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

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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°C boiling range gasoline was 40% of the liquid product, whose octane tests gave an average octane number of (Research + Motor)/2 = 81.7.

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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.

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ABSTRACT

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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

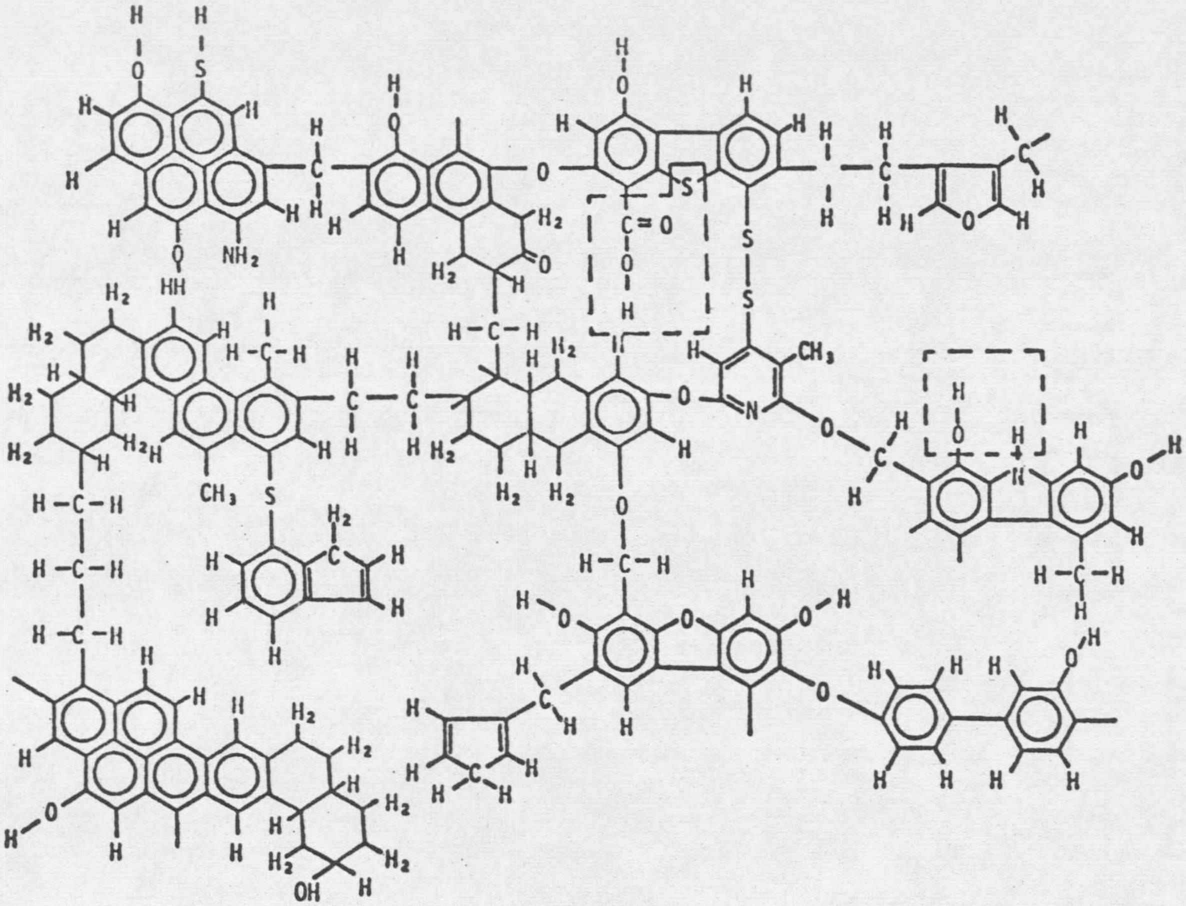


