

## ARSENIC AND NITROGEN REMOVAL DURING SHALE OIL UPGRADING

By

D. J. Curtin\*, J. D. Dearth\*, G. L. Everett  
M. P. Grosboll, and G. A. Myers\*

Atlantic Richfield Company, 400 E. Sibley Blvd., Harvey, IL 60426,  
and \*P. O. Box 2819, Dallas, TX 75221

### Introduction

Shale oils and shale oil distillates can contain high concentrations of arsenic spread throughout their boiling ranges<sup>(1)</sup>. Arsenic has been shown to rapidly and permanently deactivate commercial hydro-treating catalysts. Even where hydrotreating is not required, arsenic removal may be desirable.

### The Nature of Arsenic in Shale Oil

Table 1 shows the arsenic distribution in a raw shale oil. The gas oil fraction contains the highest average arsenic concentration, about 52 ppm. A substantial arsenic peak occurs in the 204-260°C (400-500°F) boiling range. Following this peak, the arsenic concentration decreases. A significant arsenic level is observed in the residuum.

Table 1

Arsenic Distribution in Shale Oil

<u>Boiling Range</u>	<u>Fraction Volume Percent</u>	<u>Arsenic Content ppm</u>
IBP-204°C (IBP-400°F)	18	10
204-482°C (400-900°F)	58	52
482°C (900°F) and heavier	24	38

The distribution of the arsenic throughout the boiling range implies the presence of organic arsenic compounds. Other work reported in the literature confirms that organic arsenic compounds can be present in hydrocarbon fractions formed by the thermal decomposition of naturally occurring organic solids including European brown coal<sup>(2,3,4,5,6,7)</sup>. The pyrolysis of this coal yields a tar which has a very high arsenic content. Some of the arsenic-containing compounds have been shown to be organic in nature. We also have data which suggest that inorganic arsenic compounds are present.

Many organic arsenic compounds are known to be unstable. Thus it is possible under certain conditions that shale oil samples, including distillates, may lose a significant amount of their arsenic content. Care must be taken not only in sampling but also in storage and handling to maintain representative feedstocks. Over a long period of working with shale oil distillates in the development of the Atlantic Richfield Arsenic Removal and Hydro-treating Process, we have established many techniques necessary to ensure that the arsenic compounds remain representative of those in the commercial feedstock.

## The Effect of Arsenic on Hydrotreating Catalysts

Figure 1 shows the effect of arsenic in shale oil on one commercial nickel-molybdenum hydrotreating catalyst. A shale gas oil was passed over the catalyst at 1.5 weight hourly space velocity, 2000 psig, 282°C (720°F), and 1014 m<sup>3</sup>H<sub>2</sub>/m<sup>3</sup> (6000 scf H<sub>2</sub>/bbl). Initially the arsenic was totally removed from the oil by deposition on the nickel-molybdenum catalyst. When the arsenic level on the catalyst reached 7 weight percent, the arsenic level of the effluent oil increased rapidly.

The hydrodenitrogenation (HDN) activity of the nickel-molybdenum catalyst used in this test charging untreated shale gas oil is plotted in Figure 2. The HDN activity rapidly declined to a point where about 1000 grams of oil had been treated per gram of catalyst. At this point, which corresponds to the point where arsenic began to appear in the effluent oil, the rate of catalyst activity decline became less severe. Arsenic deposition appeared to be a major factor in the catalyst deactivation. This hypothesis was confirmed by an additional test of a fresh sample of nickel-molybdenum catalyst at the same conditions but charging shale gas oil with the arsenic removed. The HDN activity, also shown in Figure 2, declined much less rapidly than was the case when the arsenic-containing raw shale gas oil was treated.

## Arsenic Removal from Shale Oil Distillates

Three alternatives were apparent for shale oil hydrotreating. First, one could attempt to develop a hydrotreating catalyst which would be resistant to arsenic poisoning. Our work indicated that existing catalysts with sufficient denitrogenation activity would be poisoned by arsenic due to its strong affinity for metals. A second possibility would be to remove the arsenic deposits from the catalyst during regeneration. Once again our data, later confirmed in tests by other companies, showed that standard regeneration procedures were ineffective in restoring HDN activity to an acceptable level. A third alternative would be to develop a new process to remove arsenic from the oil. In our preliminary studies, we determined that this third alternative was by far the most promising.

