Upgrading of solvent refined coal (SRC-II) liquids by catalytic hydrotreating and the effect of water on catalyst activity
by Turgut Sahin

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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Upgrading of SRC-II Vacuum Flash Feed (VFF) and Light Ends Column Feed (LECF), which were produced from the Pittsburg and Midway Coal Mining Company's SRC-II pilot plant, was performed by catalytic hydro-treating.

Three commercial catalysts, Nalco Mo 477, Nalco NM 502, and Harshaw HT 400, were tested for their ability to remove nitrogen and sulfur present in SRC-II liquids. Harshaw HT 400 was subjected to long runs under two different conditions; with water addition at 475°C and without water addition at 425°C.

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

Among three catalysts tested, Harshaw HT 400 gave the best performance to upgrade SRC-II VFF. Water addition to the feed (LECF). improved the performance of this catalyst. The runs with water addition gave three times longer catalyst life on the stream, higher liquid product yields and better distillation yields than the runs without water addition.

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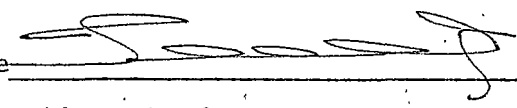
Signature 

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Approved:

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ABSTRACT

Upgrading of SRC-II Vacuum Flash Feed (VFF) and Light Ends Column Feed (LECF), which were produced from the Pittsburg and Midway Coal Mining Company's SRC-II pilot plant, was performed by catalytic hydrotreating.

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I. INTRODUCTION

When the world oil crisis started in the early seventies, many nations around the world seriously started looking for alternative energy sources.

Of course, there are several alternatives such as solar energy, nuclear energy and fossil fuels. The latter has become more attractive because of its abundant resources and promising process to utilize it for conventional use. Just for an example, the United States has 780 billion tons of recoverable coal reserves (1). However coal as a solid fuel is not a good alternative to oil because of the environmental problems and the nation's dependence on liquid fuels. Then, converting coal to a liquid fuel becomes the most favorable one (2,3).

Coal liquefaction processes are being looked into: Solvent Refined Coal (SRC), Exxon Donon Solvent (EDS), H-Coal, and Synthoil are a few examples. However each of these is merely in the development stage in the United States. Coal processes have their own problems. They require large capital investment, abundant water and have social problems (4). Of these, SRC is our major interest.

A. Historical Background

SRC Process and Pittsburg and Midway Coal Mining Co.

The SRC project was begun in 1962 when Spencer Chemical Company was awarded a research contract by the Office of Coal Research (OCR, subsequently a part of DOE) to study the technical feasibility of a coal deashing process (now called SRC process). In 1965, the process was successfully demonstrated with a 50 pound-per-hour continuous-flow unit. During the term of contract, Gulf Oil Corporation acquired Spencer Chemical Company. After reorganization, the contract was assigned to the research department of Pittsburg and Midway Coal Mining Company (5).

Construction of a 50 ton-per-day pilot plant at Fort Lewis, Washington was begun in 1972 and became fully operational in 1974. This early process is called SRC-I and produced a solid product. Later in 1977, the SRC-I process was modified to SRC-II process to produce liquid products (5). A schematic diagram of both processes are shown in Fig. 1 (6) and Fig. 2 (7).

Of major concern to this project is the SRC-II process. It is not a single product process. The percent gas and liquid product yields and composition of Powhatan #5 coal are shown in Table I and Table II respectively (8). Table III summarized the analysis of the respective SRC-II feed stocks, Vacuum Flash Feed (VFF) and Light Ends Column Feed (LECF), used in this project.

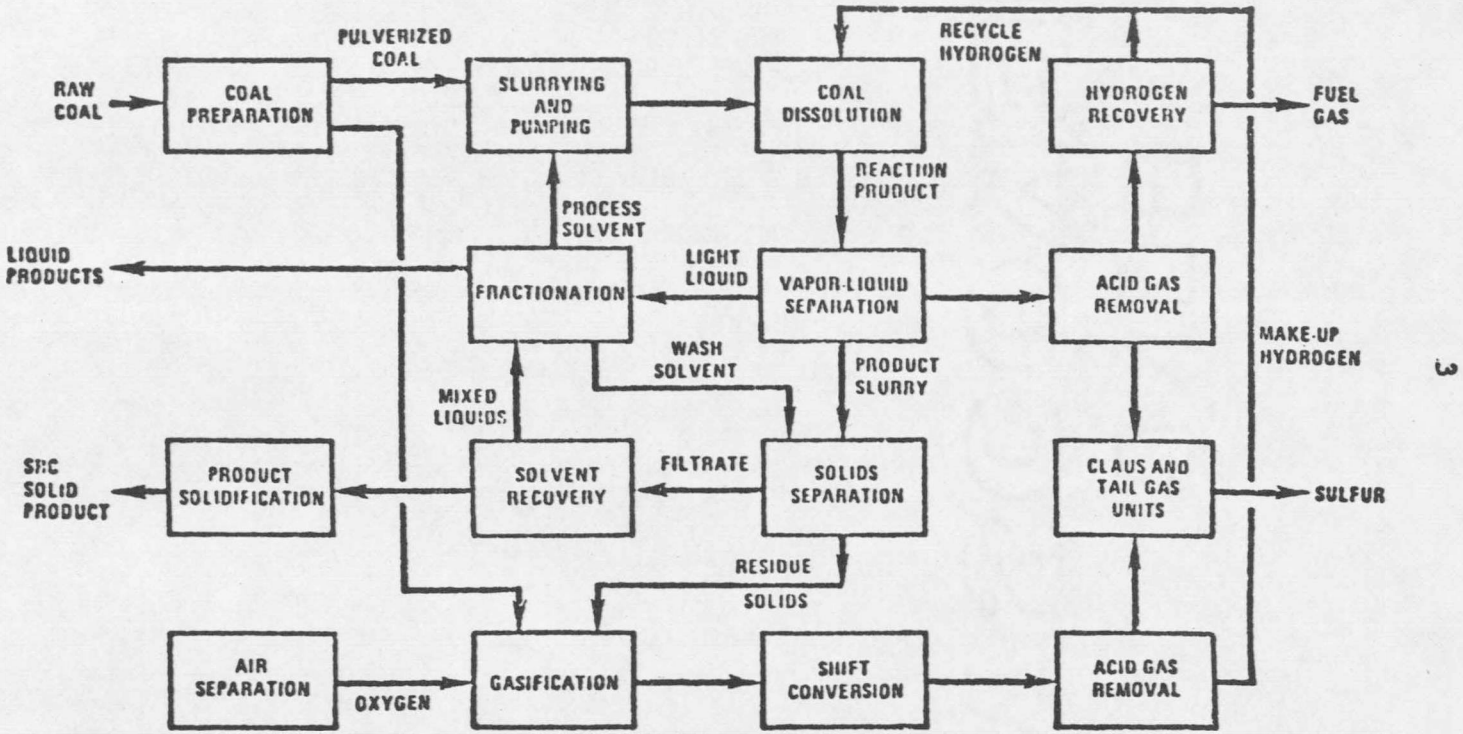

FIGURE 1. Schematic Diagram of SRC-I Process

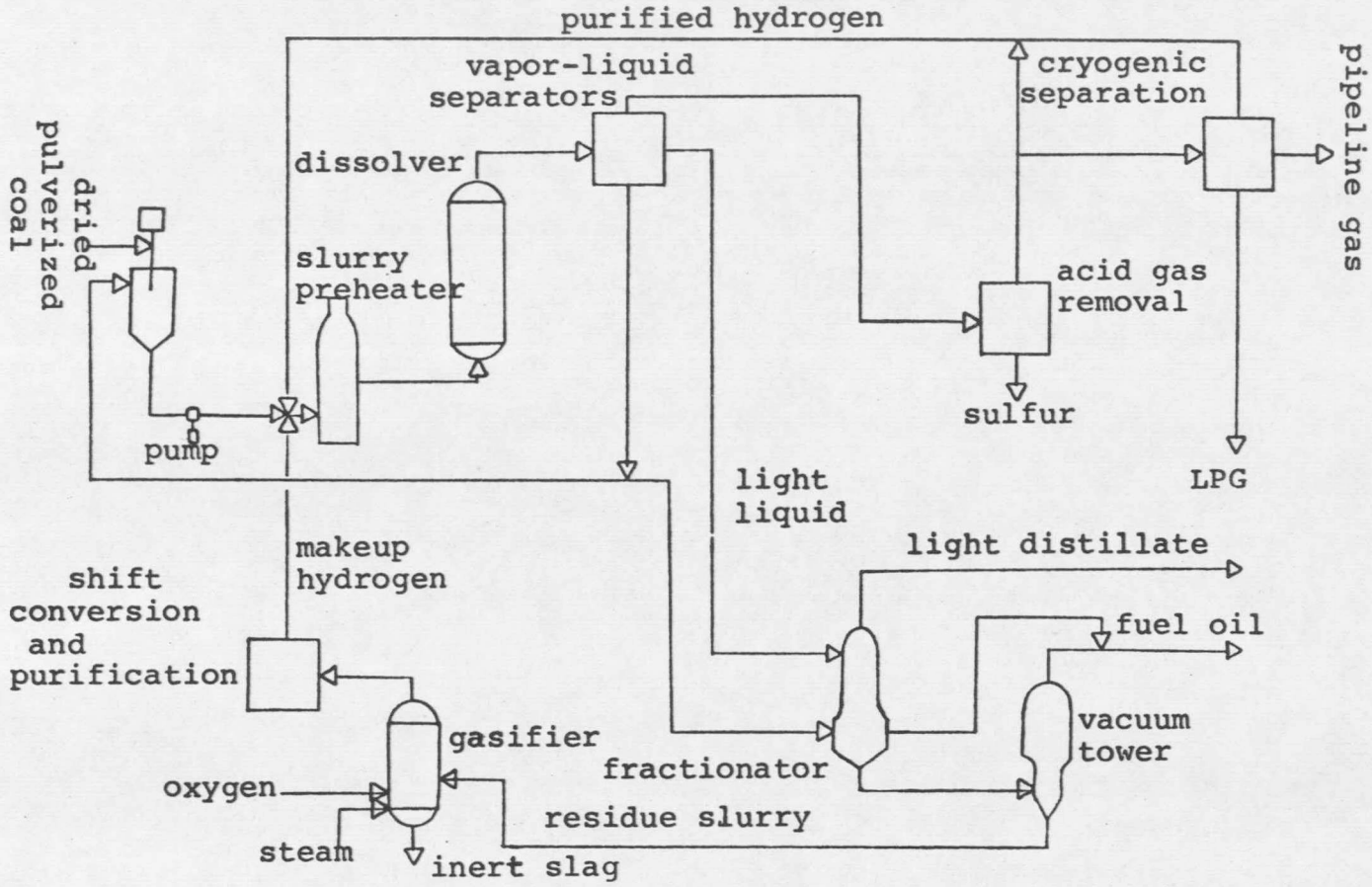

FIGURE 2. Schematic Diagram of SRC-II Process

TABLE I

SRC-II Feed Coal Analysis (Powhatan #5 Mine Coal) (8)

	weight %	
Carbon	70.18	
Hydrogen	4.99	
Nitrogen	1.23	
Sulfur	3.52	
Organic Sulfur		1.69
Pyritic Sulfur		1.68
Sulfate Sulfur		0.15
Oxygen	13.41	
Organic Oxygen		7.59
Inorganic Oxygen		5.82
Chlorine	0.04	
Metals (by specific ash)	6.63	
H/C ratio	0.85	
Moisture (as received coal)	1.20	
Volatile (as received coal)	36.50	
Ash (MF coal)	12.40	
Analysis of Coal (MMF Coal)		
Volatile Matter	42.60	
Carbon	81.90	
Nitrogen	5.40	
Oxygen	8.90	
Sulfur	2.00	

TABLE II

Distillate Yields of SRC-II Process

	weight % Moisture Mineral Free Coal	
C_1	5.53	
C_2	4.70	
C_3	5.17	
C_4 (i-)	0.29	
C_4 (n-)	2.70	
Total C_1 to C_4		18.38
NH_3 (by nitrogen balance)	0.56	
H_2S (by sulfur balance)	3.08	
HCl (by Chlorine balance)	0.02	
Total other gases		4.57
Water (by oxygen balance)	9.07	
C_5 - 193°C (naphtha)	8.57	
193 - 288°C (middle distillate)	18.05	
288 - 482°C (heavy distillate)	27.15	
Total C_5 + Distillate		53.76
482°C + Pyridine soluble	18.66	
Insoluble Organic Matter	2.11	
Total 482°C + Organic Matter		20.77
Mineral Matter		15.68

TABLE III

Properties of SRC-II Vacuum Flash Feed and Light Ends Column Feed

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

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Several catalysts, either commercial or catalysts produced at MSU, have been tested to upgrade the SRC products.

Hass tested 27 commercial catalysts and 29 catalysts produced at MSU. He first screened them in batch-autoclave tests and then tested the promising catalysts in continuous trickle bed reactor runs. Harshaw HT-400 E 1/16" (Co-Mo) and MSU STK-5-2-2-1.5 E(Ni-Co-Mo) catalysts gave the best denitrogenation. For desulfurization, Cyanamid HDS 2DA 1/16" Trilobe (Co-Mo) and MSU STK 5-2-6-1.5 E(Ni-Co-Mo) were the best (9).

He concluded that higher MoO_3, Ni-Mo and Co-Mo concentrations improved denitrogenation. He studied the temperature effect on denitrogenation and higher temperatures gave better denitrogenation at the expense of increased catalyst coking. He also found that Liquid Hourly Space Velocity (LHSV) of 1.0 was the best for denitrogenation (9).

Later, Yeh studied the effect of metal oxides and physical properties of catalyst bases. The catalyst base with an optimum combination of proper surface area and pore diameter was more significant than MoO_3 concentration on denitrogenation. He also reduced the catalyst deactivation by starting up at lower temperatures and gradually increasing to the desired operating temperature (10).

In his later studies, Yeh found that presence of Ni was insignif-

icant for denitrogenation although Co, Mo, W had a positive effect. However, higher Co concentrations increased the carbonaceous material lay down. His other important finding was that all catalyst deactivation was due to pore mouth plug up and it was restored after burning off with air (11).

Specification Grades for the Upgraded Product

The product from the upgrading process must meet certain requirements. If it is going to be used as a boiler fuel, the requirements would be hydrogen to carbon mole ratio about 1.6, and nitrogen, sulfur, and mineral levels below 0.5 wt%. The sulfur level is determined from the current EPA standards (12). If the product is to be used as a feed stock to a conventional catalytic cracker, the nitrogen requirement is much more stringent. Catalytic cracking catalysts have acid sites which play a dominant role in cracking of hydrocarbon feeds. Nitrogen neutralizes these acid sites and acts as a poison. The more nitrogen in the feed, the shorter is the life of the catalyst. The preferred nitrogen level of a catalytic cracker feed is in the range of 100-400 ppm (13). Several hydrocracking processes can tolerate nitrogen levels up to 0.3 wt%. Two of these are Standard Oil of Indiana's ultracracking process and Union Oil's uni-cracking process (14, 15).

B. Research Objective

The objective of this research was to catalytically upgrade the SRC-II products to a feedstock suitable for conventional refineries or a boiler fuel.

To achieve this objective it was planned to:

1. test commercially available catalysts which are reported to be suitable for this purpose by former researchers or others.
2. find out how to extend the catalyst life.

The main problem in this research was considered to be the nitrogen content of the SRC-II products because it is hard to remove and causes severe catalyst poisoning in further refining steps. Sulfur is also a problem in terms of pollution and catalyst poisoning but it is easier to remove.

C. Chemistry and Theory of Hydrotreating Catalysts and Catalyst Activity

Catalysts for upgrading of coal derived liquids should have both hydrogenation and hydrocracking characteristics in order to remove heteroatoms. They must be strong enough to stand up for a long time to successive regenerations.

Most of the catalysts used in heteroatom removal are metal oxide impregnated carriers. Selection of carriers is very important because they should have suitable physical properties and also promote acidity for hydrocracking purposes. It has been shown that acidic carriers such as alumina-silica and activated Fuller's earth improve the hydrocracking activity of a catalyst because of their acidic nature (16).

In general, catalysts that promote hydrocracking also promote isomerization reactions above 400°C, which are likewise strongly dependent upon the acidic characteristics of a catalyst (16).

When the acidity of a catalyst alone is considered, generally, pure compounds are less acid than combinations. Acidity of various compounds, starting from the least acid, are: silica, alumina, silica-alumina. The metals on the support also effect the acidity. It was found that nickel oxide reduces the overall acidity of a catalyst, whereas molybdenum oxide increases it (17).

The most commonly used commercial catalyst is a mixture of cobalt and molybdenum oxides on a gamma-alumina support. The others are Ni-Mo/Al_2O_3 and Ni-W/Al_2O_3. The latter is more expensive. The ratio of Mo/Co or Mo/Ni must be greater than one. Each of above is sulfided before use to increase the activity. Presulfided metal oxide catalysts are considerably more important in the case of Ni-Mo/Al_2O_3 than with Co-Mo/Al_2O_3 catalysts. If not presulfided before use, NiO may be reduced to metallic Ni by the reducing environment in the reactor, and if so, some H_2S addition is advised (18). It is also suggested that each individual catalyst may be sulfided under different conditions. In general degree of sulfiding at catalyst surface is higher at higher temperatures (375°C). This is true for bulk weight of sulfur too (19).

