Upgrading solvent refined coal by catalytic hydrotreatment
by An-Gong Yeh

A thesis submitted in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY in Chemical Engineering
Montana State University
© Copyright by An-Gong Yeh (1981)

Abstract:
Catalytic hydrotreatment was performed to upgrade SRC-II Vacuum Flash Feed (VFF) and Light Ends Column Feed (LECF) which were produced from the Pittsburg and Midway Coal Mining Company's SRC-II pilot plant.

The liquid products were analyzed for sulfur and nitrogen content. The distillation yields were also determined.

The statistical studies on the metal effects showed that Co, Mo, and W significantly increased the catalyst activity for the denitrogenation of both SRC-II coal liquids. The adding of Ni appeared to be ineffective. The effect of Co and Mo on the desulfurization of LECF was positive. The effect of Mo and W on the desulfurization of VFF was also positive but Co was negative. The interaction between Co and Mo gave a negative effect on the denitrogenation of both liquids and on the desulfurization of LECF. The interactive effects of Co-W and Mo-W were negative for the SRC-II VFF denitrogenation and desulfurization, respectively.

The catalyst deactivation was observed and moderated by starting at a lower temperature and higher space velocity. The catalyst was poisoned by the carbon laydown, whose mechanism appeared to be pore mouth plug-up.

Catalyst C-49 with metal combination of 4% CoO, 8% MoO3, 1% NiO, and 8% WO3 proved to reduce the nitrogen content to as low as 0.3 wt% for 104 hours with an average liquid product recovery of 91 wt%. The yield of 50-204°C boiling range gasoline was 40% of the liquid product, whose octane tests gave an average octane number of (Research + Motor)/2 = 81.7.

UPGRADING SOLVENT REFINED COAL BY CATALYTIC HYDROTREATMENT

by

AN-GONG YEH

A thesis submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemical Engineering

Approved:

Chairperson, Graduate Committee

Head, Major Department

Graduate Dean

MONTANA STATE UNIVERSITY
Bozeman, Montana

December, 1981

ACKNOWLEDGMENTS

The author wishes to thank the staff of the Chemical Engineering Department at Montana State University for their help. A special thanks goes to Dr. Lloyd Berg and Dr. F. P. McCandless for their guidance and encouragement with this research.

The author would like to extend his thanks to the United States Department of Energy for the financial support that made this research possible.

Special appreciation goes to Lyman Fellows for his help in the maintenance of equipment. The author would like to thank Professors J. R. Anderson and G. J. Lapeyre of the Physics Department at Montana State University for helping with surface analysis. many thanks must go to Mr. J. W. Berg of CENEX, Mr. H. Beuther of Gulf, and Mr. N. F. Boyd of Dravo Engineers and Constructors for their information supply.

The author is grateful to Hou-Yen Hsieh, M. Rameswaran, and David Nickelson for their help with the analytical work.

Finally, a special thanks goes to the author's wife, Yen-Ching, for her patience and help with typewriting.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Catalytic hydrotreatment was performed to upgrade SRC-II Vacuum Flash Feed(VFF) and Light Ends Column Feed(LECF) which were produced from the Pittsburg and Midway Coal Mining Company's SRC-II pilot plant.

The liquid products were analyzed for sulfur and nitrogen content. The distillation yields were also determined.

The statistical studies on the metal effects showed that Co, Mo, and W significantly increased the catalyst activity for the denitrogenation of both SRC-II coal liquids. The adding of Ni appeared to be ineffective. The effect of Co and Mo on the desulfurization of LECF was positive. The effect of Mo and W on the desulfurization of VFF was also positive but Co was negative. The interaction between Co and Mo gave a negative effect on the denitrogenation of both liquids and on the desulfurization of LECF. The interactive effects of Co-W and Mo-W were negative for the SRC-II VFF denitrogenation and desulfurization, respectively.

The catalyst deactivation was observed and moderated by starting at a lower temperature and higher space velocity. The catalyst was poisoned by the carbon laydown, whose mechanism appeared to be pore mouth plug-up.

Catalyst C-49 with metal combination of 4% CoO, 8% MoO_3, 1% NiO, and 8% WO_3 proved to reduce the nitrogen content to as low as 0.3 wt% for 104 hours with an average liquid product recovery of 91 wt%. The yield of 50-204^{o}C boiling range gasoline was 40% of the liquid product, whose octane tests gave an average octane number of (Research + Motor)/2 = 81.7.

INTRODUCTION

The United States is second in the world in estimated total coal resources with 3,600 billion metric tons. Of this vast amount, approximately 200 billion metric tons are estimated to be currently economically recoverable coal reserves(1). At the forecasted mining rate for 1980 of 695 million metric tons, this represents a 287 year supply(2). With the supply of petroleum becoming limited and its price increasing, coal has the potential to be converted to liquid and gaseous fuels.

Several processes have been developed for the liquefaction of coal. They can be grouped into three general categories: pyrolysis, extraction-hydrogenation, and indirect liquefaction. The Pittsburg and Midway Coal Mining Company(P&M), a wholly owned subsidary of Gulf Oil Corporation, has developed the Solvent Refined Coal(SRC-II) process as one of the extraction-hydrogenation processes to an advanced stage(3). It converts high-sulfur coal to distillate liquids, naphtha, and light hydrocarbons. Their chemical compositions and certain physical properties are considerably different from petroleum products. The carbon to hydrogen ratios are considerably higher than those for petroleum crudes and fuels. The concentration

of heteroatoms such as nitrogen and sulfur are also much higher than petroleum. Coal liquids from the SRC-II process need a secondary hydrotreatment to upgrade these liquids.

It is the objective of this research to develop a catalyst to upgrade SRC-II products into clean distillate fuels through the catalytic hydrotreatment.

BACKGROUND

Coal Structure

Coal is composed principally of organic substances, subordinately of minerals, and containing water and gases in submicroscopic pores. Coal is not a uniform mixture of carbon, hydrogen, sulfur, nitrogen, and minor proportions of other elements. Rather, it is an aggregate of high-molecular compounds differing in several proportions and in the structures. The examination of the coal molecule has been hampered by the inability to find techniques which characterize such large complex structure. This is reflected in the diversity of models proposed for coal molecular arrangement(4-9). Figure 1 shows the coal structure proposed by Hill and Lyon(8).

Mineral coals contain hundreds and even thousands of atoms in a single molecule with a multiple repetition of the basic structural grouping of atoms. The basic skeleton of coal can be visualized as a condensed aromatic carbon-atom lattice, surrounded by a typical fringe formed by molecules of the side groups. The nucleus, based on the benzene ring, possesses the highest bond strength and the highest thermal stability, whereas the surrounding side groups are hydrocarbons of different

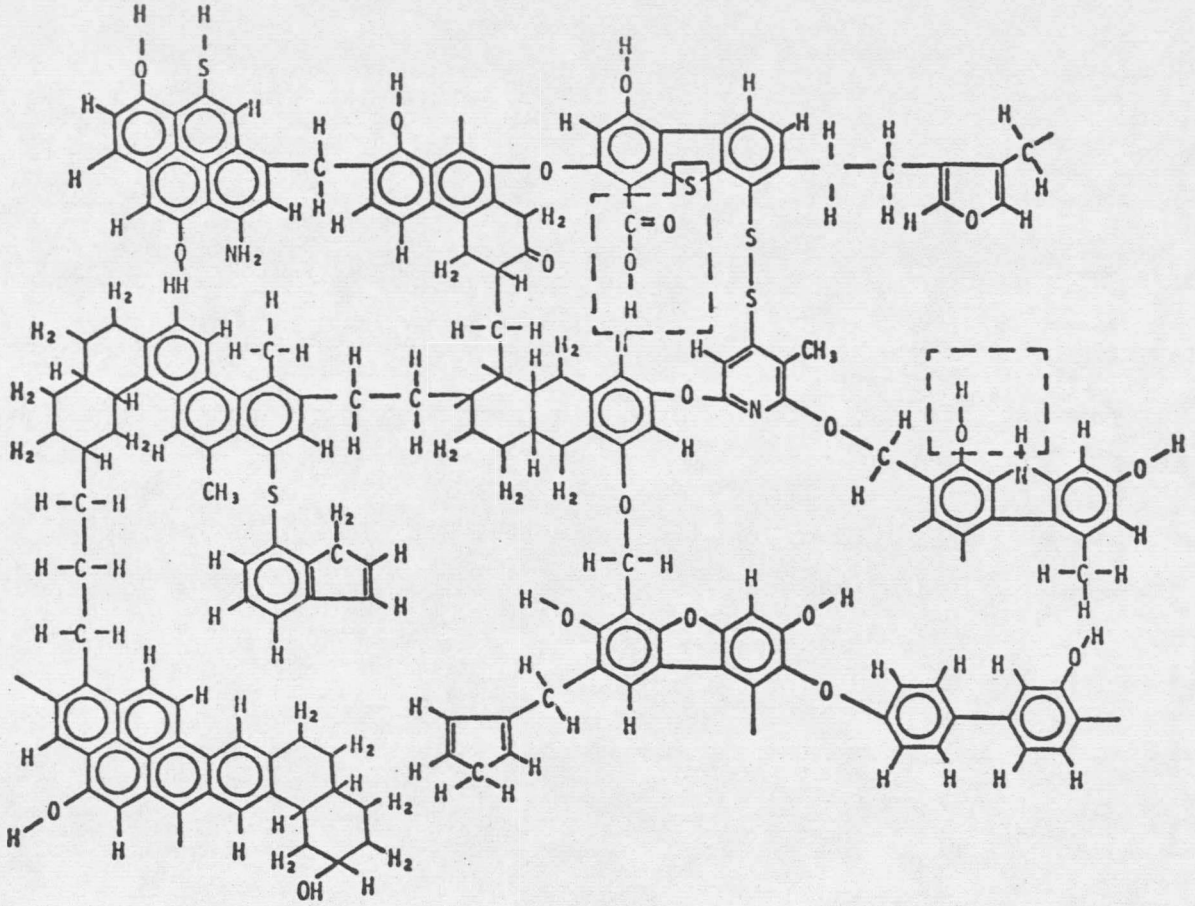

FIGURE 1. Coal Structure

degree of polymerization, of relatively low stabilities, decreasing from the center of the macromolecules to its periphery.

The organic constituents of coal are usually described in terms of its elementary composition, i.e. the percentage contents of carbon, hydrogen, oxygen, nitrogen, and sulfur. Coals with identical contents of carbon, hydrogen, and oxygen in their organic fraction may still differ in their properties. Notwithstanding, the elementary composition assists in the evaluation of the chemical nature of coal. The average elementary composition of different fuels in Table I shows that the gradual transitions from wood to anthracite occuring in nature can be arranged in a definite sequence according to the degree of carbonification.

Table I

Average elementary composition of different fuels

Fuel	Elementary composition of organic mass, %		
	C	H	O + N
Wood	44	6.0	50.0
Peat	59	6.0	35.0
Brown Coal	70	5.5	24.5
Bituminous coal.	82	5.0	13.0
Anthracite	95	2.0	3.0

Conversion of Coal to Oil and Gas

It is very difficult to use coal directly to supplant oil and natural gas in most of their usages, coal must be gasified or liquefied to offer the potential of substituting. The major difference between coal and petroleum is the ratio of hydrogen to carbon and the ash content. Coal has an atomic hydrogen to carbon ratio of approximately 0.8, while the ratio for oil is of the order of 1.8. Coal has an ash content that can be as high as 15%, whereas oil seldom has over a few tenths of a percent. The problem in coal conversion processes is to increase the hydrogen content of the material and to eliminate the ash.

The concept of coal gasification is an old one. A so-called gas producer was placed in operation as early as 1840(4). Prior to the discovery and widespread use of natural gas, manufactured or "town gas" was made from coal by a number of different gasification processes. However, most of these operated at atmospheric pressure, and recent development work has been directed toward high pressures and more efficient equipment. Coal gasification may be carried out with one of three objectives: to make low-Btu

gas; medium-Btu gas; or high-Btu gas(10). The low-Btu gas known as power gas shows its great potential for use in steam power plants and in gas turbines. The medium-Btu gas known as industrial gas or syngas is suitable for industrial use. Only the high-Btu gas is suitable for transmission in long pipelines so as to be called pipeline gas. The overall efficiency of a pipeline gas gasifier is low, the cost of pipeline gas is expected to be materially higher than other types of gas produced from coal and very much higher than the present cost of natural gas and probably even higher than the cost of natural gas a decade from now(11).

Liquid fuel from coal was first produced in the early 1900s. Coal liquefaction processes can be classified as pyrolysis, extraction-hydrogenation, and indirect liquefaction processes(12,13). In the indirect liquefaction process, the coal is first gasified and the gases are then converted to liquids. It was first developed as the Fischer-Tropsch process in Germany prior to World War II, and has been operated since 1955 in South Africa as the "SASOL" process. The process is somewhat less efficient because it is two-step conversion. The pyrolysis method

is to heat the coal in the absence of air, thus driving off the volatile matter. The volatile matter may be cleaned, the sulfur removed, and then hydrogenated to produce coal liquid. The liquid yield of pyrolysis process is as low as 25 percent. In the extraction-hydrogenation processes, a hydrogen-rich liquid solvent is added to the coal. The solvent can act as hydrogen "donors," that is, it can absorb hydrogen and in turn donate the hydrogen to the coal. Usually the use of added catalyst speeds up the reaction and improves process efficiency.

There are more than 30 gasification processes and more than 20 liquefaction processes that are currently being developed. Seven different extraction-hydrogenation processes are currently being carried out forward to the demonstration stage shown in Table II(13). Two have already been started up: the H-coal project and the Exxon Donor-Solvent(EDS) project. A German plant, using Bergius-Pier Process, is to be started up soon (13). Other two plants that are somewhat further down the road are Supercritical Gas Extraction(SGE) and Liquid Solvent Extraction(LSE) by National Coal Board in

Table II

Coal Liquefaction processes in the demonstration stage

General Type and Company	Process	Coal Feed, ton/d	Status
Extraction-Hydrogenation			
International Coal Refining Co. Newman, Kentucky	SRC-I	6,000	Detailed Engineering Stage.
Pittsburg and Midway Morgantown, West Virginia	SRC-II	6,000	Started construction recently.
National Coal Board, U.K. Point of Ayr, North Wales	SGE	25	Designs Essentially Complete; Decisions on Construction Expected Soon.
National Coal Board, U.K. Point of Ayr, North Wales	LSE	25	
Exxon Baytown, Texas	EDS	250	Coal Started in July, 1980.
Ashland Synthetic Fuels, Inc. Catlettsburg, Kentucky	H-Coal	600	Coal Started in May, 1980.
Ruhrkohle- Vega Bottrop, West Germany	Bergius-Pier	200	To be started up soon

the U.K. Two much larger demonstration plants are planned for SRC-I and SRC-II processes, the SRC-I by International Coal Refining in Newman, Kentucky, and the SRC-II by Pittsburg and Midway in Morgantown, West Virginia. However, current political and economic conditions could result in significant changes.

SRC II Process

Of major concern to this research is the SRC-II process operated by Pittsburg and Midway Coal Mining Company. A fifty ton per day pilot plant is being operated at Fort Lewis, Washington. Pulverized raw coal is dissolved in a process-derived slurry product in the presence of hydrogen at elevated temperature and pressure. The hydrogenation and hydrocracking of coal are enhanced by the catalytic activity of the inorganic matter contained in the recycle slurry as well as the inorganic matter in the feed coal. A flow diagram of the SRC-II process is shown in Figure 2(14). The hydrocracking reactions occur primarily in the reactor. Coal is converted to liquid and gaseous products; most of its ash and much of its sulfur settle out and can be removed by filtration. The reactor effluent flows through a series

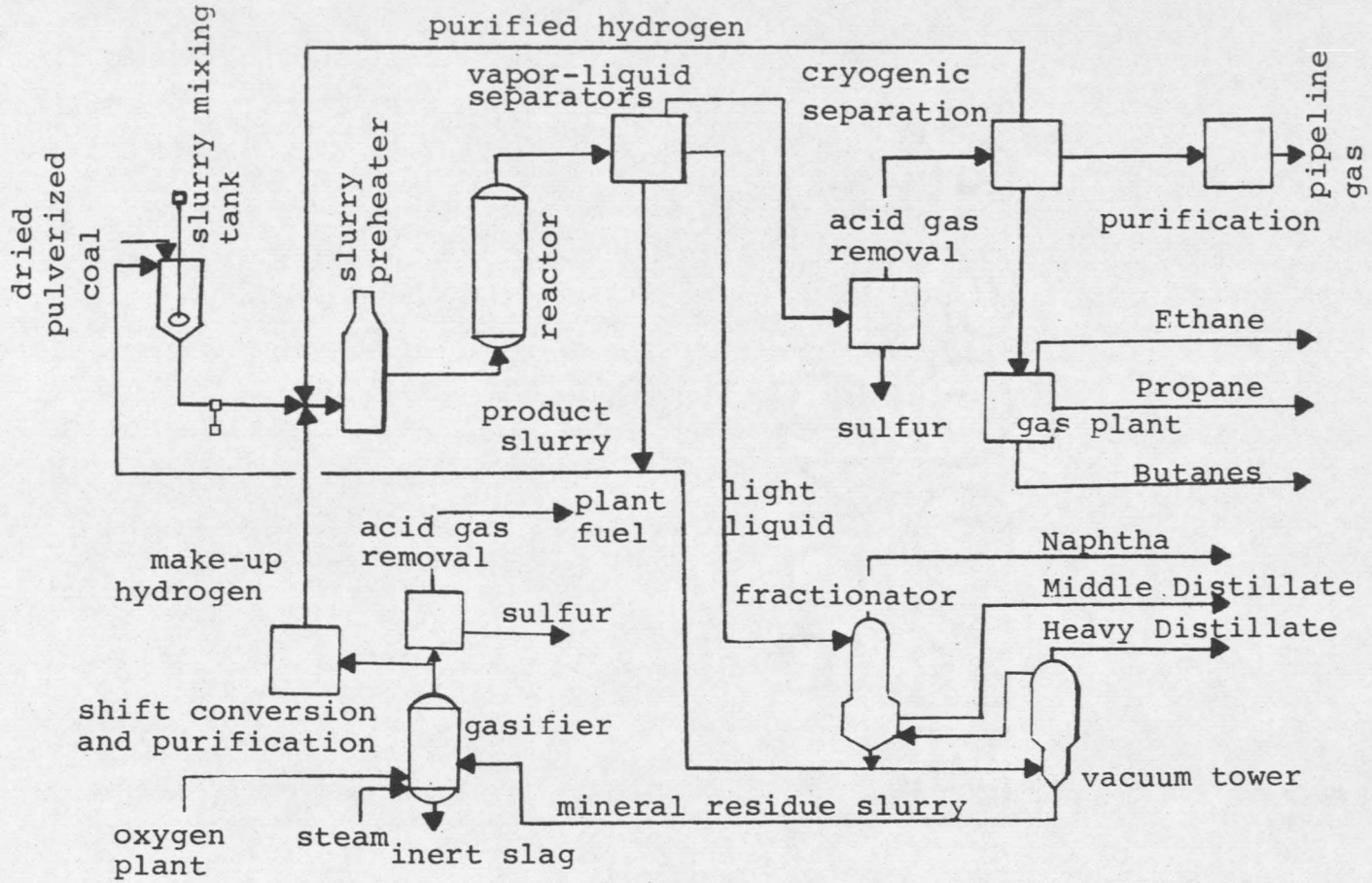

Figure 2. Flow Diagram of SRC-II Process

of vapor-liquid separators, where it is ultimately separated into process gas, light hydrocarbon liquids, and slurry. The process gas is converted and fractionated to produce pipeline gas, ethane, propane, and butane streams. All the light hydrocarbon liquids collected from the various condensation steps are called Light Ends Column Feed(LECF). The LECF plus the overhead stream from the vacuum tower is sent to a fractionator. Part of recycle oil slurry and bottom product of fractionator called Vacuum Flash Feed(VFF) are fed into the Vacuum Flash Tower. All the liquid is separated into naphtha(C_5-193°C normal boiling range), a middle distillate(193-316°C), and a heavy distillate(316-482°C). The feed coal properties are shown in Table III(15). The overall yields and hydrogen consumption are given in Table IV.

Coal Liquids from SRC-II Process

The raw coal liquids from SRC-II process are not directly interchangable with comparable products derived from petroleum. Their composition is different, and their acceptance in place of conventional fuels will require the development of somewhat different methods of use. The properties of SRC-II liquid products are listed in Table V.

TABLE III

SRC-II feed coal properties

Kentucky #9 Coal

	wt%
Carbon	71.35
Hydrogen	5.07
Nitrogen	1.44
Sulfur	3.50
O_2	7.55
Ash	10.12
Moisture	0.97

Sulfur Forms (wt% on Coal)

Pyritic sulfur	1.63%
Sulfate Sulfur	0.09%
Organic Sulfur	1.76%
Total	3.48%

Average Mineral Residue Analysis (wt%)

Carbon	27.61%
Hydrogen	1.39%
Nitrogen	0.54%
Sulfur	7.29%
Ash	63.17%
Pyridine Insoluble	96.98%

Table IV

Yields from SRC-II process

	wt% Moisture-free Coal Charge
Methane	5.8
Ethane	4.4
Propane	4.1
Iso-Butane	0.2
n-Butane	2.0
C_5-193°C Naphtha	10.2
193-316°C Middle Distillate	17.9
316-482°C Heavy Distillate	7.9
482°C + Residue	24.0
Pyridine-Insoluble Organic Material (IOM)	4.6
Ash	12.0
Residual S	1.1
Carbon Monoxide	0.1
Carbon Dioxide	1.0
Hydrogen Sulfide	2.5
Ammonia	0.4
Water	6.2
Total	104.4
Hydrogen Consumption	4.4

Table V

Properties of SRC-II liquid products

	Naphtha	Middle Distillate	Heavy Distillate
Specific Gravity	-	0.98	1.08
Viscosity, SUS	-	38@38°C	200@4°C 40@93°C
Pour Point, max.	-	-46°C	10°C
Flash Point	-	77°C	127°C
Nitrogen, wt.%	4,500 ppm	0.8	1.1
Sulfur, wt.%	1,900 ppm	0.2 to 0.25	0.3 to 0.4
Oxygen, wt.%	3.5%	-	-
High Heating Value, Btu/lb	-	17,400	Approx. 17,000
Hydrocarbon Analysis: vol.%			
Aromatics	34	-	-
Cycloparaffins	45	-	-
Paraffins	21	-	-
Distillation, °C			
IBP	38°C	188°C	304°C
10%	66°C	199°C	321°C
50%	143°C	243°C	366°C
90%	177°C	299°C	427°C
End Point	193°C	316°C	482°C

- Data not abailable

The raw naphtha(C_5-193°C), comprising about one-third of the total liquid product, needs to be severly hydrotreated to meet the specification for a naphtha reforming chargestock. Gulf is currently developing the data base to design a naphtha hydrotreater which is to be included in the SRC-II demonstration plant(15).