Many different arsenic removal process candidates were studied, and sufficient data were developed to permit us to make preliminary design and economic comparisons of the processes. The literature contains a number of patents for removal of arsenic in the parts per billion range from naphthas in order to protect very sensitive reforming catalysts. Unfortunately, such removal processes are apparently not applicable to shale oils with arsenic concentrations of 50 to 60 parts per million. As a consequence, a number of new process ideas were developed. Two processes, caustic washing and fixed-bed guard reactor, emerged from the preliminary evaluation as significantly superior to the others and were selected for further study.

A continuous bench-scale apparatus was constructed for experiments on caustic washing of shale gas oil fractions. As shown by the flow diagram in Figure 3, caustic solution and oil were pumped from storage tanks into a stirred reactor maintained at desired conditions of temperature and pressure. In the reactor a chemical

reaction occurred which resulted in the formation of arsenic compounds which were soluble in the caustic phase. The reactor effluent then flowed into a settler where the two phases were permitted to coalesce and be withdrawn through separate lines. To simulate commercial operation, a portion of the effluent caustic solution was recycled back to the feed tank. From analyses of the individual effluent phases, process conditions were evolved. This system was found to be effective for arsenic removal. Commercial design parameters were obtained from process variable studies, and economics were evaluated.

Figure 4 shows the flow diagram for the experimental guard bed apparatus. Hydrogen and oil were fed at prescribed rates into a packed reactor maintained at appropriate conditions of temperature and pressure. The hydrogen-oil mixture passed down over the catalyst bed and exited from the bottom of the reactor, at which point the gas and liquid phases were separated.

Using the data obtained from the two bench-scale units, we prepared preliminary commercial designs and calculated comparative economics for both processes. Other factors such as process operability and environmental effects were also considered. Based on our studies, the guard bed process was ultimately found to be superior to caustic washing in all three respects.

The development of the guard bed arsenic removal process was complicated by the unconventional nature of the shale oil and of the guard bed catalysts found to be most effective. For example, early catalysts tested, which were inexpensive and commercially available, performed satisfactorily in the process variable studies run to measure the effects of changing temperature and space velocity. However, in extended catalyst aging runs, problems were encountered with catalyst strength. A search for a suitable replacement catalyst was initiated, and a considerable effort was made to test commercial catalysts from a large number of different manufacturers and in several different sizes and physical configurations. Some of the candidates did exhibit performance which was superior to that for the original catalyst, but even the best catalysts did not meet our specifications. Eventually a strong, effective guard bed material was developed which was resistant to shale oil fouling and which will remove a high percentage of arsenic from shale oil distillates even at high levels of arsenic loading. The excellent effectiveness for arsenic removal provides substantial economic benefits. The use of competing materials would result in much larger and costlier processing equipment or a prohibitively high turnaround frequency to renew the guard bed material. This guard bed material, developed in a joint effort with a large catalyst manufacture using commercially projectable techniques, has been used to demonstrate this arsenic removal process for over 1000 hours charging shale gas oils at commercial process conditions. The arsenic removal dearsenation results of this demonstration run are shown in Figure 5.

This process operates over a wide range of pressures, hydrogen partial pressures and temperatures. It can process shale gas oil at high efficiency at required hydrotreating conditions for shale oil.

## Pilot Plant Denitrogenation Studies

### Experimental

Hydrodenitrogenation studies were performed in a bench scale continuous down-flow packed bed pilot plant unit. Over 60,000 reactor hours of shale oil processing were completed in our studies. Shale oil and hydrogen flowed through the packed bed and then through a high pressure water scrubber for removal of by-product ammonia and hydrogen sulfide gases. The latter stage avoids pilot plant operating problems due to ammonium sulfide formation. Gaseous and liquid products were then separated, metered, and analyzed to permit the determination of yields and weight balances.

Shale oil feedstocks containing both low and high arsenic levels were studied so that the effect on HDN of the arsenic removal co-process could be determined. Shale gas oil and naphtha fractions were treated separately since preliminary investigation showed this to be most economical for commercial applications. The gas oil work is discussed here.