FIGURE 1. Coal Structure

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

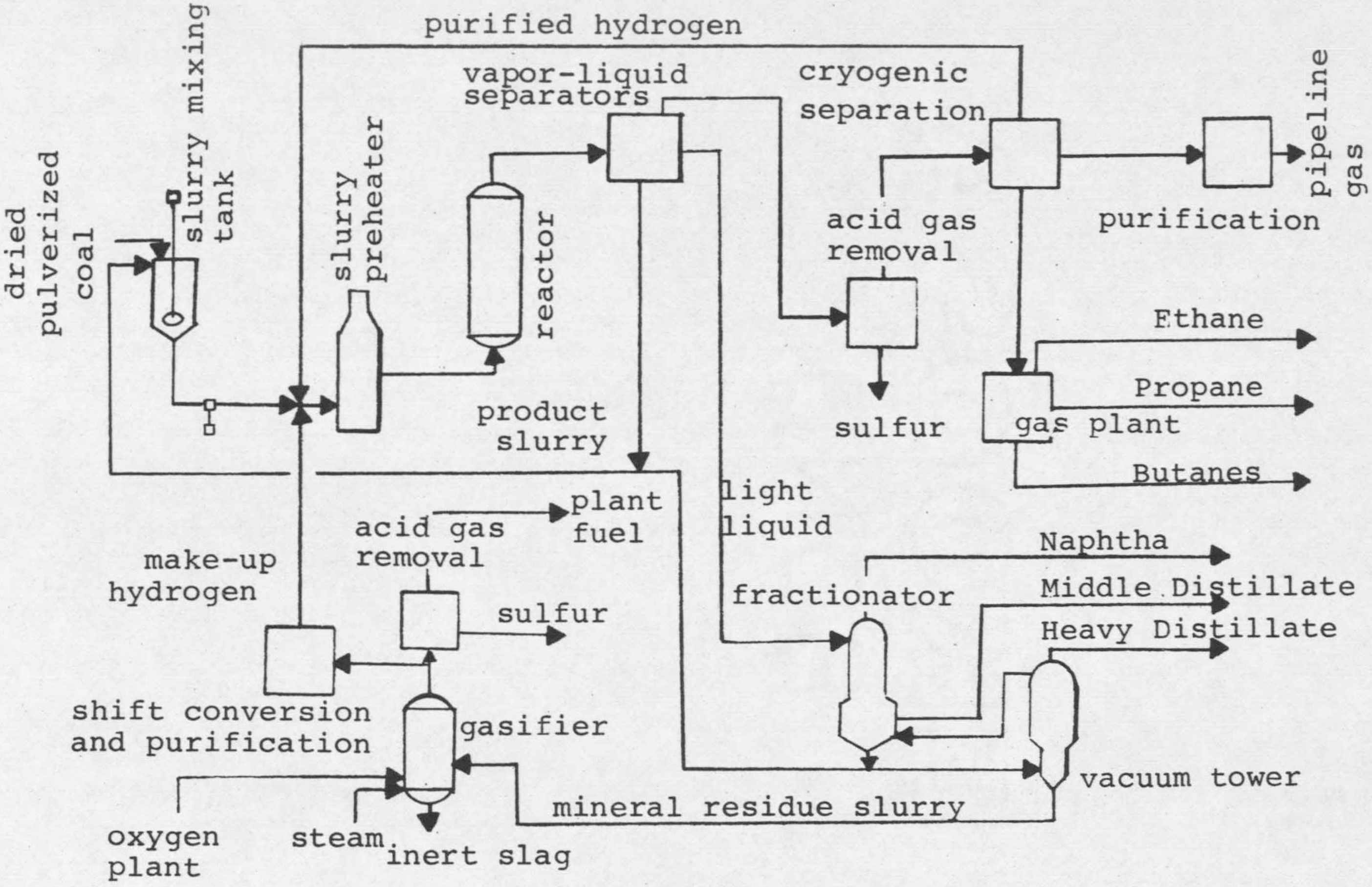


Figure 2. Flow Diagram of SRC-II Process

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^oC normal boiling range), a middle distillate(193-316^oC), and a heavy distillate(316-482^oC). 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^oC), 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^oC) 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 catalyst 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°C for 8 hours.
2. Calcine at 450°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

