



The effect of pressure on the catalytic upgrading of solvent refined coal
by I-Hsing Tsao

A thesis submitted in partial fulfillment of the requirement for the degree of Master of Science in
Chemical Engineering
Montana State University
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Abstract:

A catalytic hydrotreating (hydrodesulfurization, hydrodenitrogenation, and hydrocracking) experimental study of coal-derived liquid SRC-II was carried out at elevated pressures from 1000 psi to 2000 psi. SRC-II Light Ends Column Feed (LECF) was upgraded in a trickle-bed reactor into a liquid feedstock containing less than 0.3 wt.% nitrogen. Hydrotreating at 2000 psi extended the longevity of both commercial and MSU fabricated catalysts significantly. Results obtained from experiments carried out at various operating pressures showed that higher pressures gave better denitrogenation and hydrocracking.

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MONTANA STATE UNIVERSITY
Bozeman, Montana

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of a thesis submitted by

I-Hsing Tsao

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TABLE OF CONTENTS

	Page
APPROVAL	ii
STATEMENT OF PERMISSION TO USE	iii
ACKNOWLEDGEMENT	iv
TABLE OF CONTENTS	v
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	viii
INTRODUCTION	1
Coal	1
Coal to liquid	3
Liquid product of SRC-II	11
Upgrading SRC-II liquid product	11
Catalytic hydrotreating and pressure effect	16
Catalyst deactivation	20
Research objective	21
EXPERIMENTAL	22
Feedstock	22
Catalysts	22
Continuous trickle bed reactor	23
Catalyst pretreatment	26
Analytical procedure	27
RESULTS AND DISCUSSION	29
Catalytic hydrotreating at 2000 psi	29
Catalytic hydrotreating at various pressures	36
SUMMARY AND CONCLUSIONS	47
RECOMMENDATION FOR FUTURE RESEARCH	48
LITERATURE CITED	49

LIST OF TABLES

	Page
I. Coal conversion processes dating from at least 50 years ago	5
II. Hydrogen consumption and hydrocarbon yields from SRC processes	8
III. Properties of SRC-II Light Ends Column Feed (LECF)	12
IV. Sulfur and nitrogen removal from coal and shale liquids and three petroleum distillates, by hydroprocessing, in percent by weight	14
V. Operating conditions of Runs TS-101, TS-102, MSU-106, and T-5C1	30

LIST OF FIGURES

	Page
1. Changes in the total US energy supply and in the amounts of energy deriving from different sources are recorded for 1960-80 and projected for the year 2000	2
2. The contributions to the total US energy supply of the sources plotted in Figure 1.	2
3. Representative partial structures of different ranks of coal	4
4. SRC-I process, without the addition of catalysts	7
5. SRC-II process, with catalysts	9
6. Hydrogen/carbon ratios for various hydrocarbon sources, end products and products of coal liquefaction	10
7. Quinoline HDN reaction network	19
8. Trickle bed reactor and auxiliary equipments	24
9. Nitrogen content vs. time on stream for Run TS-102 & Run T-5C1	31
10. Nitrogen content vs. through-put for Run TS-101 & Run MSU-106	33
11. Nitrogen content vs. through-put for Runs TS-101, -102 & -103	34
12. ASTM distillation results for Runs TS-101, -102 & -103	35
13. Operating conditions of Run TS-104	37
14. Operating conditions of Run TS-105	38
15. Nitrogen content and denitrogenation vs. time on stream for Run TS-105	39
16. Nitrogen content and denitrogenation vs. time on stream for Run TS-104	40
17. Sulfur content and desulfurization vs. time on stream for Run TS-105	41
18. Sulfur content and desulfurization vs. time on stream for Run TS-104	42
19. ASTM Distillation results for Run TS-105	44
20. ASTM Distillation results for Run TS-104	45
21. Block diagram of gasoline and naphtha distilled of Run TS-104	46
22. Block diagram of gasoline and naphtha distilled of Run TS-105	46

ABSTRACT

A catalytic hydrotreating (hydrodesulfurization, hydrodenitrogenation, and hydrocracking) experimental study of coal-derived liquid SRC-II was carried out at elevated pressures from 1000 psi to 2000 psi. SRC-II Light Ends Column Feed (LECF) was upgraded in a trickle-bed reactor into a liquid feedstock containing less than 0.3 wt.% nitrogen. Hydrotreating at 2000 psi extended the longevity of both commercial and MSU fabricated catalysts significantly. Results obtained from experiments carried out at various operating pressures showed that higher pressures gave better denitrogenation and hydrocracking.

INTRODUCTION

The industrial world is in the early stages of a major energy transition. On the horizon we can clearly discern the beginning of the end of the petroleum age, and the world is starting to shift from a primary dependence on oil and gas for energy to the use of a broader, and much more diversified, mix of energy resources. Figure 1 presents a recent projection of the energy supply picture for the United States up to the year 2000 [1]. Figure 2 shows the relative contributions of various energy resources. Coal will be the most important resource as the oil contribution decreases.

COAL

Coal is the most abundant available energy resource both in the United States and worldwide. US coal production -- about 780 million tons in 1979 -- is expected to triple by the year 2000, with about 30% being used in the manufacture of synthetic fuels. Coal is a generic term covering a broad range of carbonaceous materials which differ in origin, geological age, properties, composition, and structure. Coals are classified (or ranked) as lignite, sub-bituminous, bituminous, and anthracite. This is the

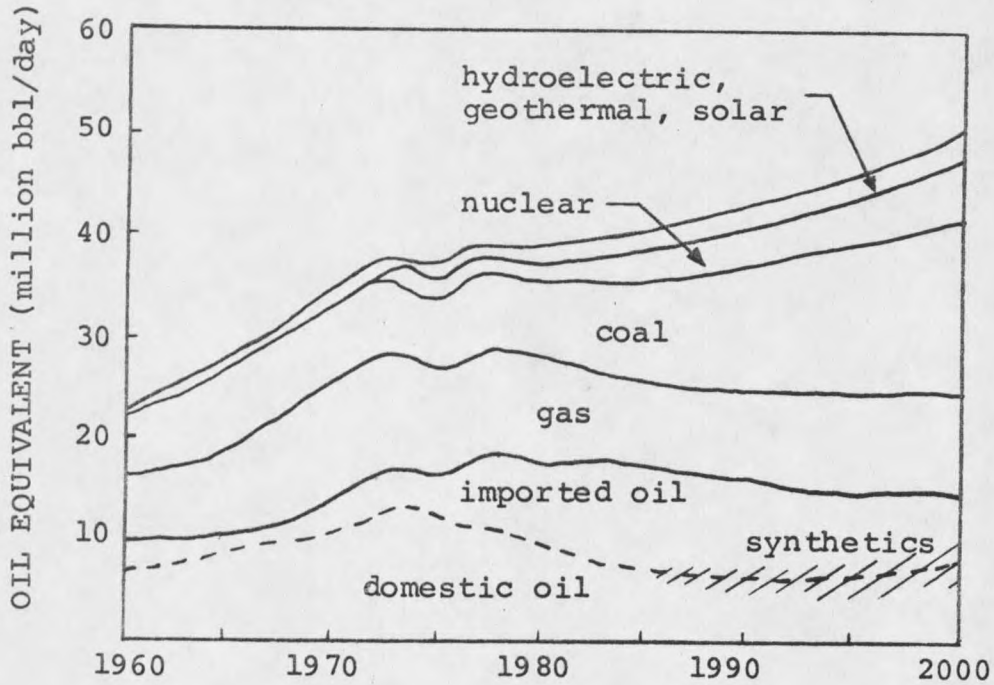


Figure 1 Changes in the total US energy supply and in the amounts of energy deriving from different sources are recorded for 1960-80 and projected for the year 2000. [1]

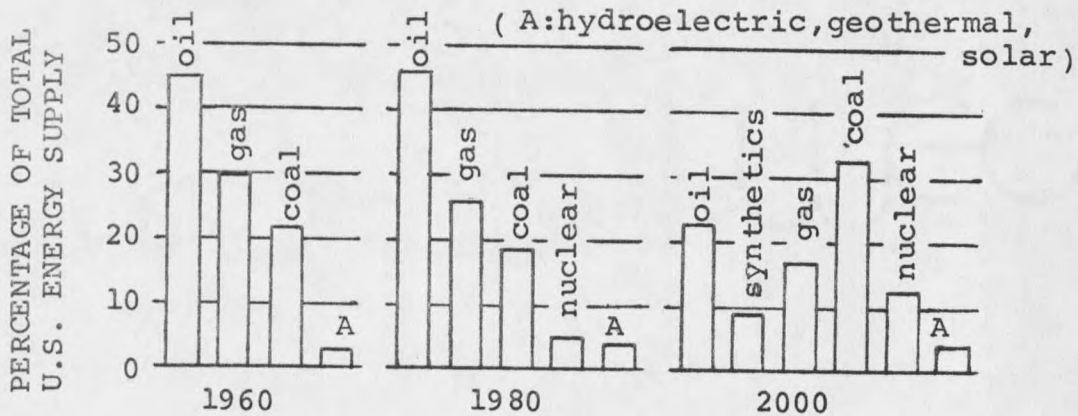


Figure 2 The contributions to the total US energy supply of the sources plotted in Figure 1.

order of increasing aromatic content and decreasing volatile matter and moisture. It is also roughly the order of increasing heat content. Wender[2] has suggested the simple structural models in Figure 3 for visualizing changes in rank.

Coal is basically an organic sedimentary heterogeneous rock with discrete inorganic inclusions and an ultrafine capillary pore-like structure. The actual organic structure of coal has been debated actively, and various molecular models have been proposed. In one such model for a bituminous vitrinite -- the principal organic component of coal -- the main types of linkage bridging the polynuclear clusters are short aliphatic groups and various kinds of heteroatom linkages, such as oxygen (ether) and sulfur (sulfide) bonds. There are also a large number of partially or wholly saturated aromatic structures, which, together with the short aliphatic bridges, impart a good deal of nonplanarity to the vitrinite structure, resulting in cavities between clusters and layers in which water or other small molecules can reside. Present also are oxygen, sulfur, and nitrogen heterocyclic structures.

COAL TO LIQUID

The conversion of coal to clear liquid fuels requires not only a reduction in molecular weight and removal of

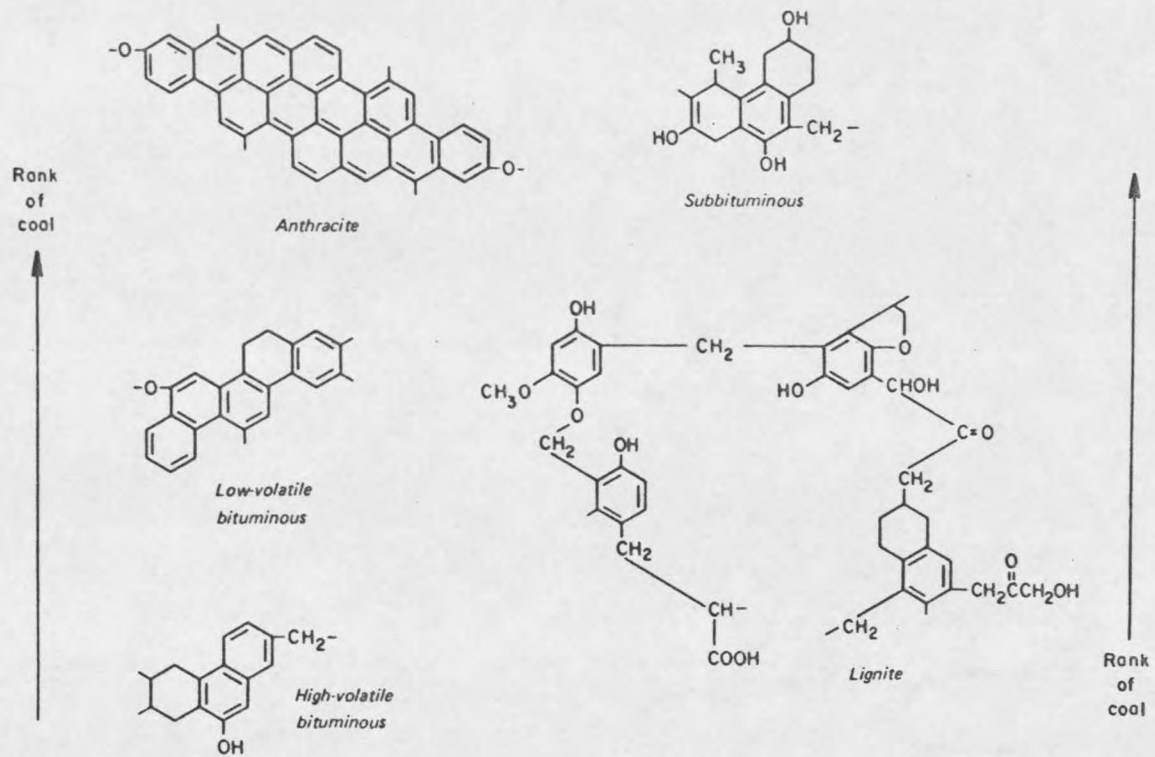


Figure 3 Representative partial structures of different ranks of coal

heteroatoms but also a substantial increase in hydrogen-to-carbon ratio. There are essentially four general methods for the liquefaction of coal: pyrolysis, gasification followed by synthesis (indirect liquefaction), hydroliquefaction (direct liquefaction), and solvent extraction. The basic technologies for each have been known for at least fifty years, and several conversion processes have been used commercially (ref. Table I). However, continued innovative research is expected to lead to more economical and more efficient technologies for the conversion and utilization of coal as a clean fuel.