The structure of sulfided metal oxides is complex. They are usually represented as MoS_2, Co_9S_8 and WS_2. MoS_2 by itself is more active than Co_9S_8 but a mixture of the two is more active than either alone. However, the mechanism of their interaction is still speculative. Compounds formed as a result of reaction of these species with alumina contribute little catalyst activity. Their role is essentially that of a support. The metal sulfides, MoS_2 and WS_2 form layered type structures in which layers of S atoms alternate with layers of metal atoms. At the edges of such a structure, atoms of Ni or Co might intercalate into the MoS_2 or WS_2 structure, forming the active sites (18).

Hydrogenitrogenation and Hydrodesulfurization

SRC-II liquids contain 1.2% to 0.8% nitrogen and 1.3% to 0.7% sulfur, depending upon the fraction of the product and source of coal used in the process. For example, SRC-II LECF contains 0.88% nitrogen and 1.21% sulfur, SRC-II VFF contains 1.17% nitrogen and 0.72% sulfur. These heteroatoms have to be reduced to certain levels (see sec. I.A) depending upon how the product is to be used.

Nitrogen and sulfur are present mostly in coal liquids as heterocyclic ring compounds. Representative nitrogen compounds and their physical properties are listed in Table IV. The basicity of these nitrogen compounds is very important for further catalytic reactions such as acid catalyzed reactions of catalytic cracking, since they will poison the catalyst.

Less is known about the hydrodenitrogenation of heterocyclic ring compounds than of the analogous reactions with heterocyclic sulfur compounds. In general, the heterocyclic ring is first saturated, and then the ring is fractured at a C-N bond. Nitrogen is removed from the resulting amine or aniline as ammonia (20). The reaction of pyridine is given as an example below (21):

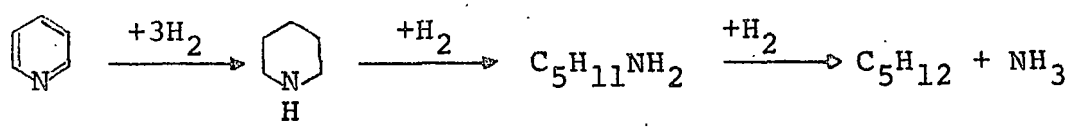
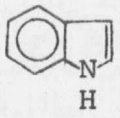
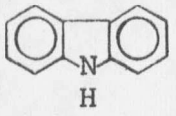
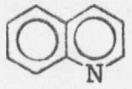
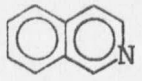
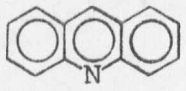


TABLE IV

Representative heterocyclic nitrogen compounds (18)

Name	Formula	Structure	Basicity	Solubility in water
Pyrrole	C_4H_5N		w/n*	insoluble
Indole	C_8H_7N		w/n	soluble hot hot
Carbazole	$C_{12}H_9N$		w/n	∞
Pyridine	C_5H_5N		s**	∞
Quinoline	C_9H_7N		s	6 pts/100
i-Quinoline	C_9H_7N		s	slightly
Acridine	$C_{13}H_9N$		s	slightly hot

* weak or not basic

** strong

On a Ni-Mo catalyst, which accelerates hydrogenation reaction, the first step can proceed to a nearly equilibrium concentration of piperidine under a wide range of reaction conditions of industrial interest (22, 23).

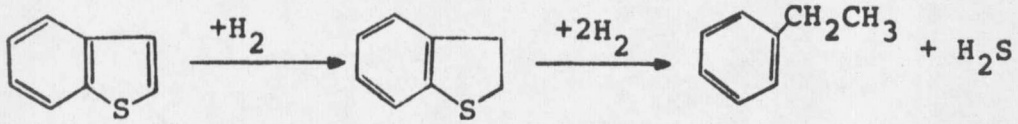
The intermediate product, piperidine is more of a catalyst poison than pyridine because it has an obstructively long absorbed life on the catalyst surface (24).

With quinoline, analogous reactions occur but a greater variety of intermediate compounds are formed. The overall reaction network is relatively complex. Quinoline is converted to 1,2,3,4-tetrahydroquinoline, 5,6,7,8-tetrahydroquinoline and decahydroquinoline, followed by hydrocracking to form aromatic and saturated cyclic amines, and then cyclic hydrocarbons (22).

Sulfur in coal liquids is present as thiophenes and thiophene derivatives. Under industrial conditions reactivity of these decreases in the following order: thiophene, benzothiophene dibenzothiophene, methyl substituted benzothiophenes. Methyl groups in the 2 and 5 position cause the greatest inhibition, presumably by steric effect. With dibenzothiophene, the presence of methyl groups in the 4 or 4 and 6 positions likewise greatly decreases the reactivity of dibenzothiophene, but the reactivity is increased when they are in the 3 and 7 or 2 and 8 positions (25).

With benzothiophene, substituted or unsubstituted, the thiophene

ring is hydrogenated to the thiophene derivative before the sulfur atom is removed, in contrast to the behavior of thiophene. In the latter case, in the presence of basic nitrogen compounds, removal of the sulfur atom and the donation of hydrogen to the structure occurs simultaneously (18, 23).



Hydrodesulfurization and hydrodenitrogenation reactions interact with each other in a complicated manner. Under some circumstances one inhibits the other, but under other circumstances H_2S formed by the HDS reaction enhances the HDN reactions (23, 26).

D. Catalyst Deactivation and Regeneration

Deactivation occurs due to carbonaceous material laydown, nitrogen bases and metallic ions. The latter is permanent and the catalyst activity can not be restored. The former two can be removed by burning off with air and activity is restored.

In poisoning by nitrogen bases, the basicity of the compound and the molecular weight play an important role but the molecular weight is the dominant one. Starting from the most effective poison, these are: quinaldine, quinoline, piperidine, decylamine and aniline (27).

During upgrading of coal liquids, the most serious and fast deactivation is caused by carboneceous material laydown (11). Catalyst is regenerated by air burnoff. The most important factor in regeneration is temperature. It has to be kept under 600°C to ensure against deactivation of the catalyst by sintering (17, 27).

II. EXPERIMENTAL

A. Outline of Research

Two areas were investigated in this research. First, three commercially available catalysts, which have large surface area, pore volume and pore diameter for free passage of liquified coal molecules, were tested. Second, the best of these, Harshaw HT 400 E 1/32", was tested by long continuous runs. The effect of water on denitrogenation was tested during these long runs by making two sets of experiments, one with water addition to the feed and the other without water addition.

Test of Commercially Available Catalysts

Three different catalysts, Nalco Mo 477 E 1/16", Nalco NM 502 E 1/16", and Harshaw HT 400 E 1/32", were tested for their denitrogenation capabilities and their life on stream. A total of eleven continuous runs were made with them; five with Nalco Mo 477, three with Nalco NM 502, and three with Harshaw HT 400. SRC-II Vacuum Flash Feed (VFF) was used for all of these runs (see Table III for its properties).

Operating conditions were relatively moderate (see Table V for details of operating conditions).

TABLE V

Operating Conditions for the Test of Commercial Catalysts

Nominal Reactor Temperature,	°C	425 ± 10
Feed Temperature ,	°C	80 ± 10
Pressure ,	psig	1000 ± 50
H_2 Flow Rate	scf/bbl of oil	10,000 ± 500
LHSV		1.0 ± 0.1

Durability Test of Harshaw HT 400 E 1/32"

As it was mentioned before, two sets of experiments were designed for this purpose. SRC-II Light Ends Column Feed (LECF) were used as feed stock for these experiemnts (see Table III for its properties). Conditions of these runs are explained below.

Water addition to the feed was proposed for the first experiment in order to see the effect of water on denitrogenation and catalyst life. Two 160-hour-runs were made with 1.5 volume% water added to the feed. Operating conditions were the same as listed on Table V except 475°C was the nominal reactor temperature. The system was operated 10 or 15 hours a day and kept under hydrogen pressure for the rest of the day or for a couple of days when the system was not operating.

The second experiment was made without any water addition to the feed to compare with the former one. Two 160 hour-runs were made. The operating conditions were the same as listed on Table V. For the first run, the system was kept under hydrogen pressure or very low hydrogen flow when the system was not operating to prevent coke formation. The second run was 160 hours non-stop.

In both experiments runs were started at 390°C and gradually increased to the desired operating temperature. LHSV was 50 for the first minute and then decreased to 1.0. The reason of this treatment was to reduce initial deactivation.

Catalyst Regenerations

The catalyst was regenerated by burning off with O_2 -N_2 mixture between each cycle of the durability tests of Harshaw HT 400. For the first 12 hours, a 5% O_2-95% N_2 mixture and for the second 12 hours, a 40% O_2-60%N_2 mixture was used. Burnoff took place in the 540-590°C temperature range. After each burnoff, the catalyst was sulfided with 10% H_2S and 90% H_2 mixture for 12 hours at 325-350°C.

B. Materials

Two kinds of SRC-II liquids, Light Ends Column Feed (LECF) and Vacuum Flash Feed (VFF), were used as feed stock (see Table III for their properties). VFF was used for the test of commercial catalysts and LECF was used for the durability tests of Harshaw HT 400.

The catalysts used were commercially produced hydrotreating catalysts (see Table VI for their properties). Both 1/4" and 1/8" Denstone inert supports were obtained from Norton Company (28).

C. Equipment

All experiments were carried out in a trickle bed reactor made of a 1-inch I.D. 40 inches long schedule 80 Inconel pipe (see Fig. 3 for details of the system). A liquid-gas separation unit is attached to the reactor. Some specific features of which are:

1. Condensing the product in a shell and tube heat exchanger.
2. A back pressure regulator which maintains the system pressure constant and lets the products go out at atmospheric pressure.
3. Two pressure gauges to indicate the system pressure and to control the back pressure regulator respectively.
4. An emergency relief valve to the vent.
5. A collection pipe to collect the heavy particles by precipitation and a valve at the end to purge these. This valve is used for cleaning purposes too.
6. A liquid-gas separator where gases go to vent and liquids are collected in a bottle continuously.

The reactor was placed in a heating unit to maintain the reaction temperature at a specified level. The heating unit is built by wrapping a 6-inch O.D. and 1-inch I.D. aluminum block which is 3-feet long,

TABLE VI

Properties of Commercial Catalysts

Catalyst	Metal Load			Surface Area	Pore Volume	Pore diameter
	MoO_3	CoO	NiO			
	wt%	wt%	wt%	m^2/gm	ml/gm	Å
Nalco Mo 477 E 1/16"	14	3.3	-	250	0.55	88
Nalco NM 502 E 1/16"	14	-	4	240	0.53	88
Harshaw HT 400 E 1/32"	15	3	-	210	0.5	95

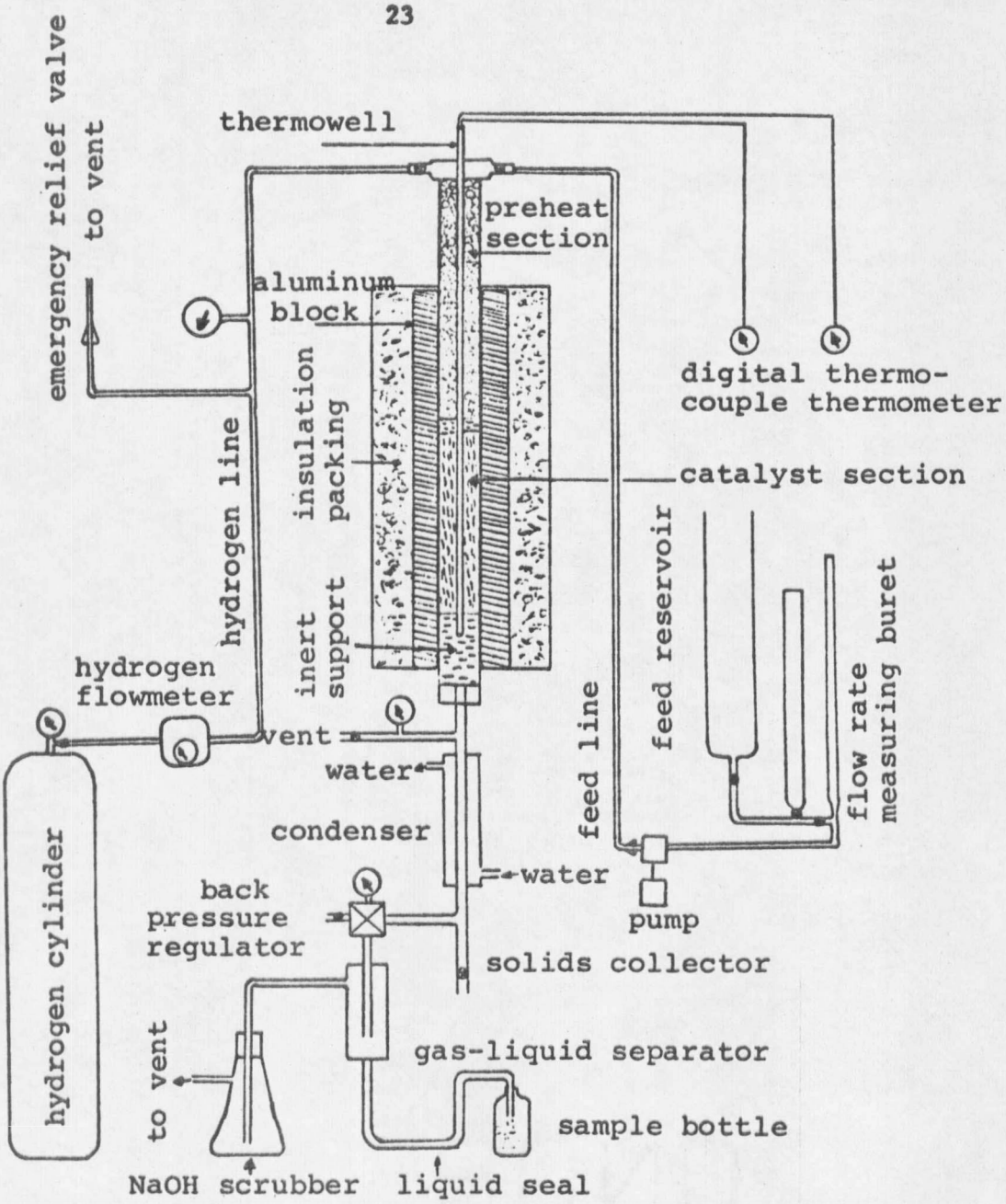


FIGURE 3. Experimental Set Up

with a nichrome wire heating coil encased in ceramic beads. Each of three coils is connected to a powerstat variable transformer which is manually controlled for temperature. The heating unit is insulated against heat losses. Two iron-constantan thermocouples were placed in the thermowell. These allow the monitoring of one temperature at the entrance of the catalyst section and another one in the catalyst section.

The SRC-II feed was pumped into the top of the reactor by a Milton Roy Model MR-1-49 Simplex packed piston pump through a 1/8" stainless steel pipe. The pump is equipped with a manually controlled micrometer adjustment for feed rate control. All oil feed lines and reservoirs (not applicable when LECF is used) were wrapped with Cole-Palmer flexible heating cords (29) to prevent the feed from freezing up.

Technical grade hydrogen is fed through a pressure regulator, a 1/8" pipe, a micrometer valve (to adjust the flow rate), a Brooks Thermal Mass Flowmeter (30), and a ball check valve to the top of the reactor.

The exit gases are first passed through water and then 10% NaOH-water solution before venting.

D. Procedures

Experimental Runs

The reactor was first cleaned and all inlets were checked for plugs before each run except after burnoffs. The reactor was loaded with inert supports and catalyst as following: first the thermowell was placed in the center of the reactor and tightened very well against leaks. The top of the reactor was filled with 175 ml of 1/4" spherical Denstone inert support, followed by 25 ml of 1/8" cylindrical Denstone inert support and a mixture of 60 ml of catalyst and 60 ml of 1/8" inert support; the rest of the reactor was filled with 1/8" inert support. A few layers of stainless steel screen was placed at the bottom to support the reactor bed. All screws were sealed with Anti-sieze or Silver Goop and Teflon tape and then tightened to prevent leakage.

The reactor was placed in the heating unit and connected to the separator. All valves were closed before pressurizing the system with nitrogen. All connections were checked for leaks with snoop. In case of any leakage, it was fixed before turning the heaters on.

The reactor was left under nitrogen pressure until the desired temperature was reached. Then the hydrogen inlet line was connected to the reactor and nitrogen pressure was released. The system was pressurized with hydrogen and checked for leaks again. If there was no leak, hydrogen flow rate was adjusted. Reservoirs were filled

with preheated SRC-II (not applicable to SRC-II LECF), the feed line heaters were turned on and the pump was started to fill the feed line by pumping into the reservoir. Then the pump was stopped and prefilled feed line was connected to the top of the reactor. After opening the feed line valve at the reactor inlet, the pump was started and the run was begun.

The feed flow rate was adjusted and measured by timing the amount of liquid pumped from the buret. For the test of commercial catalysts, samples were taken at 15-minute intervals. The flow rate was checked after each sample was taken. For the long runs, samples were taken at 5 or 10-hour intervals and the flow rate was checked only occasionally (usually at one hour intervals), because SRC-II LECF was easier to handle.

When the run was completed, the pump was shut down and hydrogen was let flow for several more hours to make sure that oil left in the reactor had time to react (not applicable for the test of commercial catalysts). Reservoirs and the feed line were cleaned by pumping acetone through the reservoirs.

At the end, the hydrogen inlet was closed and the system was depressurized. Heaters were turned up when catalyst regeneration was desired.

