

THE EFFECT OF GUARD BED MATERIAL ON THE  
HYDROTREATMENT OF USED  
LUBRICATING OILS

By

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## PREFACE

An investigation into the effectiveness of using five different guard beds in a trickle bed reactor used to hydrofinish reclaimed spent oil was made. A full evaluation of the effectiveness of the guard beds was made by studying various liquid characteristics and catalyst activity. On the basis of these analyses, one guard bed proved to be more effective than the others.

I wish to express my sincere gratitude to all of the people who assisted me in completing this study. I am especially indebted to my major adviser, Dr. Billy L. Crynes, and the other committee members. The secretaries of the Department of Chemical Engineering were also very helpful.

I am also very thankful to fellow students Troy Weiss, Jeff Mapes, John Carroll, Chad Steward, and John Beazer whose help made for the timely completion of this investigation.

The help of Dr. Z. Alshaeib in reporting metal concentrations of liquid samples was sincerely appreciated. I am also thankful to Opinder Bhan of the National Institute of Petroleum and Energy Research (NIPER) for donating the feedstock used in this study.

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## CHAPTER I

### INTRODUCTION

The dwindling supply of petroleum resources has made conservation a major national concern. Several federal agencies have revised or encouraged policies that point to the obvious benefits of environmental and resource management. The result of a considerable portion of this legislation has been to revise national policies concerning the handling and fate of used lubrication oils.

The re-refining of used lubricating oil has been successfully applied since 1915 and was practiced in both World War I and World War II for the servicing of military aircraft. Early commercial applications were largely restricted to railroads or other groups having a central collection point. Yet, by the 1960's over 150 re-refining companies were producing a total of 18 percent of the United States' lubricating oil demand. However, due to a number of economic and technological reasons, the re-refining industry provided less than five percent of the lubricating oil on the market in 1981 (Berry, 1981).

Alternate methods of utilizing waste lubricating oil that have commonly been employed include use as a dust control, an asphalt extender, and a fuel oil additive. In the past, these methods were the popular procedures used in disposing of spent oil, since the advantages of re-refining were not readily apparent. Re-refining technology was basically confined to acid/clay processes which created

acid sludges that were as environmentally objectionable as the pollutants generated by direct disposal of the spent oil. Furthermore, there was a general feeling that high quality lubricating oils could not be produced from used feedstocks. However, with the recent interest given to the recycling of wastes by the federal government and with the increase in re-refining technology, these obstacles have become insignificant. Congressional reports now point favorably toward re-refining. In addition, recycling processes have been shown to produce base stocks comparable to or better than those formulated from virgin crudes (Whisman, Reynolds, Goetzinger, Cotton, and Brinkman, 1978c; Whisman, Goetzinger and Cotton, 1974a; Whisman, Goetzinger and Cotton, 1974b; Whisman, Goetzinger and Cotton, 1974c; Bethea, Bosniack, Clayburgh, and Mohundro, 1973).

## CHAPTER II

### LITERATURE REVIEW

Until recently, literature pertaining to spent oil processing has been limited. The numerous publications now available in the open literature will be reviewed in three separate sections. The first will describe the physical and chemical characteristics of used motor oils. The second will briefly present a few of the new processes that have been proposed to regenerate waste oil. Literature comparing the benefits of the more important finishing processes will also be reviewed in the second section. The last section will briefly analyze the available literature concerning all aspects of lube oil hydrotreatment.

#### Characterization of Spent Lubricating Oils

Spent lubricating oil poses numerous environmental and economic problems. In order to properly dispose of used oil, one must fully understand the physical and chemical properties associated with the oil. Comprehensive studies of spent oil characteristics have revealed that some of these properties can be estimated with reasonable confidence (Whisman et al., 1977).

The hydrocarbon structures most desired for quality lube oil formulation are: (1) highly alkylated monoaromatic or mononaphthenic hydrocarbons (with a preference for the C<sub>5</sub> ring) and (2) iso-paraffins

(usually with 20 to 40 carbon atoms) with lateral chains that are also iso-paraffins (Billon, Franck and Peries, 1975). A feedstock that is rich in these compounds will, inevitably, produce a very high quality lubricant.

As could be expected, characterization studies have revealed that spent lubricating oils are rich in the organic compounds that are required to formulate a quality lubricating oil. In fact, spent lubricating oil contains between 53 to 70 % more lube base stock than a typical crude feedstock. Furthermore, only 30 % of a spent oil feedstock would be rejected as residue, while between 45 to 65 % is rejected when processing crudes (Cutler, 1976).

More importantly, Cotton, Whisman, Goetzinger, and Reynolds (1977) have shown that the base stock compositions of spent lube feedstocks can be estimated within very narrow 95 % confidence intervals regardless of the geographical or seasonal origin of a particular oil sample. Characterization studies conducted on 30 spent oil samples showed the average base stock composition to be 76.7 % saturates, 13.2 % monoaromatics, 3.7 % diaromatics, and 6.5 % polyaromatic-polar materials. From this information a re-refiner could produce a consistent product even though the feedstock's origin may vary.

Though the base composition of waste oils can be estimated within narrow ranges, the contaminant levels are not nearly so predictable. Contaminants such as water, fuel dilution, sediment, antifreeze, acids, and metallic elements and compounds can vary greatly. Whisman et al. (1977) gave a detailed analysis of the more significant properties associated with lubricating oils and how they can be affected by the contaminant level of the oil. Individual and average contaminant

levels of 30 used motor oils obtained randomly throughout the United States were also presented.

The metallic contaminants contained within used motor oils are largely due to the use of additives when formulating the original lubricant. This would explain the presence of metallic compounds containing phosphorous, calcium, sodium, sulfur, lead, zinc, and barium (Nowack, Tabler and Johnson, 1979). Other metals, such as aluminum, chromium, copper, iron, potassium, manganese, nickel, silicon, and tin, accumulate in the engine crankcase as engine components mechanically deteriorate. The engine lubricant also collects lead due to contact with leaded gasoline and combustion deposits. Metal concentrations were also presented by Cotton and her coworkers (1977).

While the metallic compounds used as additives have greatly increased lubricant performance, they have also increased the task of reclaiming. Resins and particulates of carbon, dirt, and wear metals are kept suspended in the circulating lubricant by the calcium and barium salts used as detergents (Nowack et al., 1979). These metallic particulates and compounds, if left in the oil, shorten hydrotreating catalyst life, affect the metallic substrates of sensitive process equipment and create fouling problems. Therefore, a successful reclamation process would be one that could economically remove both the particulates and the additive systems of the spent oil feedstock.

Other contaminants found in spent oil base stocks (i.e. sulfur, nitrogen and oxygen compounds) account for an average of 3.3 percent of the whole oil sample (Cotton et al., 1977). These compounds are also indications of the additive level, even though naturally occurring nitrogen, sulfur and oxygen compounds do exist. Although some of

these compounds give desirable properties, today's additive systems make their presence insignificant.

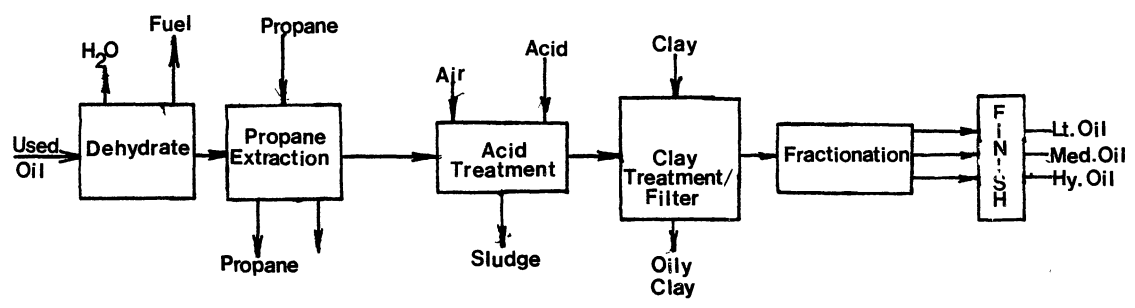
The environmentally harmful components of spent lube oil make its direct disposal an unacceptable alternative. In addition, the presence of metallic particulates and compounds create additional problems when directly burning the oil. However, with the re-refining technology that has only recently been developed, spent lubricating oil can be processed in an environmentally acceptable manner. Furthermore, spent oil characteristics insure that the production of quality motor oils is feasible.

#### Re-refining Processes

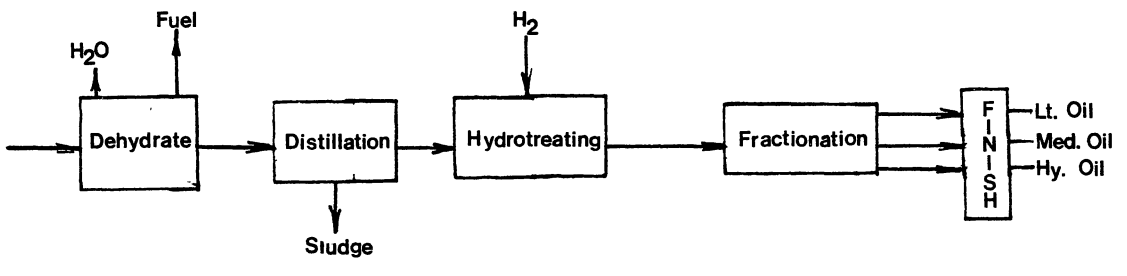
Numerous processes have been developed to re-refine spent lube oil. Presenting all of these would be too lengthy and too cumbersome for the purposes of this paper. Therefore, a general overview of the more important and promising methods will be discussed.

Most successful re-refining processes can be represented by one of the process schematics presented in Figure 1. The acid/clay operation has been the dominant process in the recycling industry and is presented here though recent technological advances have made it nearly obsolete. Due to today's difficult-to-remove additives, re-refiners using the acid/clay process have had to increase the severity of the sulfuric acid treatment and tolerate reduced yields.

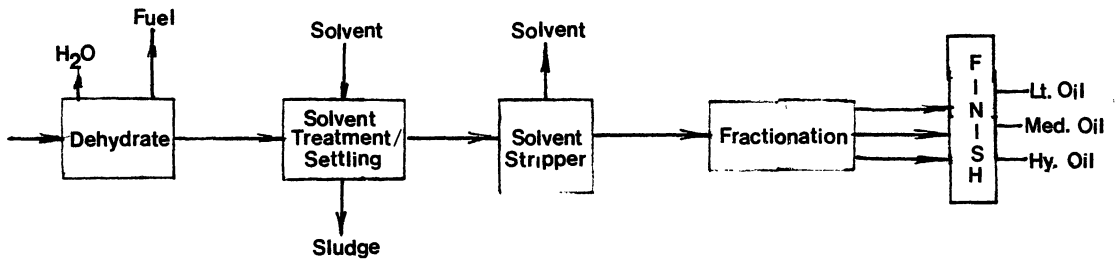
Each of the new technology systems can generally be divided into two separate stages: (1) the purification and reclaiming stage and (2) the finishing stage. The former is responsible for removing water, low-boiling contaminants, oxidation products, and other undesirable



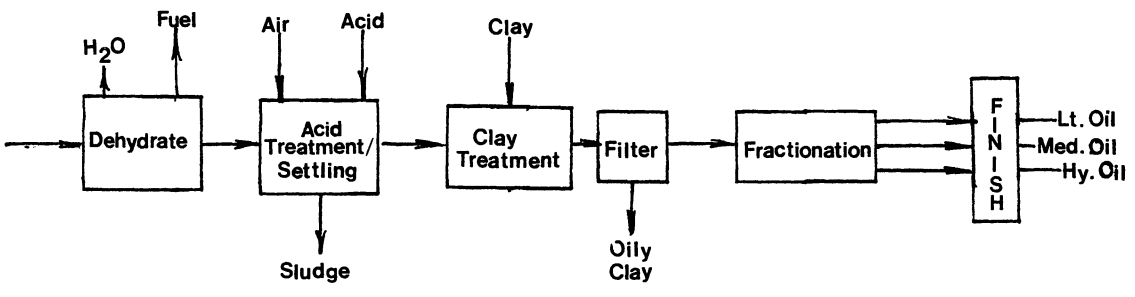
PROPANE EXTRACTION



DISTILLATION HYDROTREATING



SOLVENT EXTRACTION



ACID/CLAY

Figure 1. Modern Re-refining Processes

contaminants. The latter decolorizes, deodorizes and upgrades the reclaimed oil by removing trace amounts of sulfur, oxygen, nitrogen, and metallic elements and compounds.

The major differences between any two of these processes involve the methods employed to accomplish the purification and reclaiming stage. A number of these methods have been studied extensively and were found to adequately reclaim spent lube oil (Berry, 1981; Deutsch, 1979; Nowack, Tabler and Johnson, 1979; Whisman et al., 1978c; Quang, Bonneford and Kerdraon, 1976; Weinstein, 1974; Whisman et al., 1974b). However, the finishing stage has eluded researcher's scrutiny.

The two widely available methods of finishing the reclaimed oil are clay contacting (followed by filtration) and mild hydrotreatment. The majority of the open literature agrees that hydrofinishing has a number of distinct advantages over traditional finishing operations. The most important aspects of this literature are:

1. Since mild hydrotreating conditions appear to have a number of distinct operating advantages for the finishing of virgin crudes, it would also seem reasonable that hydrofinishing would have the same advantages when processing spent oil (Quang, Bonneford and Kerdraon, 1976).

2. The hydrofinishing of spent oils will present some problems not encountered when processing virgin feedstocks due to the contaminants (such as metallic elements and compounds, halogen compounds and oxygenated materials) contained within spent lubricating oil. Without the removal of these compounds, catalyst life and reactor metallurgy may be reduced or affected (Quang, Bonneford and Kerdraon, 1976).

3. Hydrofinishing operations reduce or eliminate disposal problems



and utilize a former refinery byproduct, hydrogen (Billon et al., 1975; Beauther, Mansfield and Stauffer, 1966; Jones, 1954).

4. The hydrofinishing of virgin feedstocks showed significant improvements in a number of lubricating oil characteristics over traditional finishing processes (Whisman et al., 1978c; Beauther, Mansfield and Stauffer, 1966; Jones, 1954).

5. Replacing clay contacting procedures with hydrofinishing as the final processing stage of virgin oils increases the yield and shifts the product from a low value oil to a high value oil (Whisman et al., 1978c; Beauther et al., 1966; Jones, 1954).

6. Hydrofinishing maintains the advantage of being a continuous operation (Jones, 1954).

7. Hydrofinishing would require more sophisticated equipment and might require the attention of more highly skilled labor (Bigda, 1978).

In general, the literature strongly suggests that the most economical and reasonable choice for the final processing stage of any lube oil manufacturing process would be hydrogen treatment. Furthermore, since the performance of today's lubricating oils relies largely on synthetic, trace-element compounds (additives), the partial conversion of "natural inhibitors" to hydrocarbon structures during hydrofinishing is not a significant disadvantage. Therefore, on today's lubricant market, hydrofinishing appears to be the most promising finishing process available.