SRC-II fuel oil(193-482°C) has been suggested for use in steam boilers and other industrial direct heating applications. A number of programs are ongoing to assess the potential problems and to seek solutions. The SRC-II fuel oils have a substantially lower hydrogen content and higher content of aromatics than petroleum fuel oils. Fuels of high aromaticity burn with a more luminous flame and have a greater tendency to produce smoke. Also, conventional combustion of SRC-II fuel oil leads to high NO_x and SO_x emissions which do not meet EPA's regulations. Two possible efforts should be made to solve the problem; one is to modify the conventional combustor, the other one, which is more efficient, is to upgrade the SRC-II fuel oils.

The chemical constituents of SRC-II liquid products is complicated. Akhtar et al.(16) identified a number of

sulfur containing compounds liberated from coal during liquefaction. They are mercaptans, sulfides, polysulfides, thiophanes, thiophenes, dibenzothiophenes, and benzonaphthothiophenes. Nitrogen is usually found in fused-ring aromatic compounds such as quinolines, acridines, and phenanthridines(17) which are very unreactive.

Upgrading SRC-II Liquid Products

Both theoretical and experimental studies conducted on the upgrading of coal liquids are based on petroleum refining technology. The upgrading of coal liquid is normally effected by hydrotreating in the presence of catalyst at elevated temperatures and pressures. The principal catalytic reactions are hydrogenation of unsaturated hydrocarbons, hydrogenolysis of heteromolecules and hydrocracking. A number of research programs are ongoing to study the basic kinetics of hydrotreating single or double compounds being found in SRC-II liquids. Several oil companies have evaluated commercially available catalysts for upgrading the raw liquid products.

Wentrcek and Wise(18) discussed the hydrodesulfurization of butyl mercaptan. Massoth(19) investigated the hydrogenolysis of thiophene. Gates and coworkers(20,21,22)

made the kinetic studies on the hydrodesulfurization of benzothiophenes, dibenzothiophenes, and benzonaphthothiophenes. Shabtai(23) presented the denitrogenation of 1,10-phenanthroline. Katzer et al.(24,25) studied the denitrogenation of quinolines and acridines. Abdou(26) and other researchers(27,28,29) showed that nitrogen removal required hydrogenation of aromatic rings prior to carbon-nitrogen(C-N) bond scission. These studies were not directly applicable to upgrading SRC-II liquids because they employed model reactants which are not truly representative of coal liquefaction products.

Most of the work conducted on the upgrading raw SRC liquid products are carried out in the industry. Bendoraitis et al.(30) compared the activity of commercial alumina-based catalysts in a shaker bomb reactor for upgrading SRC fuel oil. Potts and his coworkers(31) evaluated commercial Co-Mo, Ni-Mo, and Ni-W catalysts in an expanded bed reactor using a feed of 50% SRC blended with 50% creosote oil. Chevron Research(32) hydrotreated SRC-II in a trickle bed reactor at 2000-2500 psig and 400^{o}C. Givens(33) compared the commercial available Ni-Mo, Co-Mo, and Ni-W catalysts using SRC-I as feedstock.

Berg, McCandless, and Hass(34) tested commercial catalysts and showed the effect of the process variables on hydrotreating SRC-II. Ramer(35) and Yeh(36) discussed the effect of catalyst properties on hydrotreating SRC-II. With regard to the alumina-based catalysts, while a good deal of development work has been done, no systematic study has been published and it is hardly possible to determine the most effective catalytic compositions for upgrading SRC-II liquid products.

If SRC-II liquid products are to be used as boiler fuels, nitrogen and sulfur contents are to be lower than 0.5 wt%(37). The sulfur level is determined from the current EPA standards(38). Generally speaking nitrogen is more difficult to remove than sulfur. Liquid products from the SRC-II process can easily meet the sulfur mineral standard, therefore the major steps in upgrading are to reduce nitrogen levels to less than 0.5 wt% and to increase the hydrogen content of the fuel. If SRC-II liquid products are to be used as catalytic cracker feedstocks, the preferred nitrogen level for catalytic cracker feed is in the range of 100-400 ppm(39). There

are some hydrocrackers that are able to tolerate nitrogen levels as high as 0.3 wt% in the feedstock. Examples of these are the Standard Oil of Indiana Ultra Cracking Process and the Union Oil Co. Unicracking Process(40,41). The nitrogen content of the feedstock must be reduced to meet this requirement, otherwise it will poison the catalyst of conventional hydrocracking units.

Effect of Catalyst

The primary effect of catalyst on a chemical reaction is to increase its rate. Traditionally, hydrotreating catalysts consist of active components, usually metals, deposited on a high surface area porous support. It has been noted that the rate of a catalytic reaction should be proportional to the surface area of the catalyst(42). The increased catalytic activity with decreasing particle size has been confirmed by data presented by Malakoff(43). Rajagopalan and Luss(44) reported that a catalyst with larger pore diameter tended to sustain a longer catalyst life. It is believed that the solvent refined coal has a high asphaltene content with an

average size of 40-50Å per molecule and smaller pores of the catalyst tend to plug up. Berg, McCandless, and Yeh (45) found that the liquid product yield increased by increasing the pore volume of catalyst support. Therefore, a satisfactory catalyst should possess a good combination of high surface area, large pore diameter, and large pore volume.

The most common metals responsible for the hydrogenation and hydrogenolysis functions of a hydrotreating catalyst are molybdenum and tungsten. The metals Ni, Co, Fe, Zn, and Cr are usually described as promoters. Four metals, Co, Mo, W, and Ni have been studied for their capabilities of upgrading SRC-II liquid product in this research.

One of the best known and most annoying features of catalysts is their ability to be inactivated or poisoned. Metallic catalysts are particularly sensitive to being poisoned by compounds of sulfur and nitrogen containing lone pairs of electrons which form strong donor bonds to the metal surface(42). Frequently catalysts are also poisoned by sintering or the contamination of organometallic and carbonaceous materials in the feed. The cata-

lyst poisoning can be either temporary or permanent depending on the deactivation mechanisms. Polinski, Stiegel, and Tischer(46) have proposed four possible deactivation mechanisms of catalyst used for coal liquefaction. Catalysts can be regenerated if the poisoning is temporary, while there is no value of doing regeneration if the catalyst is poisoned permanently. In commercial practice of hydrotreating, the catalyst is advantageously regenerated with air after a certain period of time on stream to regain a large fraction of the initial catalyst activity.

The operating time between regenerations varies from hours to years. A publication in 1955 by Gulf Oil(47) described a process in which the catalyst on-stream time before regeneration was of the order of hours. Regeneration must be carried out to avoid surface area loss. Catalyst overheating may occur inadvertently with permanent loss of activity. It has been stated that the presence of small quantities of silica in the support tends to make the catalyst more stable for regeneration (42). In order to reuse the active catalyst, the development of a catalyst regeneration process is required.

Reactor System and Operating Conditions

To perform a catalytic reaction where the reactants are gaseous and liquid in a continuous manner is now almost invariably effected by the so-called "trickle" process, in which the liquid trickles down over the catalyst bed. Commercial development of the trickle bed reactor can be traced as early as in 1950s to the Shell Oil Company(48). The original "trickle" patent specifies that L/D is to be 5/1 or greater(48). In the petroleum industry trickle bed reactors have been used to hydroprocess various petroleum materials. The hydrodesulfurization, hydrodenitrogenation, and hydrocracking of heavy or residual oil have been economically tested using this type of reactor(49).

In the trickle bed reactor, the catalyst is fixed and the flow pattern is close to plug flow and the liquid to catalyst ratio is low thus limiting side reactions. The trickle bed reactor is simple, yet it can be operated at high pressures and high temperatures with relatively low capital investment(50).

Operating conditions for the reactors are a pressure range of 150-3,000 psig, a temperature range of 345-450^{o}C,

a space velocity of 0.25-20 v/v/hr, and a hydrogen flow rate range of 250-10,000 scf/bbl. Runnion(51) and Hass(52) concluded that the optimal process variables were 425°C, a space velocity of 1.0 v/v/hr, and a hydrogen flow rate of 10,000 scf/bbl of oil. In most fixed bed reactors, as the run progresses, it is necessary to raise the temperature to compensate for the loss in catalyst activity in order to increase reaction rate and maintain conversion levels. It was found that higher temperatures gave higher conversions, however the conversion of hydrocarbon to coke also increased. Thus there is no good reason to operate at a higher reactor temperature. It is understood that most of the carbon is laid down in the initial running period. Berg, McCandless, and Yeh(53) proved that catalyst deactivation was alleviated by starting at a lower temperature. The study for the effect of pressure on the catalyst activity reported that better results could be obtained by operating at a higher pressure. In this research 1,000 psig is the limiting working pressure of the equipment.

Research Objective

The objective of this research is to upgrade SRC-II liquid products into clean distillate fuels or a feedstock suitable for a conventional refinery.

The sulfur and nitrogen contents of SRC-II liquid products were to be reduced to as low as possible and the amount of product recovered in the distillation tests was to be increased. A goal was set of 0.3 wt% nitrogen and 0.5 wt% sulfur in the upgraded product.

The research plan was to systematically study the effects of metals and catalytically active components on a silica-alumina catalyst carrier and to assure the renewability of the promising catalyst through periodic regenerations.

MATERIALS, EQUIPMENT, AND PROCEDURES

Feedstock

The Pittsburg and Midway Coal Mining Company(P&M) supplied the SRC-II liquid products made by using Kentucky #9 Coal from the Colonial Mine. Two SRC-II products, P&M's SRC-II Vacuum Flash Feed(VFF) and Light Ends Column Feed(LECF), were used as feedstocks in this research. Table VI shows a representative analysis. The VFF containing 1.17 wt% N and 0.72 wt% S is a slurry at room temperature and requires preheating prior to pumping. However, the VFF tends to coke up if it is overheated. The LECF containing 0.88 wt% N and 1.21 wt% S is a mixture of 15% SRC Naphtha, 40% SRC Middle Distillate, and 45% SRC Heavy Distillate.

Catalyst Preparation

All catalysts fabricated at Montana State University were made by impregnating commercial catalyst carrier with metal salts using the incipient wetness technique. The procedure used was:

1. Dry the catalyst carrier in the oven at 110^{o}C for 8 hours.
2. Calcine at 450^{o}C for 8 hours.

TABLE VI

Properties of feedstocks

	Vacuum Flash Feed	Light Ends Column Feed
% Carbon	87.43	-*
% Hydrogen	7.15	-*
% Nitrogen	1.17	0.88
% Sulfur	0.72	1.21
% Oxygen	3.72	-*
% Ash	0.249	0.02
Sp. Gravity 60/60°F	1.08	0.983
ASTM D-86 Distillation, °F		
IBP	408	122
5%		217
10%	445	288
20%	485	381
30%	544	446
40%	598	488
50%	642	541
60%		577
70%		611
80%		660
90%		727
95%		795
End Point	684	956

* Data not available

3. Cool to room temperature in a dessicator and record the weight of catalyst carrier.
4. Impregnate the catalyst carrier in a slowly rotating jar with a specific metal solution, the concentration of which is estimated by(54):

   wt% of metal oxide on the support
   = conc. of solution x pore vol. /
   (1 + (pore vol. x conc. of solution))

   The concentration of solution is further adjusted by experience.
5. Air dry at room temperature in an air stream of 3 psig.
6. Repeat the steps from 1 to 3 for the air dried catalyst and record the weight increased after impregnation.

The catalyst compositions were reported as the weight percents of metal oxides which were the percent weight increased after impregnation of the weight of blank catalyst carrier. This procedure was repeated as needed to obtain the objective percentages of metal oxides.

One catalyst carrier, Nalco-78-6008C-1/32" obtained from Nalco Company was used in this research. It is

composed of 98% Al_2O_3 and 2% SiO_2, and possesses a surface area of 214.6 m^2/gram, an average pore diameter of 156.5Å, a median pore diameter of 161 Å, and a pore volume of 0.84 ml/gram. Four metals were loaded on the support in the order of Co, Mo, Ni, and W by using the water solution of $Co(NO_3)_2 \cdot 6H_2O$, $(NH_4)_6MO_7O_{24} \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, and $5(NH_4)_2O \cdot 12WO_3 \cdot 7H_2O$, respectively.

Catalyst Pretreatment

All catalysts were pretreated by sulfiding. This procedure was used to activate the catalyst and to prevent the reduction of catalyst activity by hot hydrogenation(55,56). The catalyst was treated with a 10% hydrogen sulfide in hydrogen mixture for 12 hours in order to sulfide the metal oxides into metallic sulfides. The stream of hydrogen sulfide was passed through the pipe reactor at approximately atmospheric pressure. Exit gases from the apparatus were scrubbed with 20% sodium hydroxide-water solution before venting to the hood. Temperature was maintained at 325°C by use of a powerstat to control an electric pipe heater. Extreme caution should be taken whenever handling

the extremely poisonous hydrogen sulfide because it can cause coma and death within a few seconds after inspiration. Hydrogen sulfide is extremely hazardous because it fatigues the sense of smell in high concentration; therefore it gives no warning(57).

Continuous Trickle Bed Reactor

The trickle bed reactor was designed and constructed by the Chemical Engineering Department at Montana State University prior to this research. The schematic diagram of the trickle bed reactor and auxiliary equipment is shown in Figure 3.

The reactor was made by a one-inch I.D. 40 inches long schedule 80 Inconel pipe. The top of the reactor was fitted with a 1/4-inch stainless steel cross. It allowed the fitting of a 36-inch stainless steel tubing serving as a thermowell, and the fitting of two feed ports, one for SRC-II feed and one for hydrogen.

The reactor was placed into a 1-inch bore hole of a 6-inch O.D. aluminum block which was about three feet long. The reactor was clamped 4-inch outside the top of aluminum block. The aluminum block was wrapped with

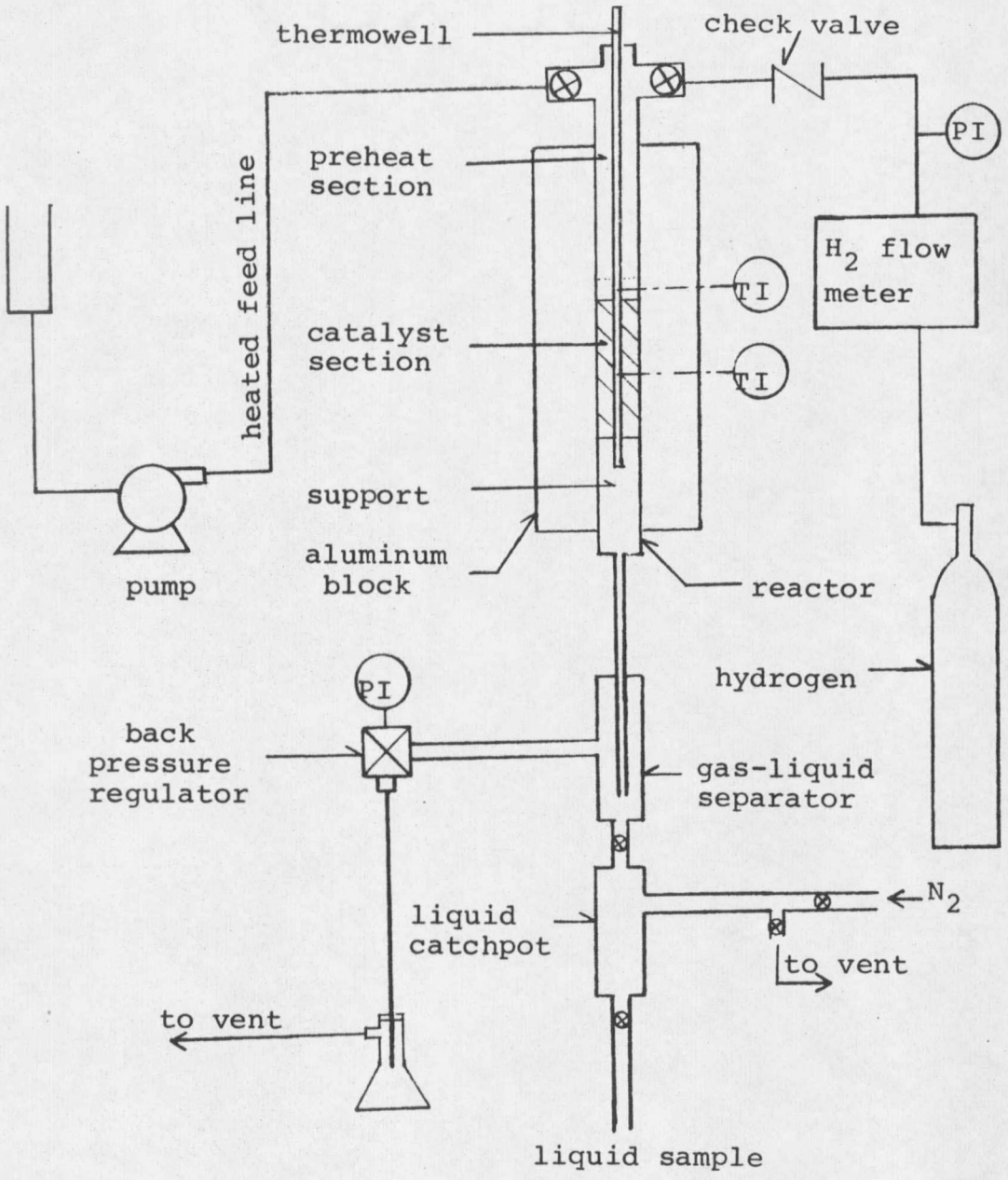

Figure 3. Trickle Bed Reactor

three sets of Nichrome wire heating coils encased in ceramic beads. Each heating coil was connected to a powerstat variable transformer which was manually controlled to adjust temperature. Two chromel-alumel thermocouples were placed in the thermowell, one in the preheat section and one in the catalyst section. The thermocouple wires were connected to Cole-Parmer Digital Thermocouple Thermometers(58). Starting from the top, the reactor was loaded with 175 ml. of 1/4" Denstone inert support(59), followed by 25 ml. of 1/8" Denstone insert support to serve as the preheating section. The sixty milliliters of catalyst mixed with 60 ml. of 1/8" inert support was loaded into the catalyst section. The remaining space at the bottom of the reactor was filled with 1/8" Denstone inert support. Then a cone of stainless steel screen was inserted as a plug support above the 1/4-inch I.D. reactor closure that was threaded into the pipe. The threaded connection was sealed with Teflon tape and Silver Goop to prevent leakage.

The SRC-II liquid products were pumped into the top of the reactor by using a Milton Roy piston pump through a 1/8" Stainless Steel feedline. The pump speed

was manually controlled by micrometer. All feedlines and reservoirs were wrapped with flexible heating cords. The liquid feed temperature was mainly adjusted by the Powerstat connected to the heating cord for the feedline from the pump to reactor. Technical grade hydrogen stored in the cylinder was fed through a pressure regulator, a Brooks Thermal Mass Flowmeter, and a micrometer to the top of the reactor(60).

Gases and liquids passed through the reactor to a gas-liquid separator. The gases passed through a condenser and through a Grove back pressure regulator which was equipped with a corrosion-resistive Teflon diaphram. Generally, the exit gases passed through a scrubber with 20% NaOH-water solution and then were vented. From Runs 7 to 22, the exit gases passed through a 30 ml. concentrated sulfuric acid, which was used for collecting nitrogen of the exit gases, before reached scrubber. A wet test meter could be connected before the gas was vented in order to calibrate the Brooks Thermal Mass Flowmeter. The liquids passed from the gas-liquid separator into a pressurized catchpot. When a liquid sample was taken, the valve between the separator

and catchpot was closed. The catchpot was depressurized and the sample was drained from the bottom of the catchpot. The catchpot was repressurized with nitrogen and the valve was reopened.

Operation of Continuous Trickle Bed Reactor

The reactor loaded with the catalyst to be tested was placed in the aluminum heat block. The liquid and hydrogen feedlines were connected at the top of the reactor and the catchpot system was attached at the bottom. The thermocouple wires were inserted into the thermowell. The whole system except the pump was pressurized to 1,000 psig with nitrogen and checked for leaks using Snoop Soap solution. If no leaks were found, the system was depressurized. Three variable Powerstats were then turned on to heat the reactor.

When the reactor reached the desired temperature, all liquid feedlines and reservoirs were preheated. The reservoir was filled and SRC-II liquid product was pumped through the feedlines. Hot SRC-II products were recirculated for a few minutes through the feed line back into the reservoir. During the recirculation

the liquid feed temperature was measured at the outlet of feedline by the thermocouple connected to a digital thermometer. Feedlines should be filled first to avoid the pump cavitation. The reactor was pressurized with hydrogen by means of a bypass valve attached to the Brooks Flowmeter. When the system approached desired pressure, the bypass valve was closed and the micrometer was adjusted to keep the desired hydrogen flow rate, The valve of the feedline was then opened and the pump started. The liquid flow rates were measured by timing the liquid level drop in the buret. The flow rate was checked frequently to maintain an even flow and the average flow rate was reported as liquid hourly space velocity(LHSV).

The first product was taken in 30 minutes after the start-up and the remainder of samples were collected at 15 or 30 minutes intervals, unless otherwise specified. The overall weight ratio of product to feed was reported as the yield of oil. Gaseous products and hold-up in the reactor were not part of the yield. The running time

varied from 2 to 10 hours. After the last sample was obtained, the pump was shut off. The liquid feed valve at the top of the reactor was closed and the feedline was disconnected. The excess SRC-II liquid products were drained and the reservoir was cleaned with acetone. The hydrogen flow was cut-off and the reactor was depressurized. The hydrogen feedline was disconnected and heaters were shut off. The catchpot system was removed and cleaned thoroughly with acetone. The reactor was then removed from the aluminum heating block. The entire contents of the reactor were emptied of catalyst and inert supports in order to measure their properties. The reactor was cleaned unless the catalyst was to be regenerated in place.