### Catalyst Screening

The denitrogenation catalyst activity and stability were shown to have a major impact on the cost effectiveness of the shale upgrading design because reactor investment is a major part of the total plant investment. To assure the selection of the best available catalyst, extensive comparison testing was done. As expected, nickel-molybdenum catalysts were better for HDN than cobalt-molybdenum catalysts. The catalyst chosen was found to have a 10-20 percent higher volume activity on shale oil than the best competitors.

### Denitrogenation

An experimental program was conducted to determine the optimum range of processing conditions for achieving the desired low product nitrogen level. Process conditions studied cover a range of temperatures, 371-454°C (700-850°F), and space velocities, 0.5-2.0 (hours)<sup>-1</sup>, at a reactor pressure found to provide an acceptable aging rate. A pyrolysis shale gas oil produced by a retort operation was tested along with a gas oil from the coking of the bottoms fraction of the pyrolysis oil. A pyrolysis-coker shale gas oil blend with low arsenic content was used for most of the studies, but high arsenic content pyrolysis-coker blends and coker only were also used to establish a feedstock effect.

Denitrogenation data from these tests were used to develop an HDN correlation based on first order kinetics:

$$\ln \frac{N_f}{N_p} = (K_{t,i} \tau) \alpha \quad (1)$$

where

- $N_f$  = nitrogen content of feedstock, ppm
- $N_p$  = nitrogen content of product, ppm
- $K_{t,i}$  = apparent rate constant at temperature  $t$  and with feed  $i$
- $\tau$  = space time  $\left(\frac{1}{\text{WHSV}}\right)$ , where WHSV, the weight hourly space velocity, is defined as the weight of feed per hour per weight of catalyst.
- $\alpha$  = catalyst relative activity

First order kinetics gives a reasonable fit to the HDN data. This is consistent with the observation of McIlvried<sup>(8)</sup> and others for the denitrogenation of various materials. Apparent rate constants calculated from equation 1) are plotted in Arrhenius form in Figure 6 showing an apparent activation energy of 26.9 Kcal/gm mole. The higher arsenic level feeds, both pyrolysis-coker blend and straight coker, showed significant HDN activity losses (5-10 percent for the blend and 35 percent for the coker alone). Figure 7 shows the actual denitrogenation data plotted in the form predicted by equation 1). Good agreement between the data and the first order kinetic form is indicated.

#### Hydrogen Consumption

The hydrogen consumption, calculated from material balance on hydrogen content of feed and product streams, is shown as a function of nitrogen removal in Figure 8. Feeds with higher hydrogen contents tend to consume less hydrogen by an amount approximately equal to the difference in hydrogen contents of the feeds. The range of hydrogen consumption observed for these shale oil HDN tests, 254-304 m<sup>3</sup>/m<sup>3</sup> (1500-1800 scf/b), approach the consumptions obtained in conventional hydrocracking operations.

#### Aging Studies

A number of catalyst aging runs were made during the process development. One of these was a pilot plant gas oil aging run set up to simulate the production of a low nitrogen level (750 ppm) product from a feed oil containing 21,500 ppm nitrogen. Start-of-cycle process condition needed to achieve this low gas oil nitrogen level was 377°C (710°F).

During the 90-day aging run, the temperature was raised 7°C (13°F) to maintain denitrogenation. After 90 days the temperature was raised to 399°C (750°F), and operated for another 30 days. Only a 1°C temperature increase was required to maintain denitrogenation as shown in Figure 9. These results show that a 1 year cycle or greater is feasible for shale oil upgrading.

#### Reactor Modeling

In order to screen various reactor designs for a given application, a reactor model which simulates the important design variables was developed. Such a model must predict the required catalyst quantity, and predict yields for each reactor temperature, pressure, and hydrogen rate chosen.

For shale oil hydrotreating, the reactor model must also take into account the effect of arsenic since arsenic is a strong catalyst poison. Even with a guard bed, arsenic is deposited continually throughout the cycle and to compensate for its poisoning effect temperature must be raised to maintain HDN activity. Because of the highly exothermic reaction, many hydrogen quench points, such as shown in Figure 10, or other means of heat removal, are required to control reactor temperature. As the catalyst activity declines, both due to arsenic and time on stream, conversion in each catalyst bed changes. The lower conversion gives less heat release and, therefore, bed temperature must be increased to maintain catalyst activity. This in turn greatly changes the required hydrogen quench after each catalyst bed as the cycle progresses.