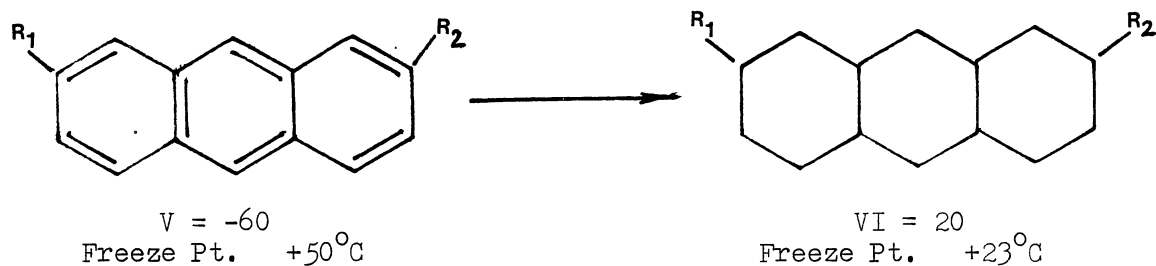
#### Hydrotreating of Spent Lubricating Oils

Beauther, Mansfield and Stauffer (1966) defined three types of

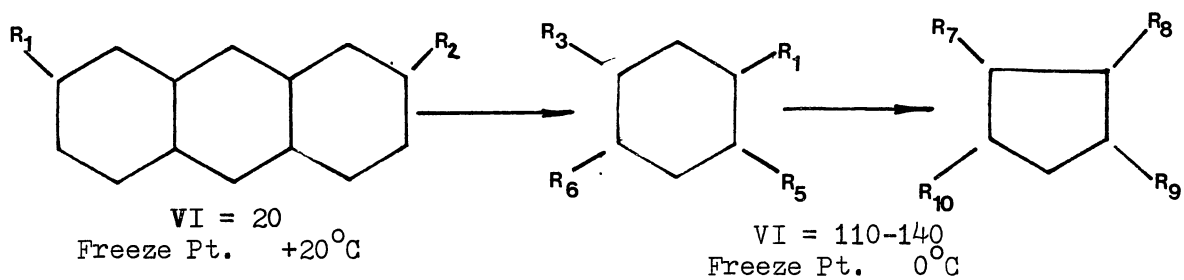
hydrogenation operations used to process lubricating oils: (1) mild hydrofinishing, (2) severe hydrofinishing, and (3) hydrotreating. Partial or complete saturation of aromatics is accomplished by both of the latter operations. The third process also includes a cracking function in the catalyst to convert condensed aromatics to alkyl naphthenes. However, spent lubes are largely composed of the organic compounds necessary to formulate a quality lubricant and do not require the conversion capabilities of the latter two operations. Mild hydrofinishing, as opposed to clay contacting, does not segregate species but transforms undesirables, resulting in higher yields.

Considering the hydrocarbon structures that give desirable lubricant properties, it becomes relatively simple to define the reactions that should be promoted. These reactions were listed by Billon, Franck and Peries (1975) and are reproduced in Figure 2. The reactions to be avoided are those leading to degradation of molecules, since they would cause a decrease in yield. Furthermore, Billon claims that the catalyst must simultaneously activate the H-H, C=C, C-C, and C-H bonds in the presence of heteromolecules that generate both hydrogen sulfide and ammonia. Catalysts conforming to these restrictions are usually made of a metal sulfide from the VIII or VIA groups of the periodic table and an acidic, silica-alumina carrier.

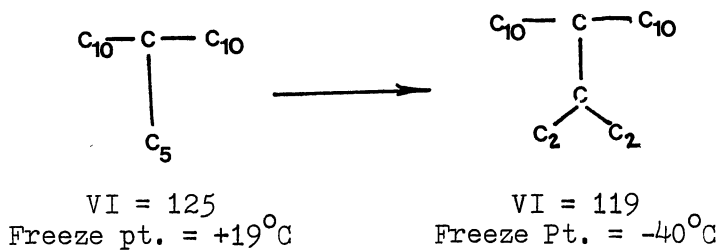
The hydrotreating of distilled spent lube oil was studied by Bethea et al. (1973). Temperatures of 287.8 °C (550 °F), 315.6 °C (600 °F) and 343 °C (650 °F) were studied all at 4481.6 kPa, 1.0 volume of catalyst/volume of oil per hour (space time) and 285.0 m<sup>3</sup> of hydrogen/m<sup>3</sup> of oil (1600 scf/bbl). An additional run was made at 315.6 °C (600 °F), 4481.6 kPa, 1.5 space time, and 285.0 m<sup>3</sup>/m<sup>3</sup> (1600



HYDROGENATION OF POLYAROMATICS INTO POLYNAPHTHENES



HYDRODECYCLIZATION OF POLYAROMATIC  
AND POLYNAPHTHENOAROMATICS INTO MONONAPHTHENES



HYDROISOMERIZATION OF N-PARAFFINS INTO ISOPARAFFINS

Figure 2. Desired Hydrotreating Reactions.

scf/bbl). The physical properties of the product oil indicated that the preferred operating conditions would be 315.6 °C (600 °F) and one hour space time. The product oil was found to have all of the physical characteristics required of a 150 vis neutral lube base stock with the exception of a marginal failure during the copper strip corrosion test. However, it was shown that hydrofinishing at 343 °C (650 °F) could correct this deficiency.

Billon et al. (1975) also suggested that lube stocks be hydro-treated by fractions. Though treating a mixture may simplify the process, it also greatly reduces the operational flexibility. By treating each fraction separately, each oil can be manufactured under well controlled operating conditions. In addition, all fractions will maintain good additive responses and a maximum reduction in feedstock consumption will be realized.

Jones (1954) reported that the mild treating conditions employed when treating extracted light and medium weight lubes result in long catalyst life. An operating lube refiner had already treated 4.4 m<sup>3</sup> of oil/kg of catalyst (25,000 bbl/ton) with the likelihood that catalyst life would allow at least 8.8 m<sup>3</sup>/kg (50,000 bbl/ton).

However, the deposition of the metallic components of spent lube oil may cause premature, permanent deactivation of the catalyst. Tamm, Harusberger and Bridge (1981) showed that feed metals caused deactivation by two mechanisms: (1) poisoning of the active catalyst surface, and (2) physically obstructing the catalyst pores.

Catalyst deactivation caused by metals deposition can be delayed by incorporating guard beds in the process scheme. A guard bed is usually composed of hydrometallizing catalyst, hydrodesulfurizing

catalyst or some inexpensive scavenging material. The purpose of a guard bed is to remove undesirable contaminants from the feedstock that would cause premature deactivation of the expensive catalyst used in the main reactor. Guard beds can also serve as an efficient feed pre-heater.

Exxon Oil Company's Baytown refinery made use of a catalytic guard bed for its operation. Pressure drops across the guard bed and the total reactor train were continuously monitored. When these became too high (approximately 150 days after startup), the guard bed was bypassed and charged with fresh catalyst. Christ, Shah and Sherman (1979) reported that the high pressure drops were caused by agglomerations of carbon, iron scale and salts in the catalyst bed interstices.

Using shale-derived oils as a feedstock, Robinson and Evin (1982) found that 1.6 mm (1/16 inches) alumina extrudates failed to adequately protect the main reactor bed. Catalyst activity had declined drastically within the 24 day run and deposits of iron, sulfur, alumina, sodium, arsenic, and calcium were found in the interstices of both the guard bed and the reactor. The main reactor bed was composed of Shell 324 (Ni-Mo-Al<sub>2</sub>O<sub>3</sub>) catalyst and was operated at 385 °C (725 °F). The low temperatures maintained in the guard bed, 216-271 °C (421-520 °F), were cited as the cause for the incomplete demetallation of the feedstock and the catalyst deactivation.

Murphy and Treese (1979) successfully used a catalytic guard bed designed to remove materials entrained within heavy petroleum residua. The main reactor catalyst was designed to inhibit the diffusion of asphaltenes and metals by maintaining a small pore structure. Richardson and Ishitawa (1979) also used a catalytic guard bed while

treating petroleum residua. After 27 months of service, the guard bed catalyst was found to be nine weight percent coke and 38 percent deposited metals (based on fresh catalyst). Furthermore, a rapid decline in metals deposition was found in the remaining reactor train.

Though the high metals content of used lubricating oil would naturally indicate the need for an effective guard bed, no studies dealing with this topic could be found. The extended catalyst life that would be realized by incorporating a guard bed into process schemes developed for hydrotreatment of spent lubricating oils could greatly improve the economic feasibility of re-refining. This suggests that there is a need for a study determining the optimum guard bed material.

#### Literature Summary

The following conclusions can be drawn from the literature reviewed:

1. Direct disposal of spent lube oil by using it as a dust control, an asphalt extender, and a fuel oil additive is an environmentally unacceptable alternative.
2. Spent lube oil contains 53 to 70 % more quality lube base stock than a typical crude feedstock.
3. The base stock compositions of spent oil samples can be estimated within acceptable confidence intervals.
4. The high metallic concentrations found in today's lubricating oils have greatly increased the task of reclaiming and quickly outdated the conventional acid/clay re-refining process.
5. Today's additive systems make the presence of natural inhibitors less significant.

6. Modern reclaiming methods have been found to adequately remove water, low-boiling contaminants, oxidation products, and some metals.

7. Hydrofinishing boast numerous advantages over traditional clay finishing while maintaining very few disadvantages.

8. Long catalyst life could be expected when using the mild operating conditions used to finish lube stocks.

9. The deposition of the metallic components of spent lubricating oil on the catalyst surface can cause permanent deactivation.

10. More information on the effect on hydrotreatment of spent lube stocks is needed.

11. Clearly there is a need to investigate guard bed materials and their effectiveness when treating used lubricating oils since little information is currently available.

## CHAPTER III

### EXPERIMENTAL EQUIPMENT

The reactor system used during this investigation was the Catalyst Life Test Unit (CLTU) located in the Hazardous Reactions Laboratory at Oklahoma State University. Wilkinson (1983) and Chang (1982) both successfully utilized the unit while studying the upgrading of coal liquids. Since the detailed equipment lists, vendor sources and full equipment information are found in these references, only a brief outline of the process is given here.

A simplified diagram of the CLTU is shown in Figure 3. The hydrogen was fed to the system from a four cylinder manifold, which allowed rapid bottle transfer during reactor operation. A regulator maintained the feed pressure at 6.89 MPa (1000 psig). Hydrogen flow rates were controlled by a micrometering valve located between the regulator and the reactor tube. The hydrogen pressure in the reactor was controlled by a Honeywell Dialatrol unit operating off of a pressure transducer located at the reactor inlet. The system was designed so that high upstream pressures caused by plugging or flow fluctuations would result in the opening of the pneumatic valve installed in the off gas line.

The oil was fed to the reactor through 0.64 cm. (0.25 inch) stainless steel tubing by a positive displacement Ruska pump. An overpressure sensor and a rupture disk were installed in the oil feed lines



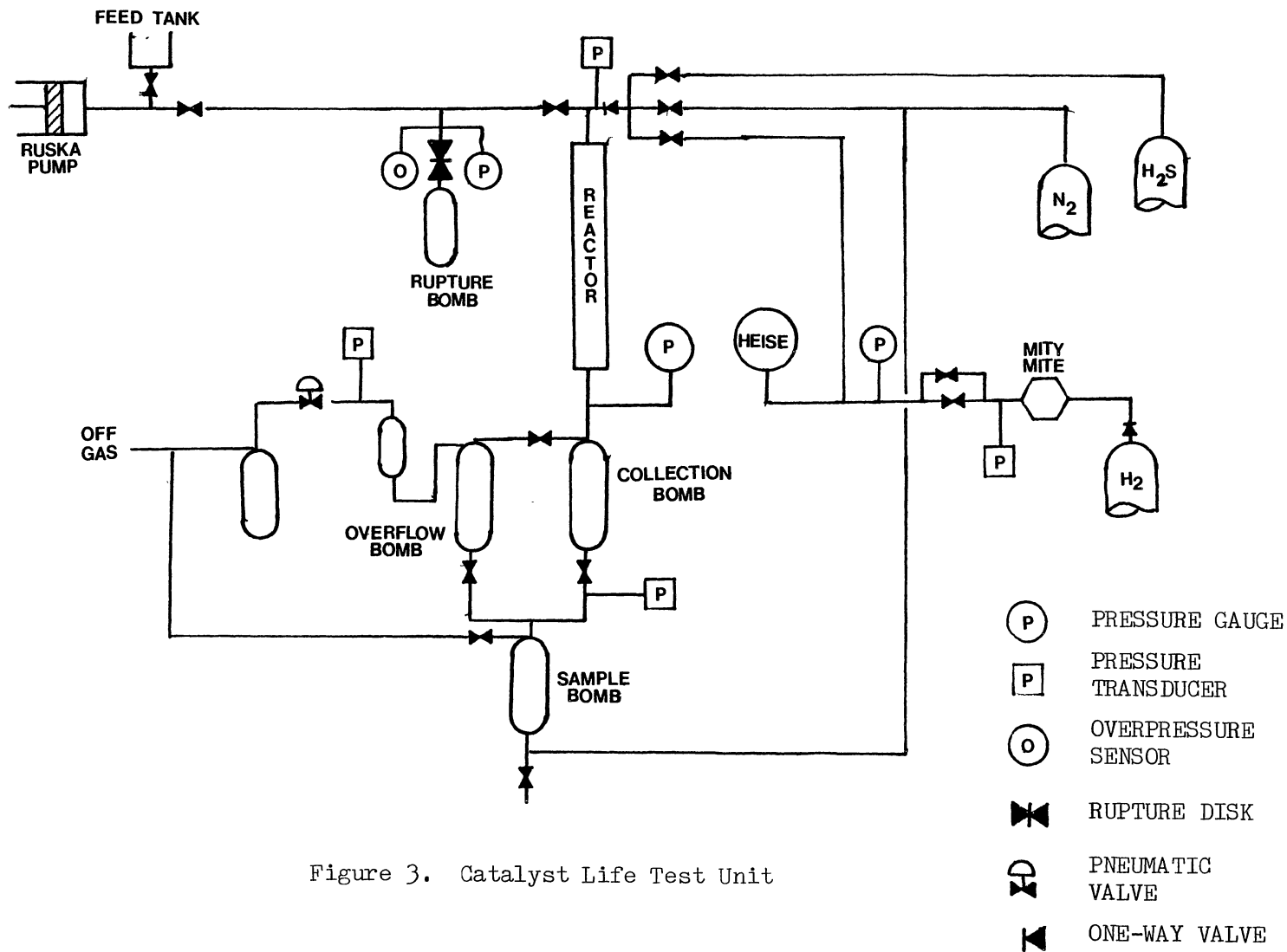


Figure 3. Catalyst Life Test Unit

to prevent any possible damage to the pump.

The actual reactor tube is shown in Figure 4. The reactor was a 1.31 cm (0.515 inch) I.D. stainless steel tube that was 86.36 cm (34 inches) in length. A solid copper cylinder surrounded the reactor tube to equally distribute heat. Heat was supplied by circular heating bands wrapped around the outside of the copper cylinder and was controlled by a Honeywell Dialatrol unit along with two variacs. The entire reactor system was then insulated with felt and fiberglass.

The outer wall temperature was monitored by seven strategically placed iron-constantan thermocouples. The thermocouple located at the center of the reactor was used to complete the feedback loop to the Honeywell controller.

The liquid product was collected in the two gas-liquid separation bombs located just below the reactor. A third bomb was put into the system prior to the pneumatic valve to prevent liquid carryover. Hydrogen sulfide was removed from the off-gas by a scrubber filled with a 20 % sodium hydroxide solution. Hydrogen flow rates were measured using a wet test flow meter located just after the scrubber.

The CLTU was designed to operate unattended and is, therefore, equipped with a number of safety devices. An alarm system would automatically shut off the hydrogen and electrical supplies to the unit if unsafe operating conditions (i.e. high temperatures, high pressures, low feed, low pressure, and presence of dangerous gases) were detected. An auto dialer was also installed to warn operators of the unit's condition.