Operation of Catalyst Regeneration

After a catalyst test was finished, the reactor was placed in the other identical aluminum heating block for regeneration. The premixed nitrogen-oxygen gas stored in the cylinder was fed into the top of the reactor. The outlet gases passed through a wet test meter, which was used for measuring the flow rate, then to the vent. The catalyst might be sampled to examine the completeness

of burn-off by measuring the pore volume. After completing the burn-off, catalyst was resulfided prior to reuse.

Analytical Procedures

The upgraded liquid products were analyzed for sulfur and nitrogen contents. The nitrogen content of sulfuric acid of Run 7 to 22 was also analyzed to determine the amount of nitrogen exiting as gas. The extent of hydrocracking was determined by distillation technique and the extent of carbon laydown was found by a pore volume determination. Auger Electron Spectroscopy(AES) was used to analyze the carbon distribution for the selected samples.

The sulfur analysis was performed on approximately 0.3 grams sample by the quartz tube combustion method using a Bico-Brown Shell design sulfur apparatus (61,62). The reported accuracy of the instrument is 0.03% error. The weight percent desulfurization(%DS) was calculated as follow:

%DS= (wt% S of feed - wt% S of product)/(wt% S of feed)

Nitrogen content was determined by Macro-Kjeldahl method(63,64,65) using 0.5 grams of samples and 40 grams of potassiun sulfate. The accuracy is about 0.3%. The denitrogenation(%DN)was calculated similarly to the desulfurization(%DS).

The extent of cracking was determined by ASTM D-86 atmospheric distillation(65). This technique measured the cumulative amount of product which boiled below 650^{o}F (434^{o}C) or when decomposition begins, whichever occurred first. The amount of the sample used for the distillation was 50 ml whenever possible.

The pore volume of the catalyst was estimated by the water saturation method. It gave a relative value rather than absolute. The procedures are as follows:

1. Dry 2-5 grams catalyst at 100^{o}C for two hours.
2. Cool the catalyst to room temperature in a desiccator, then weigh the catalyst.
3. Immerse the catalyst into the boiling water for 5 minutes to get rid of the air in pores.
4. Decant the excess water and widely spread catalyst on a sheet of paper.

5. Leave 35 minutes for natural air dry, then weigh the saturated catalyst.

The pore volume was calculated by the weight gained after saturation of the weight of dried catalyst. The weight of water absorbed by the catalyst was considered to be approximately equal to the pore volume assuming the specific gravity of water to be one. It should be noted that the unit of pore volume measured is the milliters per gram of catalyst and can be converted to milliters per gram of blank catalyst carrier by multiplying by a factor of (1 + total wt% of metals loaded).

The carbon distribution of the spent and regenerated catalysts was determined by Auger Electron Spectroscopy (66). Samples were prepared by cutting the catalyst cylinders in half as shown in Figure 4. The cross sections obtained from cutting were the surface to be analyzed. The spectra were recorded at five spots with equal length moving from center to the outer surface on the cross sections. Samples should not be touched by human hands because the resulting contamination causes difficulty in maintaining the low vacuum required in the system

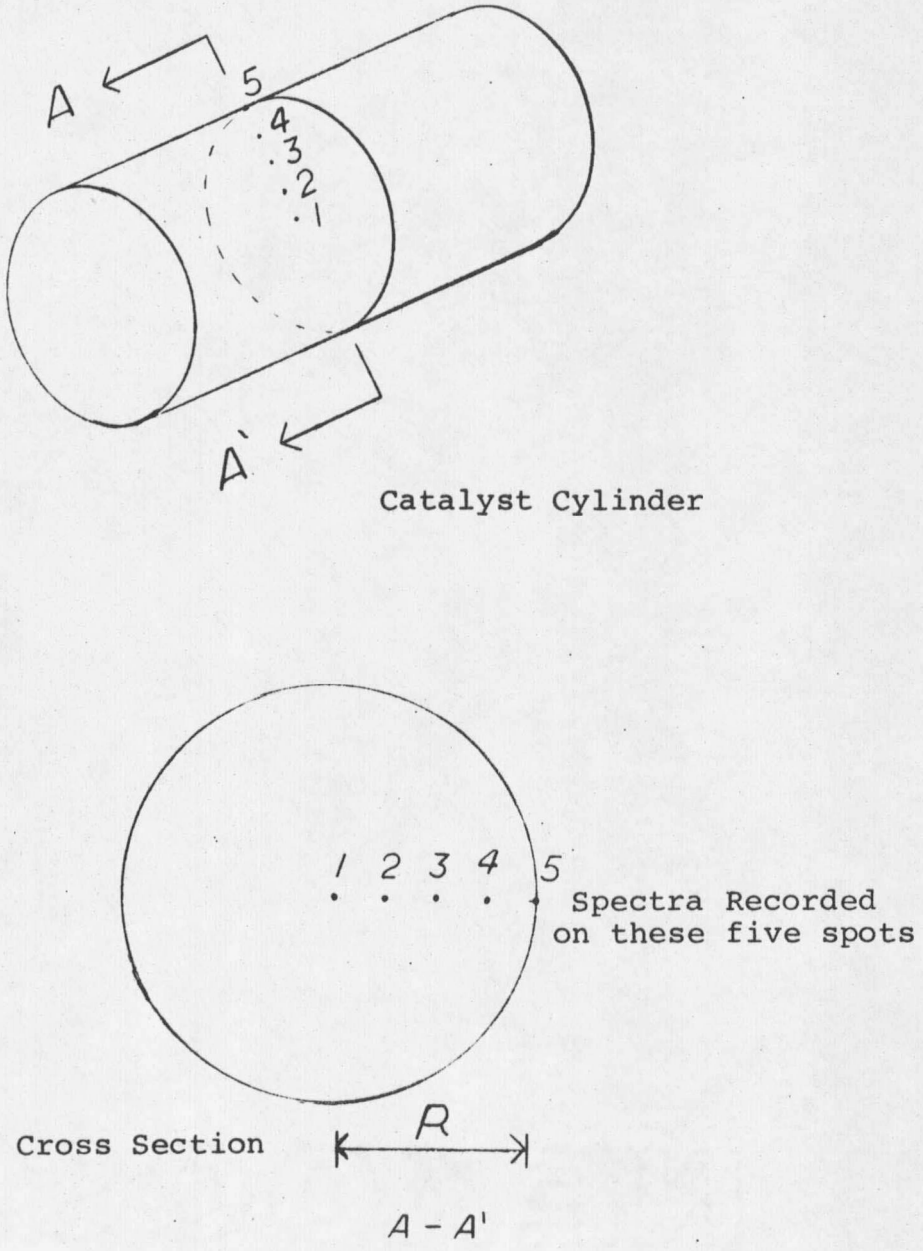

Figure 4. Sample preparation for the analysis of AES

and leads to an incorrect analysis. The extent of carbon laydown was determined by the carbon to aluminum atomic ratio measured from the peak-to peak amplitude ratio of elements on the spectrum(67). The carbon distribution was obtained by plotting the carbon to aluminum atomic ratio from spot to spot.

RESULTS AND DISCUSSION

The optimum liquid feed temperature was determined. Two feedstocks, SRC-II Vacuum Flash Feed and Light Ends Column Feed showed different behaviors with catalytic hydrotreating. The statistical study was performed to analyze the effect of catalyst composition. An attempt was made to investigate the material balance of the reactor system. Approximately 46% of input nitrogen was unaccounted for. Catalyst deactivation was observed and moderated by starting at lower temperature and higher space velocity. Pore volume of the spent catalyst was reduced due to the carbon laydown which caused catalyst deactivation. The mechanism of catalyst deactivation appeared to be pore mouth plug-up explained by Auger spectrum. A catalyst was tested for a long run through periodic regeneration and the upgraded product was further characterized.

Liquid Feed Temperature

SRC-II Vacuum Flash Feed(VFF) is too viscous to pump at room temperature but it also gives thermal cracking and coke laydown when heated too high. Four blank runs, Run 1 to 4, with blank catalyst carrier

as the catalyst were carried out to determine the optimum conditions for feeding the SRC-II VFF. Their operating conditions were 1,000 psig, 425°C, space velocity of 1.0 v/v/hr, and hydrogen flow rate of 10,000 scf/bbl of oil. The temperature of feeding SRC-II VFF varied from 85°C to 200°C, 85°C for Run 1 and 2, 105°C for Run 3, and 200°C for Run 4. Run 1 to 3 were made two hours. The first samples were collected after 45 minutes because no liquid sample was obtained after 30 minutes. All samples were analyzed for nitrogen contents and samples collected after 90 and 120 minutes were analyzed for sulfur contents. Table VII presents the results. In Run 1 the nitrogen content of SRC-II VFF, 1.17 wt%, was reduced to 0.42 wt%(65%DN) after 45 minutes and to 0.93 wt%(19%DN) after 120 minutes. Run 3 reduced the nitrogen content to 0.3 wt% after 45 minutes and to 0.72 wt% after 120 minutes. Figure 5 plots these data. Run 3 with a higher liquid feed temperature gave a slightly better denitrogenation than Runs 1 and 2. Runs 1 and 2 gave oil product yields of 45% which were lower than 63 wt% obtained from Run 3 due to the lower

Table VII

Blank runs data

Run	Feed-Stock *	Liquid Feed Temp., °C	%DN Time on Stream, min 30	45	60	75	90	105	120	180	Avg. %DN	%DS Time on Stream, min 90	120	150	Avg. %DS	wt% Yield of Product
1	VFF	85	-	65	40	36	27	27	19	-	31.2	12	33	-	22.5	45
2	VFF	85	-	40	28	26	27	24	24	-	28.2	24	31	-	27.5	44
3	VFF	105	-	74	40	28	23	39	38	-	40.3	26	20	-	23	63
4**	VFF	200	-	78	----	coked	up	-----			-	56	-	-	-	-
5	LECF	85	56	-	39	-	-	-	33	30	39.5	76	-	69	72.5	77
6	LECF	85	56	-	40	-	-	-	39	28	40.8	65	-	64	64.5	77

* VFF contains 1.17 wt% N and 0.72 wt% S; LECF contains 0.88 wt% N and 1.21 wt% S

** Run 4 coked up after 45 minutes

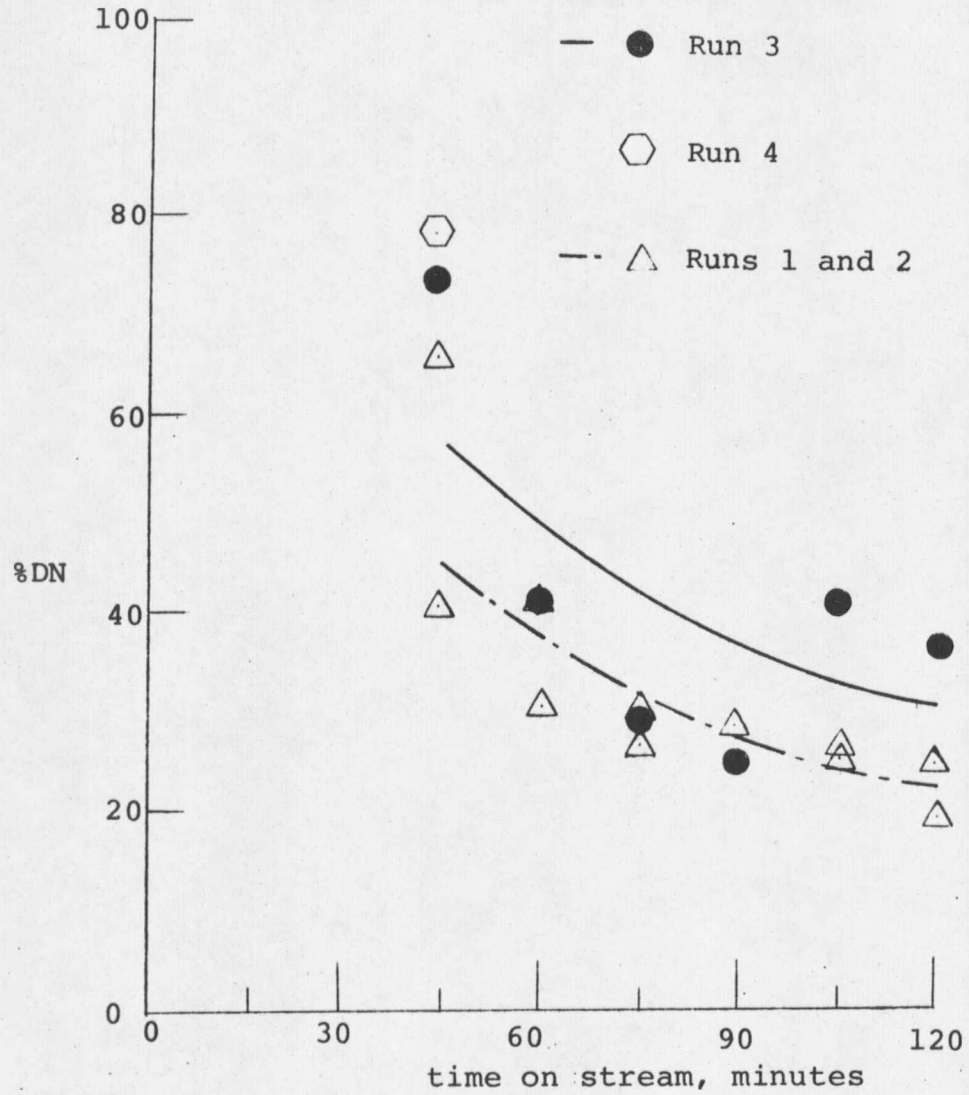

Figure 5. Effect of liquid feed temperature* on the denitrogenation.

* SRC-II VFF was fed at 85°C for Runs 1 and 2, 105°C for Run 3, and 200°C for Run 4.

liquid feed temperature. The desulfurization data for these runs seemed similar. Their desulfurization averaged to be 24%. The distillation yield of ASTM D-86 of these three runs were also fairly close. They were 66, 66, and 68 vol.% for Runs 1, 2, and 3, respectively. Samples of Run 4 were collected up to 45 minutes because the coke build-up raised the pressure to 1,300 psig necessitating shut-down. There was no oil product yield recorded for this run because of the unusual shut-down. To avoid the pumping problems and coke build-up, an SRC-II liquid feed temperature of 85°C seemed to be reasonable.

Feedstocks Comparison

SRC-II Light Ends Column Feed(LECF) was used as feedstock in Runs 5 and 6 which were operated for 3 hours and used blank catalyst carriers as the catalyst. Their operating conditions were the same as those of Run 1 and 2. In these runs, the first samples were collected after 30 minutes and the remainders were sampled every 30 minutes. Four samples collected from 30, 60, 90, and 180 minutes were analyzed for nitrogen contents and

samples collected after 90 and 150 minutes were analyzed for sulfur contents. The nitrogen analyses of Runs 5 and 6 showed an effluent oil containing an average nitrogen content of 0.38 wt%(56%DN) after 30 minutes and 0.62 wt%(29%DN) after 180 minutes. The average sulfur content of oil product was 0.38 wt%(68.5%DS). These data are listed in Table VII. Comparing with the results of upgrading SRC-II VFF in this table, sulfur content of SRC-II LECF was removed more effectively. The denitrogen data of both feedstocks was regressed on the running time and plotted in Figure 6. The regression equations

$$\%DN = 70.5e^{-0.01t} \quad \text{for VFF}$$

and

$$\%DN = 55.2e^{-0.00387t} \quad \text{for LECF}$$

with R-squares of 0.70 and 0.80, respectively, seemed appropriate to fit those data. The constants, 70.5 and 55.2, could be explained as initial activities of catalysts and the exponential terms might be the deactivation rates. The time on stream, t, is presented as a unit of minute in the equations. This indicated that the denitrogenation of VFF gave a higher initial

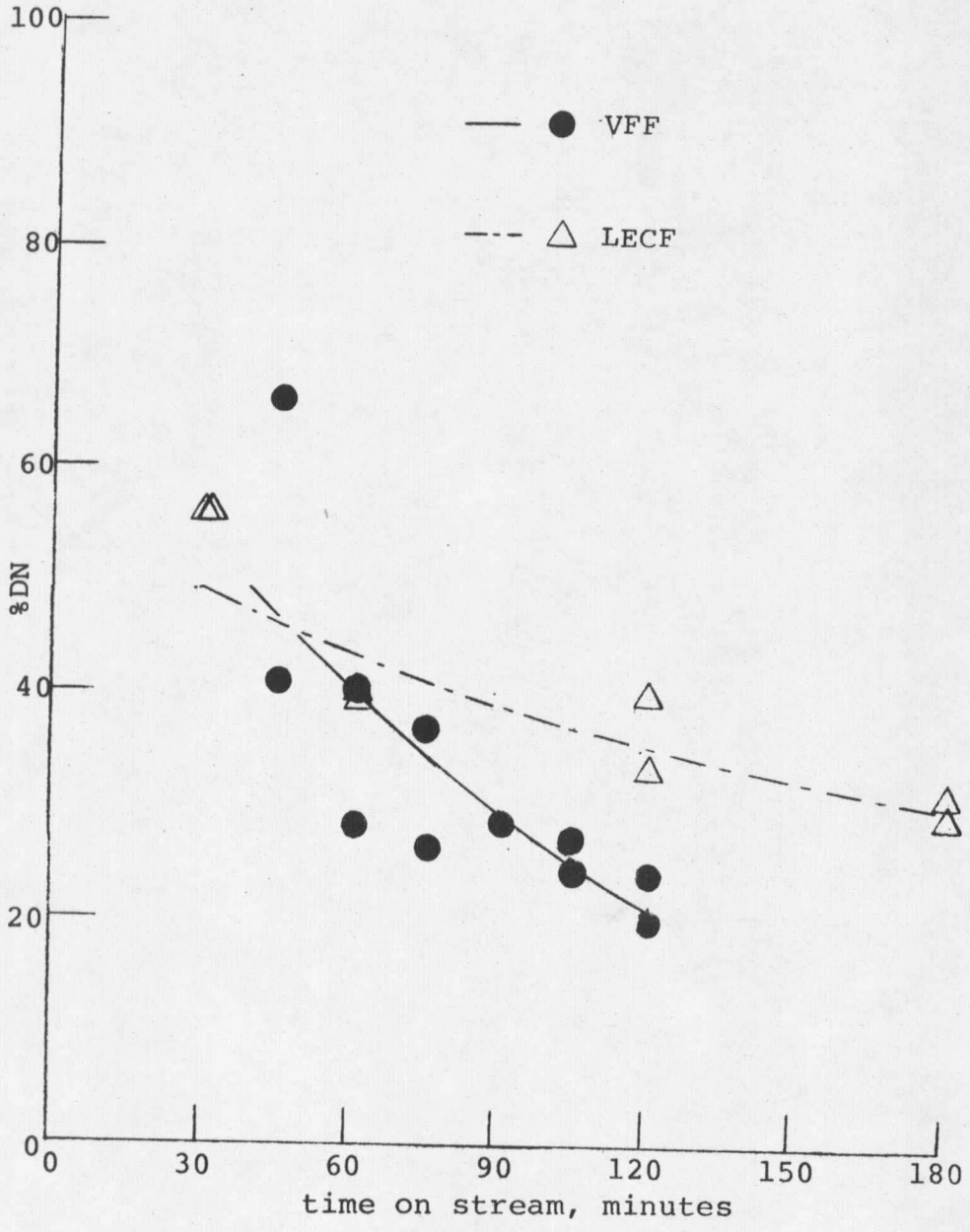

Figure 6. Feedstock comparison

activity of catalyst but much higher deactivation rate than the LECF did. It was believed that the heavier carbonaceous materials of VFF have caused the shorter active life of the catalyst. The oil product yield of LECF in Runs 5 and 6, 77 wt%, was much higher than that of VFF in Runs 1 and 2, which was 45 wt%.

Catalytic Compositions

A sixteen experiment 2^4 full two level metal-loading factorial design was developed to determine the metal effects for each feedstock. The catalysts designated from C-41 to C-56 comprising every combination of 2 and 4% CoO, 2 and 8% MoO_3, 1 and 4% NiO, and 2 and 8% WO_3 were tested in Run 7 to 22 using SRC-II VFF as feedstock and in Run 23 to 38 using SRC-II LECF. Runs 7 to 22 were made 2.5 hours, while Runs 23 to 38 were made 3 hours. The typical operating conditions were 1,000 psig, 425°C, space velocity of 1.0 v/v/hr, a hydrogen flow rate of 10,000 scf/bbl, and liquid feed temperature of 85°C.

In Run 7 to 22, samples were collected at first 45 minutes and then every 15 minutes. All samples

were analyzed for nitrogen contents and the samples collected at 90 and 150 minutes were analyzed for sulfur contents. Table VIII summarizes the denitrogenation data. The blank runs data are also included in the table for comparison. The average denitrogenation data varied from 61.9%(0.46 wt% N of product) to 81.1%(0.22 wt% N of product) and was regressed on the weight percent of metal oxides by using the forward stepwise regression technique at a confidence level of 90%. The regressed equation became

$$\%DN = 31.8 + 11.29CoO + 2.36MoO_3 + 3.26\ WO_3 - 0.589(CoO)(MoO_3) - 0.893(CoO)(WO_3)$$

The intercept, 31.8, is the average %DN for blank runs. The analysis of variance tables is shown in the Appendix A. The result showed that three metals, Co, Mo, and W, significantly increased the catalytic activity on denitrogenation and the interactive effects of Co-Mo and Co-W were negative. Effect of Ni was found to be insignificant. Figure 7 plots the denitrogenation data for these runs versus the running time. The effect of Co concentration is also shown in the plot.

