



The effects of temperature and space velocity on the catalytic upgrading of solvent refined coal (SRC-II)
by Hemant Bhatia

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE
in Chemical Engineering
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Abstract:

Long run cycle experiments ranging from 30-300 hours were made to determine the effects of temperature and space velocity on the upgrading of SRC-II Light Ends Column Feed (LECF) produced at Pittsburg and Midway Coal Mining Company's SRC-II pilot plant.

MSU's most promising catalyst C-49 with a metal loading of 4% CoO, 8% MoO₃, 1% NiO, and 8% WO₃ was used in all the experiments.

The liquid products were analyzed for their nitrogen and sulfur contents. The ASTM distillation yields were also obtained.

Higher temperature and lower space velocities gave better denitrogenation, while desulfurization was not affected by the temperatures and space velocity in the range of study. A minimum temperature of 425°C is needed to reduce the nitrogen content below the 0.3 Wt% requirement.

Higher temperatures also allowed the use of higher space velocities at the expense of greater coke formation. The best conditions for denitrogenation are an operating temperature of 500°C and a liquid hourly space velocity of 1.25 hr⁻¹.

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Date March 4 1982

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Approved


Chairperson, Graduate Committee


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ABSTRACT

Long run cycle experiments ranging from 30-300 hours were made to determine the effects of temperature and space velocity on the upgrading of SRC-II Light Ends Column Feed (LECF) produced at Pittsburg and Midway Coal Mining Company's SRC-II pilot plant.

MSU's most promising catalyst C-49 with a metal loading of 4% CoO, 8% MoO₃, 1% NiO, and 8% WO₃ was used in all the experiments.

The liquid products were analyzed for their nitrogen and sulfur contents. The ASTM distillation yields were also obtained.

Higher temperature and lower space velocities gave better denitrogenation, while desulfurization was not affected by the temperatures and space velocity in the range of study. A minimum temperature of 425°C is needed to reduce the nitrogen content below the 0.3 Wt% requirement.

Higher temperatures also allowed the use of higher space velocities at the expense of greater coke formation. The best conditions for denitrogenation are an operating temperature of 500°C and a liquid hourly space velocity of 1.25 hr⁻¹.

INTRODUCTION

The oil embargo of 1973-74 brought into sharp focus what is known and what is not known about energy flows in the United States. A great deal is known on the supply side - how much oil, gas, coal, and uranium ore are produced, where it comes from, how it is transported, and where it is used. Little is known about interfuel substitutability, and potential for conservation.

The consumption of energy in the United States has been rising rapidly and is expected to increase from 60 quadrillion (10^{15}) BTU in 1969 and 85 in 1980, to a projected 135 in 2000 (1). To supply their needs there are known recoverable resources of fuel amounting to, in the same units of quadrillion BTU, 300 for Petroleum, 300 for gas, 300 for uranium, and 4600 for coal. Overall, coal represents about 80% of known recoverable fossil fuels. (1) About 200 billion metric tons of coal are currently recoverable at today's prices. Presently U.S. coal production is 785 million tons/yr (2) while the petroleum consumption is 2700 million tons/yr (50 million barrels/day) (3). Although coal has only one half the energy value of petroleum, its reserves and production are sufficiently large to supply a part of America's petroleum needs.

Coal has an atomic hydrogen ratio of approximately 0.8 while the ratio for oil is of the order 1.8. Coal liquefaction therefore involves increasing the hydrogen content of coal. Coal liquefaction

processes can be grouped into three general categories: pyrolysis, extraction hydrogenation, or indirect liquefaction.

Of major concern to this research is the extraction-hydrogenation process. The Pittsburgh and Midway Coal Mining Company has developed the Solvent Refined Coal (SRC-II) as one of the extraction hydrogen processes (4). It converts high sulfur coal to distillate liquids, naphtha and light hydrocarbons. These raw liquid products are not directly interchangeable with comparable products derived from petroleum. The carbon to hydrogen ratio is considerably higher than petroleum crudes, as is the concentration of heteroatoms nitrogen and sulfur. The acceptance of SRC-II products in place of conventional fuels thus requires the development of a secondary catalytic hydrotreatment process.

It is the objective of this research to investigate the proper temperature and space velocity required to optimize the upgrading of SRC-II products into clean distillate fuels.

BACKGROUND

SRC-II Process

The SRC-II process converts high sulfur coal to distillate liquids, naphtha, and light hydrocarbons. A fifty tons per day pilot plant is being operated by Pittsburg and Midway Coal Mining Company at Fort Lewis, Washington. Figure 1 is a flow diagram of the SRC-II demonstration plant. (4)

Raw coal is pulverized and dried, then mixed with hot recycle slurry from the process. The coal and recycle slurry mixture is then pumped together with hydrogen through a fired pre-heater to a reactor maintained at 460°C and 13,780 kPa. The hydrocracking reactions occur primarily in the reactor, and the heat generated by these reactions rapidly raises the temperature of the reactants to the design temperature. The reactor effluent is then separated into process gas, light hydrocarbons and slurry.

The process gas is cooled to 38°C and stripped of H₂S and CO₂. The treated gas is then cryogenically separated to remove hydrocarbons. The pure hydrogen is recycled to the process while the recovered hydrocarbons become by-products of the process.

The C₁ fraction is sold as pipeline gas. The other light hydrocarbon gases are fractionated to produce ethane, propane, and butane. All the light hydrocarbon liquids, and the overhead stream

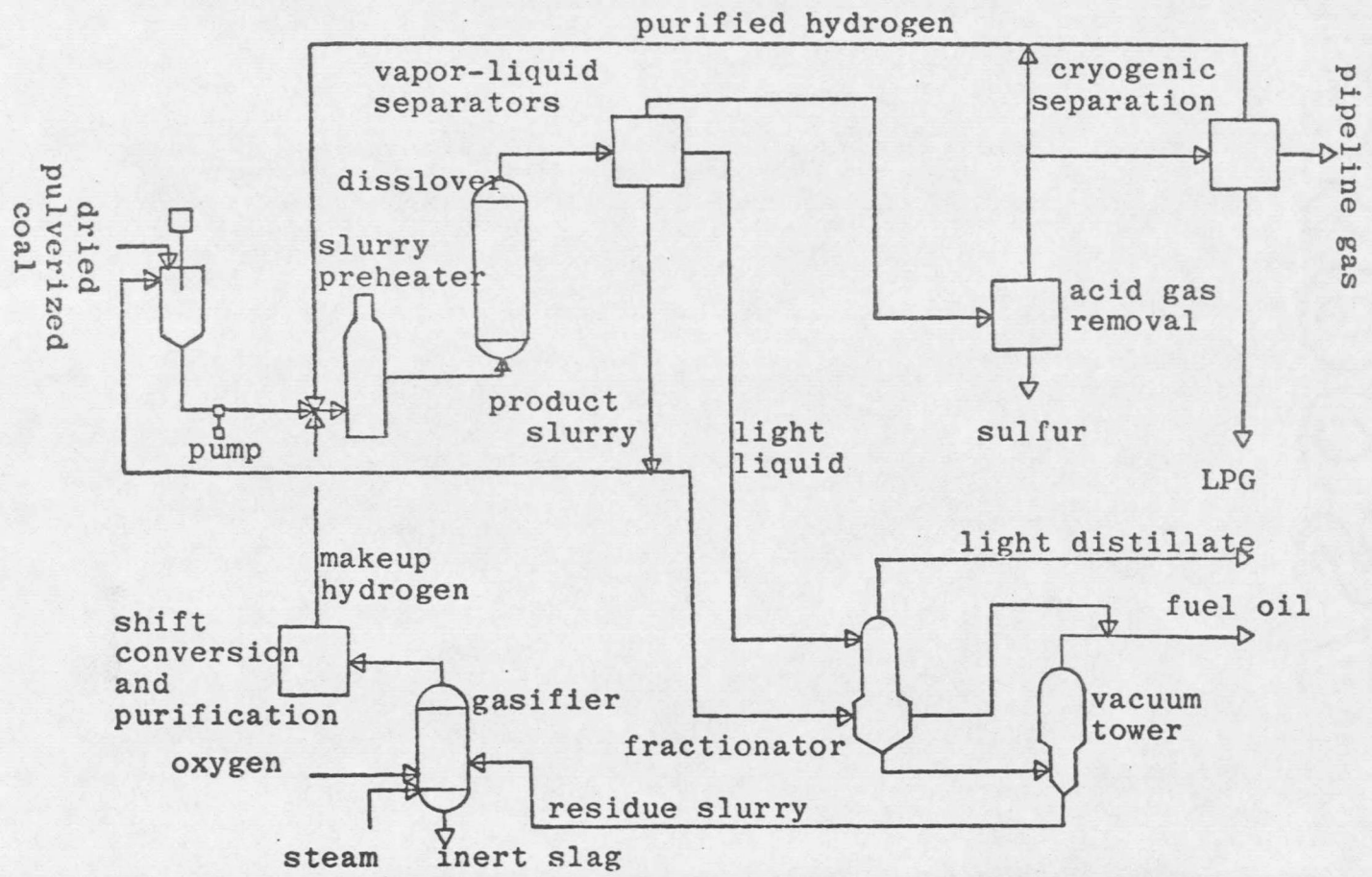


FIGURE 1. SRC-II PROCESS SCHEMATIC

from the vacuum tower are sent to a fractionator (Light Ends Column Feed) where the total liquid is separated into naphtha [C_5 -193°C nominal boiling range], a middle distillate [193-316°C], and a heavy distillate [316-482°C]

The product slurry is divided into two parts. One part is recycled to the process, while the other (Vacuum Flash Feed) goes to a vacuum tower where the lighter portion of the distillate is removed overhead and sent to the fractionator. A heavy distillate product is removed as the side stream. The residue from the vacuum tower is sent to a slagging gasifier for production of synthesis gas.

Chemical and Physical Properties of SRC-II Product

The SRC-II product cannot be considered as a single product from the process. The various products of SRC-II process are given in Table 1 (5). Properties of P&M's SRC-II product (Light Ends Column Feed) are shown in Table 2(6). The SRC-II product used in this research was made from refining Kentucky #9 coal, its analysis is shown in Table 3 (7).

Upgrading SRC-II Liquid Products

The liquid products of SRC-II contain significant amounts of organic nitrogen, and organic sulfur compounds as are commonly found in most petroleum crudes. Akhtar et al (8) have identified a number of sulfur containing compounds liberated from coal during

TABLE 1

SRC PROCESS GAS AND LIQUID YIELDS*

C ₁ - C ₄ gas, Scf**	3130
CH ₄ gal	2100
C ₅ - 350°F, gal	32
bbl	0.762
350 - 750°F distillable, gal	38
bbl	0.094
Total liquid, gal	70
bbl	1.666

**Approximate analysis of C₁ - C₄ gas cut:

	Vol %	BTU Value/ft ³ of total gas
CH ₄	67.0	680
C ₂ H ₆	19.3	340
C ₃ H ₈	10.0	260
C ₄ H ₁₀	<u>3.7</u>	<u>120</u>
	100.0	1400

* Per ton of SRC.

TABLE 2

PROPERTIES OF SRC II
LIGHT ENDS COLUMN FEED

	Light Ends Column Feed
% Carbon	-*
% Hydrogen	-*
% Nitrogen	0.88
% Sulfur	1.21
% Oxygen	-*
% Ash	0.02
Sp. Gravity 60/60°F	0.983
ASTM D-86 DISTILLATION	
IBP	122
5%	217
10%	288
20%	381
30%	446
40%	488
50%	541
60%	577
70%	611
80%	660
90%	727
95%	795
End Point	956

* Data not available.