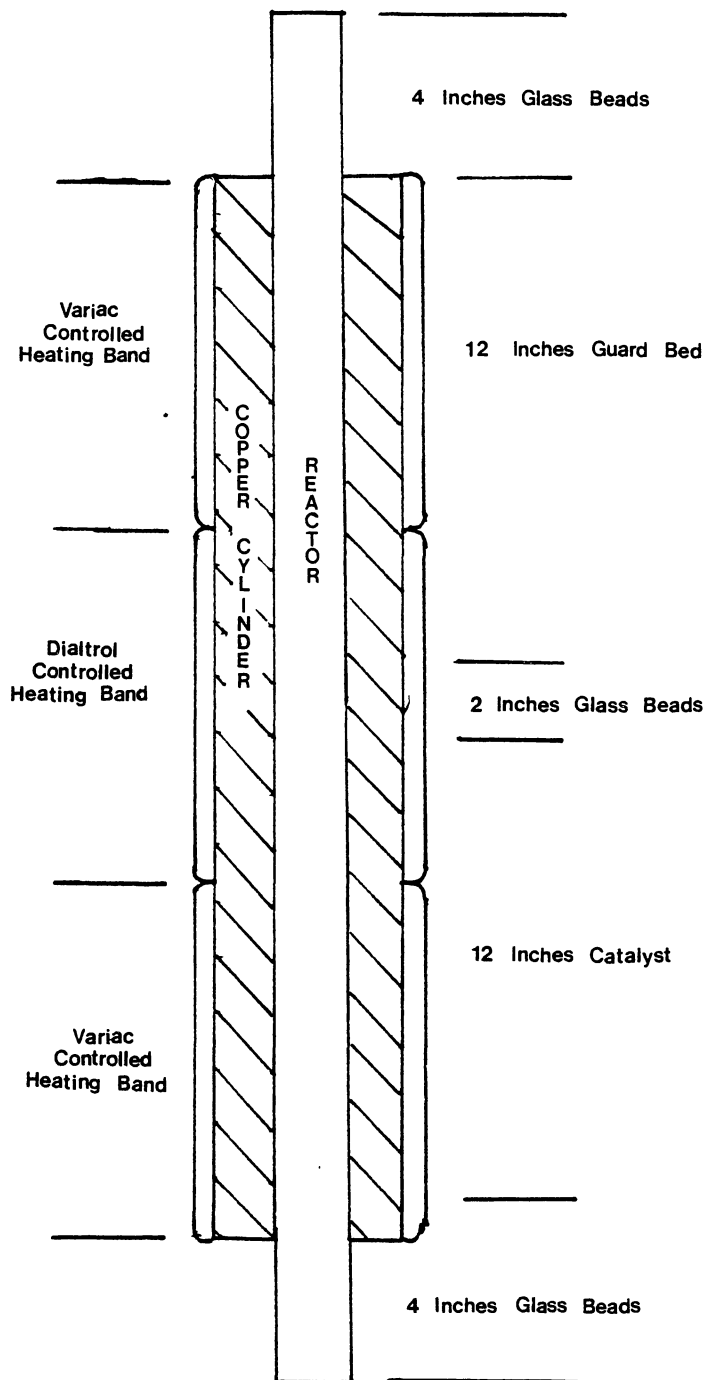


Figure 4. Heating and Packing Arrangement for the CLTU Reactor

## CHAPTER IV

### EXPERIMENTAL PROCEDURE

This investigation was designed to compare the effect of using materials with varying physical and chemical properties as guard beds in a hydrotreatment reactor. Four materials were chosen because they were believed to have good scavenging properties. Table I presents a number of characteristics of the four materials. Another experimental run utilized an atmospheric filter as the only pretreatment prior to the catalyst bed. For this run, the feedstock was first filtered using Whatman number 4 qualitative filter paper on an ASTM 40-60 ground glass filter.

In addition to the guard bed material, a catalyst bed comprised of Ketjen KF-153-S (Ni-Mo- $\text{Al}_2\text{O}_3$ ) 0.16 cm (0.0625 in) pellets was packed into the reactor tube. The properties of this catalyst are also given in Table I. During a run, the guard bed conditions were identical to the conditions within the catalyst bed. The conditions for each experimental run are listed in Table II.

The feedstock used during this investigation was first reclaimed at the National Institute of Petroleum and Energy Research (NIPER) according to the procedures described by Whisman et al. (1978a). This process utilizes a mixture<sup>s</sup> of 1-butanol, 2-propanol and methylethyl ketone as the solvent for the solvent extraction operation described previously. In addition, the oil was also distilled at NIPER to

TABLE I  
 PHYSICAL CHARACTERISTICS OF THE TESTED GUARD BED MATERIALS  
 AND THE KETJEN CATALYST

MATERIAL	PORE VOLUME ( $10^3 \text{ m}^3/\text{kg}$ )	SURFACE AREA ( $10^{-3} \text{ m}^2/\text{kg}$ )	PACKING <sup>†A</sup> DENSITY ( $10^{+3} \text{ kg}/\text{m}^3$ )	MOST FREQUENT PORE DIAMETER ( $10^{-10} \text{ m}$ ) <sup>-</sup>
Katalco Alumina Pellets	0.78	405.3	0.643	39.5
Norton Alumina Spheres	0.43	49.0	0.577	150 and 2000
Filtrol Activated Clay	0.31	271.3	0.837	1900
Darco Activated Carbon	0.94	206.6	0.370	2500
Ketjen KF-153-S Catalyst	0.42	282.3	0.894	32

<sup>†</sup>Packing Density = (Material Weight)/(Bed Volume)

TABLE II  
REACTOR OPERATING PARAMETERS

RUN NUMBER	GUARD BED MATERIAL	PRESSURE (kPag)	TEMPERATURE (°C)	LHSV (h)	HYDROGEN RATE (std m <sup>3</sup> /m <sup>3</sup> )
RIV	Katalco A-5 Alumina	4583 ± 35	325 ± 2	1.0	852 ± 72
RV	Norton 3232 Alumina	4583 ± 35	325 ± 2	1.0	797 ± 75
RVI	Filtrol Activated Clay	4583 ± 35	325 ± 2	1.0	784 ± 59
RVII	Darco Activated Carbon	4583 ± 35	325 ± 2	1.0	723 ± 86
RVIII	Katalco A-5 Alumina	4583 ± 35	325 ± 2	1.0	760 ± 49
RIX	Atmospheric Filter	4583 ± 35	325 ± 2	1.0	788 ± 86

remove alledged halide contaminants that had caused severe corrosion problems in their hydrogenation reactor.

The experimental procedure consists of catalyst loading, catalyst activation, reactor startup, normal operation, sampling, shutdown, and analysis. A detailed discussion of each step follows.

#### Reactor Loading

The reactor was loaded and installed in such a manner as to maintain constant temperature in both the guard and catalyst beds. The guard bed typically consisted of a material believed to have good scavenging properties and capable of withstanding the moderate temperatures and pressures existing in the reactor. The catalyst used was obtained from a vendor and had proven to be a good hydrogenation catalyst in a previous study (Bhan, 1983). The step-by-step procedure followed when packing the reactor tube is given in Appendix B.

After loading, the reactor tubes were placed on the CLTU and pressure tested at 6998 kPa (1000 psig). A pressure test was considered successful if the pressure recorder displayed no significant pressure losses in any individual section of the reactor. Once the system was free of leaks, the wet felt and fiberglass insulation were placed on the reactor and activation procedures were begun.

#### Catalyst Activation

The catalyst was activated in the two steps described below.

#### Calcination

Calcination procedures were begun by allowing 16.7 m<sup>3</sup>/sec

(589 ft<sup>3</sup>/sec) of nitrogen to flow into the reactor at 793 kPa (100 psig). Once this flow rate had been established, the reactor temperature was gradually raised (at the rate of 1.7 °C/min) to the operating temperature, 325 °C (617 °F). This temperature was maintained for approximately one hour to insure that all residual moisture was driven out of the catalyst bed.

### Presulfiding

In order to transform the catalyst to its active state, the nitrogen supply was shut off and a five percent mixture of hydrogen sulfide in hydrogen was introduced to the reactor at a rate of 16.7 m<sup>3</sup>/sec (589 ft<sup>3</sup>/sec). Reactor pressure and temperature were maintained at 793 kPa (100 psig) and 325 °C (617 °F), respectively. After 1.5 hours of presulfiding, the hydrogen sulfide supply was shut off and the reactor was purged with nitrogen for approximately 0.25 hours. During this time, the Ruska pump was filled with feed oil and set for the proper delivery rate.

### Reactor Startup

Once the catalyst had been activated, the reactor pressure was raised to operating conditions (4583 kPa or 650 psig) with hydrogen. The pressure controller set point was then adjusted to the proper position and the hydrogen flow rate was manipulated until 8.3 m<sup>3</sup>/sec (294 ft<sup>3</sup>/sec) was obtained. As mentioned earlier, the hydrogen flow was largely controlled by the metering valve located between the reactor and the pressure regulator.

Having set the hydrogen volumetric flow rate, the oil in the



Ruska pump was manually compressed to operating pressure and introduced into the reactor. All alarm systems were then activated and the time of oil-on-catalyst was recorded.

#### Normal Operating Procedures

As mentioned earlier, the CLTU was designed for unattended operation. Once started up, the system should not require any additional attention other than to obtain samples. However, should something fail, the unit has numerous alarm systems that automatically notify the operators.

Furthermore, temperature and pressure profiles were continuously monitored by two Honeywell pen plotters. In this manner, the operators were informed of any deviations that might occur between sample periods and were able to make corrections in order to prevent reoccurrence.

#### Sampling Procedure

Due to the capacity of the collection bomb, samples had to be collected every six hours. The procedure used to obtain each sample is presented in Appendix B. Once the samples were collected, the Ruska pump was refilled. On the average, the system restabilized within 0.25 hours after the sample had been collected.

#### Shutdown Procedure

Once a run had been completed, the oil supply was shut off, all reactor and line heaters were turned off, and the fiberglass insulation was removed from the reactor. The hydrogen flow rate during the run was maintained as the reactor was allowed to cool.

Once the system had reached ambient temperature, the hydrogen supply was shut off and the reactor was vented to the atmosphere. The reactor tube was then removed and capped.

#### Sample Analysis

Liquid samples were analyzed for metals, color, nitrogen, hydrogen, and carbon. They were also subjected to ASTM 1160 distillations to aid in determining the extent of hydrogenation. Catalyst and guard bed materials were analyzed for coke content, pore volume, surface area, and metal deposits. The procedures used for these analyses are given in Appendix B.

## CHAPTER V

### EXPERIMENTAL RESULTS AND DISCUSSION

The most significant difference in liquid characteristics occurred in the ASTM 1500 color analysis. Though the color of lubricating oils and other petroleum products do, to a limited degree, indicate desired changes in hydrocarbon structures, its major significance has to do with the final product's marketability. Even though acceptable values of color have been established, the current implication is that the lighter the color the better. Bethea et al. (1973), using Nalcomo 471 Co-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst to treat distilled used lubricating oil, reported color values ranging from 0.5 to 1.5 and that the typical color of a 150 vis neutral lube base stock is 1.5. Based on this information, the color values recorded during this investigation were considered satisfactory if they were lighter than ASTM standard number two.

Figure 6 presents the initial color of each sample for all six experimental runs. Due to a delay in receiving the color comparator, the colors of the products of runs RIV and RV had to be backdated to the time of their collection using the color aging results presented in Figure 7. The color aging plot was obtained by monitoring the change in color of the samples of runs RVII, RVIII and RIX and graphing the average change associated with a particular time interval.