Table I: Coal conversion processes dating from at least 50 years ago [1]

Gas from coal	1780 Fontana: $C + H_2O \rightarrow CO + H_2$ 1902 Sabatier: $CO + 3H_2 \rightarrow CH_4 + H_2O$
Liquids from coal	1867 Berthelot: $Coal + H_2$ 1910 Bergius: $Coal + H_2$ 1925 Fischer-Tropsch: $CO + H_2$
Chemical/tars from coal	late 1800s Coke ovens early 1800s pyrolysis

The addition of hydrogen to coal is done most simply in the solvent refined coal (SRC) process. Interestingly enough, this process was originally designed to remove ash from coal, thereby making it more economical to transport and more valuable in combustion. This involved taking the coal through a liquid phase, at which point the hot ash is separated out. But some knotty problems developed at this

point. Through a series of modifications, these problems unraveled and a new liquefaction process was born [3].

The process has two variations. In variation one (SRC-I), shown in Figure 4, crushed coal is blended with a process-derived oil and pumped through a slurry heater and reactor at temperatures of about 850°F (450°C) and hydrogen pressures of about 2000 psi (13.8 MPa). This breaks up the heavier, more carbonaceous molecular structures, producing more volatile compounds. Although the hydrogen-to-carbon ratio of the product does not differ very much from that of the coal used, considerable hydrogen is consumed (Table II) [4]. The product mixture is separated into gases and lighter oil which can be recycled to make a slurry, a heavy product called solvent refined coal (a tar-like solid used as a boiler fuel), and the unreacted coal and ash residue. The latter fraction can be gasified with oxygen and steam to make the hydrogen required. In variation two (SRC-II), shown in Figure 5, the existing ash, notably containing pyrite, is used as a catalyst to enhance conversion and the yield of a lighter distillate fraction. The product is liquid at room temperature and hydrogen consumption is greatly increased over that of SRC-I, as is the gas production. In contrast to SRC-I, the hydrogen-to-carbon ratio of the liquid is increased over that of the original coal. Figure 6 shows the hydrogen-to-carbon ratios of SRC-I and SRC-II products.

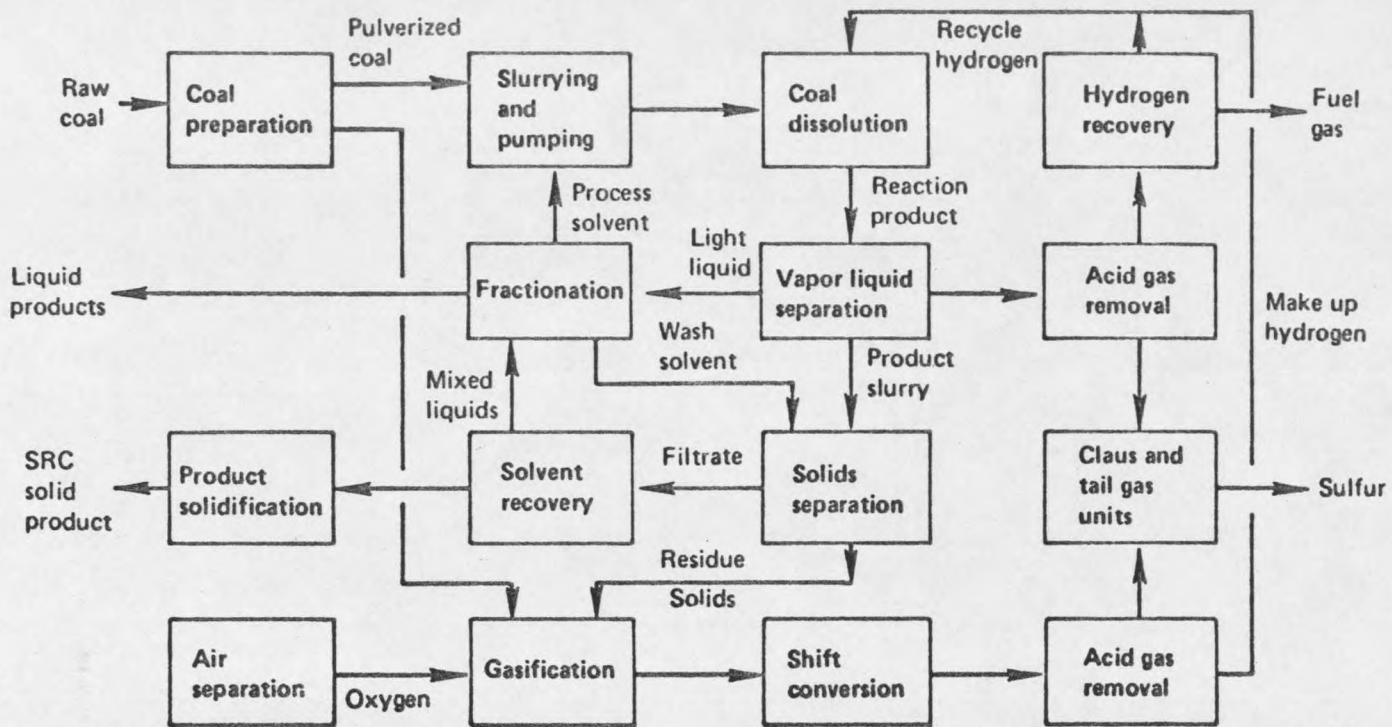


Figure 4 SRC-I process, without the addition of catalysts

Table II Hydrogen consumption and hydrocarbon yields from SRC processes

	SRC I (Kentucky No. 9)	SRC II (Kentucky No. 9)
Hydrogen consumed, standard cubic feet per ton of coal ^a	7,400	15,500
Process yields, based on coal		
Light gases, pounds per ton of coal		
CH ₄	50.7	116.8
C ₂ -C ₃	62.7	163.2
Liquid hydrocarbons, barrels per ton of coal		
C ₄ -380°F	0.44	0.96
380-650°F	0.30	1.07
650-1000°F	0.16	0.20
1000°F+ (SRC)	2.47	1.11
Total C ₄ + liquids	3.37	3.34
C ₄ -1000°F liquid, vol %	26.7	66.7
Hydrogen consumed per C ₄ -1000°F liquid, standard cubic feet per barrel	8,200	7,000
Ratio of CH ₄ to H ₂ consumption, pounds per million standard cubic feet	6.8	7.5
Ratio of CH ₄ to C ₄ -1000°F liquid, pounds per barrel	56.3	52.4

^aAs received. Hydrogen externally supplied.

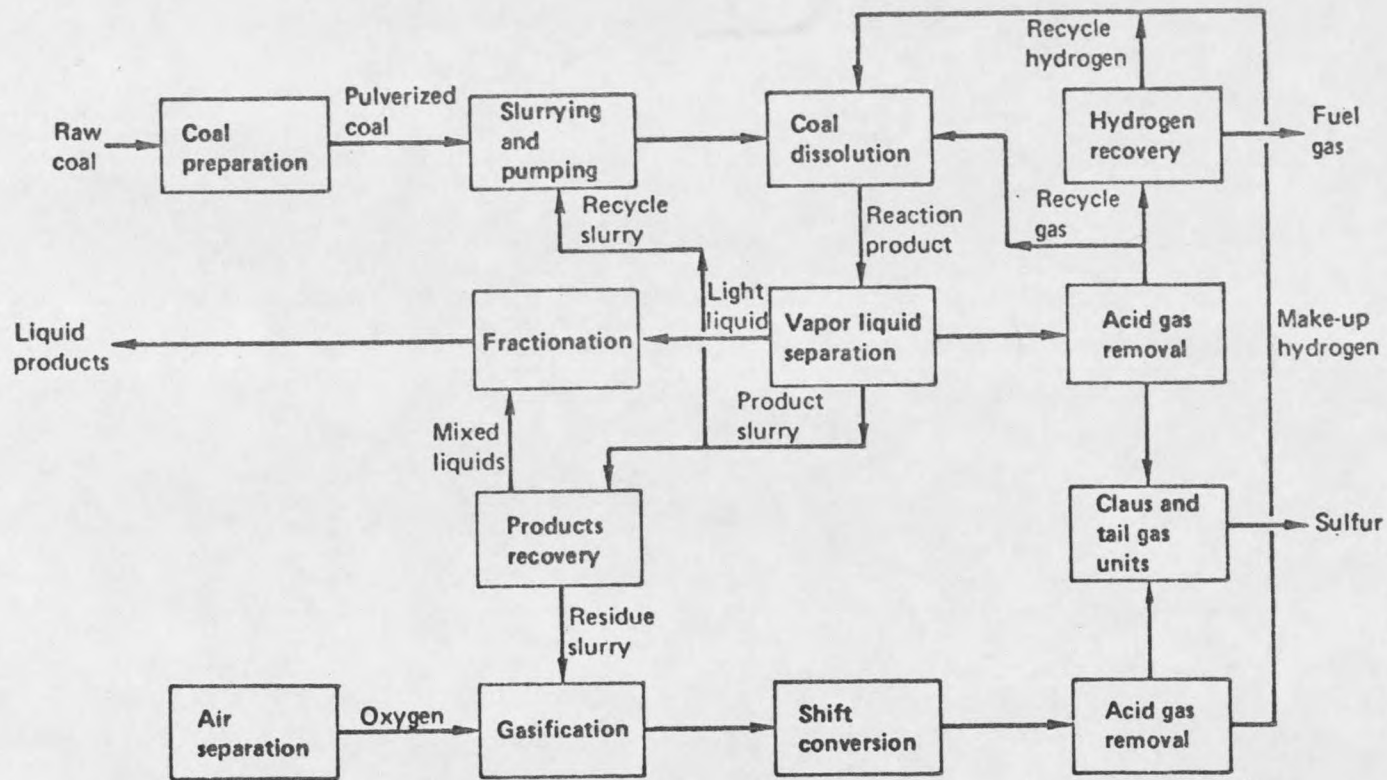


Figure 5 SRC-II process, with catalysts

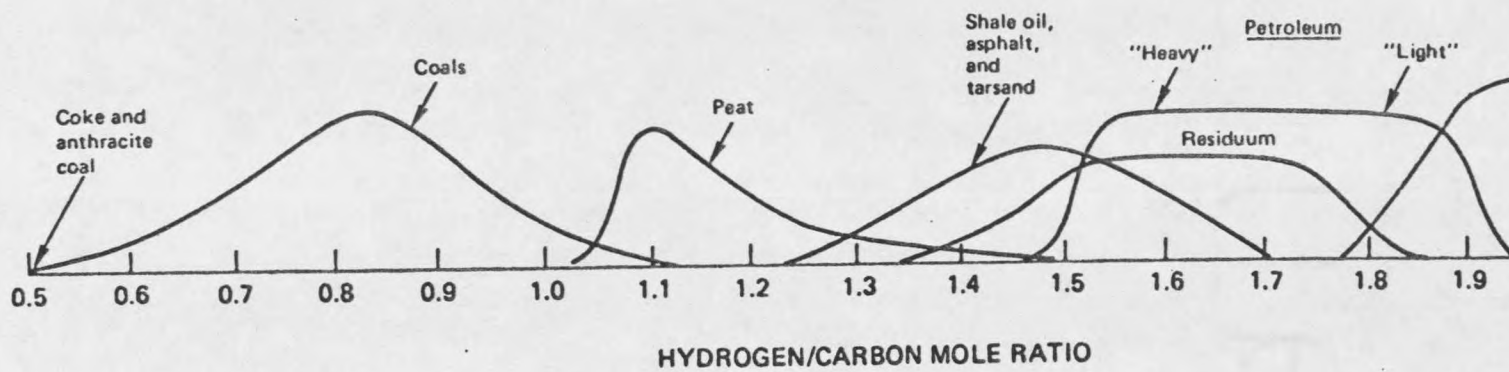
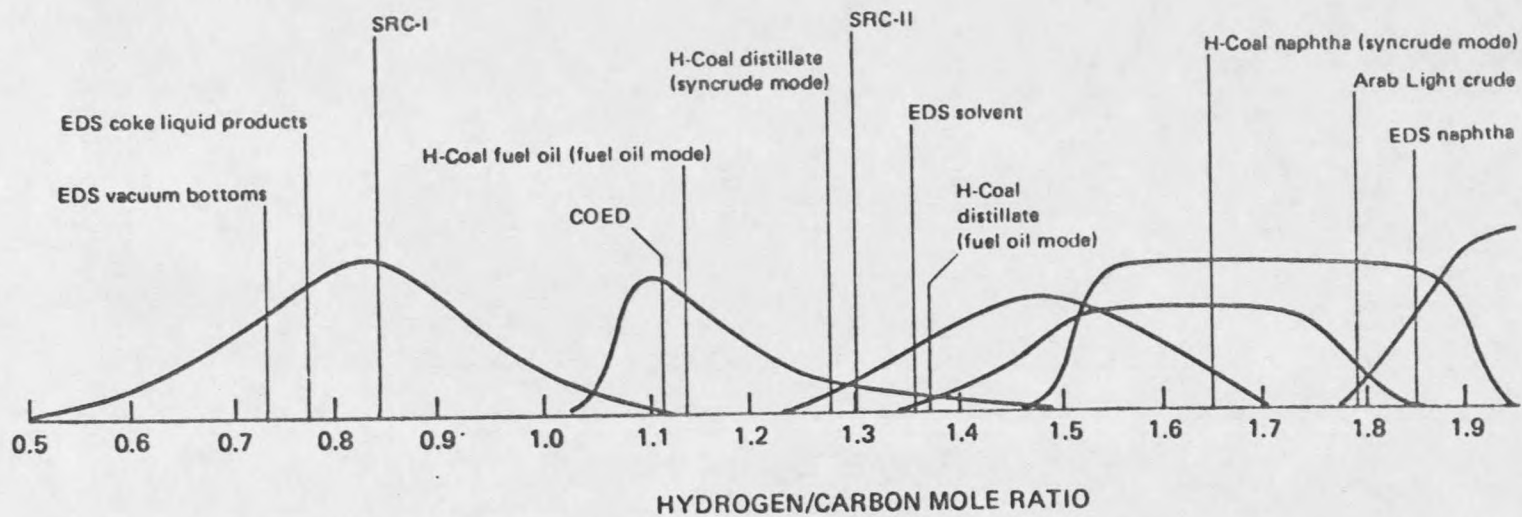


