this liquid by the time 99 percent of the nitrogen has been removed.

The processing conditions required to achieve a given hydrogen consumption and nitrogen removal are shown in Figures 5.3.6 and 5.3.7, respectively. The data are scattered as is usual in these experiments, but can be used to establish values for the temperature, pressure, and LHSV required for a given level of nitrogen removal in the range of about 94 to 99.999 weight percent.

The change in API gravity of the liquid correlates reasonably

Table 5.3.1 SRC-II Whole Liquid Product Hydrotreating
Processing Conditions

Processing Condition or Property	Range or Value
Temperature, °F	749-776
Pressure: Total, psia	1995-2506
Hydrogen, psia	1700-2300
LHSV	0.49-1.52
Recycle Gas Rate, SCF/bbl	7,504-15,811
Hydrogen Consumption, SCF/bbl	
Gross	1,741-3,301
Chemical	1,651-3,109
Nitrogen Content of the product, ppm	0.1-560
Nitrogen Removal, Wt. %	94.28-99.999
Sulfur Content of the Product, ppm	3-100
Sulfur Removal, Wt. %	99.27-99.89
Catalysts	ICR-106 (Ni, W, Si, Al) ICR-113 (Ni, Mo, Si, Al)

Source: Sullivan and Frumppkin, 1980.

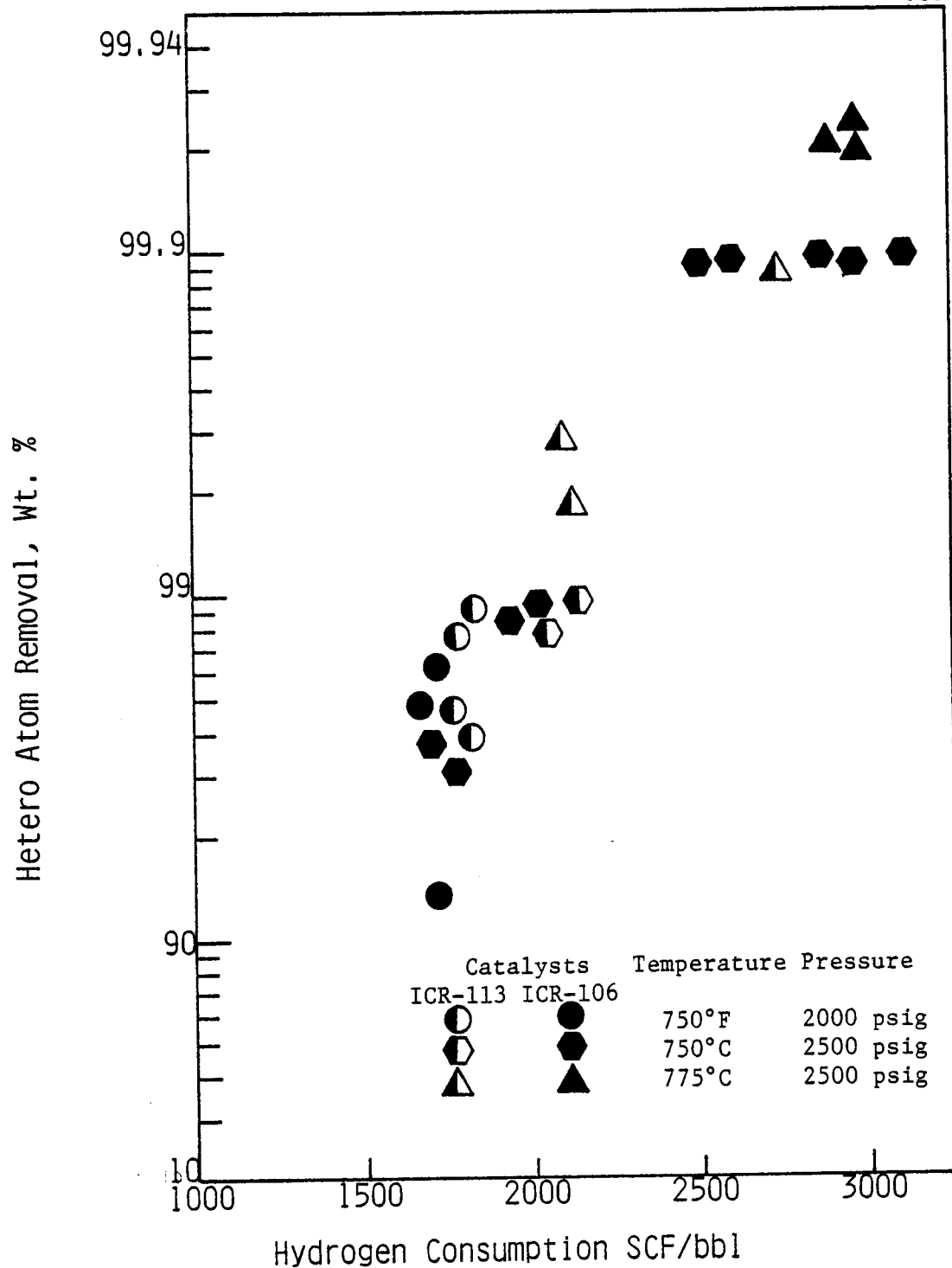


FIGURE 5.3.1 Heteroatom Removal From SRC-II Whole Liquid Product by Hydrotreating
(Sullivan and Frumpkin, 1980)