Catalyst Regenerations

While the system was heating up, the reactor was flushed with nitrogen to remove hydrogen left in it. Otherwise hydrogen could cause a sudden temperature jump at the beginning of the burnoff.

When the reactor temperature reached 550°C, the 5% O_2 cylinder was connected to the top of the reactor. The flow rate was adjusted so that the reactor temperature was below 590°C. After 12 hours of burningoff, it was switched to 40% O_2 to complete the process faster. When the burnoff was completed, usually after another 12 hours, the oxygen line was disconnected and the reactor was removed from the heating unit for sulfiding.

The completion of burnoff was tested by increasing the oxygen input and/or by checking the presence of smoke at the vent stream. If there was no temperature increase when the oxygen input increased, completed burnoff was indicated. A clear vent stream also indicated the same thing.

To sulfide the catalyst, the reactor was placed in the heater of the sulfiding unit so that the catalyst section was at the center of the heater. The heater was turned on and the hydrogen sulfide inlet and outlet lines were connected to the reactor. Extreme precautions were taken during sulfiding because H_2S is highly poisonous. All connections were checked for leaks before the gas was flowed through the reactor. Outlet gases were scrubbed with 20% NaOH-H_2O solution before

venting.

Sulfiding was carried out under very slow H_2S flow rate and at 325-375°C for 12 hours. When sulfiding was over, inlet and outlet lines were disconnected and the reactor was removed from the sulfiding unit for a new run. The reactor was placed in the heating unit of the experimental set up as described above. Then it was flushed with nitrogen to remove unreacted H_2S. Otherwise it might cause corrosion in the moist reaction environment.

Sample Pretreatments

After taking each sample, the weight and volume of the product was recorded. Water was separated from the oil by decantation and called residual water (not applicable to the test of commercial catalysts). Then the oil was washed with excess water to remove water soluble nitrogen compounds. The water was separated from the oil by freezing.

Oil, residual water and wash water were analyzed for their nitrogen content. Only oil samples were analyzed for sulfur content.

Analytical Procedures

Nitrogen analysis was done by the Macro-Kjeldhal method (31, 32, 33). The percent denitrogenation was calculated with the following equation:

$$\text{wt\% DN} = \frac{\text{wt\% N in the Feed} - \text{wt\% N in Oil}}{\text{wt\% N in the Feed}}$$

Sulfur analysis was done by the quartz tube combustion method using a Bico-Braun Shell design sulfur apparatus (31, 34, 35). Percent desulfurization was calculated with a similar equation by replacing wt% N with wt% S in above equation.

The extent of cracking was determined by ASTM D-86 atmospheric distillation (36). This technique measures the cumulative amount of product which boils below 700°F or when decomposition begins, which ever occurs first.

III. RESULTS AND DISCUSSIONS

As it was mentioned above (sec. II), three different commercial catalysts were tested for their denitrogenation capability and best of them, Harshaw HT 400, was subjected to long runs. Two sets of experiments, one with water addition and the other one without water addition, were made with it to find the best condition.

A. Test of Commercially Available Catalysts

The three catalysts tested are discussed case by case below. For an easy comparison the best results from each catalyst are plotted in Fig. 11. Although the conditions were different for different runs the comparison of the results are still meaningful. The reason why conditions were not the same is the difficulty in handling the SRC-II VFF and the problems in flow rate measurements. SRC-II VFF always caused pumping system plug ups and problems in reading buret divisions. Making at least three runs with each catalyst eliminated some of the potential errors. The detailed data of each run are listed in Appendix.

Denitrogenation Results

Since denitrogenation of SRC-II liquids was considered to be the major problem, all catalyst evaluations were based on their ability to remove nitrogen present in the feed and to protect their activity

longer. Generally the longer a catalyst lasts the more economical it is for commercial use. A total of 11 runs were made with the previously mentioned three commercial catalysts (see Table VI for their properties).

In runs T-1A to T-5A, Nalco Mo 477 E 1/16" was tested. All nitrogen results are plotted in Fig. 4 as wt% nitrogen in the product vs. time of run. Run T-1A was made with unpresulfided catalyst to see the difference between unpresulfided and presulfided catalyst. As it can be seen from Fig. 4 and Fig. 5, nitrogen content of the product was higher, but the rate of deactivation was lower than the presulfided catalyst. However, deriving a conclusion from a single run can be misleading.

Run T-2A was made with presulfided catalyst but because of a failure in controlling the flow rate, the average LHSV was 1.9 for this run. As a result, the catalyst was deactivated within an hour.

Run T-3A was made to repeat the former one. However, some of the samples were lost during lab analysis due to defective bottles. At the same time, very fluctuating nitrogen analysis were obtained mainly because of non-homogeneous samples. During the process, some water was produced by a deoxygenation reaction and water soluble nitrogen compounds, such as NH_3, piperidine, and etc., were dissolved in this water layer. There was a great possibility that the test samples were

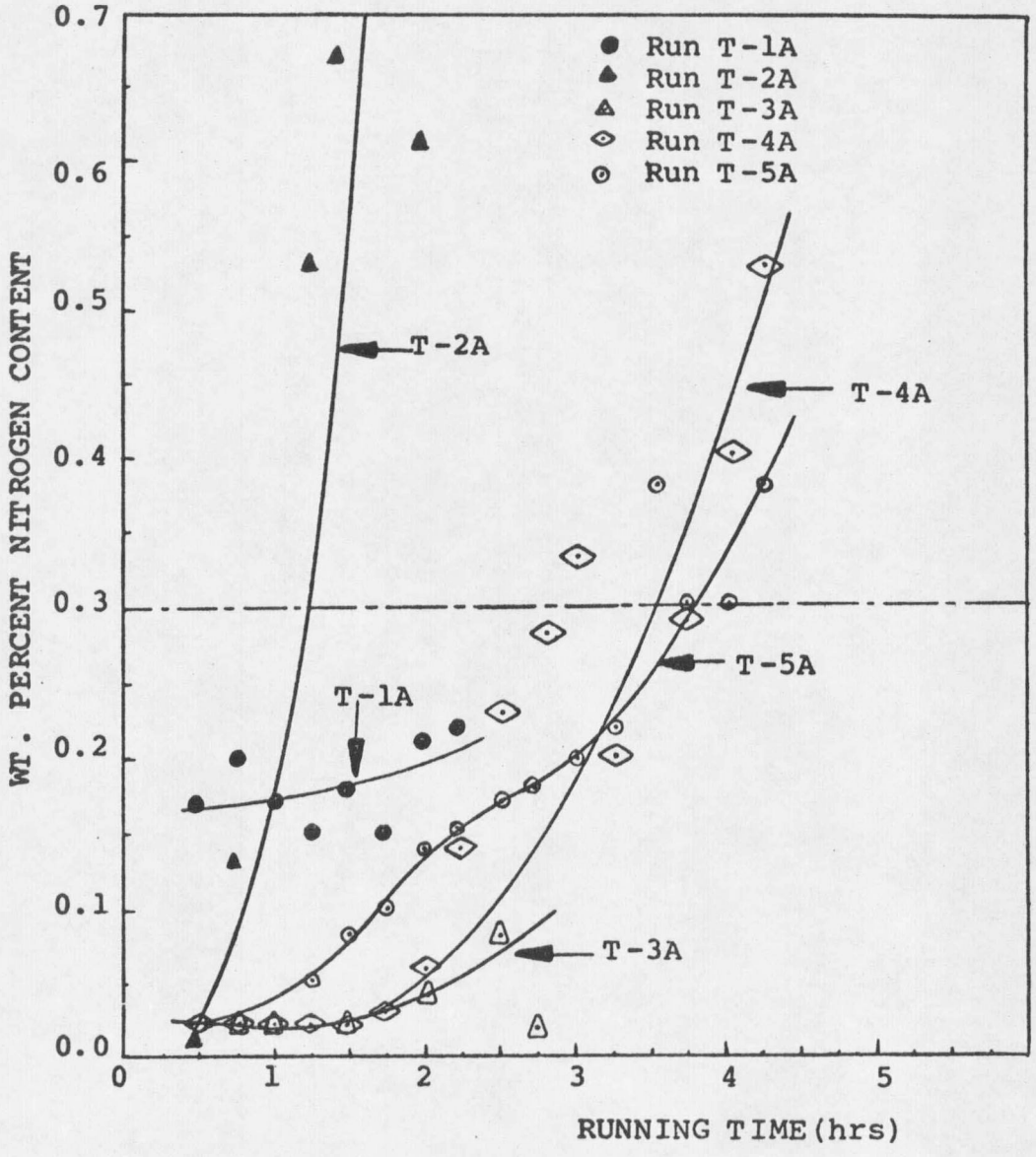


FIGURE 4. Percent Nitrogen Content of Oil vs. Running Time for Nalco Mo 477

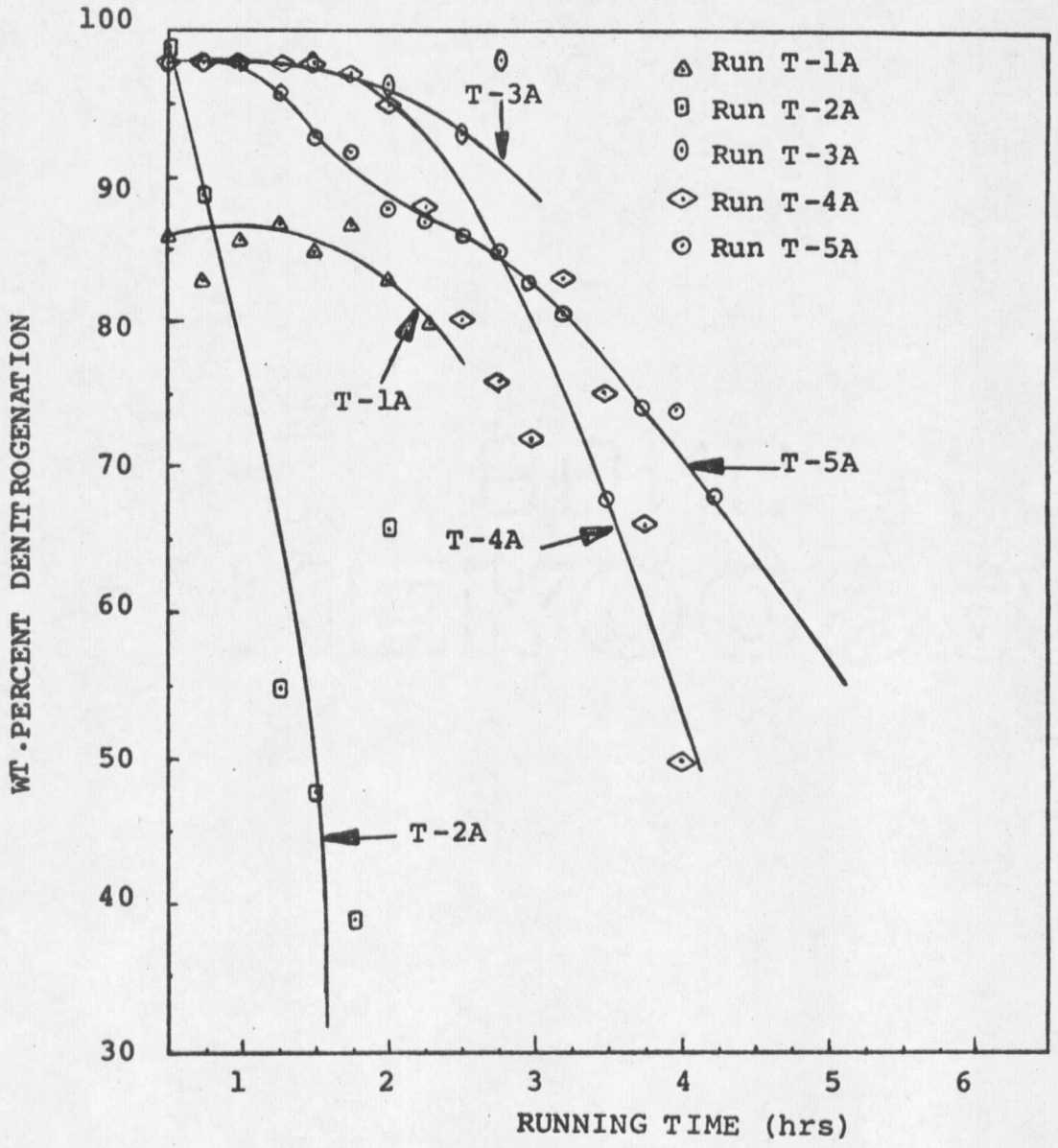


FIGURE 5. Percent Denitrogenation vs. Running Time for Nalco Mo 477

taken from that water layer in lab analysis. The smooth distribution of the nitrogen content in the oil throughout the entire running time intervals, when the samples washed with water and oil separated for analysis, proved this argument. There were also more nitrogen in the water than in the oil (see Table XI in Appendix). The results from the washed samples are plotted in Fig. 5.

Run T-4A was made to repeat the previous one but the micrometer valve at the hydrogen flowmeter inlet was broken during the run and plugged the hydrogen line. As a result hydrogen flow rate steadily decreased to 5,000 scf/bbl of oil. Figure 5 shows the sharp increase in nitrogen content as hydrogen flow rate decreases.

Then Run T-5A was prepared to make a run under the desired conditions and it was succesful until a pumping failure occured 30 minutes before the desired completion time (5 hours). Four hours were enough to see the trend of deactivation of the catalyst. Samples were washed again and both oil and wash water were analyzed for nitrogen content (see Fig. 4 for nitrogen content of oil). Percent nitrogen removal from the product by washing as a function of running time is plotted in Fig. 6. The removal of nitrogen by washing decreases as running time increases because production of water soluble nitrogen compounds decreases as the catalyst deactivates. An average of 57% of the nitrogen in the product was removed by washing.

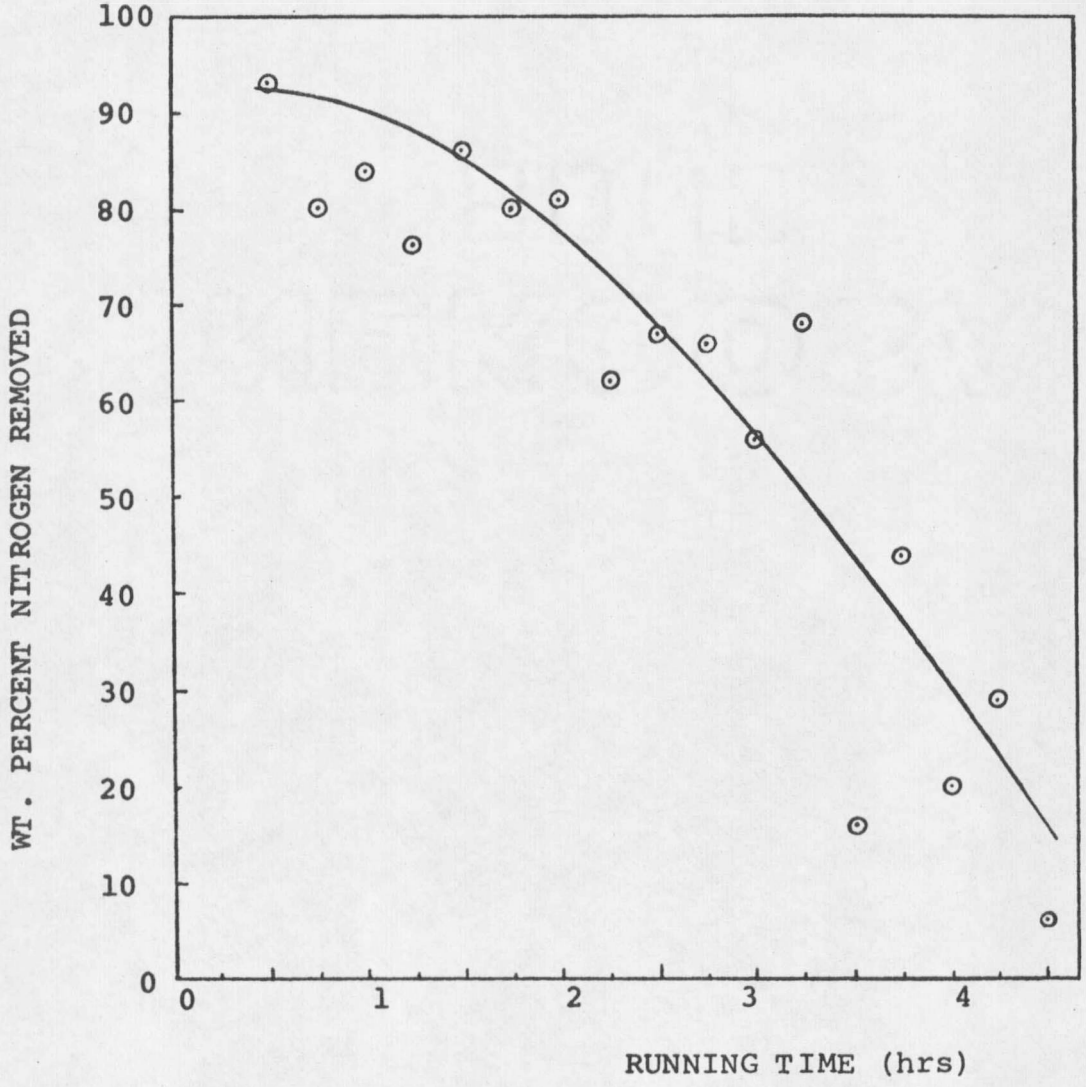


FIGURE 6. Percent Nitrogen Removal from the Product by Washing

In this research, the activity of the catalysts was measured by percent denitrogenation. Results of five runs are plotted in Fig. 5 as percent denitrogenation vs. time to determine rate of deactivation as a run continues.