Figure 6 Hydrogen/carbon ratios for various hydrocarbon sources, end products and products of coal liquefaction [4]

LIQUID PRODUCT OF SRC-II

The SRC-II product cannot be considered as a single product from the process. Various products of SRC-II process are produced in different plants. Of major concern to this research are the products from the SRC-II process operated by Pittsburg and Midway Coal Mining Company (P&M). Properties of P&M's SRC-II Light Ends Column Feed (LECF) are shown in Table III. The chemical constituents of SRC-II liquids products are complicated. Unlike conventional petroleums, coal-derived liquids are characterized by the presence of significant quantities of polynuclear aromatic hydrocarbons and heteroatom-containing polynuclear aromatics [5,6]. These differences in chemical composition necessitate that synthetic crudes be subjected to hydrogenation/hydrogenolysis in order to remove most of the polynuclear aromatic hydrocarbons and sulfur-, nitrogen-, and oxygen-containing aromatic compounds prior to refining.

UPGRADING SRC-II LIQUID PRODUCT

The most effective way to use SRC-II liquid products at first may be to replace petroleum fractions now being used for boiler fuels with solvent refined coal that has undergone a minimum of refining. The petroleum fractions now used in boilers could then be refined to lighter products. If SRC-II liquids are put through a mild to moderate hydrotreating step to stabilize them and remove

Table III Properties of SRC-II Light Ends
Column Feed (LECF)

% Carbon	—*
% Hydrogen	—
% Nitrogen	0.67
% Sulfur	1.21
% Oxygen	—
% Ash	0.02
Sp. Gravity 60/60 F	0.983

ASTM D-86 Distillation	F
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

sulfur and nitrogen, the product will be usable not only as an environmentally acceptable boiler fuel but also as a refining feed.

If SRC-II liquid products are to be used as boiler fuels, nitrogen and sulfur contents should be lower than 0.5 wt%. If they are to be used as refining feedstocks, the preferred nitrogen level is 100-400 ppm range. There are some hydrocrackers that are able to tolerate nitrogen levels as high as 0.3 wt% in the feedstock [7]. The upgrading of coal liquids will require many of the processing steps now used in refining petroleum. Catalytic hydroprocessing should be given the greatest attention. It is essential for the removal of heteroatoms (particularly nitrogen and sulfur), and for the cracking of the high-molecular-weight coal liquids to more usable fractions.

While one of the major concerns with petroleum has been the sulfur in the crude, there are problems with nitrogen in coal liquids as well, because of increasing restrictions on NO_x emissions from fuels and severe poisoning effect that nitrogen-containing compounds have on refinery catalysts. The concentration of organically bound nitrogen in coal liquids is several times higher than that found in petroleum. In practice, the removal of nitrogen is generally more difficult than the removal of sulfur. Table IV shows that a lower percentage of the nitrogen is

Table IV Sulfur and nitrogen removal from coal and shale liquids and three petroleum distillates, by hydroprocessing, in percent by weight 8,9,10

	Sulfur			Nitrogen		
	In original	In product	Percent removed	In original	In product	Percent removed
Shale oil	0.6	0.0025	99.6	2.2	0.07	97
Solvent Refined Coal	0.29	0.001	99.6	0.85	0.05	94
H-Coal	0.32	0.001	99.6	0.46	0.014	70
Three petroleum distillates	0.8	0.05	94	0.015	0.007	53
	1.19	0.07	94	0.056	0.041	27
	1.58	0.14	91	0.012	0.007	42

removed even when the hydroprocessing removes a higher percentage of sulfur [8,9,10].

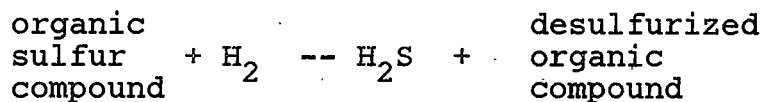
Typical catalysts for the processes described here consist of combinations of cobalt, nickel, molybdenum, and tungsten supported on alumina. Such catalysts are normally 3-6 percent cobalt or nickel and 12-18 percent molybdenum or tungsten. Under operating conditions, these metals are in the form of sulfides on the alumina.

Most work of upgrading SRC-II liquid products has been done at Montana State University (MSU). Catalyst C-49, MSU fabricated, with a metal combination of 4% CoO, 8% MoO₃, 1% NiO, and 8% WO₃ has been proven to reduce the nitrogen content in SRC-II LECF to as low as 0.3 wt% for 104 hours with regeneration of the catalyst every eight hours [11]. Several kinds of commercial hydrotreating catalysts were also tested. Harshaw HT-400 E 1/16" (Co-Mo) Catalyst gave the best nitrogen removal at 450°C of all commercial catalysts tested by Hass [12]. Sahin [13] proved that Harshaw HT-400 E 1/32" (Co-Mo) catalyst reduced the nitrogen content to as low as 0.3 wt% for approximately 40 hours without regeneration. A systematic study of the effects of temperatures and liquid hourly space velocities for catalyst C-49 has been done. The result showed that higher temperature and lower space velocity gave better denitrogenation [14]. However, the effect of pressure has

not been studied. It is hoped that this research will contribute in this respect.

CATALYTIC HYDROTREATING AND PRESSURE EFFECT

Hydrodesulfurization (HDS) is generally carried out in the temperature range of 260 to 450°C, with hydrogen pressures of 150-3000 psi, and feed space velocities usually in the range of 0.5 to 5.0 volumes of liquid per volume of catalyst per hour (v/v/hr), with extremes from 0.25 to 20 v/v/hr. A catalyst comprised of a metallic sulfide supported on alumina or silica-alumina is invariably used [15]. Under these conditions, mercaptans, sulfides, polysulfides, thiophanes, and thiophenes are reacted to produce hydrogen sulfide and hydrocarbons. The reaction,



is inhibited by product H_2S and might be first order in hydrogen partial pressure at sufficiently low values [16]. The data of Cecil et al. [17], for example, demonstrated that with an unidentified catalyst, the rate of HDS of a Middle Eastern residuum was proportional to hydrogen partial pressure over a range of 0- 1.4×10^7 Newton/sq m (about 0-2000 psi). However, Beuther and Schmid [18], for example, observed that beyond 7×10^6 Newton/sq m (about

1000 psi) there was only a small effect of increased hydrogen partial pressure on rate of residuum HDS. Spare and Gates [19] studied the reaction rate of a model reactant, biphenyl, in a pressure range of 1000-3000 psi and a temperature range of 300-375°C. Biphenyl was chosen as the reactant because it is representative of the least reactive aromatic hydrocarbons derived from coal; further, it is a primary product of the HDS of dibenzothiophene, which is typical of the least reactive sulfur-containing compounds found in coal-derived liquids and heavy feedstocks [20]. At lower temperatures, the rate was almost linearly dependent on the hydrogen concentration, whereas at high temperatures, the dependence was more than first order.

The sparse and conflicting results suggest a dependence of the kinetics on catalyst composition and on the nature of the feedstocks.

All the HDS reactions are essentially exothermic and irreversible under most industrial conditions; if extremely low sulfur content (for example, less than 1 ppm) is desired, thermodynamic reversibility may be important.

Hydrodesulfurization of coal-derived liquids is usually accompanied by hydrodenitrogenation (HDN) since nitrogen compounds are often present in these liquids. There are interactions between the sulfur and nitrogen compounds [21]. Organonitrogen compounds in solvent

refined coal are mostly the nitrogen-containing aromatic compounds such as pyrrole, indole, carbazole, pyridine, quinoline, acridine, and their derivatives. The presence of amino polycyclic aromatic nitrogen heterocycles (for example, aminoquinoline) was confirmed by high-resolution mass spectrometry [22]. Less is known about the HDN of heterocyclic ring compounds than of the analogous reactions with heterocyclic sulfur compounds. Generally speaking, the heterocyclic ring is first saturated, followed by ring fracture at a carbon-nitrogen bond. Nitrogen is removed from the resulting amine or aniline as ammonia [23]. The mechanisms of HDN of some model compounds, pyridine, quinoline, isoquinoline, acridine, etc., were studied [24,25].

Anilines and substituted anilines are often formed as intermediate compounds during HDN of multi-ring aromatic, nitrogen-containing compounds such as quinoline, carbazole, and acridine. These aniline compounds are very unreactive; therefore, nitrogen removal from anilines can become a rate-limiting step in total nitrogen removal. Katzer, Stiles and Kwart [26] studied HDN of anilines and showed that was a positive order dependence on hydrogen pressure. Quinoline has received considerable study since it contains both a heterocyclic ring and a benzene ring. The steps currently believed to be significant in its overall HDN reaction network are shown in Figure 7. The effect of

hydrogen pressure on the equilibrium concentration of Py-tetrahydroquinoline (PyTHQ) or Bz-tetrahydroquinoline (BzTHQ) depends on the temperature. For instance, at 420°C an increase in hydrogen pressure from 530 psi to 1050 psi increased the equilibrium concentration of PyTHQ or BzTHQ, but the opposite effect occurred at 330°C [27]. Both PyTHQ and BzTHQ are converted to DHQ. The conversion of DHQ to hydrocarbons and ammonia is facile [25].

Because of the complicated composition of coal-derived liquid, the HDS and HDN reaction mechanisms or experimental observations from model compounds cannot be applied to SRC-II LECF without some doubt, although they do give some suggestions.

CATALYST DEACTIVATION

A catalyst may become deactivated for a variety of reasons, such as poisoning, fouling, reduction of active area by sintering or migration, and loss of active species [28]. Polinski, Stiegel, and Tischer [29] suggested that poisoning of catalysts occurred by several possible modes. The modes included poisoning by coking (carbon deposits), poisoning by metallization, and parallel poisoning by "irreversible" nitrogen compound adsorption. Catalyst deactivation due to the carbon deposits on the catalyst was studied by Auger Electron Spectrum analysis. Yeh [11] found that the mechanism of catalyst poisoning during the

upgrading of SRC-II liquids appeared to be pore-mouth plugging.

RESEARCH OBJECTIVE

The objective of this research was to study the effect of pressure on the catalytic upgrading of SRC-II liquid product to a clean distillate fuel or a suitable feedstock for a conventional refinery. The sulfur and nitrogen contents in the upgraded product have to be reduced to as low as 0.5 wt% and 0.3 wt%, respectively. Since the removal of nitrogen is generally more difficult than the removal of sulfur, the denitrogenation was the major concern of this research.

EXPERIMENTAL

FEEDSTOCK

SRC-II Light Ends Column Feed received from Pittsburgh and Midway Coal Mining Company was used as the feedstock in this research. Its representative analysis was listed in Table III. The sulfur and nitrogen contents of this feedstock were 1.21 wt% and 0.67 wt%, respectively.

CATALYSTS

Three catalysts, C-49, KT-14, and Harshaw HT-400 E 1/32", were used to evaluate the effect of increased operating pressure on hydrotreating of SRC-II LECF.