TABLE 3

PROPERTIES OF KENTUCKY # 9 COAL*

<u>Average Raw Coal Analysis (Wt%)</u>	
Ash	9.55
Moisture	6.14

<u>Average Dried Pulverized Coal Analysis, (Wt%)</u>	
Carbon	70.76
Hydrogen	5.18
Nitrogen	1.53
Sulfur	3.57
Oxygen (by difference)	8.60
Ash	9.97
Moisture	6.39

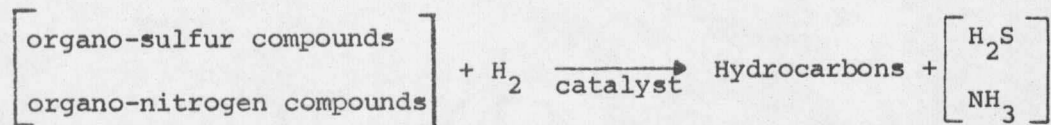
<u>Average Analysis of Forms of Sulfur, (Wt%)</u>	
Pyritic Sulfur	2.03
Sulfate Sulfur	0.27
Organic Sulfur	1.27
Total Sulfur	3.57

*Analyzed in June, 1979.

liquefaction. They are mercaptans, sulfides, polysulfides, thiophanes, thiophenes, dibenzothiophenes, and benzoapthothiophenes. Nitrogen is usually found in fused ring compounds such as quinoline, acridines, and phenanthridines (9). The concentrations of both groups of compounds must be greatly reduced to meet air pollution standards (10), and to prevent catalyst poisoning in subsequent refining. This is effected by catalytic hydroprocessing.

Hydrodesulfurisation (HDS) and hydrodenitrogenation (HDN) occur simultaneously. The overall chemical reactions involved are

(11)



Sulfided cobalt-molybdenum on alumina or nickel - molybdenum on alumina are typical catalysts.

Satterfield et al (12) used mixtures of thiophene and pyridine as model compounds for the two groups of reactions and showed that thiophene and H₂S inhibit the hydrogenation of pyridine to piperidine, the first step in the overall sequence of HDN reactions, but that H₂S enhances hydrogenolysis of piperidine and hence accelerating the overall series of reactions. Also Satterfield and Cocchetto (13) showed that the overall rate of HDN of pyridine is greatly affected by an equilibrium limitation on the formation of piperidine as an intermediate.

and 7.0 MPa.

These studies are not directly applicable to upgrading SRC-II liquids because model reactants such as thiophene and pyridine are not truly representative of SRC-II products.

Chevron Research (16) hydrotreated SRC-II in a trickle bed reactor at 13.5 - 16.9 MPa and 400°C. Givens (17) compared the commercially available Ni - Mo, Co - Mo, and Ni - W catalysts using SRC-1 as feedstock. Ramer (18) and Yeh (19) discussed the effect of catalyst properties on hydrotreating SRC-II. Further Yeh (20) made a systematic study of the effects of metals and catalytically active components on a silica-alumina catalyst carrier. While Berg, McCandless and Hass (21) tested commercial catalysts, and showed the effect of process variables on hydrotreating SRC-II, no systematic study has been done to determine the optimum operating conditions. It is hoped that this research will contribute in this respect.

Selection of Catalyst

Hydrotreating catalysts consist of active components, usually metals, deposited on a high surface area porous support. Berg, McCandless and Yeh (22) found that the liquid product yield increased by increasing the pore volume of the catalyst support. The most common metals used in hydrotreating catalysts are molybdenum and tungsten. The metals nickel, cobalt, iron, zinc, and chromium are

promoters. Yeh (20) studied four metals, cobalt, molybdenum, tungsten and nickel for their capabilities of upgrading SRC-II liquid product. He concluded that a metal combination of 4% CoO, 8% MoO₃, 1% NiO, and 8% WO₃ was the optimum for reducing the nitrogen content.

One of the disadvantages of metallic catalysts is their sensitivity to being poisoned by sulfur and nitrogen compounds. Catalyst poisoning may be either temporary or permanent depending on the mechanism of deactivation. Polinski, Stiegel, and Tischer (23) have proposed four possible deactivation mechanisms of catalysts used for coal liquefaction. Catalysts can be regenerated if the poisoning is temporary. The operating time between regeneration varies greatly. The catalyst is regenerated with air after a certain time on stream to regain a large fraction of the original activity.

Effect of Temperature

As the temperature of the reaction increases, the rate controlling the overall rate of reaction will pass from the surface chemical kinetic step to control by a combination of the surface kinetic step and pore diffusion and at higher temperatures to control by film diffusion (24). Hass (25) found that higher distillate yields were obtained at the expense of increased catalyst coking. It is necessary to operate at a sufficiently high temperature

so as to obtain a high yield of products with low nitrogen and sulfur content, but low enough temperatures so as to prolong the on-stream life of the catalyst in between regenerations.

RESEARCH OBJECTIVE

The objective of this research was to catalytically upgrade SRC-II products to clean distillate fuels. Since sulfur and nitrogen contents of SRC-II liquid products were to be reduced as low as possible a criterion of 0.3 wt % nitrogen and 0.5 wt% sulfur in the upgraded product was set.

The research plan consisted of using MSU's most promising catalyst in making a composite study on the effects of temperature and liquid hourly space velocity and thus determine the optimum operating conditions for the catalytic hydrotreatment of SRC-II.

MATERIALS, EQUIPMENT, AND PROCEDURES

Feed Stock

The Light Ends Column Feed (LECF) from Pittsburg and Midway Coal Mining Company's SRC-II process was used as the feed stock in this research. A representative analysis is shown in Table 4. The LECF is a slurry at room temperature and requires preheating prior to pumping, it is a mixture of 15% SRC - Naphtha, 40% SRC - middle distillate, and 45% SRC - heavy distillate.

Catalyst Preparation

The catalyst was fabricated by impregnating a commercial catalyst carrier with metal salts using the incipient wetness technique. The procedure used was as follows:

- 1) Dry the catalyst carrier in the oven at 110°C for 8 hours.
- 2) Calcine at 450°C for 8 hours.
- 3) Cool to room temperature in a dessicator and record the weight of the catalyst carrier.
- 4) Impregnate the catalyst carrier in a slowly rotating jar with a specific metal solution, the concentration of which is estimated by (26):

weight % of metal oxide on the support

= concentration of solution x pore volume / (1 + (pore volume x con. of solution))

TABLE 4

PROPERTIES OF SRC-II LIGHT ENDS COLUMN FEED

% Carbon	*
% Hydrogen	*
% Nitrogen	0.88
% Sulfur	1.21
% Oxygen	*
% Ash	0.02
Sp. Gravity 60/60°F	0.983

ASTM D-86 DISTILLATION

1BP	122
5%	217
10%	288
20%	381
30%	446
40%	488
50%	541
60%	577
70%	611
80%	660
90%	727
95%	795
End Point	956

* Data not available.

the concentration of the 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 - 3 for the air dried catalyst and record the weight increased after impregnation.

The catalyst composition was reported as the weight percent of metal oxides which were the percent weight increased after impregnation of the weight of blank catalyst carrier.

The catalyst carrier Nalco - 78 - 6008C - 1/32" obtained from Nalco Company was used in this research. It comprises 98% Al_2O_3 and 2% SiO_2 . It has a surface area of $214.6 \text{ m}^2 \text{ g}^{-1}$, an average pore diameter of 156.5 Å, a median pore diameter of 161 Å, and a pore volume of 0.84 ml g^{-1} . Four metals were loaded in the order of Co, Mo, Ni, W by using the water solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $5(\text{NH}_4)_2\text{O} \cdot 12\text{WO}_3 \cdot 7\text{H}_2\text{O}$ respectively.

Catalyst Pretreatment

The catalyst was activated by sulfiding with a 10% hydrogen sulphide in hydrogen mixture for 12 hours at 325°C. This procedure was used to activate the catalyst and to prevent reduction of catalyst activity by hot hydrogenation (27,28). The metal oxides were converted into metallic sulfides. A stream of hydrogen sulfide was passed through a pipe reactor at atmospheric pressure. Exit gases were scrubbed with 20% $\text{NaOH} - \text{H}_2\text{O}$ solution. Temperature was

maintained by the use of two powerstats.

Extreme care should be used whenever handling hydrogen sulphide. It is highly toxic and causes death within a few seconds of inhalation. In high concentrations it fatigues the sense of smell and therefore gives no warning (29).

Continuous Trickle Bed Reactor

The trickle bed reactor used in this research was designed and fabricated by the Chemical Engineering Department at M.S.U. prior to this research. A schematic diagram of the trickle bed reactor and auxiliary equipment is shown in Figure 2.

The reactor was made by a 25 mm I.D., 1.1 m long schedule 80 Inconel pipe. The top of the reactor was fixed with a 6 mm stainless cross. It allowed the fitting of a 0.91 m stainless steel tubing which served as a thermowell. It also allowed the fitting of two feed ports, one for the LECF feed and the other for hydrogen.

The reactor was placed in a 25 mm bore hole of a 150 mm O.D. aluminum block which was about 0.9 m long. The reactor was clamped 100 mm outside the top of the aluminum block. The aluminum block was wrapped with three sets of Nichrome wire heating coils, encased in ceramic beads. Each heating coil was connected to a powerstat variable transformer which could be used to manually control the temperature. Two chromel-alumel thermocouples were placed in the thermowell, one in the preheat section and the other in the catalyst