The best of these five runs was Run T-5A which was made under the desired conditions and gave specification grade product for four hours. This shows that this catalyst has an active life around four hours.

The second commercial catalyst tested was Nalco NM 502 E1/16". A total three runs were made with this catalyst and the nitrogen content of the product is plotted in Fig. 7.

Run T-1B was made with unpresulfided catalyst. Because of a problem in the flow rate measuring system, it was hard to obtain a steady flow rate, so the LHSV fluctuated around 1.5. Samples were washed and analyzed for nitrogen content (see Fig. 7). Figure 7 shows how a high LHSV causes fast deactivation.

Run T-2B was made with presulfided catalyst but discarded because of an undesired high LHSV.

Run T-3B was made to repeat the former run and it was succesful. It was a four-hour-run and gave specification grade product for three hours. As a result, this catalyst was not as effective as the former one for denitrogenation.

The percent denitogenation vs. time for two runs are plotted in

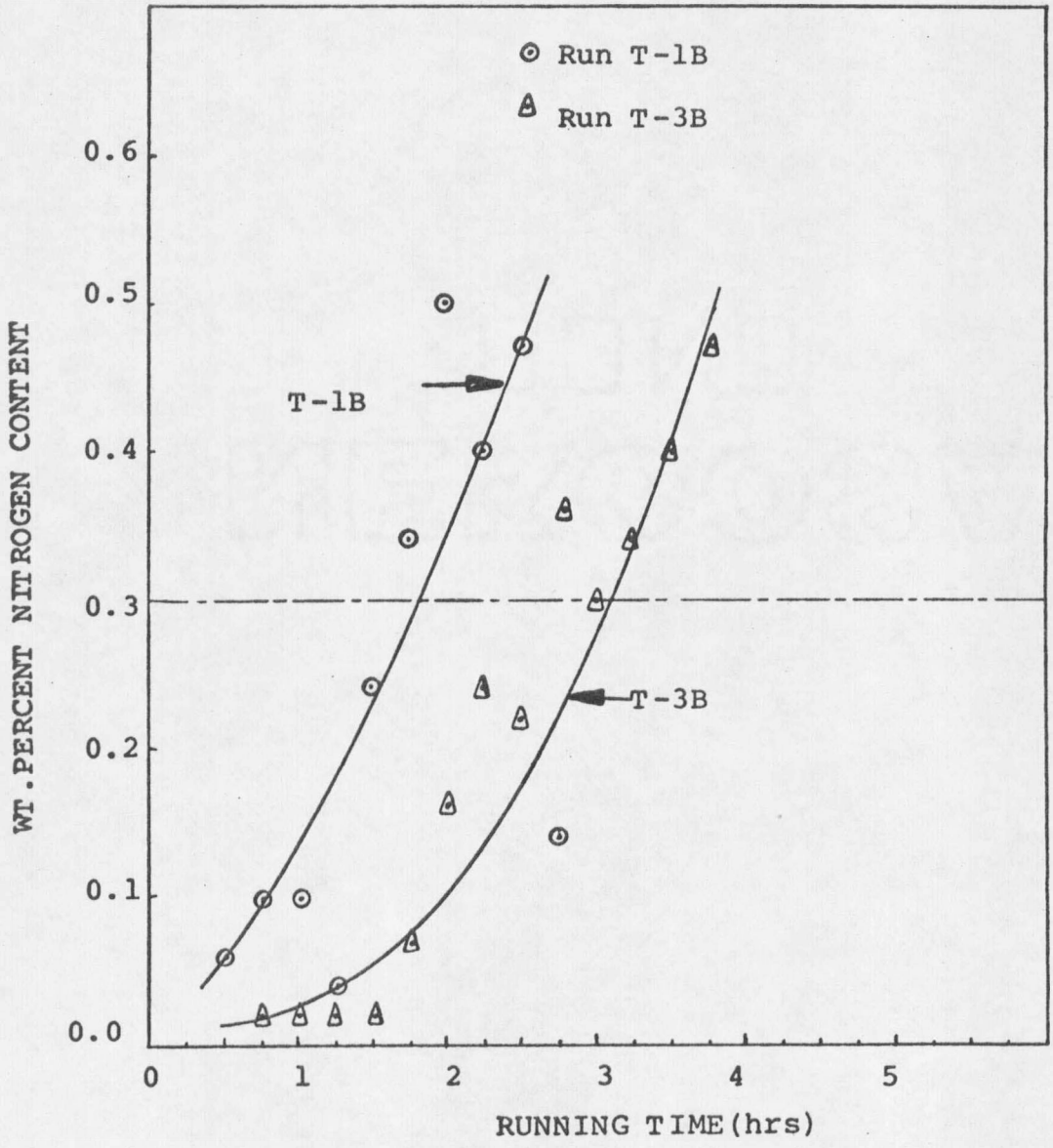


FIGURE 7. Percent Nitrogen Content of Oil vs. Running Time for Nalco NM 502

Figure 8 to determine the rate of deactiviation. This catalyst deactivated faster than the former one.

The last commercial catalyst tested was Harshaw HT 400 E 1/32" and three runs were made under different operating conditions. Figure 9 and Fig. 10 show the percent nitrogen in the oil and the percent denitrogenation as a function of running time for these runs. All of the samples were washed before nitrogen analysis.

The first of these three, Run T-1C, was made with presulfided catalyst and it was a 6.5-hour-run. It gave specification grade product for 4.5 hours. One important factor, presence of water in the feed, was observed during this run. The water was in the SRC-II VFF itself and estimated to be around 1%. In previous runs the SRC-II VFF was heated on a heater before putting it into the feed reservoir to increase its fluidity. In this case it was put into the feed reservoir as received from the storage drum so the water in it was preserved.

As it can be seen from Fig. 10 and Fig. 11 the rate of deactivation of the catalyst is lower than the others. That could have been because of presence of water in the feed.

To see the effect of water, Run T-2C was made with presulfided catalyst and preheated feed was used. The catalyst was deactivated within three hours and deactivation was faster. This was an indication of the positive effect of water in the feed on catalyst activity.

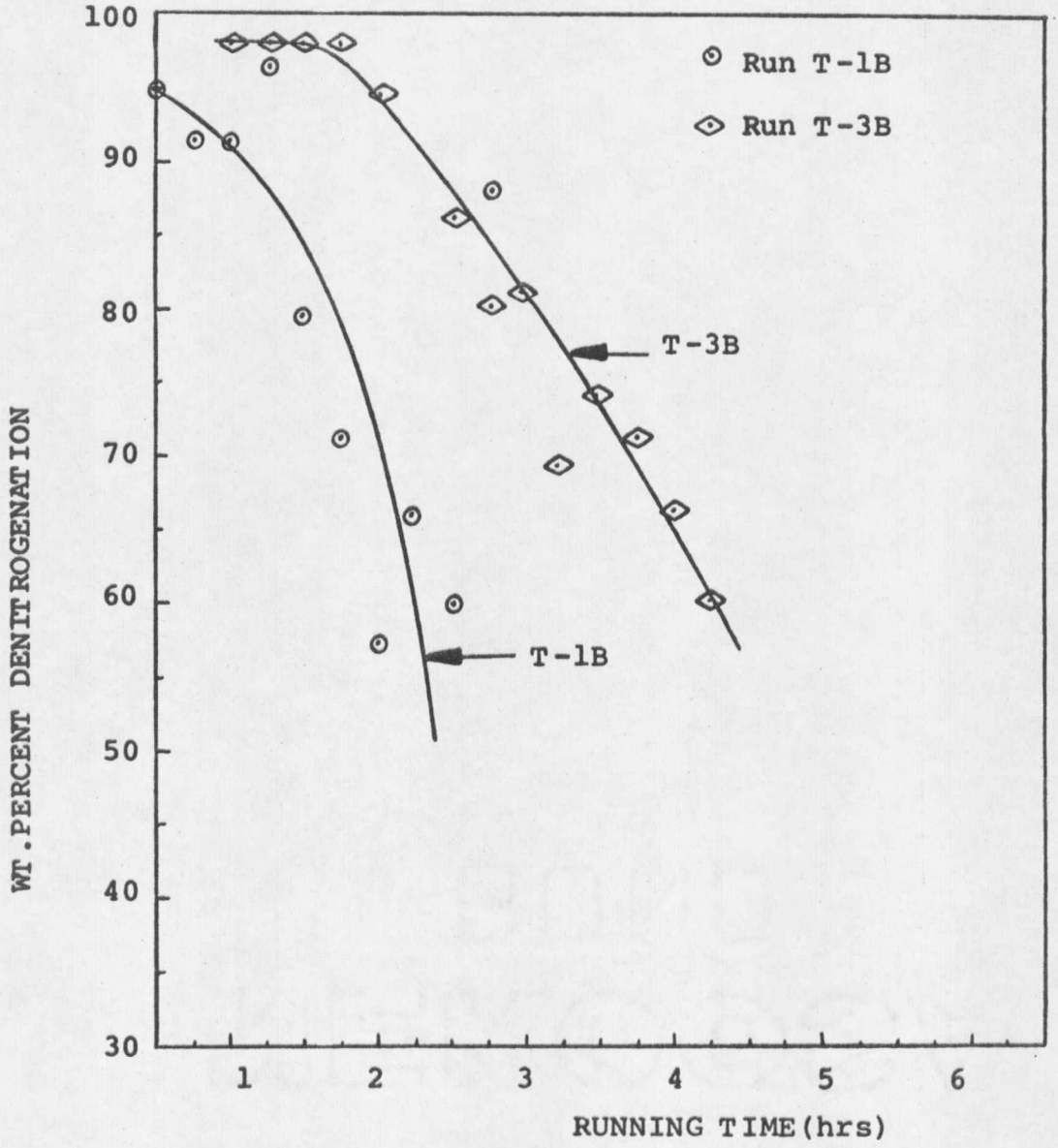


FIGURE 8. Percent Denitrogenation vs. Running Time for Nalco NM 502

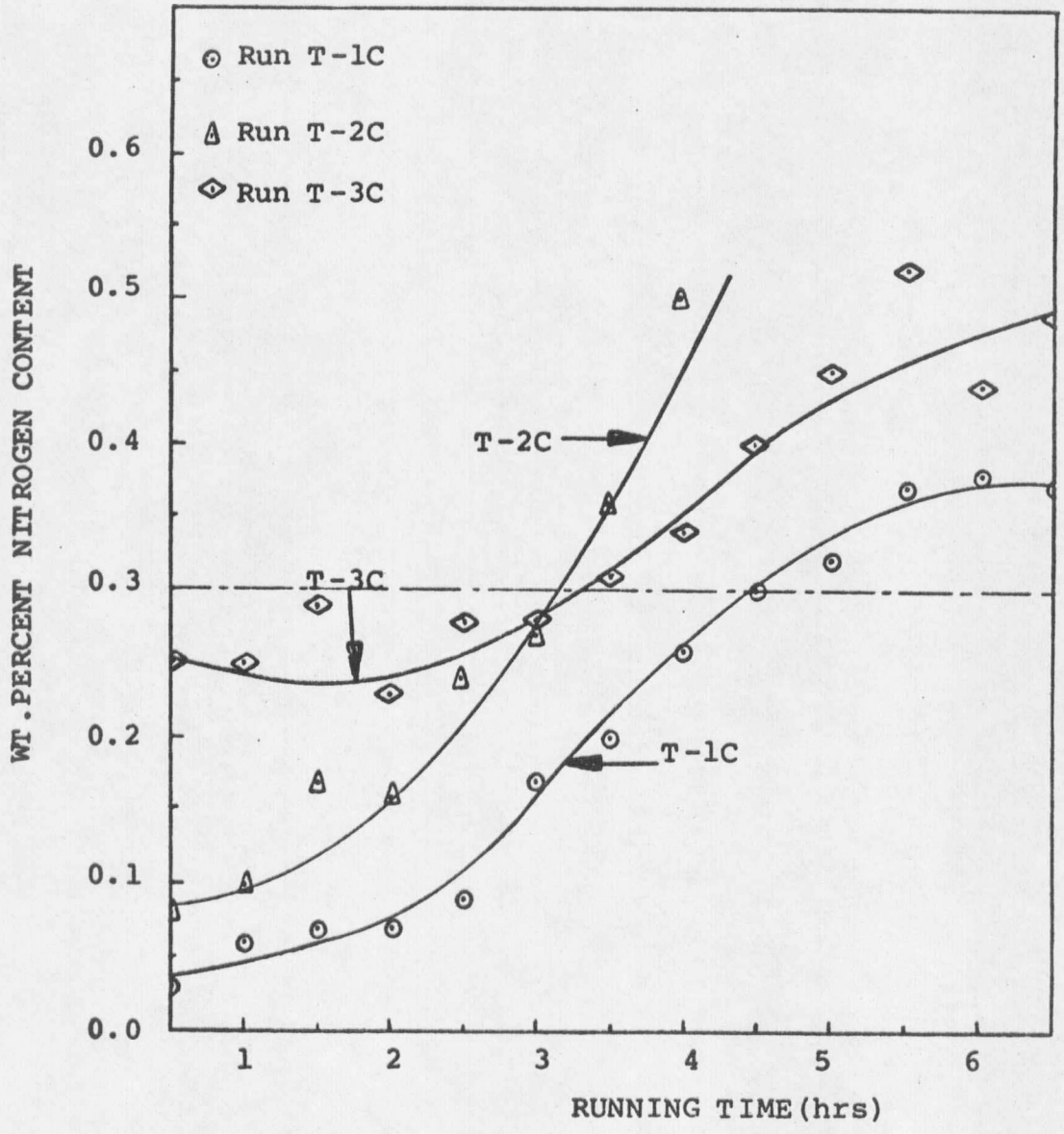


FIGURE 9. Percent Nitrogen Content of Oil vs. Running Time for Harshaw HT 400

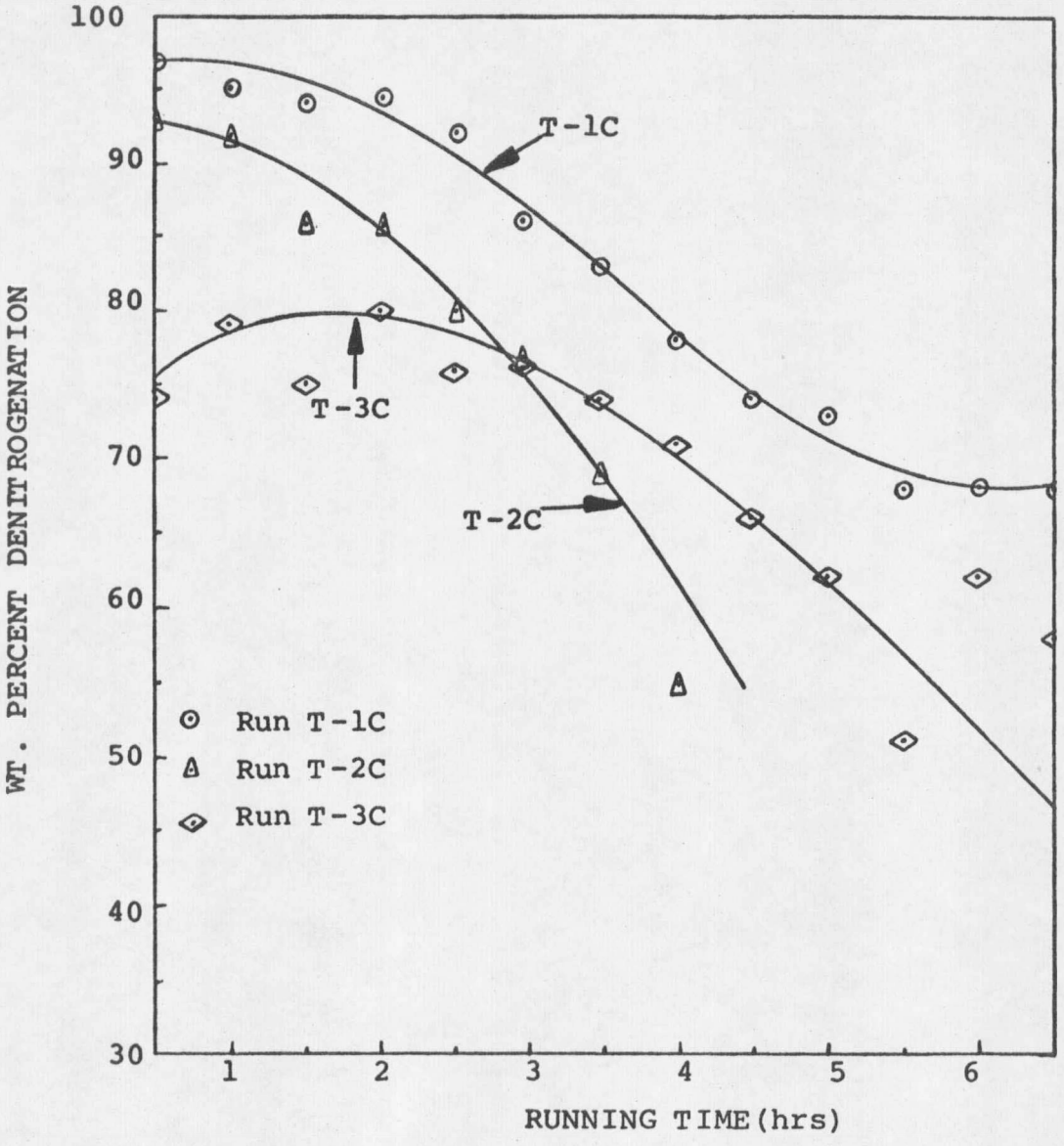


FIGURE 10. Percent Denitrogenation vs. Running Time for Harshaw HT 400

However, it was too early to make a conclusion.