Catalyst C-49 has a metal loading of 4% CoO, 8% MoO₃, 1% NiO, and 8% WO₃ on the catalyst carrier Nalco 78-6008C 1/32". The carrier comprises 98% Al₂O₃ and 2% SiO₂. It has a surface area of 214.6 sq m/gm, an average pore diameter of 156.5 Å, and a pore volume of 0.84 ml/gm. The preparation and pretreatment of catalyst C-49 followed the procedure of Yeh [11]. Metals were loaded in the order of Co, Mo, Ni, and W by using water solutions of Co(NO₃)₂·6H₂O, (NH₄)₆Mo₇O₂₄·4H₂O, Ni(NO₃)₂·6H₂O, and 5(NH₄)₂O·12WO₃·7H₂O. Catalyst KT-14 with a metal loading of 4% CoO, 10% MoO₃, and 8% WO₃ was fabricated by Kim [30] at Montana State University. The catalyst carrier, Katalco 81-6731,

has a surface area of 223 sq m/gm, an average pore diameter of 169 Å, and a pore volume 0.933 ml/gm. Metals were loaded with the same metallic aqueous solutions used for catalyst C-49 but in a different order of Mo, Co, and W. Kim improved the impregnation method of catalyst preparation by draining off the excessive metallic solution before drying. This improvement may avoid the excess metallic compounds precipitating in the catalyst pore and then plugging the pore mouth. Commercial catalyst Harshaw HT-400 E 1/32" was tested for its longevity and catalytic performance at several different pressures. It is loaded with 3% CoO and 15% MoO₃ and has a surface area of 210 sq m/gm, an average pore diameter of 95 Å, and a pore volume of 0.5 ml/gm.

The catalyst composition was reported in the weight percent of metal oxides which were added on impregnation to the blank catalyst carrier.

CONTINUOUS TRICKLE BED REACTOR

Trickle beds are employed commercially for the hydrodesulfurization of petroleum stocks. Basically, trickle bed means a reactor in which a liquid phase and a gas phase flow cocurrently downward through a fixed bed of catalyst particles while reaction is taking place [31].

Figure 8 shows the trickle bed reactor and auxiliary equipment used in this research. The trickle bed reactor was designed and fabricated by the Chemical Engineering

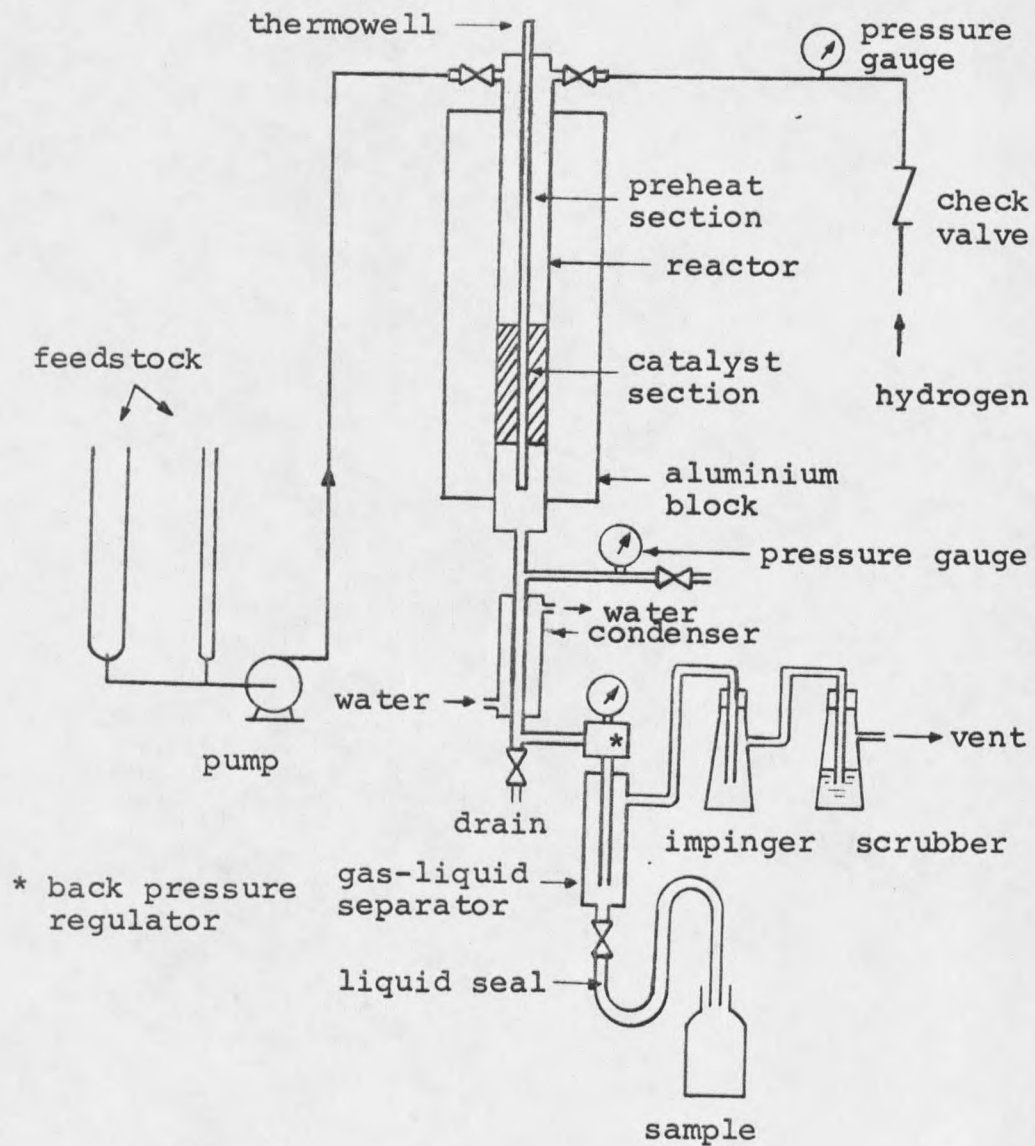


Figure 8 Trickle bed reactor and auxiliary equipment

Department of MSU. The reactor is about 40 inches long made of a 1-inch I.D. Schedule 80 Inconel pipe. At the top, there is a quarter inch stainless steel cross attached. It allowed the fitting of a 33-inch piece of stainless steel tubing, which served as a thermowell, and the fitting of two feed ports, one for feedstock and another for hydrogen. At the bottom, the reactor connected with a continuous sampling system which is composed of a pressure gauge, a water cooling condenser, a back pressure regulator, and a gas-liquid separator. In this reactor, from the top to the bottom, 175 ml of 1/4" Denstone inert support [32] and 25 ml of 1/8" Denstone inert support were loaded to serve as the preheating section, a mixture of 60 ml of catalyst and 60 ml of 1/8" inert support was loaded into the catalyst section. The remaining space was filled with 1/8" inert support. The reactor was placed into a six inches diameter, three foot long aluminum block. Three sets of Nichrome wire heating coils were wrapped around the block. Each heating coil was connected to a powerstat variable transformer for manually controlling the temperature. The temperature was detected by the chromel-alumel thermocouple placed in the thermowell of the reactor, and temperature was indicated by a Cole-Parmer digital thermocouple thermometer [33].

Liquid feedstock was pumped into the top of the reactor by a Milton Roy Simplex piston pump. The feed flow rate was controlled by adjusting the micrometer on the pump. Technical grade hydrogen was stored in the tailor-made, high pressure cylinder and then fed into the top of the reactor. Hydrogen and liquid feedstock were passed cocurrently through the reactor and then to a gas-liquid separator through a Grove back-pressure regulator equipped with a corrosion-resistive Teflon diaphragm. The exit gases passed through an impinger and through a scrubber with 10 percent sodium hydroxide-water solution and then vented. Liquid products were sampled by the overflow of the liquid seal which formed at the bottom of the separator.

CATALYST PRETREATMENT

In processing a feedstock containing sulfur compounds, a metallic or oxide catalyst will usually become converted to a sulfide either as a bulk compound or as a chemisorbed surface sulfide. Metal sulfides possess catalytic activity for hydrogenation and dehydrogenation reactions. They may be more resistant than metallic catalysts to the formation of coke deposits. They may also resist poisoning by sulfur compounds more readily than metallic catalysts. Generally superior performance is obtained by converting the catalyst to the sulfide form under controlled conditions rather

than allowing the catalyst to become sulfided by contact with sulfur compounds in the reaction mixture [28]. The catalysts were sulfided in a stream of 10% hydrogen sulfide in hydrogen at 350°C for 12 hours. The sulfiding was operated at atmospheric pressure. The spent gas from the sulfiding tube was scrubbed with 20% NaOH-water solution before venting to the hood.

Previously, it was thought that during sulfiding of the catalyst, sulfur is formed which could block the active sites of the catalyst and inactivate it. However, Katzer, Stiles, and Kwart [34] found that there was no significant difference in the nitrogen removal rate between the sulfided and unsulfided catalyst, indicating that sulfiding of these catalyst does not deactivate them.

ANALYTICAL PROCEDURE

The liquid products taken from experimental Run TS-102 to Run TS-105 were pretreated as follows:

1. Water was separated from the oily part of the liquid product by decantation.
2. The oily part of the liquid product was washed with the same amount of water in order to remove the water-soluble sulfur/nitrogen compounds. Then the water part was removed by freezing.

Upgraded SRC-II LECF liquid products were analyzed for sulfur and nitrogen content. The extent of hydrocracking was determined by distillation technique. The sulfur analysis was carried out by the quartz tube combustion method using a Bico-Brown Shell design sulfur apparatus [35]. The reported accuracy of the instrument is 0.03 %. The nitrogen analysis was performed by Macro-Kjeldahl method [36]. The accuracy of this method is around 0.3%. ASTM D-86 atmospheric distillation method [37] was used to determine the extent of hydrocracking. This method measures the cumulative amount of distillate which boiled below 650°F or when decomposition starts, whichever occurs first.

RESULTS AND DISCUSSION

The SRC-II Light Ends Column Feed was catalytically upgraded in a continuous trickle bed reactor. Three catalysts, one commercial and two MSU fabricated, were tested in extended time experiments to evaluate the performances of increasing the pressure from the usual 1000-1100 psi range to 2000 psi. The quantitative effect of pressure on the removal of nitrogen, removal of sulfur, and hydrocracking of SRC-II LECF was demonstrated by varying pressure during a single continuous run.

CATALYTIC HYDROTREATING AT 2000 PSI

In order to determine the effect of increased hydrogen pressure, the conditions and catalysts of two runs made by former workers were repeated, except that a pressure of 2000 psi was now used. Table V lists the operating conditions of those former runs, MSU-106 and T-5C1, and repeated runs, TS-101 and TS-102.

The average nitrogen content after 160 hours duration was 0.37 wt% in Run T-5C1, however it was only 0.12 wt% in Run TS-102. The nitrogen content of the product vs. time on stream of Runs TS-102 & T-5C1 is shown in Figure 9. The beneficial effect of the higher pressure is significant.

Table V Operating conditions of Runs TS-101, TS-102, MSU-106, and T-5C1

RUN*	CATALYST	TEMPERATURE (C)	DURATION (hrs)	PRESSURE (psi)	LHSV (v/v/hr)
TS-101	C-49	425	60	2000	1.25
MSU-106**	C-49	425	60	1100	1.25
TS-102	Harshaw HT-400E	425	160	2000	1.02
T-5C1***	Harshaw HT-400E	425	160	1000	1.01