The only run that produced unsatisfactory color values in the

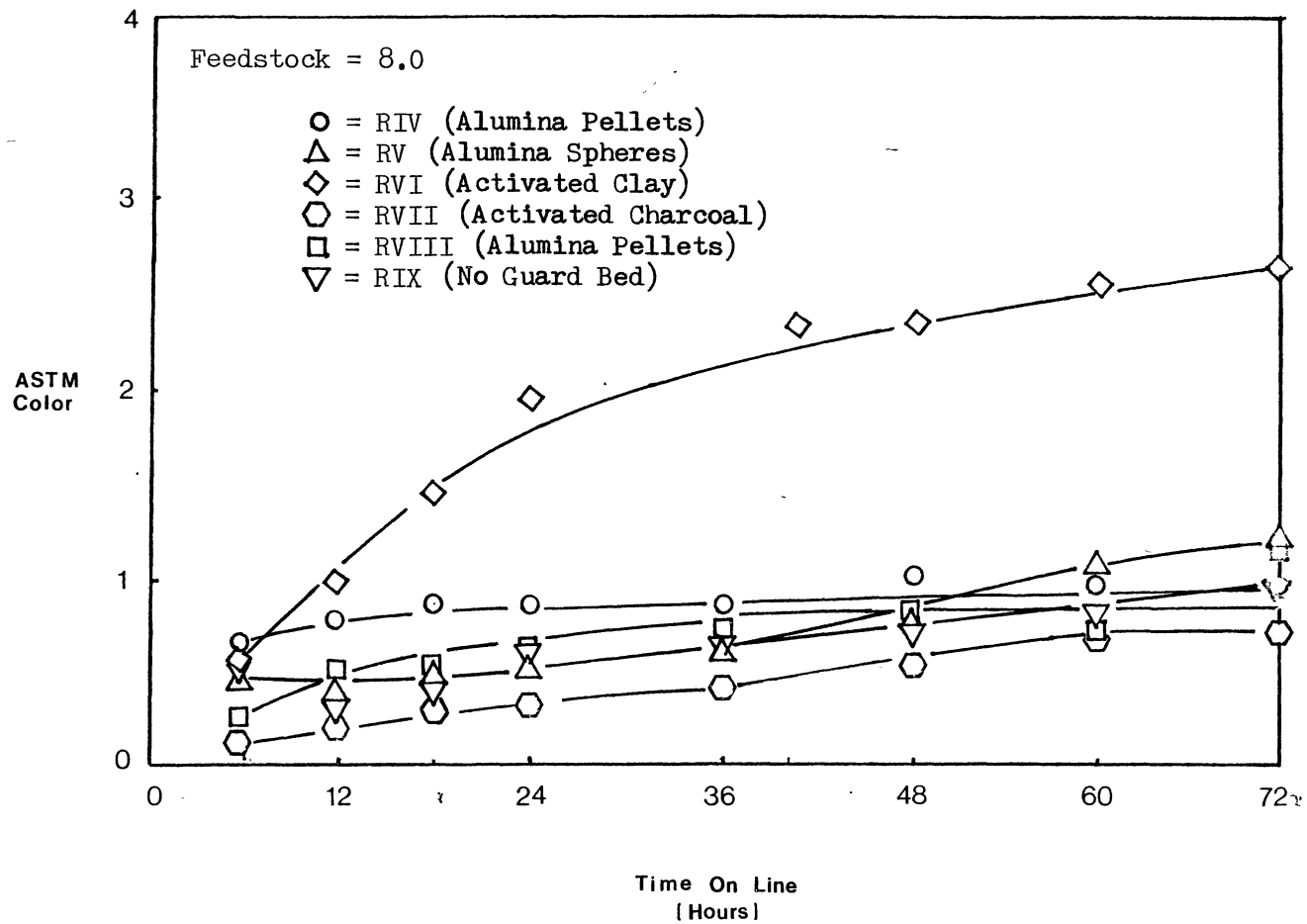


Figure 5. Comparison of Product Colors Upon Their Collection

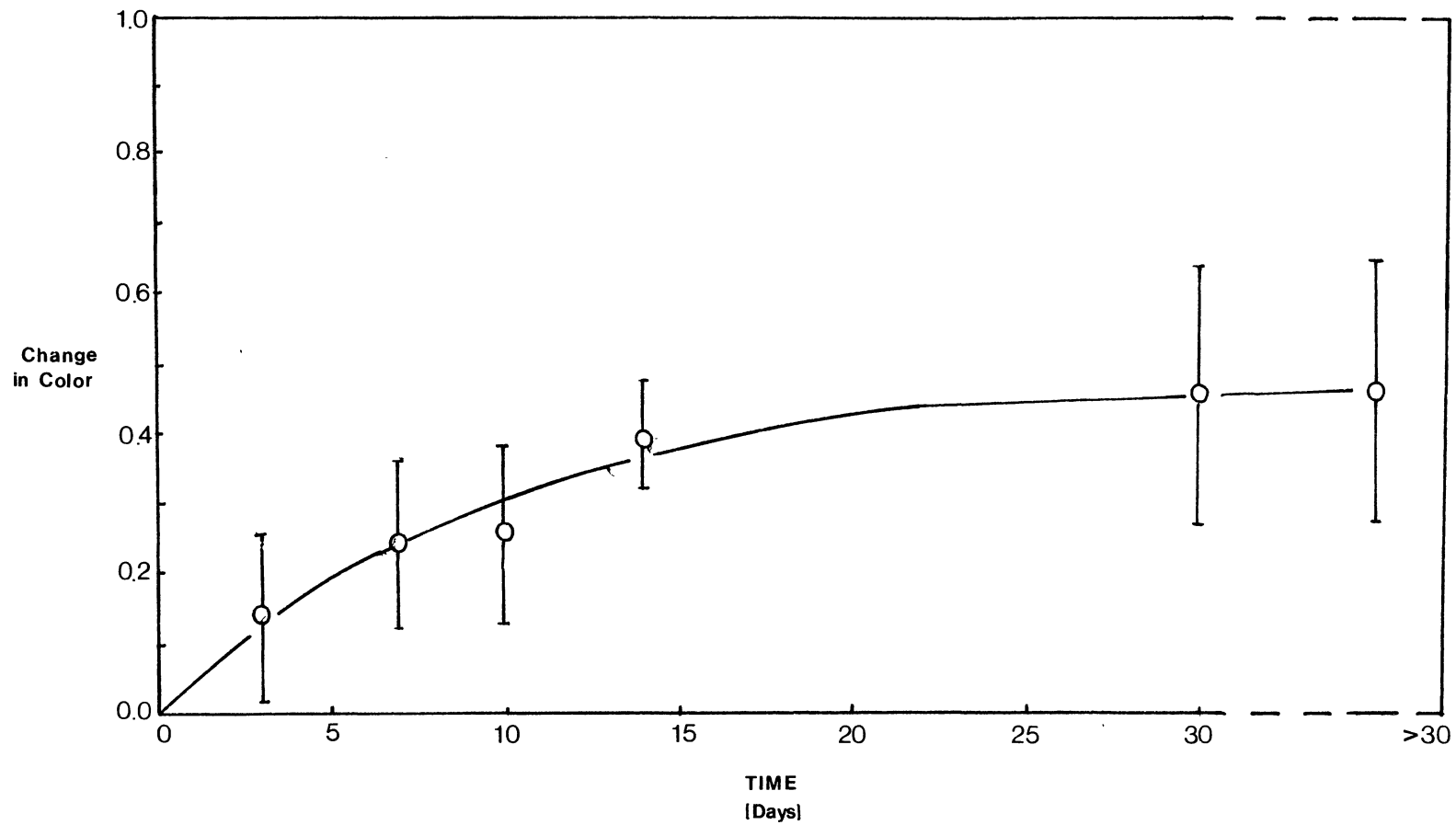


Figure 6. Change in Product Color During Aging

product oil was series RVI in which Filtrol grade 25 activated clay was used as a guard bed. This was surprising as Filtrol grade 20 clay had already proven to be a successful clay contacting agent in a study conducted by Whisman and his co-workers (1978c). Furthermore, series RIX, which was made without a guard bed, produced a lube base stock with a color between 0.4 and one. This would seem to imply one of three things: (1) Activated clay somehow inhibits color improvement, or (2) The filter of run RIX removed some color bodies that the activated clay could not, or (3) Some discrepancy in operating conditions or catalyst activation occurred during run RVI. However, in light of the clay's success as a contacting agent, it would seem highly unlikely that it would inhibit the color improvement realized in the catalyst beds. In addition, no deviations in reactor operating parameters were recorded and catalyst activity (in terms of hydrodemetallation and hydrogenation rates) appeared to be comparable to other runs. Therefore, it would appear that the paper and ground glass filters used in run RIX were more effective in removing color bodies than was the activated clay of series RVI.

Experimental series RVII tended to produce the greatest color improvement. Though no published data predicting this behavior could be found, it would appear that the activated carbon of series RVII may possess some additional catalytic or scavenging activity that is not present in the other materials. The large pores and high total pore volume of the carbon would enhance scavenging activities while the fairly large surface area would contribute to any catalytic activity that might exist on the carbon.

The choice of guard beds appeared to have little effect on either

the distillation curves or the hydrogen-to-carbon atomic ratio of the product oils. This is to be expected since the reactor was operated under mild hydrotreating conditions. The ASTM 1160 distillation results are presented in Appendix A. The recorded temperature was found to be accurate to within  $\pm 3$  °C. The only visible difference between the feedstock and the product oils usually appeared at the lower boiling temperatures. However, even these differences were small and indicated only small changes in base stock hydrocarbon structures. Many authors (Whisman et al., 1974b; Cutler, 1976) claim this result is desired since spent lubricating oil already contains the necessary base stock and more severe treatments could reduce yields.

The hydrogen-to-carbon ratios were measured using a Perkin-Elmer elemental analyzer that was found to be accurate to within two percent of the recorded value. Wilkinson (1983) and Chang (1983) studied the instrument's accuracy and a detailed procedure of the methods used can be found in their papers. The data obtained from this equipment are presented in the figures of Appendix A. Though the results do show a slight increase in the hydrogen-to-carbon atomic ratios (which would be expected during mild hydrogenation studies), they fail to demonstrate any significant differences between runs. These figures also show no evidence of catalyst deactivation during any of the 72 hour runs and confirm that the compositional characteristics of the base stock had been preserved.

The Perkin-Elmer analyzer used to determine the hydrogen-to-carbon ratios was also capable of predicting the nitrogen content. However, the nitrogen content of the feedstock was found to be

approximately 0.05 % and was too low to accurately measure or to consider as a significant property. The sulfur contents of spent lubricating oils have proven to be insignificant in previous studies (Cotton et al., 1977; Bethea et al., 1973) and were not determined.

Liquid samples were analyzed for metal contamination by two methods: Atomic absorption and Inductively Coupled Argon Plasma Spectrometry. Atomic absorption procedures were used to determine the concentrations of aluminum, barium, calcium, copper, iron, lead, magnesium, and zinc. Phosphorous contamination was determined using the latter piece of analytical equipment.

The only metals found to exist in the feedstock were iron, lead, zinc, and phosphorous. However, zinc and lead concentrations were also very low. The relative concentrations of these metals in the original feedstock and in the samples collected after 72 hours of reactor operation are given in Table III. The data show no significant iron or phosphorous breakthrough in any of the runs though series RVI (activated caly) allowed 8.7 % of the feedstock iron to remain in the product oil. No indication of metals contamination was detected in the product of series RVII (activated carbon).

The metal contaminants present in the feedstock were in low concentrations due to the method of reclaiming used. Whisman et al. (1974b) found that by reclaiming spent oil using a solvent extraction process combined with distillation, metal contamination could be greatly reduced and clogging problems in distillation equipment could nearly be eliminated. The effectiveness of this treatment in removing metallic contaminants was presented by Whisman and his coworkers (1974a) and is comparable to the results presented in this investigation.



TABLE III

METALS AND PHOSPHOROUS CONCENTRATIONS  
IN THE FINAL LIQUID PRODUCTS

LIQUID SAMPLE	GUARD BED MATERIAL USED	ELEMENTS, ppm			
		Fe	Zn	Pb	P
FEED	N/A	23	1.1	0.6	80
RIV-8	Alumina Pellets	0.8	0.5	ND	L5
RV-8	Alumina Spheres	0.2	ND	ND	L5
RVI-8	Clay	2.0	0.6	ND	L5
RVII-8	Carbon	ND	ND	ND	L5
RVIII-8	Alumina Pellets	0.3	0.6	ND	L5
RIX-9	None	0.6	0.3	ND	L5

N/A = Not Applicable  
 ND = Not Detected  
 L5 = Less than 5 ppm

However, the low concentrations of metallic substances do make the feedstock of this investigation atypical. Other types of reclamation processes may not be as effective in chemically demetallizing the spent oil. While studying a number of process schemes and alternatives, Whisman et al. (1974a) reported that a solvent-distillation reclaiming process would give the best results in terms of removal of inorganics, acidic components, organometallic additives, wear metals, and lead. Other reclaiming methods would produce oils with higher concentrations of metallic compounds and could present additional difficulties in hydrofinishing processes.

Iron and phosphorous were the only two inorganics present in high enough concentrations to be used to study the effects of metallic deposition on catalyst and guard bed activity. However, these two elements represent the two types of detrimental components that exist in used lubricating oil. Iron is a wear metal that accumulates in the engine crankcase, while phosphorous exists as an organic compound used as an additive in the original lubricant formulation.

While the EDAX is only semi-quantitative, it can indicate large differences in metallic deposits. The numerical values shown in Tables IV and V represent the intensity of iron and phosphorous X-rays produced at the catalyst surface, respectively. The intensities are roughly proportional to the compositional make-up of the deposit analyzed and can be used to make comparisons.

Phosphorous deposits found in the guard beds demonstrated varying profiles over the beds' lengths. However, iron deposits tended to concentrate at the guard bed entrances. The most noticeable results of the EDAX was that the activated carbon of series RVII had collected

TABLE IV

SEMI-QUANTITATIVE DETERMINATION OF THE  
EXTENT OF IRON DEPOSITION \*

RUN NUMBER	GUARD BED MATERIAL USED	GUARD BED			CATALYST BED		
		TOP	MIDDLE	BOTTOM	TOP	MIDDLE	BOTTOM
RIV	Alumina Pellets	37	5	6	9	6	2
RV	Alumina Spheres	65	20	87	55	2	2
RVI	Activated Clay	21	0	7	1	2	1
RVII	Activated Carbon	240	155	23	9	4	1
RVIII	Alumina Pellets	44	9	9	11	2	5
RIX	None				220	10	6

\* All Numbers Represent Intensities Of X-Rays Produced at the Deposits Surface

TABLE V

SEMI-QUANTITATIVE DETERMINATION OF THE  
EXTENT OF PHOSPHOROUS DEPOSITION \*

RUN NUMBER	GUARD BED MATERIAL USED	GUARD BED			CATALYST BED		
		TOP	MIDDLE	BOTTOM	TOP	MIDDLE	BOTTOM
RIV	Alumina Pellets	2	1	4	0	0	0
RV	Alumina Spheres	0	1	10	23	0	0
RVI	Activated Clay	7	0	0	0	0	0
RVII	Activated Carbon	22	78	11	6	0	0
RVIII	Alumina Pellets	15	3	0	2	0	2
RIX	None				118	3	0

\* All Numbers Represent Intensities of X-Rays Produced at the Deposits Surface

significantly larger amounts of iron and phosphorous than did the other guard beds. The absence of iron and phosphorous compounds in the liquid samples of this run also indicate this increase in effectiveness.

Both phosphorous and iron deposits detected in the catalyst bed tended to be greater at the reactor entrance. Series RIX, which utilized a prefiltered feedstock and no guard bed, showed significantly larger deposits in the catalyst than in any other run. This result is especially significant since it provides some insight into guard beds and their effectiveness on catalyst deactivation. Though this investigation showed no significant catalyst deactivation during any of the 72 hour runs, the appearance of metallic deposits on catalyst surfaces has been shown to be detrimental to catalyst activity (Tamm, 1981). Ultimately, these deposits will deactivate the catalyst.

The coke content of the catalyst and guard bed materials was determined by the amount of tetrahydrofuran insolubles deposited on the pellet surfaces. The results are presented in Figures 9 and 10 and were found to be accurate within  $\pm 3\%$  coke based on the spent pellet weight. The weight percent coke deposited on the decolorizing carbon of series RVII was not determined since the oxidation process involved would have destroyed the guard bed material itself. Catalyst coking showed no significant differences between runs, though some runs seemed to establish lower levels of coking.

The constant coking profiles produced in this investigation were predicted by Chang (1983). Chang found that the amount of carbonaceous material deposited on catalyst surfaces while hydrotreating certain coal liquids tended to be evenly distributed over the reactor length after 72 hours of on line operation.

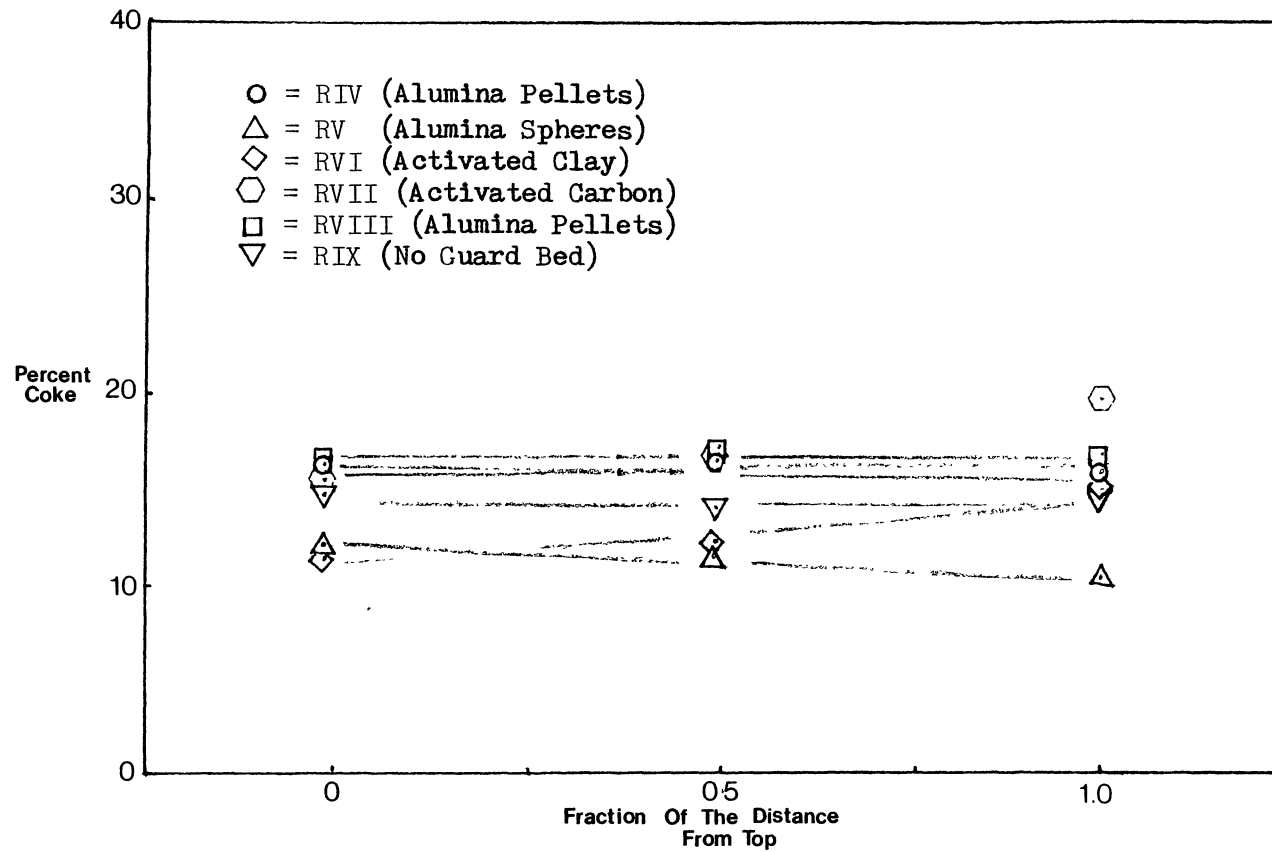


Figure 7 . Coking Profiles for the Main Catalyst Bed.