The third run, Run T-3C, was made with 5% (vol.) water addition to the feed. Unfortunately, at the beginning of the run, the LHSV was higher than that desired. Water in the feed caused fog formation and made it hard to read the flow rate. The average LHSV was around 2.0 for the first thirty minutes. That caused some initial deactivation of the catalyst but the result was better than the second run. This run also showed that deactivation of the catalyst was slower with water in the feed.

These runs were not sufficient to conclude the positive effect of water in the feed on catalyst activity. There were two reasons for that; first, it was found that SRC-II VFF was polymerized and longer heating at higher temperatures caused solidification of it; second, replication of these runs was needed.

The results of the best runs from these catalysts are plotted in Fig. 11 as percent denitrogenation vs. time to compare the activities of the three catalysts. As Harshaw HT 400 (Run T-1C) showed a lower rate of deactivation and leveling after a certain period of time, Nalco Mo 477 and Nalco NM 502 showed higher rate of deactivation and no leveling. Nalco NM 502 gave very good denitrogenation for the first two hours and very sharp decrease in activity after that. However, it is not possible to derive absolute conclusions from these results because of unequal conditions.

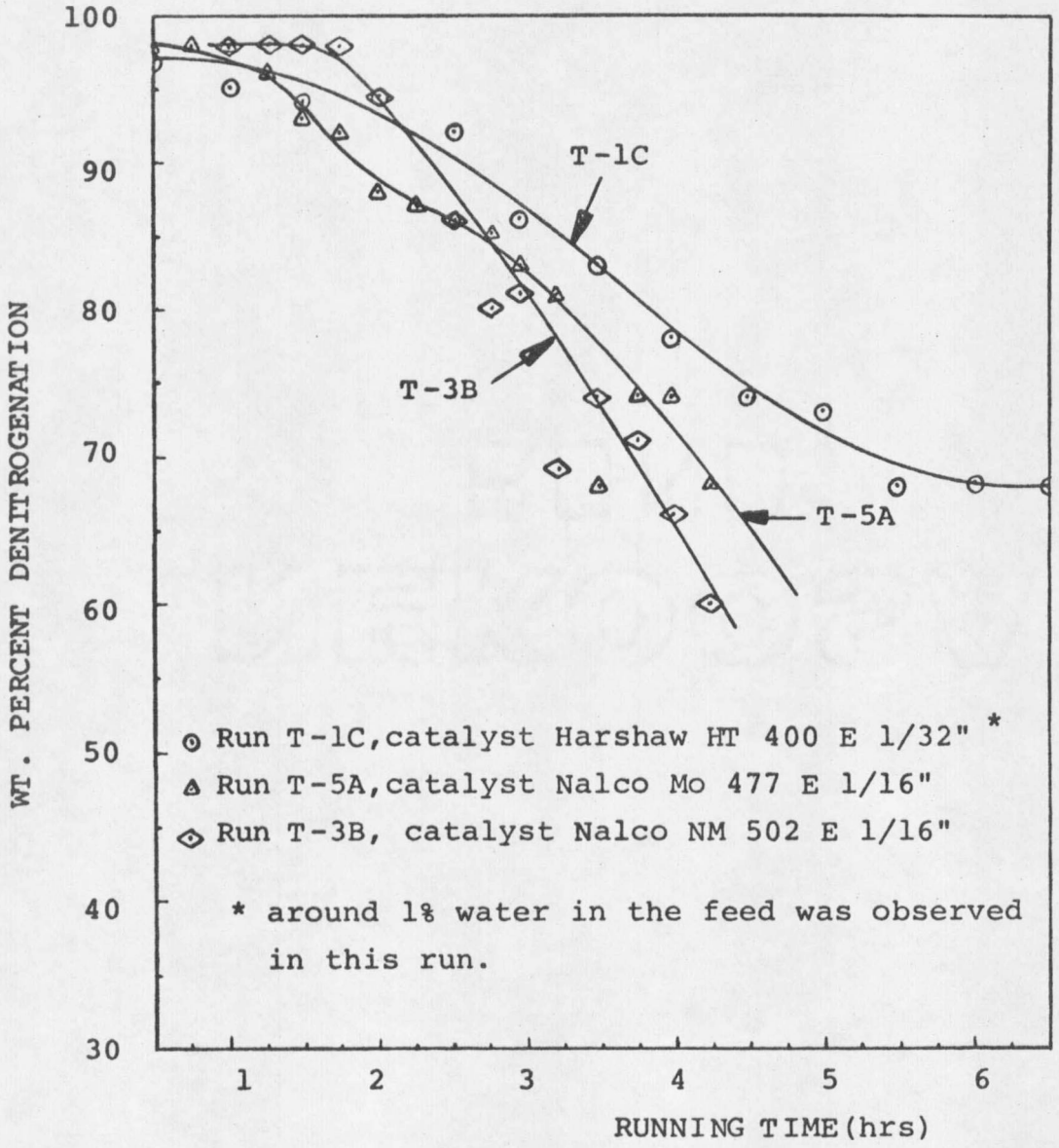


FIGURE 11. Percent Denitrogenation vs. Running Time for the Best Runs From Each Catalyst

The summary of averaged results is shown in Table VII. When the results are compared in this table, time of run and operating conditions have to be taken into account otherwise they can be misleading.

Desulfurization Results

Although the aim of this work was to achieve the best denitrogenation, sulfur also has to be removed as much as possible. That is why some of the samples were analyzed for their sulfur content. Table VII summarizes the averaged percent sulfur content and desulfurization for each run. Catalysts in general retained their activity in terms of desulfurization for a longer time and the rate of deactivation was lower.

Figure 12 shows percent sulfur content of oil and percent desulfurization as a function of running time for Nalco Mo 477. As can be seen, different conditions affected the desulfurization activity of the catalyst similar to the denitrogenation activity. Run T-5A gave the best desulfurization for this catalyst.

Samples from Run T-3B were analyzed for sulfur (see Fig. 13) and desulfurization was better than denitrogenation for Nalco NM 502 as it was for the other catalysts. Samples from all three runs with Harshaw HT 400 were analyzed for sulfur content of oil (see Fig. 14) and Run T-3C was the best for desulfurization. Desulfurization activity of the catalyst was similar to denitrogenation activity under different conditions. It can be said that they are interrelated.

TABLE VII

Summary of the Averaged Results from the Test of Commercial Catalysts

Catalyst	Run No.	Total Time (hrs)	Average LHSV (hr^{-1})	Ave. N (wt%)	Ave. DN (wt%)	Ave. S (wt%)	Ave. DS (wt%)	Ave. wt% N Remov.
NALCO	T-1A	2.5	1.0 ± 0.1	0.18	84.5	0.22	70.0	-
Mo 477	T-2A	2.00	1.9 ± 0.1	0.57	51.4	0.28	61.2	-
E 1/16"	T-3A	2.75	1.0 ± 0.1	0.04	96.6	0.-	-	-
	T-4A	4.25	1.0 ± 0.1	0.11	91.0	0.22	69.6	56
	T-5A	4.50	1.0 ± 0.1	0.19	83.9	0.19	73.4	57
Nalco NM 502 E 1/ 16"	T-1B	2.75	1.5 ± 0.2	0.33	72.2	-	-	27
	T-3B	4.25	1.0 ± 0.2	0.23	80.3	0.26	64.3	30
Harshaw	T-1C	6.50	1.0 ± 0.1	0.22	81.2	0.22	69.0	42
HT 400	T-2C	4.00	1.0 ± 0.1	0.26	77.6	0.27	63.0	5
E 1/32"	T-3C	7.00	1.1 ± 0.1	0.35	70.1	0.23	68.8	26

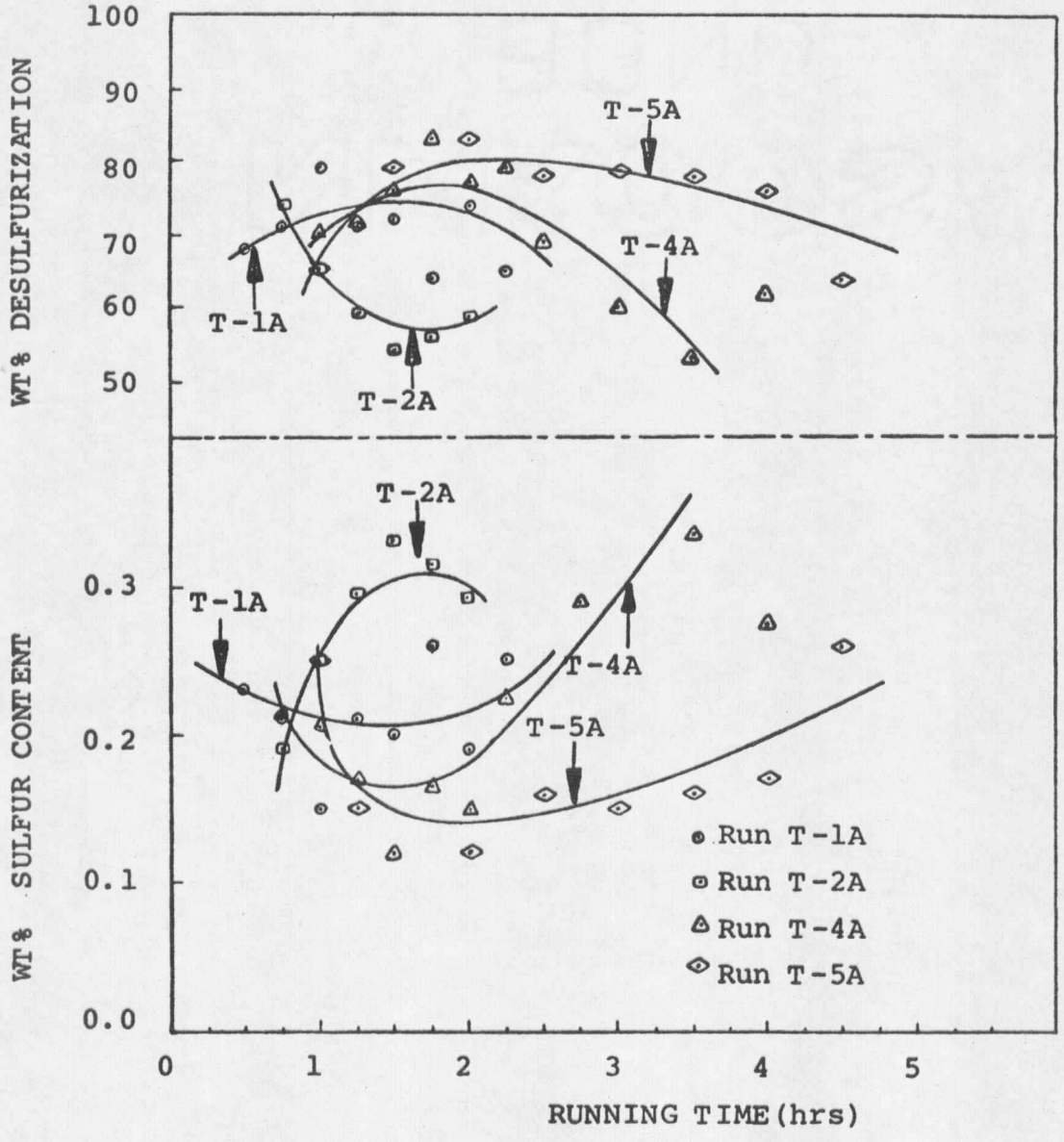


FIGURE 12. Percent Sulfur Content of Oil and Desulfurization vs. Running Time for Nalco Mo 477

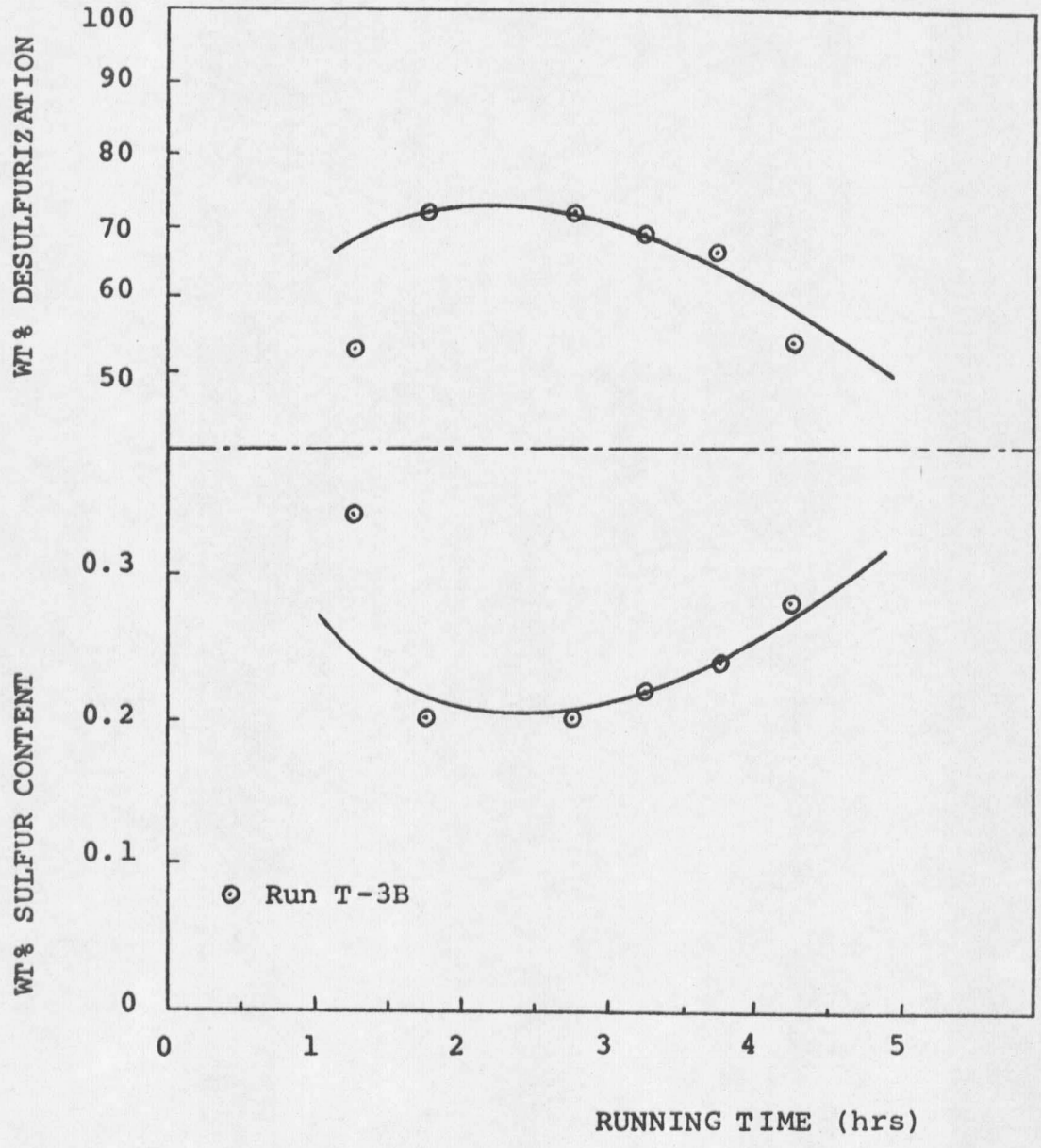


FIGURE 13. Percent Sulfur Content of Oil and Desulfurization vs. Running Time for Nalco NM 502

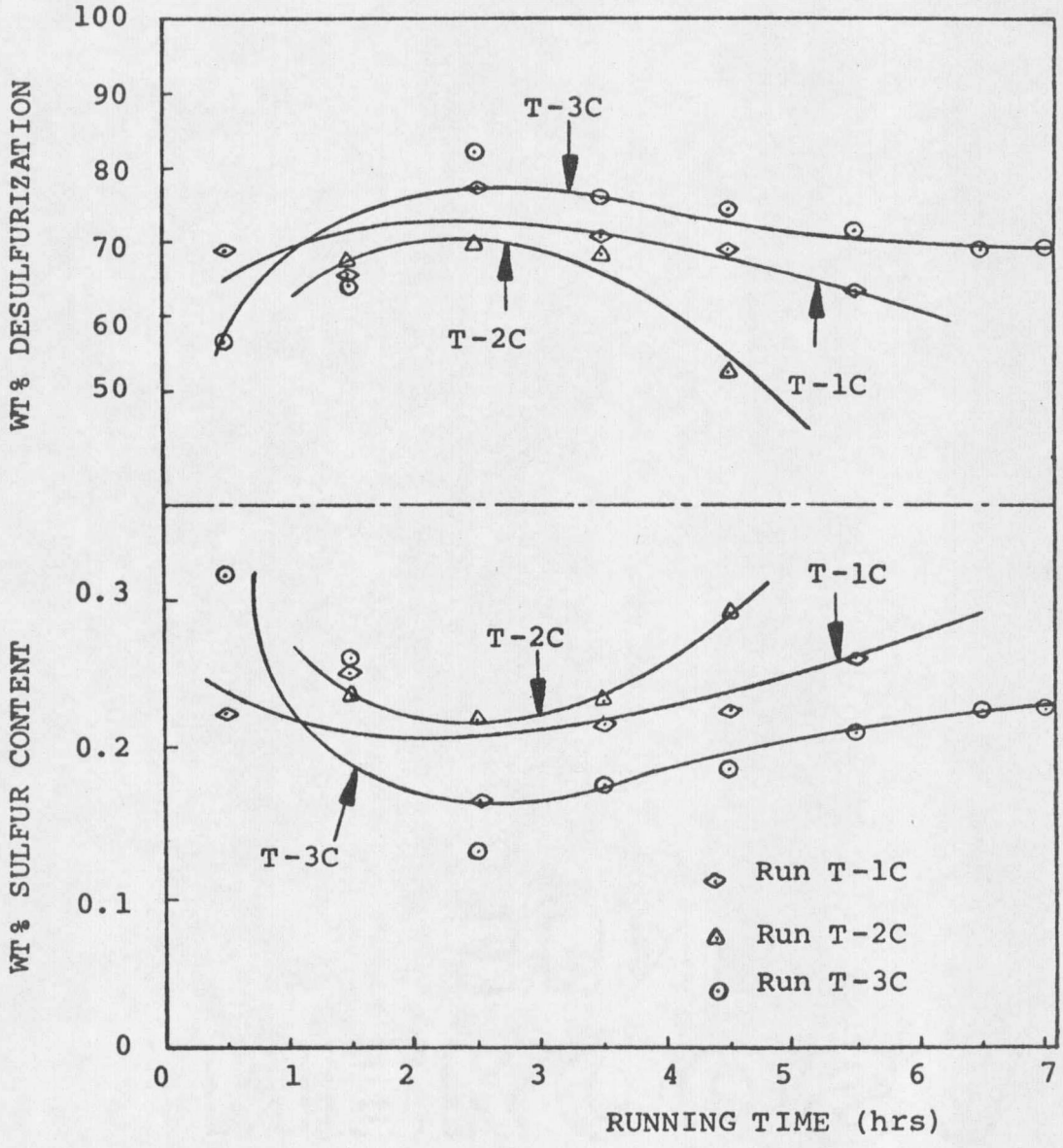


FIGURE 14. Percent Sulfur Content of Oil and Desulfurization vs. Running Time for Harshaw HT 400

B. Durability Test of Harshaw HT 400

Two successive runs were made with water addition to the feed and the catalyst was regenerated between the cycles. Two runs were made without water addition in the same way. The operating temperature was 475°C for the former pair and 425°C for the latter. SRC-II Light Ends Column Feed (LECF) was used as feed stock for these runs (see Table III for the properties of the feed).