The variations are substantial, as illustrated in Figure 11. Since hydrogen quench rate varies significantly with time on stream, the quench system must be designed to handle a wide range of flows. Most conventional hydrotreaters would be unable to handle the quench rate variation along with the high heat release for shale oil processing. Flexibility must also be provided so the reactor inlet temperature can be raised. The model enables the designer to accurately take these effects into account for an optimum design.

The complexity in modeling arises when attempting to simultaneously take into account the effect on conversion of temperature, WHSV per bed and arsenic, when the amount of arsenic laydown itself is a function of WHSV and temperature. The actual system is further complicated in that the catalyst ages with time on stream as well, even if no arsenic were present.

For each catalyst bed the model does the following:

- o Calculates the severity and conversion.
- o Predicts yields including H<sub>2</sub> consumption needed to estimate the exothermic heat of reaction.
- o Performs heat balances to predict outlet temperature and quench rates.
- o Predicts HDS, HDN, hydrocracking, aromatic saturation, and olefin saturation.
- o Predicts catalyst activity as a function of arsenic and time on stream.

#### Design Studies

With such a model, the overall shale upgrading process can be optimized. Since arsenic removal and HDN are highly interdependent, the reactor design needs to be studied in order to minimize overall processing costs.

One use of the model is to determine the optimum conditions for arsenic removal since any arsenic leakage directly affects the required severity and cycle life for HDN. As the arsenic removal is increased via increased guard reactor size, capital costs increase but catalyst usage decreases. The optimum design for HDN can be found using the model. Conditions are chosen so arsenic removal and coke deposition are balanced to minimize costs.

The model has been used for two commercial designs, one for Colony Development Operation, a joint venture of which Atlantic Richfield is the operator, and another for a client of this shale oil hydro-treating technology.

#### Literature Cited

1. Burger, E. D., D. J. Curtin, G. A. Myers and D. K. Wunderlich, "Prerrefining of Shale Oil", Am. Chem. Soc., Div. Pet. Chem., Aug. 24-29, 1975.

2. Svajgl, O., Collection Czech Chem. Commun., 24, 3829 (1959).
3. Ibid., 28, 11 (1963).
4. Svajgl, O., Freiberger Forschung-H, A340, 89 (1964).
5. Svajgl, O., Scientific Papers of the Institute of Chemical Technology. Prague; Tech. of Fuels, 7, 187 (1965).
6. Ibid., D13, 163 (1967).
7. Svajgl, O., Sbornik praci z vyzkumu chernicke ho vyuziti, dehtu a ropy, 8, 83 (1968).
8. McIlvried, H. G., "Kinetics of the Hydrodenitrication of Pyridine", Industrial Engineering Chemistry, Process Design and Development, 10, 1, 125-130 (1971).