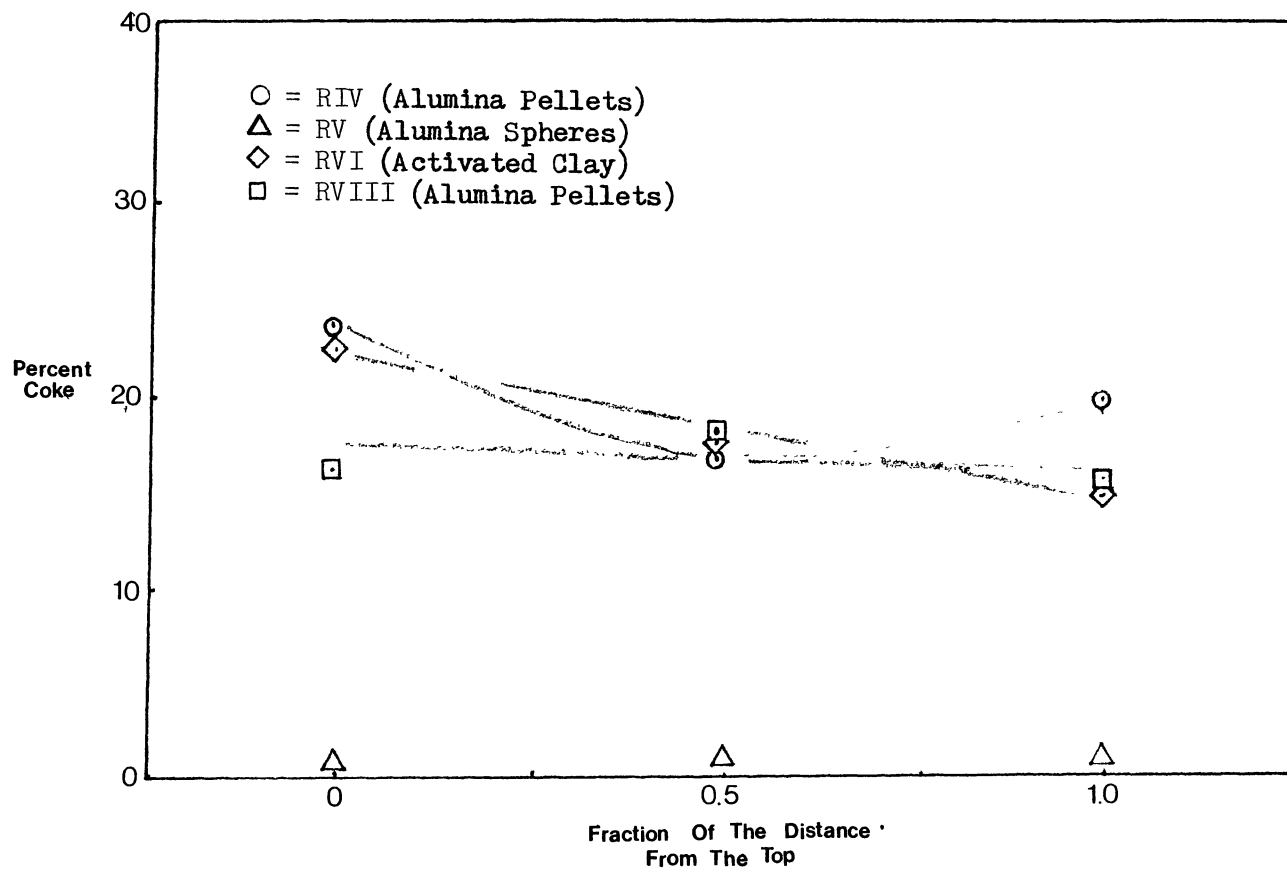


Figure 8. . Coking Profiles for the Guard Beds.

The most noticeable aspect of the coking results was the fact that the alumina spheres of series RV developed less than one percent coke. However, upon retrieving the alumina from the guard bed, it was found that a black, viscous substance had accumulated in the bed's interstices. Elemental analysis of this material showed that the hydrogen-to-carbon atomic ratio was 0.153 and that 61.7 % of the sample fed to the analyzer was recovered. This implies that 38.3 % of the substance was composed of undetectable elements such as iron, phosphorous, oxygen, sulfur, chlorine, and other oil contaminants.

The existence of this material in the guard bed interstices of run RV is unprecedented. However, the similarity in the chemical compositions of the Katalco pellets and the Norton spheres suggests that the differences in their physical properties are important. The major differences between these two guard bed materials lie in their physical characteristics (see Table I). The spheres had larger pores, smaller overall pore volume, a lower surface area, and a significantly different geometric shape. The smaller pore volume of the alumina spheres (almost half of that of the Katalco pellets) could explain the plugging evidenced in the guard bed of series RV (A smaller pore volume would tend to fill up faster in materials of equal scavenging activity). The only other explanation would imply that the difference in geometric shapes could cause the plugging. However, no literature could be found that would predict or support such behavior.

The surface area and pore volume analysis of the spent catalyst and guard bed samples verified the results of the coking analysis (see Table VI). Those catalysts and guard beds that developed higher levels



TABLE VI

PHYSICAL PROPERTIES OF SPENT CATALYSTS AND  
GUARD BED MATERIALS

SAMPLE *	MATERIAL	PORE VOLUME ( $10^{-3}$ M <sup>3</sup> /KG)	SURFACE AREA ( $10^3$ M <sup>2</sup> /KG)	PORE SIZE ( $10^{-10}$ M)	PERCENT OF PORE VOLUME UNOCCUPIED
CIV-T	Spent Catalyst	0.24	155	30	56
CV-T	Spent Catalyst	0.33	239	27	77
CVI-T	Spent Catalyst	0.39	236	32	92
CVII-T	Spent Catalyst	0.21	148	33	50
CVIII-T	Spent Catalyst	0.27	157	32	65
CIX-T	Spent Catalyst	0.30	199	31	71
GIV-T	Spent Alumina	0.36	207	31	46
GV-T	Spent Alumina	0.46	42	28	100
CVI-T	Spent Clay	0.12	53	2000	38
CVII-T	Spent Carbon	0.49	66	2000	52
GVIII-T	Spent Alumina	0.30	170	32	38

\* All Samples Were Taken From The Top Zones of Their Respective Beds

of coke also showed a significantly larger decrease in surface area and overall pore volume. The total pore volumes and surface areas of each of the guard bed materials except the alumina spheres (series RV) were all greatly reduced during reactor operation (Table VI). This also supports the data obtained from the coking analysis since run RV (alumina spheres) acquired less than one percent coke on the guard bed surfaces. The pore volume of the spent catalyst of run RVII is probably lower than the other runs due to the breakthrough of small carbon particles originating in the activated carbon itself.

In review of the data, the most significant analyses made were those that determined product color and metals contamination and those that detected metallic and carbonaceous deposits on catalyst surfaces. Based on these results, the guard bed materials can be arranged in order of their decreasing effectiveness as follows: (1) the activated carbon of series RVII, (2) the alumina pellets of series RIV and RVII, (3) the atmospheric filter of series RIX, and (5) the alumina spheres of series RV. Series RVII produced results superior to those of the other runs in all analyses except that determining coke content, where the catalyst was found to have acquired a slightly higher level of coke than in the other runs. The alumina spheres of series RV were considered the least effective guard bed since they caused visible plugging in only 72 h of reactor operation.

#### Data Accuracy and Reproducibility

The accuracy of the results presented in this investigation depended not only on the accuracy of the analytical equipment, but also on the ability to minimize variations in overall reactor operating

conditions. Reactor temperature during each of the experimental runs was maintained at  $325^{\circ}\text{C}$  ( $617^{\circ}\text{F}$ ) with a standard deviation of  $\pm 2^{\circ}\text{C}$  ( $3.6^{\circ}\text{F}$ ). The total pressure in the reactor was held at 4583 kPa (650 psig) and had a standard deviation of  $\pm 35$  kPa ( $\pm 5$  psi). The average hydrogen flow rates of the runs varied from 723 std  $\text{m}^3/\text{m}^3$  of oil (4063 scf/bbl) to 852 std  $\text{m}^3/\text{m}^3$  (277 scf/bbl)  $\pm 86$   $\text{m}^3/\text{m}^3$  (483 scf/bbl). These effects were found to be negligible at rates above 531 std  $\text{m}^3/\text{m}^3$  (3000 scf/bbl) by both Wan (1974) and Sooter (1975) while conducting hydrotreating studies on coal liquids.

The elemental analyzer used to determine hydrogen-to-carbon ratios and nitrogen contents was periodically calibrated using standards with known compositions. In addition, each of the liquid samples was analyzed three times and the average composition was reported. Standard deviations of 9.0 % to 20.0 % of the average were reported for hydrogen-to-carbon ratios. Nitrogen contents were very low and high standard deviations (sometimes greater than 100 % of the reported average) indicated that the limits of the equipment had been reached.

The distillation equipment used to obtain the curves of Appendix A was initially tested for accuracy by boiling pure compounds with known boiling points. After these results proved that the equipment was reliable, the feedstock was subjected to three separate distillations. The results of comparing the three distillation curves showed an average standard deviation of  $\pm 3^{\circ}\text{C}$  ( $\pm 5.4^{\circ}\text{F}$ ) could be expected.

Metals analysis in the liquid products also produced reliable results. Two separate samples of the feedstock were prepared in varying amounts of Methyl Isobutyl Ketone (MIBK) and analyzed. Iron concentrations of 23.1 and 21.8 ppm were reported indicating the

reproducibility of this specific analysis.

The accuracy of the coking analysis was determined by calculating the coke contents of samples from the same reactor zone three separate times. This procedure resulted in standard deviations ranging from one to three weight percent.

The overall reproducibility of this investigation can be seen by comparing the results of runs RIV and RVIII. These two runs were made with identical guard beds (comprised of Katalco A-5 alumina) and produced results with negligible differences. There was very good agreement between these two runs. The coke profiles of the guard beds did show some differences toward the upper and lower portions of the beds, but the levels of coking that had been established were similar. These results, along with the small deviations produced within the analytical equipment, indicate the high reproducibility and accuracy of this study.

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

In this investigation, the effectiveness of four different materials used as guard beds in a hydrotreating reactor was evaluated. The four materials included Katalco A-5 alumina pellets, Norton 3232 alumina spheres, Darco activated carbon, and Filtrol grade 25 activated clay. In addition, another run was made using an atmospheric filter to remove feedstock components that would be harmful to the catalyst. The operating conditions maintained within the guard and catalyst beds were a temperature of 325 °C (617 °F), a pressure of 4583 kPa (665 psia), a liquid hourly space time of 1.0 h, and a hydrogen flow rate of 748 m<sup>3</sup>/m<sup>3</sup> of oil (4200 scf/bbl). Liquid properties and catalytic activity were then determined and used to draw the following conclusions:

1. All of the materials used, except the activated clay, produced satisfactory improvements in the liquid properties (i.e. color, hydrogen-to-carbon atomic ratio, metals concentrations, nitrogen content, and ASTM distillation curves).
2. The hydrofinishing of reclaimed used lube oils produces desired changes in liquid characteristics without creating severe changes in the hydrocarbon structure of the oil. A more severe treatment would greatly reduce yields.
3. The activated carbon was more effective at protecting the

catalyst bed and improving liquid characteristics than the other materials. The presence of the carbon seemed to provide some additional scavenging or catalytic activity that the other materials lacked.

4. Metallic elements appeared to be more effectively removed by highly porous materials with large diameter pores.

5. Both iron and phosphorous deposits tend to accumulate at the top of the catalyst bed. The deposition of these on the different guard beds demonstrated varying profiles and appeared to be largely dependent on the guard bed material. Of the materials tested, the activated carbon proved to be the most effective guard bed, while the alumina spheres proved to be the least effective.

6. The deposition of carbonaceous materials on catalyst surfaces did not show a significant reliance on guard bed properties.

Based on the literature and the results of this investigation, further studies are encouraged. The following recommendations for future projects are made:

1. To accurately study the deactivation of the catalyst, longer runs should be made. The length of the runs should be such that significant catalyst deactivation is evident.

2. The effects of temperature, pressure, and space time should be determined in order to optimize the hydrofinishing process.

3. Other materials could be tested for their ability to protect the catalyst bed. Some suggested materials would include fly ash, bauxite, charcoal, used hydrodesulfurization catalyst, and diatomaceous earth.

4. A feedstock more typical of other reclaiming processes should be used to expand on the results of this study. A feedstock

with higher concentrations of contaminants could provide more conclusive results on guard bed effectiveness.

5. Since the activated carbon appeared to effectively reduce metal concentrations, it may not be necessary to distill the lube oil before it enters the guard bed. This would greatly increase the importance of the guard bed and reduce the cost associated with producing a satisfactory product. This should be evaluated.

6. A controlled investigation into the effects of guard bed material shape and physical characteristics (pore volumes, surface areas and pore sizes) should be made to assist in determining prospective guard bed materials.

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APPENDIX A

DISTILLATION AND HYDROGEN-TO-CARBON  
ATOMIC RATIO CURVES

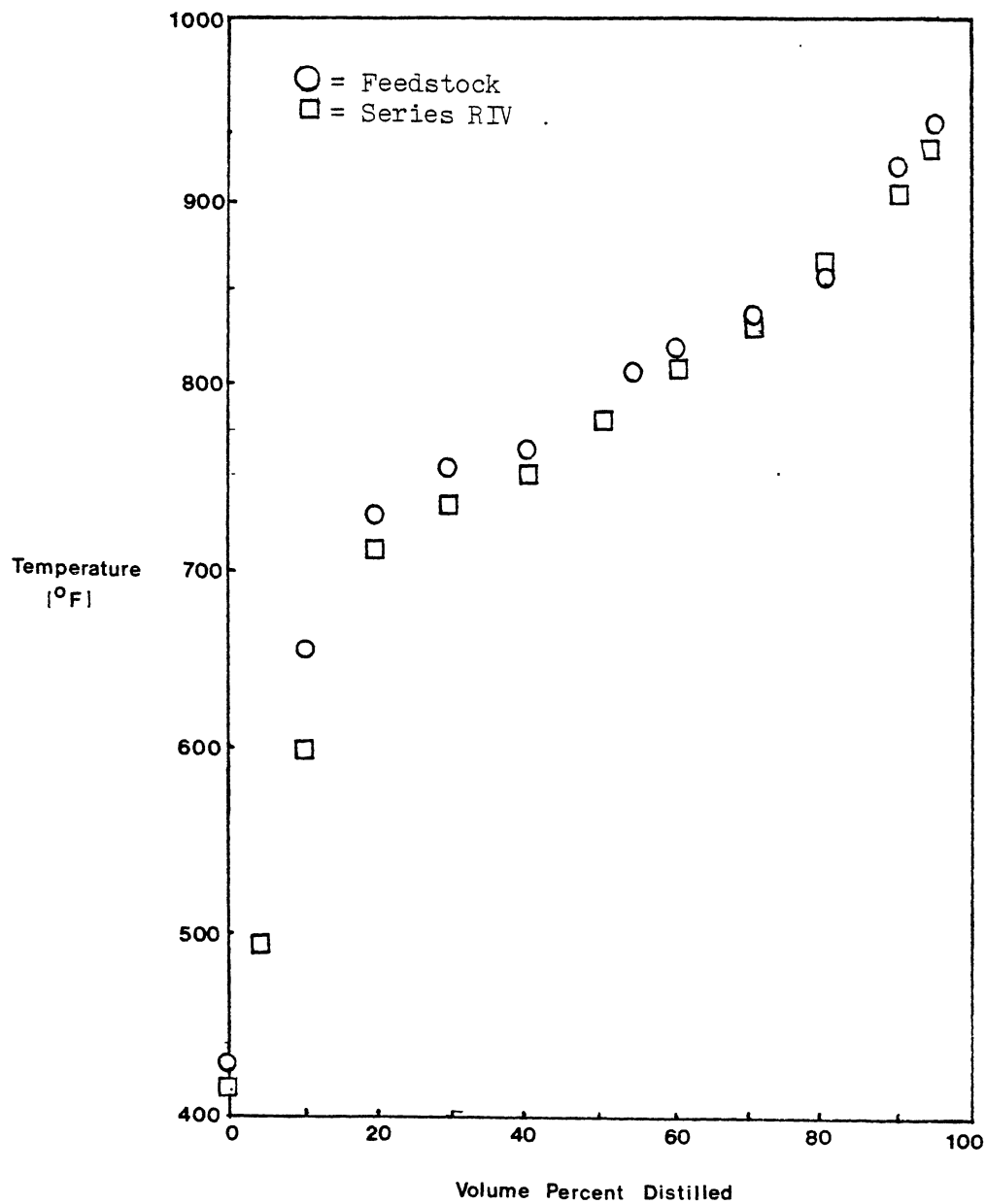


Figure 9 . Comparison of the Distillation Curves of the Feedstock and the Final Liquid Product of Series RIV.