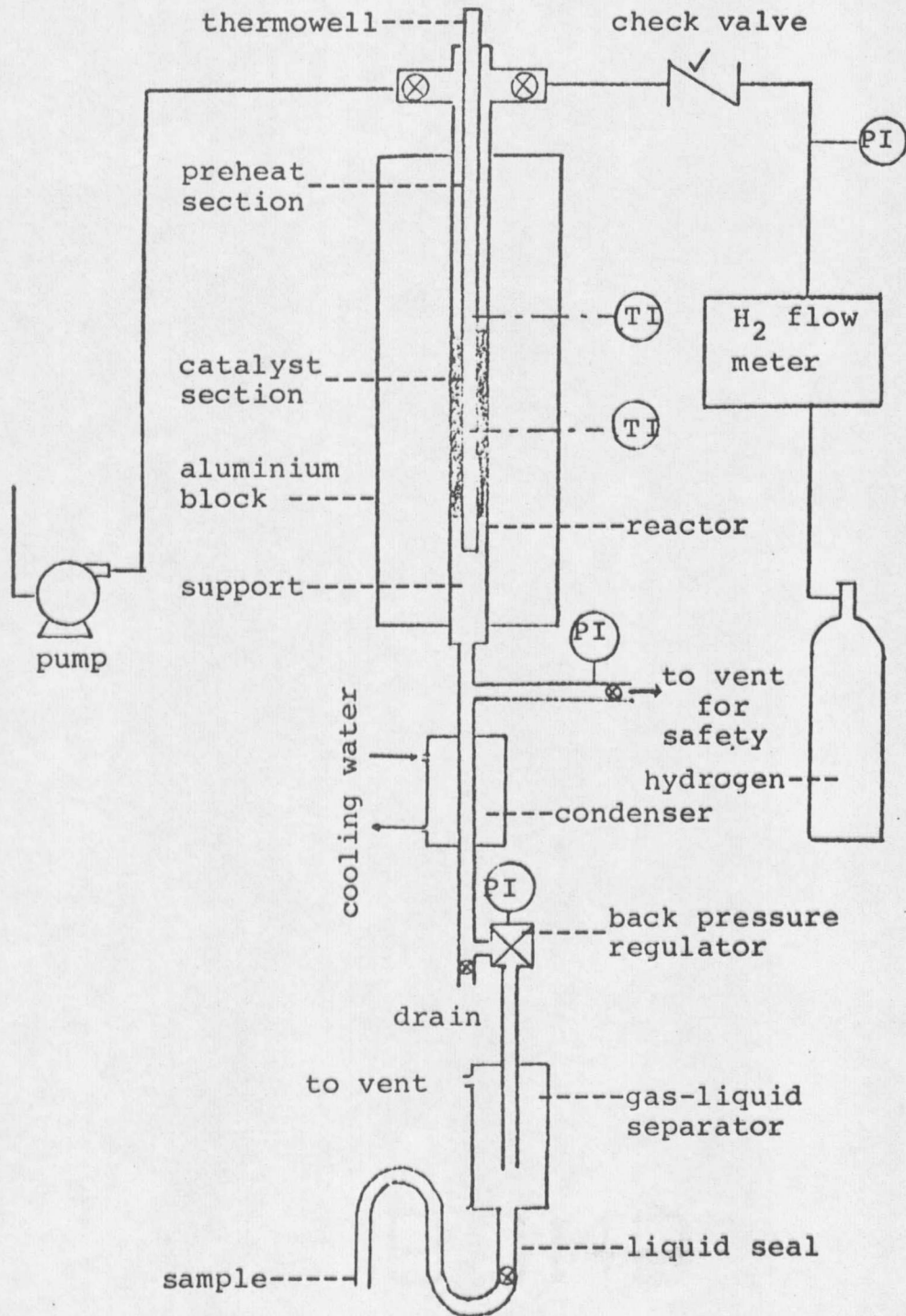


FIGURE 2. TRICKLE BED REACTOR

section. The thermocouple wires were connected to two Cole-Parmer Digital Thermocouple Thermometers (30). Starting from the top, the reactor was loaded with 175 ml of 6 mm Denstone inert support (31), followed by 25 ml of 3 mm Denstone inert support. This served as the preheating section. A mixture of 60 ml of catalyst and 60 ml of 3 mm inert support was loaded into the catalyst section. The remaining space at the bottom of the reactor was filled with 3mm Denstone inert support. A stainless steel screen was then inserted as a plug support. The threaded connection was sealed with Teflon tape and Silver Goop to prevent leakage.

The LECF feed was pumped into the top of the reactor by using a Milton Roy piston pump through a 3 mm stainless steel feedline. The pump speed could be manually controlled by a micrometer adjustment. The feedline was wrapped with flexible heating cords. The liquid feed temperature was adjusted by a powerstat, connected to the heating cord. Technical grade hydrogen was fed to the top of the reactor through a pressure regulator, and a Brooks Thermal Mass Flowmeter. Fine adjustments to the flow rate was made by a micrometer screw (32).

Gases and liquids from the reactor pass through a gas-liquid separator. The gases are sent through a condenser to a Grove back pressure regulator equipped with a corrosion resistant Teflon dia-

phragm. The exit gases were then scrubbed with a 20% NaOH-H₂O solution before venting.

The liquids passed from the gas-liquid separator into a catchpot. The catchpot was modified to collect liquid samples continuously by adding a double U-bend copper tube. The U-bend formed a liquid seal, allowing the sampling to take place continuously. Sampling bottles were changed every 450 ml of LECF through-put.

Operation of the Continuous Trickle Bed Reactor

The reactor was loaded with the catalyst and 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 thermocouples were inserted into the thermowell. The whole system was then pressurized with nitrogen to 7 MPa. Snoop soap solution (33) was used to check for leaks. If no leaks were detected, the system was depressurized, and three variable powerstats were turned on to heat the reactor. When the desired temperature was attained, all liquid feedlines and reservoirs were preheated to 85°C. Hot SRC-II LECF was recirculated for a few minutes through the feed line back into the reservoir. Feedlines should be filled first in order to avoid pump cavitation.

Next, the reactor was pressurized with hydrogen by means of a by-pass valve attached to the Brooks Flowmeter. At the desired pressure, the by-pass valve was closed and the micrometer was ad-

justed to the desired hydrogen flow rate. Hass (25) concluded that a hydrogen to oil ratio of 10,000 scf/bbl of oil is optimal. Based on the LHSV, the hydrogen flow rate was suitably adjusted. The valve of the feedline was then opened and the pump started. The liquid reservoir consisted of three burettes connected in parallel to the feedline. The largest had a capacity of 1 liter, and had graduations every 10 ml. The next burette had a capacity of 250 ml, and had graduations every 1 ml. The last burette had a capacity of 50 ml and graduations at 0.1 ml. The smallest burette was used for precisely adjusting the flow rate. Once the flow rate had stabilized to the desired LHSV, the small burette valve was closed and the middle burette (250 ml) valve was opened. The flow rate was periodically checked to maintain an even flow. The average flow rate was reported as the liquid hourly space velocity (LHSV).

Sampling was done continuously, and the sample bottles were changed after every 450 ml of Light Ends Column Feet (LECF) had been fed. The overall weight ratio of product to feed was reported as the yield of oil. As it was desired to keep the through-put of LECF constant for every run, (4500 ml) while the temperature and LHSV were varied, the running time varied from 300 hours (for a LHSV of 0.25 hr^{-1}) to 30 hours (for a LHSV of 2.50 hr^{-1}).

At the end of the run, the pump was shut off. The liquid feed valve was closed, and the feedline disconnected. The excess LECF

was drained, and reservoirs were cleaned with acetone. The hydrogen flow was stopped and the reactor was depressurized. The heaters were shut off and the hydrogen feedline was disconnected. The catchpot system was removed and thoroughly cleaned with acetone. The reactor was removed from the aluminum heating block. Next the contents of the reactor were emptied. The spent catalyst was preserved for measuring its pore volume. The reactor was cleaned and reloaded for the next experiment.

Analytical Procedures

The upgraded liquid products were analysed for sulfur and nitrogen. The gasoline yield and extent of hydrocracking was determined by distillation and the extent of carbon laydown was determined by pore volume measurements.

The sulfur content was determined by the quartz tube combustion method using a Bico-brown Shell design sulfur apparatus (34,35). About 0.3 grams of sample are needed. The reported error of the instrument is 0.03%. The weight percent desulfurization (%DS) was calculated as follows:

$$\%DS = \text{Wt\% S of feed} - \text{Wt\% S of Product} / (\text{Wt\% of S in feed})$$

The Nitrogen content was determined by the Macro-Kjeldahl method (36,37). About 0.5 grams of sample and 40 grams of potassium sulfate are needed for the analysis. The percent denitrogenation was calculated in the same way as the percent desulfurization.

The extent of hydrocracking was determined by ASTM D-86 atmospheric distillation (38). This method measured the cumulative amount of product which boiled below 370°C (700°F) or when decomposition began, depending on whichever occurred first. 50 ml of sample was used for the distillation.

The pore volume of the catalyst was estimated by the water saturation method. It gave a relative value rather than absolute (39).

The method is outlined below:

1. Dry 4-5 grams of catalyst at 110°C for two hours.
2. Cool to room temperature in a dessicator and record the weight of catalyst.
3. Immerse the catalyst into boiling water for 5 minutes. This will ensure that all the air in the pores has been expelled.
4. Decant the excess water and widely spread the catalyst on a sheet of paper.
5. After air drying for 35 minutes, weigh the catalyst.

The pore volume was determined by the weight gained by the dried catalyst after saturation. Since the specific gravity of water can be assumed to be one, the weight of water absorbed by the catalyst can be considered to be equal to the pore volume measured in milliliters per gram of catalyst. The catalyst sample was then placed in an oven at 425°C for two hrs. The loss in the weight of catalyst corresponded to the carbon laydown.

RESULTS AND DISCUSSION

Experiments were conducted to investigate the effects of temperature and space velocity. (vol. of LECF per unit vol. of catalyst per hour) on denitrogenation, desulfurization, yield of oil product, and the amount of distillable liquids. The spent catalyst was analyzed for its pore volume and the amount of carbon laydown.

These experiments were carried out in a continuous trickle bed reactor as illustrated in Figure 2. The total through-put of the feed, the temperature of the feed, the volume and height of the catalyst bed, the composition of the catalyst, the pressure, and hydrogen to oil ratio were kept constant for all the runs. A summary of the constant operating conditions is given in Table 5.

Eleven experiments were performed. The run time varied from 300 hours for a LHSV of 0.25 hr^{-1} to 30 hours for a LHSV of 2.5 hr^{-1} . The Appendix contains a summary of the data from all these runs, all obtainable catalyst description data, and ASTM distillation data.

A. The Effect of Temperature

Denitrogenation

The average nitrogen content of the products for each run is given in Table 6. Runs 107, 108 and 111 are the only ones with an average nitrogen content below 0.3 Wt%. From this we see that a minimum temperature of 425°C is needed to reduce nitrogen below the 0.3 Wt% requirement. Figure 3 and 4 further illustrate the effect of

TABLE 5

SUMMARY OF CONSTANT OPERATING CONDITIONS

Feed Temperature	85°C
H ₂ to Oil Ratio	10,000 scf/bbl
Run Pressure	7.7 MPa
LECF Through-put	4.5 liter
Catalyst Composition	4% CoO, 8% MoO ₃ , 1% NiO, 8% WO ₃
Volume of Catalyst	60 ml
Volume of 1/8" Denstone in Catalyst Bed	60 ml
Height of Catalyst Bed	250 mm.
Catalyst Base Composition	98% Al ₂ O ₃ , 2% SiO ₂
Pore Volume of Fresh Catalyst	0.62 ml/gram
Surface Area of Catalyst	214.6 m ² /gram

TABLE 6

THE AVERAGE NITROGEN CONTENT OF THE PRODUCTS

Run No.	Temperature °C	LHSV hr ⁻¹	Run Time hrs.	Nitrogen Content Wt %
101	350	0.25	300	0.50
102	350	1.25	60	0.70
103	375	0.75	100	0.45
104	375	1.75	42.9	0.55
105	425	2.00	37.5	0.45
106	425	1.25	60	0.38
107	425	0.50	150	0.30*
108	475	0.75	100	0.26*
109	475	1.75	42.9	0.36
110	500	2.50	30	0.38
111	500	1.25	60	0.22*

* Spec. grade - i.e. nitrogen content below 0.3 Wt%.