Table VIII

Denitrogenation data of factorial design for SRC-II VFF

Run	Catalyst	%DN* time, minutes							%DN Avg.	Metal Oxides on the Catalyst, wt%			
		45	60	75	90	105	120	150		CoO	MoO_3	NiO	WO_3
1	carrier	64.4	39.7	35.9	27.4	26.6	18.8	-	35.6	0	0	0	0
2	carrier	40.2	27.8	25.6	27.4	23.5	23.5	-	28.0	0	0	0	0
7	C-41	92.0	89.3	85.5	77.8	72.6	61.5	50.0	75.5	2	8	1	8
8	C-42	85.5	92.8	69.2	61.5	48.7	44.0	35.9	62.5	2	8	1	2
9	C-43	97.0	96.2	91.0	80.3	65.4	56.4	51.7	76.8	2	8	4	8
10	C-44	98.6	92.2	80.8	68.8	51.3	42.7	43.6	68.3	2	8	4	2
11	C-45	98.3	87.2	79.5	62.8	56.4	45.3	30.3	65.7	2	2	1	8
12	C-46	93.8	79.5	65.8	57.7	49.1	44.9	42.3	61.9	2	2	1	2
13	C-47	95.5	89.7	81.6	66.7	58.5	52.1	35.9	68.6	2	2	4	8
14	C-48	93.2	80.0	70.5	64.1	57.7	54.3	48.7	67.0	2	2	4	2
15	C-49	98.6	93.8	88.9	80.3	66.7	60.7	56.8	77.9	4	8	1	8
16	C-50	97.3	91.7	84.6	78.6	69.7	60.3	57.3	77.1	4	8	1	2
17	C-51	97.9	92.1	81.2	70.9	62.0	55.6	57.3	73.8	4	8	4	8
18	C-52	89.7	87.2	82.0	72.2	68.4	66.7	50.8	73.8	4	8	4	2
19	C-53	95.1	88.9	79.1	70.1	57.7	52.6	57.3	71.5	4	2	1	8
20	C-54	92.3	99.1	97.4	73.5	71.8	70.1	63.2	81.1	4	2	1	2
21	C-55	97.4	88.6	70.1	75.2	72.6	68.4	57.3	75.6	4	2	4	8
22	C-56	94.9	91.4	79.5	58.1	91.4	47.0	28.2	70.1	4	2	4	2

* Nitrogen content of SRC-II VFF is 1.17 wt%

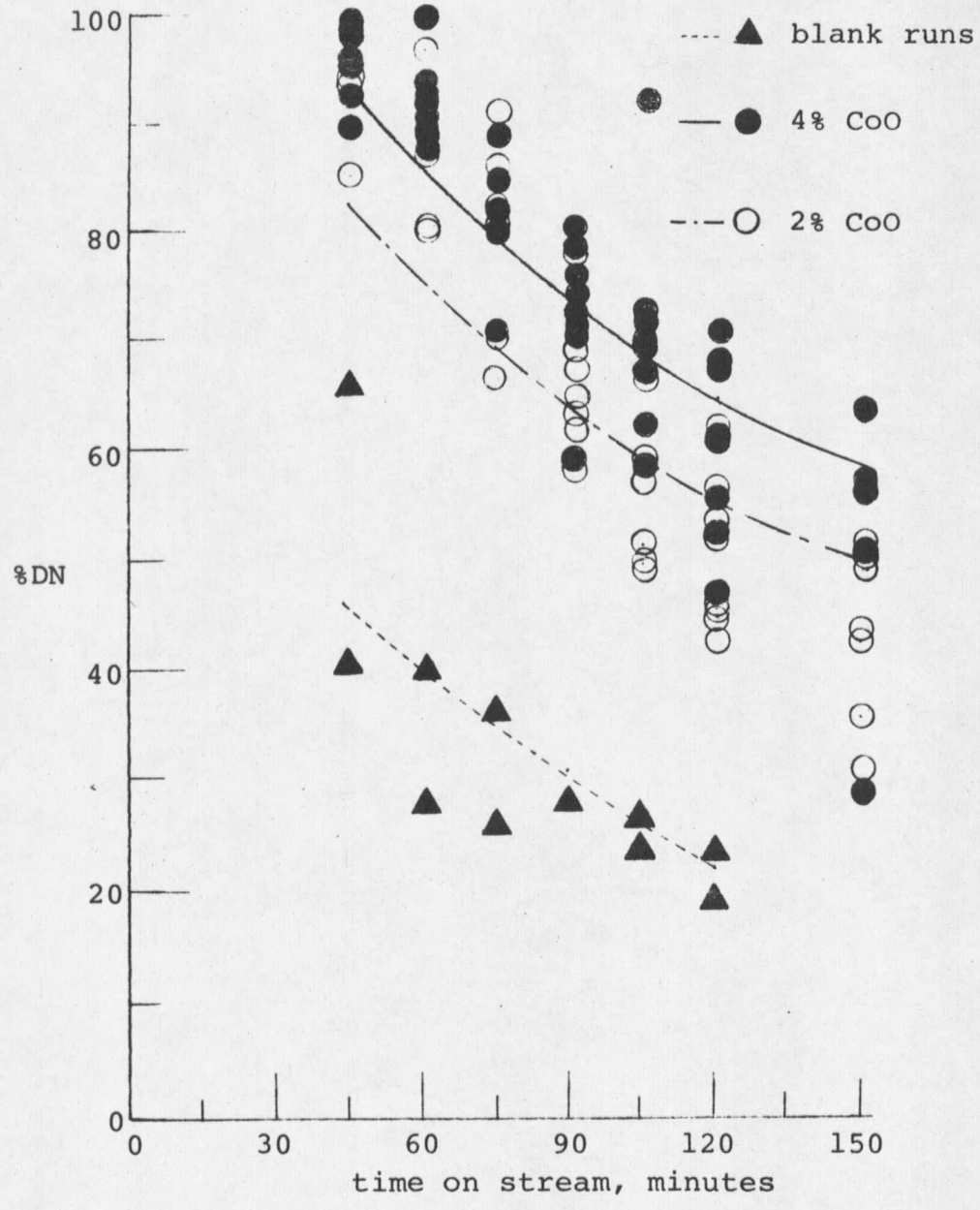

Figure 7. Denitrogenation of SRC-II VFF from Run 7 to 22.

The average desulfurization, ASTM D-86 distillation yield at 650°F, and oil product yield data shown in Table IX were also regressed on the catalyst compositions using a confidence coefficient of 0.90. The average desulfurization for blank runs were 24.95% and the average desulfurization in Runs 7 to 22 varied from 14.9%(0.61 wt% S) to 77.4%(0.16 wt% S). The regression equation for desulfurization of VFF was

$$\%DS = 24.95 - 6.43\ CoO + 6.66\ MoO_3 + 4.8\ WO_3 - 0.556(MoO_3)(WO_3),$$

which showed the main effects of Mo and W to be positive and Co giving a negative effect. The interactive effect of Mo-W was found to be negative. The effect of Ni turned out to be insignificant. Tungsten was found to effect the oil product yield negatively. The effect of metals on the ASTM D-86 distillation yield was found to be insignificant. The average ASTM D-86 distillation yield at 650°F of Run 7 to 22 was 78.9 vol.%. The average oil product yield for catalysts with 2% and 8% WO_3 were 76.1 wt% and 70.3 wt%, respectively. The analysis of variance tables are shown in Appendix A.

In Run 23 to 38, liquid samples were collected

Table IX

Desulfurization and yields data of factorial design for SRC-II VFF

Run	Catalyst	%DS 90 min.	%DS 150 min.	Avg.[@] %DS	ASTM D-86 Yield[@] at 650°F, vol.%	Yield of Oil Product, wt%	Metal Oxides on Catalyst, wt% CoO	MoO_3	NiO	WO_3
1	carrier	-	-	22	66	45	0	0	0	0
2	carrier	-	-	28	66	44	0	0	0	0
7	C-41	85	70	77	77	72	2	8	1	8
8	C-42	60	68	64	75	77	2	8	1	2
9	C-43	65	70	67	82	62	2	8	4	8
10	C-44	74	68	71	80	70	2	8	4	2
11	C-45	62	68	65	80	64	2	2	1	8
12	C-46	0	69	34	74	76	2	2	1	2
13	C-47	35	58	46	74	76	2	2	4	8
14	C-48	18	66	42	82	75	2	2	4	2
15	C-49	31	64	48	85	76	4	8	1	8
16	C-50	42	44	43	80	74	4	8	1	2
17	C-51	46	66	56	83	79	4	8	4	8
18	C-52	46	66	56	81	84	4	8	4	2
19	C-53	17	65	41	76	75	4	2	1	8
20	C-54	17	53	35	77	76	4	2	1	2
21	C-55	13	60	37	76	58	4	2	4	8
22	C-56	0	30	15	80	77	4	2	4	2

@ Sulfur content of SRC-II VFF is 0.72 wt%, distillation yield at 650°F for SRC-II VFF is 55 vol%.

every 30 minutes. For each run two samples were analyzed for sulfur contents and remainders were analyzed for nitrogen contents. The denitrogenation data is shown in Table X. The nitrogen content of LECF, 0.88 wt%, has been reduced to an average of 0.07 wt% N(91.8%DN) in Run 33 and 0.28 wt%(67.6%DN) in Run 36. The fitted equation for the average denitrogenation data became

$$\%DN = 40.1 + 6.47\ CoO + 5.23\ MoO_3 + 1.56\ WO_3 - 0.86(CoO)(MoO_3)$$

with a confidence level of 90%. The intercept of the equation is the averaged %DN for Runs 5 and 6. The analysis of variance table is shown in the Appendix B. It was found that the adding of Co, Mo, and W significantly increased the catalyst activity on denitrogenation and the interactive effect of Co-Mo was negative. The denitrogenation data of LECF is plotted in Figure 8 as a function of time on stream. The effect of CoO concentration and the data for blank runs are also plotted for comparison. The data for desulfurization and oil product yield is shown in Table XI. These two

Table X

Denitrogenation data of factorial design for SRC-II LECF

Run	Catalyst	%DN time on stream, min. 30	60	120	180	avg.	Catalyst Composition, wt% CoO	MoO_3	NiO	WO_3
5	carrier	56	39	33	30	39.2	0	0	0	0
6	carrier	56	40	39	28	40.6	0	0	0	0
23	C-41	98	98	86	80	90.3	2	8	1	8
24	C-42	98	89	73	67	81.5	2	8	1	2
25	C-43	86	93	80	77	81.3	2	8	4	8
26	C-44	98	93	84	84	89.8	2	8	4	2
27	C-45	98	98	83	77	88.9	2	2	1	8
28	C-46	88	74	61	55	69.3	2	2	1	2
29	C-47	93	93	80	75	85.2	2	2	4	8
30	C-48	92	89	59	58	74.4	2	2	4	2
31	C-49	98	93	88	83	90.3	4	8	1	8
32	C-50	98	98	85	80	90.0	4	8	1	2
33	C-51	98	98	88	84	91.8	4	8	4	8
34	C-52	98	94	77	72	85.2	4	8	4	2
35	C-53	98	62	68	68	74.1	4	2	1	8
36	C-54	98	70	50	52	67.6	4	2	1	2
37	C-55	98	92	52	47	72.2	4	2	4	8
38	C-56	97	75	57	56	71.0	4	2	4	2

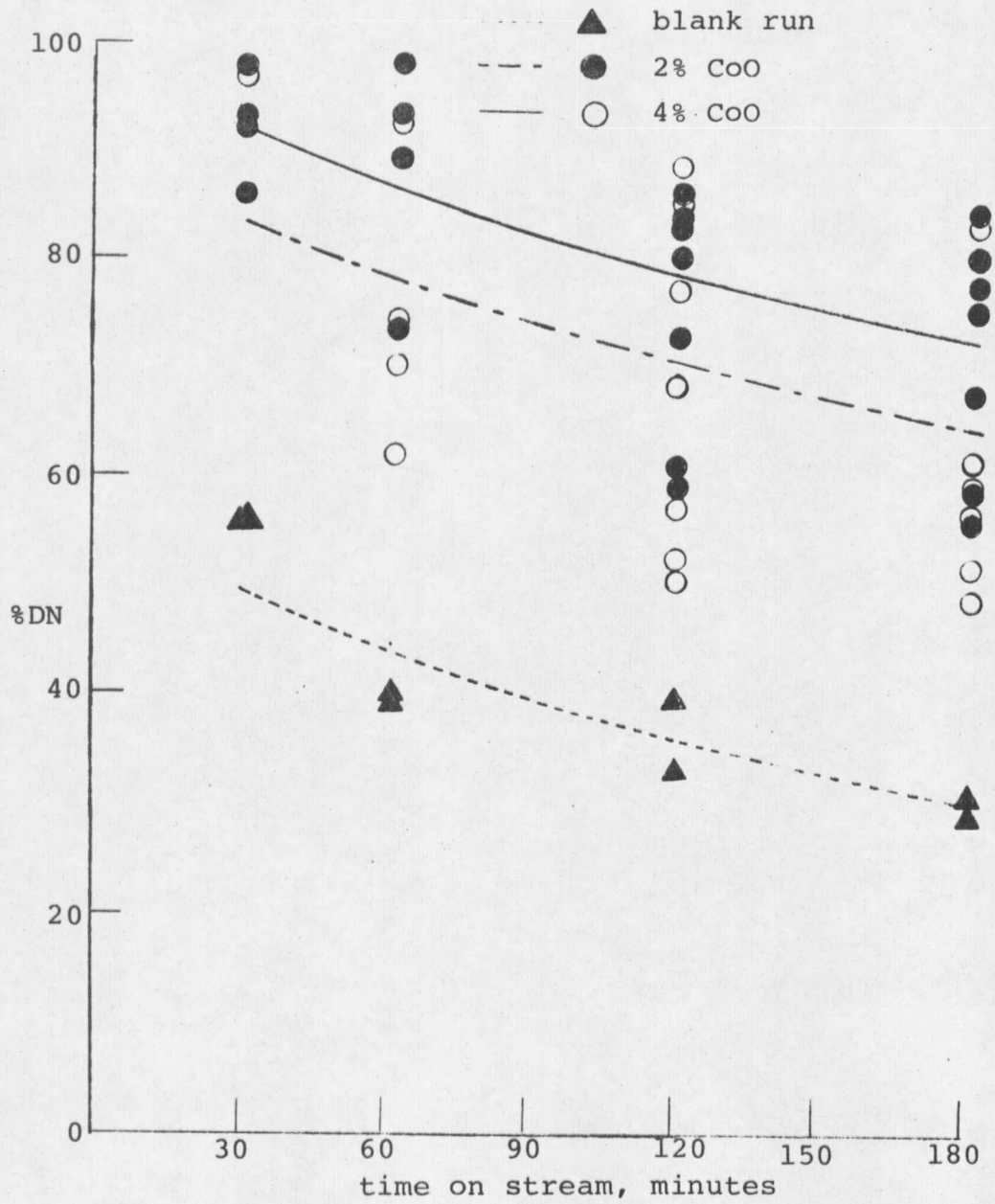

Figure 8. Denitrogenation of SRC-II LECF from Run 23 to 38.

Table XI

Desulfurization and product yield data for SRC-II LECF

Run	Catalyst	%DS on stream, min. 90	150	avg.	Oil Product Yield, wt%	Catalyst Composition, wt% CoO	MoO_3	NiO	WO_3
5	carrier	76	69	72.5	77	0	0	0	0
6	carrier	65	64	64.5	77	0	0	0	0
23	C-41	82	87	84.7	89	2	8	1	8
24	C-42	90	86	88.2	100	2	8	1	2
25	C-43	90	84	87.0	96	2	8	4	8
26	C-44	79	77	78.1	98	2	8	4	2
27	C-45	83	86	83.9	88	2	2	1	8
28	C-46	80	84	82.0	89	2	2	1	2
29	C-47	83	82	82.4	86	2	2	4	8
30	C-48	89	88	88.8	100	2	2	4	2
31	C-49	77	83	80.0	91	4	8	1	8
32	C-50	86	87	86.6	87	4	8	1	2
33	C-51	80	73	76.2	94	4	8	4	8
34	C-52	90	92	91.1	88	4	8	4	2
35	C-53	86	76	81.0	80	4	2	1	8
36	C-54	73	81	77.1	84	4	2	1	2
37	C-55	86	85	85.7	84	4	2	4	8
38	C-56	91	80	85.5	100	4	2	4	2

variables were regressed on the catalyst compositions at a confidence level of 90%. The regressed equation for desulfurization was

$$\%DS = 68.5 + 4.175\ CoO + 2.38\ MoO_3 - 0.63(CoO)(MoO_3)$$

The intercept, 68.5% S, was the averaged activity of Runs 5 and 6. The analysis of variance table is shown in the Appendix B. Co and Mo were found to increase the catalyst activity significantly on desulfurization of LECF. The interactive effect of Co-Mo was negative. The adding of Ni on the catalyst appeared to be ineffective. The effect of metals on oil product yield was found to be insignificant.

The above regression equations were used for analyzing the factorial designs but were not appropriate to use for prediction because the experiments were not designed for this. There were some similarities of metal effects for both feedstocks. Three metals, Co, Mo, and WO_3 affected the catalyst activity on denitrogenation significantly, while Ni did not. The interactive effects of certain metals on both denitrogenation and desulfurization were negative. The effect of Ni on

desulfurization on both feedstocks was found to be insignificant.

Material Balance

An attempt was made to study the material balance of nitrogen for the reactor system. The work was performed on Run 7 to 22 by a coworker. The amount of nitrogen fed with SRC-II VFF, laid down in the reactor, and collected from the outlet liquid and gases was recorded. The spent catalysts and inert supports were analyzed for nitrogen contents so as to obtain the total weight of nitrogen laydown. The exit gases from the reactor were passed through a flask filled with 30 ml. conc. H_2SO_4 before venting. At the end of runs the sulfuric acid solutions were analyzed for nitrogen contents to determine the amount of nitrogen existing in a gas phase. Hsieh(68) has reported in Table XII the distribution of nitrogen in the products. The percent of the feed nitrogen laid down on the catalyst was correlated with catalyst composition. This correlation was found to be insignificant. The average percent of the feed nitrogen laydown on the catalyst was 12.0 wt%. The unaccounted portion of the feed

Table XII

Material balance of nitrogen from Run 7 to 22

Run	space Velocity, v/v/hr	wt.of Nitrogen in the feed*, grams	% laydown Inert Supports	% laydown Catalyst	% in the exit gas	% in the liquid product	unaccounted wt.%
7	0.92	1.7	24.7	14.4	1.7	13.8	45.4
8	0.99	1.9	20.7	10.6	0.5	13.3	54.8
9	1.00	1.9	18.9	10.0	1.6	13.2	56.3
10	1.10	2.0	19.2	11.1	2.6	20.2	46.9
11	1.00	1.9	22.6	11.1	1.6	20.5	44.2
12	0.83	1.6	25.5	12.7	2.0	19.1	40.7
13	1.00	1.9	20.0	9.0	1.6	24.7	44.7
14	0.93	1.8	19.3	12.5	1.7	18.8	47.7
15	1.00	1.9	21.0	12.1	1.6	14.2	51.1
16	0.88	1.7	24.0	11.4	2.4	14.4	47.9
17	0.97	1.8	23.4	10.9	1.6	15.8	48.4
18	0.90	1.7	24.0	10.5	1.2	15.2	49.1
19	0.91	1.7	25.6	12.8	2.9	15.7	43.0
20	0.87	1.7	29.7	15.8	2.2	11.2	41.2
21	0.96	1.8	26.9	14.3	1.0	15.9	41.9
22	0.96	1.8	26.4	13.2	1.0	22.0	37.5

* Feedstock was SRC-II VFF which contained 1.17 wt% N

nitrogen was averaged to be 46.3% which was believed to be the uncollected nitrogen in the exit gases.

Temperature and Initial Space Velocity Observations

Four experiments, Runs 39 to 42, were made to survey the effect of starting at a lower temperature and a higher space velocity. The blank catalyst carrier was used in Runs 39, 40, and 41, while catalyst C-49 was used in Run 42. SRC-II VFF served as the feedstock for these runs.

Runs 39, 40, and 41 were started at 425°C and space velocities of 5, 20, and 10 v/v/hr, respectively, for the first five minutes. Then the temperature increased to 475°C in two hours and the space velocities reduced to 1.0 hr^{-1}. Run 39 coked up after 6 hours due to the increased temperature and low initial space velocity. Runs 40 and 41 were made 8 and 10 hours, respectively, without pressure build-up. Table XIII summarizes the nitrogen contents of liquid product. The denitrogenation of those runs using blank catalyst carrier were poor. The denitrogenation data for Runs 39 and 40 is plotted in Figure 9. The data of Runs 1 and 2 is also

Table XIII

Temperature and initial space velocity observations

Run No.	39	40	41	42
Catalyst	Blank	Catalyst	Carrier	C-49
Temperature*	475	475	475	475
Space Velocity at first 5 min., hr^{-1}	5.0	20.0	10.0	10.0
Space Velocity after 5 min., hr^{-1}	1.0	1.0	1.0	1.0
Time on Stream, minutes	Nitrogen content of liquid product**, wt%			
30	.46	.73	.45	.08
45	-	.56	.52	.11
60	.56	.63	.55	.20
75	.55	.59	.54	.22
90	-	.79	.57	.22
105	.70	.68	.59	.32
120	.63	.67	.37	.29
135	.64	.78	.57	.31
150	.59	.73	.61	.28
165	.66	.67	.82	.25
180	.61	.77	.63	.22
210	.61	.64	.63	.36
240	.60	.69	.60	.27
270	.62	.64	.69	.42
300	.66	.63	.66	.27
330	.62	.69	.68	.31
360	.73	.69	.65	.40
390	coked	.61	.57	.48
420	up	.69	.64	.49
450	.	.89	.62	.42
480	.	.87	.68	.42
510	.	.	.76	.
540	.	.	.64	.
570	.	.	.68	.
600	.	.	.87	.