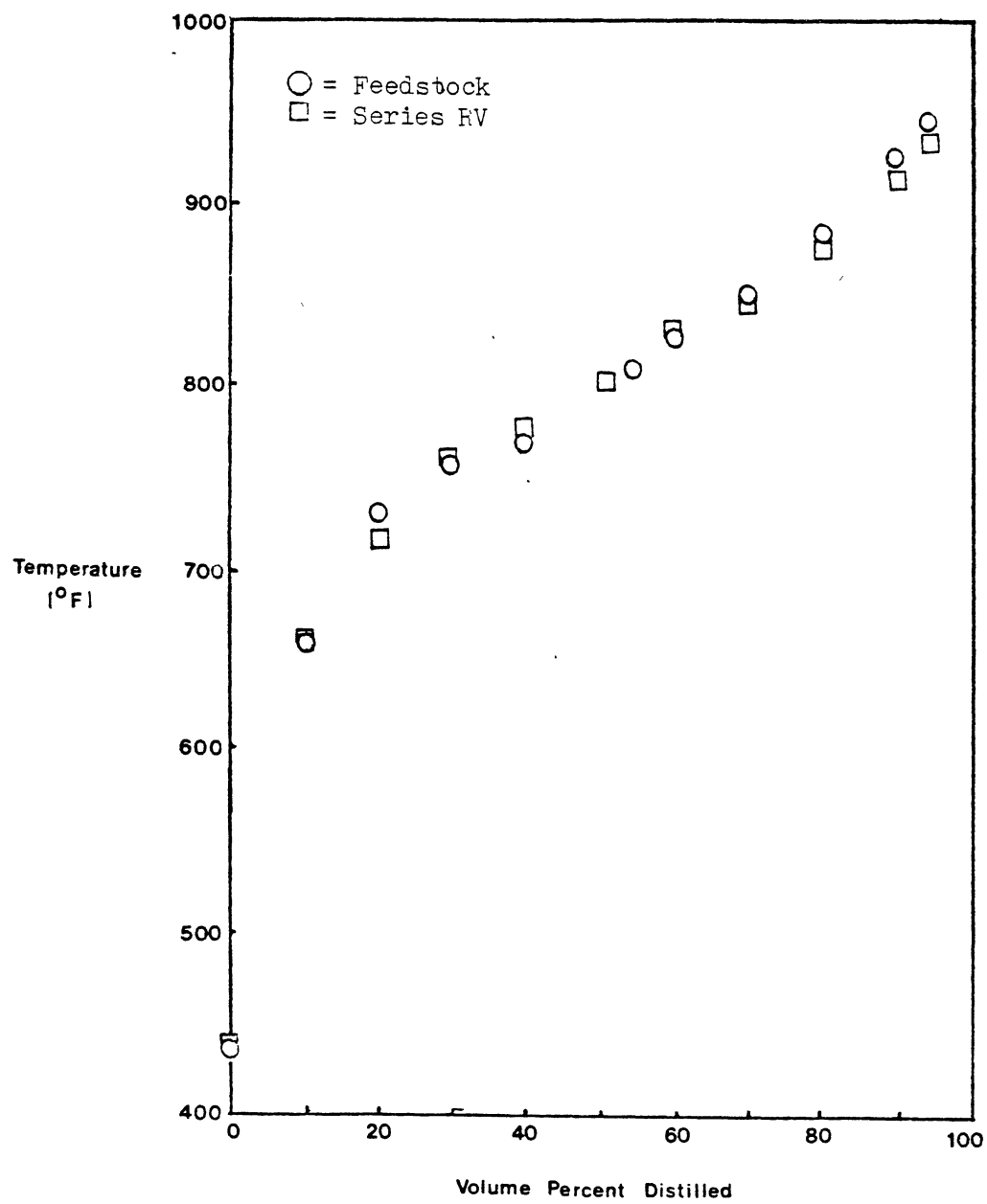


Figure 10. Comparison of the Distillation Curves of the Feedstock and the Final Liquid Product of Series RV.

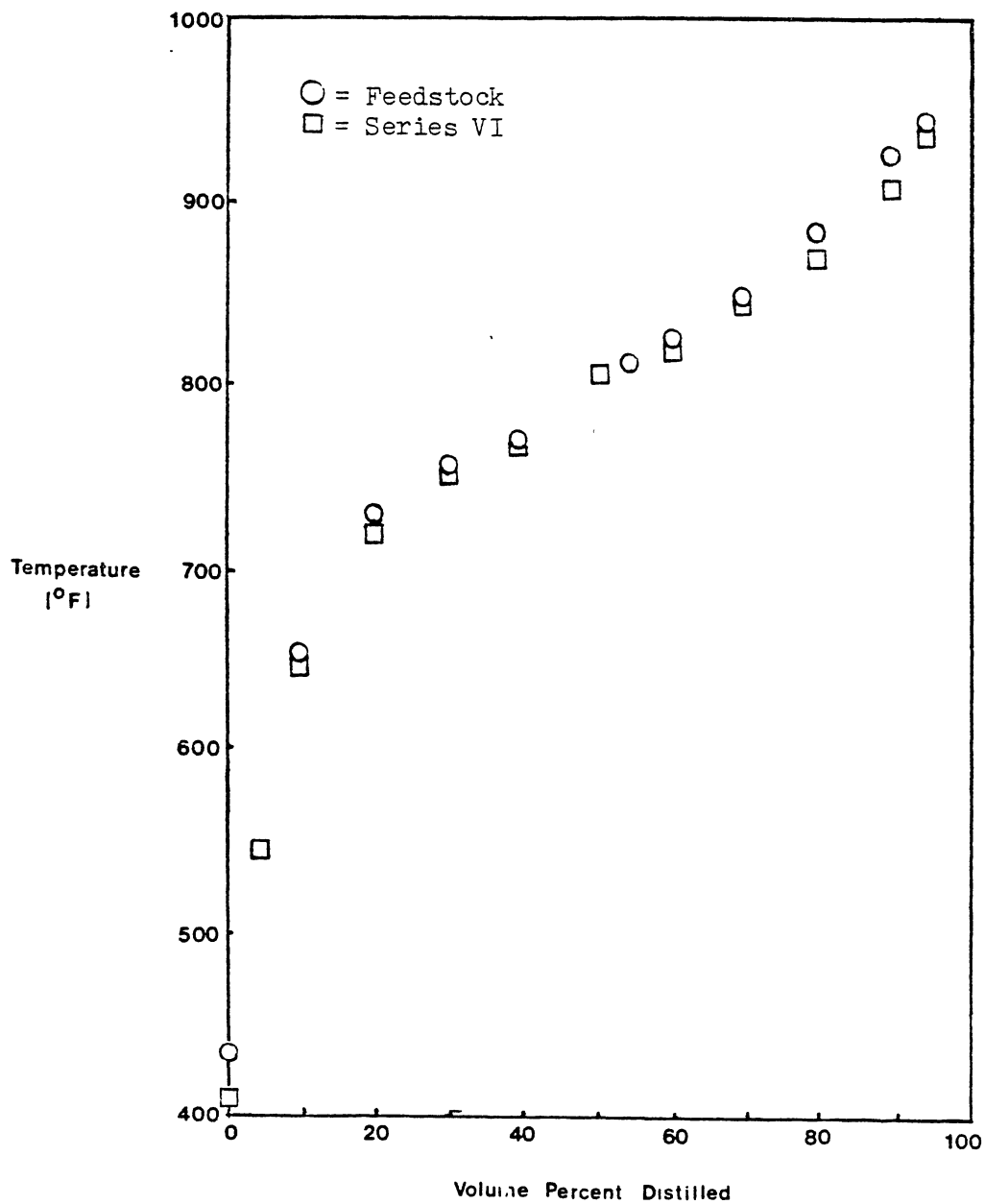


Figure 11. Comparison of the Distillation Curves of the Feedstock and the Final Liquid Product of Series VI.

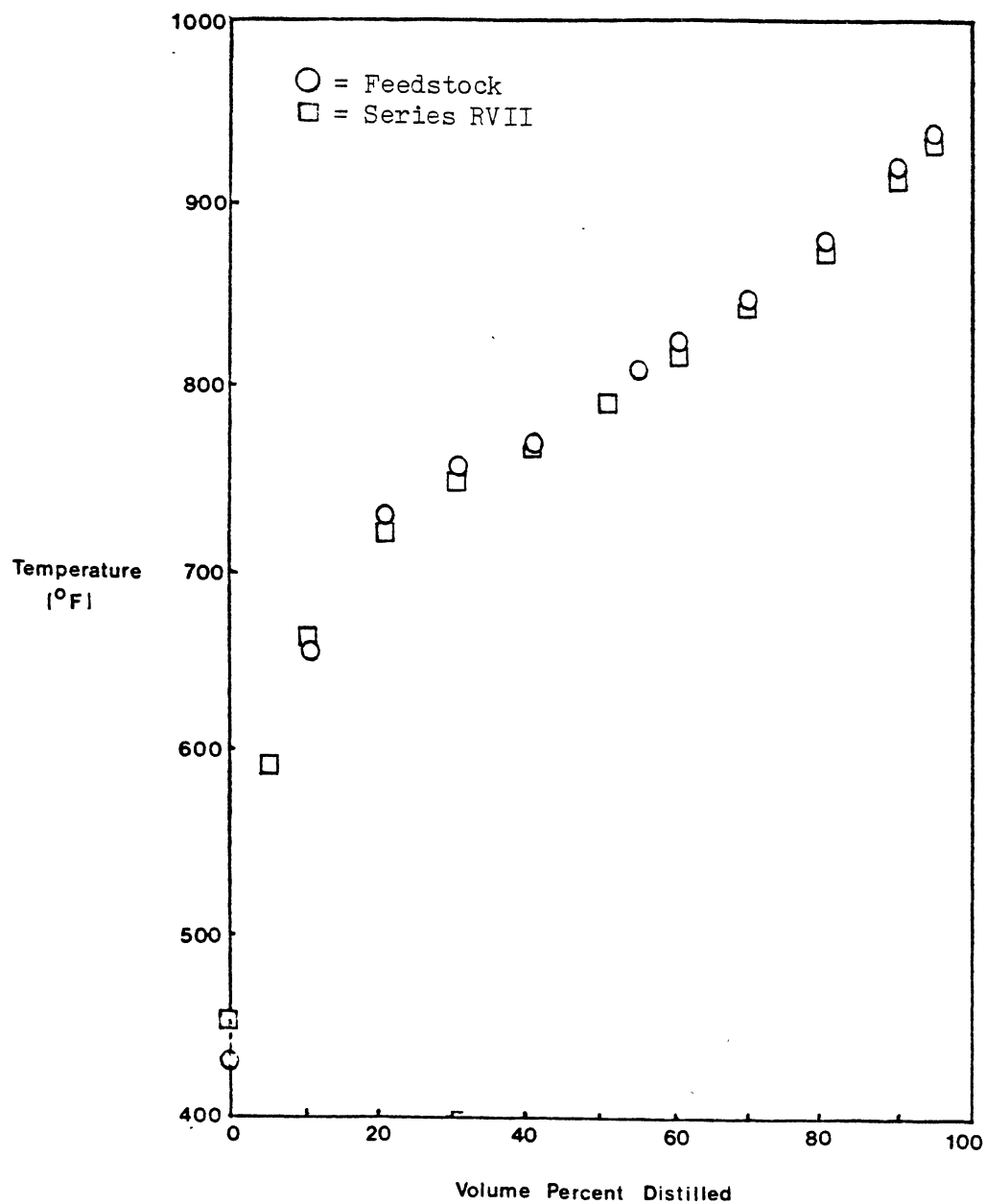


Figure 12. Comparison of the Distillation Curves of the Feedstock and the Final Liquid Product of Series RVII.



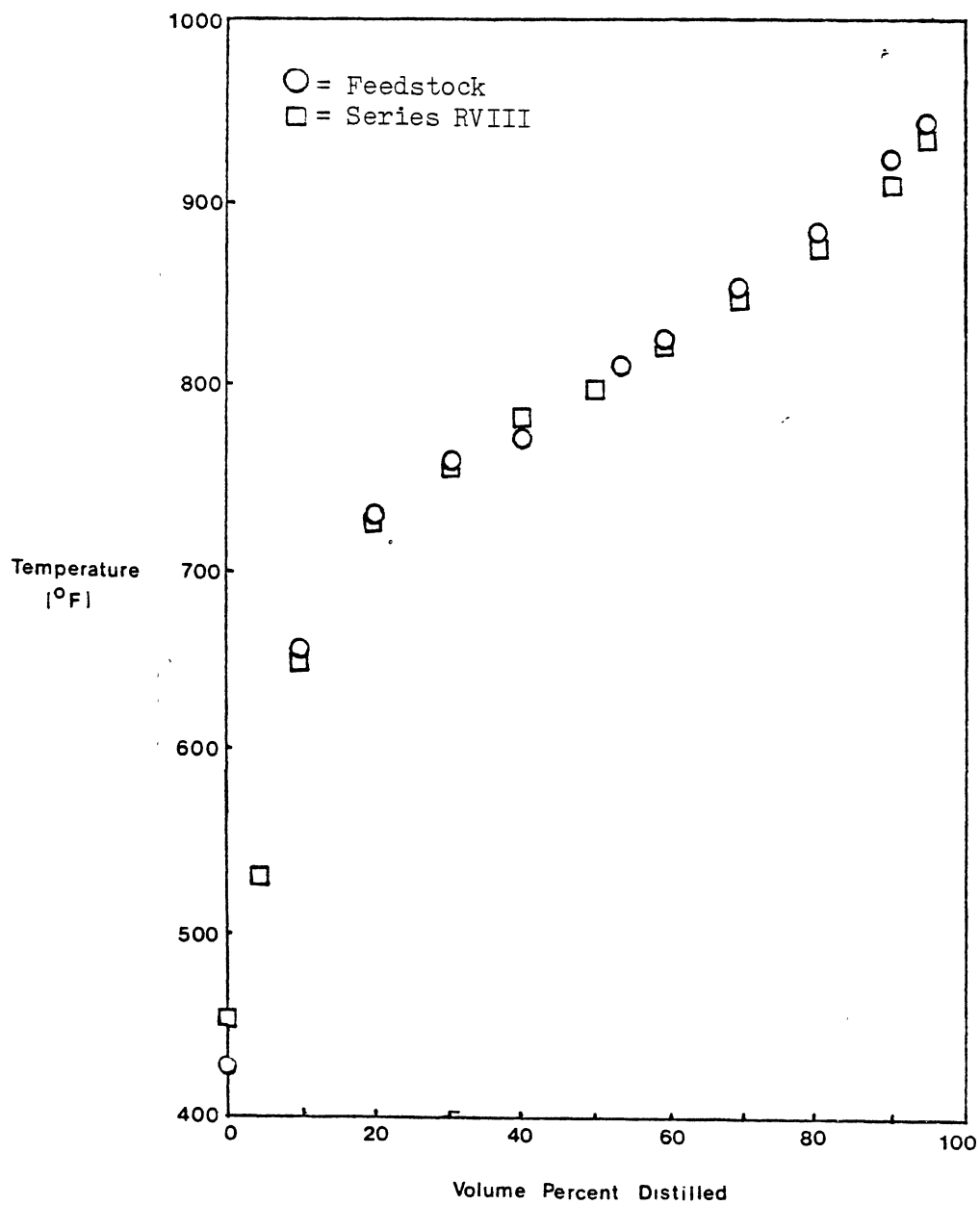


Figure 13. Comparison of the Distillation Curves of the Feedstock and the Final Liquid Product of Series RVIII.