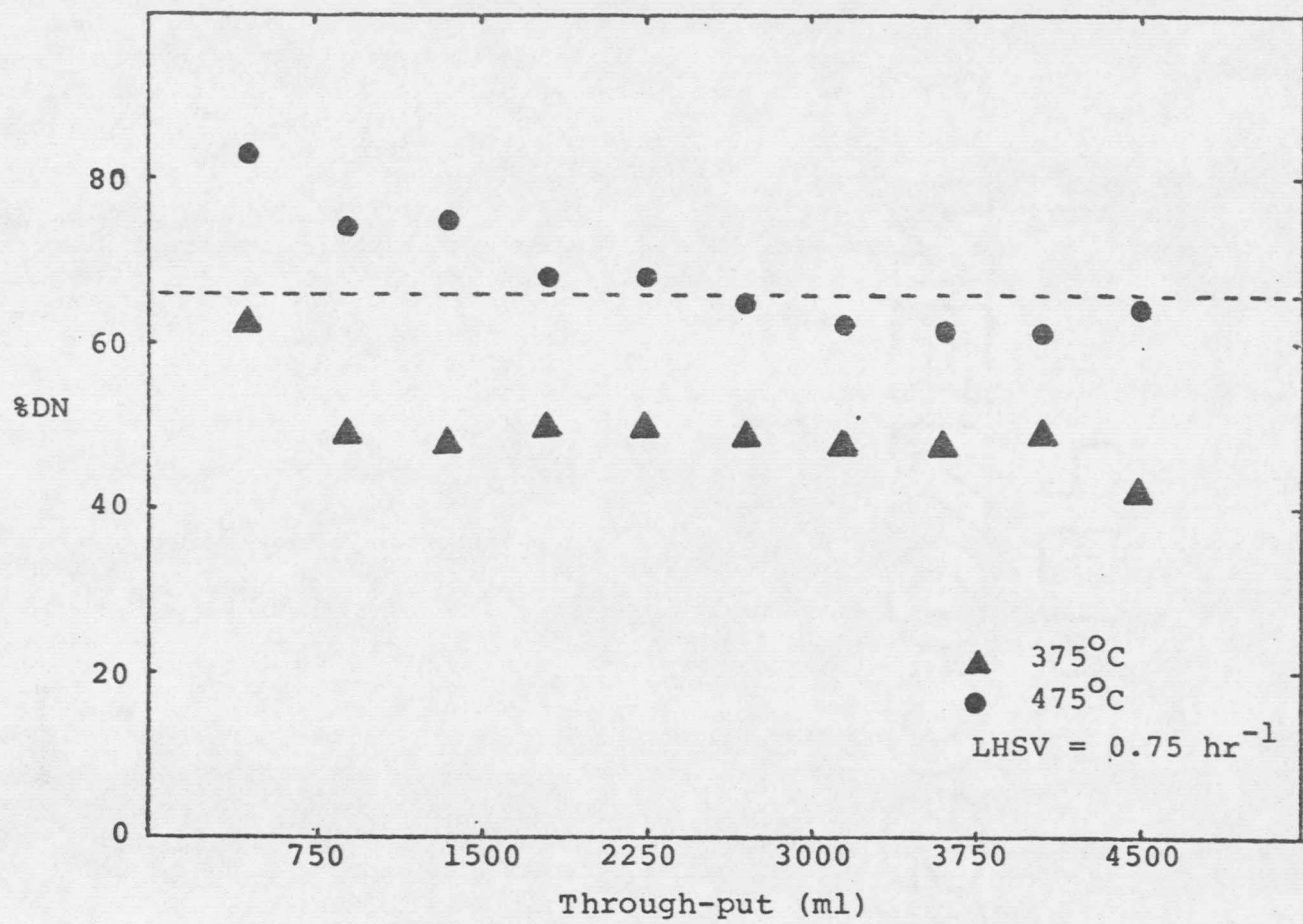


FIGURE 3. THE EFFECT OF TEMPERATURE ON DENITROGENATION

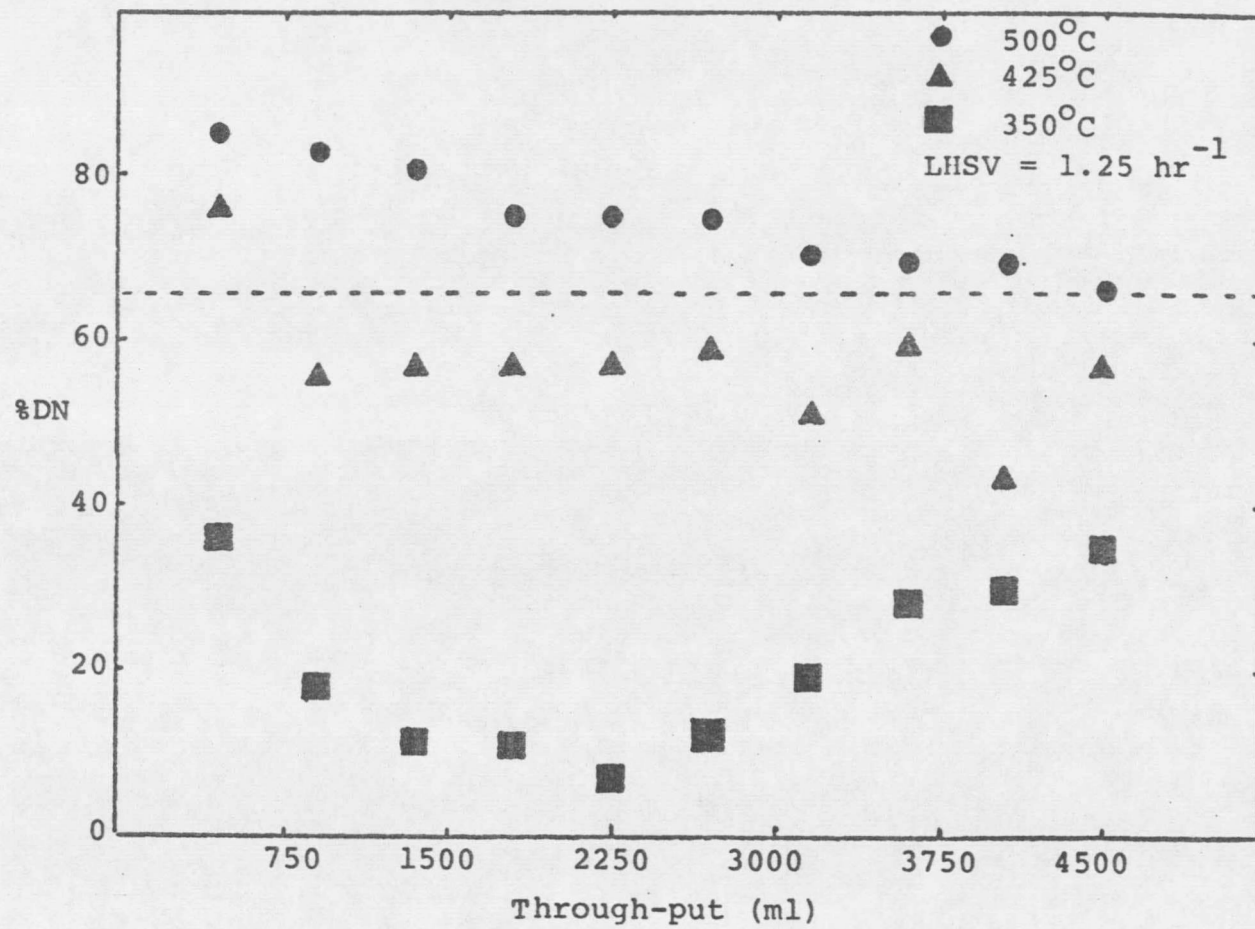


FIGURE 4. THE EFFECT OF TEMPERATURE ON DENITROGENATION

temperature on denitrogenation. Figure 4 compares the denitrogenation of the product at three different temperatures; 500°C, 425°C, 350°C. The LHSV in each case is 1.25 hr⁻¹. The dashed line represents the minimum denitrogenation required to achieve the 0.3 Wt% requirement. Clearly higher temperatures are needed for denitrogenation. Higher temperatures also allow the use of higher space velocities. The conditions for greatest denitrogenation were an operating temperature of 500°C and a LHSV of 1.25 hr⁻¹.

Desulfurization

The average sulfur contents of the products for each run is given in Table 7. All the runs reduced the sulfur to below the 0.5 Wt% requirement. From this we can see that desulfurization is much easier than denitrogenation. The data indicates the desulfurization does not follow any kind of trend with respect to parameters such as temperature and space velocity.

Yield of Oil

The total amount of product expressed as a percentage of the total through-put of the feed was reported as the yield of oil. Table 8 gives the Wt% yield of oil for all eleven runs. Higher temperatures result in lower yields. Figure 5 compares the yield of oil at three different temperatures; 500°C, 425°C, 350°C. The LHSV in each case is 1.25 hr⁻¹.

TABLE 7

THE AVERAGE SULFUR CONTENT OF THE PRODUCTS

Run No.	Temperature °C	LHSV hr ⁻¹	Run Time hrs	Sulfur Content Wt %
101	350	0.25	300	0.20
102	350	1.25	60	0.21
103	375	0.75	100	0.09
104	375	1.75	42.9	0.29
105	425	2.00	37.5	0.09
106	425	1.25	60	0.14
107	425	0.50	150	0.18
108	475	0.75	100	0.13
109	475	1.75	42.9	0.22
110	500	2.50	30	0.16
111	500	1.25	60	0.17

TABLE 8

CARBON LAYDOWN AND OIL PRODUCT YIELD FOR SRC-II LECF

Run No.	Temperature °C	LHSV hr ⁻¹	Run Time hrs	Oil Product Yield, Wt%	Carbon Lay- down, %
101	350	0.25	300	86.6	16.0
102	350	1.25	60	89.1	12.5
103	375	0.75	100	94.9	12.1
104	375	1.75	42.9	90.2	11.4
105	425	2.00	37.5	87.9	10.6
106	425	1.25	60	87.2	13.3
107	425	0.50	150	84.2	13.6
108	475	0.75	100	77.3	12.9
109	475	1.75	42.9	84.5	12.2
110	500	2.50	30	82.4	14.5
111	500	1.25	60	75.9	16.3

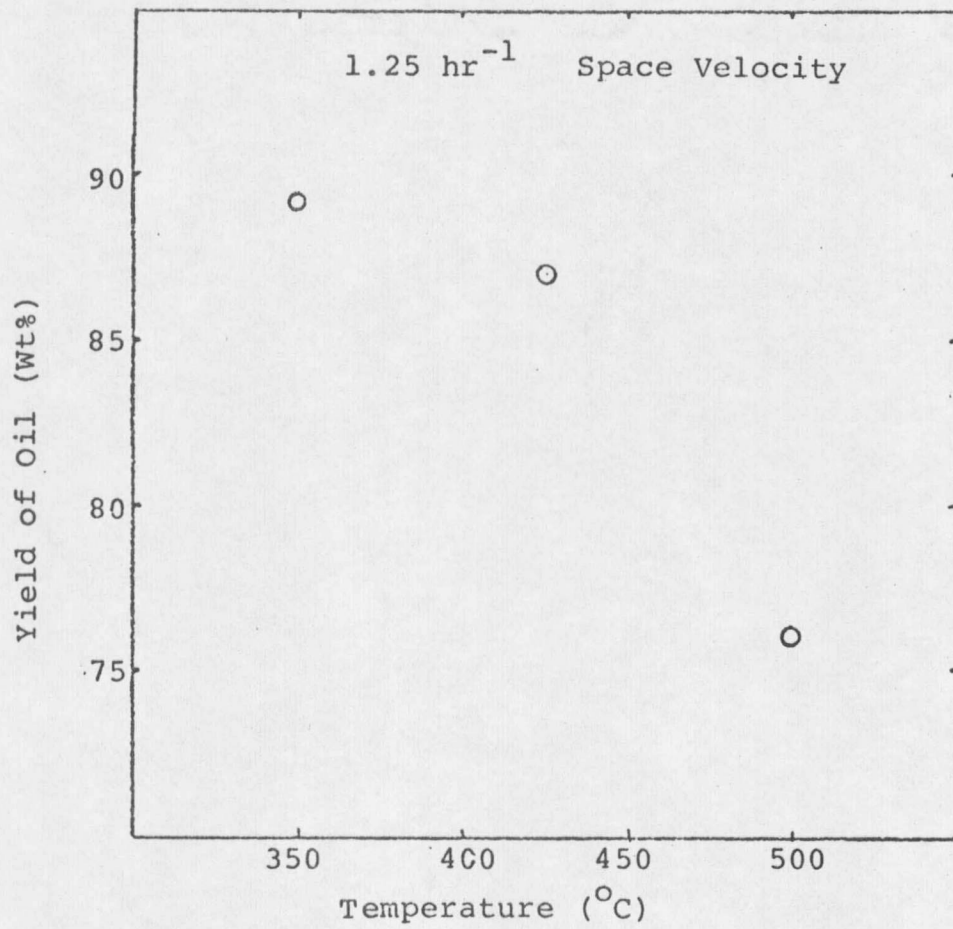


FIGURE 5. THE EFFECT OF TEMPERATURE ON THE YIELD OF OIL

The total amount of carbon laydown per 100 grams of catalyst was reported as the percent carbon laydown. Table 8 also gives the percent carbon laydown for all runs. Figure 6 compares the percent carbon laydown at the same three temperatures and space velocity as figure 5. Clearly higher temperatures result in greater amounts of coke formation, thus decreasing the Wt% yield of oil.