* SRC-II LECF was the feedstock for all runs

** [14]

*** [13]

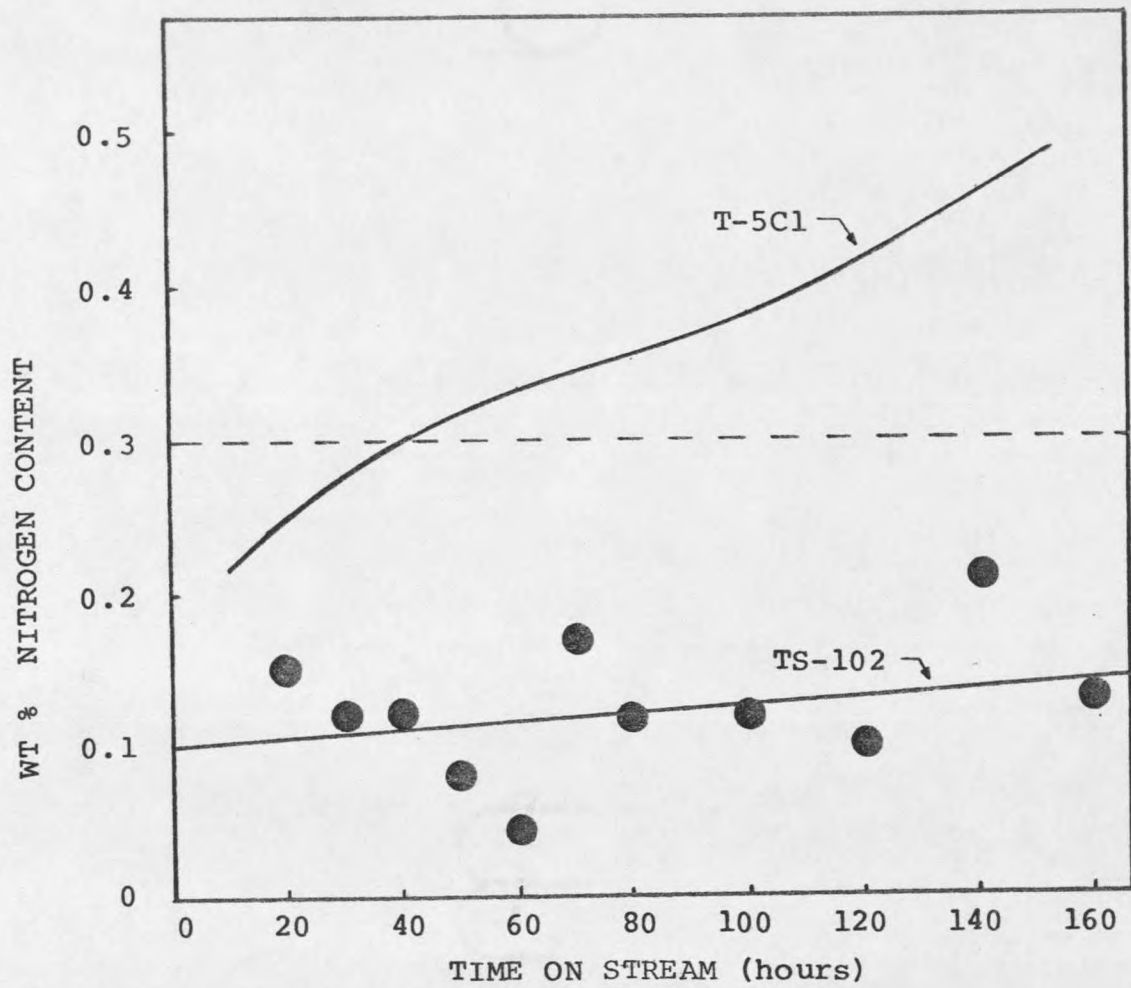


Figure 9 Nitrogen content vs. time on stream for Run TS-102 & Run T-5C1

Run TS-102 will go far beyond 160 hours producing specification grade denitrogenation, while Run T-5C1 exceeded the 0.3 wt% nitrogen content after 40 hours. In Figure 10 we also can see the beneficial effect of increasing pressure by comparing the nitrogen contents of Run TS-101 and MSU-106.

Catalyst KT-14 was tested in Run TS-103. The operating conditions were 425°C, 2000 psi, and 2.0 v/v/hr. The average nitrogen content of the liquid product after space time 320 hours was as low as 0.17 wt%. This is the best performance of a catalyst tested at MSU. Therefore, the positive effect of increased pressure on denitrogenation was noted for all three catalysts, C-49, Harshaw HT-400 E and KT-14, although these catalysts have different catalyst carriers, metal loadings, and preparation methods. The results of Run TS-103 are presented in Figure 11 & 12 and compared with those of Runs TS-101 & -102. Even though Run TS-103 has twice as a high space velocity as Run TS-102, it gave much the same result for denitrogenation. However Run TS-103 has a much lower nitrogen content in the product than does Run TS-101. The possible reason is the different impregnation methods of preparing the catalysts. The gasoline yield by the ASTM distillation from Run TS-103 is about 40 volume percent which is better than that from Runs TS-101 & -102. The higher extent of hydrocracking of