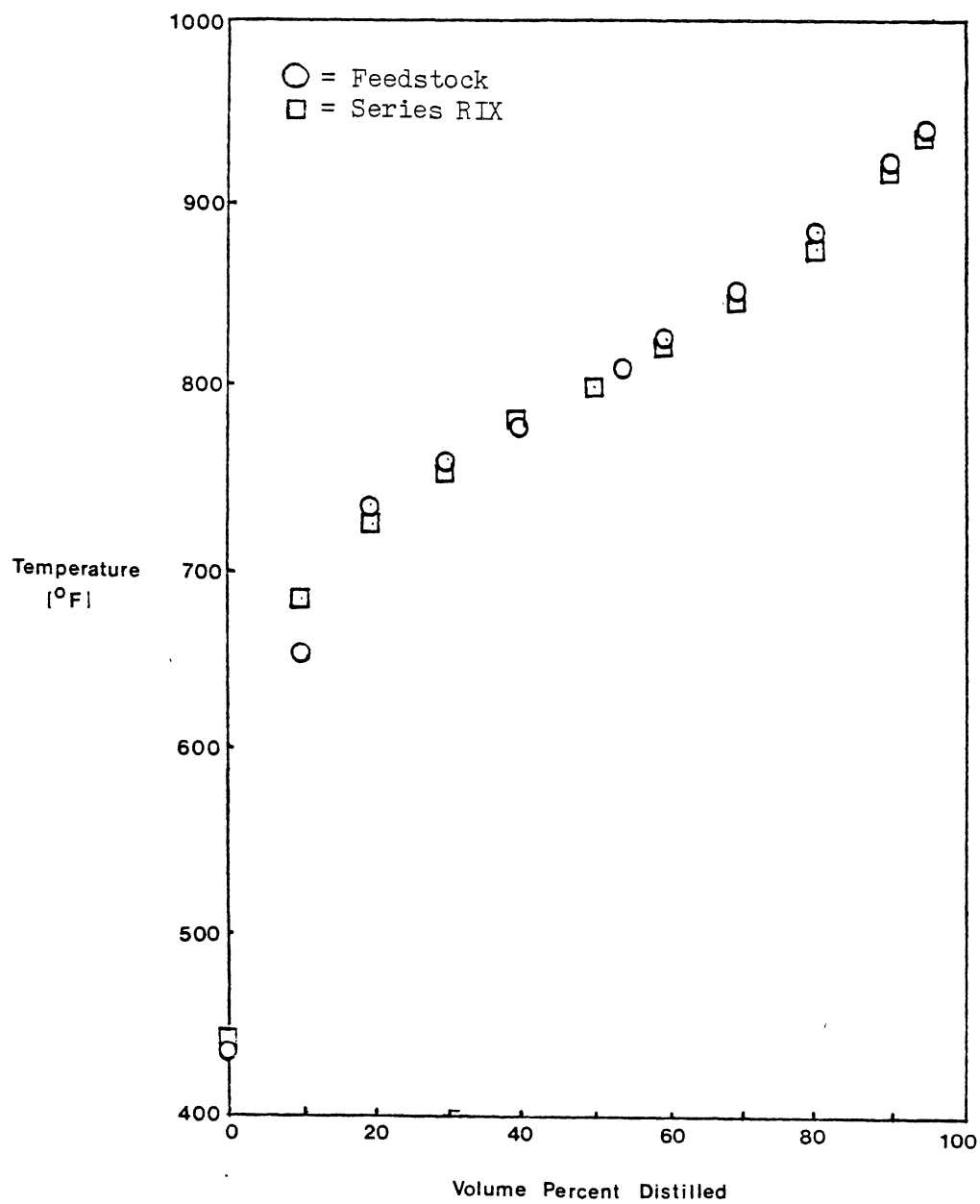


Figure 14. Comparison of the Distillation Curves of the Feedstock and the Final Liquid Product of Series RIX.

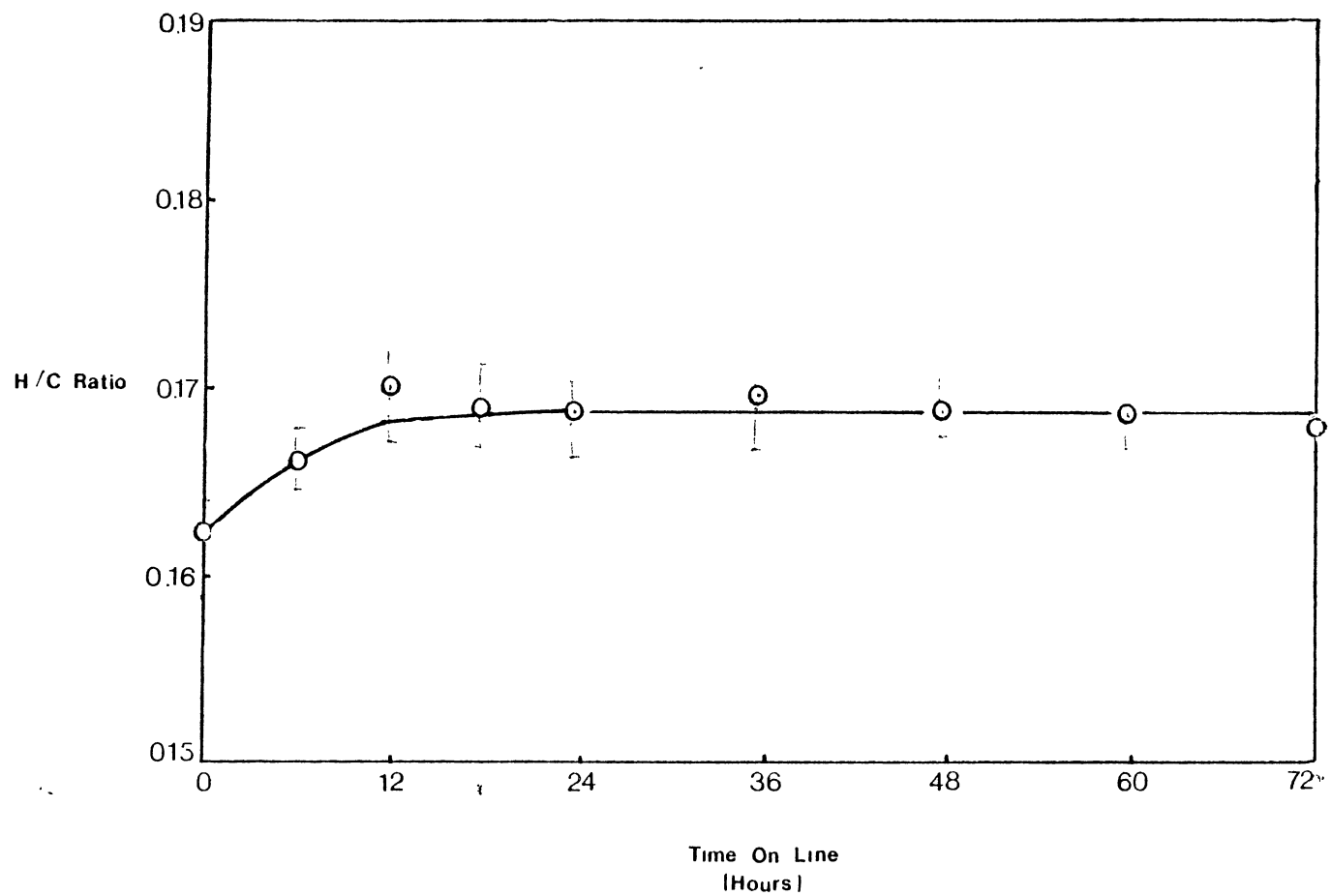


Figure 15. Hydrogen-to-Carbon Ratio of the Product Oil of Series RIV As a Function of the Time On Line.

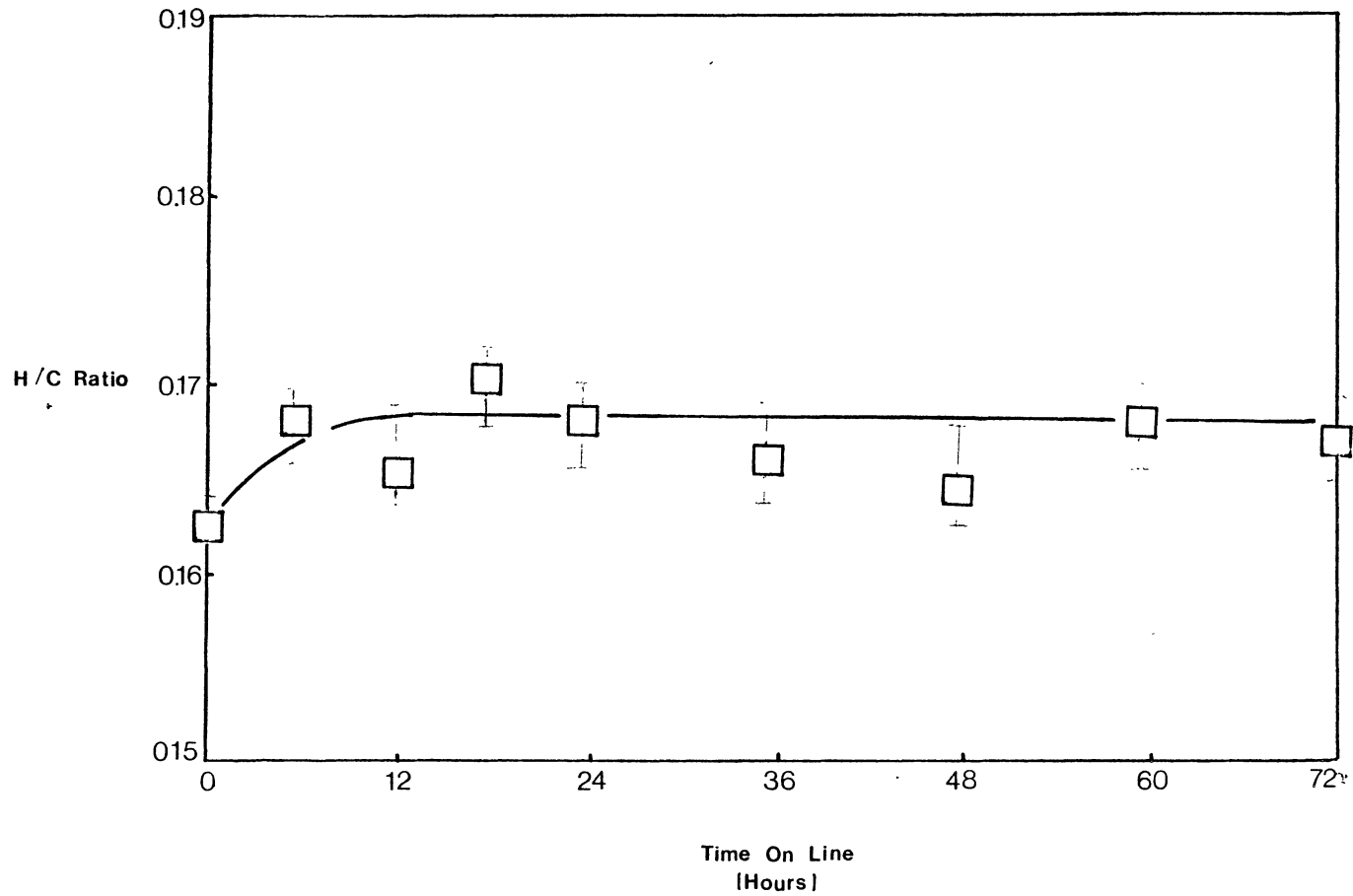


Figure 16. Hydrogen-to-Carbon Ratio of the Product Oil of Series RV As a Function of the Time On Line.

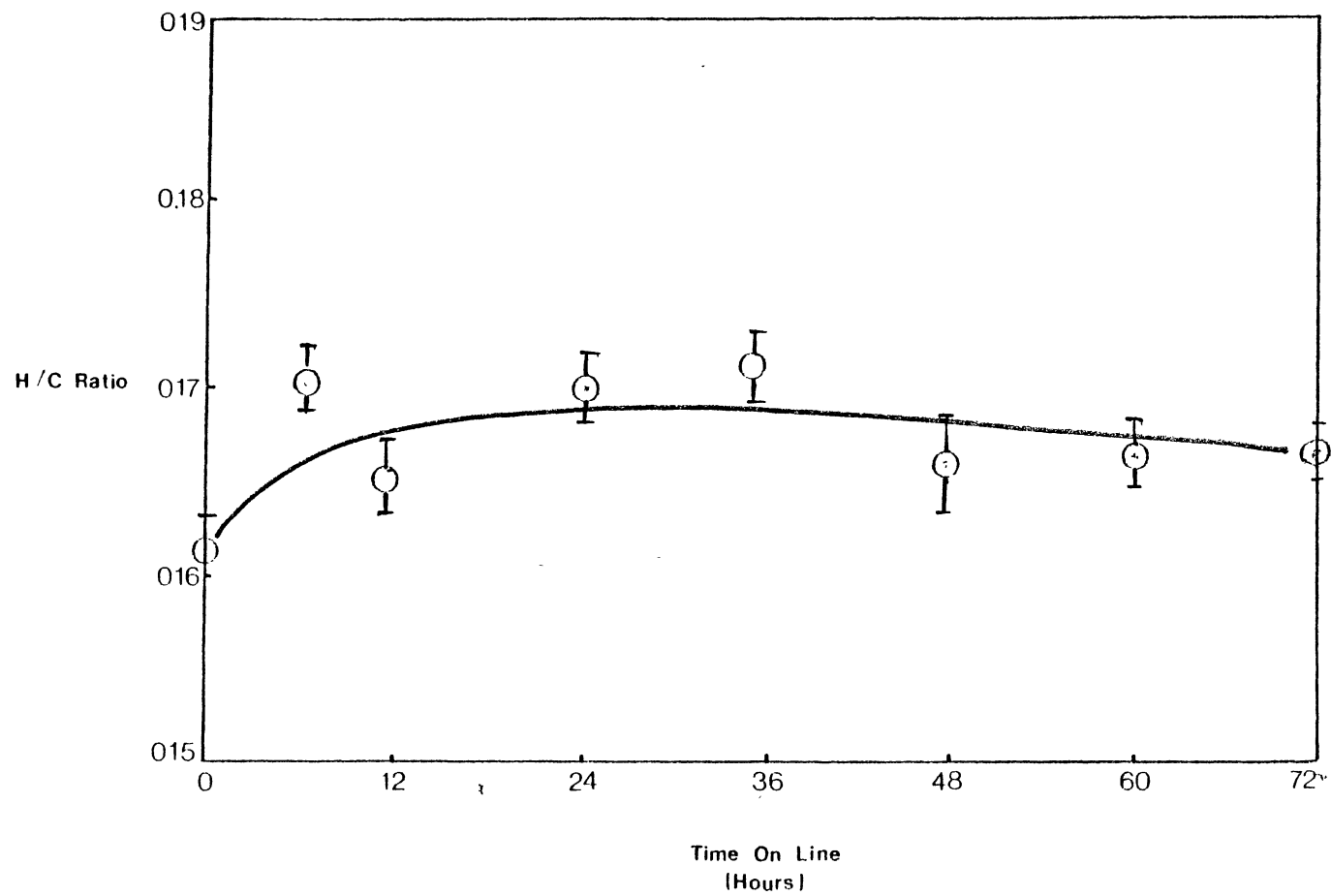


Figure 17. Hydrogen-to-Carbon Ratio of the Product Oil of Series RVI As a Function of the Time on Line.