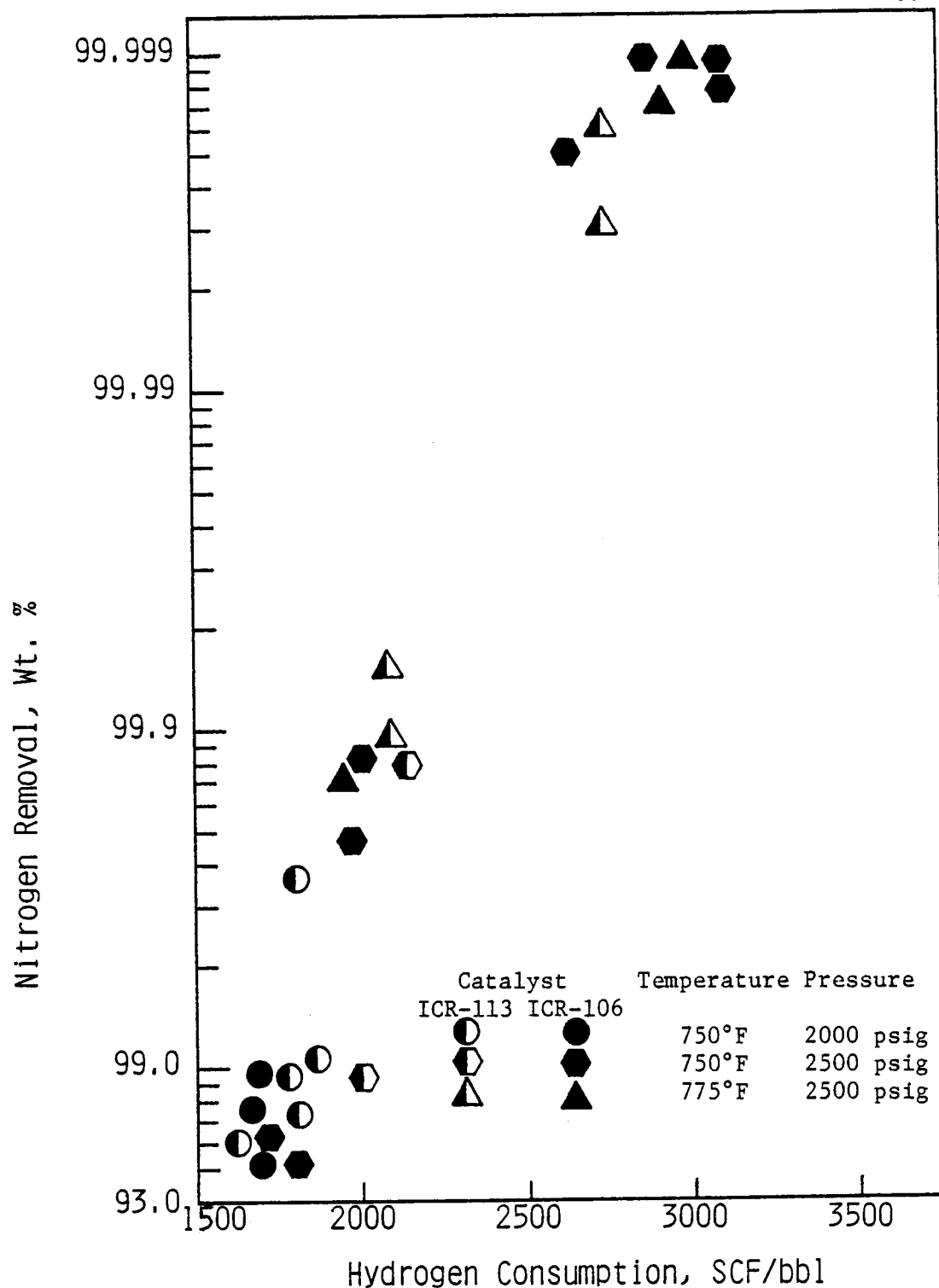


FIGURE 5.3.2 Nitrogen Removal From SRC-II Whole Liquid Product by Hydrotreating (Sullivan and Frumpkin, 1980)