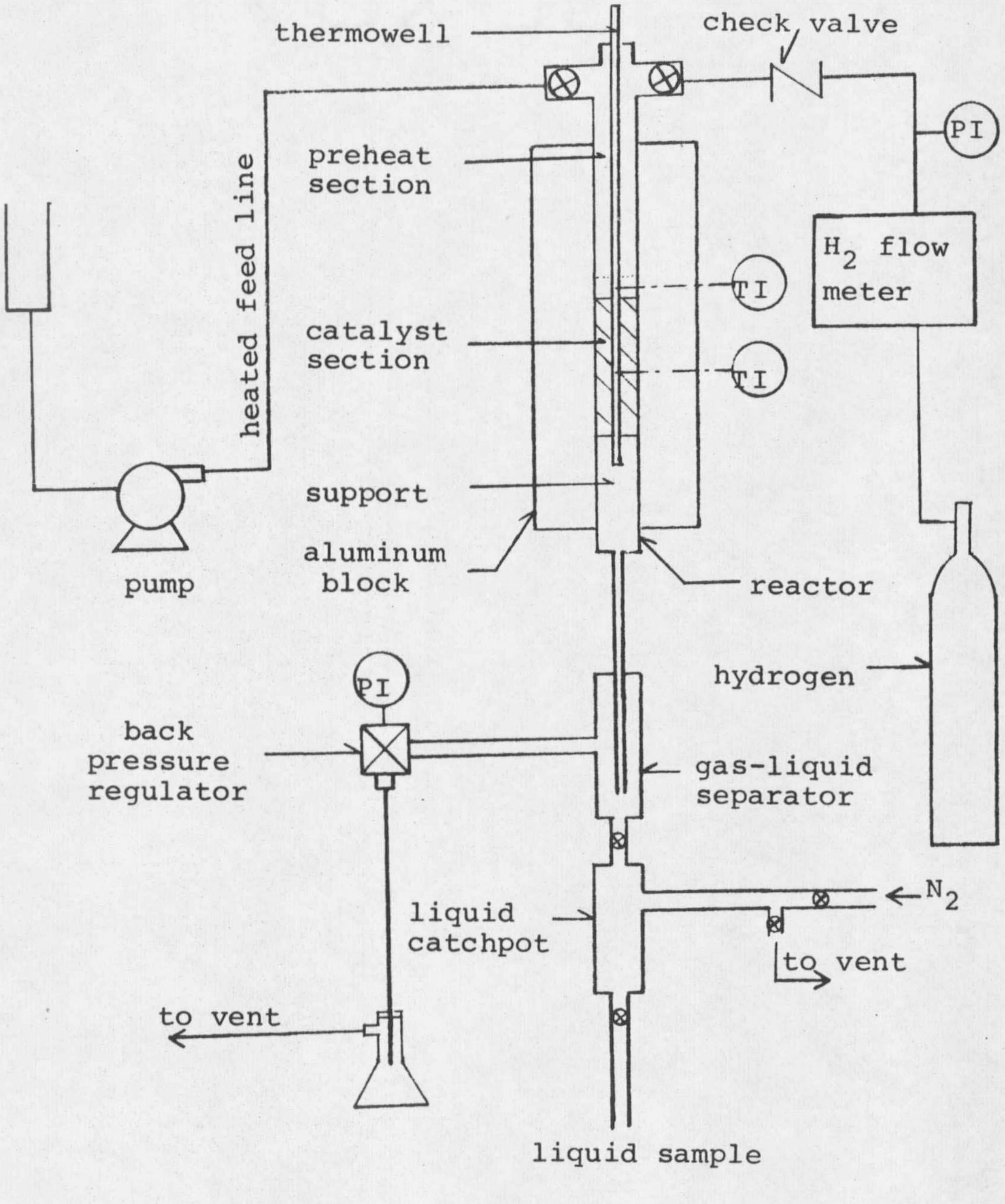


Figure 3. Trickle Bed Reactor

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 milliters 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.

<u>Operation of Catalyst Regeneration</u>

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.

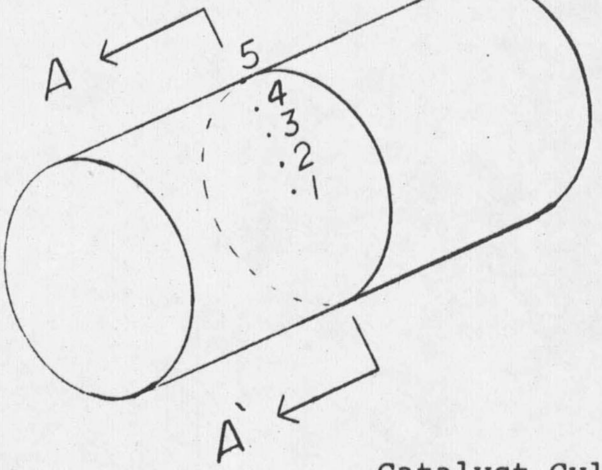
The pore volume of the catalyst was estimated by the water saturation method. It gave a relative value rather than absolute. The procedures are as follows:

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.

