The effect of hydrogenated creosote oil as a hydrogen donor agent on upgrading of solvent refined coal (SRC-II)

by Chia-Ren Jack Pan

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering

Montana State University

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Abstract:
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The effect of high concentration of creosote oil on catalytic upgrading of SRC-II is nonbeneficial. As the percentage of creosote oil is increased the activity in denitrogenation and desulfurization decreased. Harshaw HT-400 is more active for denitrogenation and desulfurization than either Shell NM324 or MSU-C-49.

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ABSTRACT

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The hydrogenated creosote oil was added in three different ratios to SRC-II Light End Column Feed product: 25%:75%, 50%:50%, 75%:25%. MSU-C-49 catalyst which was developed at Montana State University, and two commercial catalysts, Shell NM324 and Harshaw HT-400, were evaluated in a small scale trickle bed reactor.

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CHAPTER I

INTRODUCTION

The thirty years of success in coal liquefaction technology has demonstrated coal's feasibility as a new energy source. However, no commercial plant has been constructed since the technology has become a reality. Politics, economics and environmental considerations have influenced its progress.

The most efficient use of coal is when it is burned directly in furnaces or under boilers. The problem of combustion is the emission of noxious gases such as sulfur oxides and nitrogen oxides. Indeed, this concern was one reason for initiating the shift from coal to oil for electrical power generation.

Liquifying coal has been proved to be the most efficient way(1) to provide liquid fuel from coal. However, liquified coal has too high a sulfur and nitrogen content to be accepted either by the EPA(2,3) or in conventional petrochemical refining processes. The petroleum refining industries do not accept liquified coal because of equipment and pollution problems. Nitrogen contained in the feedstock for Fluid Catalytic Cracking(FCC) would be a major source of pollution and equipment damage.

Hydrogen blistering is an example of the extensive damage possible in equipment. Another important reason for the upgrading of coal liquids is that high nitrogen and sulfur content in organic compounds cause undesirable poisoning of the acidic functions of catalysts in refining processes (5). Poisoning shortens catalyst life and increases the cost of investment. From economic considerations, price determines the feasibility of substituting coal liquid for petroleum. The upgrading of coal liquids became a necessary procedure if the liquids are to be used as substitutes for petroleum.

The purpose of this research is to investigate the effect of different catalysts on the upgrading of Solvent Refined Coal(SRC-II) by the addition of hydrogenated creosote oil. The creosote oil acts as a hydrogen donor agent.

CHAPTER II

COAL CONVERSION

Coal has been used in many different ways for more than a century. In the beginning it was used primarily for heat by combustion. Direct combustion is the most straightforward and convenient use of coal. Coal gasification was introduced as a substitute for natural gas. However, the energy supply and the resource structure has changed over the years. It was not until World War II when people needed much more energy. Because of the petroleum shortage, coal again became an important energy resource. It was during World War II that the non-petroleum producing countries were forced to develop a substitute for petroleum. However, consumers currently use about 75% of their petroleum products in the form of distillates(6). The enormous consumption of distillates in transportation and heating fuel has become a major reason to the liquify coal.

Coal Liquefaction

Coal is converted to a liquid product through either direct or indirect liquefaction techniques. Indirect liquefaction is the most developed. First, coal is gasi-

fied to produce a mixture of hydrogen and carbon monoxide which is then combined by catalysts to form liquid compounds. Currently, the only commercial process is the Fisher-Tropsch being used in South Africa in conjunction with Koppers-Totzek, Texaco, Winkler-Lurgi and Shell-Koppers gasifiers.

Two different processes of direct liquefaction are catalytic hydrogenation and the use of a donor solvent. The latter was characterized as the Solvent Refined Coal (SRC) process developed by Pittsburg and Midway Coal Co. and the Exxon Donor Solvent(EDS) process. Both processes produce liquified coal by solvent extraction.

Direct catalytic hydrogenation essentially reduces molecular weight and increases the H/C ratio of the parent coal molecule to a ratio similar to that of a petroleum crude. The process used catalysts comprising cobalt and molybdenum oxide on alumina or molten $ZnCl_2$(5). The Synthoil and H-coal processes are examples of direct catalytic hydrogenation.

Solvent Refined Coal (SRC)

In 1974, Pittsburg & Midway Coal Mining Company owned by the Gulf Oil Company was awarded a contract by the Department of Energy(DOE) for the SRC-I pilot plant start-up operation. Figure 1 shows the flow scheme of the SRC-I process. SRC-I was designed to produce low ash and low

sulfur solid boiler fuel(7) to meet the sulfur emission requirement. The pulverized coal and anthrancene oil was introduced into a slurry tank and pumped to the slurry preheater, where slurry was preheated to above 800°F at 100 atm. The preheated slurry was fed to a dissolver and the solvent in the slurry from the dissolver was recovered as a recycle stream which went back to the slurry tank. The SRC-II mode was connected to SRC-I in 1977(8). Figure 2 shows the SRC-II flow scheme. The final product in SRC-II is liquid at room temperature. This makes SRC-II considerably different from SRC-I. The overall yield and hydrogen consumption of the SRC-II process are given in Table I. The feed for this research is Light End Column Feed(LECF), a light liquid from the vapor-liquid separators of the SRC-II process.

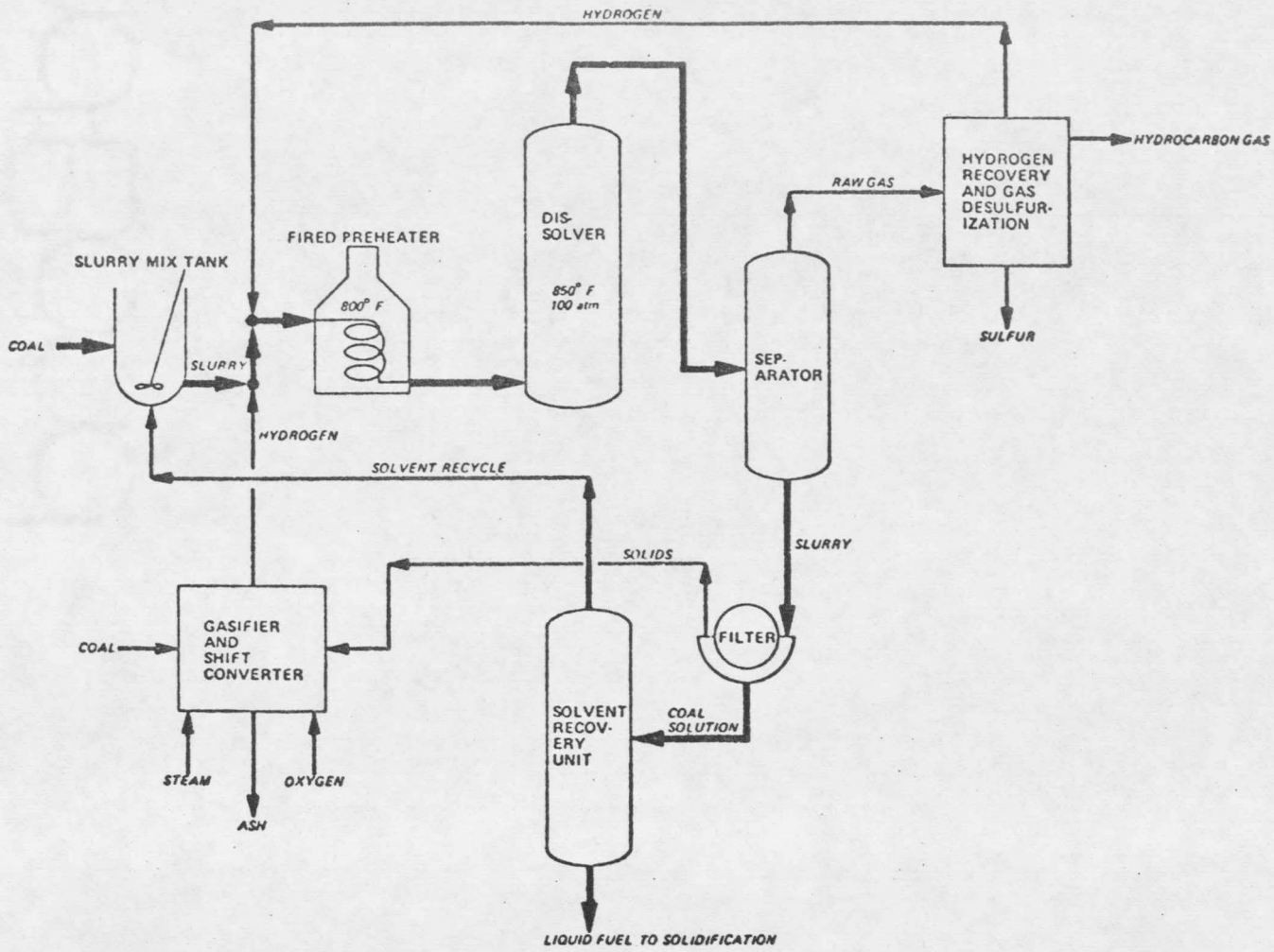


Figure 1. Flow Scheme of SRC-I Process.

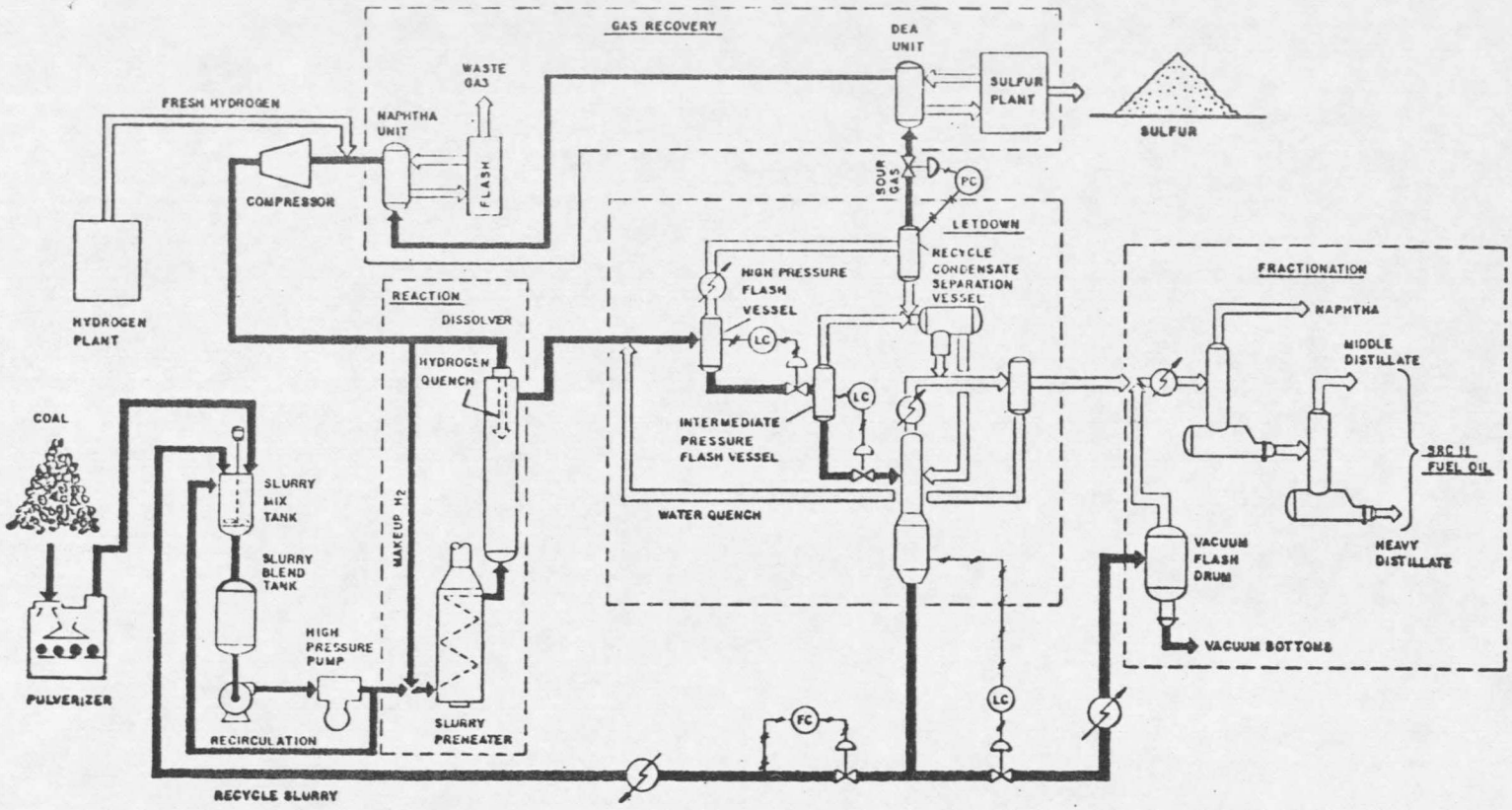


Figure 2. Flow Scheme of SRC-II Process.

Table I

Yields from SRC-II process

	wt% Moisture-free Coal Charge
Mathane	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

CHAPTER III

USE OF HYDROGENATED CREOSOTE OIL IN SRC-II UPGRADING

History

Because of the large amount of polyaromatic content, creosote oil, a coal-derived solvent once widely used for wood protection, became a favorite in the start-up of the SRC process. Several studies have investigated the use of creosote oil as a hydrogen donor solvent in the liquefaction of coal. It was not an attractive agent in the upgrading of liquified coal until Givens et al.(8) and Potts et al.(9) introduced creosote oil in 1978 as a solvent in a study of deriving liquid fuels from SRC-I product and in the evaluation of commercial catalysts. In 1982 Stiegel et al.(10) used creosote oil for the screening of upgrading catalysts for SRC-I.