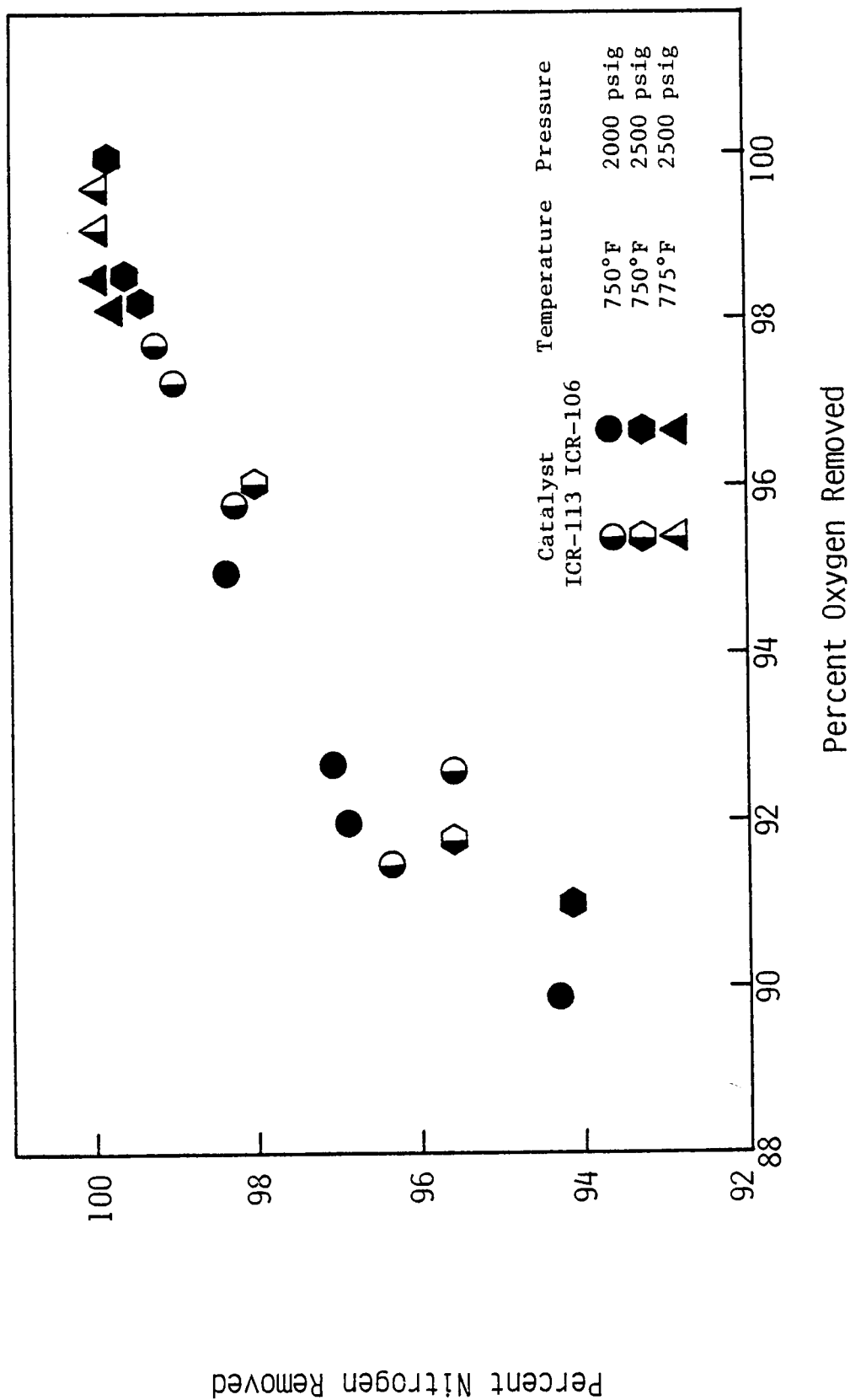


FIGURE 5.3.4 Oxygen Removal Correlation for SRC-II Whole Liquid Product
Hydrotreating
(Sullivan and Frumarkin, 1980)

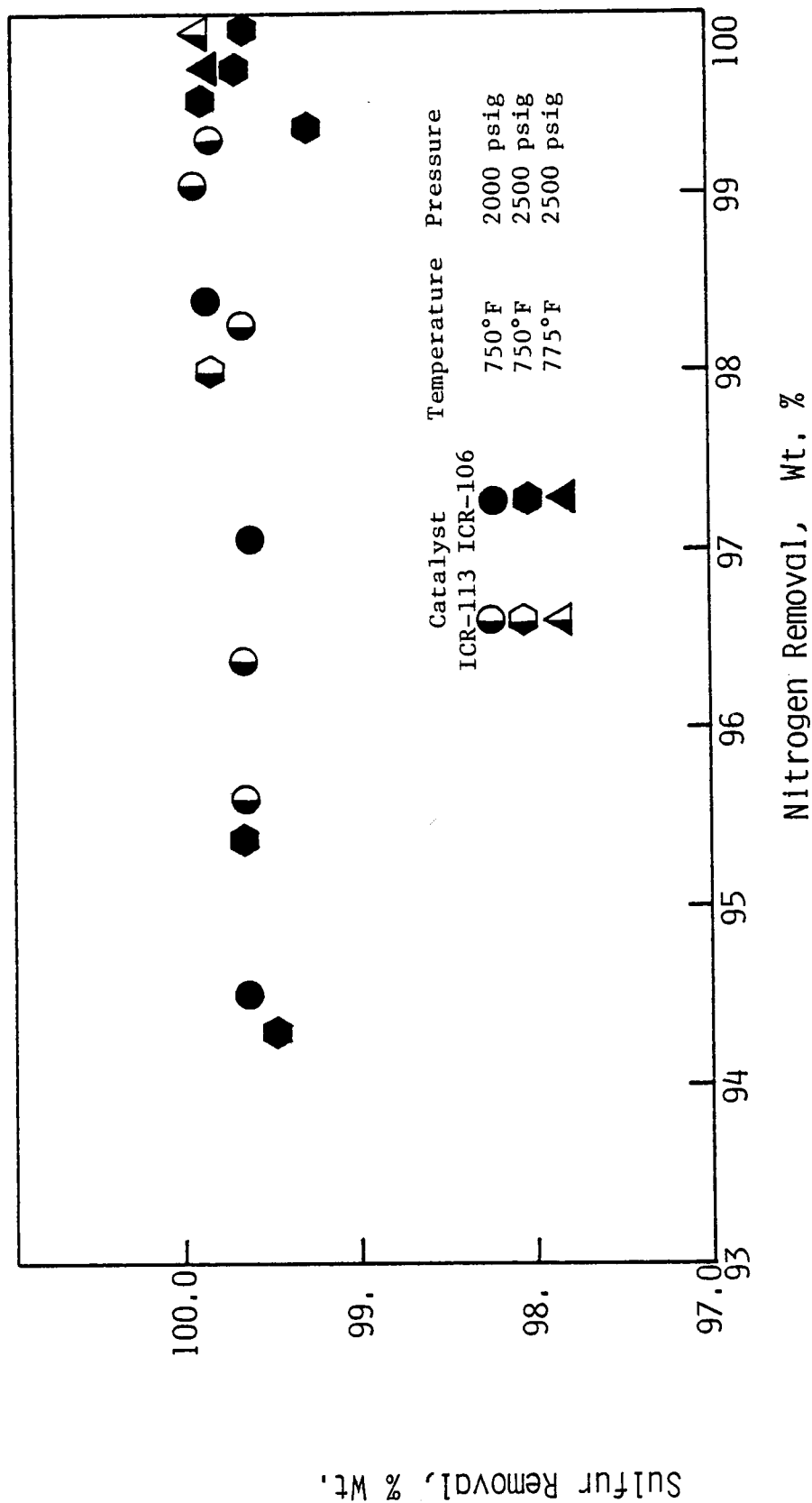


FIGURE 5.3.5 Sulfur-Nitrogen Removal Correlation for SRC-II Whole Liquid Product
Hydrotreating
(Sullivan and Frumpkin, 1980)

