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LC-FINER CATALYST TESTING

Final Report

By
D. Garg
J. C. Bronfenbrenner

Work Performed Under Contract No. AC05-78OR03054

International Coal Refining Company
Allentown, Pennsylvania

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FINAL REPORT

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for the

UNITED STATES DEPARTMENT OF ENERGY
Office of Solvent-Refined Coal Products
under Contract DE-AC05-78-OR-03054

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ABSTRACT

The activity and aging rate of modified Shell 324 Ni-Mo-Al catalyst were studied in ICRC's process development unit (PDU) under SRC-I Demonstration Plant hydroprocessing conditions. The studies determined variations in SRC conversion, hydrocarbon gas production, hydrogen consumption, and heteroatom removal at both constant and increasing reaction temperatures. Samples of spent catalyst were analyzed to ascertain the reasons for catalyst deactivation. Finally, the PDU hydroprocessing results were compared with those generated at Lummus and Wilsonville pilot plants.

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EXECUTIVE SUMMARY

ICRC has completed its research program to determine the activity and aging rate of the LC-Finer Ni-Mo-Al catalyst under SRC-I Demonstration Plant design conditions in the ICRC PDU.

As previously reported by Garg (1, 2, and 3), results showed that SRC conversion, hydrocarbon gas production, and hydrogen consumption increased with increasing reaction temperature from 775 to 825°F. However, oil production did not increase with temperature. The increase in hydrocarbon gas production and hydrogen consumption resulted in a severe decline in the selectivities for oil production over both hydrocarbon gas production and hydrogen consumption. Heteroatom removal did not improve significantly by increasing the reaction temperature from 775 to 825°F.

Catalyst aging experiments showed that SRC conversion, hydrocarbon gas and oil production, hydrogen consumption, overall desulfurization, denitrogenation, and deoxygenation, and first-order rate constant for the conversion of SRC changed slightly during 294 hours of operation at 775°F temperature, but changed significantly thereafter. The catalyst aging experiment at 825°F experienced several operational problems, resulting in a much shorter period of constant catalyst activity than that observed in the aging experiments conducted at 775°F.

Analysis of spent catalyst revealed a significant reduction in surface area, pore volume, and pore diameter. In addition, the analysis showed an unusually high level of sodium deposition on the catalyst, probably resulting from the presence of a large amount of sodium in the feed. A mass balance around the system revealed that only small amounts of iron and titanium present in the feed SRC were deposited on the catalyst, whereas a major portion of sodium in the feed was retained by the catalyst.

The decline in catalyst activity is attributed mainly to the significant reduction in surface area and pore size resulting from coke and metal deposition. The decrease in activity may have also been partly due to sodium deposition on the catalyst. However, it is not intended to add sodium carbonate in the demonstration plant; therefore sodium

levels in the SRC feed to the demonstration plant hydrotreater should normally be lower.

Finally, the decline in activity of Ni-Mo-Al catalyst observed in the PDU was comparable with that noted with Co-Mo-Al catalyst at the Wilsonville facility during run 235.

INTRODUCTION

Production of distillate liquids by catalytic hydrocracking of solvent-refined coal (SRC) is a major processing step in the SRC-I Demonstration Plant. One of the few commercially available hydrocracking processes capable of handling SRC is the Lummus-Cities expanded-bed (LC-Fining) process. Design plans are to install an LC-Finer in the SRC-I Demonstration Plant that is capable of handling 14,000 barrels per day (bpd) total feed, of which 30% is recycle distillate diluent oil.

The LC-Finer process was chosen because of its proven application for processing residual petroleum oils. The process employs conventional hydroprocessing catalysts in an ebullated-bed reactor, in which gas and slurry are fed upwardly through a bed of catalyst expanded by pumping liquid around and through the reactor at a high rate. This process is thought to be exceptionally well-suited to the processing needs of a refractory or very high molecular weight feedstock because catalyst can be continuously added or withdrawn from the reactor without having to depressurize or cool it. Because SRC consists essentially of high-molecular-weight asphaltenes and preasphaltenes, its composition may be the major contributor to rapid catalyst aging. The high metal content of SRC may also contribute significantly to catalyst deactivation.