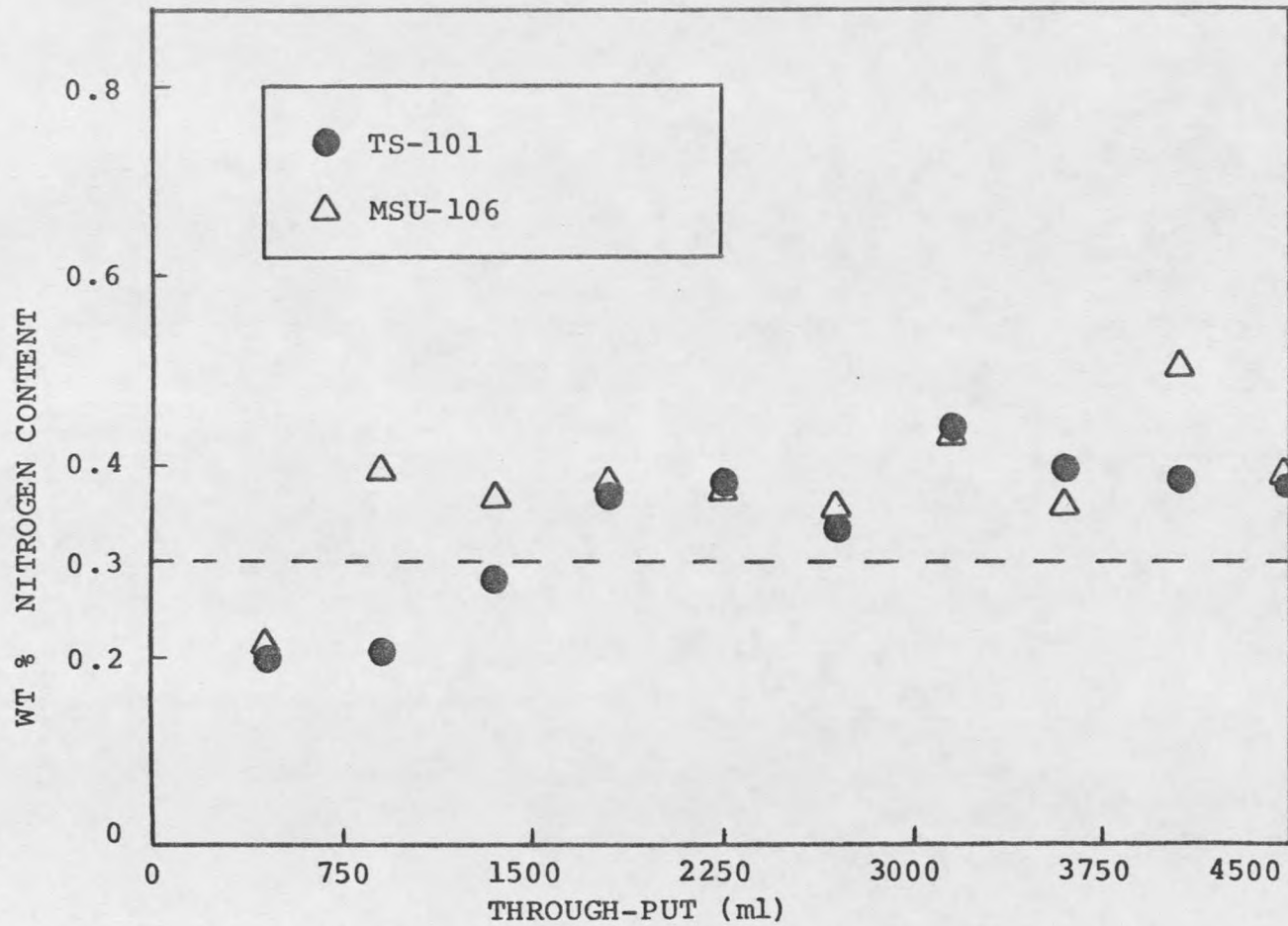


Figure 10 Nitrogen content vs. through-put for Run TS-101 & Run MSU-106

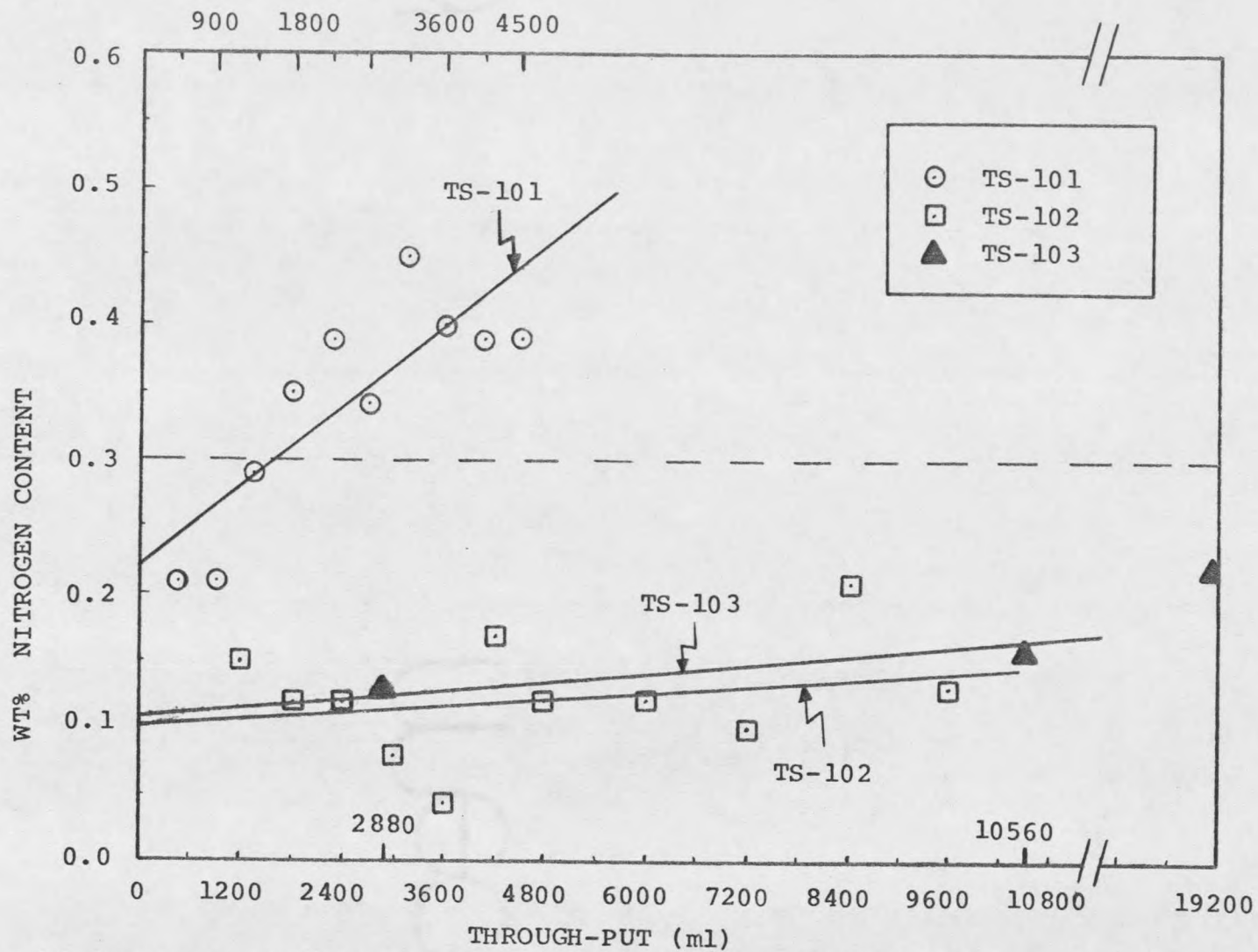


Figure 11 Nitrogen content vs. through-put for Runs TS-101 -102 &-103

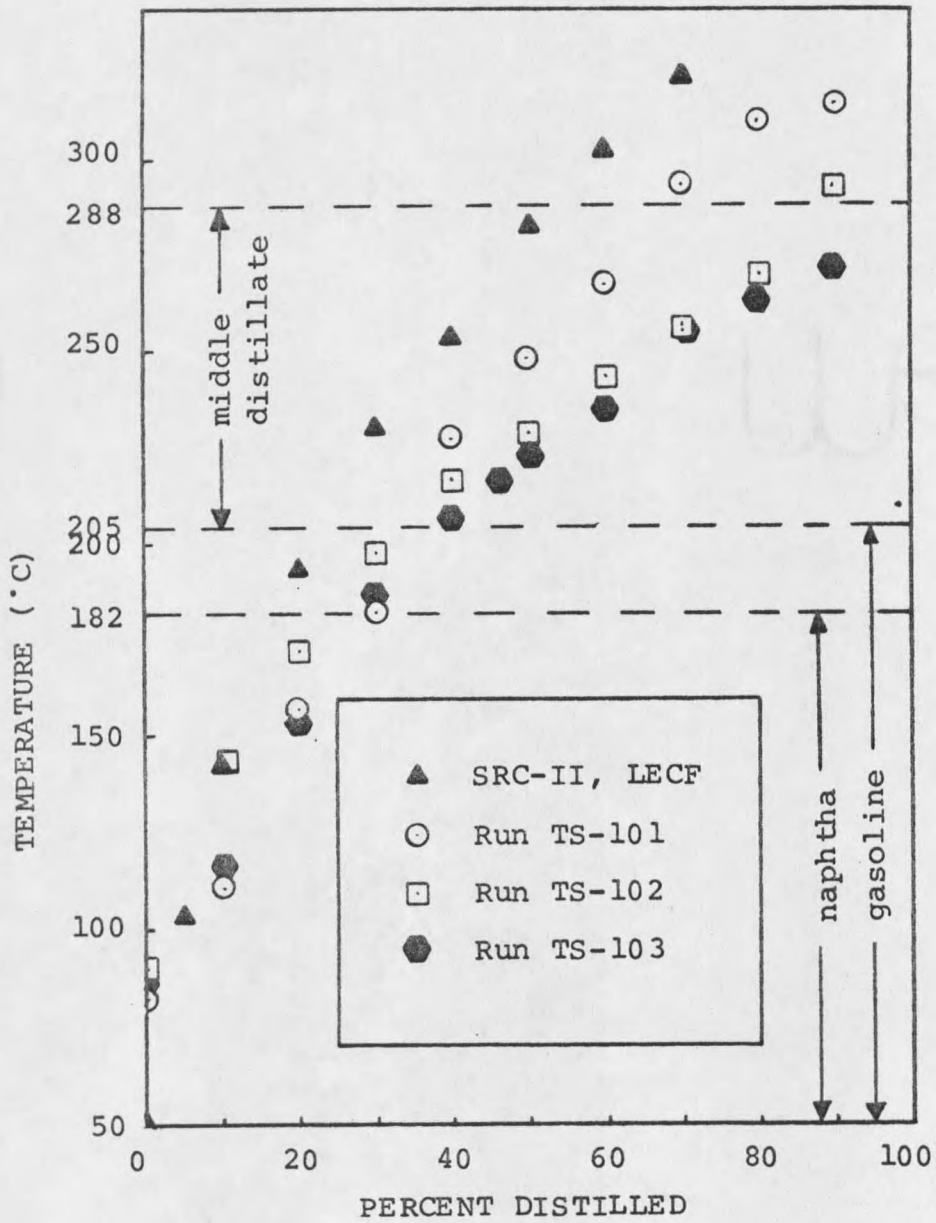


Figure 12 ASTM distillation results for Runs TS-101, -102 & -103

Run TS-103 might be due to the larger amount of active metal (Co and Mo) loaded on catalyst KT-14.

CATALYTIC HYDROTREATING AT VARIOUS PRESSURES

Runs TS-104 & -105 were carried out at several different pressures. The operating conditions of both runs are shown in Figure 13 & 14. Catalyst Harshaw HT-400 E (1/32") was used in both Runs TS-104 & -105. Temperature was also varied at 2000 psi in Run TS-104.

Figure 15 shows the nitrogen content in upgraded product as a function of time on stream at various pressures. There is a positive order dependence of denitrogenation on operating pressure, or on hydrogen pressure since the vapor pressures of the liquid reactants are very low. During the period of 48 to 72 hours, the nitrogen content exceeded 0.3 wt% due to rapid catalyst deactivation at 1000 psi [11]. However, when pressure was elevated after 72 hours, the nitrogen content was reduced gradually. It suggests that the catalyst might be partially recovered from deactivation by applying increased pressure. Figure 16 shows similar results for Run TS-104. The higher temperature gives a slight advantage to denitrogenation at 2000 psi.

The sulfur content of the product obtained from Runs TS-104 & -105 are presented in Figures 17 & 18. The effect of pressure is not as significant as for denitrogenation.