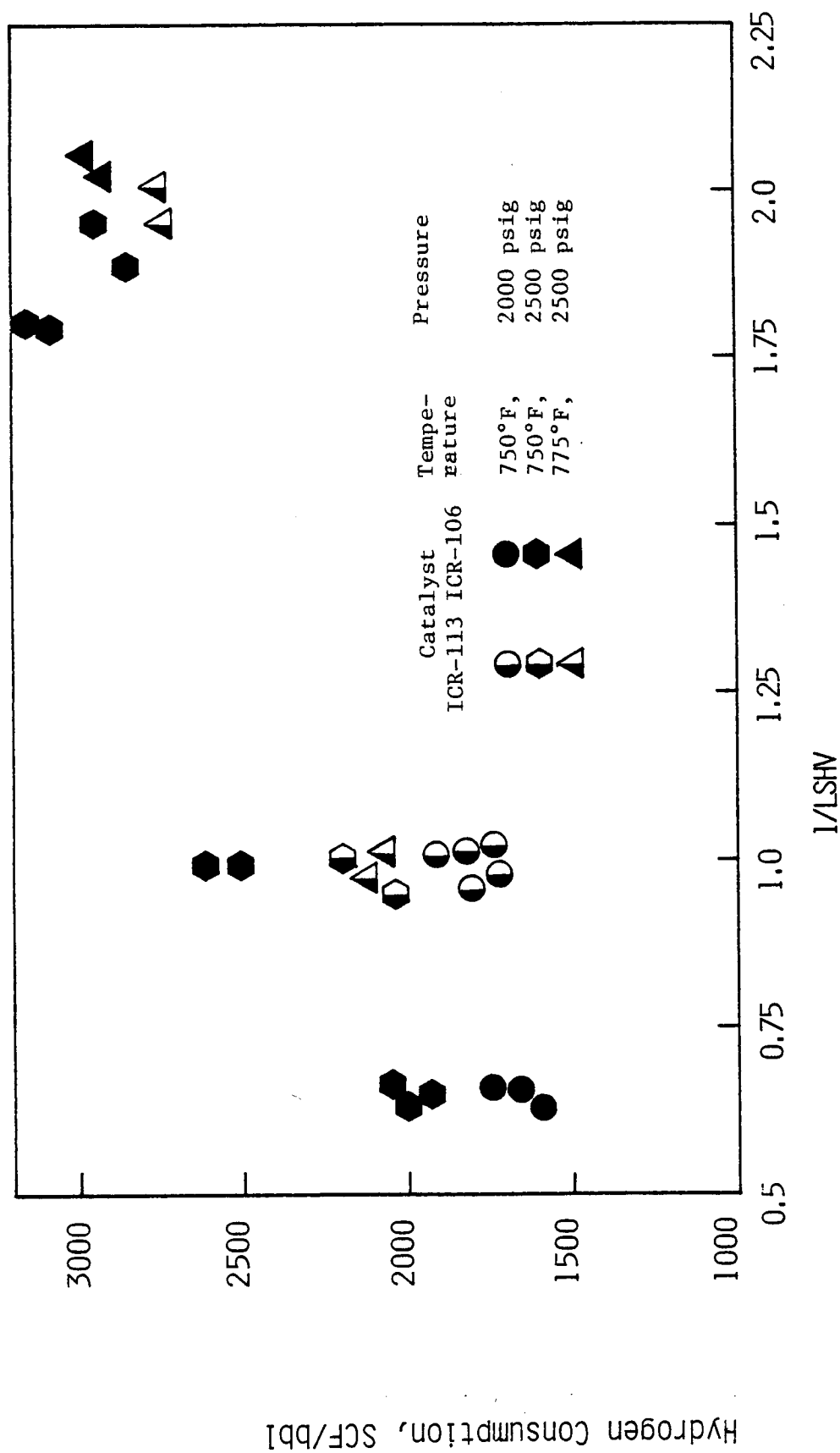


FIGURE 5.3.6 Hydrogen Consumption as a Function of Processing Conditions for SRC-II Whole Liquid Hydrotreating (Sullivan and Frumpkin, 1980)