* Temperature started at 425°C, then increased to 475°C in two hours

** Nitrogen content of feedstock, SRC-II VFF, was 1.17wt%

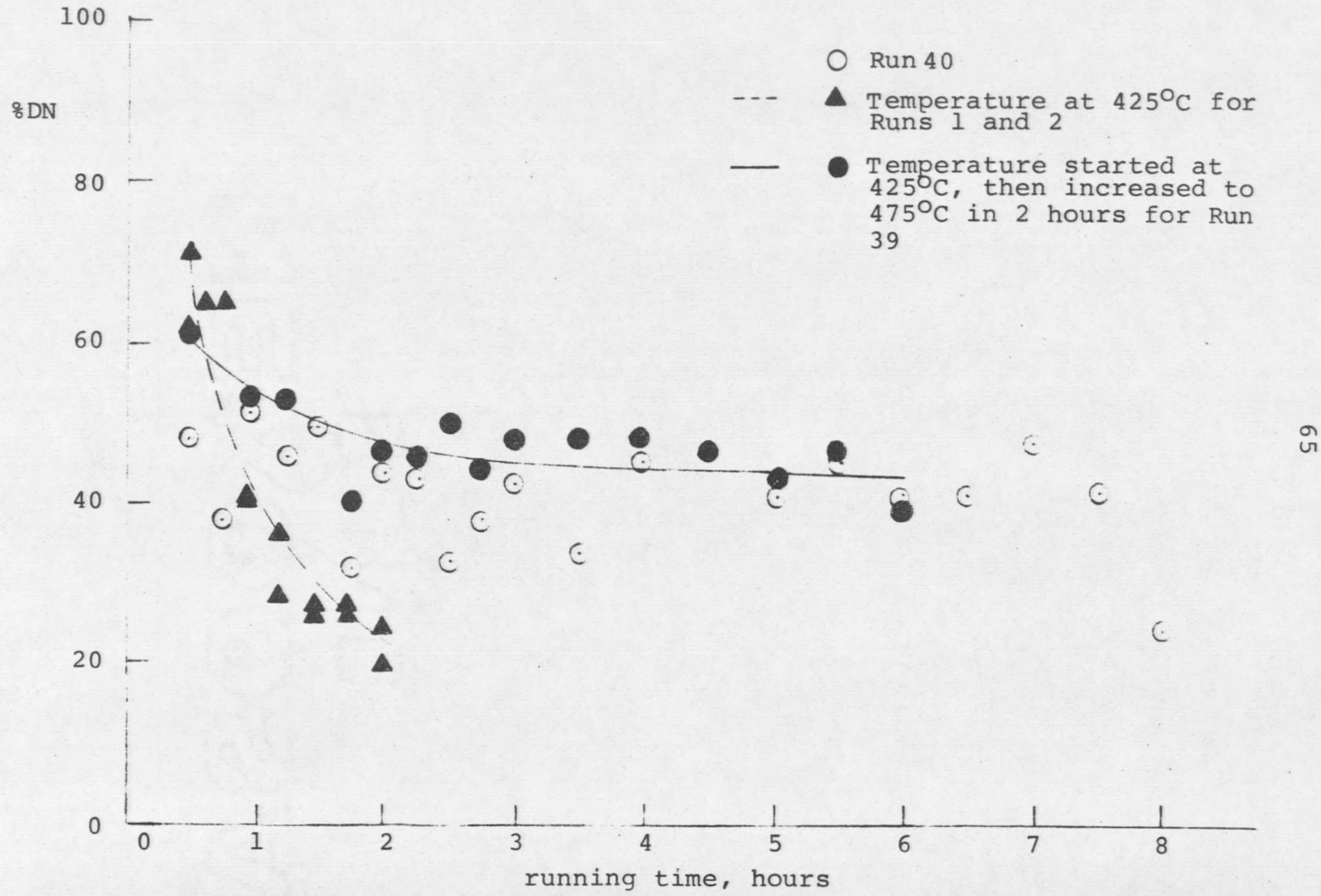

FIGURE 9. Effect of temperature and initial space velocity on denitrogenation

plotted for comparison. The activities of Runs 39 and 40 were slightly lower at the beginning but much less deactivated than those of Runs 1 and 2 which were made a constant temperature of 425°C and a space velocity of 1.0 hr^{-1}. Run 39 gave a better denitrogenation than Run 40 due to its lower initial space velocity.

Run 42 using the same operating conditions as Run 41 but different catalysts was made 8 hours. The data in Table XIII shows that Run 42 gave a better denitrogenation, in which the nitrogen content of SRC-II VFF, 1.17 wt%, was reduced to 0.08 wt% after 30 minutes and to 0.42 wt% after 8 hours. The average nitrogen contents of liquid product for Run 41 and 42 were 0.62 wt% and 0.30 wt%, respectively. The denitrogenation data for these two runs is plotted in Figure 10. It showed that catalyst C-49 gave a better catalyst activity than its blank carrier and that the use of starting at higher space velocity decreased the catalyst deactivation rate.

Catalyst Deactivation

Catalyst deactivation due to the carbon laydown on

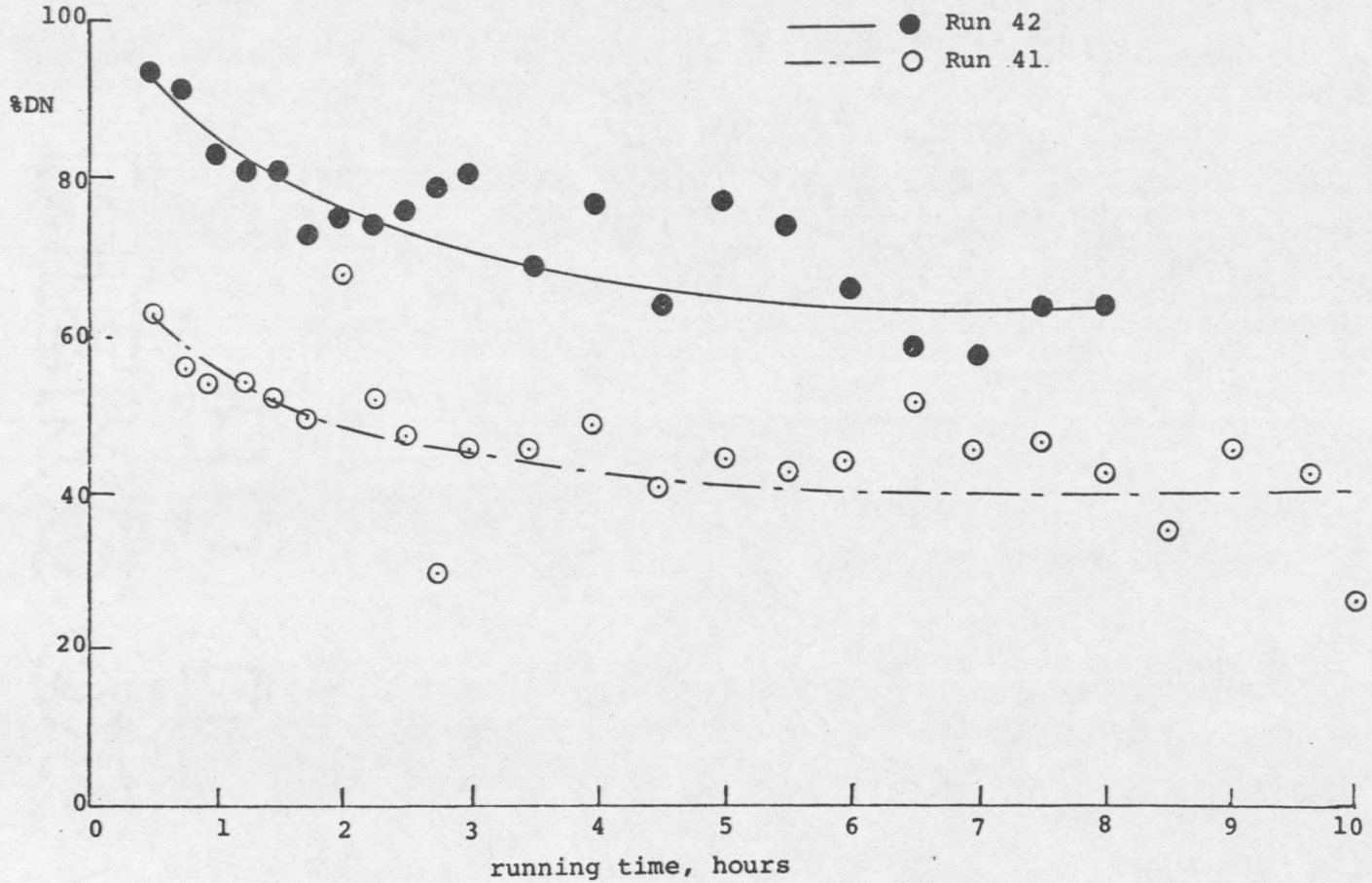

FIGURE 10. Comparison of catalyst C-49 and its carrier for denitrogenation at 475°C.

the catalyst was studied by the pore volume reduction and Auger Electron Spectrum analysis which also provided the information for examining the completeness of catalyst regeneration.

Carbon laydown in the reactor from Run 7 to 22 was determined by a coworker. Spent catalysts and inert supports were burned-off in the oven until their weights reached constant. Rameshwaran(68) reported the portions of carbon laydown on the catalysts and inert supports shown in Table XIV in which the total percent carbon laydown varied from 19.7 wt% to 25.9wt% of feed. The percent carbon laydown on the catalyst section varying from 9.0 wt% to 14.2 wt% was correlated with the catalyst composition. The result indicates that catalysts with 4 wt% CoO give more carbon laydown than those with 2 wt%. The analysis of variance table is shown in Appendix A. In the catalyst section, carbon laydown were recorded at three different positions, top, middle, and bottom. It appeared that there was more carbon laydown on the upstream than on the downstream.

Table XIV

Carbon laydown of Run 7 to 22

Run	Space Velocity v/v/hr	Total Feed* grams	wt.% carbon laydown Catalyst Top	Middle	Bottom	Supports	Total wt.% carbon laydown
7	0.92	149.0	3.76	3.36	3.27	10.8	21.2
8	0.99	160.4	3.33	3.14	3.19	10.3	20.0
9	1.00	162.0	3.51	3.98	3.71	10.2	21.4
10	1.10	178.2	3.74	3.76	3.56	9.3	20.3
11	1.00	162.0	3.96	3.74	3.74	10.5	21.9
12	0.83	134.5	4.08	3.99	3.78	11.7	23.6
13	1.00	162.0	3.10	2.98	2.95	10.8	19.8
14	0.93	150.7	3.56	3.34	3.70	10.4	21.0
15	1.00	162.0	4.31	4.22	4.03	10.3	22.9
16	0.88	142.6	3.73	3.66	3.47	11.4	22.2
17	0.97	157.1	3.64	3.44	3.42	10.8	21.3
18	0.90	145.8	3.92	3.83	3.69	11.6	20.1
19	0.91	147.4	4.89	4.81	4.51	11.7	25.9
20	0.87	140.9	4.70	4.29	4.14	11.4	24.6
21	0.96	155.5	3.67	3.72	3.99	10.6	21.9
22	0.96	155.5	4.03	4.07	3.73	11.2	23.1

* Feedstock was SRC-II VFF

The self-developed water saturation procedure was performed to measure the pore volume of blank catalyst carrier. A value of 0.80 ml./gram was obtained to compare with the reported data of 0.84 ml./gram. The same measurement procedures were applied to measure the pore volume of fresh catalysts from C-41 to C-56. Table XV shows the data. It was found that the pore volume decreased after the impregnation and that there was a strong correlation between the pore volume and the total metal loading. Figure 11 plots the data and the regressed line. It is interesting to note that the pore volumes of fresh catalyst shown in Figure 11 become a constant of 0.75 when the ml./gram catalyst is converted to milliters per gram of catalyst carrier by multiplying by the (1 + total wt% metal loaded) conversion factor. The converted data is also presented in Table XV, which shows the pore volume has been reduced 6% after the impregnation. The spent catalysts of Run 7 to 22 using VFF and of Run 23 to 38 using LECF were measured for the pore volume by the same method. The results are listed in Table XV. The pore volume of catalysts being used for

Table XV

Pore volume of catalysts measured by water saturation

Catalyst	Pore Volume: Fresh Catalyst ml./gram of Catalyst	Pore Volume: Fresh Catalyst ml./gram of Catalyst carrier	Pore Volume: Spent Catalyst Used for VFF, ml./gram Catalyst	Pore Volume: Spent Catalyst Used for LECF, ml./gram Catalyst	Total Metal Loaded, wt.%
carrier	0.80 ± 3%		-	-	0
C-41	0.63	0.75	0.20	0.49	19
C-42	0.64	0.72	0.14	0.54	13
C-43	0.60	0.73	0.18	0.51	22
C-44	0.65	0.75	0.11	0.53	16
C-45	0.68	0.77	0.13	0.58	13
C-46	0.69	0.74	0.18	0.56	7
C-47	0.65	0.75	0.17	0.58	16
C-48	0.68	0.75	0.14	0.59	10
C-49	0.62	0.75	0.20	0.44	21
C-50	0.65	0.75	0.14	0.47	15
C-51	0.60	0.74	0.13	0.60	24
C-52	0.64	0.76	0.18	0.52	18
C-53	0.68	0.78	0.12	0.45	15
C-54	0.68	0.74	0.12	0.45	9
C-55	0.64	0.76	0.09	0.48	18
C-56	0.71	0.80	0.09	0.59	12

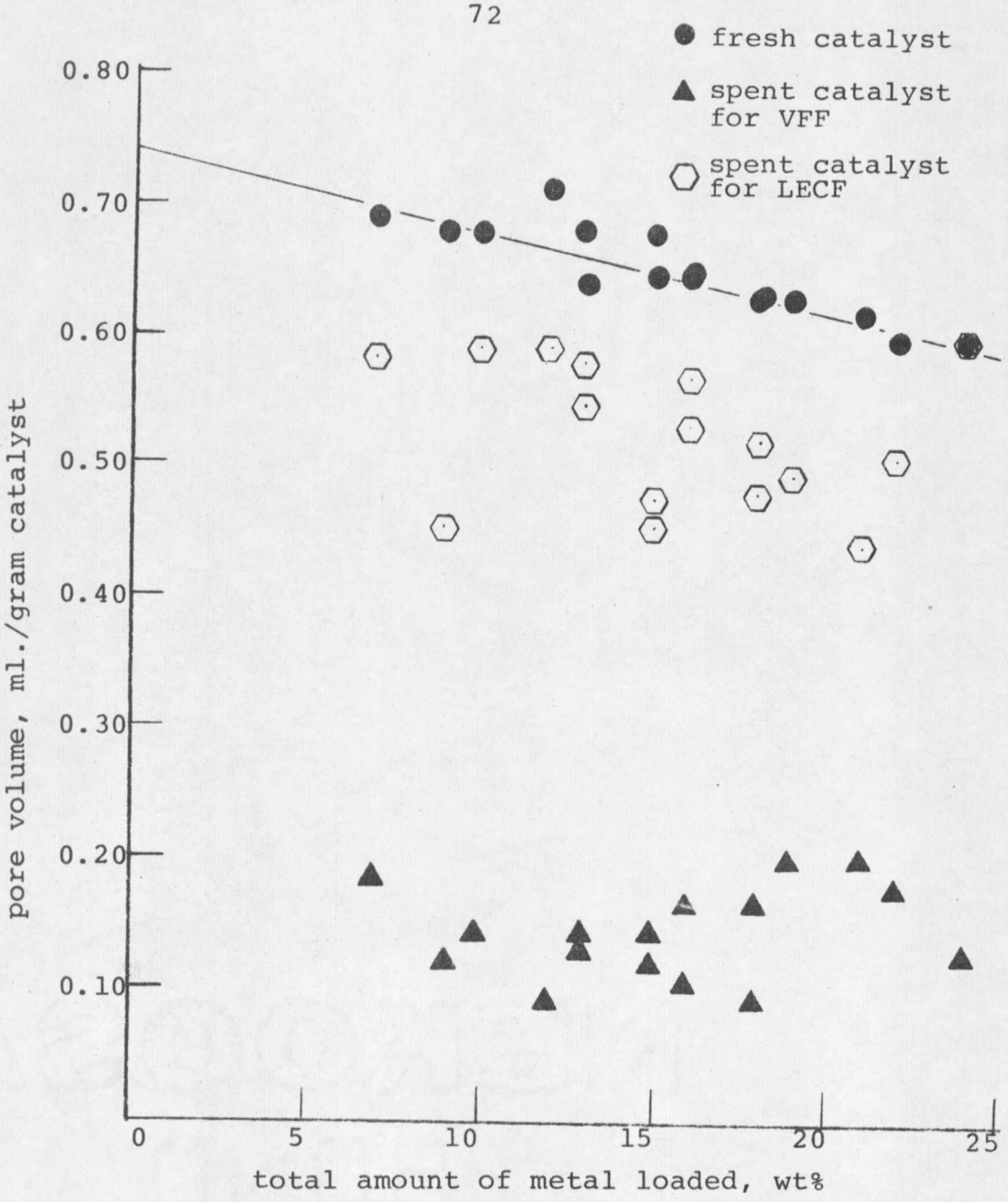

Figure 11. Correlation between pore volume and total metal loading.

upgrading SRC-II VFF was largely reduced because of carbon laydown. Their pore volume reductions ranged from 70% to 87%. Catalysts being used for SRC-II LECF had an average pore volume reduction of 20%. These data are plotted in Figure 11 for comparison. Carbon laydown on the catalyst could be burned-off by the air or oxygen to restore the catalyst activity. However, if the organometallic compounds have laid down with carbon, the catalyst would be poisoned permanently.

The Auger Electron Spectroscopy was applied to analyze the selected samples for carbon distribution on the individual catalyst cylinder. Figure 12 shows Auger spectra for the spent catalyst C-49 of Run 42. By referring to the standard spectra of the elements, peaks at 272^{ev} and 1396^{ev} were identified as carbon and aluminum, respectively. Spectra at different spots were obtained from the same electron beam energy and current. Table XVI shows the peak-to-peak heights of carbon and aluminum measured from the spectra. The C/Al atomic ratio was approximately obtained by multiplying

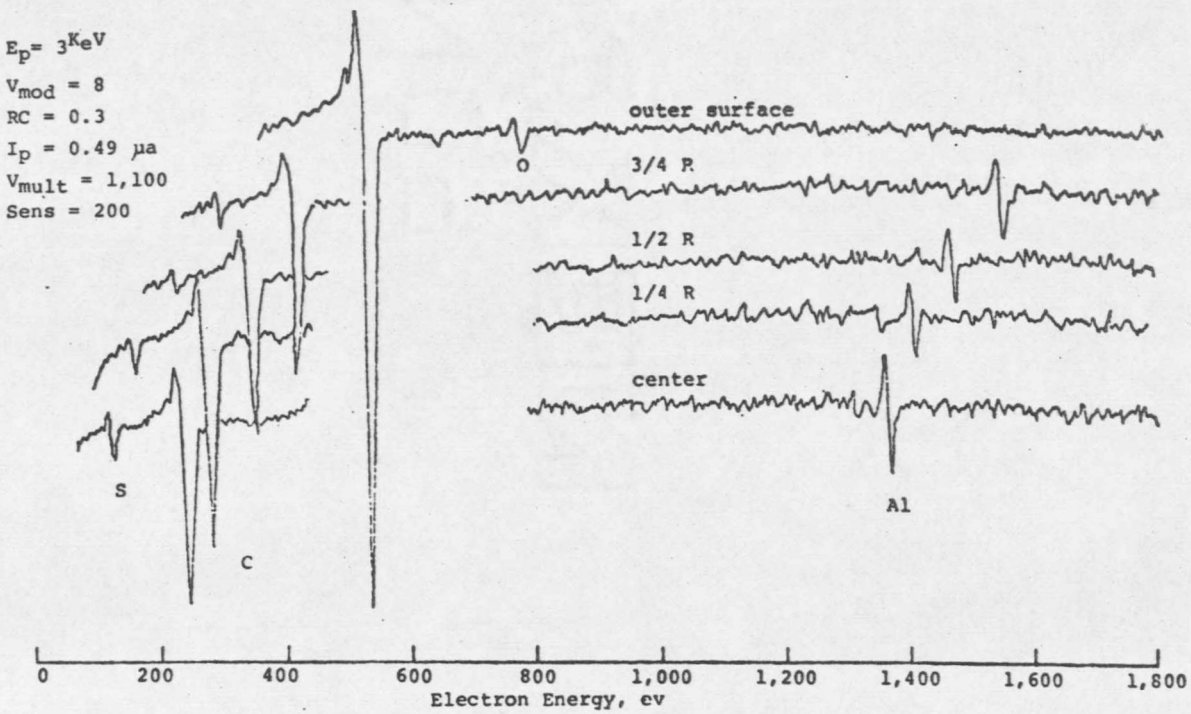

FIGURE 12. Auger spectra of the spent catalyst C-49 of Run 42.

Table XVI

Carbon distribution data for the spent catalyst C-49 of Run 42

Run No.	Distance from the center	Peak-to peak height Carbon	Aluminum	C/Al Atomic ratio**
	R*	12.0	0.2	15.0
	3/4R	5.4	1.5	0.9
42	1/2R	4.0	1.5	0.7
	1/4R	4.4	1.6	0.7
	0	4.8	2.5	0.5

* R, radius of catalyst cylinder, was 1/64".

** C/Al atomic ratio = $I_C/I_{Al} \times I^H_{Al}/I^H_C \times K_C/K_{Al}$

$= 0.25 \times I_C/I_{Al}$

I_C and I_{Al} are peak-to-peak heights of carbon and aluminum, respectively, measured from the spectrum in Figure 12. I^H and K are amplitude height and scale factors of elements, respectively, obtained from the handbook(67).

the peak-to-peak height ratio by a factor of 0.25 which was calculated from the amplitude heights and scale factors shown in the handbook(67). The C/Al atomic ratio increased from 0.5 at the center of catalyst particle to 15 at the outer surface. The carbon distribution in Figure 13 shows that the mechanism of catalyst poisoning appears to be the pore mouth plug-up. The carbon laydown on the outer surface was tremendously higher than on the inner side.

Catalyst Regeneration and Reutilization

To pursue the feasibility of reusing a promising catalyst, a process which reactivates the spent catalyst via periodic air burn-off and resulfiding is required. The completeness of catalyst burn-off was determined by the pore volume recovery and proved by the Auger spectra. Catalyst C-49 was tested for about 100 hours by reusing the catalyst periodically through regenerations.