Runs with Water Addition

The first run, Run T-4C1, was made with presulfided catalyst and 1.5 vol.% water added to the feed during the entire run. The run was carried out for 10 to 15 hours a day and kept under hydrogen pressure for the rest of the day when the system was not operating to avoid coke formation. Samples were taken for each five hours and the water layer at the bottom was separated from the oil. Then oil was washed with excess water to remove water soluble nitrogen compounds left in oil. Oil, residual water (water from the process), and wash water were analyzed for their nitrogen content. Based on total nitrogen in the product, oil, residual water, and wash water share 61 wt%, 35 wt%, and 4 wt% of the nitrogen present in the product respectively. The percent nitrogen content of oil is plotted in Fig. 15 as a function of running time. The catalyst retained its activity for 115 hours. Deactivation of the catalyst was relatively slow and a linear function of time (see Fig. 16).

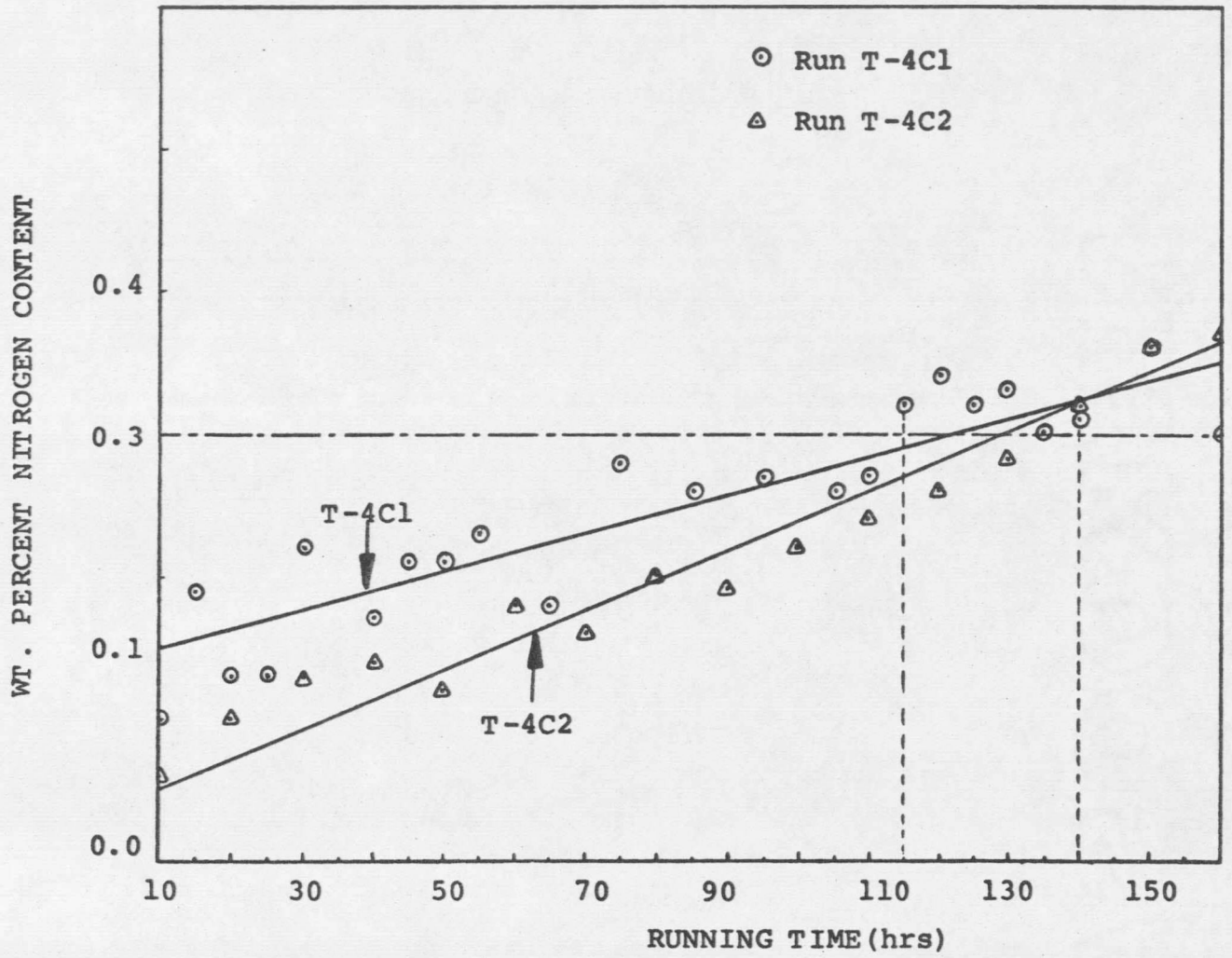


FIGURE 15. Percent Nitrogen Content of Oil vs. Running Time for the Runs With 1.5% Water Addition

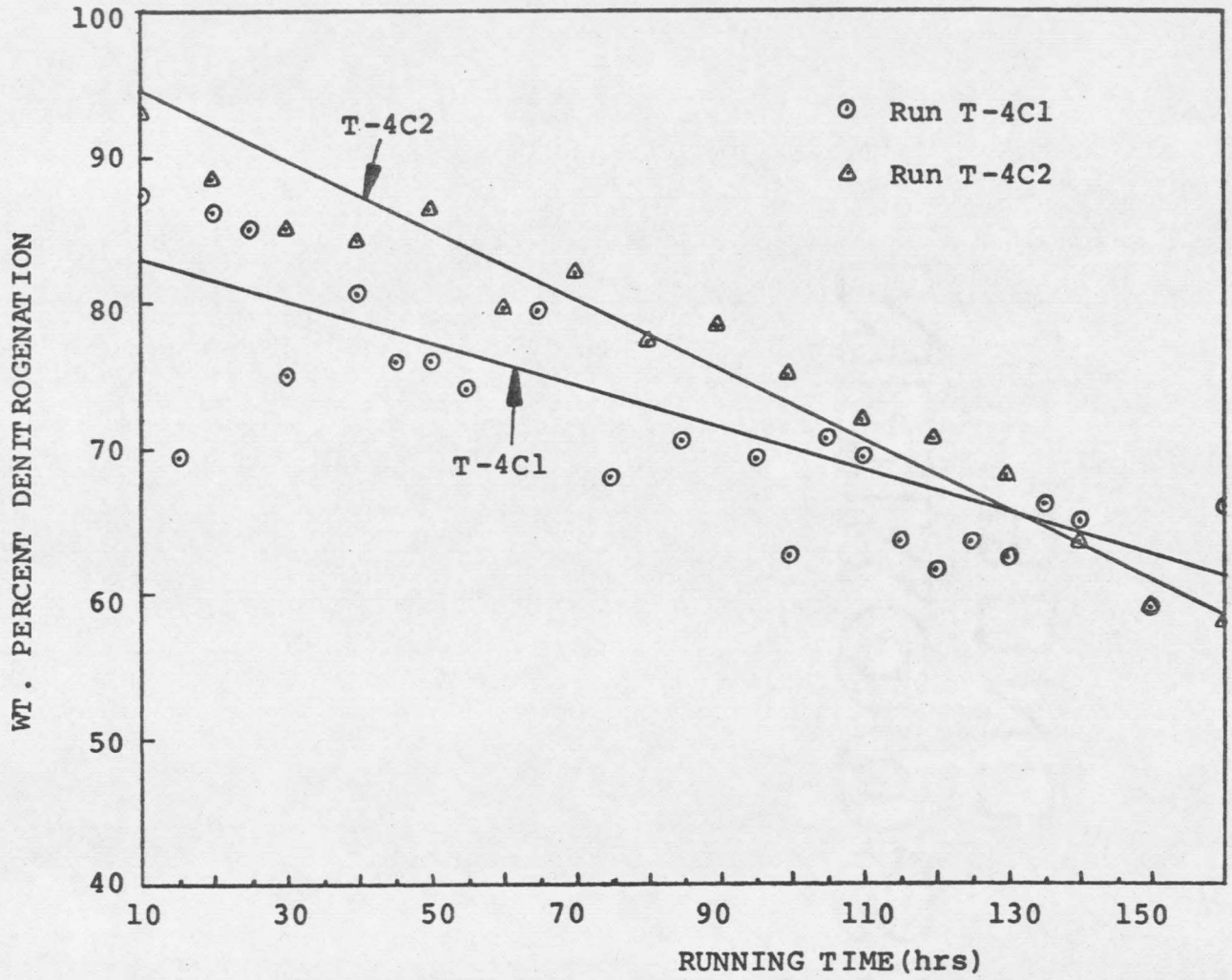


FIGURE 16. Percent Denitrogenation vs. Running Time for Runs With 1.5% Water Addition

The second run, Run T-4C2, was made after burning off the same catalyst used in the former run. The catalyst was burned off with 5% O_2-N_2 mixture for the first 12 hours then with 40% O_2-N_2 mixture for another 12 hours at a temperature range of 540-590°C. Catalyst was presulfied after the burnoff. The samples were taken for each 10 hours and treated in the same way as before. In this case, oil had 41%, residual water had 53%, and wash water had 6%, of the total nitrogen present in the product. The catalyst retained its activity for 140 hours (see Fig. 15). Percent denitrogenation vs. time is shown in Fig. 16. Deactivation was similar to the former one.

The second cycle was better than the first one for denitrogenation. Averaged results are summarized in Table VIII.

Samples from both runs were analyzed for their sulfur content also. Figure 17 shows percent sulfur content and desulfurization as a function of running time. The second cycle gave better desulfurization than the first one. The slopes of the desulfurization lines are very small and the activity of the catalyst for desulfurization is scarcely effected by the duration of the catalyst on stream.

Runs Without Water Addition

The first run, T-5C1, was made with presulfided catalyst and the catalyst retained its activity for only 40 hours. Oil similarly was separated from the water layer, washed with excess water, and separated again. Oil, residual water, and wash water were analyzed

TABLE VIII

Summary of the Averaged Results from the Durability Test of Harshaw HT 400

Run No:	Water Added vol%	Time hrs	Ave. LHSV hr^{-1}	Ave. N wt%	Ave. DN wt%	Ave. S wt%	Ave. DS wt%	Yield wt%
T-4C1	1.5	160	1.02	0.24	72.7	0.110	90.9	93.8
T-4C2	1.5	160	1.00	0.21	76.0	0.090	92.7	91.1
T-5C1	-	160	1.01	0.37	58.0	0.104	91.4	86.6
T-5C2	-	160	1.00	0.35	60.5	0.112	90.7	86.7

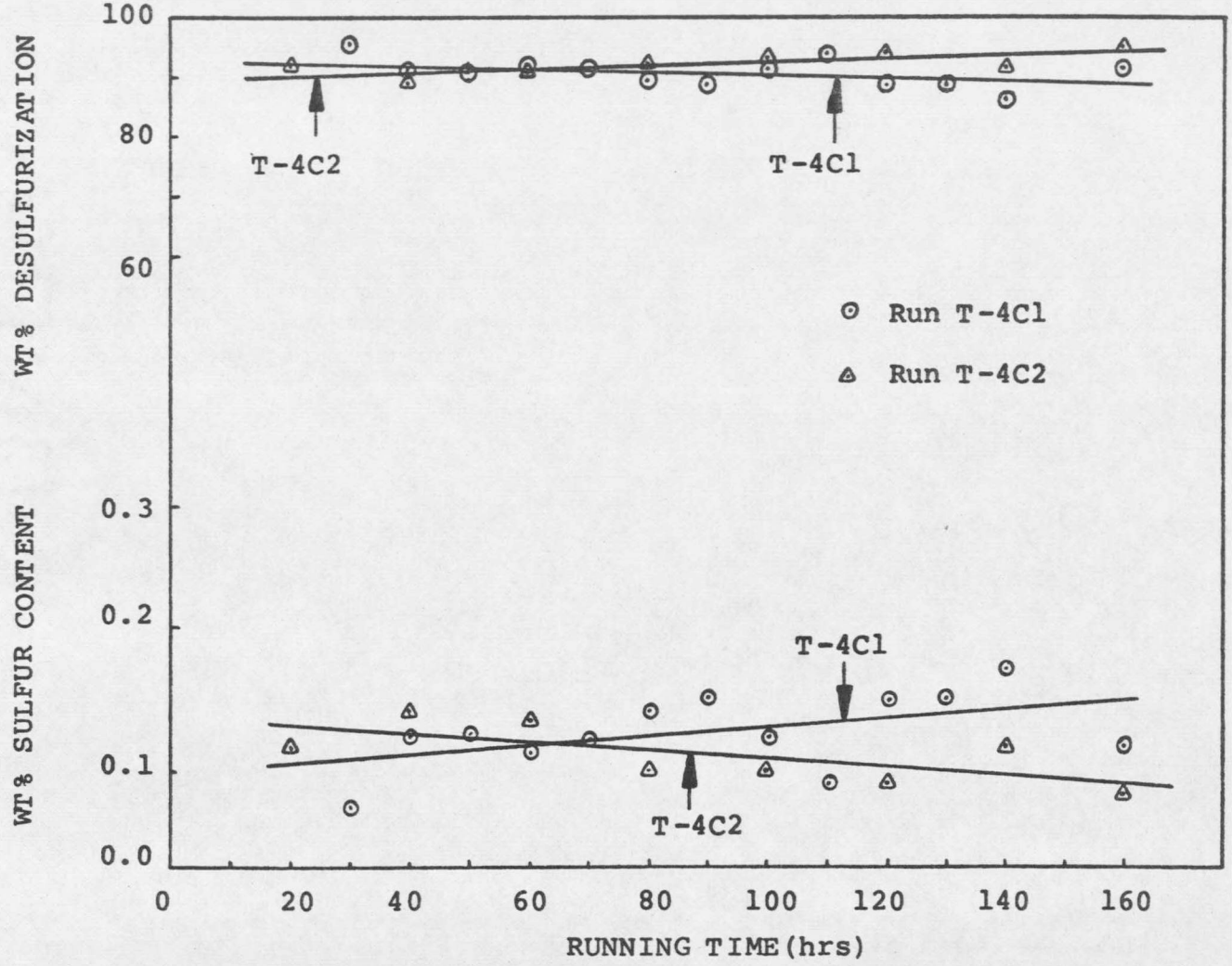


FIGURE 17. Percent Sulfur Content of Oil and Desulfurization vs. Running Time for the Runs With 1.5% Water Addition

for nitrogen content, and contained 68%, 31%, and 1% of total nitrogen in the raw product. Percent nitrogen content of the oil is plotted in Fig. 18 as a function of running time. This time, it showed a curved pattern. Figure 19 demonstrates percent denitrogenation as a function of running time. The figure shows that deactivation was very sharp for the first 50 hours and then leveled off slowly.

The second run, Run T-5C2 was made with the same catalyst used in the first run after burning off and sulfiding. The product was treated and analyzed similarly, and oil, residual water, and wash water contained 73.5%, 23.5% and 3% of the total nitrogen present in the raw product. Figure 18 and Figure 19 show percent nitrogen content of oil and percent denitrogenation as a function of time, respectively. Curves in both figures showed a pattern similar to the first run. The only difference in this case is a sharp decrease in activity after leveling off. The catalyst gave specification grade product for 40 hours.