The Amount of Distillable Liquids

The products from all the runs were subjected to ASTM D-86 distillation. 50 ml was used for each distillation. The amount of liquid boiling below 182°C (360°F) was identified as the Naphtha fraction. The amount of liquid boiling in the range 182 - 288°C (360 - 550°F) was identified as the Middle fraction, the amount of liquid boiling in the range 288 - 371°C (550 - 700°F) was identified as the Heavy fraction. The remaining amount consisting of gases and coke was called the residue. The volume percent of each fraction is given in table 9. A more complete ASTM distillation data may be found in the Appendix. The data indicates that 475°C gives the maximum amount of distillable liquids when operating at a LHSV of 0.75 hr^{-1} . This condition also results in the widest distribution of the product into the Naphtha, Middle, and Heavy fractions. Figure 7 compares the ASTM distillation data from the three runs that produced a nitrogen content of 0.3 Wt% or less.

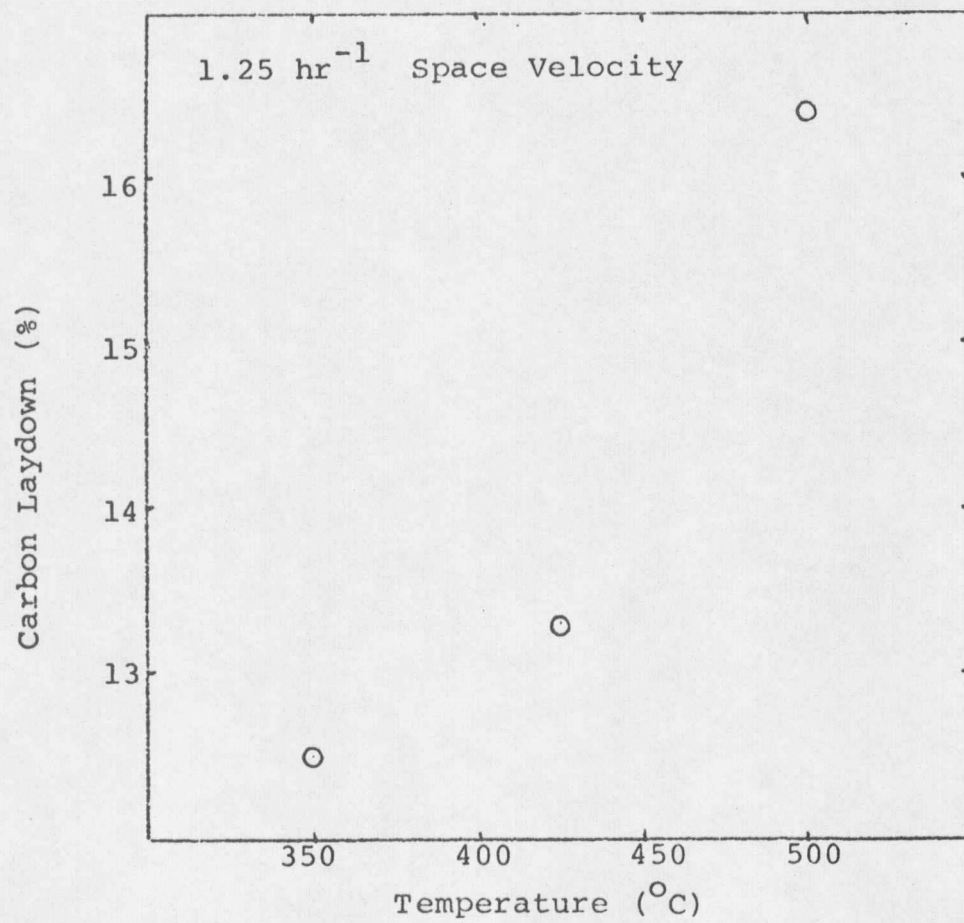


FIGURE 6. THE EFFECT OF TEMPERATURE ON CARBON LAYDOWN

TABLE 9

ASTM D-86 DISTILLATION DATA OF THE OIL PRODUCT

Run No.	Temperature °C	LHSV hr ⁻¹	ASTM DISTILLATION				
			% Naphtha 1BP-182°C	% Middle 182-288°C	% Heavy 288-371°C	% Total 1BP-371°C	% Residue
101	350	0.25	25.6	44.4	18.0	88.0	12.0
102	350	1.25	20.9	41.9	22.1	84.9	15.1
103	375	0.75	23.4	38.6	23.0	85.0	15.0
104	375	1.75	20.0	42.4	25.6	88.0	12.0
105	425	2.00	30.2	36.5	18.3	85.0	15.0
106	425	1.25	30.0	35.6	19.4	85.0	15.0
107	425	0.50	24.6	40.6	20.7	85.9	14.1
108	475	0.75	30.5	39.5	23.0	93.0	7.0
109	475	1.75	30.8	34.5	24.7	90.0	10.0
110	500	2.50	28.1	40.2	21.8	90.1	9.9
111	500	1.25	29.3	36.3	22.4	88.0	12.0

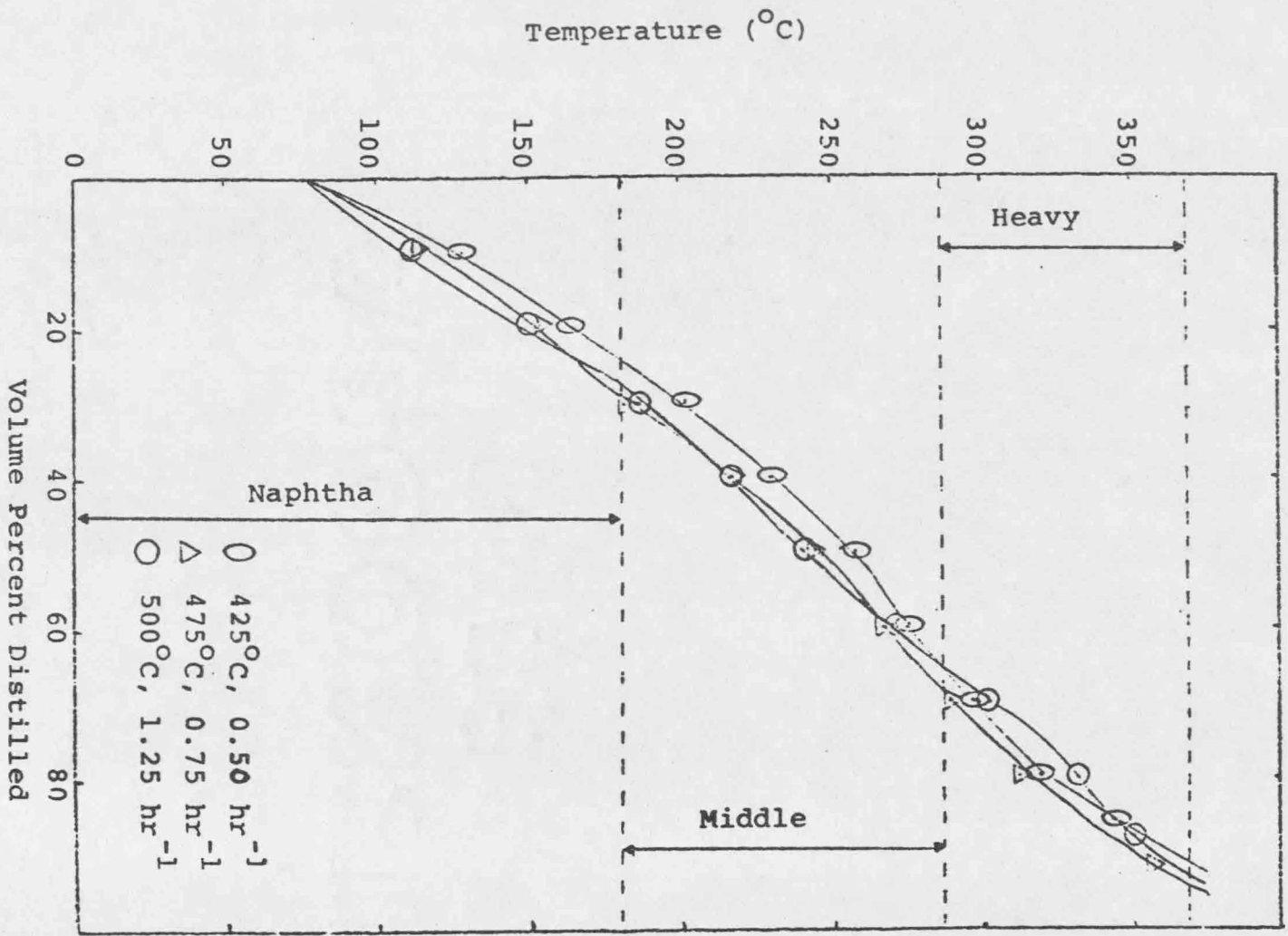


FIGURE 7. ASTM DISTILLATION DATA FOR RUNS 107, 108, AND 111

Pore Volume

The pore volume of the spent catalyst was measured by the method outlined on page 24. Table 10 gives the pore volume and percent carbon laydown for all the runs. Figure 8 compare the pore volume and percent carbon laydown at three different temperatures, 350°C, 425°C and 500°C. The space velocity in each case is 1.25 hr^{-1} . Clearly higher temperatures cause the formation of greater amounts of coke which deposit in the pores of the catalyst causing a decrease in the pore volume and thus deactivating the catalyst.

B. The Effect of Space Velocity

Denitrogenation

The average nitrogen content of the products for each run is given in Table 6. The effect of space velocity is shown in Figures 8, 9, and 10. Figure 9 compares the denitrogenations of the product at three different space velocities, 2.00 hr^{-1} , 1.25 hr^{-1} , and 0.50 hr^{-1} . The temperature in each case is 425°C. Clearly lower space velocities give better denitrogenation when compared at the same temperature. Comparing Figures 9, 10 and 11 we see that this was true at all the temperatures investigated.

Yield of Oil

The total amount of product expressed as a percentage of the total through-put of the feed was reported as the yield of oil.