It is reasonable to use hydrogenated creosote oil in the upgrading of SRC-I because it is a solid product and needs to be dissolved before it can be handled. Hydrogenated creosote oil can act as a hydrogen donor solvent in the upgrading.

The basic concept in using hydrogenated creosote oil in SRC-I upgrading is simply an application of its hydrogen-transfer capacity. However, since SRC-II end products are liquids, the introduction of hydrogenated creosote oil in upgrading is being studied because of the anticipation of its synergistic-hydrogen donor effect.

Hydrogen Donor Solvent in Coal Liquefaction

The essence of coal processing to liquid fuels is to increase the H/C ratio of the coal ($\cong$0.8) to that of motor fuel ($\cong$2.0). This is accomplished with a specific solvent in a hydrogen-gas atmosphere.

Although the mechanism of how a solvent helps in increasing the H/C ratio of coal is not completely understood, it is well accepted that the efficiency of certain hydrogen-rich solvents is a function of their ability to donate hydrogen atoms to coal and coal products. A commonly suggested route involving free radicals and hydrogen transfer is:(11)

$$\text{coal-coal} \longrightarrow 2\ \text{coal}\cdot$$

$$\text{coal}\cdot \xrightarrow[\text{donor}]{\text{hydrogen}} \text{coal}\cdot\text{H}$$

In 1981, Derbyshire et al.(13) further proposed a "synergistic effect" between pyrene-tetralin mixtures and molecular hydrogen by which coal conversion was enhanced. It can be explained by following reactions:

tetralin + coal ⟶ naphthalene + coalH

tetralin + pyrene ⟶ naphthlene + dihydropyrene

pyrene + H_2 ⟶ dihydropyrene

dihydropyrene+ coal ⟶ pyrene + coalH

There is a reduction in the hydrogen tranferred from tetralin, and hydrogenation of coal by pyrene is enhanced by hydrogen and pyrene.

Actually, the usual criterion for solvent selection is the solvent's hydrogen-donation ability. Hydrogenated solvents have been shown by Furlong et al.(14) to be better solvents in coal conversion than the original unhydrogenated material. Davies and others(15) also showed that extraction efficiencies of hydrogenated anthracene oils are consistently higher over the entire boiling range than the original anthracene oil, presumably due to the presence of polycyclic hydroaromatic compounds. These compounds are known to be reactive solvents and effective donors of hydrogen to coal fragments. Meanwhile, it is worth noting that the unhydrogenated anthracene oil have a higher solvent power than would be expected from the

extraction efficiencies of its main components such as naphthalene, anthracene, phenanthrene and dibenzofuran(15).

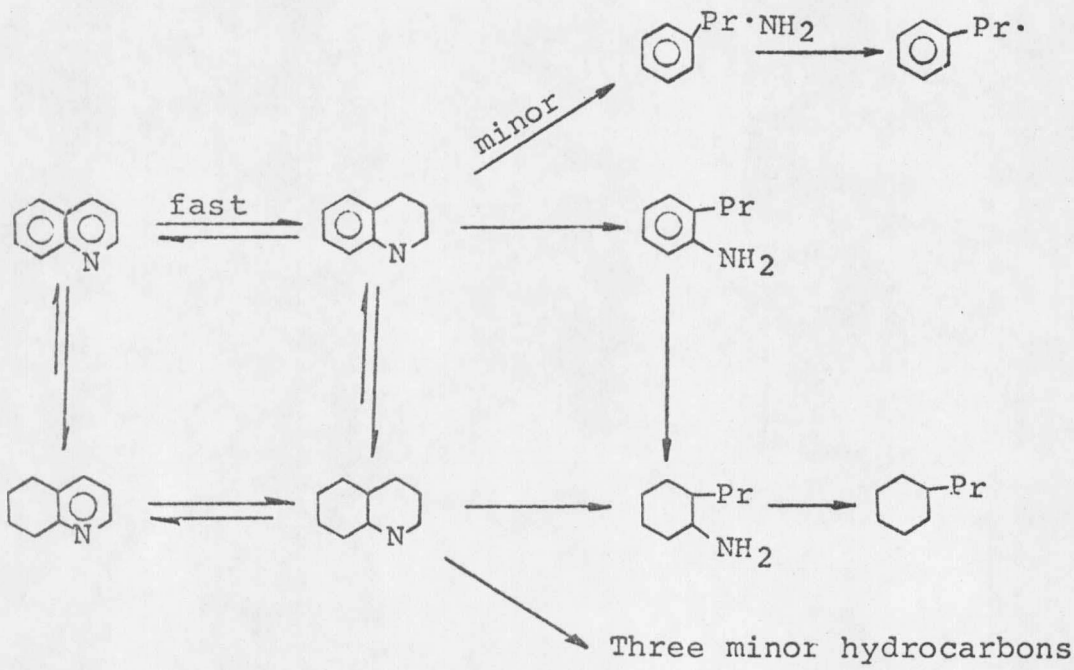
Hydroprocessing of Coal Liquids

This research is concerned with the hydroprocessing of coal liquids with special emphases on denitrogenation and desulfurization as well as the production of a greater fraction of light products.

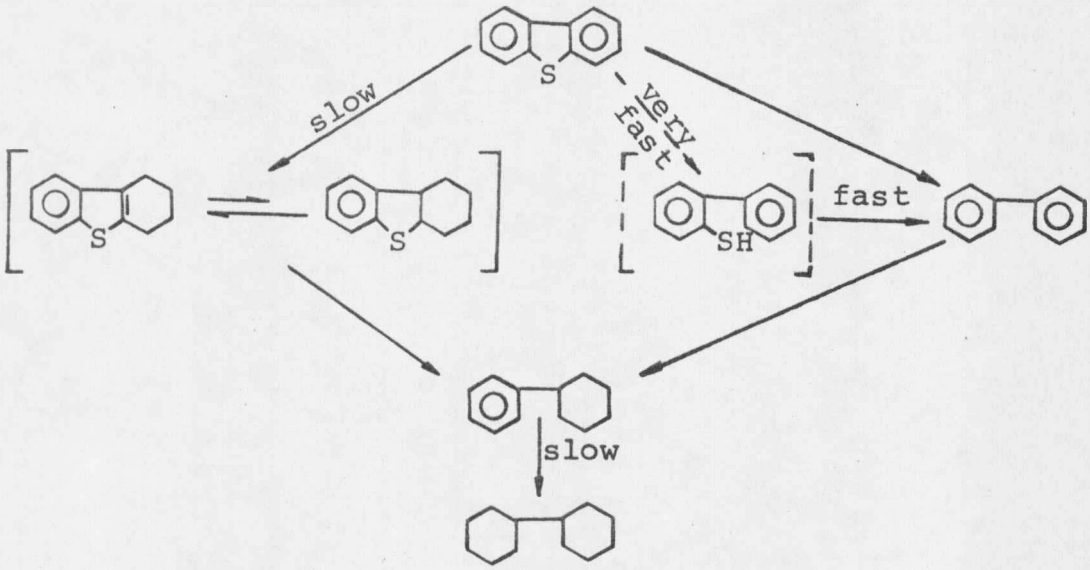
In conventional petroleum refining industries denitrogenation is greatly overshadowed by desulfurization, because crude oil generally contains little or no nitrogen. However, the high content of nitrogen in coal products can not be ignored. Since the hydrotreating catalysts developed for petroleum refining industries show little denitrogenation activity, a separate development of catalysts for hydrotreating of coal liquids is needed. Metals such as Mo, Co, Ni, and W have been proven to be workable.

Unlike desulfurization, denitrogenation requires the saturation of the aromatic ring prior to the cleavage of the carbon-nitrogen bond. Therefore, hydrogen consumption is usually high for feedstocks with high concentrations of nitrogen because of the saturation of aromatic rings.

Most of the studies on denitrogenation mechanism used a specified nitrogen compound instead of the coal liquid. Gates et al.(16) proposed a mechanism for the hydrodenitrogenation of quinoline as follows:

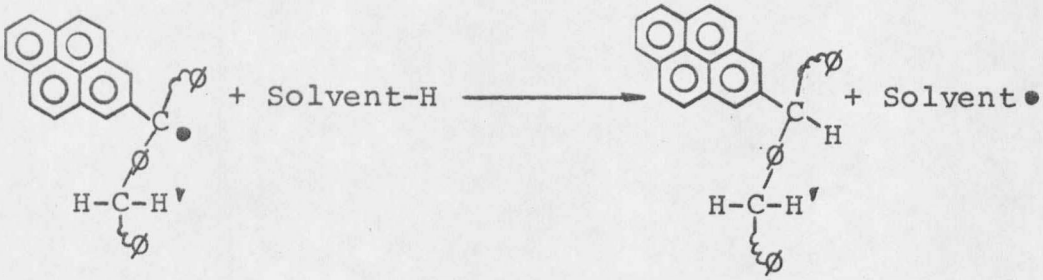


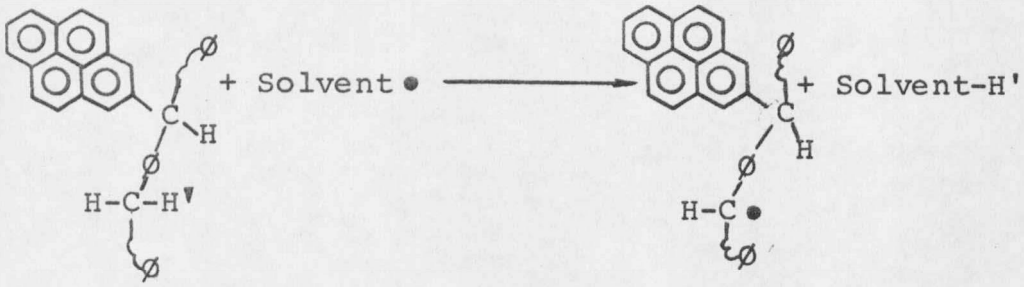
The proposed mechanism for hydrodesulfurization of dibenzothiophene(DBT) is as follows:



Coal is first cleaved into radical fragments by the solvent under high temperature and pressure, then the hydrogen donor solvent gives up a hydrogen radical to the coal fragment permanently reducing the coal molecular size. In this option, the solvent is a hydrogen-transfer agent which donates hydrogens to massive coal molecules.

However, there is another important role wherein the solvent aids in the redistribution of hydrogen, but wherein no net transfer of hydrogen occurs. In order to distinguish it from "hydrogen transfer", it is called "hydrogen shuttling" which is shown as follows:(12)





* Ø is any part of coal molecule.

Berg and McCandless(17) have been investigating the upgrading of coal liquids since the 1970's. Their results show that pore size and the amount of metal loading of the catalyst are some of the most important factors in determining the effectiveness of a catalyst. Nevertheless, hydrogen consumption is not a negligible factor in the consideration of the economics of coal-liquid upgrading.

From understanding the mechanisms for hydrotreating in coal liquefaction, it is reasonable to expect that hydrogenated creosote oil might be used in upgrading of coal liquid and give some improvement in the activity of hydrotreating.

Research on Upgrading of SRC-II

Many variables influence the upgrading of SRC-II, including temperature, pressure, catalyst, liquid hourly space velocity(LHSV), and hydrogen flow rate. Catalytic effectiveness is influenced by pore diameter distribution, surface area, metal loading, catalyst deactivation, and the presence of a promotor or inhibitor.

Several different commercial catalysts, new catalysts with various metals, metal-loading amounts and pore size distribution were all investigated by Yeh(18). The study showed that a combination of 4% CoO, 8% MoO_3, 1% NiO, 8% WO_3 based on Nalco-78-6008c-1/32" was the most effective in hydrodenitrogenation of SRC-II. Bhatia(19) used the same catalyst(MSU-C-49) in his research and further showed that at the operating condition of 425°C temperature and a LHSV of 1.25hr^{-1}, the weight percent denitrogenation is about 57.2% and weight percent desulfurization is about 88.3%.

Results of a concurrent investigation by Sahin(20) were utilized in this research in the comparision of results. In Sahin's research, Harshaw HT-400 gave the best performance in upgrading SRC-II VFF(Vacuum Flash Feed). The study showed 77% denitrogenation and 65% desulfurization using the Harshaw HT-400 catalyst without water addition.

Creosote Oil

In this research Koppers creosote oil, a coal-derived solvent used as a start-up solvent in SRC process, was introduced as a hydrogen donor agent. Koppers tar creosote oil is comprised primarily of two, three and four ring polynuclear aromatic components, and its hydrogen content is lower than for conventional recycle solvents. However, when used as solvent in the SRC process the hydrogen donor capacity of creosote oil was improved by hydrotreating(21).

The creosote oil was analyzed by Allied Chemical Co. (22) as shown in Table II. Because it is a solid-liquid mixture, its viscosity at 200°F is about 6 centipose(8), which causes handling problems that were overcome by the modification of the feed system with heating tapes and coils.