Samples from both runs were analyzed for sulfur content and the results are plotted in Fig. 20 as percent sulfur content of oil and percent desulfurization vs. running time. Sulfur content was almost constant for duration of the entire run for both cases and so was desulfurization. As a result sulfur removal is very easy under these conditions.

All results are summarized in Table VIII for both runs and detailed data are listed Tables XVI-XIX in Appendix.

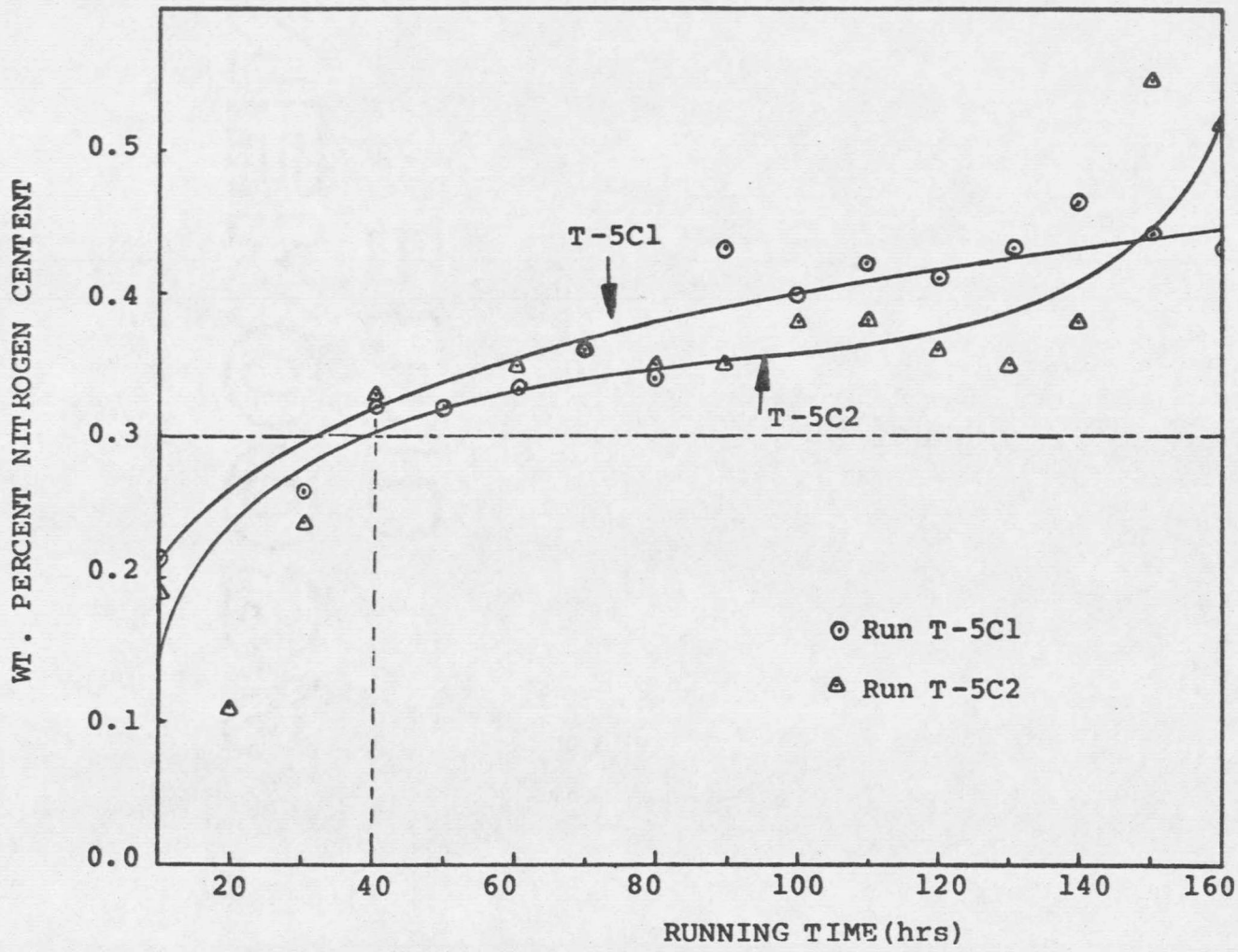


FIGURE 19. Percent Denitrogenation vs. Running Time for the Runs Without Water Addition

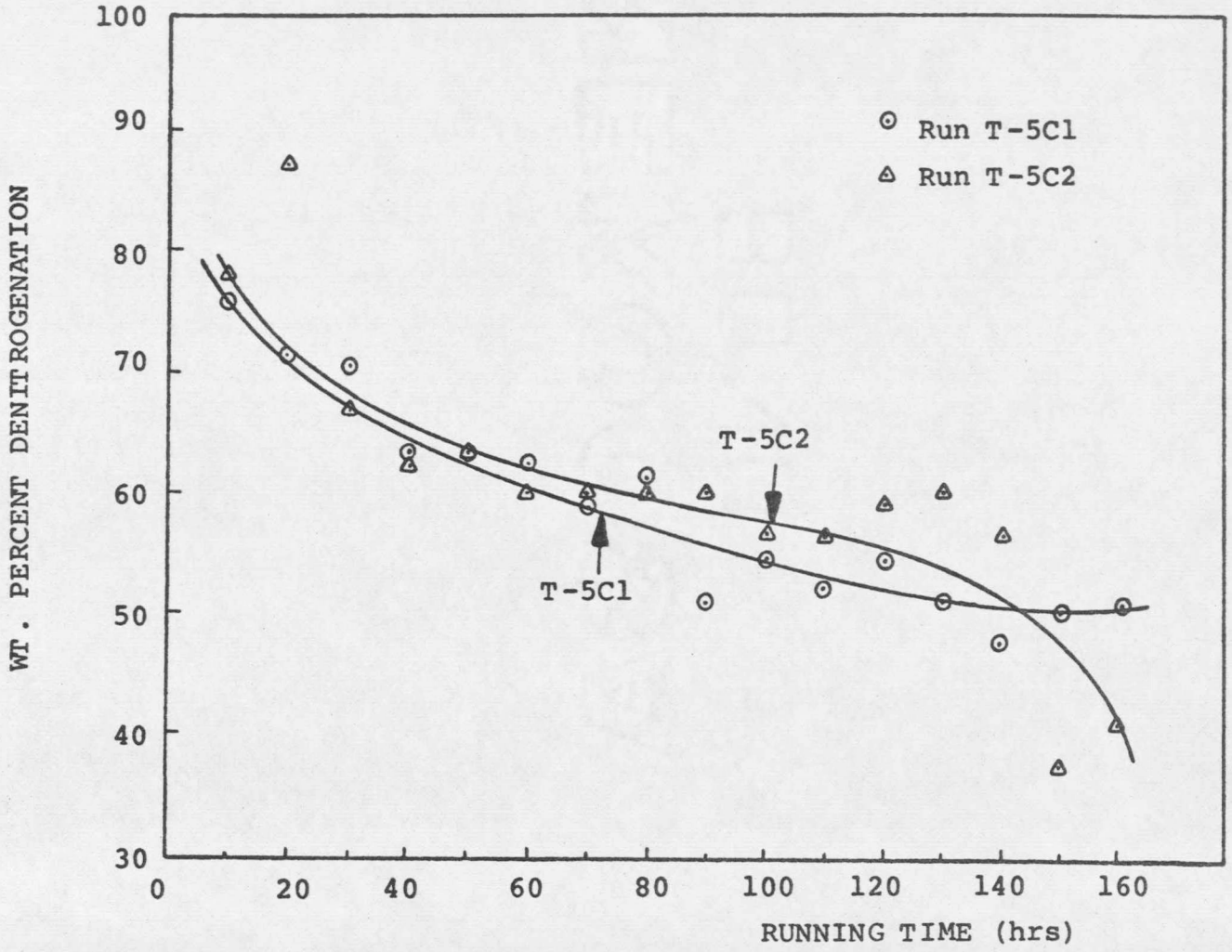


FIGURE 18. Percent Nitrogen Content of Oil vs. Running Time for the Runs Without Water Addition

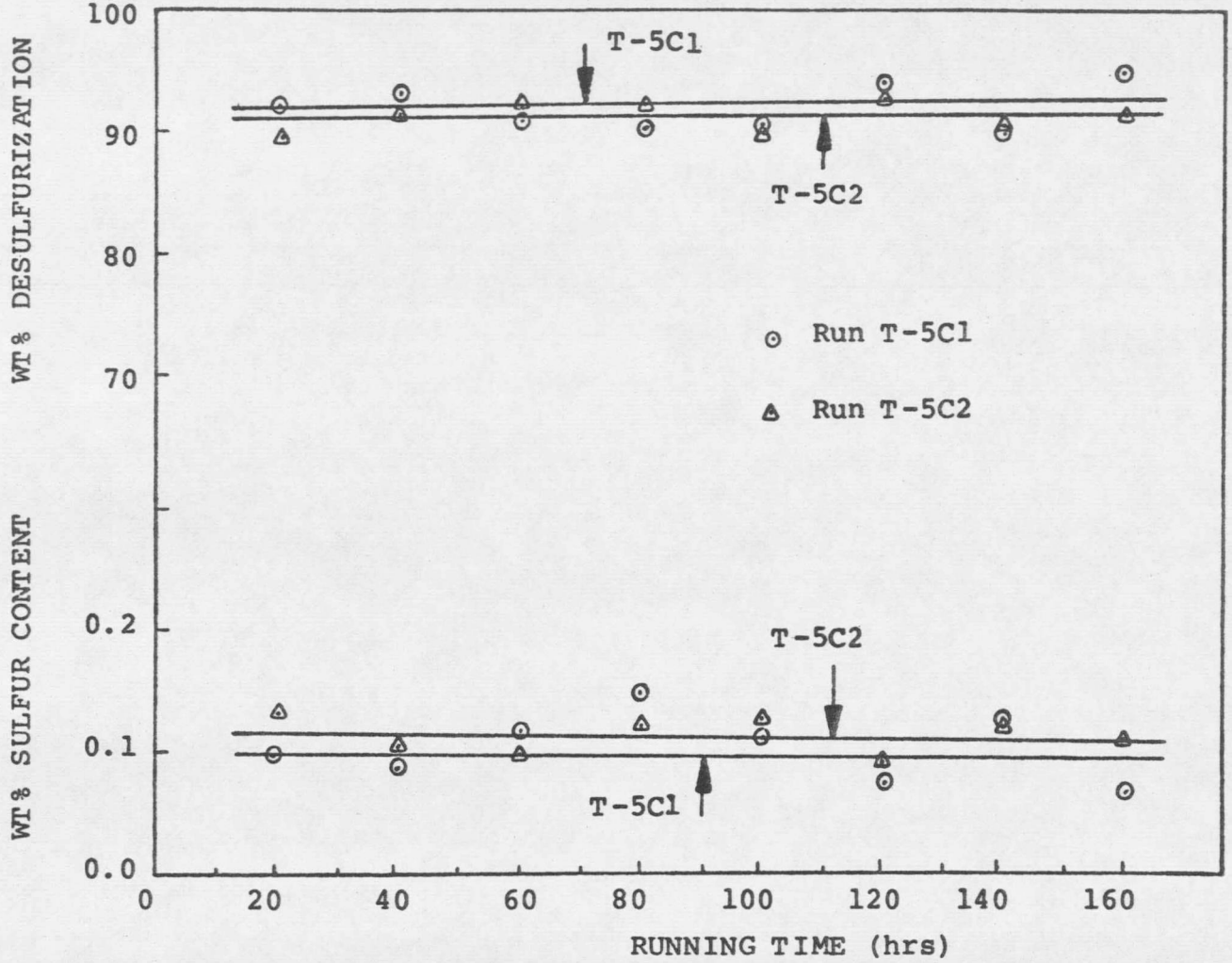


FIGURE 20. Percent Sulfur Content of Oil and Desulfurization vs. Running Time for the Runs Without Water Addition

Comparison of the Two Conditions

When these two conditions are compared for denitrogenation activity of the catalyst, the difference is great. 1.5 vol.% water addition to the feed improves the activity of the catalyst and extends the catalyst life more than three times.

It is not known how water improves the activity of the catalyst. Deriving a conclusion without any further studies will be speculative. However, possible interactions of water with the catalyst and/or reactions are; inhibition of coke formation (which is a side reaction), increasing the acidity of the catalyst by interacting with catalyst carrier or with metal sulfides, and washing out the intermediate nitrogen compounds from denitrogenation reactions from the catalyst surface. The reason can be one of these or a combination of these. The only way to find out which of these is the reason is to study the case further.

It is known that in some hydrocarbon processes steam is used as a decoking agent (37). Testing with the catalyst carrier can answer the second question. It is known that low partial pressure of steam increases the activity of alumina-silica hydrocracking catalysts (38).

When two conditions are compared for desulfurization, there is no appreciable difference. It can be concluded that water does not have a significant effect on desulfurization activity of the catalyst

for the first 160 hours of the run.

On the other hand, water improved the liquid product yields (see Table VIII). While runs with water addition gave 93-91 wt% liquid yields, the runs without water addition gave 86.6-86.7 wt% liquid yields. This can be either because of less coke formation or less gaseous product yield or both.

When ASTM distillation results are compared, the results obtained from the runs with water addition are better than the others (see Table IX and Fig. 21). Runs with water addition gave lower boiling range product. This can be either because of high temperature (475°C vs. 425°C) or of improving the catalyst activity with water. A slight decrease in low boiling range product yield was obtained in the second cycle of both conditions. This can be as a result of activity (in other words acidity) loss during the air burnoff.

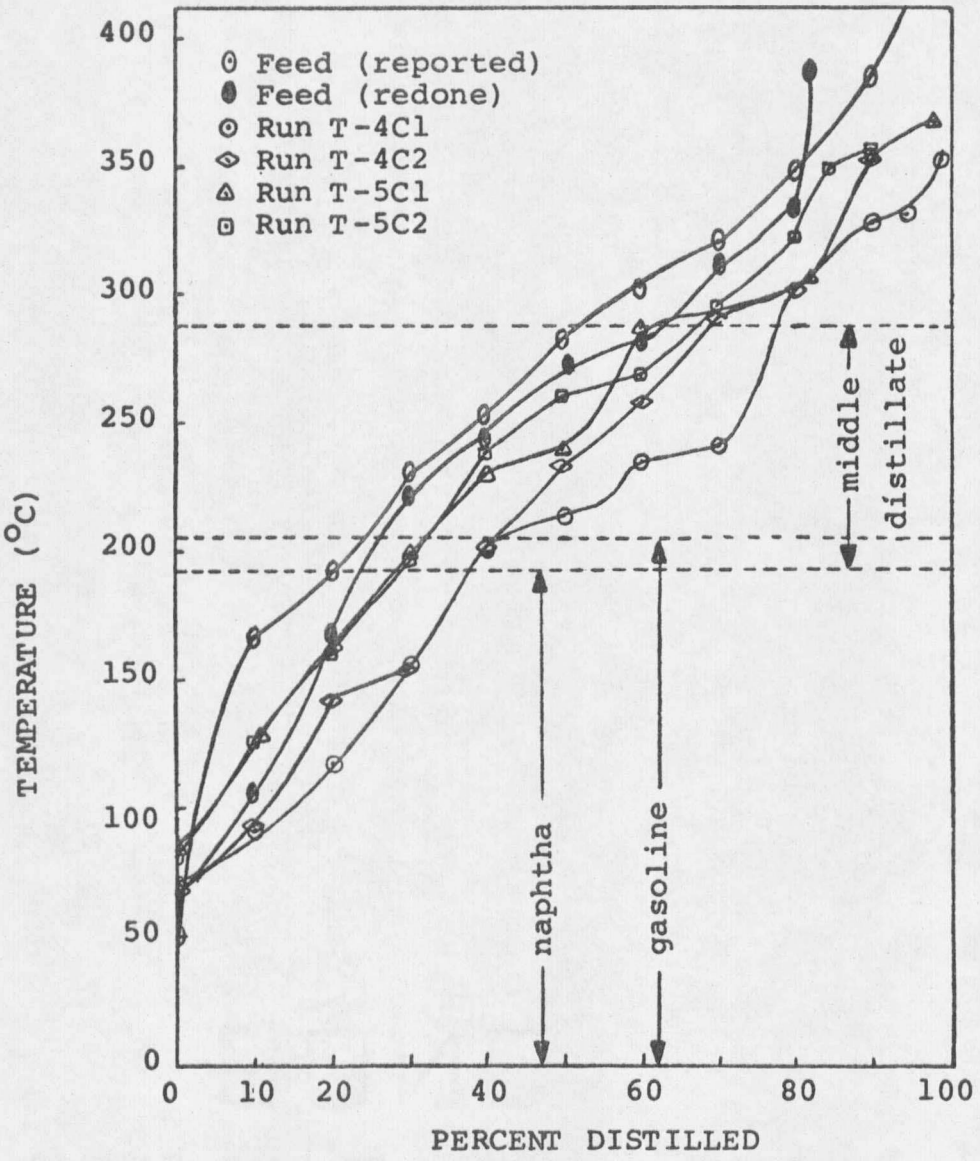


FIGURE 21. ASTM Distillation Curves of the Runs for Durability Test of Harshaw HT 400

TABLE IX

Summary of ASTM Distillation Results

Temperature Range (^{o}C)	Run No.				Feed	
	T-4C1	T-4C2	T-5C1	T-5C2	Reported	Redone
IBP, ^{o}C	83	67	85	85	50	65
IBP-193 Naphtha (vol%)	37	37	32	32	20	23.5
193- 298 Middle (vol%)	41	32	29	35	33	38
298-482 Heavy (vol%)	20	21	33	23	42*	21.5
Residue (vol%)	2	10	6	10	5*	18
FBP, ^{o}C	352	352	357	357	512	388
Gasoline Yield (vol%) (IBP-205)	42(46)**	41	32	32	25	26

* Estimated

** Value in parenthesis is obtained from a multi stage distillation equipment

N.B. All values listed here are produced from Fig. 21.