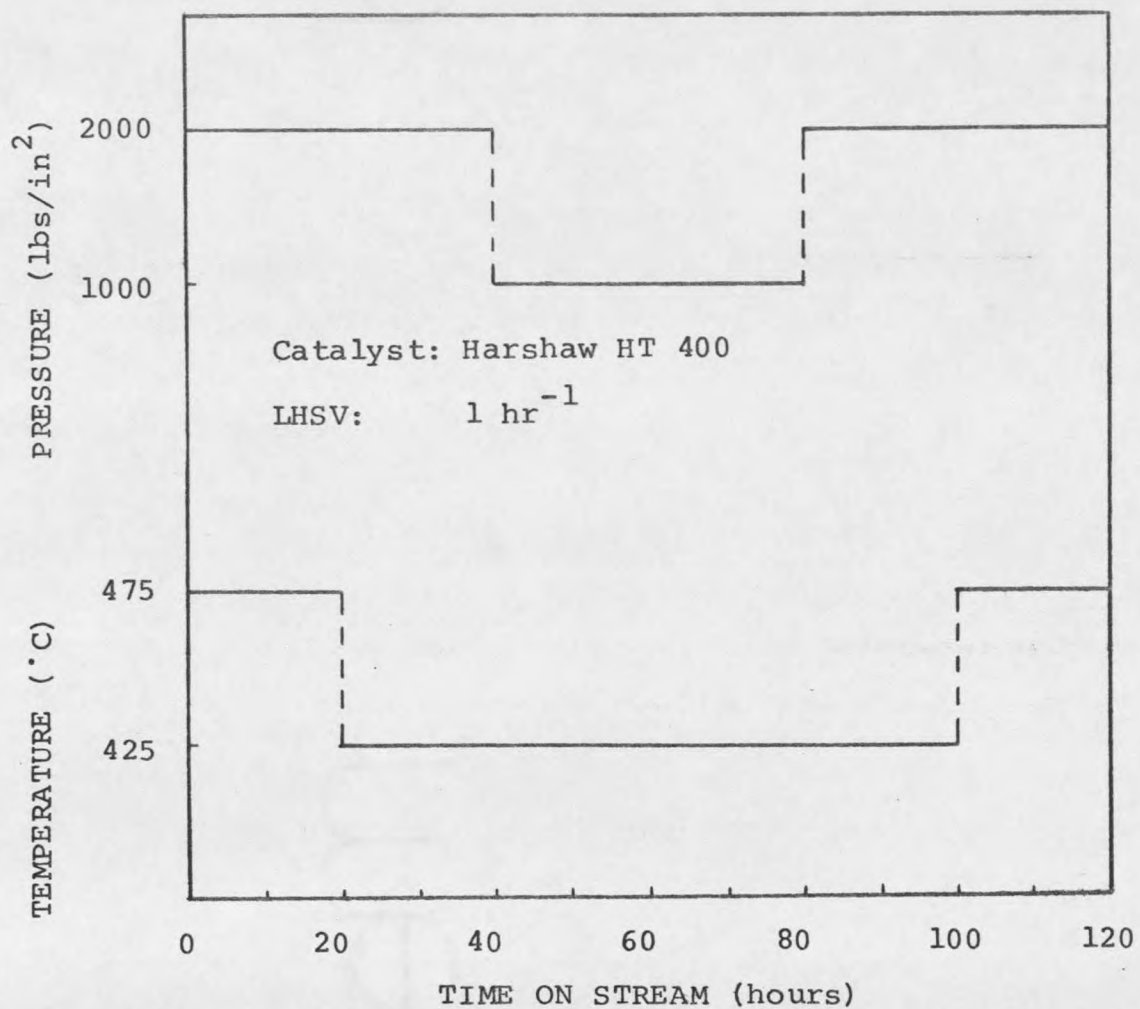


Figure 13 Operating conditions of Run TS-104

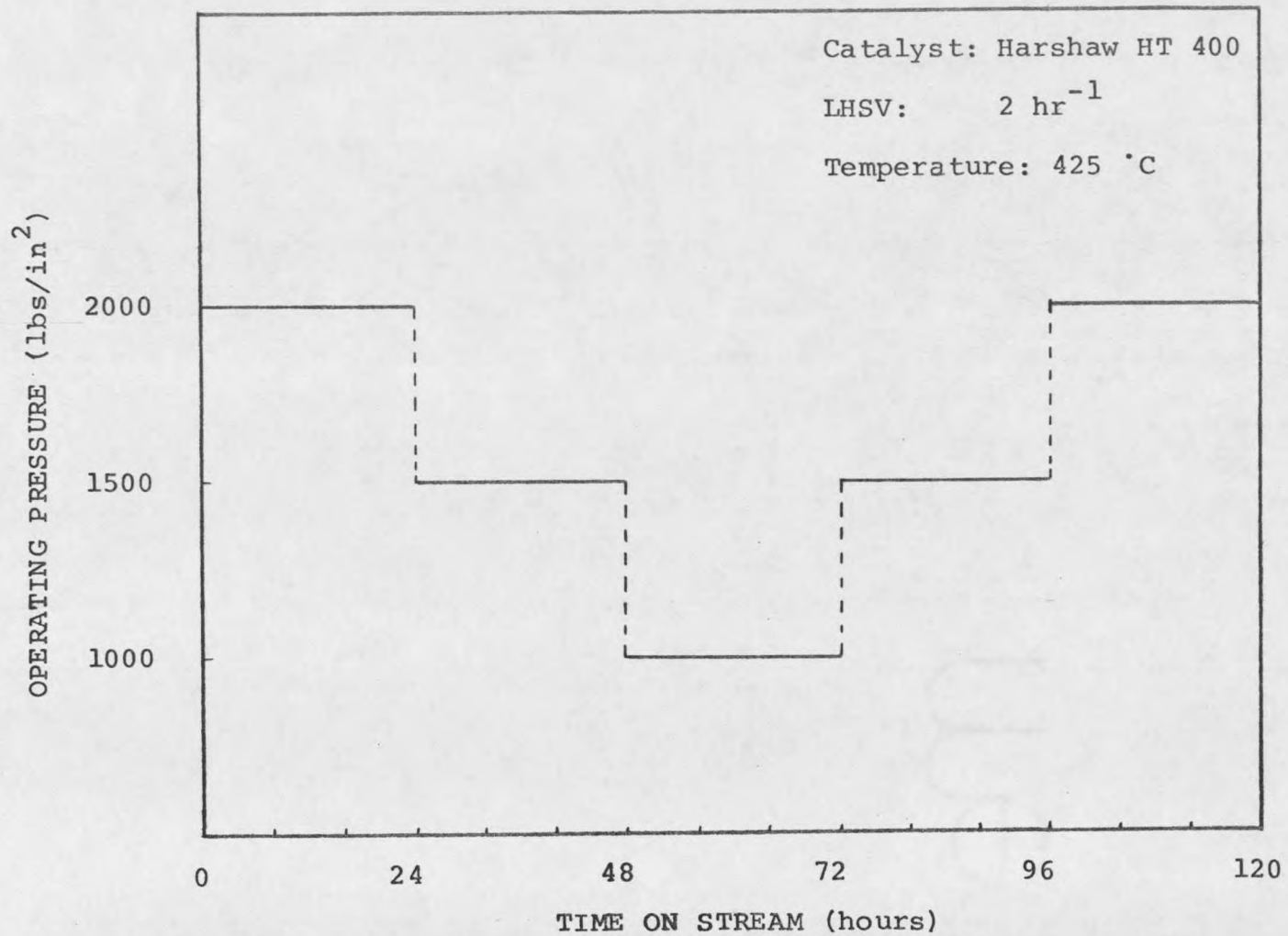


Figure 14 Operating conditions of Run TS-105

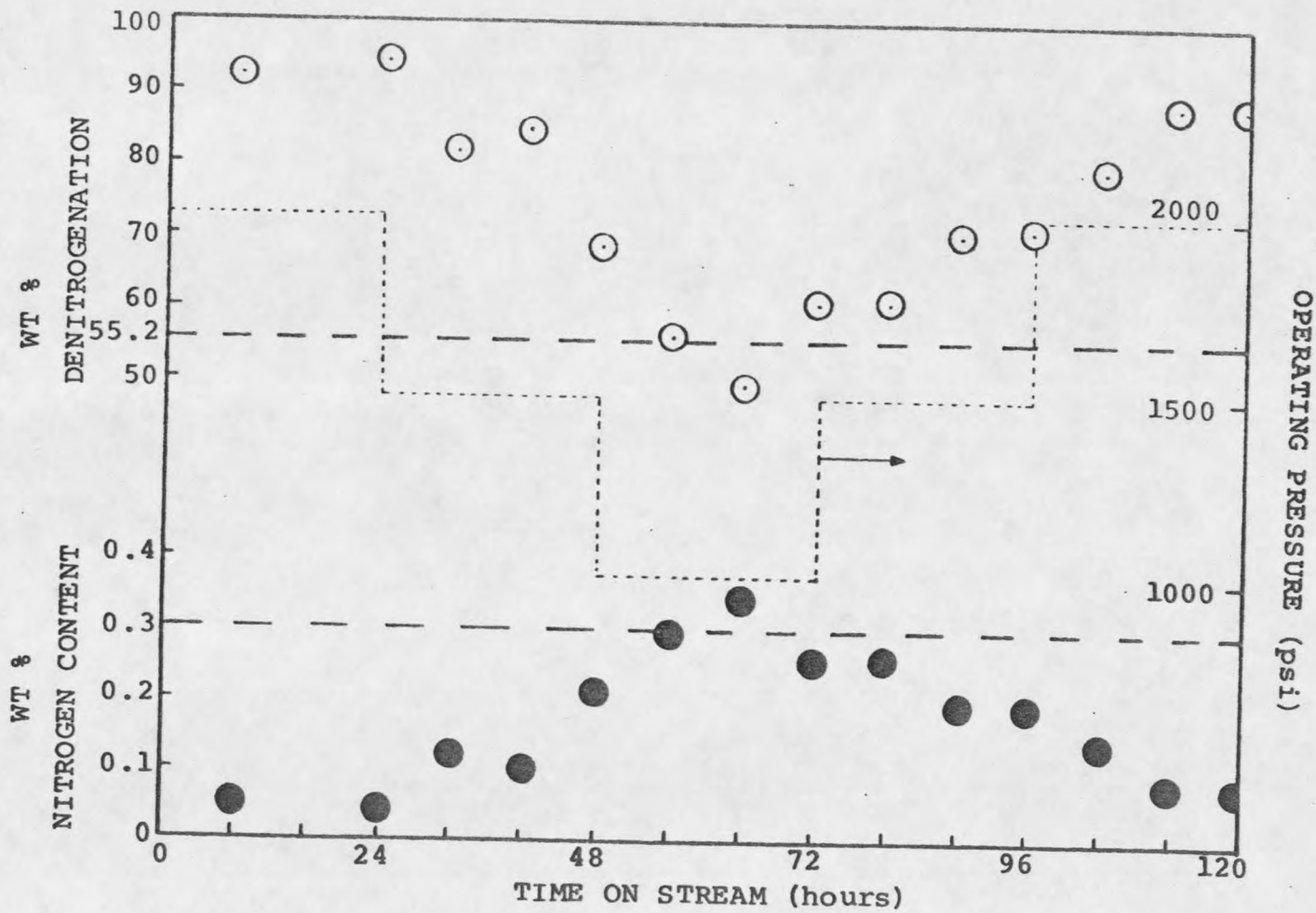


Figure 15 Nitrogen content and denitrogenation vs. time on stream for Run TS-105

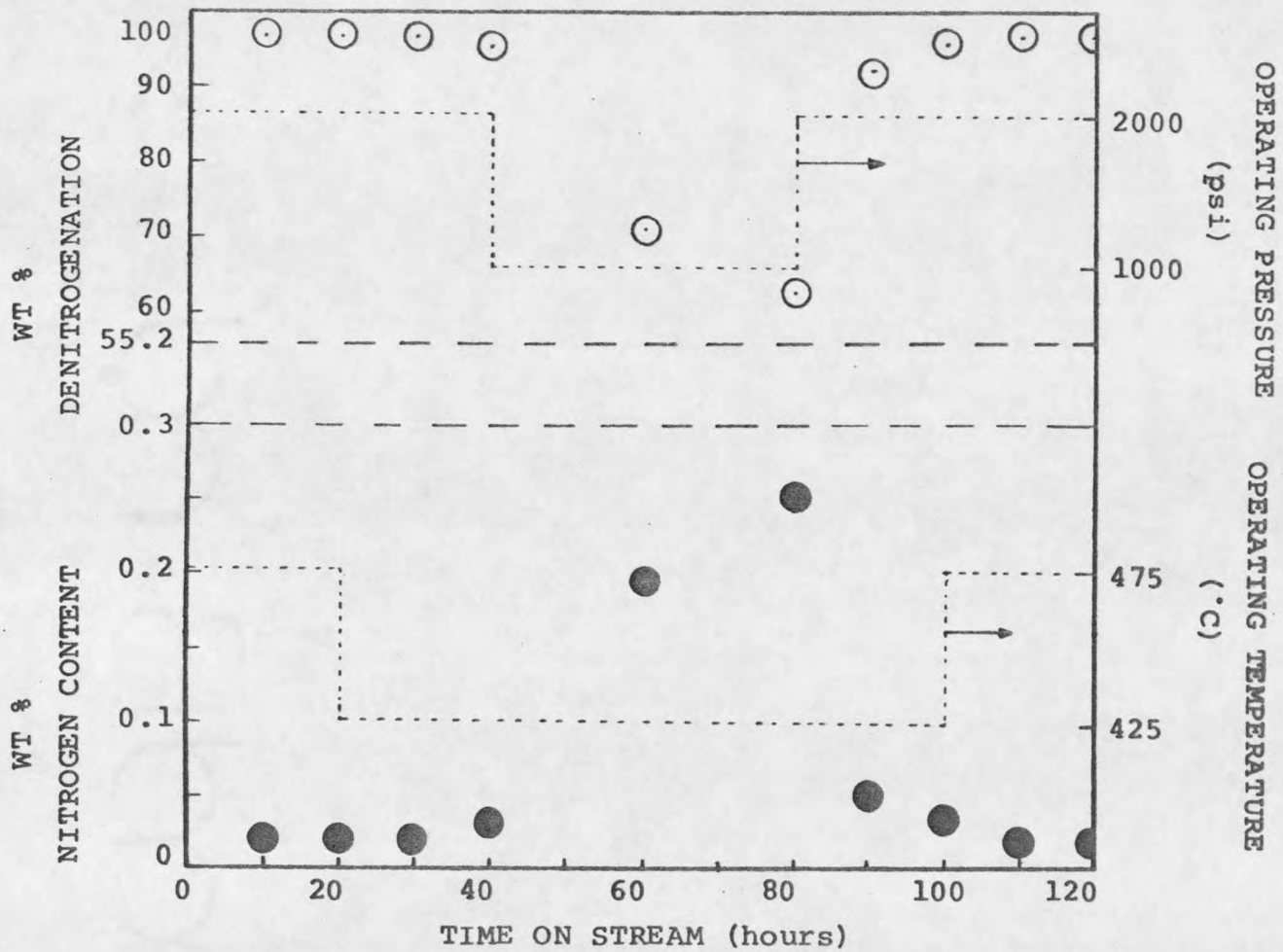


Figure 16 Nitrogen content and denitrogenation vs. time on stream for Run TS-104

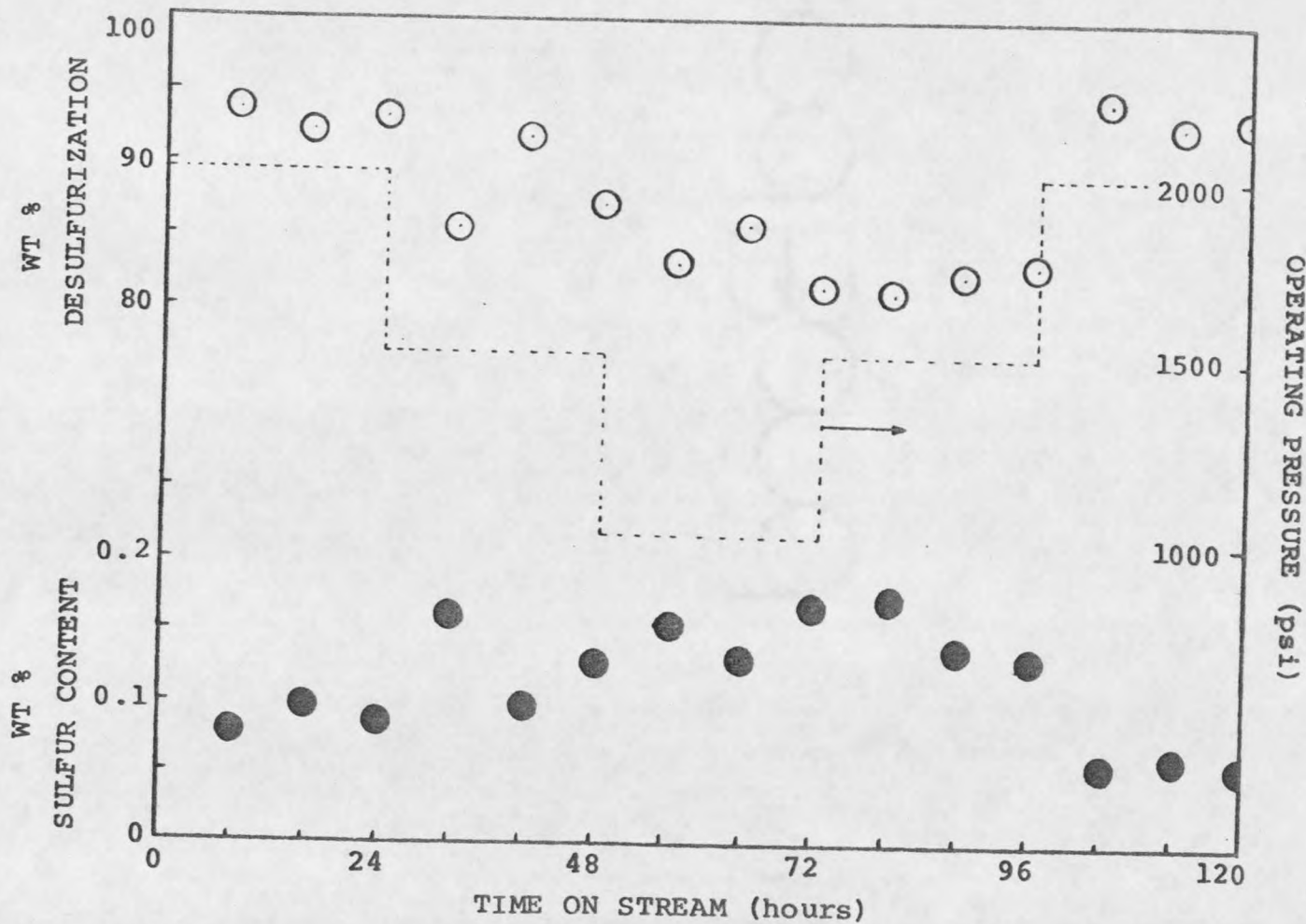


Figure 17 Sulfur content and desulfurization vs. time on stream for Run TS-105

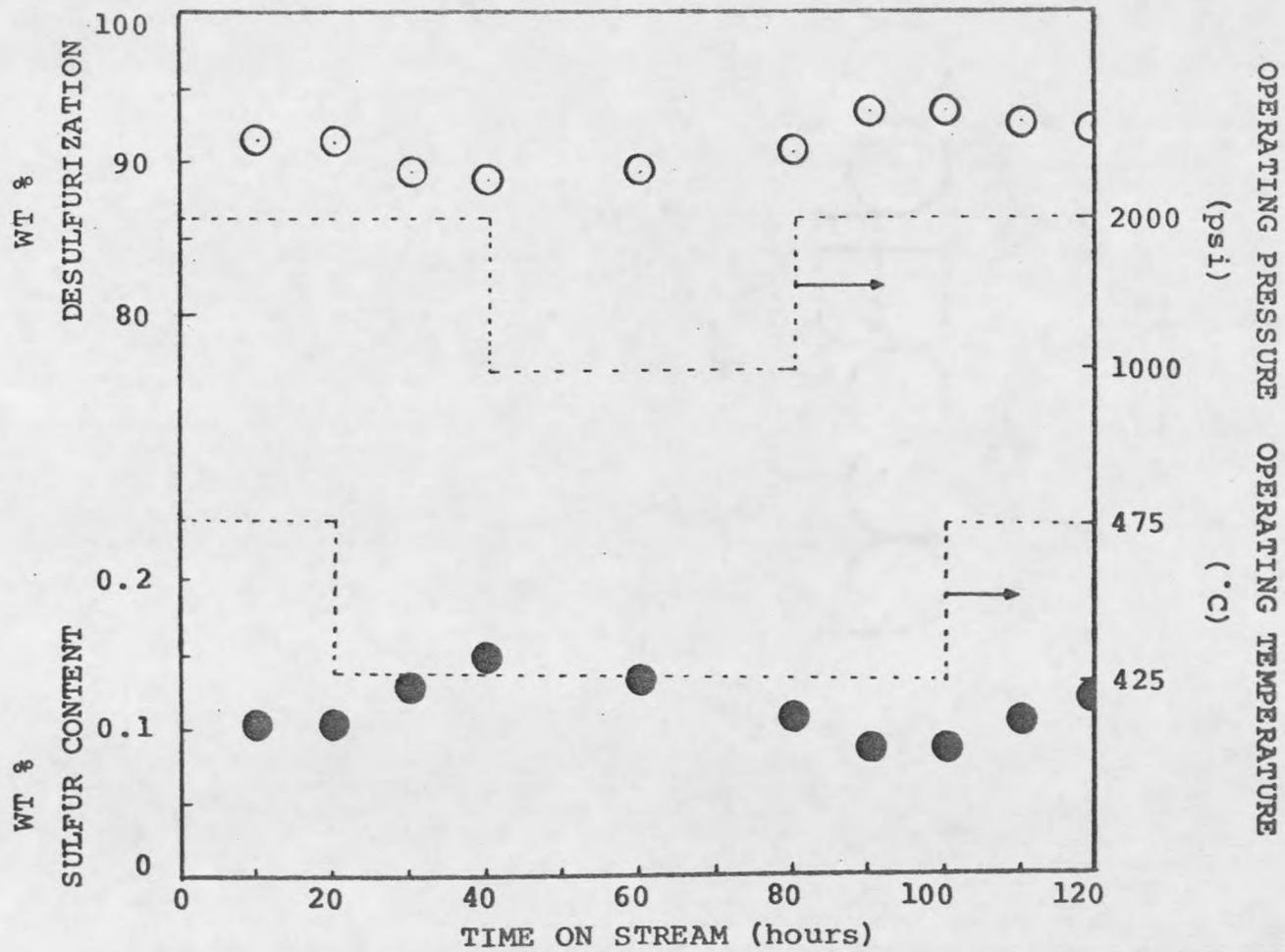


Figure 18 Sulfur content and desulfurization vs. time on stream for Run TS-104

When operating at 1000 psi Bhatia [14] found that there is no dependence of desulfurization on temperature. This study found none at 2000 psi either.