Table II. Gas Chromatographic Analysis of Creosote Oil*

Compound	Wt%
Nitrogen Compounds	
Benzonitrile	0.12
o-Ethylaniline	0.03
Quinoline	0.37
Isoquinoline	0.30
2-Methylquinoline	0.42
Indole	0.21
1-Napthonitrile	0.19
2-Naphthonitrile	0.14
Acridine	0.19
Carbazole	2.2
2-Methylcarbazole	1.7
Sulfur Compounds	
Thianaphthene	0.08
Diphenylene sulfide	0.52
Oxygen Compounds	
Coumarone	0.10
Dibenzofuran	6.7
3-Methyldiphenylene oxide	1.7
1,2-Benzodiphenylene oxide	0.96
Phenol	0.12
o-Cresol	0.05
p-Cresol	0.37
m-Cresol	0.16
4-Indanol	0.55

* Guin, J. A. et al., Ind. Eng. Chem. Process Des. Dev., Vol. 17, No. 2, 1978.

Table II. (Continued)

Compound	Wt%
Hydrocarbons	
p-Cymene	0.02
Indan	0.11
Naphthalene	5.1
2-Methylnaphthalene	1.3
1-Methylnaphthalene	0.38
Diphenyl	0.49
1,6-Dimethylnaphthalene	0.39
2,3-Dimethylnaphthalene	0.19
Acenaphthene	6.0
Fluorene	10.3
9,10-Dihydroanthracene	2.4
2-Methylfluorene	0.85
Phenanthrene	18.6
Anthracene	4.3
3-Methylphenanthrene	0.98
4,5-Methylenephenanthrene	2.5
2-Methylanthracene	0.24
9-Methylanthracene	1.2
Fluoranthene	5.5
Pyrene	2.6
Unidentified compounds in distillate	7.56
Total distillate	88.18

CHAPTER IV

EXPERIMENTAL

Catalysts

Two commercial catalysts (Shell NM324 and Harshaw HT-400) and MSU-C-49 which had been developed by Yeh(18) were applied in this research. The properties of these catalysts are shown in Table III.

All catalysts were presulfurized with a 10% hydrogen sulfide in hydrogen mixture for 10 hours in order to prevent the reduction of catalyst activity by high temperature hydrogenation(23).

Equipment

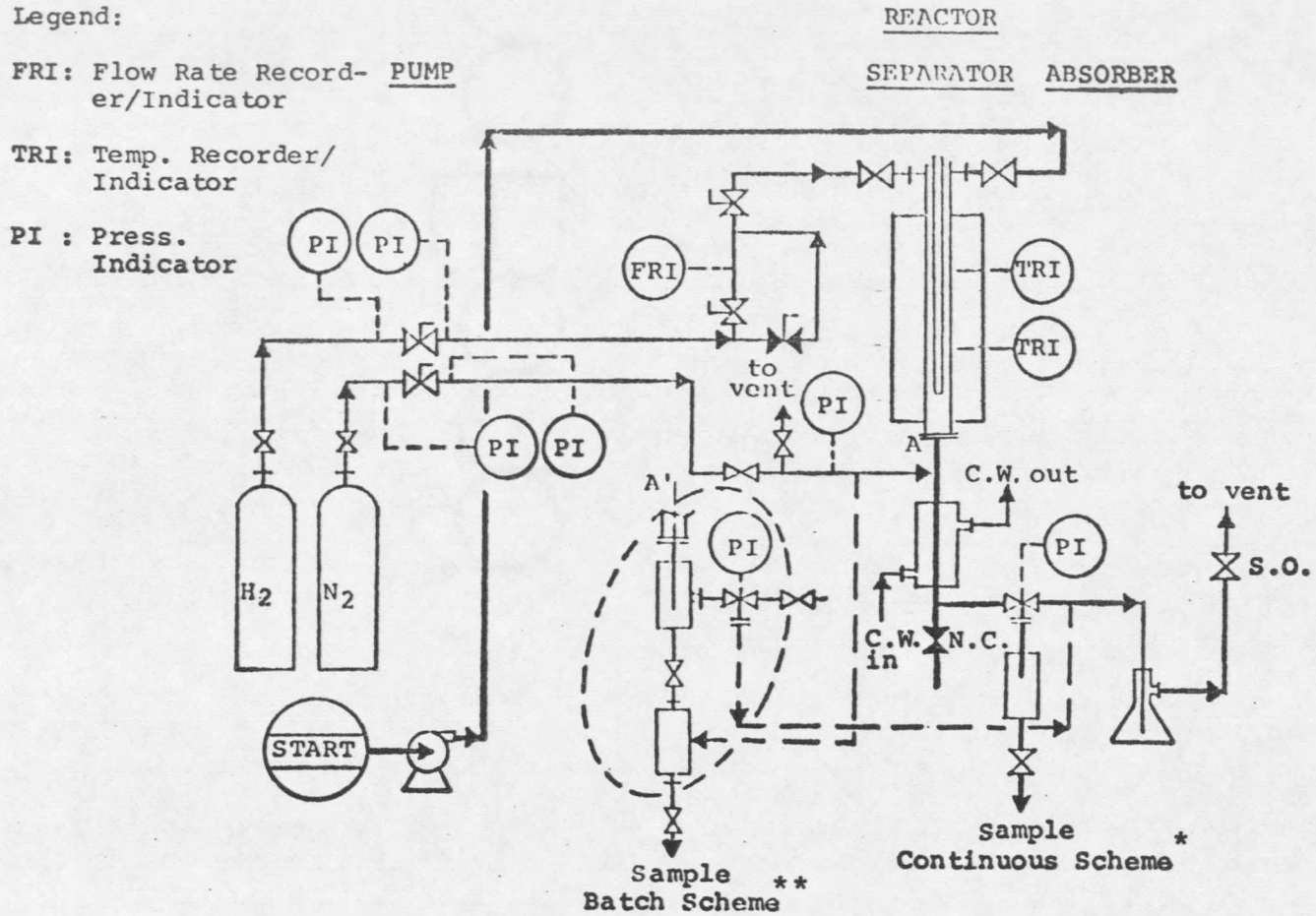
A small-scale, trickle-bed reactor as showen in Figure 3 was used throughout this research. The trickle-bed reactor is 40 inches long and made of 1" ID, schedule 80 inconel pipe.

At the top of reactor a cross was welded to the reactor and fitted with a 36-inch long stainless steel tube into the reactor to serve as a thermowell. The other two openings were for SRC-II feed and the hydrogen inlet.

Table III. Catalyst Properties

	MSU-C-49	Shell NM324	Harshaw HT-400
Type	Extruded	Extruded	Extruded
Size	1/32"	1/16"	1/32"
Bulk Density(g/cc)		0.855	0.801
Pore Volume(ml/gram)	0.84	0.396	0.5
Surface Area(m^2/gram)	214.6	188	220
Average Pore Diameter (A^o)	156.5	98	110
Metal Content(wt%)			
NiO	1.0	2.72	
MoO_3	8.0	13.16	15.0
CoO	4.0		3.0
WO_3	8.0		

Note: Catalyst support of MSU-C-49 is Nalco-78-6008C.



* Continuous Scheme is Used for Experimental Runs

** Batch Scheme is Used for Hydrotreating Creosote Oil

Figure 3. Flow Scheme of Small Scale Trickle-Bed Reactor.

At the bottom of the reactor was a threaded cap fitted with an outlet for product release and/or loading and unloading of the catalyst.

The reactor was heated by an electric winding which was wrapped around a 6-inch O.D. aluminum block surrounded by insulated material. The block had a 1-inch bore hole for the reactor.

Temperature was measured by two chromel-alumel thermocouples which were connected to digital thermocouple readouts. The thermocouples were located in the perheat and reaction sections.

Liquid feed was pumped through a 1/8-inch stainless steel tube by a metering pump. In hydrotreating of creosote oil, the feed system was heated by wrapping electric tapes or coils around the tubes to reduce the high viscosity of the creosote oil.

Gaseous phase product was condensed by a double-pipe type condenser and collected after a gas-liquid separator either continuously or by batch. The latter was used in hydrotreating of creosote oil because of its high viscosity and high boiling point. In this case, liquid was allowed to be collected in a catchpot first. Whenever the liquid product was removed, the valve between the separator and the catchpot was closed and the catchpot was depressurized through a vent. After the liquid product was drained from the bottom, the catchpot was repressurized

with nitrogen and the valve was reopened.

Hydrotreating Creosote Oil

The hydrogen to carbon ratio of creosote oil can be increased by hydrotreating, it can then be used as a solvent in the SRC process. Hydrotreating increased the hydrogen content about 1% from 6.1% to 7.5%. The hydrotreating conditions were suggested by Wright et al.(21) in 1975 as shown in Table V.

To increase pumpability of creosote oil in the existing equipment, the LHSV was increased to 1.0 c.c./c.c. of catalyst/hr, and the hydrotreating was repeated under the same conditions until the product was liquid.

Theoretically, the feed flow rate can be increased by increasing the volume of catalyst instead of increasing the LHSV. However, the capacity of the reactor restricts usage to no more than 100ml of catalyst, hence, the LHSV was increased.

The catalyst and inert packing distribution in the reactor is shown in Figure 4.

Analysis

The nitrogen and sulfur content of creosote oil are similar to that of SRC-II, and this makes it difficult to differentiate the contribution of SRC-II and creosote oil in the mixture. Therefore, it was assumed that

catalysts produce the same degree of hydrotreating on SRC-II and creosote oil. The analysis of the products for sulfur and nitrogen content was based on overall products in lieu of specifying it for SRC-II or creosote oil.

Sulfur content was analyzed and reported to 0.03% accuracy using a quartz tube combustion method which was developed by Shell Development Co.(24), and weight percent desulfurization was calculated by assuming no weight change between feed and product.

The material balance equation for sulfur in this process is shown as follows:

$$W_s \cdot C_{sf} \cdot (1-X) + (1-W_s) \cdot C_{cf} \cdot (1-X) = C_p$$

After arrangement, it becomes:

$$1-X = \frac{C_p}{W_s \cdot C_{sf} + (1-W_s) \cdot C_{cf}}$$

$$X = 1- \frac{C_p}{W_s \cdot C_{sf} + (1-W_s) \cdot C_{cf}}$$

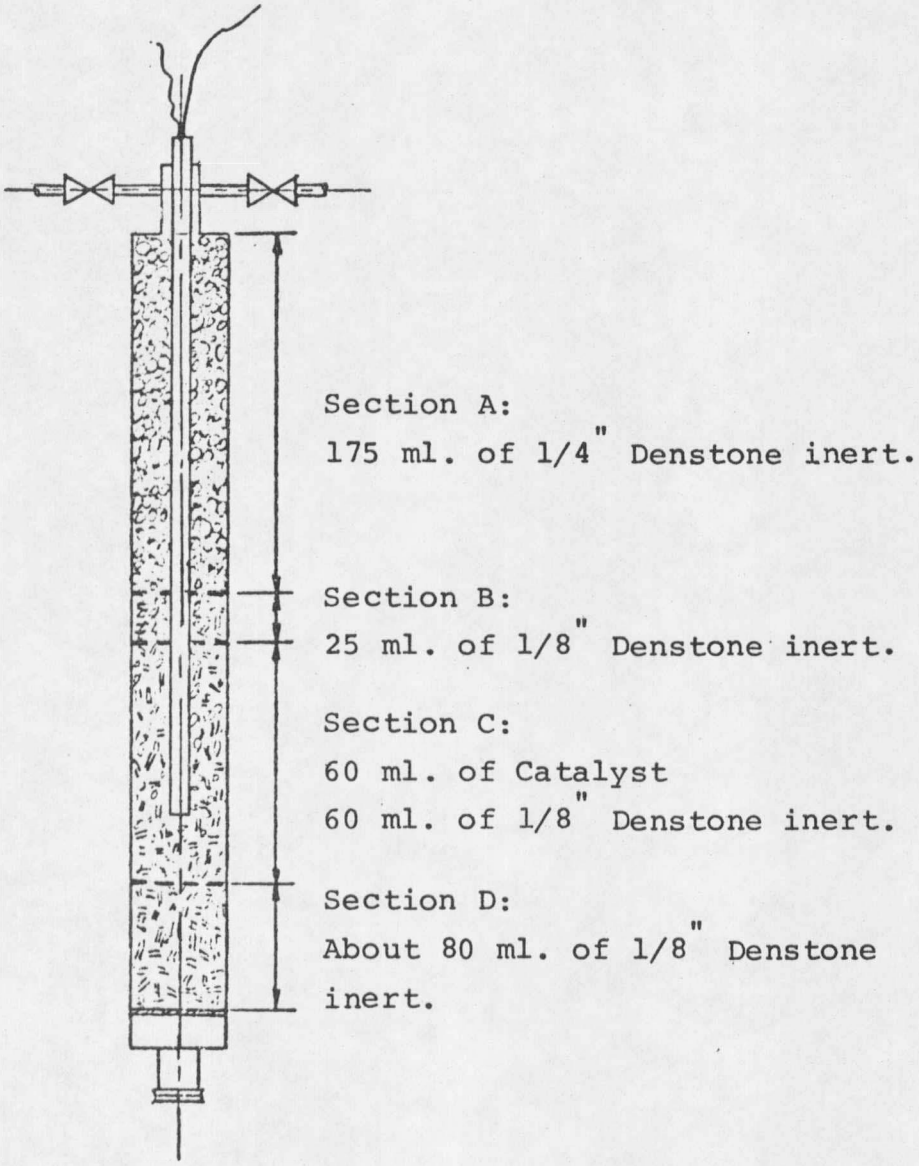


Figure 4. Catalyst and Packing Distribution in Trickle-Bed Reactor.