IV. CONCLUSIONS

1. Water addition to the feed at 475°C improved the denitrogenation activity of Harshaw HT 400 catalyst and three times longer catalyst life was obtained between regenerations.

2. Water addition did not have any significant effect on desulfurization for 160 hours of run.

3. Liquid product yield was higher with water addition.

4. Separation of water in the product from oil removed considerable amount of nitrogen from the product. This showed that nitrogen compounds in the feed were reduced to lower molecular weight, water soluble nitrogen compounds (mostly ammonia).

5. While deactivation of the catalyst followed a linear pattern in runs with water addition, it followed a nonlinear pattern in runs without water addition.

6. Activity of the catalyst was almost constant for desulfurization in both cases.

7. Three commercial catalysts tested could be listed in the following order for their denitrogenation capability under the conditions discussed (see sec. III. A); Harshaw HT 400, Nalco Mo 477, and Nalco NM 502.

8. Runs with water addition gave more low boiling product.

V. RECOMMENDATIONS

1. In order to be able to explain how water improves the denitrogenation activity of the catalyst, further studies have to be done. More runs with catalyst support, unsulfided catalyst, and sulfided catalyst at different temperatures must be done.
2. The optimum amount of water to be added to the feed must be experimentally determined.
3. Since water can have a negative effect on catalyst structure, it must be tested with successive regenerations.
4. Other commercial catalysts or catalysts produced at MSU can be tested with water addition to see how their activities are affected.

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APPENDIX

TABLE X

Data for Runs T-1A and T-2A. Catalyst was Nalco Mo 477 E 1/16".

Time	Run T-1A*				Run T-2A**			
hrs	N	S	DN	DS	N	S	DN	DS
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
0.50	0.17	0.23	86	68	0.01		99	
0.75	0.20	0.21	83	71	0.13	0.19	89	74
1.00	0.17	0.15	81	79	0.87	0.25	26	65
1.25	0.15	0.21	87	71	0.53	0.30	55	59
1.50	0.18	0.20	85	72	0.67	0.33	48	54
1.75	0.15	0.25	87	64	0.71	0.32	39	56
2.00	0.21	0.19	83	74	0.51	0.30	66	59
2.25	0.23	0.25	80	65				
Ave.	0.18	0.22	85	70	0.57	0.28	51	61

OPERATING CONDITIONS

Temperature , ^{o}C	425 ± 10
Pressure , psig	1,000 ± 50
H_2 flow rate , scf/bbl of oil	10,000 ± 500
LHSV , hr^{-1}	1.0 ± 0.1 ***

* Run T-1A was made with unpresulfided catalyst.
** Run T-2A was made with presulfided catalyst.
*** LHSV for the Run T-2A was 1.9

TABLE XI

Data for Run T-3A. Catalyst was presulfided Nalco Mo 477 E 1/16".

Time	Before washing				After washing			
hrs	N	S	DN	DS	N in oil	DN	N in water	%N removal
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
0.50	0.41		64.9					
0.75	0.21		82.1		0.02	98.3	0.02	94.6
1.00	0.03		97.4		0.02	98.3	0.02	88.4
1.25	0.81		30.8					
1.50	0.44		62.4		0.02	98.3	0.02	84.1
1.75	1.02		12.8					
2.00	0.05		95.7		0.04	96.6	0.06	79.7
2.25	1.06		9.4					
2.50	1.43		-		0.08	93.2	0.11	73.4
2.75	0.12		89.7		0.02	98.3	0.11	89.7
Ave.	-		-		0.04	96.6	0.05	80.8

OPERATING CONDITIONS

Temperature , ^{o}C	425 ± 10
Pressure , psig	1,000 ± 50
H_2 flow rate , scf/bbl of oil	10,000 ± 500
LHSV , hr^{-1}	1.0 ± 0.1

TABLE XII

Data for Runs T-4A and T-5A. Catalyst was presulfided Nalco Mo 477 E 1/16".

Time	Run T-4A				Run T-5A				
hrs	N	S	DN	DS	N	S	DN	DS	N re-* moval
	w wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
0.50	0.03		97.4		0.02		98.3		93
0.75	0.02		98.3		0.02		98.3		80
1.00	0.02	0.22	98.3	70	0.02	0.25	98.3	65	84
1.25	0.02	0.21	98.3	72	0.05	0.	95.7		76
1.50	0.02	0.17	98.3	76	0.08	0.15	93.2	79	86
1.75	0.03	0.12	97.4	83	0.10		91.5		80
2.00	0.06	0.17	94.9	77	0.14	0.12	88.0	83	81
2.25	0.14	0.15	88.0	79	0.15		87.2		62
2.50	0.23	0.23	80.3	67	0.17	0.16	86.0	78	67
2.75	0.28		76.2		0.18		84.6		66
3.00	0.33	0.29	71.8	60	0.20	0.15	82.9	79	56
3.25	0.20		82.9		0.22		81.2		68
3.50	0.29	0.34	75.2	53	0.38	0.16	67.5	78	16
3.75	0.40		65.8		0.30		74.4		44
4.00	0.59	0.28	49.6	77	0.30	0.17	74.4	76	20
4.25					0.38		67.5		29
4.50					0.30	0.26	74.4	64	6
Ave.	0.11	0.22	91.0	70	0.19	0.19	83.9	73	57

OPERATING CONDITIONS

Temperature , ^{o}C	425 $\pm$ 10
Pressure , psig	1,000 $\pm$ 50
H_2 flow rate , scf/bbl of oil	10,000 $\pm$ 500
LHSV , hr^{-1}	1.0 $\pm$ 0.1

* Percent nitrogen removal from the product by washing

TABLE XIII

Data for the Runs T-1B and T-3B. Catalyt was unsulfided and sulfided Nalco NM 502 E 1/16", respectivly.

Time	Run T-1B				Run T-3B			
hrs	N	S	DN	DS	N	S	DN	DS
	wt%	wt%	wt%	wt %	wt%	wt%	wt%	wt%
0.50	0.06		94.9					
0.75	0.10		91.5					
1.00	0.10		91.5		0.02		98.3	
1.25	0.04		96.6		0.02	0.34	98.3	53
1.50	0.24		79.5		0.02	0.	98.3	
1.75	0.34		70.9		0.02	0.20	98.3	72
2.00	0.50		57.3		0.07		94.0	
2.25	0.40		65.8					
2.50	0.47		59.8		0.16		86.3	
2.75	0.14		88.0		0.24	0.20	79.5	72
3.00					0.22		81.2	
3.25					0.36	0.22	69.2	69
3.50					0.30		74.4	
3.75					0.34	0.24	70.9	67
4.00					0.40		65.8	
4.25					0.47	0.33	59.8	54
Ave.	0.33		72.2		0.23	0.26	80.3	64

OPERATING CONDITIONS	
Temperature , ^{o}C	425 $\pm$ 10
Pressure , psig	1,000 $\pm$ 50
H_2 flow rate, scf/bbl of oil	10,000 $\pm$ 500
LHSV , hr^{-1}	1.0 $\pm$ 0.2*

* LHSV was around 1.5 for the Run T-1B.

TABLE XIV

Data for Runs T-1C and T-2C. Catalyst was sulfided Harshaw HT 400 E 1/32".

Time	Run T-1C*				Run T-2C**			
hrs	N	S	DN	DS	N	S	DN	DS
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
0.5	0.03	0.23	97.4	69	0.08		93.1	
1.0	0.06	0.	94.9		0.10		91.5	
1.5	0.07	0.25	94.0	65	0.17	0.24	85.5	67
2.0	0.07		94.0		0.16		86.3	
2.5	0.09	0.17	92.3	77	0.24	0.22	79.5	69
3.0	0.17		85.5		0.27		76.9	
3.5	0.20	0.22	82.9	70	0.36	0.23	69.2	68
4.0	0.26		77.8		0.53	0.35	54.7	52
4.5	0.30	0.23	74.4	69				
5.0	0.32		72.7					
5.5	0.37	0.26	68.4	64				
6.0	0.38		67.5					
6.5	0.37	0.	68.4					
Ave.	0.22	0.22	81.2	69	0.26	0.27	77.6	63

OPERATING CONDITIONS	
Temperature , ^{o}C	425 ± 10
Pressure , psig	1,000 ± 50
H_2 flow rate , scf/bbl of oil	10,000 ± 500
LHSV , hr^{-1}	1.0 ± 0.1

* This run was made with preheated feed and there was nowater in it

** In this run 1% water was estimated in the feed.

TABLE XV

Data for Run T-3C. Catalyst was sulfided Harshaw HT 400 E 1/32".

Time	N	S	DN	DS	
hrs	wt%	wt%	wt%	wt%	
0.5	0.30	0.315	74.4	56.3	
1.0	0.25	0	78.6		
1.5	0.29	0.260	75.2	63.9	
2.0	0.23		80.3		
2.5	0.28	0.130	76.1	81.9	
3.0	0.28		76.1		
3.5	0.31	0.175	73.5	75.7	
4.0	0.34		70.9		
4.5	0.40	0.185	65.8	74.3	
5.0	0.45		61.5		
5.5	0.52	0.21	55.6	70.8	
6.0	0.44		62.4		
6.5	0.49	0.225	58.3	68.8	
7.0	0.50	0.225	57.3	68.8	
Ave.	0.35	0.23	70.1	68.8	

OPERATING CONDITIONS	
Temperature, ^{o}C	425 ± 10
Pressure, psig	1,000 ± 50
H_2 flow rate, scf/bbl of oil	10,000 ± 500
LHSV, hr^{-1}	1.0 ± 0.1 *

* LHSV was 2.0 for the first 30 minutes.

TABLE XVI

Data for the Run T-4C1. Fresh presulfided catalyst Harshaw HT 400 was used.

Time	Nitrogen	Sulfur	%DN	%DS	LHSV	Yield	Yield
hour	wt%	wt%	wt%	wt%	hr^{-1}	vol.%	wt%
1	0.22	0.19	75.0	84.3	1.97	80.0	71.1
5	0.18		79.6	79.6	1.00	112.0	101.4
10	0.10		88.6		1.00	97.3	90.1
15	0.19		78.8		1.00	103.7	95.1
20	0.13		85.2		0.93	99.6	92.2
25	0.13		85.2		0.98	96.3	90.3
30	0.22	0.05	75.0	95.9	1.13	98.5	91.9
35					0.98	99.7	91.7
40	0.17	0.11	80.7	90.9	1.10	98.8	91.7
45	0.21		76.1		1.04	101.9	94.4
50	0.21	0.11	76.1	90.9	1.06	102.8	95.3
55	0.23		73.9		1.16	97.7	91.4
60		0.095		92.2	1.00	105.2	96.7
65	0.18		79.6		1.02	93.8	87.0
70		0.105		91.3	1.01	99.7	92.4
75	0.28		68.2		0.98	104.7	97.1
80		0.13		89.3	1.07	102.6	91.0
85	0.26		70.5		0.99	100.0	93.2
90		0.14		88.4	0.99	104.8	97.2
95	0.27		69.3		1.06	96.2	89.4
100		0.105		91.3	0.96	105.2	97.4
105	0.26		70.5		0.98	96.6	89.9
110	0.27	0.07	69.3	94.2	0.99	103.0	95.7
115	0.32		63.6		1.03	97.7	92.1
120	0.34	0.14	61.4	88.4	0.98	108.8	100.9
125	0.32	0	63.6		1.00	95.0	88.6
130	0.33	0.14	62.5	88.4	0.91	102.6	95.8
135	0.30		65.9		1.05	98.7	92.0
140	0.31	0.165	64.8	86.4	0.99	105.4	96.2
150	0.36		59.1		1.00	106.8	99.5
160	0.30		65.9		0.98	99.2	92.7
Ave.	0.24	0.11	72.7	90.9	1.02	101.2	93.8

TABLE XVI

(Continued)

OPERATING CONDITIONS	
Temperature, ^{o}C	475 ± 10
Pressure, psig	1,000 ± 100
H_2 flow rate, scf/bbl of oil	10,000 ± 500
Water addition, vol. %	1.5

TABLE XVII

Data for the Run T-4C2. Catalyst Harshaw HT 400 was was regenerated after used in the Run T-4C1.

Time	Nitro-gen	Sulfur	%DN	%DS	LHSV	YIELD	YIELD
hour	wt%	wt%	wt%	wt%	hr^{-1}	vol. %	wt%
1	0.29	-	67.0	-	2.05	49.6	44.5
10	0.06	-	93.3	-	0.99	97.6	86.8
20	0.10	0.10	88.6	91.7	0.98	104.6	95.0
30	0.13	-	85.2	-	0.96	97.2	88.6
40	0.14	0.13	84.1	89.3	1.05	99.4	90.5
50	0.12	-	86.4	-	0.97	99.3	90.7
60	0.18	0.12	79.5	90.1	1.03	93.2	85.7
70	0.16	-	81.8	-	1.01	99.5	92.1
80	0.20	0.08	77.3	93.4	1.00	100.8	93.3
90	0.19	-	78.4	-	0.94	98.2	89.8
100	0.22	0.08	75.0	93.4	1.00	99.7	94.4
110	0.24	-	72.7	-	0.97	103.6	94.8
120	0.26	0.07	70.5	94.2	1.02	97.4	90.7
130	0.28	-	68.2	-	1.01	99.3	92.7
140	0.32	0.10	63.6	91.7	1.02	99.2	92.3
150	0.36	-	59.1	-	1.01	101.8	95.2
160	0.37	0.06	58.0	95.0	1.01	101.0	94.2
Aver-age	0.21	0.09	76.0	92.7	1.00	98.9	91.1

OPERATING CONDITIONS

Temperature , ^{o}C	475
Pressure , psig	1000
H_2 flow rate, scf/bbl of oil	10,000
Water addition , vol. %	1.5

TABLE XVIII

Data for Run T-5C1. Fresh presulfided catalyst Harshaw HT 400 was used.

Time	Nitrogen	Sulfur	%DN	%DS	LHSV	Yield	Yield
hour	wt%	wt%	wt%	wt%	hr^{-1}	vol.%	wt%
1	0.22		75.0		2.08	49.6	44.4
10	0.21		76.1		1.01	92.1	86.3
20	0.25	0.095	71.6	92.2	1.01	83.9	79.4
30	0.26		70.3		0.96	93.4	88.0
40	0.32	0.085	63.6	93.5	1.00	96.7	91.3
50	0.32		63.6		0.99	86.7	81.9
60	0.33	0.115	62.5	90.5	1.00	85.5	82.3
70	0.36		59.1		1.03	105.5	99.7
80	0.34	0.095	61.4	92.2	1.02	86.1	81.6
90	0.43		51.1		0.96	97.9	94.7
100	0.40	0.110	54.6	90.9	1.01	70.7	68.0
110	0.42		52.3		1.03	106.8	102.7
120	0.41	0.075	53.4	93.8	1.00	85.3	81.8
130	0.43		51.1		1.01	95.4	91.3
140	0.46	0.125	47.7	89.7	0.95	91.8	88.0
150	0.44		50.0		1.05	79.9	76.8
160	0.43	0.065	51.1	94.6	1.03	103.7	100.0
Average	0.37	0.104	58.0	91.4	1.01	90.7	86.6

OPERATING CONDITIONS

Temperature , ^{o}C	425
Pressure , psig	1,000
H_2 flow rate , scf/bbl of oil	10,000
Water addition , vol. %	0.0

TABLE XIX

Data for the Run T-5C2. Catalyst Harshaw HT 400 was regenerated after used in the Run T-5C1.

Time	Nitrogen	Sulfur	%DN	%DS	LHSV	Yield	Yield
hour	wt%	wt%	wt%	wt%	hr^{-1}	vol.%	wt%
1					2.47	55.4	50.7
10	0.19		78.4		1.01	95.8	89.9
20	0.11	0.13	87.5	89.3	0.97	95.0	92.2
30	0.29		67.1		0.97	91.3	86.3
40	0.33	0.105	62.5	91.9	0.99	87.0	81.9
50	0.32		63.6		0.93	83.6	80.7
60	0.35	0.095	60.2	92.2	1.02	105.6	99.9
70	0.36		59.1		1.01	79.8	75.6
80	0.35	0.120	60.2	90.1	0.99	101.4	95.9
90	0.35		60.2		0.99	90.2	85.9
100	0.38	0.125	56.8	89.7	1.02	91.5	87.0
110	0.38		56.8		0.98	89.3	85.0
120	0.36	0.090	59.1	92.6	0.96	86.1	81.2
130	0.35		60.2		1.04	95.8	91.1
140	0.38	0.120	56.8	90.1	0.97	88.5	84.5
150	0.55		37.5		1.02	88.4	86.0
160	0.52	0.110	40.9	90.9	0.95	97.2	92.4
Average	0.35	0.112	60.5	90.7	1.00	91.1	86.7

OPERATING CONDITIONS

Temperature , ^{o}C	425
Pressure , psig	1,000
H_2 flow rate , scf/bbl of oil	10,000
Water addition , vol. %	0.0

Sahin, T.
Upgrading of solvent refined coal (SRC-II) liquids by catalytic...

DATE	ISSUED TO