TABLE 10
PERCENT CARBON LAYDOWN AND PORE VOLUME OF CATALYST

Run No.	Temperature °C	LHSV hr ⁻¹	Pore Volume of fresh catalyst ml g ⁻¹	Pore Volume of Used catalyst ml g ⁻¹	Carbon Laydown %
101	350	0.25	0.62	0.28	16.0
102	350	1.25	0.62	0.46	12.5
103	375	0.75	0.62	0.43	12.1
104	375	1.75	0.62	0.42	11.4
105	425	2.00	0.62	0.51	10.6
106	425	1.25	0.62	0.49	13.3
107	425	0.50	0.62	0.44	13.6
108	475	0.75	0.62	0.44	12.9
109	475	1.75	0.62	0.45	12.2
110	500	2.50	0.62	0.38	14.5
111	500	1.25	0.62	0.37	16.3

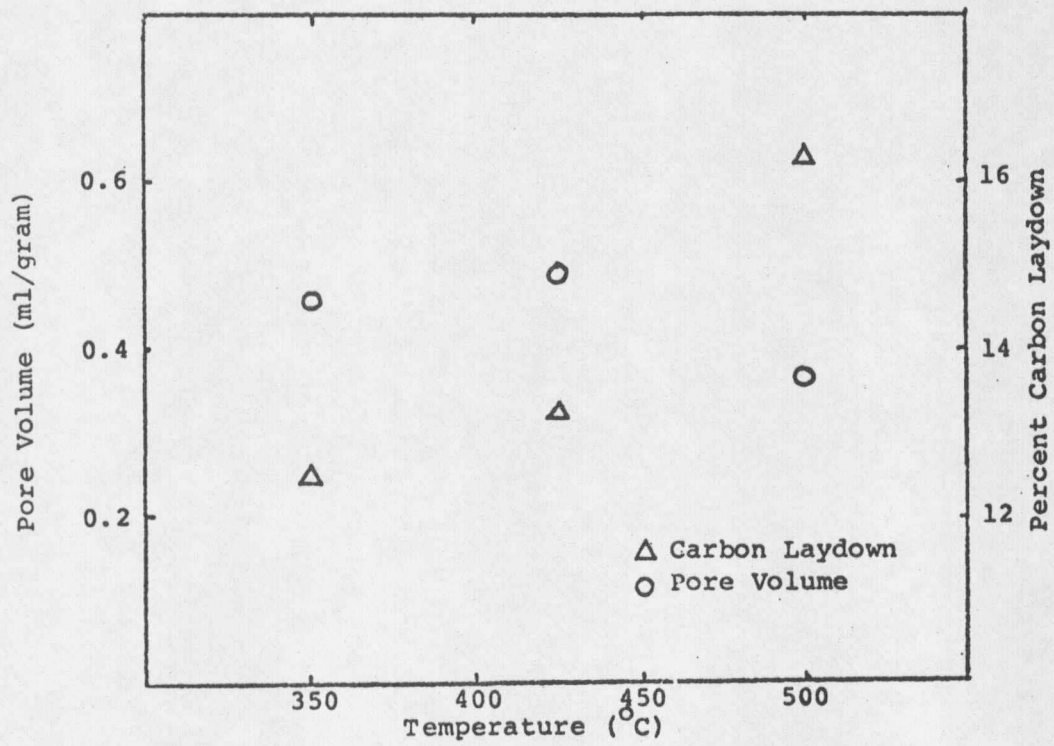


FIGURE 8. THE EFFECT OF TEMPERATURE ON PORE VOLUME AND CARBON LAYDOWN

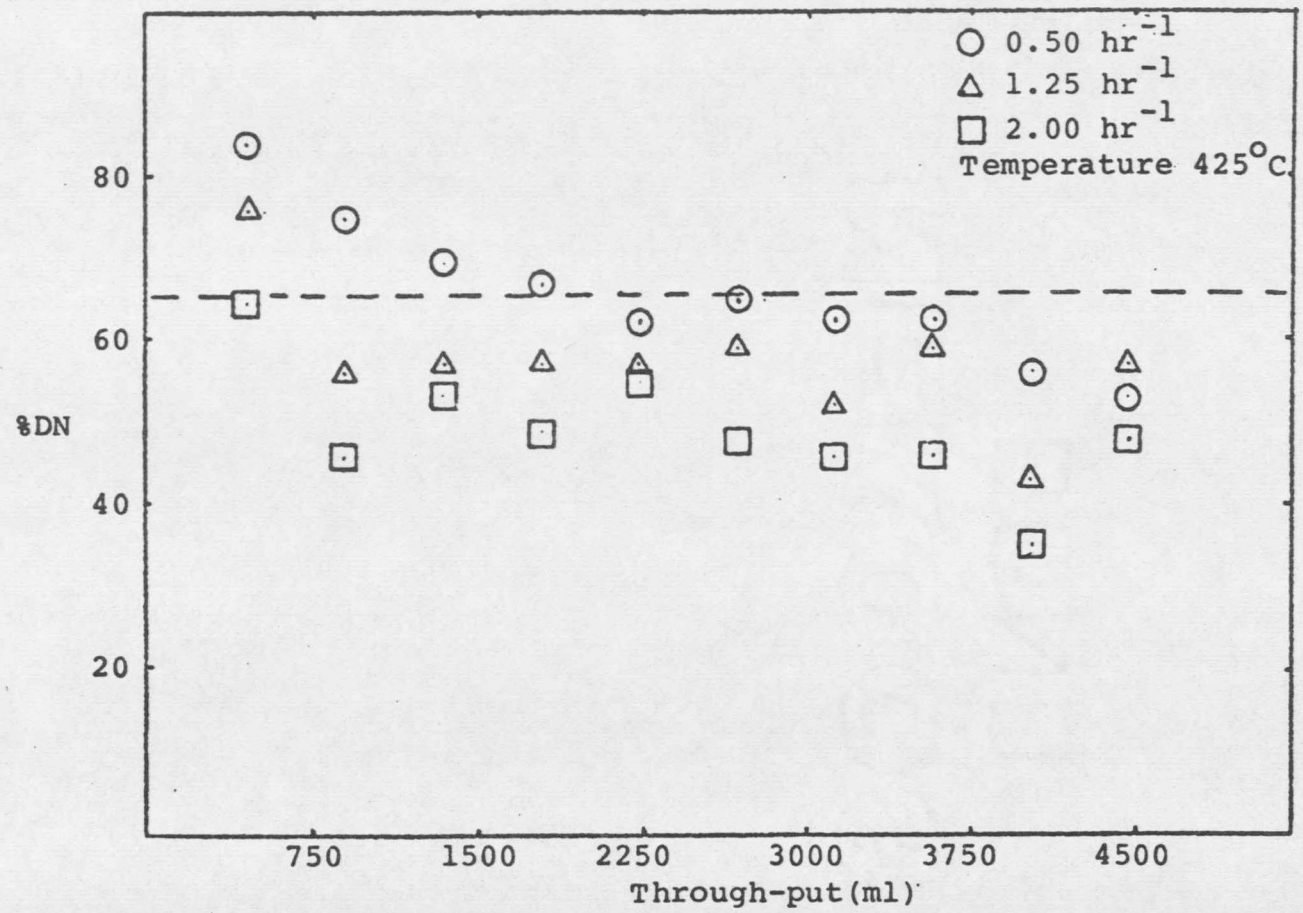


FIGURE 9. THE EFFECT OF SPACE VELOCITY ON DENITROGENATION

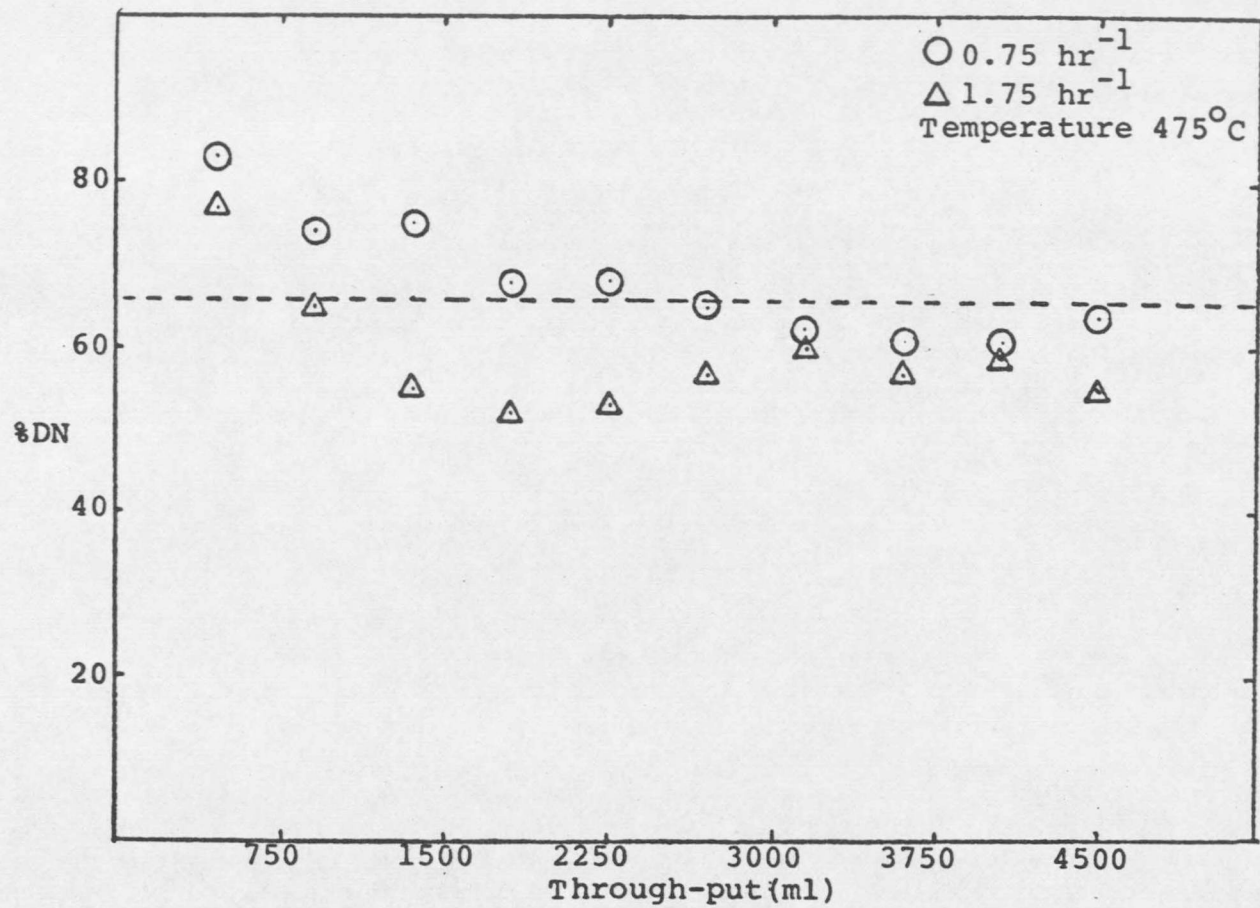


FIGURE 10. THE EFFECT OF SPACE VELOCITY ON DENITROGENATION

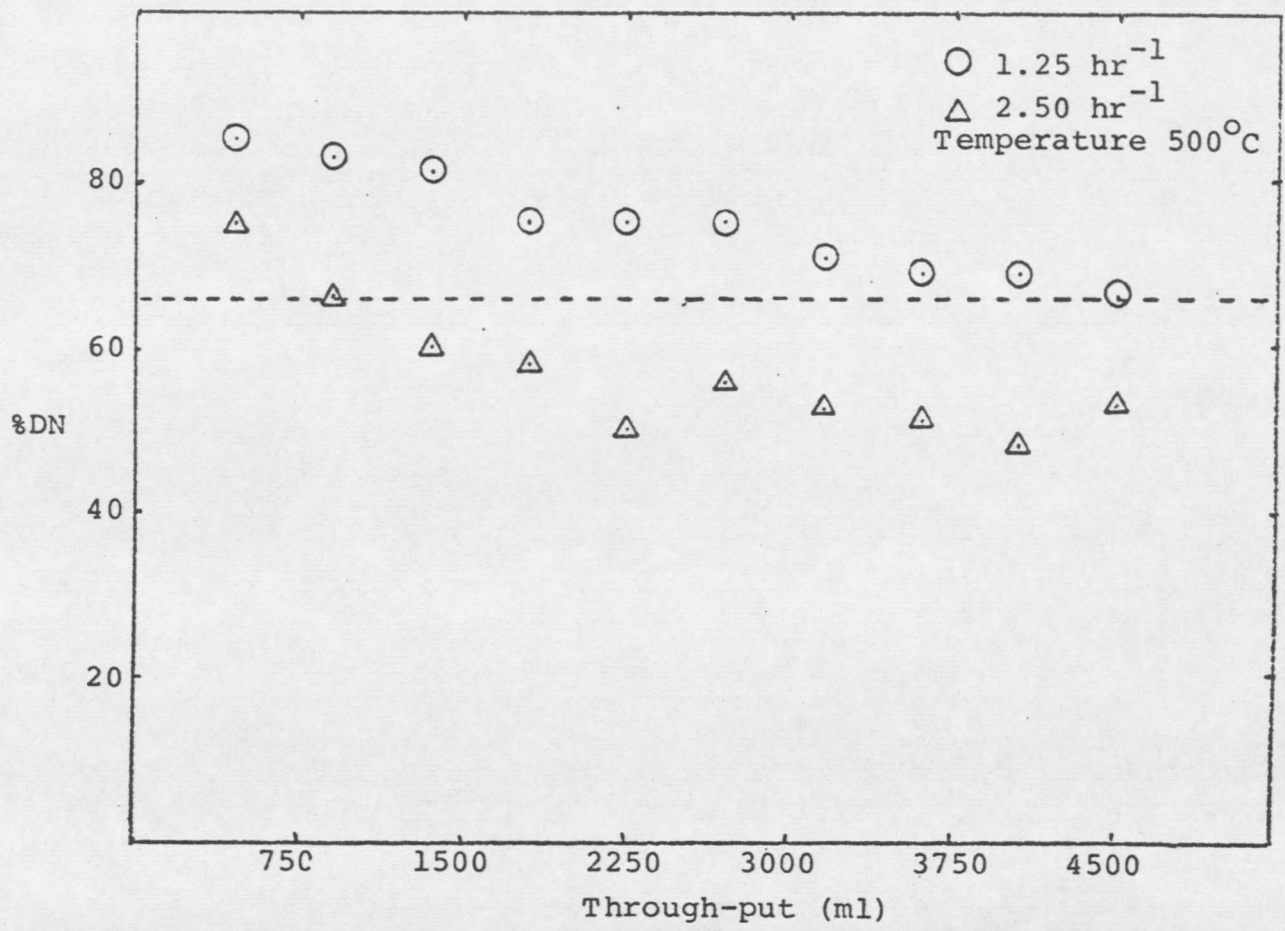


FIGURE 11. THE EFFECT OF SPACE VELOCITY ON DENITROGENATION

Table 8 gives the Wt% yield of oil for all the runs. Figure 12 compares the yield of oil at three different space velocities; 2.00 hr^{-1} , 1.25 hr^{-1} , 0.5 hr^{-1} . The temperature in each case was 425°C . Higher space velocities result in higher yields. This applied to all the temperatures investigated with the exception of 375°C where a lower space velocity resulted in a higher Wt% yield of oil.