Likewise, weight percent denitrogenation was determined by an improved Kjeldahl Method(25) and followed the equation:

$$Y = 1 - \frac{C'_p}{W_s \cdot C'_{sf} + (1-W_s) \cdot C'_{cf}}$$

ANSI/ASTM D86-77 standard distillation was applied in the determination of the extent of cracking(26).

CHAPTER V

RESULTS AND DISCUSSION

The first three runs using MSU-C-49 were conducted at three different ratios of creosote oil to SRC-II, and the last two runs used Shell NM324 and Harshaw HT-400 catalysts, keeping the creosote oil to SRC-II ratio at 25%:75%. The other conditions of all runs were kept constant and are shown in Table IV and Table V.

Table IV. Materials for Experimental Runs

Run No.	Catalyst	Creosote Oil / SRC-II
CPC-C25	MSU-C-49	25%:75%
CPC-C50	MSU-C-49	50%:50%
CPC-C75	MSU-C-49	75%:25%
CPS-C25	Shell NM324	25%:75%
CPH-C25	Harshaw HT-400	25%:75%

Table V. Reaction Conditions

Upgrading of SRC-II	
Temperature (^{o}C), (^{o}F)	425, (797)
Pressure (Kg/m^2), (psig)	7.03×10^5, (1,000)
Liquid Hourly Space Velocity (c.c. SRC-II/c.c. catalyst/hr)	1.25
Hydrogen Flow Rate (SCF/bbl. of SRC-II)	10,000
Running Time (hr)	60 (=4,500ml SRC-II)
Hydrogenating Creosote Oil	
Temperature (^{o}C), (^{o}F)	415, (780)
Pressure (Kg/m^2), (psig)	1.05×10^6, (1,500)
Liquid Hourly Space Velocity (c.c. creosote oil/c.c. catalyst/hr)	1.0
Hydrogen Flow Rate (SCF/bbl. of creosote oil)	10,000
Catalyst	Shell NM324

Raw data for nitrogen and sulfur analyses and ASTM distillations are shown in Appendix. The data is plotted in Figure 5 to Figure 18. Every product was separated by ASTM distillation into three fractions which ranged from up to 400°F, 400°F---700°F, and above 700°F. Each fraction was analyzed for nitrogen and sulfur content.

Hydrotreating Creosote Oil

First, the Koppers creosote oil was hydrogenated to increase its hydrogen content. In this research two batches of hydrogenated creosote oil were made at the same conditions with the same catalysts. Results showing the consistency between these two batches are in Table VI. Actually, these two products can be combined into one. However, for comparision, the results are shown separately.

Denitrogenation

Figures 5-7 show the nitrogen content in the products and the weight percent denitrogenation. Figure 5 and Figure 6 are plots for nitrogen content vs. throughput of SRC-II. Except for the CPH-C25 run which is obviously low, the nitrogen content in the products is about 0.35%. The CPC-C25, CPS-C25 and CPH-C25 runs have a higher nitrogen content in the feedstock because of the high content in SRC-II. However, referring to Figure 7, the extent of nitrogen removal shows some variation.

In CPH-C25 run, there is a higher denitrogenation than in CPC-C25. This fact can be explained by the high molybdate concentration in the catalyst which is shown in Table III. The same catalyst used by Sahin in his research revealed the conclusion that Harshaw HT-400 catalyst has a higher activity in denitrogenation than the MSU catalyst.

Figure 7 shows the same tendency of denitrogenation with throughput for different catalysts. Nevertheless, each run shows a lower activity than when investigated by previous coworkers with no creosote oil added. The lower activity of denitrogenation in this research obviously shows that the effect of adding creosote oil in 1:3, 1:1 and 3:1 ratios to SRC-II is not beneficial.

Desulfurization

In the same manner as the denitrogenation results shown above, the sulfur content and weight percent desulfurization in each product are plotted in Figures 8,9 and 10. In general, desulfurization is easier to achieve for coal liquids than denitrogenation.

The three test runs show only slight variation in desulfurization activity. Compared to 90% desulfurization reported in the literature, the activity for these runs has been reduced to 60%. Like denitrogenation, Figure 10 shows that desulfurization decreases as percent of creosote oil in the feed increases.

Table VI. SRC-II LECF and Two Batches of Hydrogenated Creosote Oil

	SRC-II LECF	Hydrogenated Creosote Oil	
		Batch 1	Batch 2
Nitrogen Content(wt%)	0.63	0.35	0.39
Sulfur Content(wt%)	0.67	0.32	0.30
Density(g/cm^3)	0.983	1.05	1.05
ASTM Distillation			
IBP(^oF)	122	205	210
5%	217	490	495
10%	288	575	580
20%	381	645	650
30%	446	690	695
40%	488	---	700
43%	---	700	
50%	541		
60%	577		
70%	611		
80%	660		
87%	700		
Residue and loss (vol. %)	13	57	60

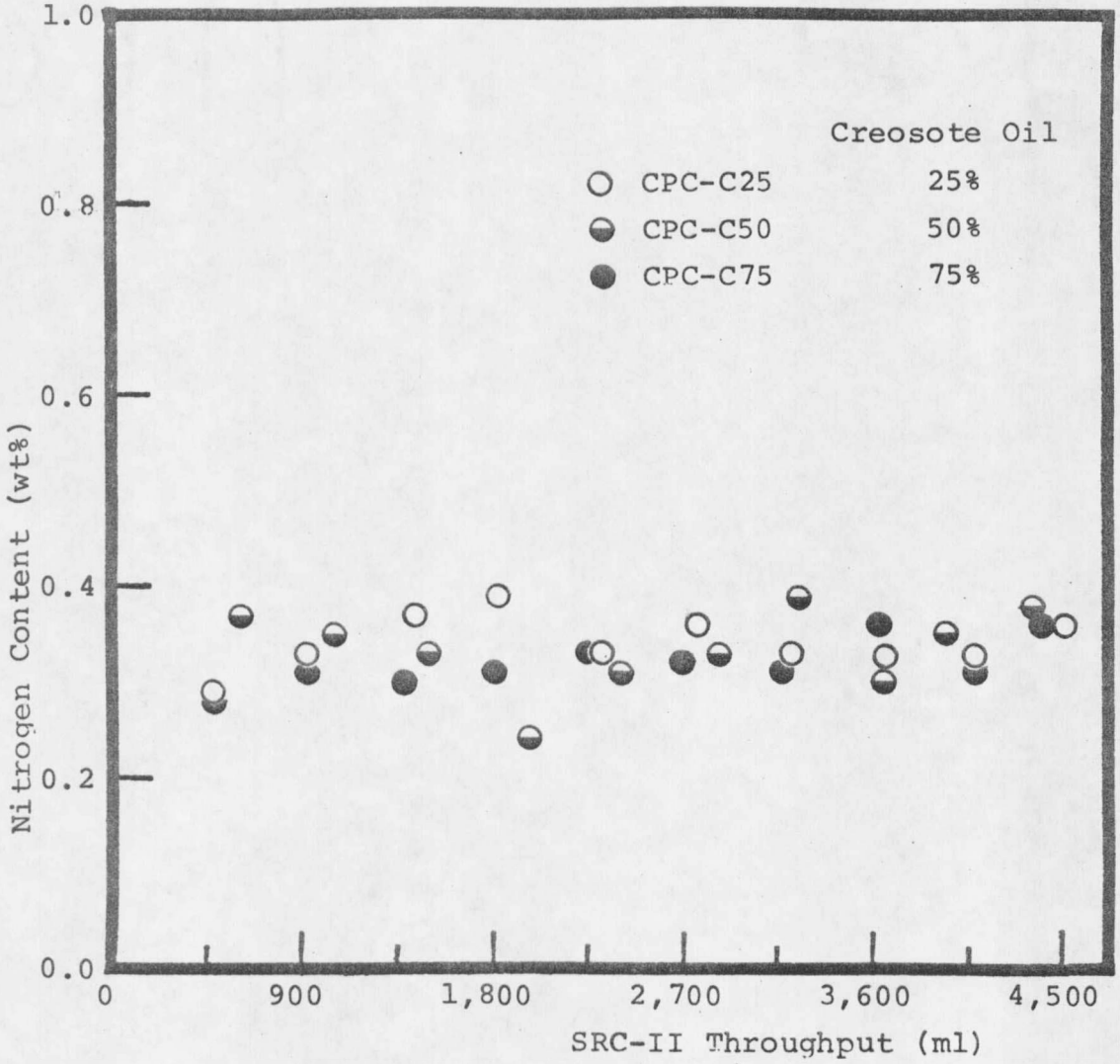


Figure 5. Nitrogen content in products upgraded by MSU-C49 with different concentrations of creosote oil.

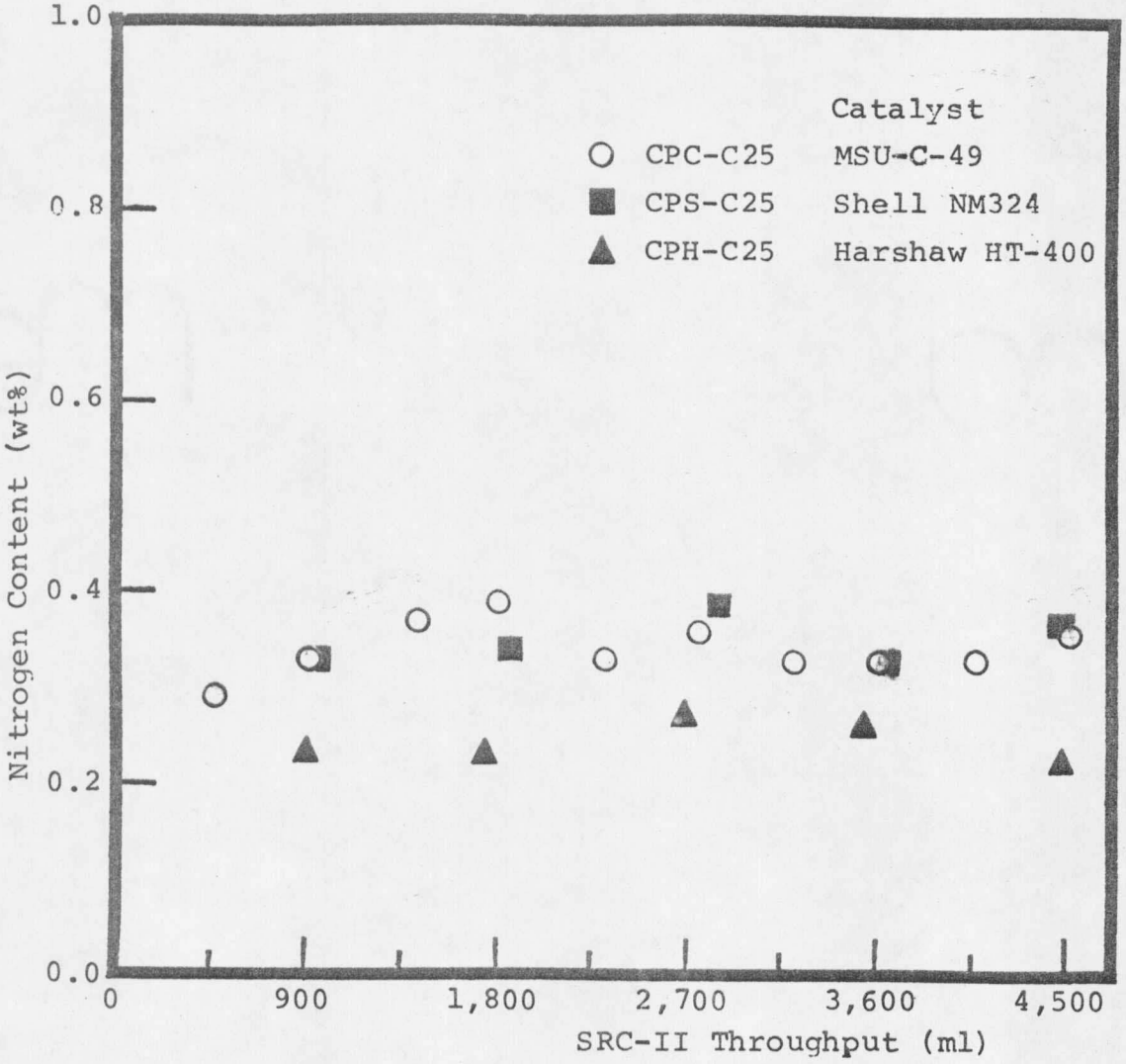


Figure 6. Nitrogen content in products upgraded by different catalysts with 25% creosote oil.