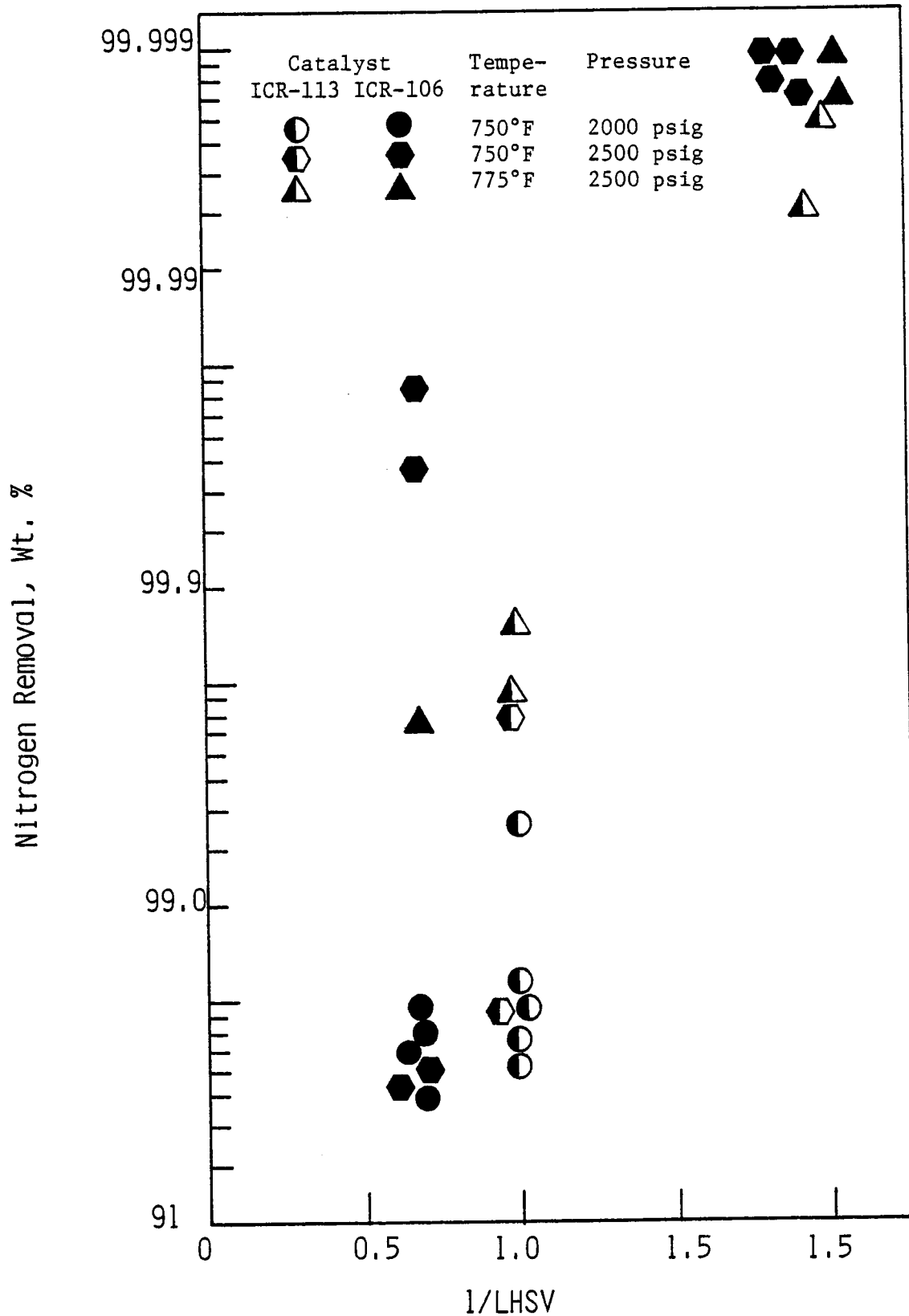


FIGURE 5.3.7 Nitrogen Removal as a Function of Processing Conditions for SRC-II Whole Liquid Hydrotreating (Sullivan and Frumpkin, 1980)

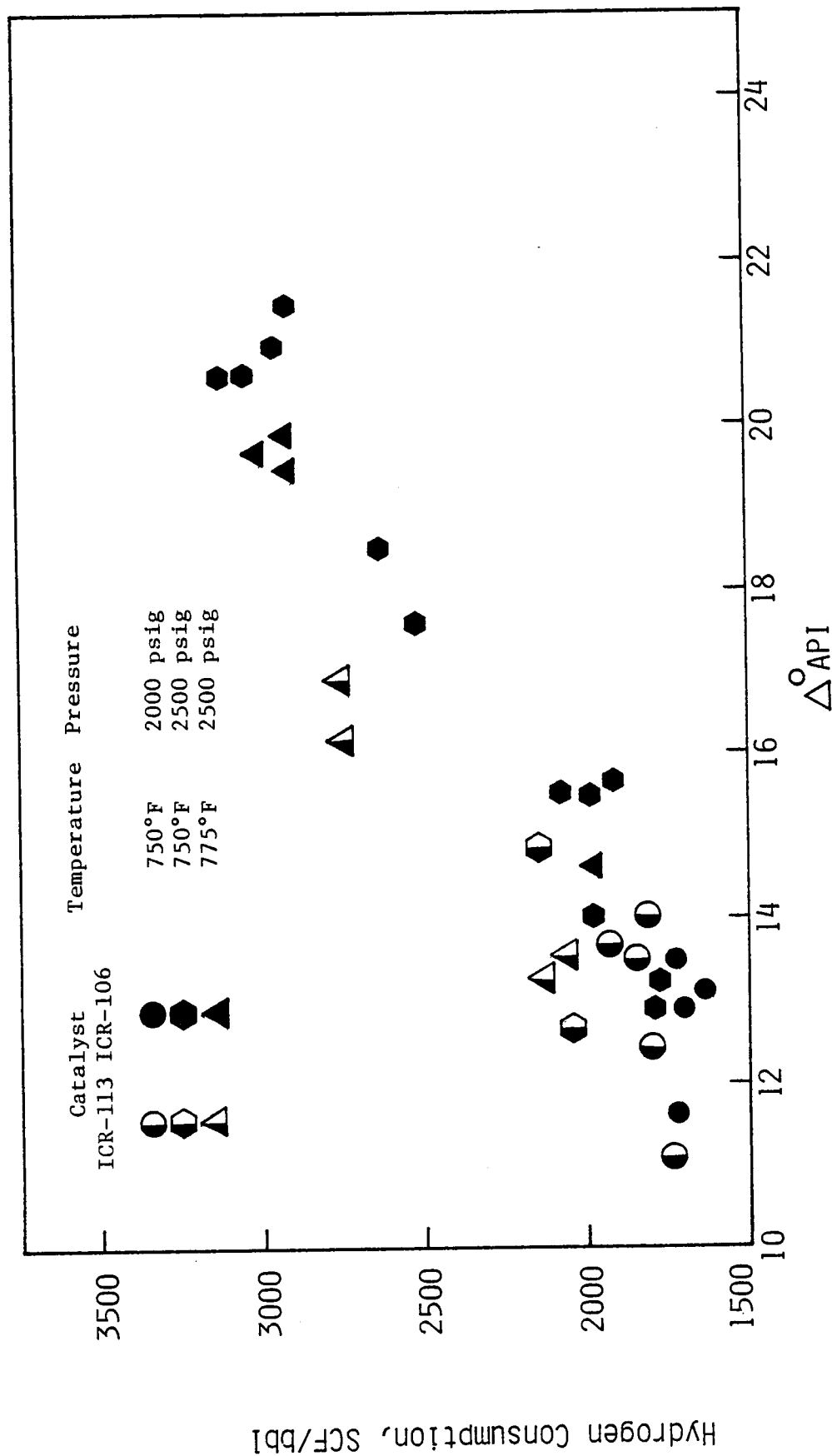


FIGURE 5.3.8 Effect of Hydrogen Consumption on Change in API Gravity of SRC-II Whole Liquid Product During Hydrotreating (Sullivan and Frumpkin, 1980)