The ASTM distillation data for Runs TS-104 & -105 are shown in Figures 19 & 20. The amount of naphtha fraction (boiling below 182°C) and gasoline fraction (boiling below 205°C) are presented in Figures 21 & 22. The extent of hydrocracking increased at both higher pressure and higher temperature.

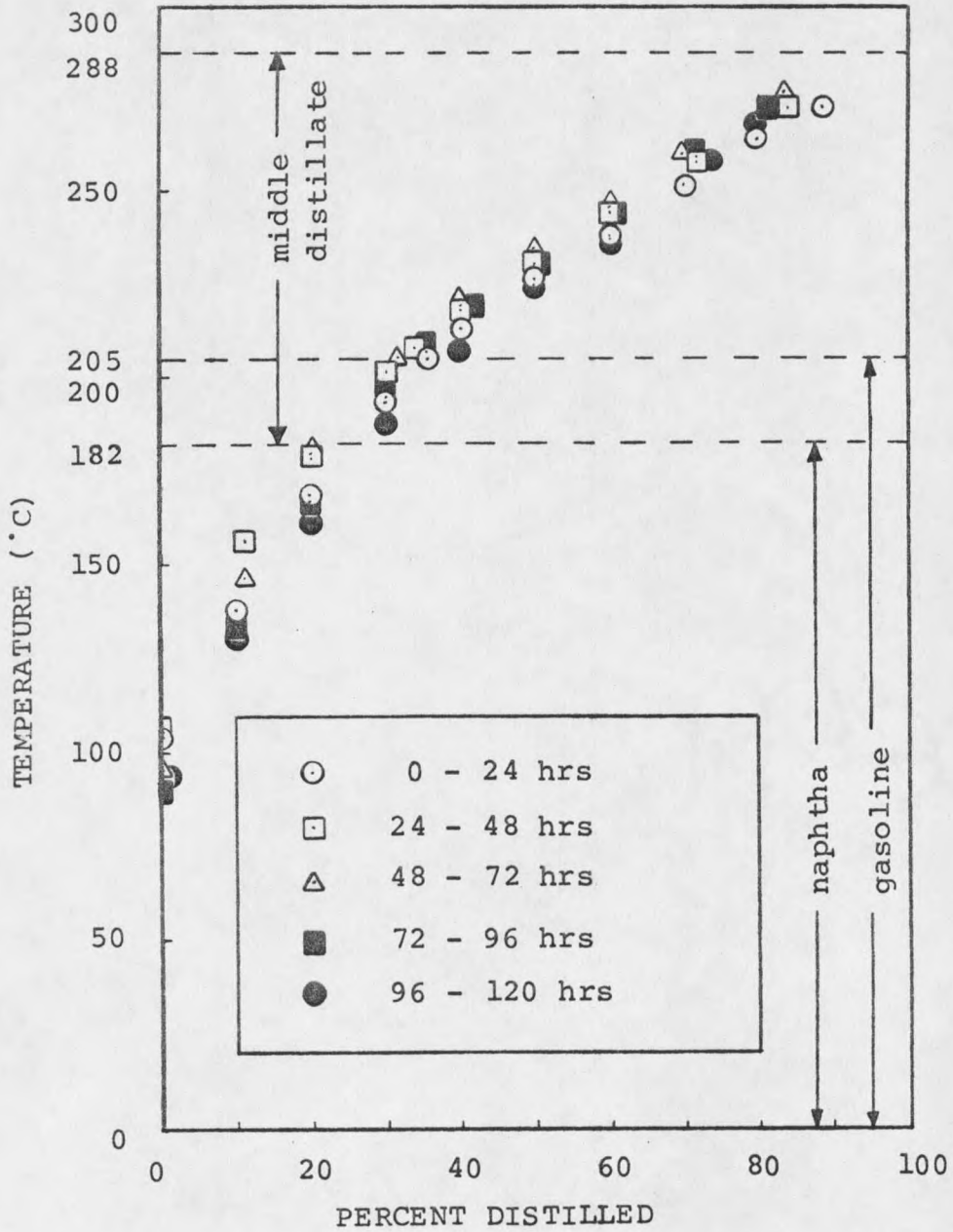


Figure 19 ASTM Distillation results for Run TS-105

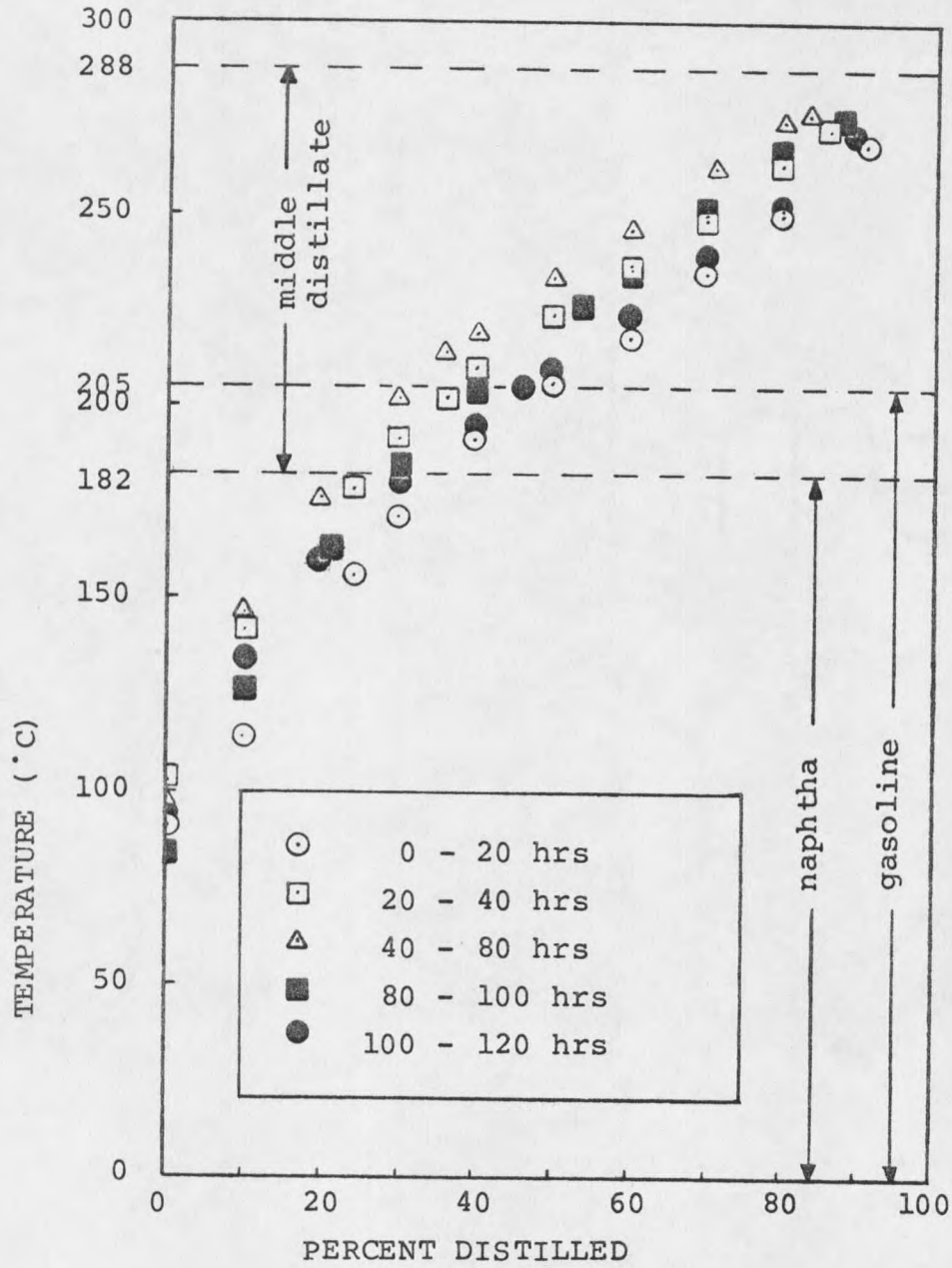


Figure 20 ASTM Distillation results for Run TS-104

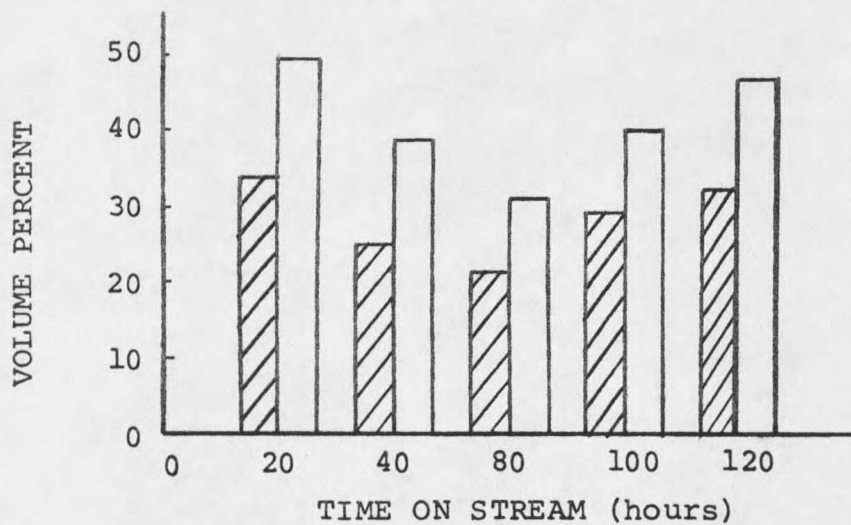


Figure 21 Block diagram of gasoline and naphtha distilled of Run TS-104

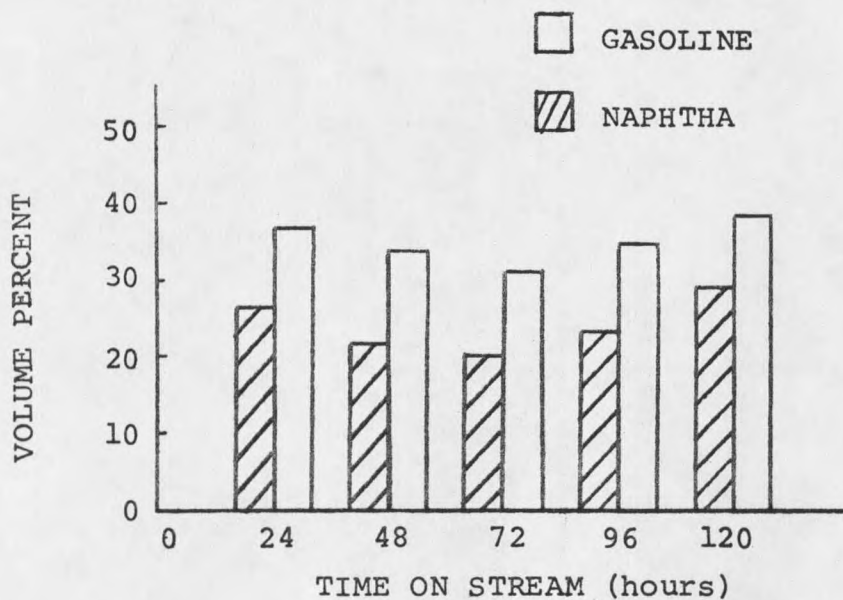


Figure 22 Block diagram of gasoline and naphtha distilled of Run TS-105

SUMMARY AND CONCLUSIONS

1. Catalyst longevity can be extended by operating at 2000 psi. It is valid for both commercial and lab fabricated catalysts. The nitrogen content can be reduced to as low as 0.3 wt% when operating beyond space time 160 hours with catalyst Harshaw HT-400 E or beyond space time 320 hours with catalyst KT-14.
2. Higher pressure gives greater denitrogenation. However, there is no significant dependence of desulfurization on pressure and temperature.
3. The extent of hydrocracking increases with operating pressure.
4. Catalyst longevity is significantly affected by the catalyst impregnation method. Catalyst C-49 can only reduce the nitrogen content to as low as 0.3 wt% for space time 20 hours, while catalyst KT-14 gives more than 320 hours with a similar metal loading but improved impregnation method.

RECOMMENDATION FOR FUTURE RESEARCH

A systematic study for investigating the optimum combination of pressure, space velocity, and temperature is suggested. Since the cost of equipment for hydro-treating increases with the operating pressure, the optimum cost has to be a concern in practice.

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