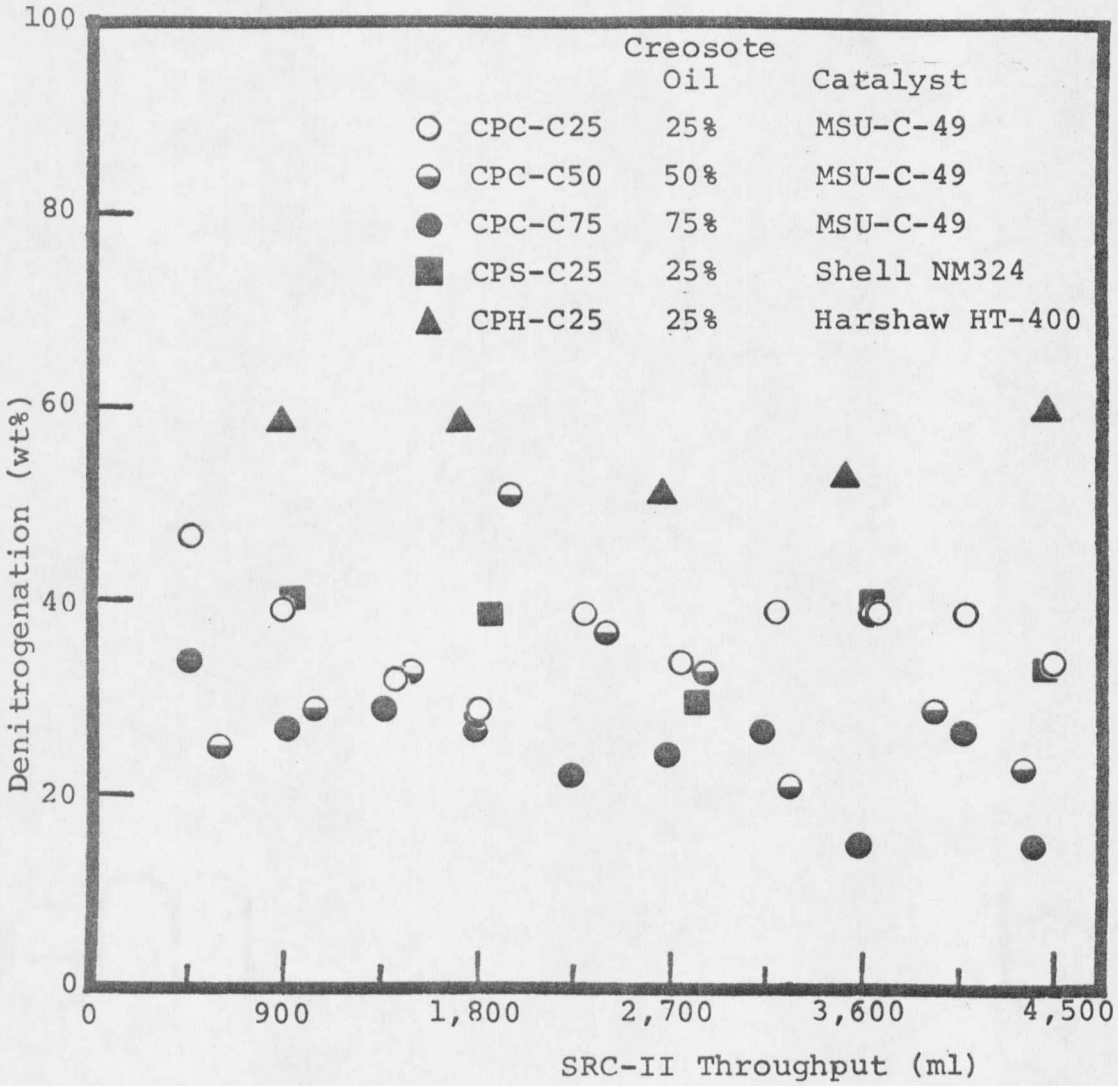


Figure 7. Weight percent denitrogenation.

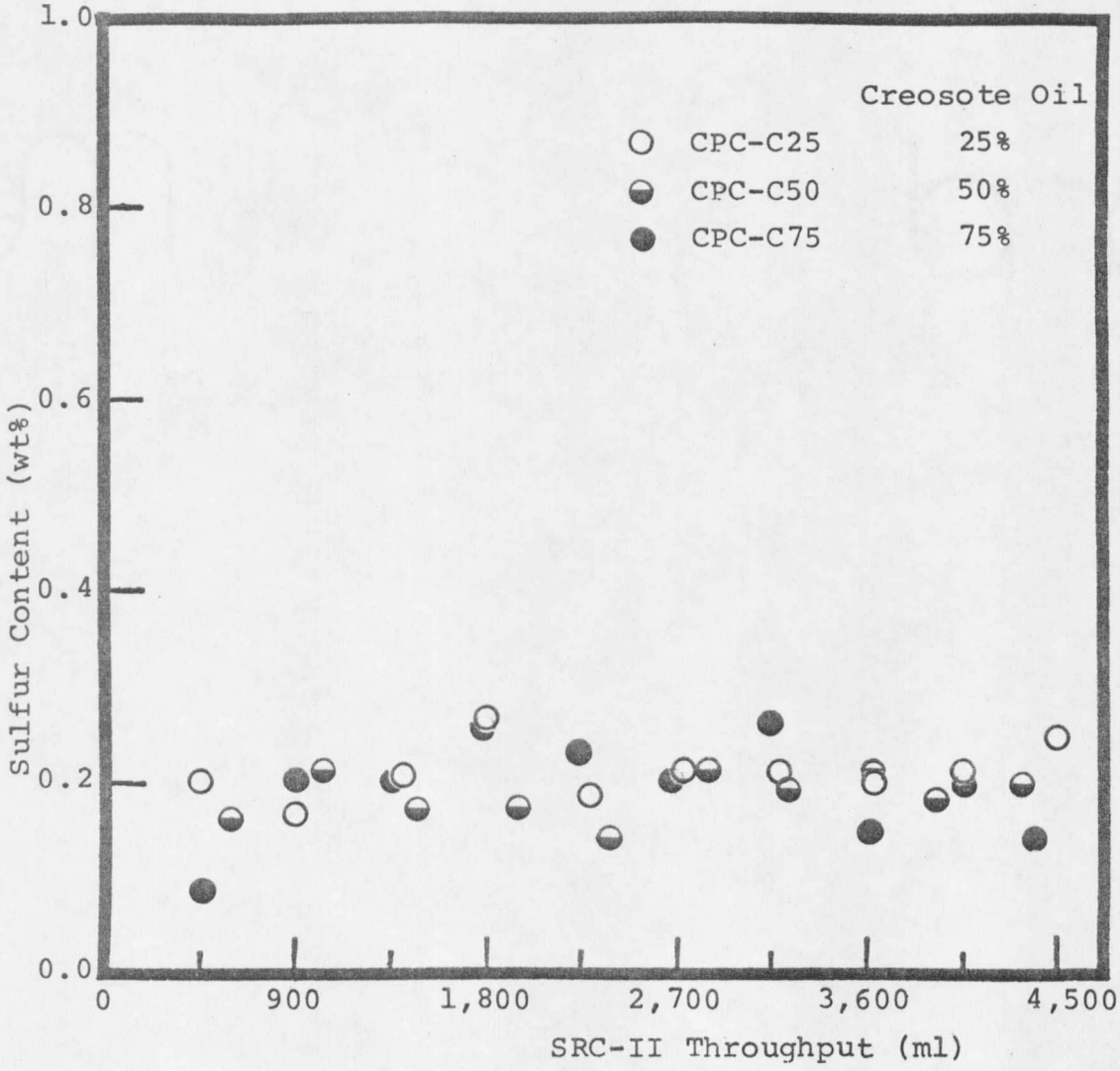


Figure 8. Sulfur content in products upgraded by MSU-C49 with different concentration of creosote oil.

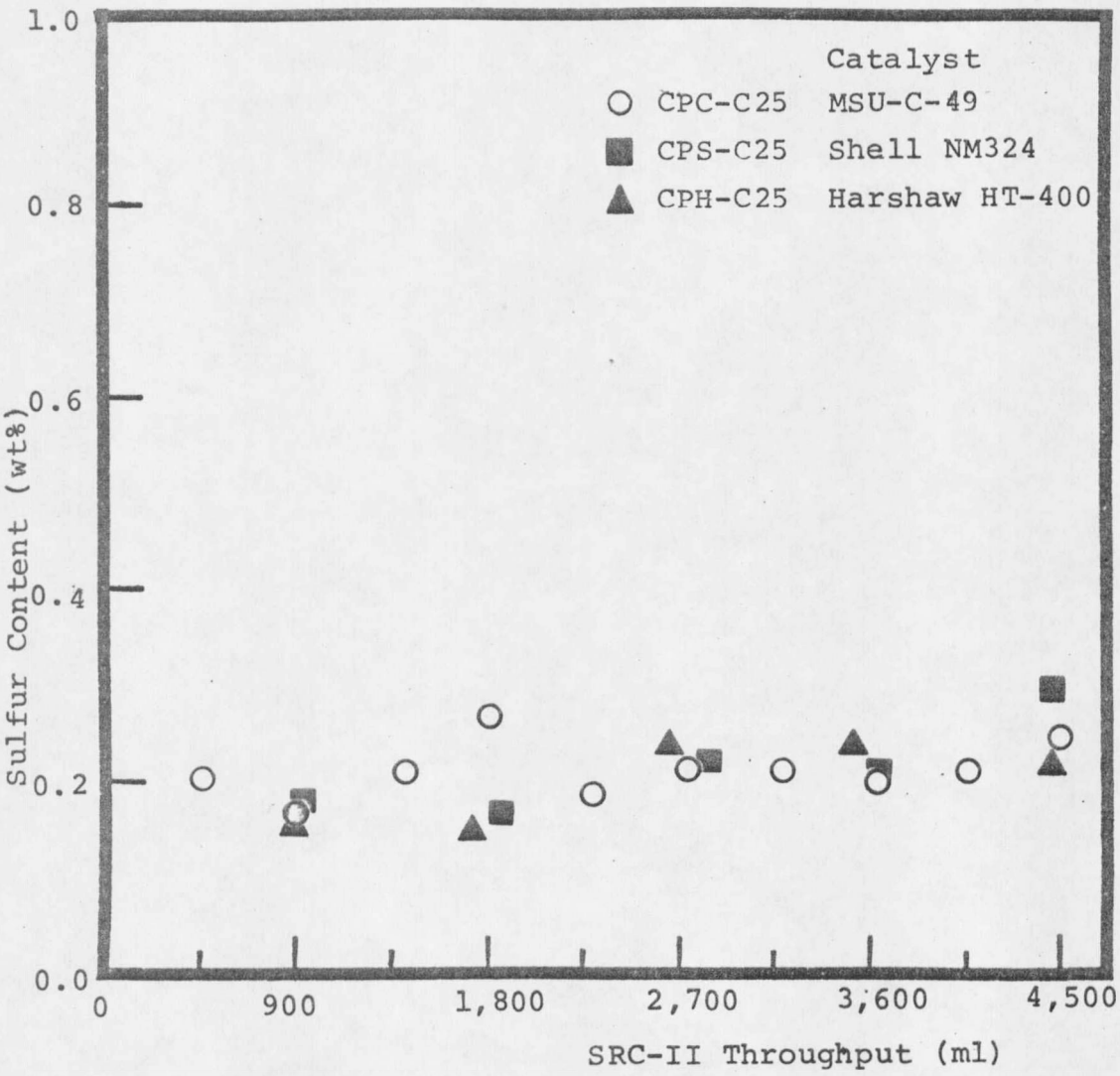


Figure 9. Sulfur content in products upgraded by different catalysts with 25% creosote oil.

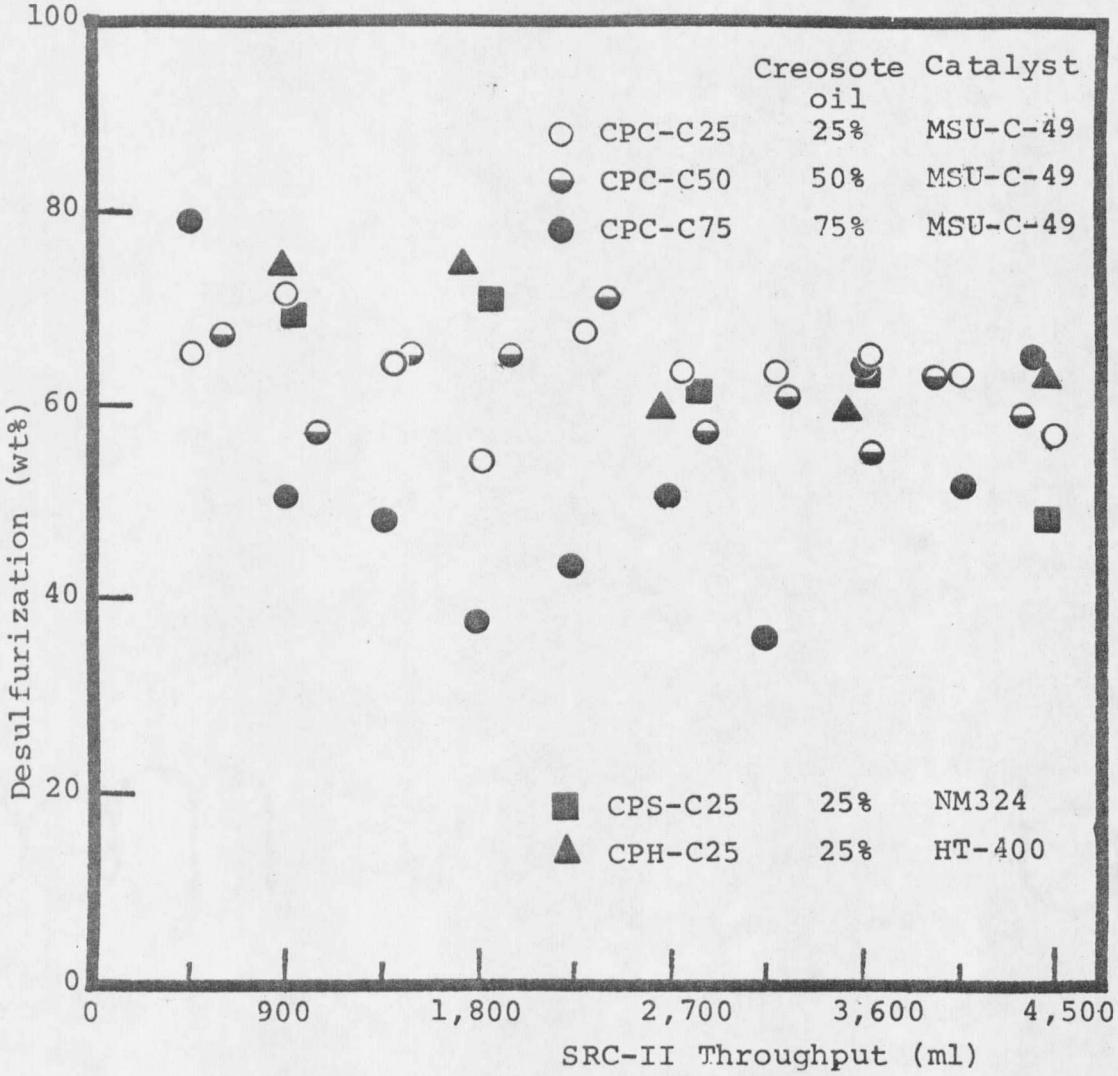


Figure 10. Weight percent desulfurization.