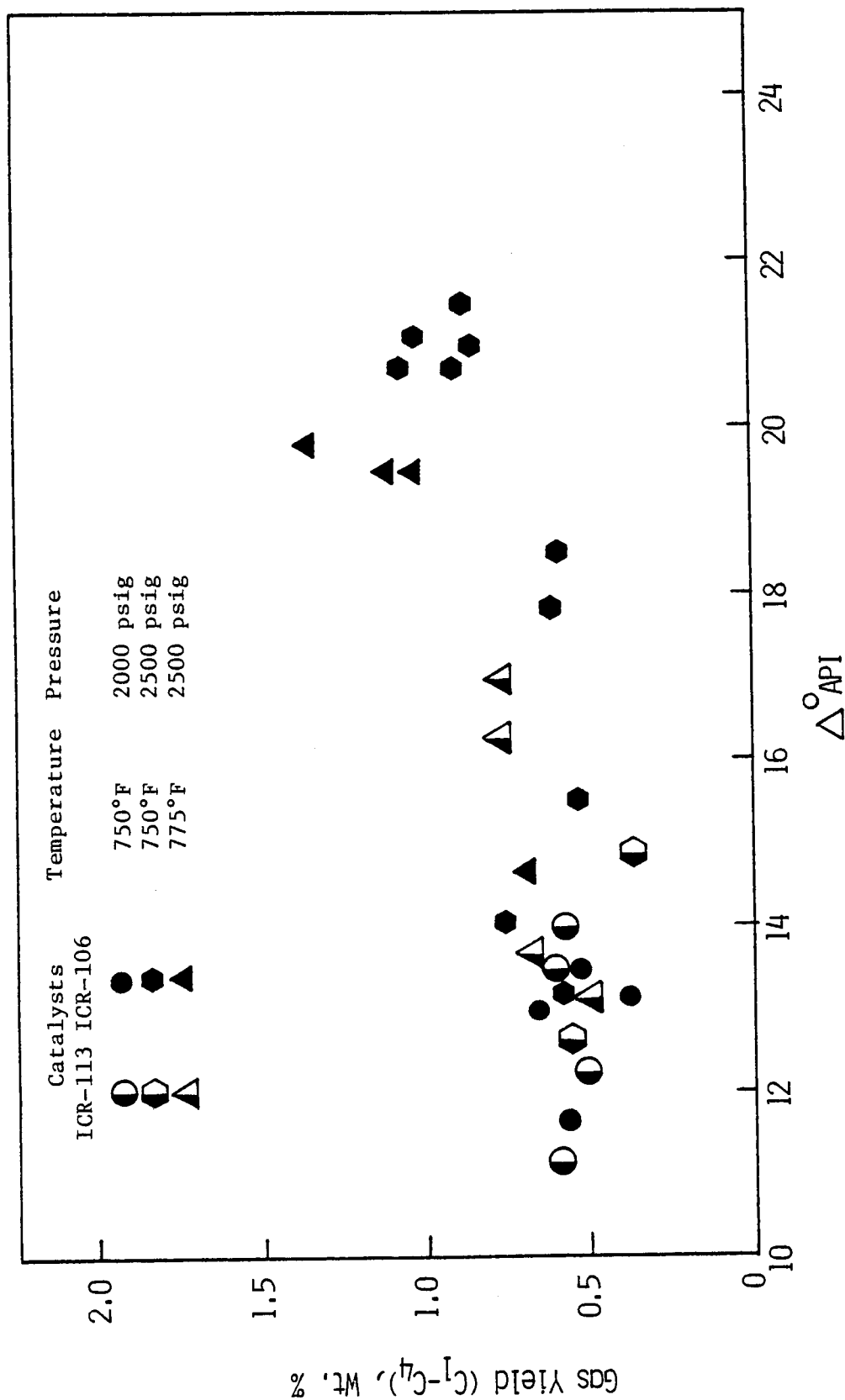


FIGURE 5.3.9 Gas Yield From SRC-II Whole Liquid Product During Hydrotreating
(Sullivan and Frumkin, 1980)