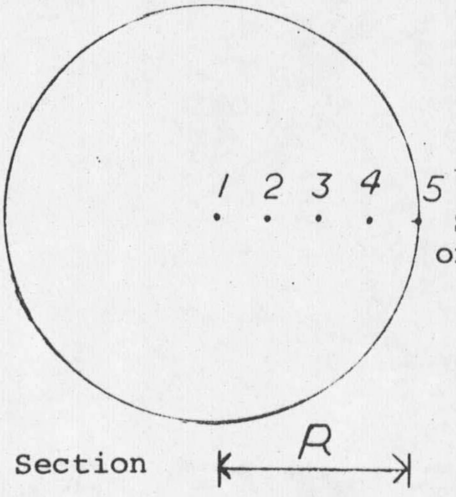
5. Leave 35 minutes for natural air dry, then weigh the saturated catalyst.

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



Catalyst Cylinder



Spectra Recorded on these five spots

Cross Section

A - A'

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^{o}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^{o}C to 200^{o}C, 85^{o}C for Run 1 and 2, 105^{o}C for Run 3, and 200^{o}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

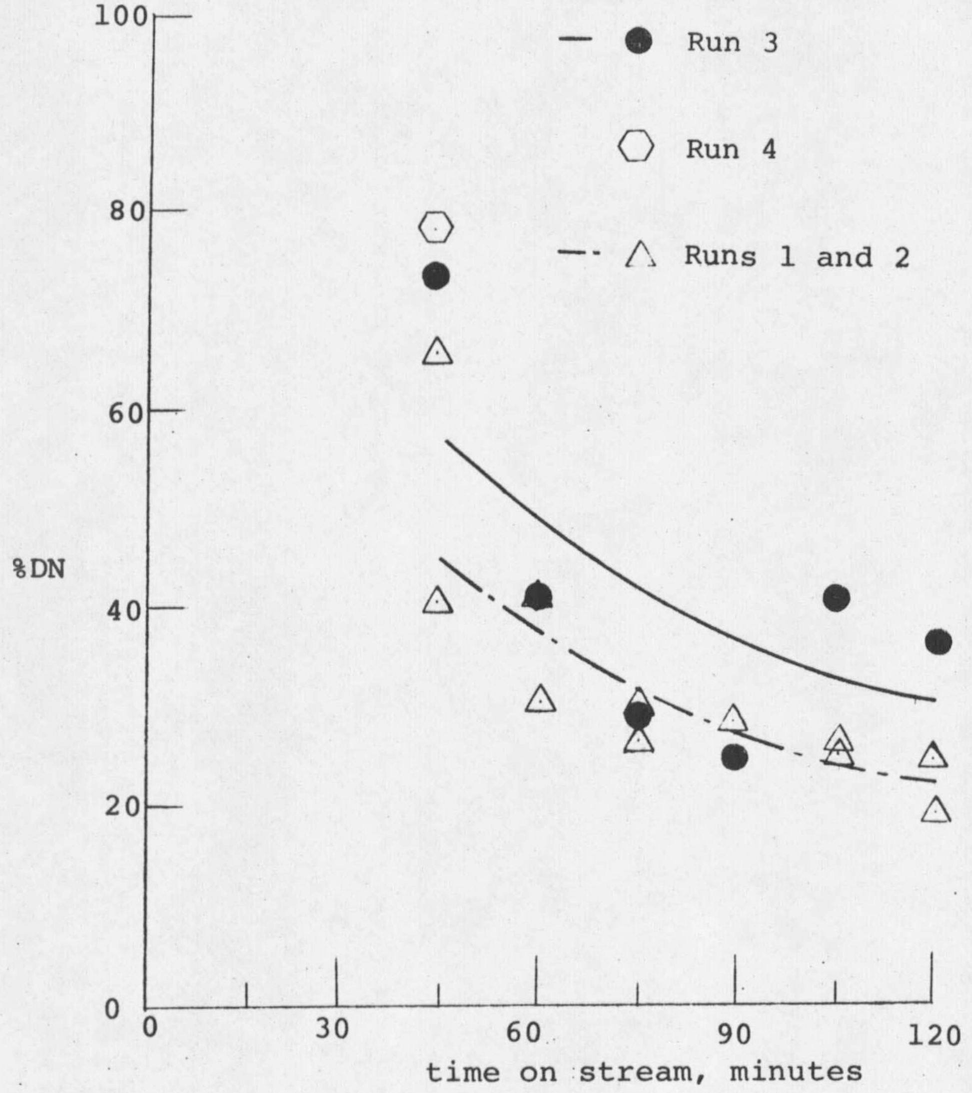


Figure 5. Effect of liquid feed temperature* on the denitrogenation.