The data presented in Figure 10 shows that the Harshaw HT-400 catalyst has higher desulfurization activity than Shell NM324 or MSU-C-49.

ASTM Distillation Result

Hydrotreating SRC-II liquified coal not only reduced the nitrogen and sulfur content, but also increased the quantity of the lower boiling point fraction. For comparative convenience, we plotted the ASTM distillation data for each run individually in Figure 11 to Figure 14. Runs of CPS-C25 and CPH-C25 used the same ratio of hydrogenated creosote oil to SRC-II in the feed--1 to 3. The increased shift from a higher product boiling point range to a lower one with the Harshaw catalyst, run CPH-C25, than with the Shell catalyst, run CPS-C25, is consistent with the fact that better denitrogenation and desulfurization was obtained with Harshaw HT-400 in this research. For the three different mixing-ratio runs, the distillation curves in Figure 13 and Figure 14 show only a tiny effect in increasing the lower boiling point fraction of upgraded SRC-II for CPH-C75 and CPC-C50 runs.

The ASTM distillations reveal the fact that it is not beneficial for a high percentage of creosote oil to be added in hydroprocessing SRC-II.

Figure 15 and Figure 16 show the nitrogen and sulfur content in each product fraction vs. percentage of added creosote oil after treatment using MSU-C49 catalyst. The medium boiling fraction has a slightly higher nitrogen content for each of the three different blending-ratio runs. It reveals that the effect of creosote oil on denitrogenation is different from that of desulfurization.

Figure 17 and 18 show the distribution of nitrogen and sulfur in the products of distillation for the different runs.

Summary

In summary, the negative effect of hydrogenated creosote oil on upgrading SRC-II liquified coal is obvious for blends of 25%:75%; 50%:50%; and 75%:25%. This fact can be explained by the competition between the creosote oil and SRC-II molecules being adsorbed on the active sites of catalyst. The less creosote oil added, the less competition comes from creosote oil for the active sites and the more molecules of SRC-II that will be adsorbed by the catalyst. A higher activity in upgrading SRC-II is obtained when less creosote oil is added, and the effect of creosote oil is not beneficial at this point.

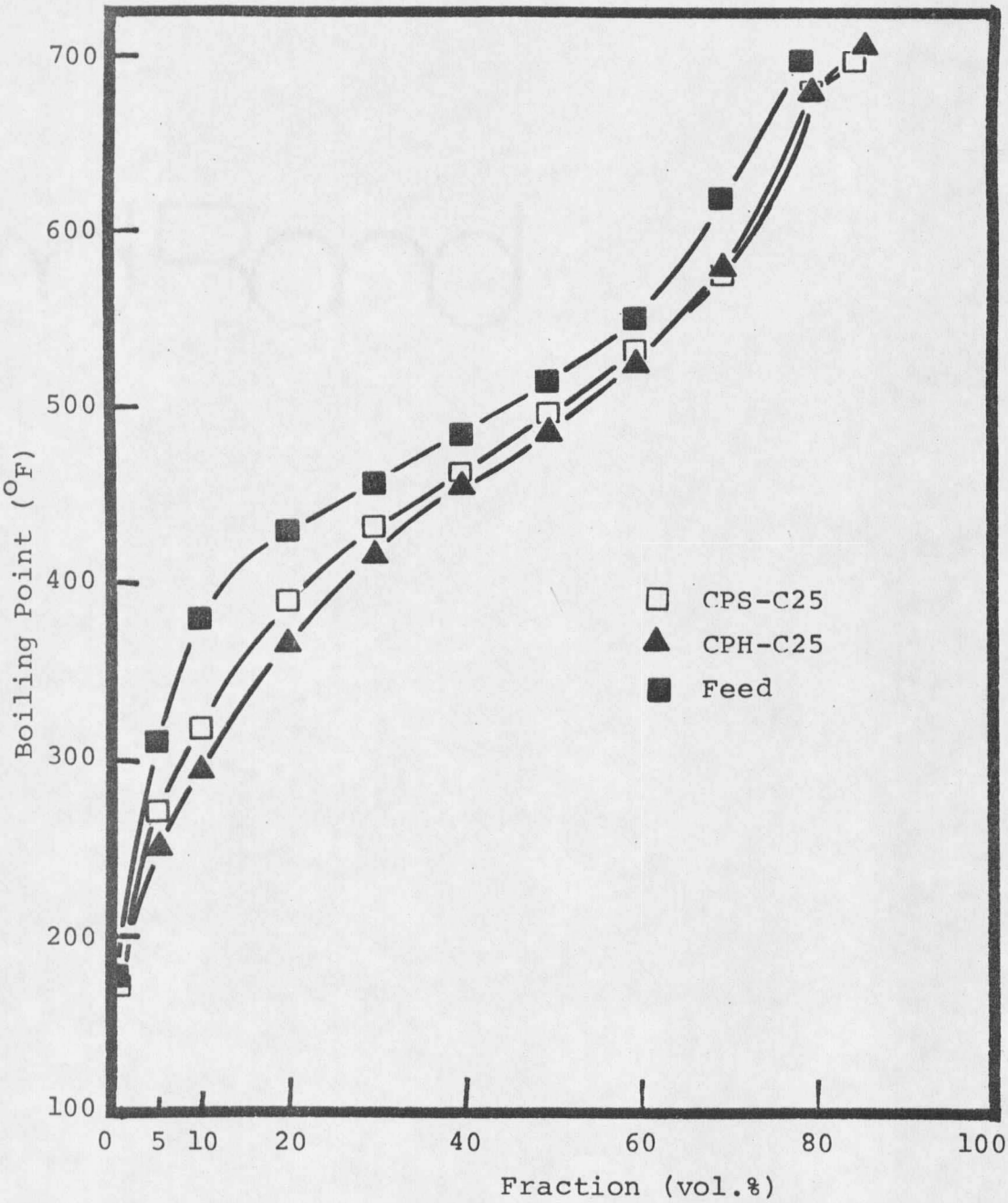


Figure 11. ASTM distillation for CPS-C25 and CPH-C25.

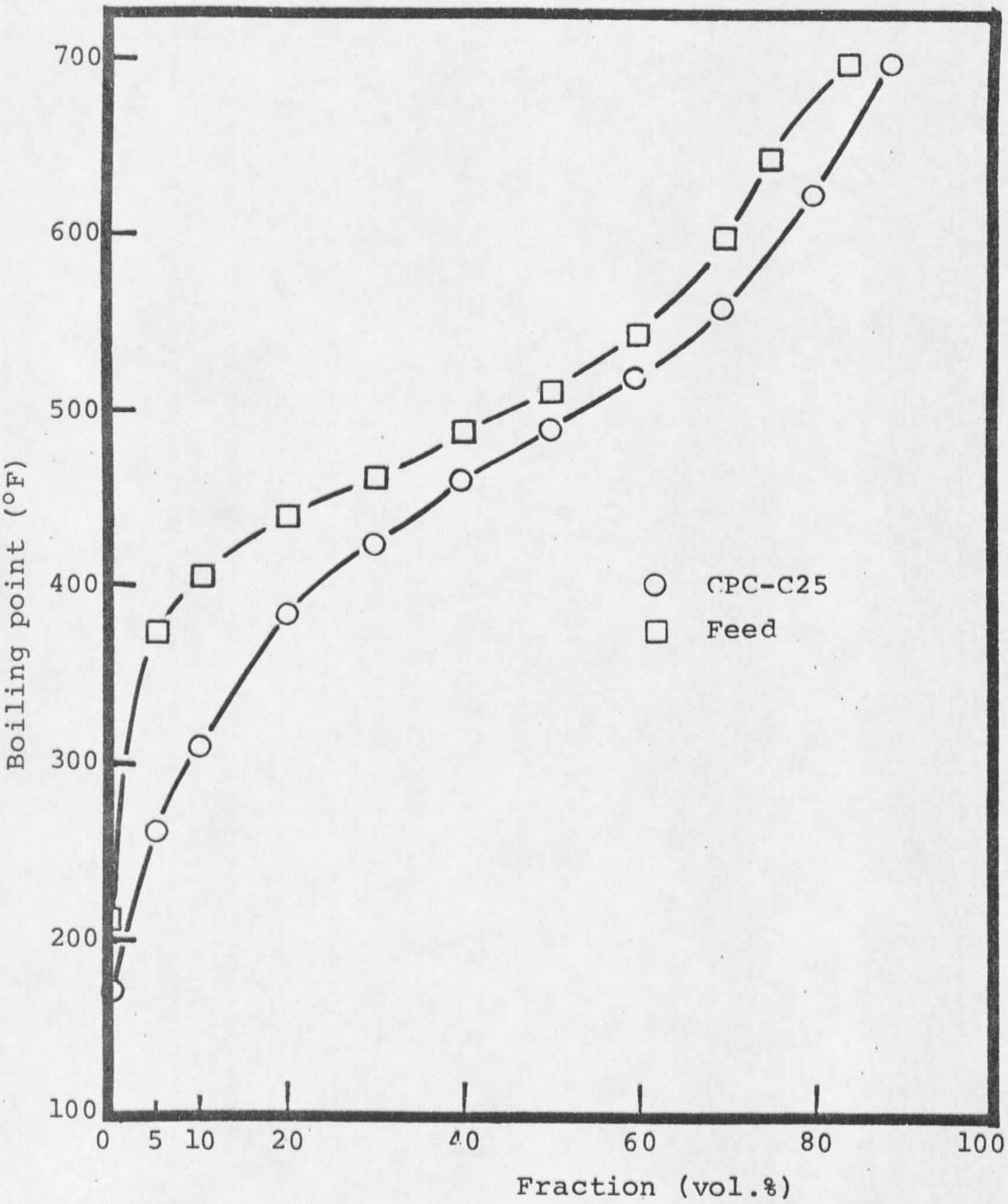


Figure 12. ASTM distillation for CPC-C25.