FIGURE 1  
ARSENIC IN HYDROTREATED PRODUCT OIL

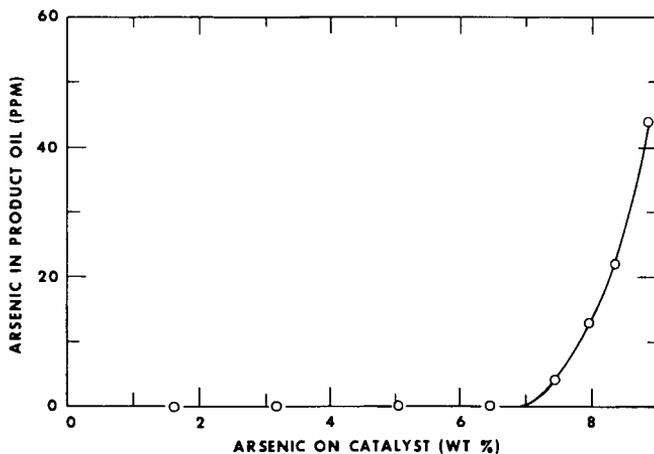


FIGURE 2  
 CATALYST ACTIVITY OF A NICKEL-MOLYBDENUM  
 CATALYST TREATING SHALE OIL

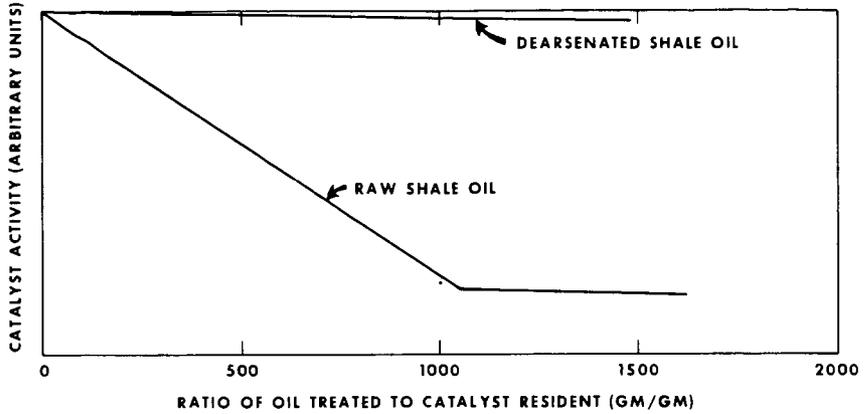


FIGURE 3  
 CONTINUOUS CAUSTIC SODA WASH APPARATUS (WITH RECYCLE)

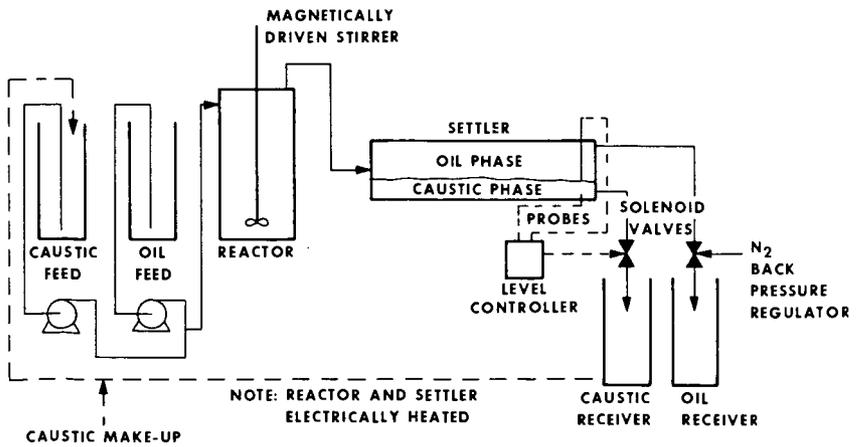


FIGURE 4  
 FLOW DIAGRAM FOR EXPERIMENTAL GUARD BED SYSTEM

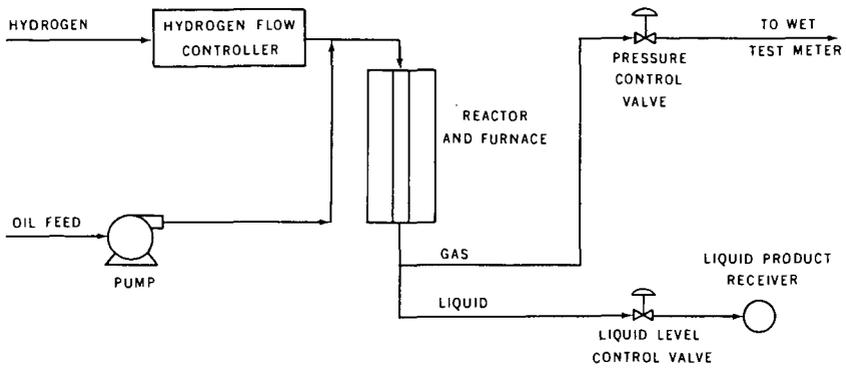
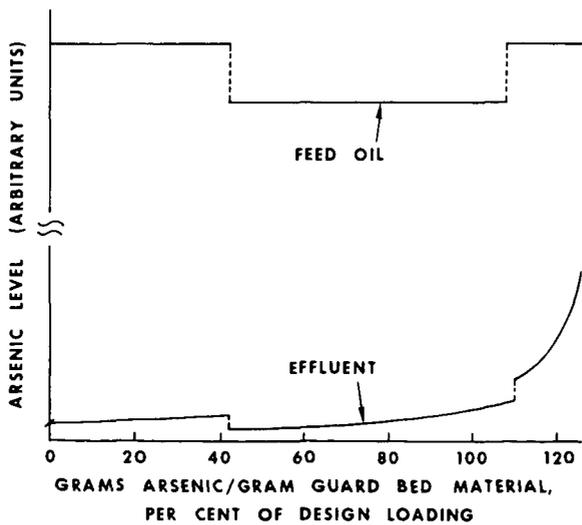