* SRC-II VFF was fed at 85^{o}C for Runs 1 and 2, 105^{o}C for Run 3, and 200^{o}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^{o}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

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

and

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

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

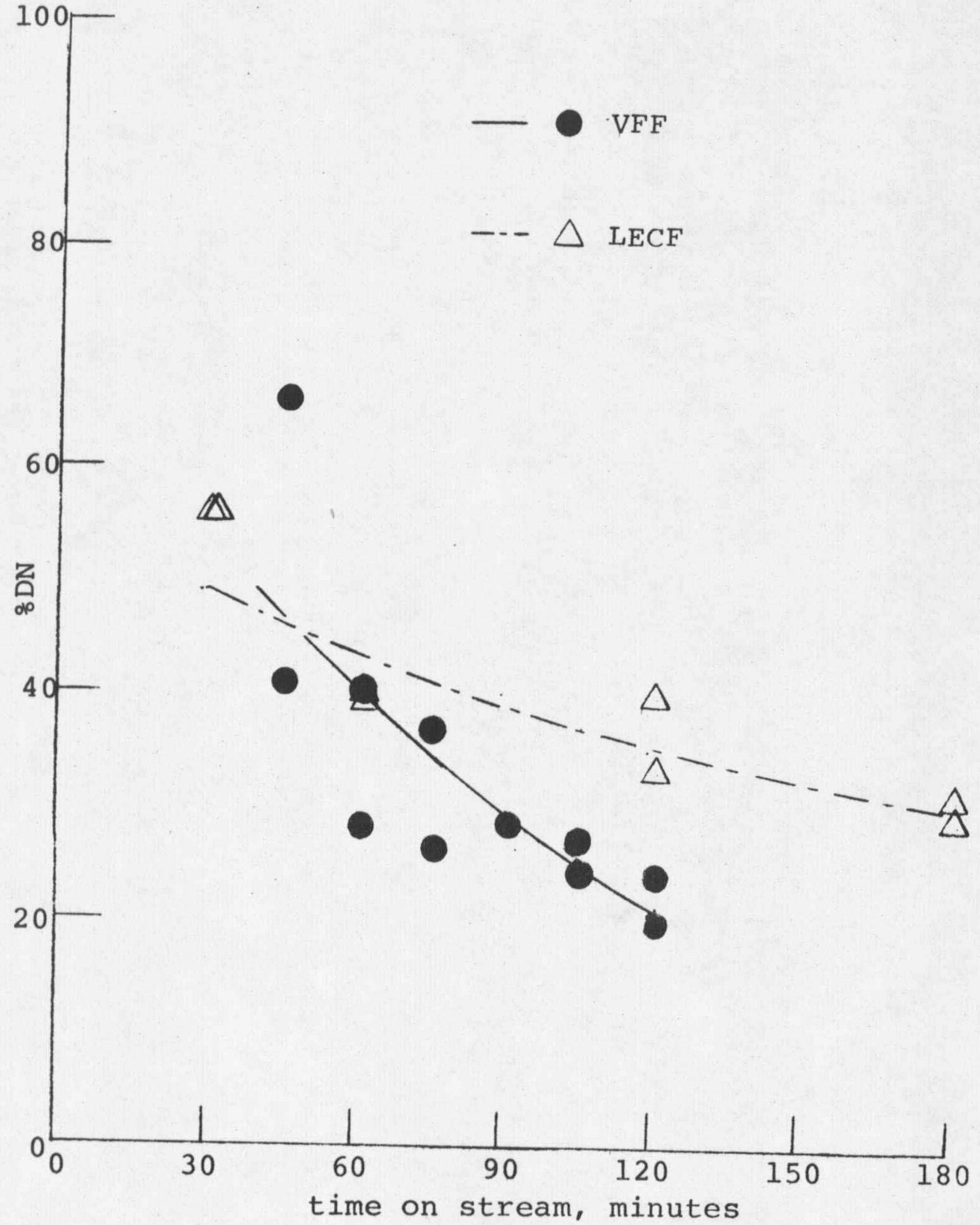


Figure 6. Feedstock comparison

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	Metal Oxides on the Catalyst, wt%			
		45	60	75	90	105	120	150	Avg.	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%