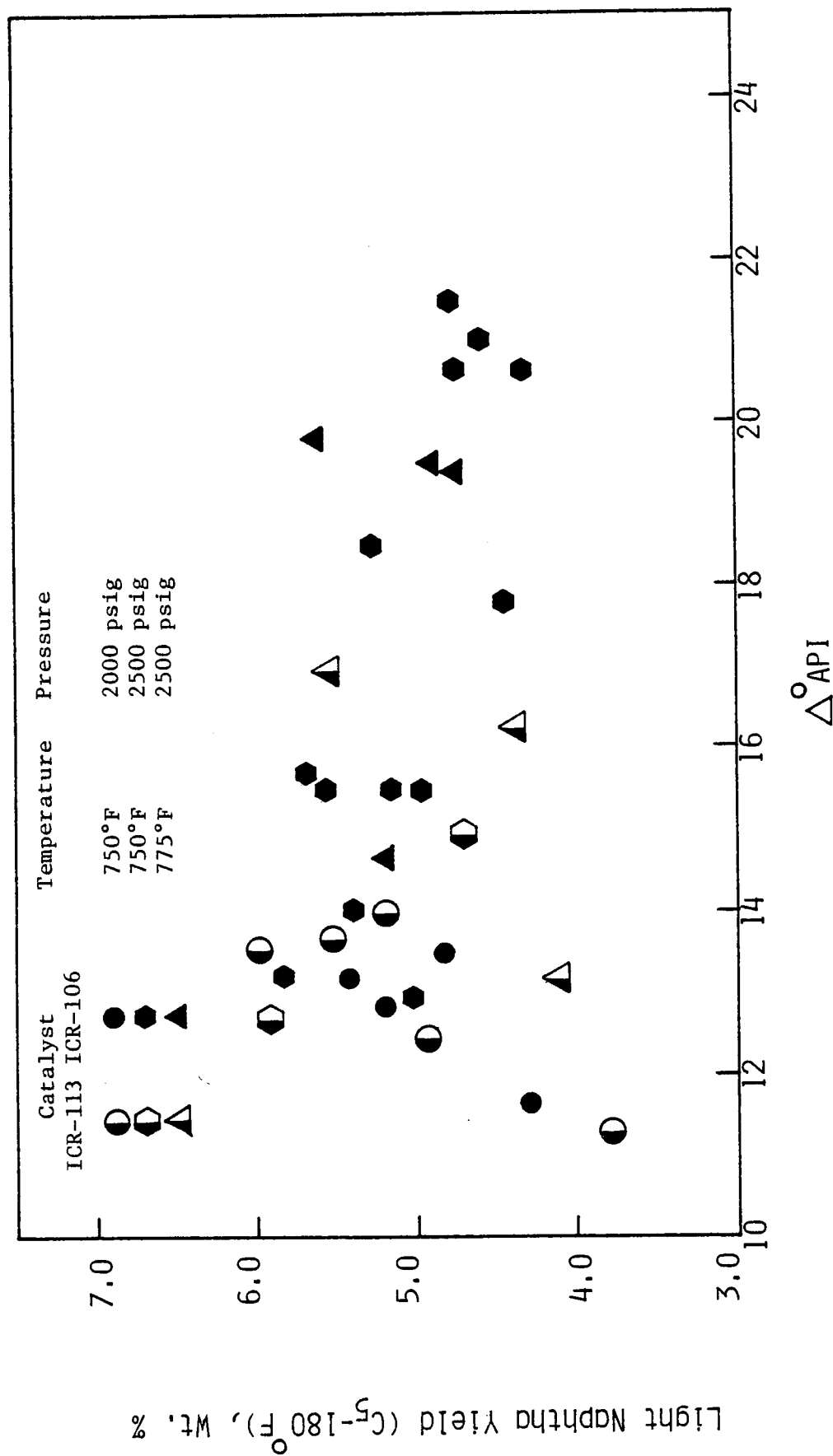


FIGURE 5.3.10 Light Naphtha Yield From SRC-II Whole Liquid Product During Hydrotreating (Sullivan and Frumpkin, 1980)

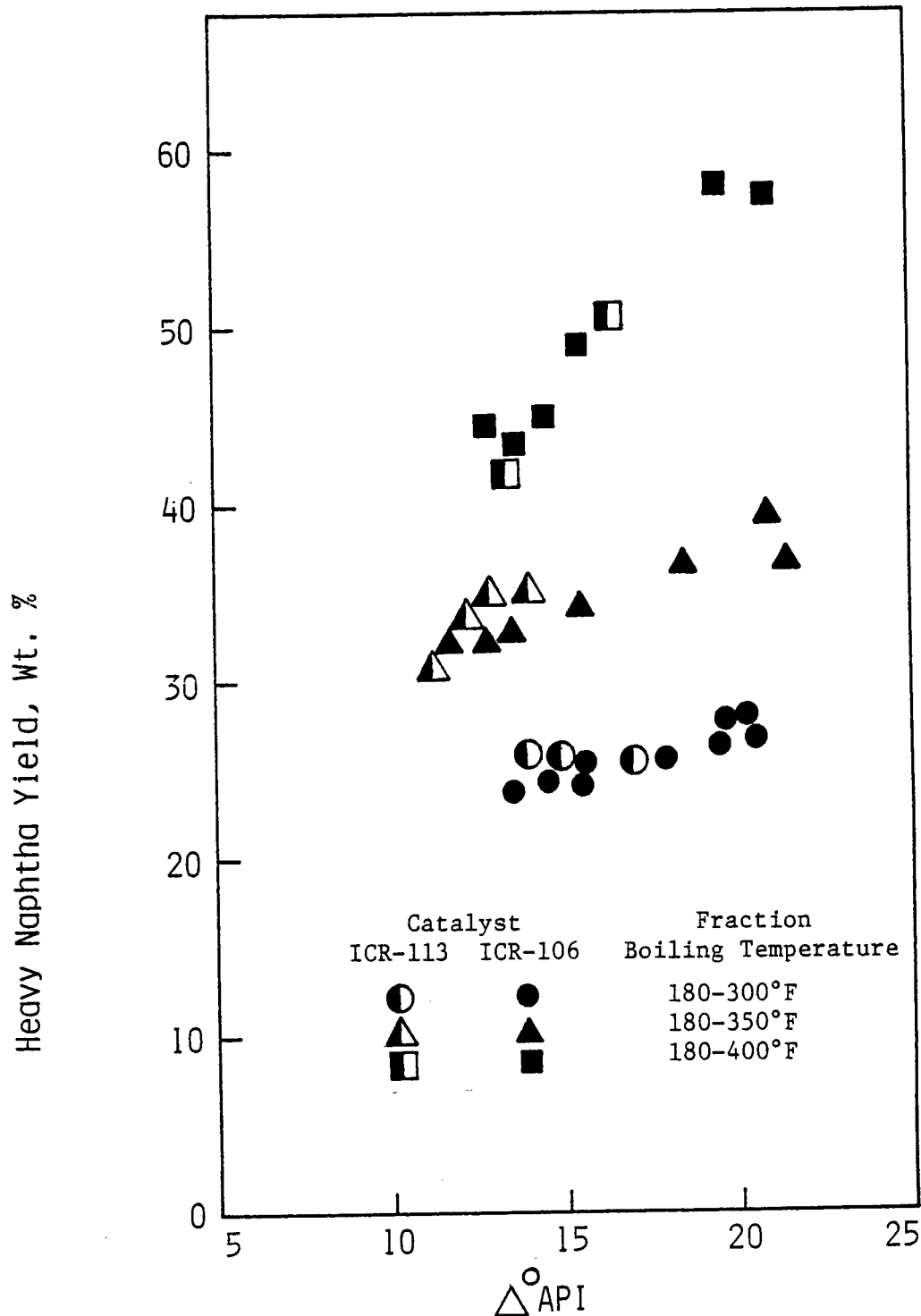


FIGURE 5.3.11 Heavy Naphtha Yield From SRC-II Whole Liquid Product During Hydrotreating (Sullivan and Frumpkin, 1980)

well with hydrogen consumption, Figure 5.3.8. The gas yield for a given change in API gravity can be estimated from Figure 5.3.9. Naptha yields are shown in Figures 5.3.10 and 5.3.11.