Fresh catalyst C-49 was again tested in Run 43 for 3 hours using SRC-II VFF as feedstock. The operating conditions were 1,000 psig, 425^{o}C, a hydrogen flow rate of 10,000 scf/bbl, a space velocity of 1.0 hr^{-1},

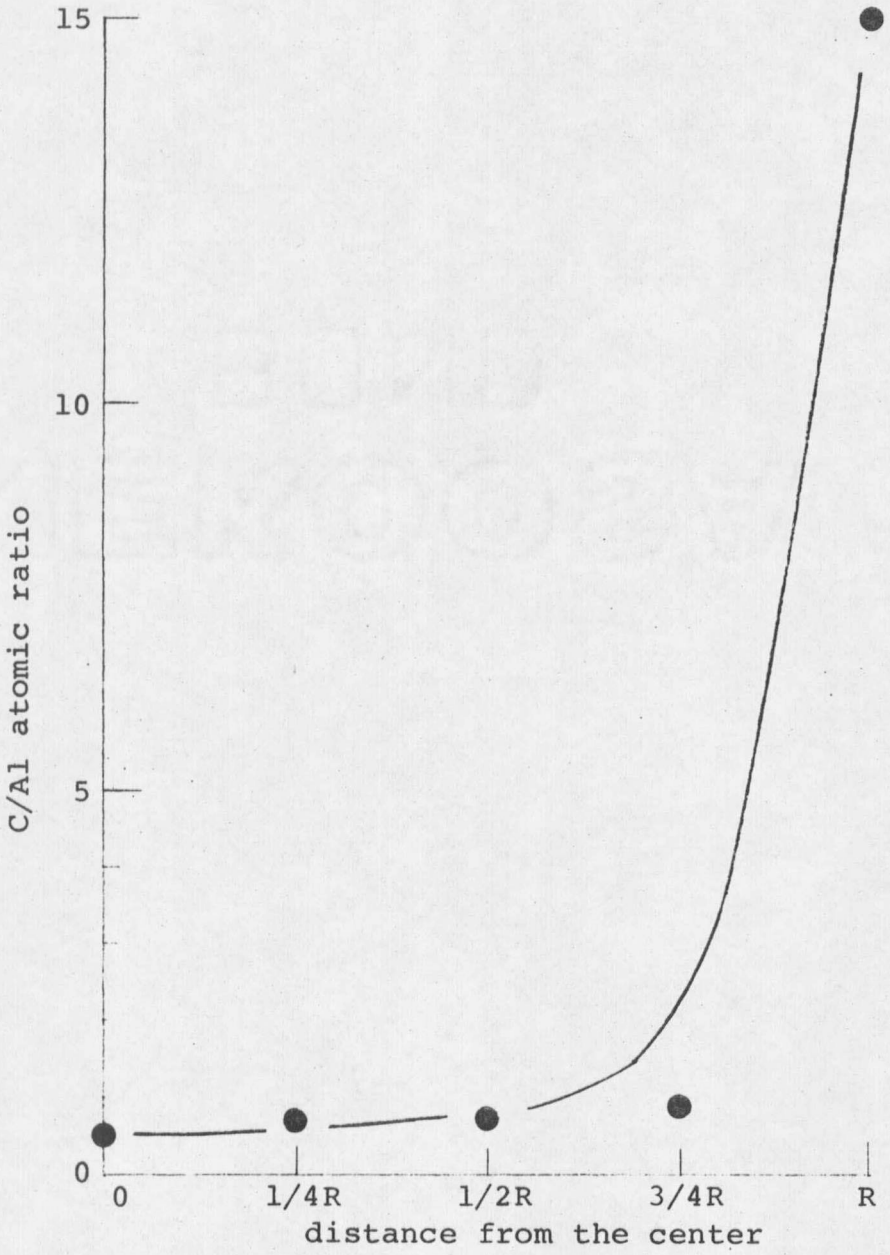

FIGURE 13. Carbon distribution of spent catalyst C-49 of Run 42.

and liquid feed temperature of 85°C. The results showed that the nitrogen content of SRC-II VFF, 1.17 wt%, was reduced to an average of 0.22 wt%. The sulfur content was reduced to an average of 0.25 wt% and oil product yield was 77 wt%. The spent catalyst was measured for the pore volume and analyzed by the Auger spectra. The pore volume turned out to be 0.20 ml./gram of catalyst. The Auger spectra are shown in Figure 14. The carbon to aluminum atomic ratios from the center of catalyst cylinder to the outer surface are plotted in Figure 15. The carbon distribution observed was similar to the one obtained from Run 42. The outer surface of the catalyst particle was almost fully covered with carbon.

The spent catalyst was burned-off under atmospheric pressure at 550°C with 5% O_2 in nitrogen. Catalyst was sampled every four hours and analyzed for pore volume. The gas flow rate was kept at 5 scf/hr for the first 12 hours and no temperature increase was found. The pore volume was increased from 0.2 to 0.33 ml./gram in four hours but then leveled off. Figure 16 plots the pore volume recovery during burn-off. The gas flow

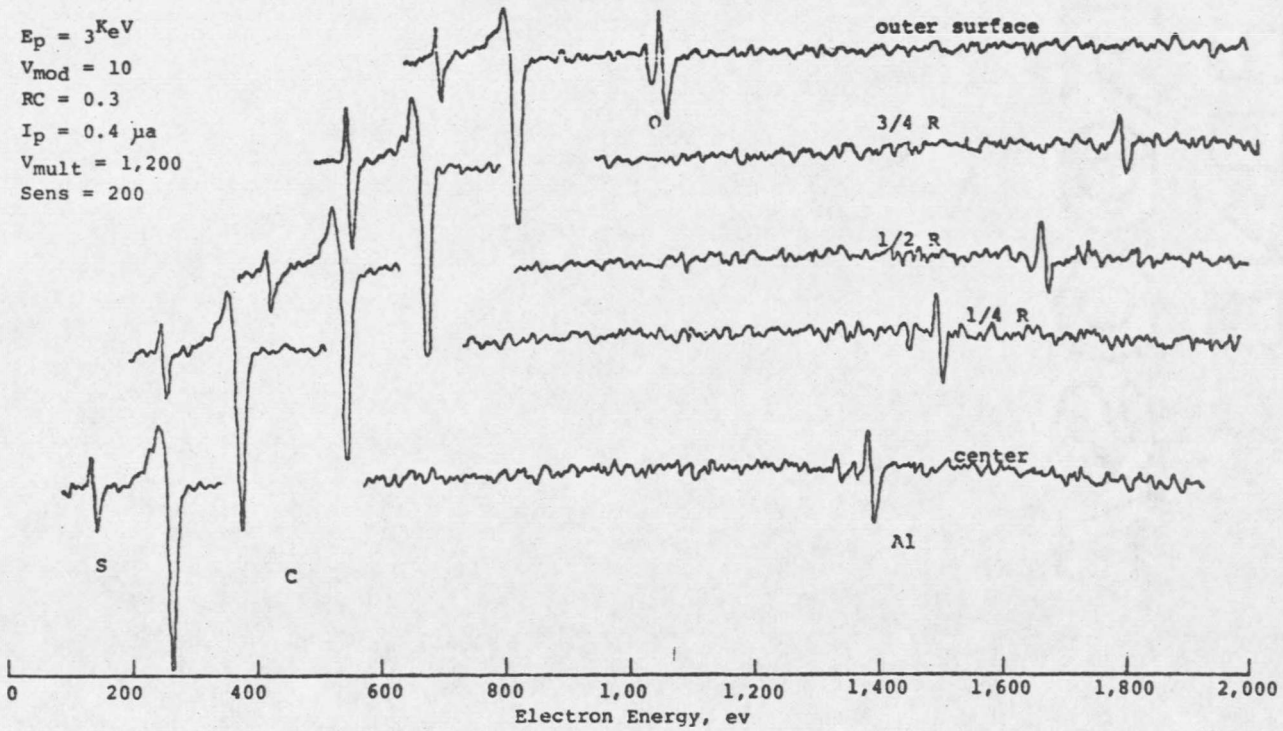

FIGURE 14. Auger spectra of spent catalyst C-49 of Run 43.

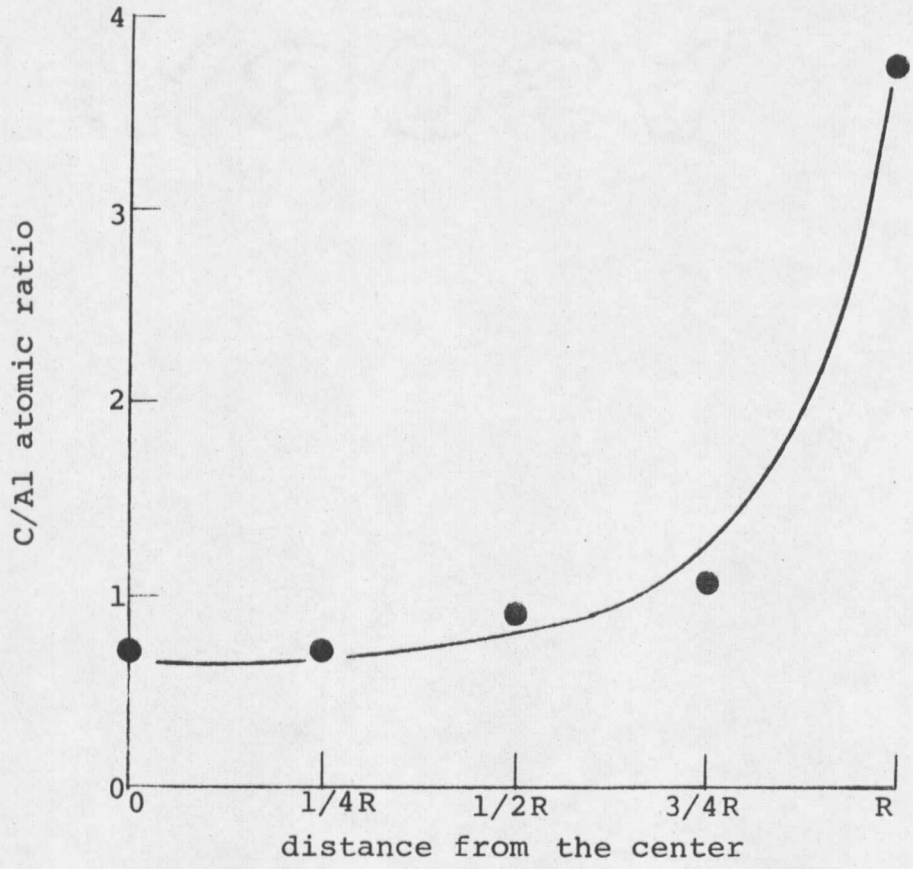

FIGURE 15. Carbon distribution of spent catalyst C-49 of Run 43

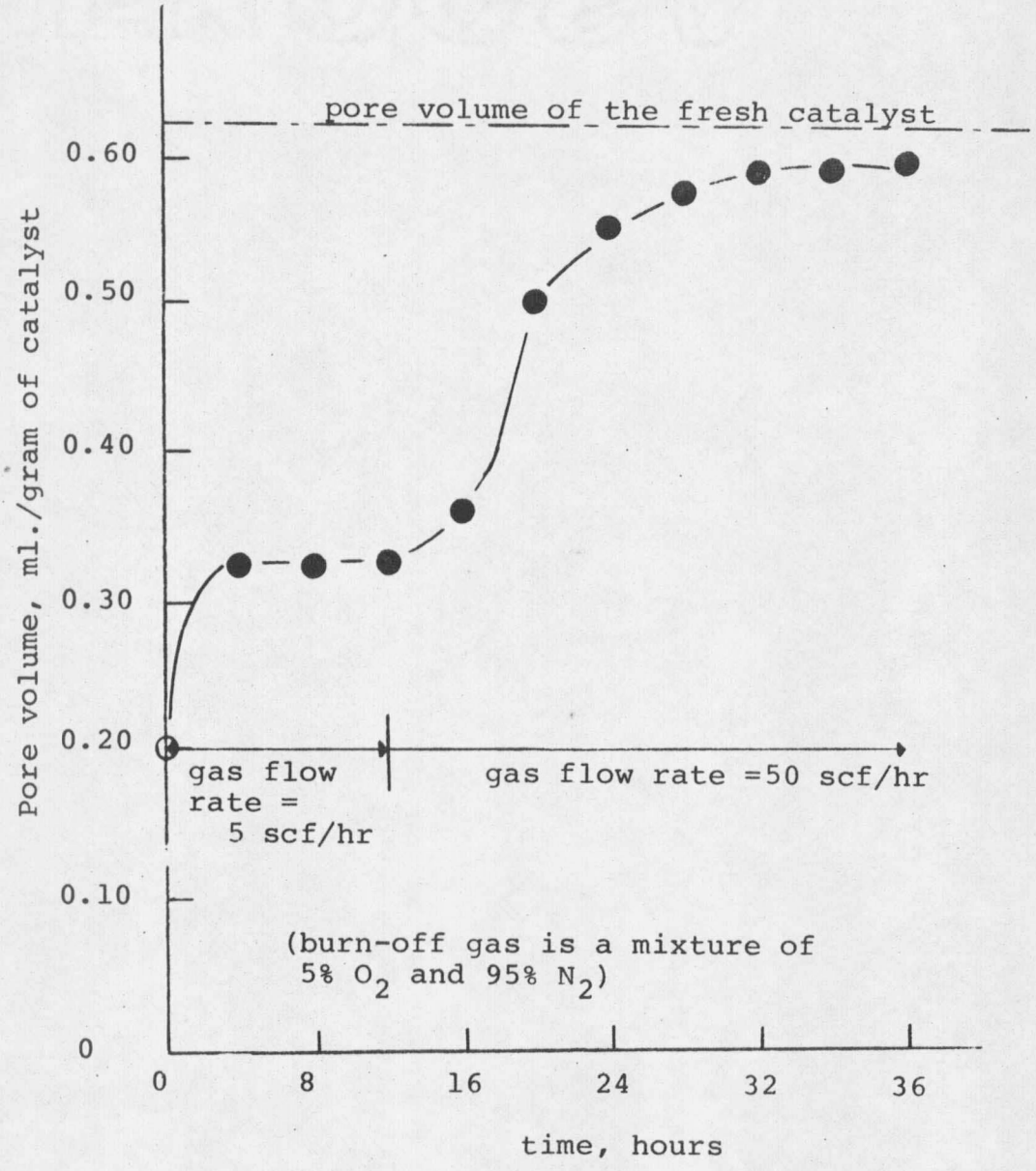

Figure 16. Pore volume recovery through burn-off for the spent catalyst C-49 of Run 43

rate was then increased to 50 scf/hr for the following 24 hours. The pore volume was increased more rapidly to 0.59 ml./gram after 36 hours, which was a pore volume recovery of 95% compared with a pore volume of 0.62 ml./gram for the fresh catalyst. The catalyst was then analyzed for the Auger spectrum. Figure 17 shows that the signal of carbon of Auger Spectrum was undetectable. It agreed with the result of pore volume measurement. This catalyst was reactivated by sulfiding and reused in Run 44.

The average nitrogen content of the liquid product was again reduced to 0.21 wt% in Run 44, which indicated that the catalyst activity for denitrogenation was fully restored. The data for denitrogenation is shown in Table XVII and data for desulfurization and oil product yield is shown in Table XVIII. The spent catalyst of Run 44 was burned-off for 8 hours with 40% O_2 in the nitrogen at 550°C and a gas flow rate of 1.5 scf/hr. The temperature increased to 580°C in ten minutes, then leveled-off to 565°C. The pore volume of the catalyst has been recovered to 94% after 4 hours burn-off. The Auger Spectrum in Figure 17 shows that the amount of

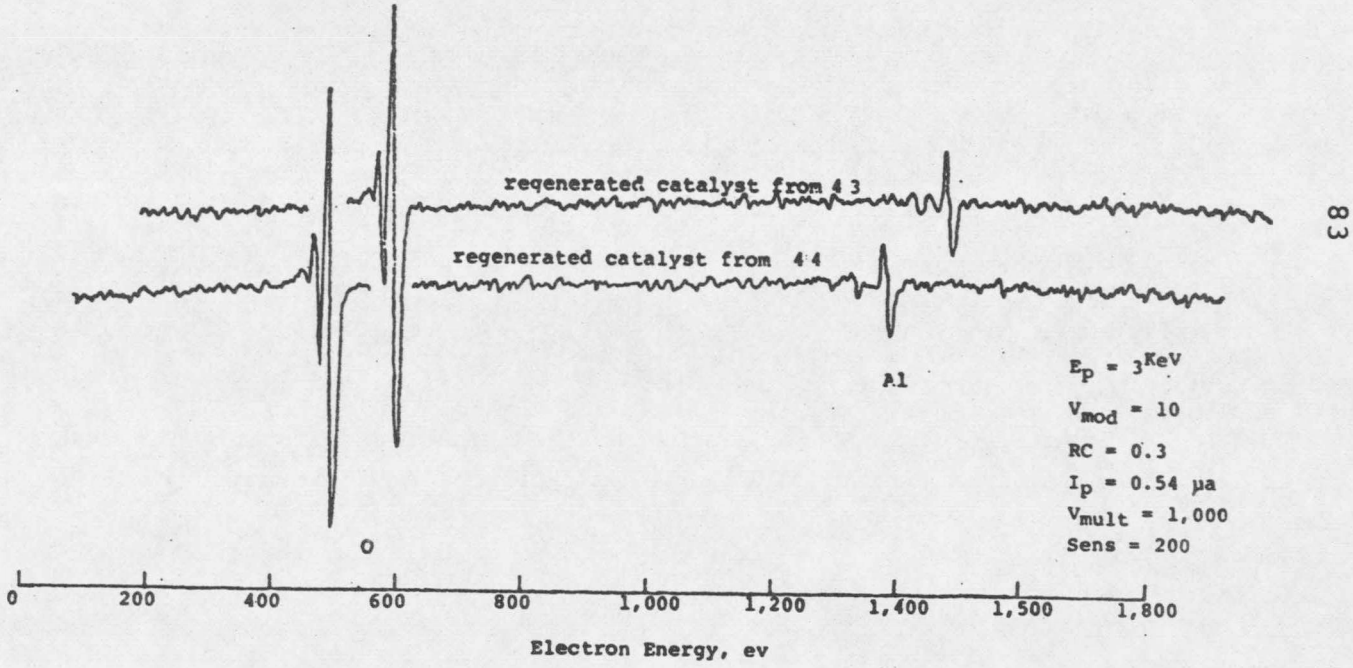

FIGURE 17. Auger spectra of regenerated catalyst C-49.

Table XVII

Nitrogen content of product from Run 43 to 76

Run	Temp., °C	LHSV, hr^{-1}	Nitrogen content of product, wt% time on stream, minutes 30	45	60	120	180	Avg. wt% N
43	427	1.10	.	0.06	0.39	0.36	0.30	0.22
44	433	1.00	.	0.03	0.16	0.15	0.43	0.22
45	428	0.93	.	0.19	0.29	0.45	0.45	0.42
46	423	1.10	.	0.04	0.10	0.52	0.57	0.40
47	420	1.00	.	0.07	0.25	0.53	0.76	0.50
48	431	0.90	.	0.07	0.20	0.34	0.60	0.36
49	434	1.10	0.06	.	0.16	0.28	0.31	0.19
50	423	0.94	0.12	.	0.23	0.22	0.33	0.24
51	425	1.10	0.09	.	0.15	0.30	0.30	0.24
52	428	1.00	0.12	.	0.09	0.20	0.24	0.19
53	425	0.98	0.09	.	0.15	0.27	0.26	0.21
54	428	0.94	0.09	.	0.12	0.25	0.42	0.27
55	426	1.10	0.09	.	0.22	0.29	0.38	0.27
56	427	1.00	0.02	.	0.09	0.22	0.44	0.21
57	417	1.00	0.09	.	0.23	0.34	0.32	0.26
58	462	1.00	0.04	.	0.36	0.30	0.10	0.22
59	426	0.96	0.02	.	0.08	0.18	0.28	0.28
60	455	0.95	0.02	.	0.04	0.12	0.13	0.08

Table XVII (continued)

Run	Temp., °C	LHSV, hr^{-1}	Nitrogen content of product, wt% time on stream, minutes 30	45	60	120	180	Avg. wt% N
61	420	0.98	0.03	.	0.24	0.21	0.21	0.19
62	448	0.97	0.08	.	0.06	0.14	0.19	0.15
63	422	0.90	0.02	.	0.26	0.16	0.19	0.19
64	449	0.95	0.02	.	0.10	0.16	0.19	0.13
65	425	0.96	0.07	.	0.09	0.20	0.24	0.18
66	454	0.92	0.02	.	0.06	0.11	0.15	0.11
67	429	0.88	0.05	.	0.04	0.15	0.23	0.12
68	450	0.99	0.03	.	0.03	0.15	0.16	0.09
69	425	0.97	0.10	.	0.11	0.21	0.24	0.17
70	442	0.86	0.02	.	0.17	0.39	0.27	0.21
71	424	0.89	0.33	.	0.26	0.37	0.43	0.35
72	446	0.92	0.20	.	0.27	0.41	0.47	0.34
73	413	1.00	0.23	.	0.25	0.35	0.40	0.31
74	451	1.00	0.09	.	0.28	0.38	0.41	0.29
75	423	0.86	0.15	.	0.28	0.43	0.44	0.33
76	455	0.98	0.25	.	0.15	0.24	0.26	0.23

Table XVIII

Sulfur content of product and oil product yield from Run 43 to 76

Run	Temp., °C	LHSV. hr^{-1}	Sulfur content of product, wt% time on stream, min. 75	105	Avg. wt% S	Oil product yield wt%
43	427	1.10	0.26	0.24	0.25	77
44	433	1.00	0.35	0.27	0.31	71
45	428	0.93	0.45	0.39	0.42	76
46	423	1.10	0.37	0.42	0.40	70
47	420	1.00	0.33	0.21	0.31	74
48	431	0.90	0.24	0.33	0.28	79
49	434	1.10	0.20	0.19	0.19	94
50	423	0.94	0.23	0.17	0.20	97
51	425	1.10	0.29	0.23	0.26	88
52	428	1.00	0.21	0.24	0.22	89
53	425	0.98	0.21	0.27	0.24	89
54	428	0.94	0.29	0.28	0.29	86
55	426	1.10	0.13	0.35	0.24	87
56	427	1.00	0.23	0.29	0.26	90
57	417	1.00	0.17	0.18	0.17	93
58	462	1.00	0.21	0.22	0.21	86
59	426	0.96	0.16	0.12	0.14	88
60	455	0.95	0.28	0.14	0.21	84

Table XVIII (continued)

Run	Temp., °C	LHSV. hr^{-1}	Sulfur content of product, wt% time on stream, min. 75	105	Avg. wt% S	Oil product yield
61	420	0.98	0.15	0.40	0.28	92
62	448	0.97	0.22	0.29	0.25	88
63	422	0.90	0.17	0.12	0.14	89
64	449	0.95	0.28	0.13	0.20	92
65	425	0.96	0.12	0.11	0.12	93
66	454	0.92	0.14	0.11	0.13	97
67	429	0.88	0.11	0.08	0.09	92
68	450	0.99	0.11	0.20	0.15	89
69	425	0.97	0.24	0.18	0.21	94
70	442	0.86	0.15	0.10	0.13	84
71	424	0.89	0.13	0.16	0.14	85
72	446	0.92	0.12	0.13	0.13	93
73	413	1.00	0.11	0.10	0.11	88
74	451	1.00	0.15	0.15	0.15	98
75	423	0.86	0.19	0.19	0.19	92
76	455	0.98	0.12	0.10	0.11	97

carbon left on the catalyst was negligible. The catalyst was then further reused for periods of 3 hours between regenerations via 4 hours burn-off with 40% O_2 in the nitrogen at the gas flow rate of 1.5 scf/hr. Figure 18 plots the denitrogenation data from Runs 43 to 48. The results show that the catalyst activity has been restored through the regeneration process and follows the same pattern from period to period.