Figure 13 compares the percent carbon laydown at three different space velocities 2.00 hr^{-1} , 1.25 hr^{-1} , 0.50 hr^{-1} . The temperature in each case was 425°C . Clearly lower space velocities cause a greater amount of carbon laydown thus decreasing the yield of oil.

The Amount of Distillable Liquids

The ASTM distillation data for all the runs can be found in Table 9. A more complete set of data may be found in the Appendix. From the data we can see that space velocity has negligible effect on the amount of distillable liquids.

Pore Volume

The pore volume of the spent catalyst was measured by the method outlined on page 24. Table 10 gives the pore volume and percent carbon laydown for all the runs. Figure 14 compares the pore volume and percent carbon laydown at three different space velocities, 2.00 hr^{-1} , 1.25 hr^{-1} , 0.50 hr^{-1} . The temperature in each case was 425°C . As can be expected lower space velocities cause the formation

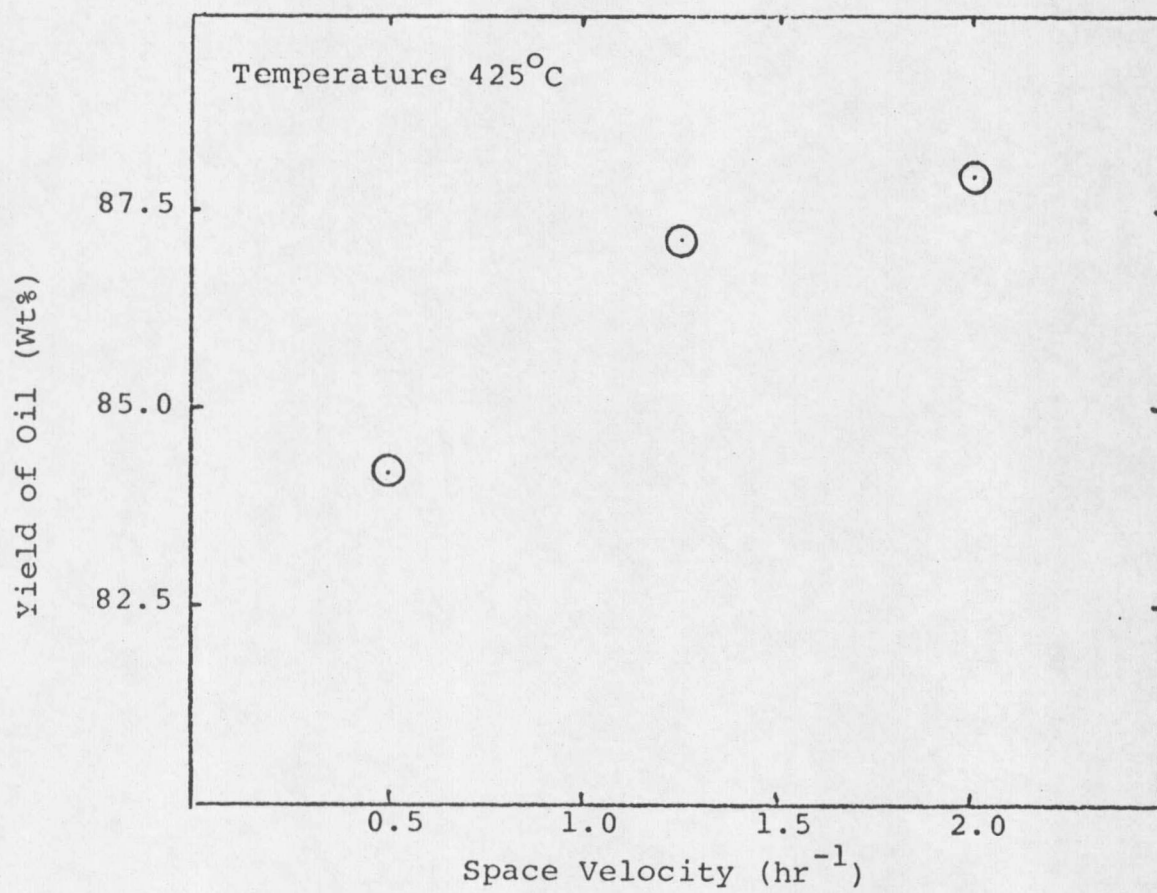


FIGURE 12. THE EFFECT OF SPACE VELOCITY ON YIELD OF OIL

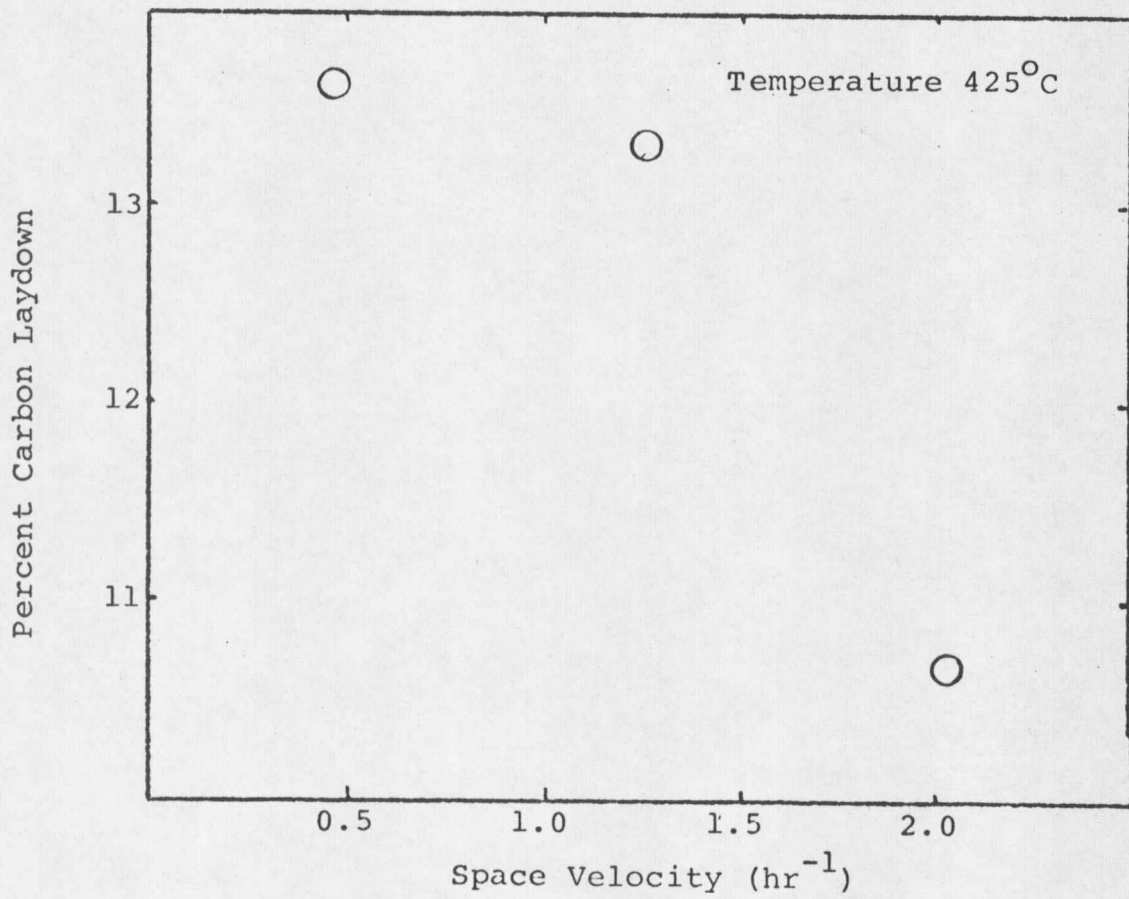


FIGURE 13. THE EFFECT OF SPACE VELOCITY ON CARBON LAYDOWN

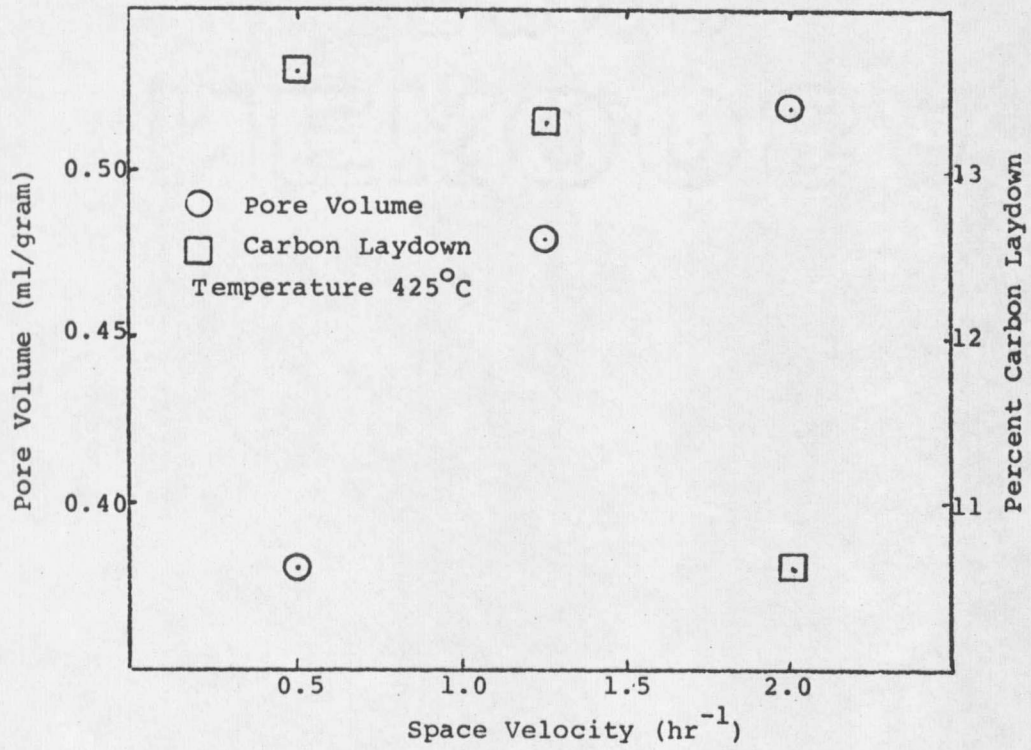


FIGURE 14. SPACE VELOCITY VS PORE VOLUME AND CARBON LAYDOWN

amounts of coke which deposit in the pores of the catalyst thus causing a decrease in the pore volume.