FIGURE 5  
 ARSENIC REMOVAL DEMONSTRATION RUN RESULTS



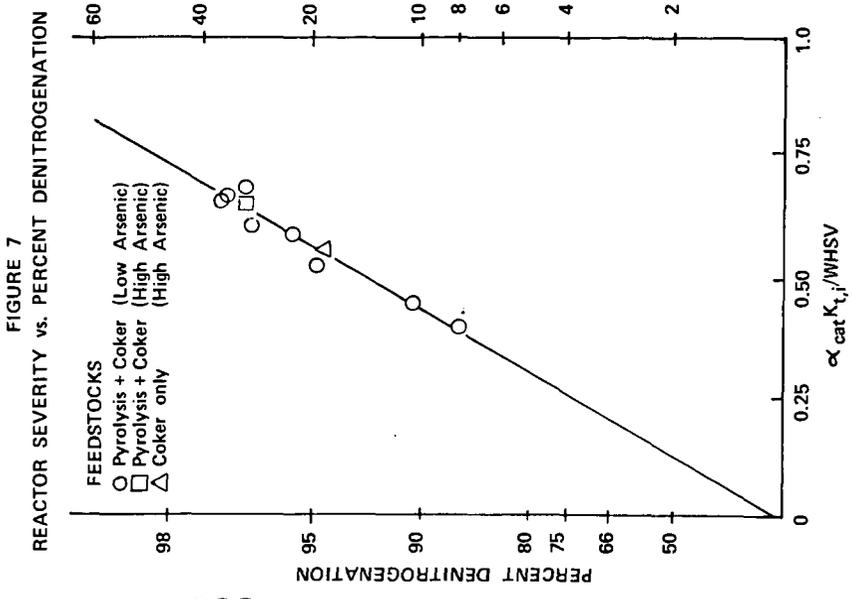
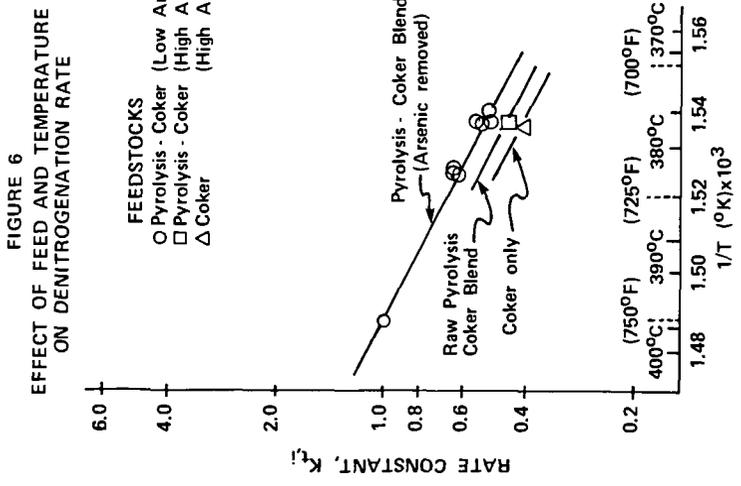