Starting with Run 49, the feedstock was changed to SRC-II Light Ends Column Feed because of the lack of Vacuum Flash Feed supply. The periodic reuse of the catalyst was extended to 102 hours. Tables XVII and XVIII summarize the results. The temperature ranged from 417 to 462^{o}C and the space velocity kept about 1.0 hr^{-1}. The results show that the average nitrogen content of the liquid product has been consistently reduced to less than 0.3 wt% and that the liquid product yields approximately 90 wt%. Figure 19 plots the data for nitrogen content of the liquid product. By observing the relationship between the reactor temperature and the nitrogen content in the liquid product, it seemed that the higher temperature gave the better

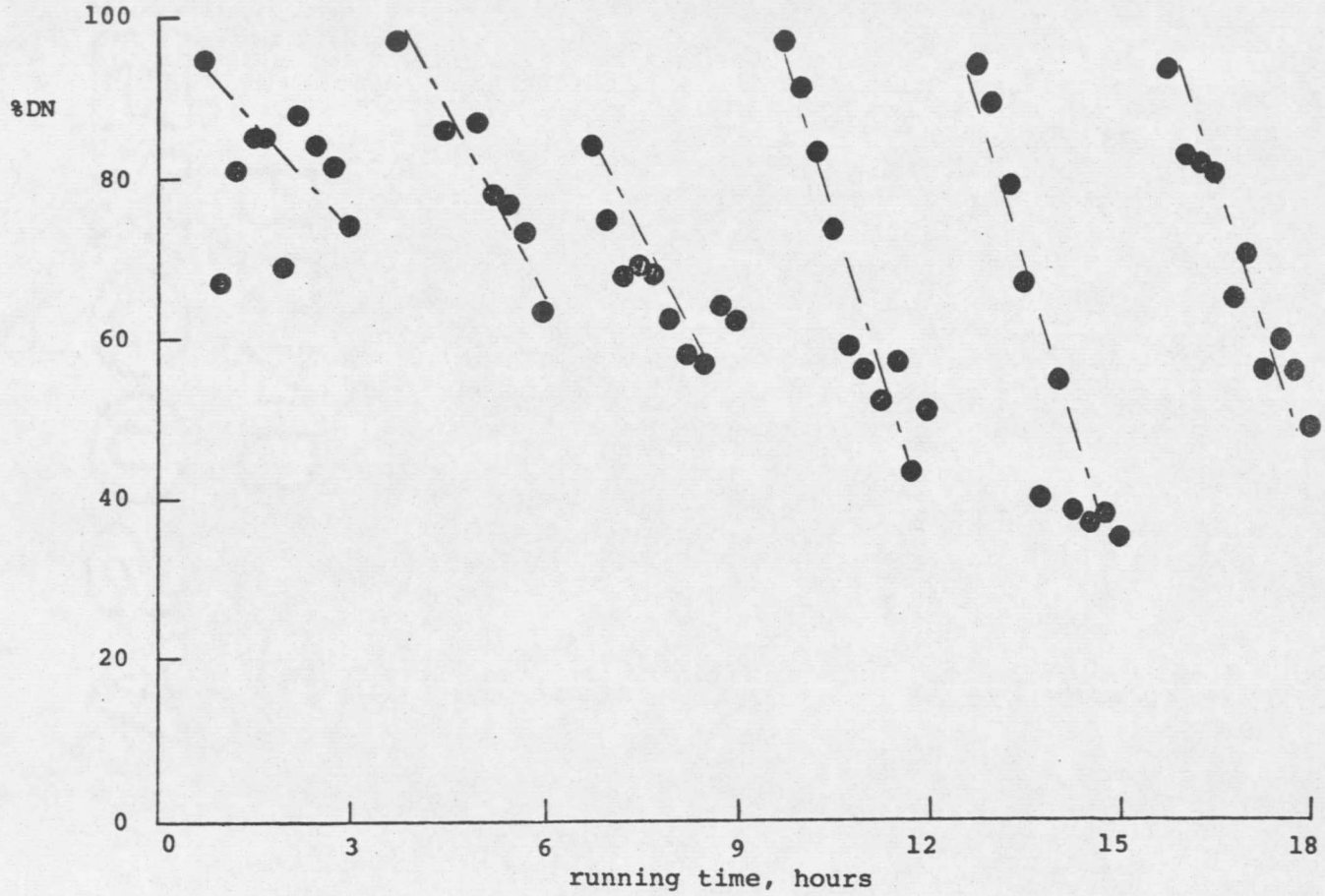

FIGURE 18. Denitrogenation of Run 43 to 48.

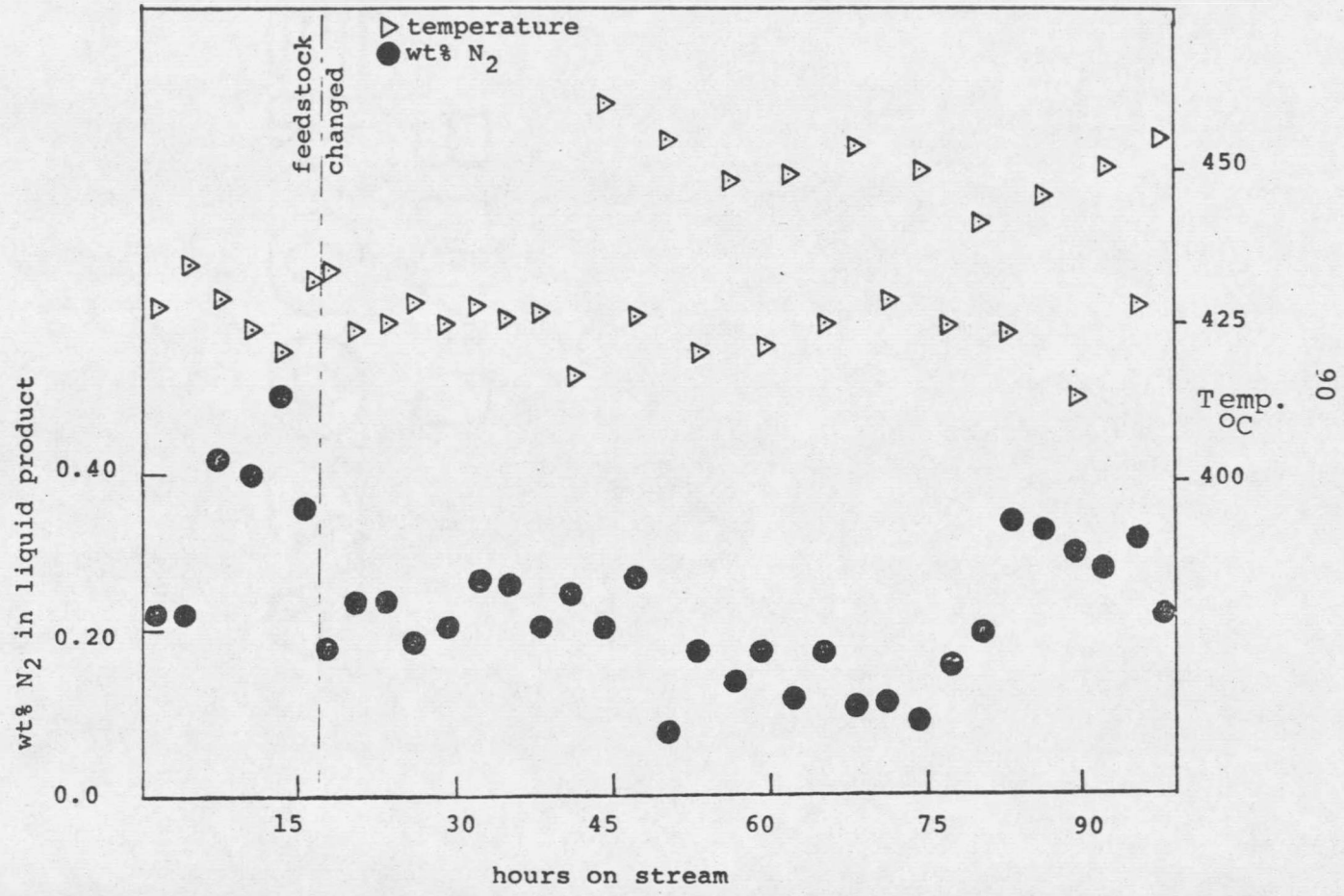

FIGURE 19. Nitrogen content of liquid product from Run 43 to 76.

denitrogenation. The data for sulfur content of the liquid product is plotted in Figure 20.

Catalyst C-49 was again used for 104 hours through periods of 8 hour runs from Runs 77 to 89 using SRC-II LECF as feedstock. The fresh catalyst was used in Run 77 and the spent catalyst was burned-off for the first 4 hours with 5% O_2 in nitrogen at a gas flow rate of 5 scf/hr. and for another 4 hours with 40% O_2 in the nitrogen at the gas flow rate of 1.5 scf/hr. Table XIX and XX summarize the data. Figure 21 plots the average nitrogen and sulfur contents of the liquid product as function of time. The average nitrogen and sulfur contents were reduced to less than 0.25 wt%. The liquid product recovered averaged 91 wt%.

Characterization of Liquid Product and Cost Estimation

Liquid products collected from Runs 23 to 38 and from Runs 43 to 76 were combined to obtain a gasoline sample for the octane tests. The yield of 50-204^{o}C boiling range gasoline was 40% of the liquid product, whose octane tests gave an average octane number of

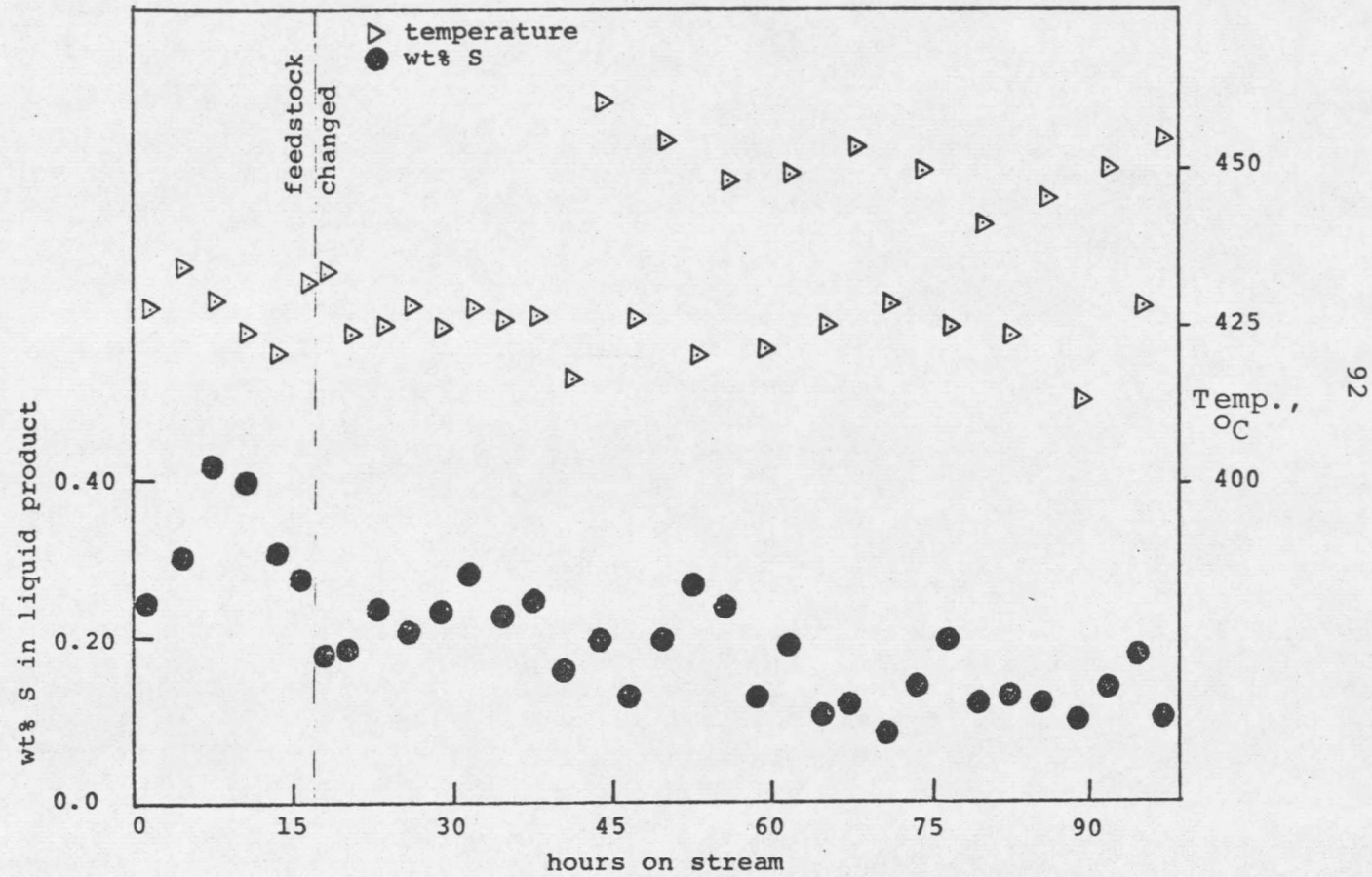

FIGURE 20. Sulfur content of liquid product form Run 43 to 48.

Table XIX

Nitrogen content of product from Run 77 to 89

Run No.	Avg. Temp., °C	LHSV	Nitrogen Content, wt% time on stream, hours 1	2	3	4	5	6	7	8	Avg. wt.%
77	440	1.00	0.05	0.17	0.30	0.16	0.25	0.20	0.20	0.27	0.23
78	433	1.00	0.02	0.15	0.28	0.25	0.28	0.31	0.29	0.35	0.24
79	433	0.84	0.11	0.15	0.19	0.24	0.27	0.24	0.28	0.22	0.21
80	429	1.00	0.08	0.22	0.24	0.23	0.26	0.26	0.29	0.27	0.21
81	431	0.92	0.29	0.20	0.23	0.26	0.26	0.30	0.30	0.28	0.24
82	426	0.95	0.09	0.18	0.24	0.35	0.27	0.27	0.30	0.29	0.21
83	434	0.97	0.11	0.21	0.24	0.25	0.26	0.29	0.28	0.30	0.22
84	456	0.97	0.11	0.19	0.21	0.23	0.27	0.29	0.27	0.31	0.24
85	424	0.94	0.13	0.23	0.26	0.33	0.26	0.26	0.32	0.27	0.22
86	428	1.00	0.15	0.16	0.16	0.28	0.29	0.22	0.22	0.24	0.21
87	425	1.00	0.09	0.20	0.23	0.30	0.25	0.25	0.24	-	0.22
88	425	0.96	0.05	0.20	0.17	0.22	0.18	0.30	0.32	0.35	0.23
89	427	0.94	0.08	0.15	0.20	0.23	0.19	0.20	0.24	0.28	0.22

Table XX

Sulfur content of product and oil product yield from Run 77 to 89

Run	Temp., °C	LHSV, hr^{-1}	Sulfur content, wt% time on stream, hours 1.5	3.5	5.5	7.5	Avg. wt% S	wt% Oil product yield
77	440	1.00	0.20	0.17	0.17	0.16	0.17	93
78	433	1.00	0.17	0.17	0.19	0.19	0.18	95
79	433	0.84	0.17	0.18	0.18	0.19	0.18	89
80	429	1.00	0.22	0.06	0.10	0.22	0.15	93
81	431	0.92	0.24	0.22	0.15	0.08	0.17	91
82	426	0.95	0.24	0.22	0.16	0.20	0.21	85
83	434	0.97	0.28	0.15	0.28	0.27	0.24	89
84	456	0.97	0.10	0.11	-	0.19	0.13	93
85	424	0.94	0.19	0.22	0.10	0.13	0.16	89
86	428	1.00	0.16	0.17	0.16	0.26	0.19	91
87	425	1.00	0.14	0.19	0.11	0.20	0.16	90
88	425	0.96	0.08	0.08	0.20	0.19	0.14	92
89	427	0.94	0.10	0.06	0.08	0.11	0.09	93

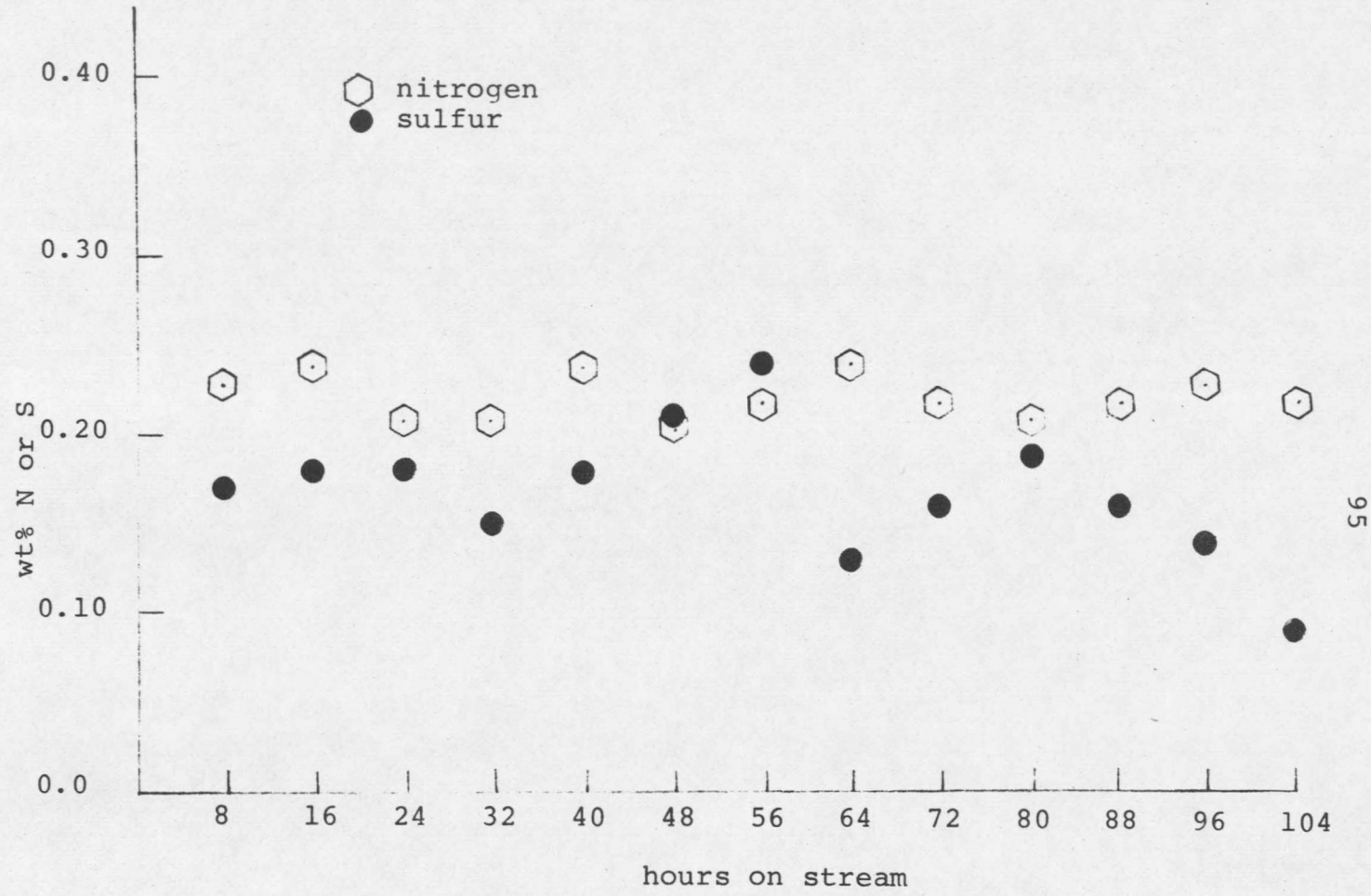

Figure 21. Average nitrogen and sulfur contents from Run 77 to 89

81.7. The result of octane tests was provided by CENEX(69).

Samples from Run 76 to 89 were collected together and sent to Gulf Research & Development Company for the detailed characterization(70). The results indicated that the specific gravity of SRC-II LECF, 0.983, was reduced to 0.945 and that the liquid product consisted of 27.1 wt% naphtha, 36.3% middle oil, and 36.6% bottoms. The distillation yield of the liquid product is shown in Table XXI.

The distillation fractions were further analyzed to determine their elemental and aromatic contents. Table XXII gives the ultimate analysis for each fraction and the liquid product. The liquid product contained an atomic H/C ratio of 1.28 while having a sulfur content of 0.24 wt%, nitrogen, 0.33% and oxygen, 0.3%. The H/C ratio of the naphtha fraction was increased to 1.61, the sulfur content, 0.20 wt%, was about the same as the liquid product and the nitrogen and oxygen contents were reduced to 0.09 and 0.12%, respectively. The middle oil fraction had the similar elemental properties as the liquid product had.

Table XXI

Distillation of product *

Cut Fraction	Temp., °F	Yield, wt%	Gravity °API	Gravity Specific
Naphtha	IBP-360	27.1	40.9	0.8208
Middle Oil	360-550	36.3	17.2	0.9516
Bottoms	550+	36.6	2.7	1.0544
Upgraded Product	--	--	18.3	0.9446

* Distillation was made at ATD with a mini-cal unit at atmospheric and reduced pressure of 100 mm Hg.

Table XXII

Ultimate analysis of distilled fraction@

Fraction	C	H	H/C	N	S	O*	Ash
Upgraded product	89.63	9.58	1.28	0.33	0.24	0.3	0.03
Naphtha	87.68	11.73	1.61	0.09	0.20	0.12	--
Middle Oil	89.19	9.52	1.28	0.39	0.16	0.3	--
Bottoms	91.38	7.90	1.04	0.57	0.19	0.5	0.04

@ Weight percent.

* Oxygen was determined by Gulf Test 2610.

However, most of the nitrogen compounds were accumulated in the bottoms fractions. A low H/C ratio of 1.04 and a high nitrogen content of 0.57 wt% were observed in this heavy fraction.