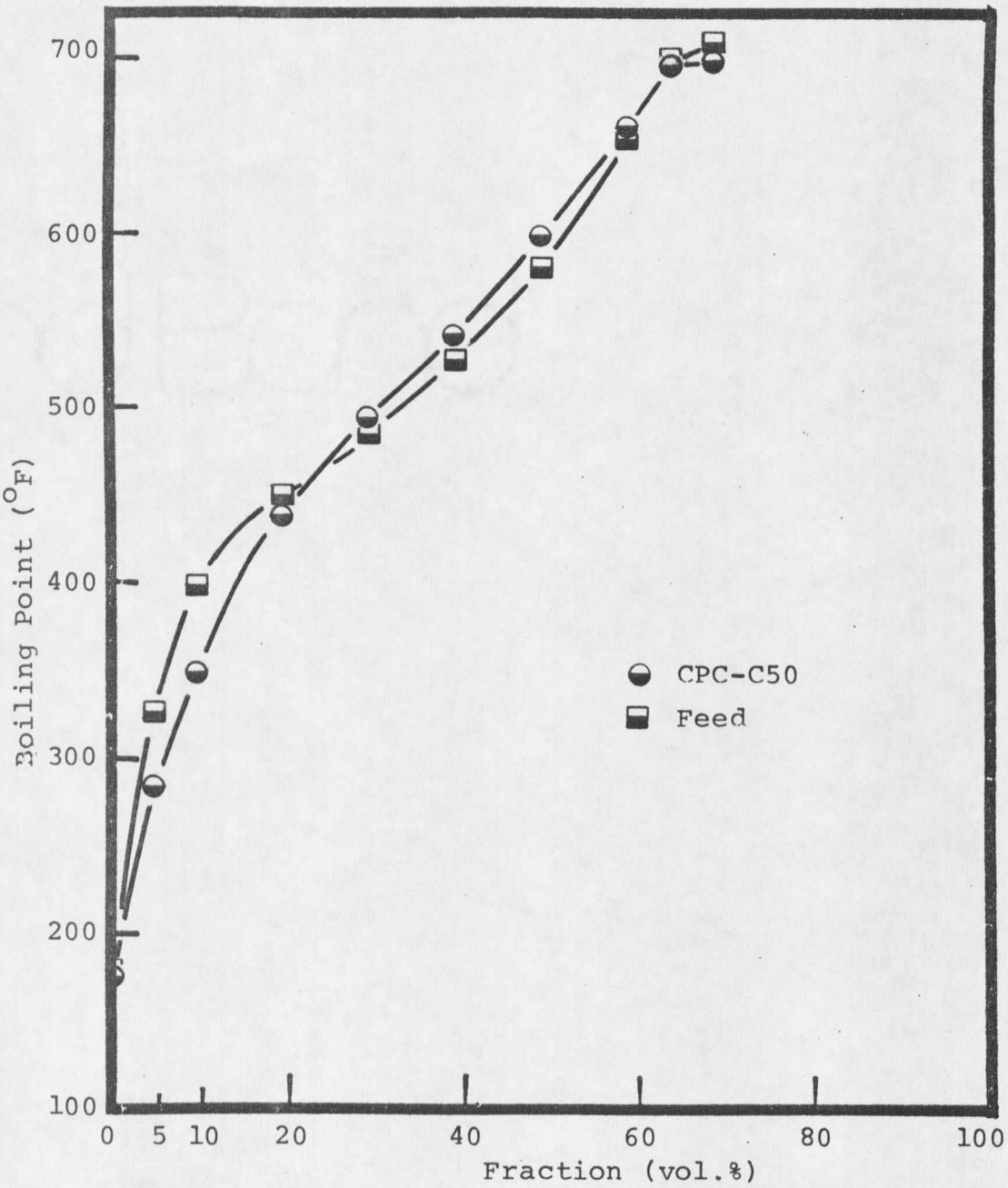


Figure 13. ASTM distillation for CPC-C50.

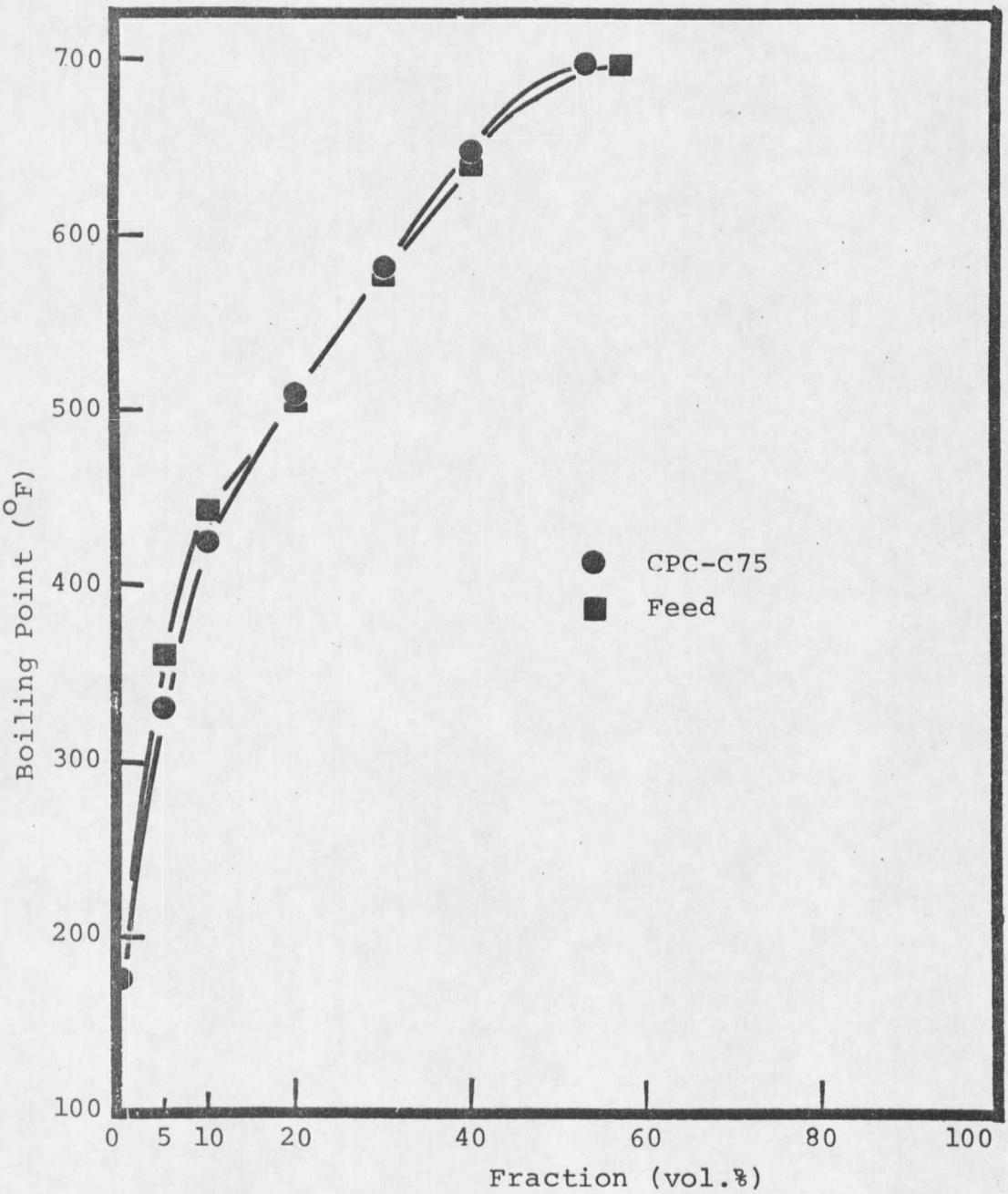


Figure 14. ASTM distillation for CPC-C75.

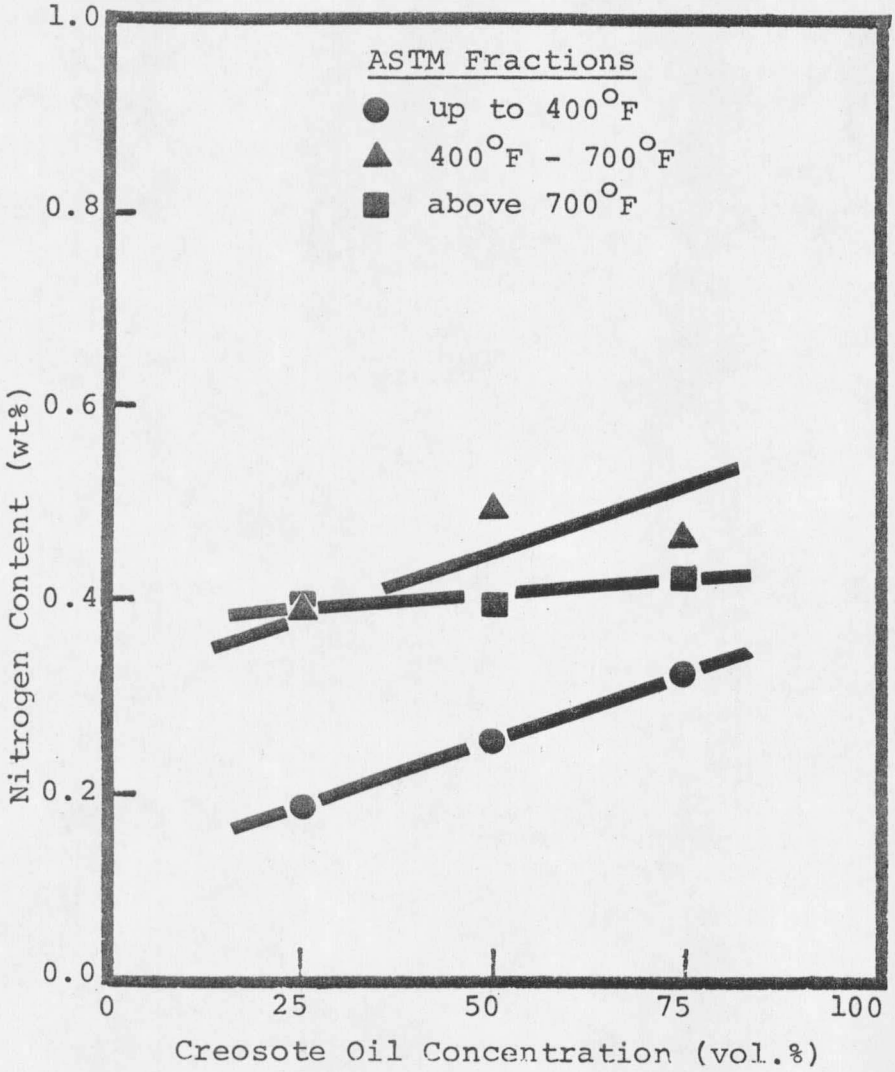


Figure 15. Nitrogen content in different fractions.

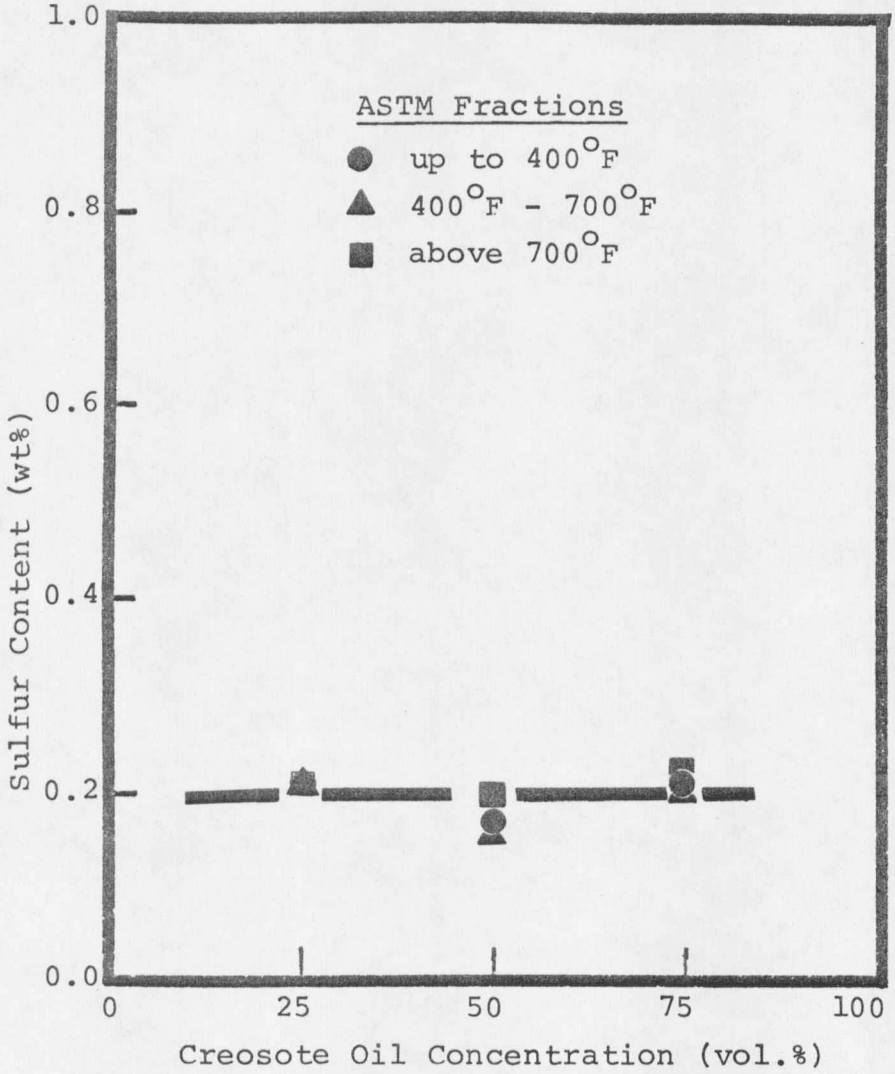


Figure 16. Sulfur content in different fractions.