FIGURE 8

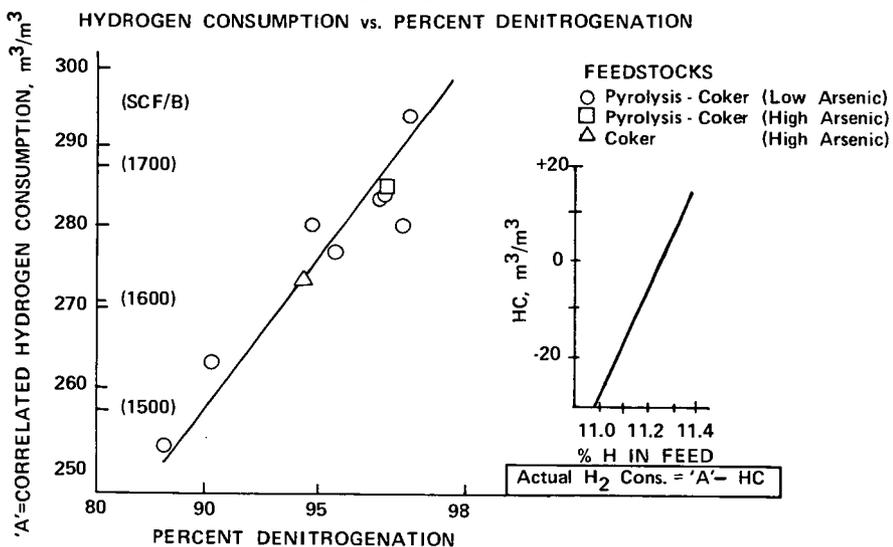


FIGURE 9  
CATALYST AGING STUDY

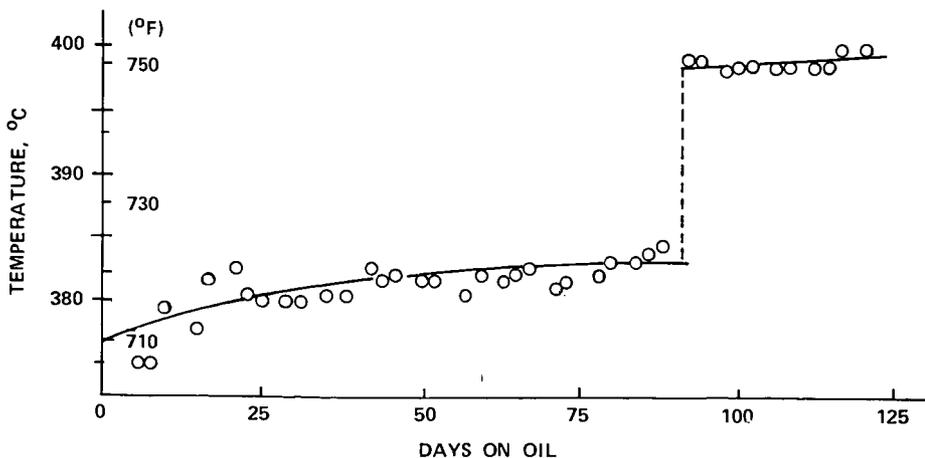


FIGURE 10  
SHALE OIL UPGRADING

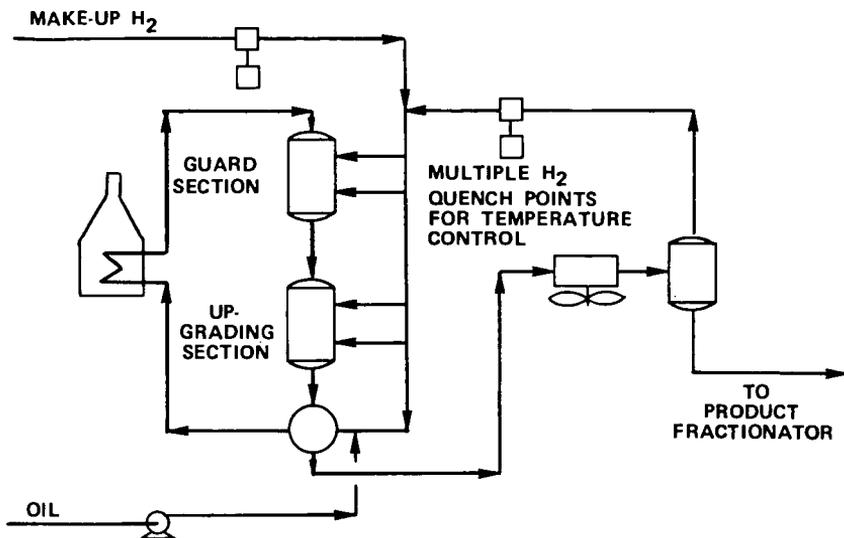


FIGURE 11  
QUENCH RATE VARIABILITY