Analyses of group compounds in Table XXIII indicate that over 90 vol% of the bottoms fraction is aromatics, compared to 49.0% in the naphtha fraction, 85.5% in the middle oil, and 78.0% in the liquid product. A slightly higher olefins content, 2.5 vol%, was found in the naphtha fraction. The content of olefins in the liquid product was 0.5 vol%. The naphtha fraction gave a great potential to be a catalytic reforming feedstock. The middle distillate fraction is very aromatic and would need aromatic saturation for use as home heating oil and for diesel application. The bottoms product would probably find its principle use as a fuel oil.

The cost estimates of a coal liquid hydrotreater in Table XXIV was provided by Dravo Engineers and Constructors(71). The estimated capital costs for a 1,000 psig reactor depend on the hydrogen consumption per barrel of feedstock and the capacity. Interpolation between H_2

Table XXIII

Group compound analysis*

Fraction	Aromatics	Saturates	Olefins
Upgraded product	78.0	21.5	0.5
Naphtha	49.0	48.5	2.5
Middle Oil	85.5	13.5	1.0
Bottoms	91.1	8.9	--

* Volume percent

Table XXIV

Cost estimate for a coal liquid hydrotreater

H_2 consumption scf/bbl. Feed	Capital Cost- $ Millions 1,000 psig Reactor- 1981 costs	
	20,000 bbl./day	50,000 bbl./day
1,000	46.2	75.7
4,400	206	338

consumption values is linear for H_2 versus the log of capital. The capacity(bbl./day) exponent factor at fixed H_2 consumption is 0.53. The estimates have included the costs of hydrogen compressors, reactors, catalyst handling, and product flash and stabilization equipment.

CONCLUSION

1. Keeping the SRC-II Vacuum Flash Feed at 85°C for feeding avoids the pumping problem.
2. The SRC-II VFF gives a higher initial catalyst activity and a higher deactivation rate than does the SRC-II LECF.
3. The catalyst activity on the denitrogenation of SRC-II VFF and LECF was significantly increased by the adding of Co, Mo, and W but decreased by the interactive effect of Co-Mo. The interaction between Co and W gave a negative effect on denitrogenation of VFF.
4. The effect of Co and Mo on the desulfurization of LECF was positive. The effect of Mo and W on the desulfurization of VFF was also positive but Co was negative. The interaction between Mo and W gave a negative effect on the desulfurization of VFF, while between Co and Mo gave a negative effect on the desulfurization of LECF.
5. The adding of Ni was ineffective.
6. The study of nitrogen material balance showed 46 wt% being unaccounted for, which was believed to be the nitrogen unabsorbed in the exit gases.

7. The catalyst deactivation was moderated by starting at a lower temperature and higher space velocity.
8. The catalyst was poisoned by the carbon laydown, whose mechanism proved to be the pore mouth plug-up.
9. Catalyst C-49 with a metal combination of 4% CoO, 8% MoO_3, 1% NiO, and 8% WO_3 reduced the nitrogen content to as low as 0.3 wt% for 104 hours with an average liquid product recovery of 91 wt%. The yield of 50-204°C boiling range gasoline was 40% of the liquid product, with an average octane number was 81.7.

RECOMMENDATIONS

1. The more severe operating conditions with a reactor pressure in the range of 1,500 to 3,000 psig should be tested to improve the hydrogenation of SRC-II liquid products and to lengthen the catalyst active life.
2. The process variables such as temperature and space velocity should be studied on upgrading SRC-II Light Ends Column Feed for a long run cycle, for example 50 to 100 hours.
3. A multistage reactor system could be used. The first reactor using an inexpensive cracking catalyst such as chromia alumina to knock down poisoning materials in feedstock before they can deposit on the active catalyst in the second reactor.
4. Auger Electron Spectroscopy should be applied to determine the metal concentration on the catalyst more accurately.
5. Chromatographic analysis of the exit gases should be performed so that the material balance and the estimation of hydrogen consumption might be made on the reactor.

6. Analyses of carbon, hydrogen, and oxygen should be carried out for both feedstock and product to determine the extent of hydrogenation and oxygen removal.
7. A trickle bed reactor system could be modified to collect the sample automatically to reduce the operation cost. The suggested reactor system is shown in the Appendix C.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. "Steam Coal Prospect to 2000," International Energy Agency of Organization for Economic Cooperation and Development, 1978.

2. Fryback M. G., "Synthetic Fuels: Promises and Problems," CEP, May 1981, p. 39.

3. "Solvent Refined Coal(SRC) Process," The Pittsburg & Midway Coal Mining Co., U.S. Dept. of Energy Report, DOE/ET/10104-5.

4. Agroskin, A.A., "Chemistry and Technology of Coal," English translation from Russian, Israel program for Scientific Translations, Jerusalem, 1966, p. 201.

5. Breger, I. A., "Chemical and Structural Relationship of Lignin to Humic Substances," Fuel, 9, 204(1951).

6. Durie,R., "Chemistry of Brown Coals," Coal Research in C.S.I.R.O., 6, 12(1959).

7. Dragunor, S. S., "Soil Organic Matter," Pergamon, London(1961), p. 65.

8. Hill, G. R. and Lyon L. B., "A New Chemical Structure for Coal," Industrial and Engineering Chemistry, 1962, Vol. 54, No. 6, p. 36.

9. Huntington, M. G.; U.S. Patent No. 3,244,615; April 5, 1966.

10. Bodle W. and Vyas K., "Clean Fuels from Coal," Oil and Gas Journal, August 1974.

11. Doolite, J. S., "Energy," Matrix Inc., 1977, p.220.

12. Storch, N. H., "Hydrogenation of Coal and Tar," New York, Wiley, 1963, suppl. vol.

13. Conn, A. L., "Conversion of Coal to Oil and Gas," CEP, May 1981.

14. Fossil Energy Research and Development Program of the U.S. Dept. of Energy, DOE/ET-0013(78), March 1978, pp. 75-78, 99-101.

15. Freel, J., Jackson, D. M., and Schmid, B. K., "SRC-II Demonstration Project," CEP, May 1981, pp.86-91.

16. Akhtar, S., Sharkey, A. G., Schultz, J. C., and Yavorsky, P. M., Paper Presented at ACS meeting, Los Angeles, March-April 1974.

17. Tschamber, H. and DeRuiter, E., "Coal Science, Advanced in Chemistry, Series 55." Am. Chem. Soc. 350(1966).

18. Wentrcek, P. R. and Wise, H., "Hydrodesulfurization Activity and Defect Structure of Co-Mo Sulfide Catalyst," J. Catalysis 51, pp. 80-85(1978).

19. Massoth, F. E. and Kibby, C. L., J. Catalysis 51, pp. 300-316(1977).

20. Schmit, G. C. A. and Gates, B. C., AIChE J., Vol.19, No. 3, pp. 417-437(1973).

21. Gates, et al., J. Catalysis 61, pp. 523-527(1980).

22. Broderick, D. H. and Gates, B. C., "ACS, DW. of Fuel Chem.," Vol. 25, No. 1, pp. 53-65(1980).

23. Shabtai, J., Russell, C., and Pai, Z., U.S. Dept. of Energy Report, DOE/ET/14700(1981).

24. Shih, S. S., Katzer, J. R., Kwart, H., and Stiles, A. B., presented before the Div. Petrol. Chem. Inc., Am. Chem. Soc. Chicago(1977).

25. Katzer, J. R., Stiles, A. B., and Kwart, H.,"Development of Unique Catalysts for Hydrodenitrogenation of Coal-derive liquids," U.S. Dept. of Energy Report, FE-3297-6, June 1980.

26. Aboul-Gheit, A. K. and Abdou, I. K., J. Inst. Petrol. 59, 568, 188(173).

27. Doelman, J. and Vlugter, J. C., Proc. 6th World Petrol. Cong. Frankfurt, III, 247(1963).

28. Sonnemans, J., Ph.D. Thesis, Twente U. of Technology, The Netherlands, 1974.

29. Flinn, R. A., Larson, O. A., and Benther, H., Hydro. Proc. and Petrol. Refiner 42, No. 9, p. 129(1963).

30. Bendoraitis, J. G. et al., "Upgrading of Coal Liquids for use as Power Generation Fuels," Mobil Research and Development Corporation, U.S. Dept. of Commerce, Report No. EPRI 361-1, Jan. 1976.

31. Potts, J. D. et al., "Commercial Scale Expanded Bed Hydroprocessing of Solvent Refined Coal(SRC) Extract," U.S. Dept. of Energy Report, No. FE-2038-25, August 1978.

32. Sullivan, R. F. and O'Rear, D. J., Chevron Research Company, U.S. Dept. of Energy contract Report No. FE-2315-52, March 1980.

33. Givens, E. N., Collura, M. A., Skinner, R. W., and GresKovich, F. I., "Hydroprocess Solvent Refined Coal," Hydrocarbon Processing, Nov. 1978, p. 195.

34. Berg, L., McCandless, F. P., and Hass, G. R., "Catalytic Hydrogenation of Coal Derived Liquid," U.S. Dept. of Energy Report No. FE-2034-12, Sept. 1978.

35. Ramer, R. J., "Catalysts for Hydrotreating Solvent Refined Coal(SRC-II)," Master's Thesis, Montana State University, August 1979.

36. Yeh, A. G., "Catalytic Hydrotreating of Solvent Refined Coal(SRC-II)," Master's Thesis, Montana State University, Nov. 1979

37. Foster, A. D., Doering, H. von E., and Hickey, J. W., "Gas Turbine Fuels," General Electric Co. Report GER-2222, 1972 and GER-2222J, 1974.

38. U.S. Energy Research and Development Administration, "Scientific Resources Relevant to the Catalytic Problems in the Conversion of Coal, Part III, pp.301-351.

39. Exxon Research and Engineering, U.S. Patent No. 3, 928,176.

40. Hydrocarbon Processing, Vol. 55, No. 9, pp. 121-128.

41. Cheadle, G. D. et al., "Unicracking-JHC Process Extends Commercial Applications," Oil and Gas Journal, pp. 76-82, July 18, 1966.

42. Bond, G. C., "Heterogeneous Catalysis: Principles and Applications," Oxford, 1974.

43. MalaKoff, H. L., Seventh World Petroleum Congress, Mexico City, 1967.

44. Kuppuswamy Rajagopalan and Dan Luss, "Influence of Catalyst Pore Size on Demetallation Rate," I & EC Pro. Des. and Dev., Vol. 18, No. 3, 1979, p. 459.

45. Berg, L., McCandless, F. P., and Yeh, A. G., " "Catalytic Hydrogenation of Coal- Derived Liquids, U.S. Dept. of Energy Report No. FE-2034-16, Sep. 1979.

46. Polinski, L. M., Stiegel, G. J., and Tischer, R. E., "Hydroliquefaction of coal with supported catalysts," U.S. Dept. of Energy Report No. DOE/PETC/TR-81/2, June 1981.

47. McAfee, J. et al., 20th Midyear Meeting of Am. Pet. Inst., St. Louis, May 11, 1955.

48. Hoog, H., U.S. Patent 2,608,521(1952).

49. Ross, L. D., "Performance of Trickle Bed Reactors," CEP, October 1965, Vol. 61, No. 10, pp. 77-82.

50. Satterfield, C. N., "Trickle Bed Reactor," AIchE J., March 1975, Vol. 21, No. 2, pp.208-228.

51. Runnion, K. N., "Catalytic Hydrogenation of Synthoil," Master's Thesis, Montana State Univ. March 1977.

52. Hass, G. R., "Catalytic Hydrogenation of Solvent Refined Coal," Ph.D. Dissertation, Montana State Univ., August 1978.

53. Berg, L., McCandless, F. P., and Yeh, A. G., U.S. Dept. of Energy Report No FE-2034-18, Dec. 1978.

54. Emmet, P. H., "Catalysis," Vol. 3, p. 123 and Vol. 1, p. 315, Reinhold 1975.

55. Meyers, R. A., "Coal Desulfurization," Marcel Dekker Inc., New York, 1977.

56. Product Data Bulletin, Armak Catalyst Division, Arizona. Inc., No. 76-4(1976), p. 4.

57. Stecher, P. G., Merck Index, 8th ed., Merk & Co., Inc., Rahway, N.J., pp.345-346.

58. Digital Thermocouple Thermometers Model 8520-40 and 8520-50, Cole-Parmer Instrument Co., 1979.

59. Norton Denstone 57 Catalyst Bed Supports, Bulletin D-12, Norton Company, Calgary, Canada.

60. Instructions for Operation of Brooks Thermal Mass Flowmeter, Brooks Instrument Division, Emerson Electric Co., Hatfield, PA, April 1975.

61. American Society for Testing and Materials, " Standard Method of Testing for sulfur in Petroleum Oils(Quartz tube Method)," 1974 Annual Book of ASTM Standards, Part 23, ASTM Designation D1551.

62. Fritz, J. S. and Schenk, G. H., Quantitative Analytical Chemistry 3rd, ed.(Boston, 1974), pp. 44-69, 191-193.

63. American Society for Testing and Materials, "Standard Method of Testing for Nitrogen in Organic Material by Modified Kjeldahl Method, 1974 Annual Book of ASTM Standards, Part 30, Designation D258.

64. Lake, G. R. et al., "Effect of Digestion Temperature of Kjeldahl Analysis," Analytical Chemistry, Vol. 23, No. 11, Nov. 1951, pp. 1634-1638.

65. American Society for Testing and Materials, "Standard Method of Test for Distillation of Petroleum Products," Annual Book of ASTM Standards, Part 23, ASTM Designation D86.

66. Bhasin, M. M., "Applications of Auger and ESCA Spectroscopies," CEP, March 1981, pp.60-67.

67. Handbook of Auger Electron Spectroscopy, 2nd ed. Physical Electronics Industries, Inc., Eden Prairie, Minnesota.

68. Berg, L., McCandless, F. P., Rameswaran, M., and Hsieh, H. Y., U.S. Dept. of Energy Report, FE-2034-22, April 1981.

69. Berg, J. W., CENEX, P. O. Box 126, Laurel Mont. 59044, Personal Communication, August 28, 1981.

70. Beuther, H., Gulf Research & Development Co., P. O. Drawer 2038, Pittsburgh, PA 15230, Personal Communication, September 24, 1981.

71. Boyd, N. F., Dravo Engineers and Constructors, One Silver Plaza, Pittsburgh, PA 15222, Personal Communication, November 2, 1981.

APPENDICES

APPENDIX A.

ANOVA TABLES FOR SRC-II VFF

DEPENDENT VARIABLE = 7

INDEPENDENT VARIABLES= 3,4,6,9,11

FIT:	VAR	R-PART	B	SE(B)	T	P-VALUE
	3	.9724	11.29	.8175	13.82	0.000
	4	.6606	2.358	.8080	2.918	.1398E-01
	6	.7723	3.258	.8080	4.032	.1974E-02
	9	-.5569	-.5687	.2647	-2.224	.4806E-01
	11	-.7130	-.8928	.2647	-3.373	.6224E-02

INTERCEPT = 0.000

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	5	.2578E+05	5155.	316.0	0.000
RESIDUAL	11	179.4	16.31		
TOTAL	16	.2596E+05			

Variable 7 = %DN of catalyst - %DN of catalyst carrier
3 = wt% CoO
4 = wt% MoO_3
6 = wt% WO_3
9 = (CoO)(MoO_3)
11= (CoO)(WO_3)

DEPENDENT VARIABLE = 8

INDEPENDENT VARIABLES= 3,4,6,13

FIT:	VAR	R-PART	B	SE(B)	T	P-VALUE
	3	-.7561	-6.430	1.606	-4.002	.1755E-02
	4	.8899	6.657	.9848	6.760	0.000
	6	.8153	4.803	.9848	4.877	0.000
	13	-.6523	-.5556	.1864	-2.981	.1146E-01

INTERCEPT = 0.000

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	4	.1313E+05	3282.	48.75	0.000
RESIDUAL	12	808.0	67.33		
TOTAL	16	.1394E+05			

Variable 8 = %DS of catalyst - %DS of catalyst carrier
3 = wt% CoO
4 = wt% MoO_3
6 = wt% WO^3
13 = $(MoO_3)(WO_3)$

DEPENDENT VARIABLE = 1

INDEPENDENT VARIABLES= 3

FIT:	VAR	R-PART	B	SE(B)	T	P-VALUE
	3	-.4538	-.9792	.5139	-1.905	.7747E-01

INTERCEPT = 78.08
R-SQUARED = .2059

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	1	138.1	138.1	3.631	.7747E-01
RESIDUAL	14	532.4	38.03		
TOTAL	15	670.4			

VARIABLE DESCRIPTION
1 = oil product yield, wt%
3 = wt% WO_3

DEPENDENT VARIABLE = 2

INDEPENDENT VARIABLES= 4

FIT:	VAR	R-PART	B	SE(B)	T	P-VALUE
	4	.5413	.6606	.2743	2.409	.3035E-01

INTERCEPT = 9.345
R-SQUARED = .2930

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	1	6.983	6.983	5.802	.3035E-01
RESIDUAL	14	16.85	1.203		
TOTAL	15	23.83			

VARIABLE DESCRIPTION
2 = wt% carbon laydown on the catalyst
4 = wt% CoO

APPENDIX B.

ANOVA TABLES FOR SRC-II LECF

DEPENDENT VARIABLE = 7

INDEPENDENT VARIABLES= 3,4,9,6

FIT:	VAR	R-PART	B	SE(B)	T	P-VALUE
	3	.7162	6.466	1.819	3.555	.3961E-02
	4	.7386	5.227	1.377	3.795	.2552E-02
	9	-.4590	-.8600	.4805	-1.790	.9872E-01
	6	.5151	1.559	.7488	2.082	.5943E-01

INTERCEPT = 0.000

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	4	.2769E+05	6921.	79.85	0.000
RESIDUAL	12	1040.	86.68		
TOTAL	16	.2873E+05			

DEPENDENT VARIABLE = 8

INDEPENDENT VARIABLES= 3,4,9

FIT:	VAR	R-PART	B	SE(B)	T	P-VALUE
	3	.8051	4.175	.8531	4.894	0.000
	4	.6589	2.377	.7527	3.158	.7552E-02
	9	-.5443	-.6294	.2691	-2.339	.3594E-01

INTERCEPT = 0.000

ANALYSIS OF VARIANCE:

SOURCE	DF	S.S.	M.S.	F-VALUE	P-VALUE
REGRESS	3	3694.	1231.	39.95	0.000
RESIDUAL	13	400.7	30.82		
TOTAL	16	4095.			

Variable 3 = CoO
4 = MoO_3
6 = WO_3

Varialbe 7 = % denitrogenation
8 = % desulfurization
9 = (CoO) (MoO_3)

APPENDIX C.

Reactor System Rearrangement

Trickle bed reactor system might be arranged to collect the liquid sample automatically. The proposed arrangement is shown in Figure 22. The gases and liquid would pass through the reactor, a condenser and the back pressure regulator to a separator. Gases and liquid could be separated in the separator at atmospheric pressure when the liquid seal forms. The valve underneath the separator might be closed during the start-up and reopened until the liquid seal forms. Gases would go to the vent and liquid could be sampled by the overflow of liquid seal. This would remove the frequent depressurization and nitrogen repressurization of the catchpot during sampling in this research and reduce the operation cost.

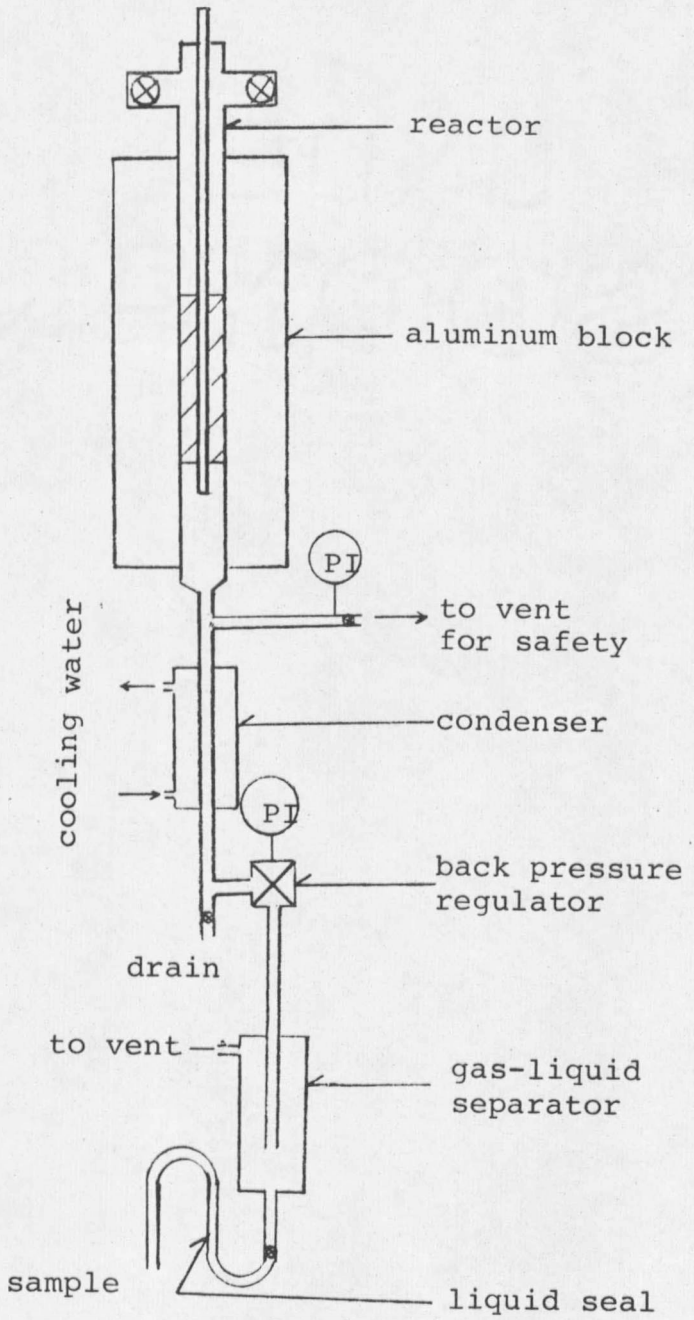

Figure 22. Trickle bed reactor rearrangement

MONTANA STATE UNIVERSITY LIBRARIES
stks D378.Y346@Theses
Upgrading solvent refined coal by cataly
RL
3 1762 00113704 9

D378
Y346
cop.2

Yeh, An-Gong
Upgrading solvent refined coal by Catalytic Hydrotreatment

DATE	ISSUED TO

-D378
Y346
Cop. 2