Although these data appear to exhibit a fair amount of scatter, the scatter is probably no worse than usual in a newly developing technology, or the application of an existing technology to a new area. Factors which can be reduced as additional data become available, can be introduced in the design process to account for the data scatter.

5.3.1 Effect of Hydrotreating on SRC-II Whole Liquid Product Bio Activity

No data could be found on the mutagenic response of the SRC-II whole liquid product. However, experts in this area might be able to make an assessment of this response on the basis of the SRC-II mutagenic response data, in view of the fact that the nitrogen content of the naptha fraction of the product should be essentially depleted of nitrogen under the relatively severe hydrotreating conditions used for the whole liquid product.

5.3.2. Effect of Hydrotreating on SRC-II Whole Liquid Product Storage Stability

Again, data were not found which would indicate the extent to which this liquid is stabilized in time as a function of hydrogen added during hydrotreatment. There is apparently no quantitative way to establish the level of hydrogen addition required to produce a given extent of stabilization.

5.3.3 Physical and Thermal Property Data

The situation here appears to be the same as for the other coal-derived liquid fractions. Based on the Econergy Associates study (1980), we conclude that the hydrotreating heat balances can be off as much as 7 percent, based on the use of thermal property correlations from the petroleum industry.

5.3.4 SRC-II Whole Liquid Hydrotesting Assessment

The SRC-II whole liquid product can be hydrotreated by commercial technology up to chemical hydrogen consumptions of about 3,100 SCF/bbl. This level of hydrotreatment can remove as much as 99.999 percent of the nitrogen and 99.89 of the sulfur, from the pilot plant SRC-II samples. The heteroatom removal data provide reasonably good correlation with hydrogen consumption, as well as the change in API gravity. The lack of thermal property data may introduce errors in the process heat balances by as much as about 7 percent, according to a previous study by Econergy Associates (1980). Mutagenic response test data for the whole liquid were not found, but it should be possible to make at least approximate estimates based on the Weimer, Pelroy and Wilson (1980) data on the SRC-II gas oil.

Stability data as a function of hydrogen added during hydro-treatment are not available. There appears to be no quantitative criteria which a designer can use to establish the extent to which this material should be hydrotreated, if at all, on site. In spite of these shortcomings, however, a hydrotreating process for the whole liquid product could probably be designed for a pilot plant, recognizing that the gas yields and thermal balances may contain a moderate amount

of error. The hydrotreating experience on the heavier gas oils, such as the EDS and the H-Coal products can supplement the SRC data through appropriate correlations.

6. CONCLUSION

Although sparse in some instances there is a growing data base in the literature dealing with heteroatom removal from coal liquids by the use of conventional petroleum hydrotreating technology. The data available are primarily for liquids derived from Illinois No. 6 and Pittsburgh Seam Coals, that is, bituminous coals. Generally, more severe conditions are required for processing coal-derived liquids to remove the sulfur, nitrogen and oxygen than petroleum liquids. Hydrogen consumption is generally considerably higher in coal liquid hydrotreating than petroleum hydrotreating, due primarily to the greater aromaticity. For example, for coal-derived naphthas, to remove the nitrogen content to the range of a few tenths of a part per million, the level required for reformer feed stocks, hydrogen consumption are required in the range of 560 to 1,100 scf/bbl of naphtha.

A limited amount of kinetic modelling has been done for the hydrotreating process, based primarily on the data for coal liquids derived by the SRC-II and H-Coal processes, on catalysts composed of Co-Mo and Ni-Mo metals on Alumina. Some of the main results obtained from the kinetic model are as follows:

- For heteroatom removal, the reaction is second order with respect to the concentration of heteroatom in the coal liquid. Also the reaction is Nth order with respect to hydrogen pressure, while "N" is in the range of 0.84 to 1.49.
- For reduction in aromaticity of the coal liquids, the rate of conversion of aromatic carbon atoms is first order in

aromatic carbon concentration and Nth order in pressure, with "N" being very nearly equal to one.

The data also suggests that liquids derived from three major processes under development at this time, EDS, H-Coal, and SRC-II, and from different bituminous coals, may respond to hydrotreating in similar ways. That is the data for the different liquids appear to correlate. Should this be verified by further experimental data and model development, will mean that hydrotreating of one liquid could very well be used to predict the hydrotreating response of other liquids. However, whether or not such modelling and predictions can be extended to liquids derived from coals of different ranks is unknown at this time.

Some catalysts which have been shown to be useful for hydrotreating are different combinations of Co-Mo-Ni and W on silica alumina. The life of hydrotreating catalysts is an unknown factor at this time. Additional testing will be required to establish effective catalyst life time, but initial indications are that life will be less for coal liquids than the life of same catalyst for petroleum liquids, due primarily to the higher metals (ash) content of coal-derived liquids compared with most petroleums.

Coal-derived naphthas can be readily hydrotreated and reformed to produce high octane (90-100 RON) gasoline blending stocks. Also the aromaticity of gas oils can be reduced by hydrotreating, but there still may be a problem meeting existing smoke point specifications for jet and diesel fuels.

7. RECOMMENDATIONS

In view of the fact that the several coal-derived liquids appear to correlate, the kinetic modelling work should be extended to include the recent data for EDS, H-Coal and SRC-II liquids.

The data base collected here should be updated periodically in view of the fact that data is still being generated by various investigators.

A similar data base and kinetic modelling study should be initiated for hydrocracking and reforming process data.

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