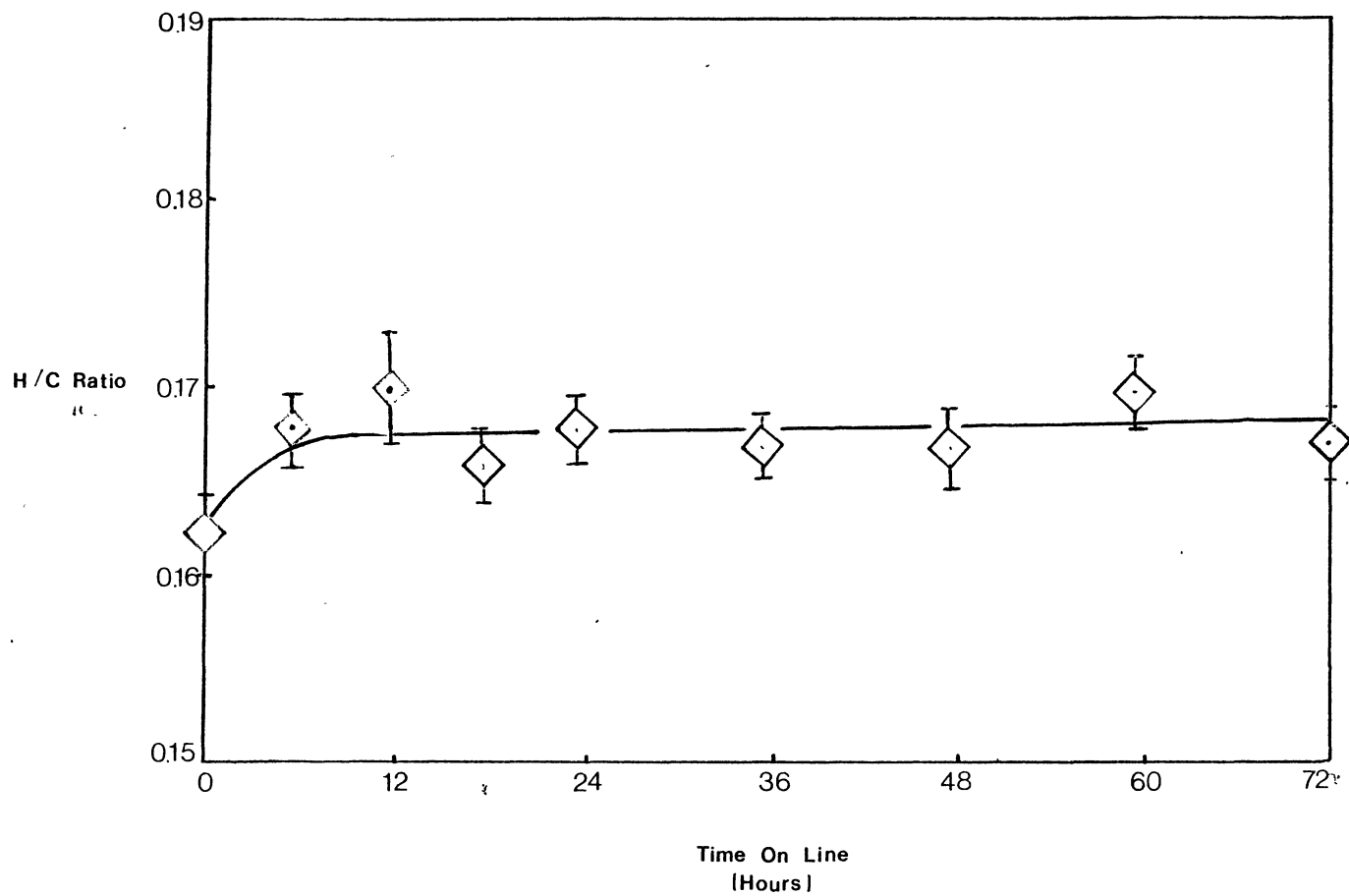


Figure 18 . Hydrogen-to-Carbon Ratio of the Product Oil of Series RVII As a Function of the Time On Line.

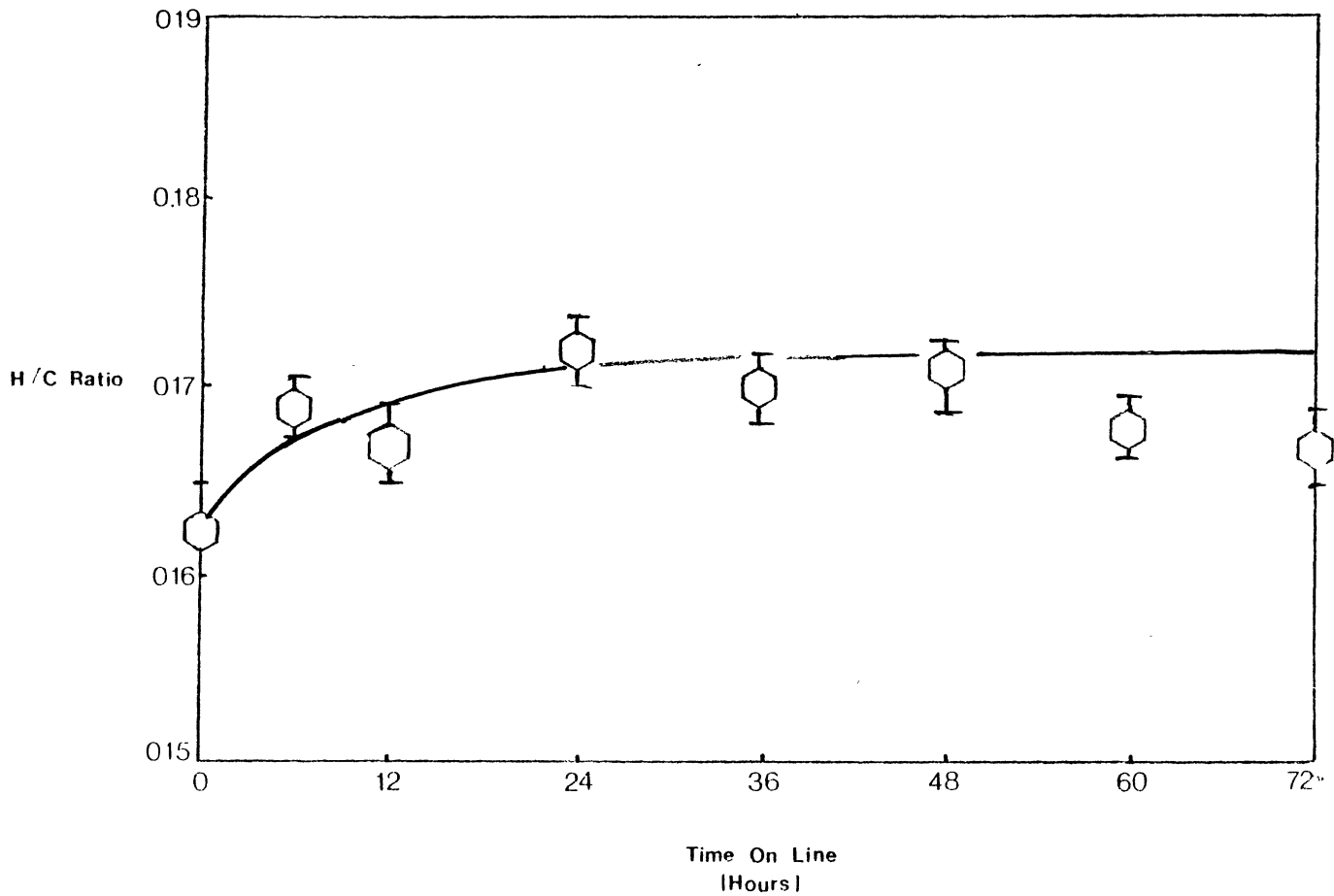


Figure 19. Hydrogen-to-Carbon Ratio of the Product Oil of Series RVIII As a Function of the Time On Line.

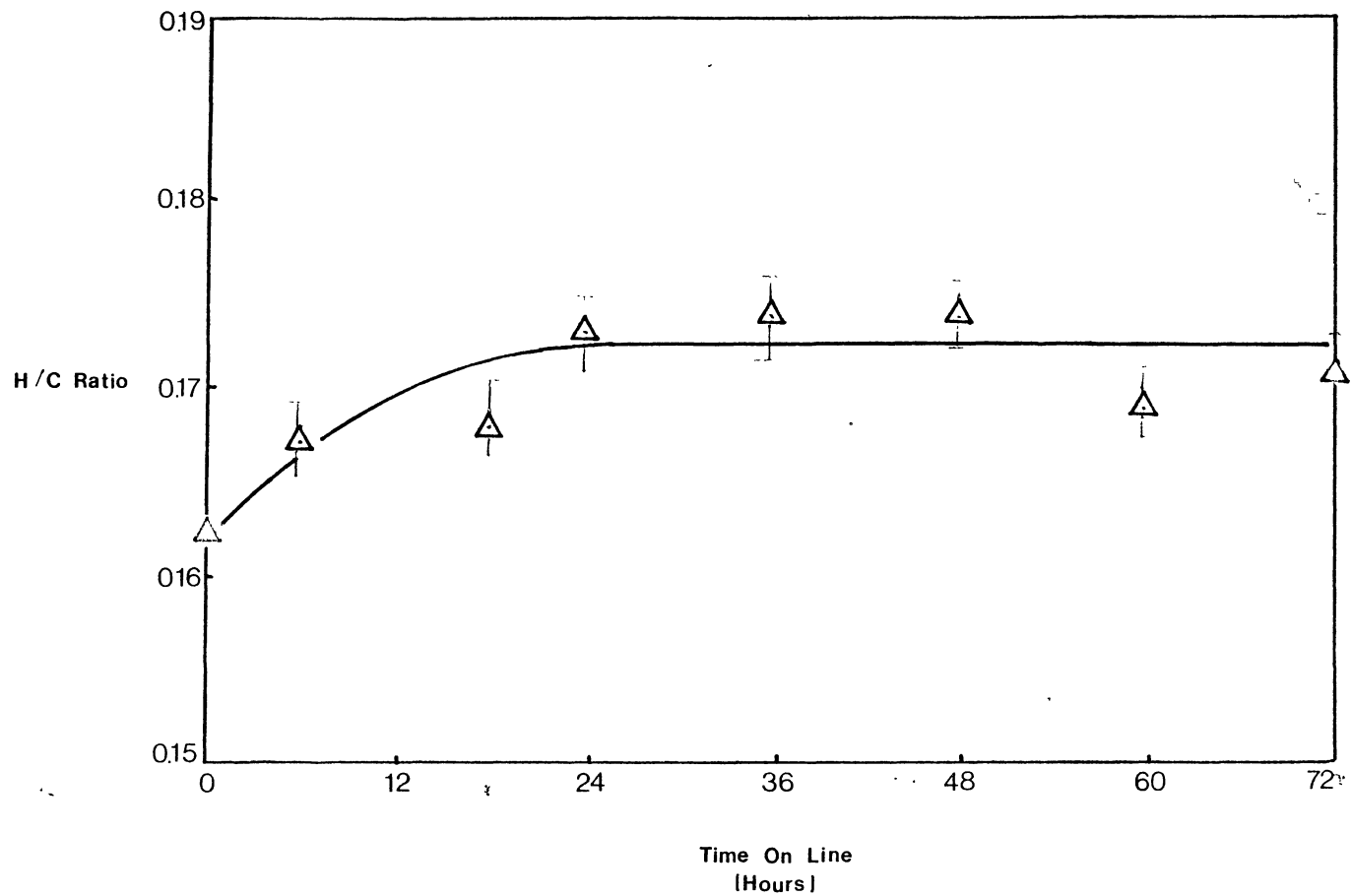


Figure 20. Hydrogen-to-Carbon Ratio of the Product Oil of Series RIX As a Function of the Time On Line.



APPENDIX B

DETAILED EXPERIMENTAL PROCEDURES

## APPENDIX B

### EXPERIMENTAL PROCEDURES

The experimental procedures listed here include only those referenced in the main body. Other procedural information is given in Chapter IV.

#### Reactor Loading

The following procedure was used to pack the reactor tubes:

1. A fifty mesh screen was placed in the bottom of the reactor tube and held in place by a small stainless steel expansion ring.
2. Three millimeter solid glass spheres were poured into the reactor while gently tapping on the sides of the tube. The reactor tubes were packed with 0.1 m (4 in.) of beads for every experimental run except RIX, which was packed with 0.275 m (11 in.).
3. Thirty centimeters (12 in.) of Ketjen KF-153-S catalyst was then packed into the reactor tubes.
4. For every experimental run except RIX, the reactor was then loaded with 0.05 m (2 in.) of glass beads. Run RIX was filled with 27.5 cm (11 in.).
5. Each reactor tube, except the one for run RIX, was then packed with its respective guard bed material. Run RIX was made without a guard bed.
6. Lastly, 0.1 m (4 in) of the glass beads were added to fill

the reactor tubes.

### Sampling Procedure

The following is a step-by-step procedure followed when liquid samples were collected:

1. The gas residing in the sample bomb was bled off by opening the vent valve.
2. The vent was then closed and the valve between the collection bomb and the sample bomb was opened. This forced the liquid sample into the sample bomb. When the liquid had completely reached this bomb, the pressure in the bomb would suddenly jump. The sample valve was then shut and the sample bomb briefly vented. The overflow bomb was then emptied in the same manner.
3. The reactor was quickly repressurized with hydrogen by bypassing the inlet metering valve.
4. The sample was then purged for approximately ten minutes with nitrogen. After purging, 793 kPa (100 psig) of nitrogen was allowed to remain in the sample bomb.
5. The sample was then collected by opening the sample exit valve.
6. Once the sample had been collected, the sample bomb was repressurized to 4583 kPa (650 psig) with nitrogen through the purge line.

### Liquid Sample Analysis

Liquid samples were analyzed for metals, color, nitrogen, hydrogen, and carbon. They were also subjected to ASTM 1160 distillations to aid in determining the extent of hydrogenation.

### Nitrogen, Carbon and Hydrogen Analysis

The analytical system consisted of a Perkin-Elmer model 240 B elemental analyzer, a model AD-2 Perkin-Elmer autobalance, a model 56 Perkin-Elmer one millivolt range recorder, and a model 04-1280 Perkin Elmer sealer. The Perkin-Elmer instruction manuals described the general procedures for use of this equipment and were directly followed.

### Color Analysis

The color of each sample was determined using a Hellige model 607 oil comparator in compliance with ASTM 1500 procedures. Numbered standard disks made the analysis simple, quick and accurate. The instruction manual describes the general procedure employed.

### ASTM Distillations

Liquid samples were also characterized by their distillation curves. The curves were obtained in accordance with ASTM 1160 distillation procedures for petroleum products. Vacuum distillation at a pressure of 10 mm Hg was required to obtain the distillation curves without cracking the hydrocarbon structures. The boiling points of each fraction were then converted to normal boiling points using ASTM 2892 conversion tables.

### Metals Analysis

Aluminum, zinc, copper, iron, barium, calcium, magnesium, and lead concentrations were all determined using an atomic absorption spectrometer. Liquid samples were first dissolved in methyl isobutyl ketone (MIBK) and then compared to standard solutions of MIBK and

Conostan metallo-organic compounds. Dr. Zohair Alshaeib of the Geology Department at Oklahoma State University conducted the analysis.

Phosphorous content could not be determined using University equipment and was therefore analyzed at the National Institute of Petroleum and Energy Research in Bartlesville, Oklahoma. Mr. Mike Crocker conducted the analysis on an Inductively Coupled Argon Plasma Spectrometer.

#### Catalyst Analysis

Catalyst and guard bed materials were analyzed for coke content and metals deposition. The procedures used in determining each of these analysis are given here.

#### Coke Content

Coke contents of the catalyst and guard bed materials were defined as the amount of tetrahydrofuran insolubles residing on the pellet surfaces. Spent catalyst samples obtained from the upper, middle and lower sections of both the guard bed and catalyst regions of the reactor were first extracted with tetrahydrofuran for 24 hours. The catalyst was then regenerated by burning off the residual coke in a Thermolyne model CP-12910 oven operating at  $500^{\circ}\text{C}$  ( $932^{\circ}\text{F}$ )  $\pm 10^{\circ}\text{C}$  ( $\pm 18^{\circ}\text{F}$ ) over a period of 24 hours. Weights of the regenerated and spent catalyst were obtained in weighted pyrex flasks that had been heated and evacuated for three hours. The weight percent difference between the moisture free regenerated and the moisture free spent pellets was recorded as the percent coke of the catalyst.

### Metals Deposition

Metals deposition on catalyst and guard bed surfaces was determined using electron dispersing X-ray analysis (EDAX). By keeping the operating parameters of this equipment constant, semiquantitative comparisons of metal compositions could be made. The EDAX was conducted by Denise Rex of the Veterinary Medicine Department of Oklahoma State University.

VITA 2

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Candidate for the Degree of

Master of Science

Thesis: THE EFFECT OF GUARD BED MATERIAL ON THE HYDROTREATMENT OF  
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