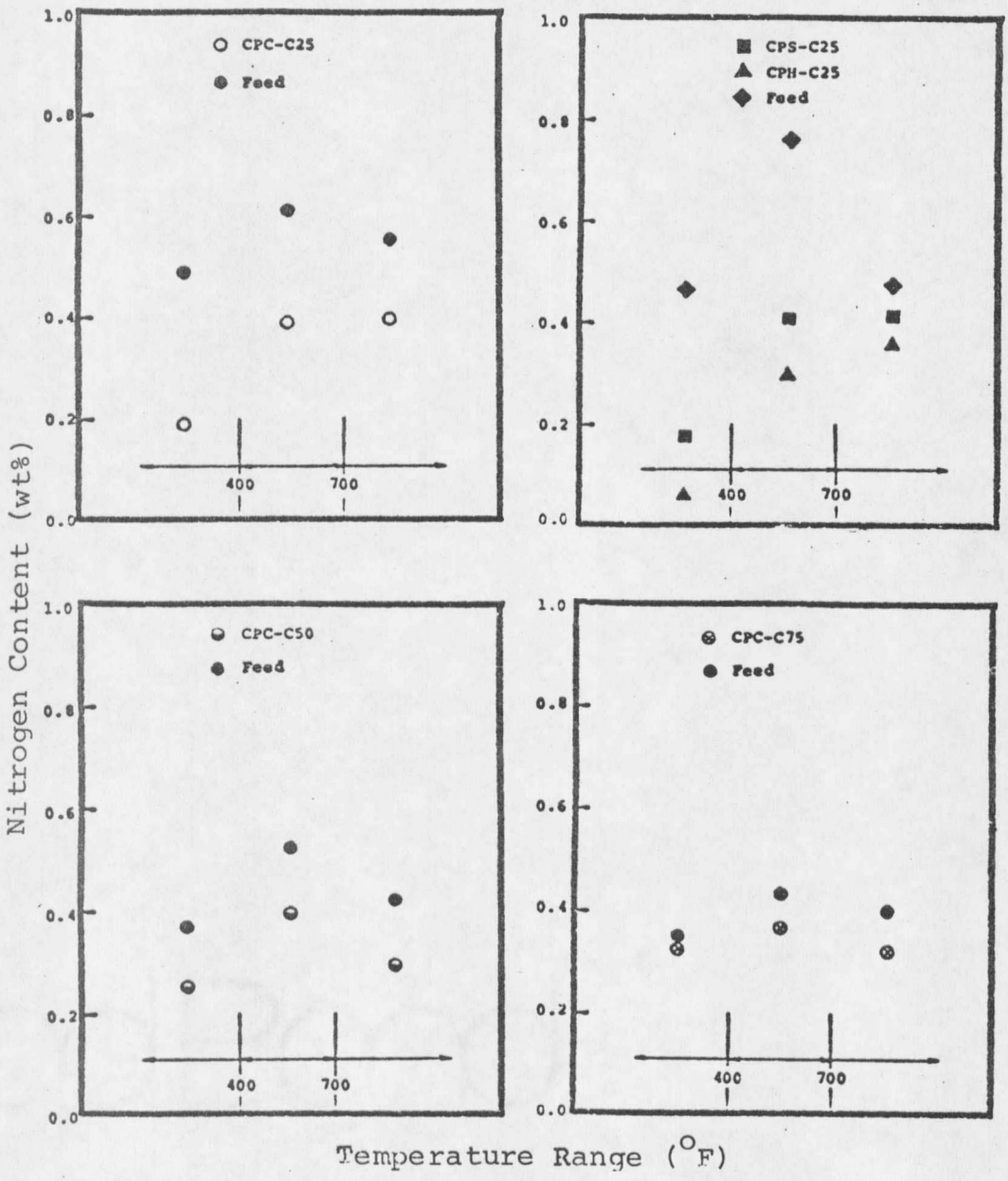


Figure 17. Nitrogen Content in Fractions for Each Run.

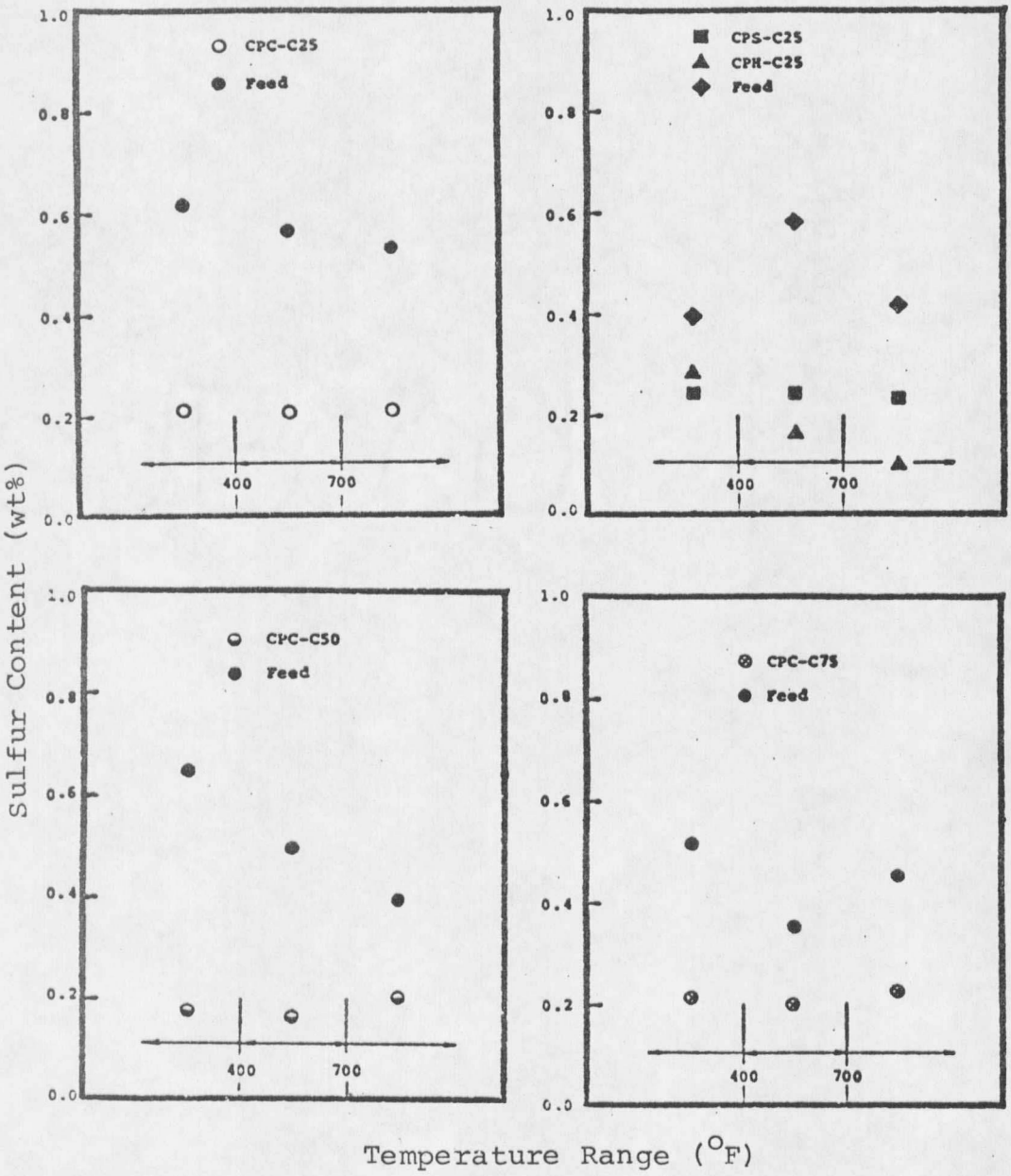


Figure 18. Sulfur Content in Fractions for Each Run.

CHAPTER VI

CONCLUSION

1. The effect of hydrogenated creosote oil as a hydrogen donor agent on upgrading of SRC-II is not benecifial.

2. The extent of hydrodenitrogenation and hydrodesulfurization of SRC-II with hydrogenated creosote oil varies with the percentage of the blending ratio. The more hydrogenated creosote oil added, the lower the extent of denitrogenation.

3. ASTM distillation is an index of extent of hydrotreating the coal liquid. The more hydrogenated creosote oil added, the less low-boiling point fraction obtained.

4. Harshaw HT-400 catalyst had the most significant effect on hydrotreating SRC-II coal liquids of the catalysts studied.

NOMENCLATURE

C_{cf}: Sulfur content of creosote oil in feed (wt fraction)

C'_{cf}: Nitrogen content of creosote oil in feed (wt fraction)

C_{sf}: Sulfur content of SRC-II in feed (wt fraction)

C'_{sf}: Nitrogen content of SRC-II in feed (wt fraction)

C_p : Sulfur content in product (wt fraction)

C'_p : Nitrogen content in product (wt fraction)

W_s : Concentration of SRC-II (wt fraction)

X : Weight fraction removal of sulfur

Y : Weight fraction removal of nitrogen

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APPENDIX

Table VII. Run CPC-C25

Catalyst: MSU-C-49

Creosote Oil / SRC-II: 25%:75%

Analysis:

Sample No.*	Nitrogen (wt%)	Sulfur (wt%)
1	0.29	0.20
2	0.33	0.16
3	0.37	0.21
4	0.39	0.26
5	0.33	0.19
6	0.36	0.21
7	0.33	0.21
8	0.33	0.20
9	0.33	0.21
10	0.36	0.25
Avg.	0.34	0.21
Feed	0.54	0.58
Wt% Removal	37.04	63.79

* Sample was taken every 6 hours.

Table VIII. Run CPC-C50

Catalyst: MSU-C-49

Creosote Oil / SRC-II: 50%:50%

Analysis:

Sample No.*	Nitrogen (wt%)	Sulfur (wt%)
1	0.37	0.16
2	0.35	0.21
3	0.33	0.17
4	0.24	0.17
5	0.31	0.14
6	0.33	0.21
7	0.39	0.19
8	0.30	0.21
9	0.35	0.18
10.	0.38	0.20
Avg.	0.335	0.184
Feed	0.49	0.49
Wt% Removal	31.63	62.36

* Sample was taken every 6 hours.

Table IX. Run CPC-C75

Catalyst: MSU-C-49

Creosote Oil / SRC-II: 75%:25%

Analysis:

Sample No.*	Nitrogen (wt%)	Sulfur (wt%)
1	0.28	0.08
2	0.31	0.20
3	0.30	0.21
4	0.31	0.25
5	0.33	0.23
6	0.32	0.20
7	0.31	0.26
8	0.36	0.14
9	0.31	0.19
10	0.36	0.14
Avg.	0.319	0.19
Feed	0.42	0.40
Wt% Removal	24.05	52.50

* Sample was taken every 6 hours.

Table X. Run CPS-C25

Catalyst: Shell NM324

Creosote Oil / SRC-II: 25%:75%

Analysis:

Sample No.*	Nitrogen (wt%)	Sulfur (wt%)
1	0.33	0.17
2	0.34	0.17
3	0.39	0.22
4	0.33	0.21
5	0.37	0.30
Avg.	0.352	0.214
Feed	0.55	0.58
Wt% Removal	36.00	63.10

* Sample was taken every 12 hours.

Table XI. Run CPH-C25

Catalyst: Harshaw HT-400

Creosote Oil / SRC-II: 25%:75%

Analysis:

Sample No.*	Nitrogen (wt%)	Sulfur (wt%)
1	0.23	0.15
2	0.23	0.14
3	0.27	0.23
4	0.26	0.23
5	0.22	0.21
Avg.	0.242	0.192
Feed	0.55	0.58
Wt% Removal	56.00	66.90

* Sample was taken every 12 hours.

Table XII. ASTM Distillation for Run CPC-C25

Fraction	Temperature (^{0}F)	
	Product	Feed
IBP	170	230
5%	265	375
10%	310	405
20%	385	440
30%	425	465
40%	460	488
50%	490	512
60%	520	545
70%	560	600
80%	625	695
84%	---	700
89%	700	---
Residue & Loss	11%	16%

Fractions	N (wt%)	S (wt%)	N (wt%)	S (wt%)
---400°F	0.187	0.209	0.488	0.618
400°F--700°F	0.391	0.204	0.615	0.566
700°F---	0.397	0.208	0.557	0.582

Table XIII. ASTM Distillation for Run CPC-C50

Fraction	Temperature (^{o}F)	
	Product	Feed
IBP	175	167
5%	285	327
10%	350	400
20%	440	450
30%	495	485
40%	543	527
50%	600	580
60%	662	655
65%	---	700
70%	700	---
Residue & Loss	30%	35%

Fractions	N (wt%)	S (wt%)	N (wt%)	S (wt%)
---400°F	0.255	0.170	0.458	0.647
400°F--700°F	0.400	0.157	0.530	0.496
700°F---	0.299	0.195	0.428	0.392

Table XIV. ASTM Distillation for Run CPC-C75

Fraction	Temperature (^{o}F)	
	Product	Feed
IBP	175	175
5%	330	360
10%	425	443
20%	510	505
30%	582	578
40%	650	643
50%	696	694
53%	700	---
57%	---	700
Residue & Loss	47%	43%

Fractios	N (wt%)	S (wt%)	N (wt%)	S (wt%)
---400°F	0.327	0.210	0.351	0.518
400°F--700°F	0.370	0.201	0.438	0.354
700°F---	0.326	0.226	0.404	0.456

Table XV. ASTM Distillation for Run CPS-C25

Fraction	Temperature (°F)	
	Product	Feed
IBP	172	177
5%	271	310
10%	318	380
20%	390	430
30%	432	458
40%	463	485
50%	495	515
60%	528	550
70%	575	620
79%	---	700
80%	683	---
85%	700	---
Residue & Loss	15%	21%

Fractions	N (wt%)	S (wt%)	N (wt%)	S (wt%)
---400°F	0.178	0.243	0.466	0.396
400°F--700°F	0.412	0.242	0.767	0.586
700°F---	0.420	0.234	0.478	0.418

Table XVI. ASTM Distillation for Run CPH-C25

Fraction	Temperature (°F) Product	Feed
IBP	175	177
5%	250	310
10%	295	380
20%	365	430
30%	417	458
40%	455	485
50%	487	515
60%	525	550
70%	578	620
79%	---	700
80%	683	---
86%	700	---
Residue & Loss	14%	21%

Fractions	N (wt%)	S (wt%)	N (wt%)	S (wt%)
---400°F	0.059	0.280	0.466	0.396
400°F--700°F	0.295	0.160	0.767	0.586
700°F---	0.357	0.100	0.478	0.418

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