CONCLUSIONS

1. Higher temperatures give greater denitrogenation when compared at the same space velocity.
2. A minimum temperature at 425°C is needed to reduce the nitrogen content below the 0.3 Wt% requirement.
3. Higher temperatures allow the use of higher space velocities.
4. The conditions for greatest denitrogenation are an operating temperature of 500°C and a liquid hourly space velocity of 1.25⁻¹.
5. Lower space velocities give greater denitrogenation when compared at the same temperature.
7. Higher temperatures and lower space velocities increase the formation of coke and gases and thus decrease the overall Wt% yield of oil.
8. Desulfurization is easier than denitrogenation and does not follow any kind of trend with respect to parameters such as temperature and space velocity.

RECOMMENDATIONS FOR FUTURE RESEARCH

1. Experiments should be conducted at higher operating pressures in the range 14 - 21 MPa to attempt to improve the denitrogenation at temperatures lower than 425°C.
2. The parameters temperature and space velocity should be studied on upgrading other feed stock such as EXXON Donor Solvent, and H-coal. In order to compare with the data of this research, experiments should be conducted for long run cycles in the range 50 - 150 hours.
3. Operating conditions of 475°C and 0.75 hr⁻¹ space velocity and of 500°C and 1.25 hr⁻¹ space velocity both resulted in keeping the average nitrogen content below the 0.3 Wt% requirement. However, the percent carbon laydown was greater at the higher temperature, hence experiments should be conducted to determine the degree of catalyst deactivation caused by the carbon laydown and thus determine the life of the catalyst at these two conditions before conclusively arriving at an optimum condition recommendation.
4. Pore volume should be measured by more accurate methods such as the Mercury Penetration Method. Otherwise the percent carbon laydown should be used as the more reliable indicator of catalyst deactivation.

5. Both the product and feed should be analysed for their carbon to hydrogen ratio to determine the extent of hydrogenation.

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APPENDIX

TABLE 11. SUMMARY OF CONTINUOUS RUN DATA

Run No.	Temp. °C	LHSV hr ⁻¹	Yield Wt %	% DS	% DN	ASTM DISTILLATION			Distillate Yield**	Pore Vol. ml g ⁻¹	% Carbon Laydown
						% Naptha	% Middle	% Heavy			
101	350	0.25	86.6	83.1	43.2	25.6	44.4	18.0	.80	0.28	16.0
102	350	1.25	89.1	82.3	20.9	20.9	41.9	22.1	.80	0.46	12.5
103	375	0.75	94.9	92.6	49.4	23.4	38.6	23.0	.85	0.43	12.1
104	375	1.75	90.2	76.0	38.0	20.0	42.4	25.6	.84	0.42	11.4
105	425	2.00	87.9	92.2	49.1	30.2	36.5	18.3	.79	0.51	10.6
106	425	1.25	87.2	88.3	57.2	30.0	35.6	19.4	.78	0.49	13.3
107	425	0.50	84.2	85.3	65.7*	24.6	40.6	20.7	.76	0.44	13.6
108	475	0.75	77.3	88.9	69.9*	30.5	39.5	23.0	.76	0.44	12.9
109	475	1.75	84.5	81.8	59.1	30.8	34.5	24.7	.80	0.45	12.2
110	500	2.50	82.4	86.4	57.0	28.1	40.2	21.8	.78	0.38	14.5
111	500	1.25	75.9	85.6	74.9*	29.3	36.3	22.4	.70	0.37	16.3

* Spec. grade - i.e. Nitrogen content below 0.3 Wt %.

** ml per gram LECF

All temperatures are ± 5°F.

All LHSV are ± 10%.

Naptha 1BP-360°F
 Middle 360 - 550°F
 Heavy 550 - 700°

TABLE 12. CONSTANT OPERATING CONDITIONS

Feed Temperature	:	85°C
Hydrogen to Oil Ratio	:	10,000 scf/bbl
Run Pressure	:	7.7 MPa
LECF Through-put	:	4.5 liter
Catalyst Composition	:	4% CoO, 8% MoO ₃ , 1% NiO, 8% WO ₃
Volume of Catalyst in Reactor	:	65 ml

TABLE 13. CATALYST DESCRIPTION DATA

Base	:	NALCO-78-6008C-1/32"
Base Surface Area m ² g ⁻¹	:	214.6
Base Pore Volume ml g ⁻¹	:	0.84
Base Pore Diameter (4V/A), Å	:	156.6
Base Median Pore Diameter Å	:	161.0
Base Composition	:	98% Al ₂ O ₃ , 2% SiO ₂
Metals:		4% CoO, 8% MoO ₃ , 1% NiO, 8% WO ₃

TABLE 14. ASTM DISTILLATIONS

101		102		103	
Vol %	Temp (°F)	Vol %	Temp (°F)	Vol %	Temp (°F)
IBP	160	IBP	165	IBP	175
10	241	10	272	10	245
20	322	20	365	20	334
30	390	30	410	30	410
40	447	40	465	40	460
50	482	50	502	50	512
60	515	60	540	60	541
70	550	70	575	70	585
80	593	80	620	80	640
88	605	84.5	695	84.5	665

104		105		106	
Vol %	Temp (°F)	Vol %	Temp (°F)	Vol %	Temp (°F)
IBP	173	IBP	180	IBP	162
10	285	10	253	10	250
20	359	20	320	20	285
30	415	30	358	30	360
40	469	40	445	40	427
50	509	50	490	50	485
60	540	60	507	60	527
70	581	70	571	70	568
80	626	80	575	80	612
88	690	84.5	595	84.5	650

107		108		109	
Vol %	Temp (°F)	Vol %	Temp (°F)	Vol %	Temp (°F)
1 BP	173	1BP	177	1BP	167
10	265	10	244	10	253
20	330	20	298	20	310
30	395	30	357	30	353
40	447	40	422	40	440
50	495	50	472	50	485
60	530	60	512	60	525
70	568	70	551	70	572
80	610	80	593	80	619
86	650	92.5	673	90	670

Table 14. (Continued)

110		111	
Vol %	Temp (°F)	Vol %	Temp (°F)
1BP	158	1BP	174
10	240	10	245
20	297	20	295
30	375	30	365
40	432	40	421
50	472	50	465
60	517	60	520
70	557	70	574
80	605	80	627
90	675	88	660

TABLE 15. NITROGEN CONTENT OF OIL PRODUCTS

<u>Description of Sample</u>	<u>Nitrogen</u>
MSU 101 (1)	0.50
MSU 101 (2)	0.60
MSU 101 (3)	0.68
MSU 101 (4)	0.51
MSU 101 (5)	0.46
MSU 101 (6)	0.56
MSU 101 (7)	0.61
MSU 101 (8)	0.56
MSU 101 (9)	0.52
MSU 102 (0)	0.56
MSU 102 (1)	0.72
MSU 102 (2)	0.78
MSU 102 (3)	0.78
MSU 102 (4)	0.82
MSU 102 (5)	0.77
MSU 102 (6)	0.71
MSU 102 (7)	0.63
MSU 102 (8)	0.62
MSU 102 (9)	0.57
MSU 103 (0)	0.33
MSU 103 (1)	0.45
MSU 103 (2)	0.46
MSU 103 (3)	0.44
MSU 103 (4)	0.44
MSU 103 (5)	0.45
MSU 103 (6)	0.46
MSU 103 (7)	0.46
MSU 103 (8)	0.45
MSU 103 (9)	0.51
MSU 104 (0)	0.44
MSU 104 (1)	0.55
MSU 104 (2)	0.61
MSU 104 (3)	0.57
MSU 104 (4)	0.52
MSU 104 (5)	0.52
MSU 104 (6)	0.51

Table 15. (Continued)

<u>Description of Sample</u>	<u>% Nitrogen</u>
MSU 104 (7)	0.53
MSU 104 (8)	0.59
MSU 104 (9)	0.62
MSU 105 (0)	0.31
MSU 105 (1)	0.47
MSU 105 (2)	0.41
MSU 105 (3)	0.45
MSU 105 (4)	0.40
MSU 105 (5)	0.46
MSU 105 (6)	0.47
MSU 105 (7)	0.48
MSU 105 (8)	0.57
MSU 105 (9)	0.46
MSU 106 (0)	0.21
MSU 106 (1)	0.39
MSU 106 (2)	0.38
MSU 106 (3)	0.38
MSU 106 (4)	0.38
MSU 106 (5)	0.36
MSU 106 (6)	0.43
MSU 106 (7)	0.36
MSU 106 (8)	0.50
MSU 106 (9)	0.38
MSU 107 (0)	0.14
MSU 107 (1)	0.22
MSU 107 (2)	0.27
MSU 107 (3)	0.29
MSU 107 (4)	0.33
MSU 107 (5)	0.31
MSU 107 (6)	0.33
MSU 107 (7)	0.33
MSU 107 (8)	0.39
MSU 107 (9)	0.41

Table 15. (Continued)

<u>Description of Sample</u>	<u>% Nitrogen</u>
MSU 108 (0)	0.15
MSU 108 (1)	0.23
MSU 108 (2)	0.22
MSU 108 (3)	0.28
MSU 108 (4)	0.28
MSU 108 (5)	0.31
MSU 108 (6)	0.33
MSU 108 (7)	0.34
MSU 108 (8)	0.34
MSU 108 (9)	0.32
MSU 109 (0)	0.20
MSU 109 (1)	0.31
MSU 109 (2)	0.40
MSU 109 (3)	0.42
MSU 109 (4)	0.41
MSU 109 (5)	0.38
MSU 109 (6)	0.35
MSU 109 (7)	0.38
MSU 109 (8)	0.36
MSU 109 (9)	0.39
MSU 110 (0)	0.22
MSU 110 (1)	0.30
MSU 110 (2)	0.35
MSU 110 (3)	0.37
MSU 110 (4)	0.44
MSU 110 (5)	0.39
MSU 110 (6)	0.42
MSU 110 (7)	0.43
MSU 110 (8)	0.46
MSU 110 (9)	0.41
MSU 111 (0)	0.13
MSU 111 (1)	0.15
MSU 111 (2)	0.17
MSU 111 (3)	0.22
MSU 111 (4)	0.22
MSU 111 (5)	0.22
MSU 111 (6)	0.26

Table 15. (Continued)

<u>Description of Sample</u>	<u>% Nitrogen</u>
MSU 111 (7)	0.27
MSU 111 (8)	0.27
MSU 111 (9)	0.30