Two different severity design cases have been proposed for LC-Finer operation. Both produce essentially the same yield of distillate product from SRC. SRC conversion is defined as the amount of 850°F+ material converted to 850°F- products. In the high-severity design case, in which about 80% of the SRC is converted, the reactant flow rate is about one-half that of the alternate design low-severity case. The conversion of SRC in the alternate design case is approximately 46%. Yield structures for the two severity cases are given in Table 1.

To prove SRC hydrocracking technology in the demonstration plant, a catalyst having a suitable life for hydrocracking SRC must be specified before demonstration plant start-up. Prior LC-Finer process studies claimed that a modified Shell 324 Ni-Mo-Al catalyst met all the desired

Table 1

LC-Finer Design Basis

Yield distribution (wt % of fresh feed)	High-severity	Low-severity
Fresh feed		
Oil	5.10	5.09
SRC	94.90	94.91
Total	100.00	100.00
Recycle stream		
Oil	106.70	42.86
SRC	75.44	0.00
Total	182.14	42.86
Net product		
H_2S	0.87	0.78
NH_3	1.72	0.79
H_2O	4.79	3.90
C_1-C_4	14.08	8.91
C_5-400°F	16.72	9.28
400-500°F	18.94	7.26
500-650°F	12.29	8.27
650-850°F	15.27	9.34
SRC	20.29	53.97
H_2	-5.00	-2.50
Total	100.00	100.00
SRC conversion (vol %)	79.2	45.6
Desulfurization (wt %)	96.7	86.2
Denitrogenation (wt %)	85.9	39.6
Deoxygenation (wt %)	93.7	76.5

design specifications. However, the catalyst consumption level is such that catalyst cost is a major factor in the hydrocracking process.

The major purpose of this program was to develop a data base that would increase confidence in the process design by verifying the performance of the modified Shell 324 Ni-Mo-Al catalyst. Specifically, the program was designed to determine intrinsic catalyst activity and stability, in addition to changes in conversion and product distribution with catalyst age under SRC-I Demonstration Plant design conditions.

EXPERIMENTAL PROGRAM

Feed Materials

Heavy solvent-refined coal (HSRC) from Kentucky #9 Fies mine coal and process solvent from the catalytic hydrocracker used in the program were supplied by the Wilsonville Advanced Coal Liquefaction Facility. Both the HSRC and the process solvent were collected during the operation of run 235. Detailed analyses of HSRC and process solvent are reported in Table 2. The process solvent was completely soluble in pentane, whereas approximately 6 wt % of the HSRC was soluble in pentane. The feed HSRC also contained high levels of metals, especially sodium. The high sodium level was due to Na_2CO_3 addition in the initial liquefaction step during run 235 to prevent chlorine corrosion.

Modified Shell 324 Ni-Mo-Al catalyst used in the program was supplied by Shell Development Company, Houston, Texas. The detailed analysis of the catalyst is summarized in Table 3.

Reactor Design

A reactor having an annular fixed catalyst basket fitted into a 2-liter stirred autoclave was specifically designed and constructed for the program (Figure 1). Alternative reactor designs may have been considered, and in fact should be investigated in the future in order to effect efficient mixing of reactants and catalyst and homogeneity of temperature. One possibility is to use rotating cages of catalyst on the stirrer shaft. Due to limitations of time and other considerations, such a study has not been attempted. Specific measurements of the fixed catalyst basket reactor are provided in Table 4. The reactor was heated

Table 2

Detailed Analysis of Feed HSRC and Process Solvent

	Wt %	
	HSRC	Hydrotreated process solvent
Pentane solubles	6.0	100.0
Pentane insolubles	94.0	0.0
Carbon	86.9	89.3
Hydrogen	6.0	9.7
Oxygen	4.1	0.5
Nitrogen	2.0	0.5
Sulfur	1.0	<0.1
Metals[a] (ppm)		
Arsenic	<1	
Vanadium	12	
Iron	150	
Sodium	200	
Titanium	120	
Chlorine	44	

[a] Data from Catalytic, 1981.

Table 3

Analysis of Shell 324 Ni-Mo-Al Catalyst

Ni	2.7 wt %
Mo	15.9 wt %
P	3.0 wt %
Size	1/16 in.
Surface area	152 m^2/g
Median pore diameter	96 Å
Median pore volume	0.38 mL/g

FIGURE 1

FIXED BASKET CATALYTIC REACTOR DESIGN

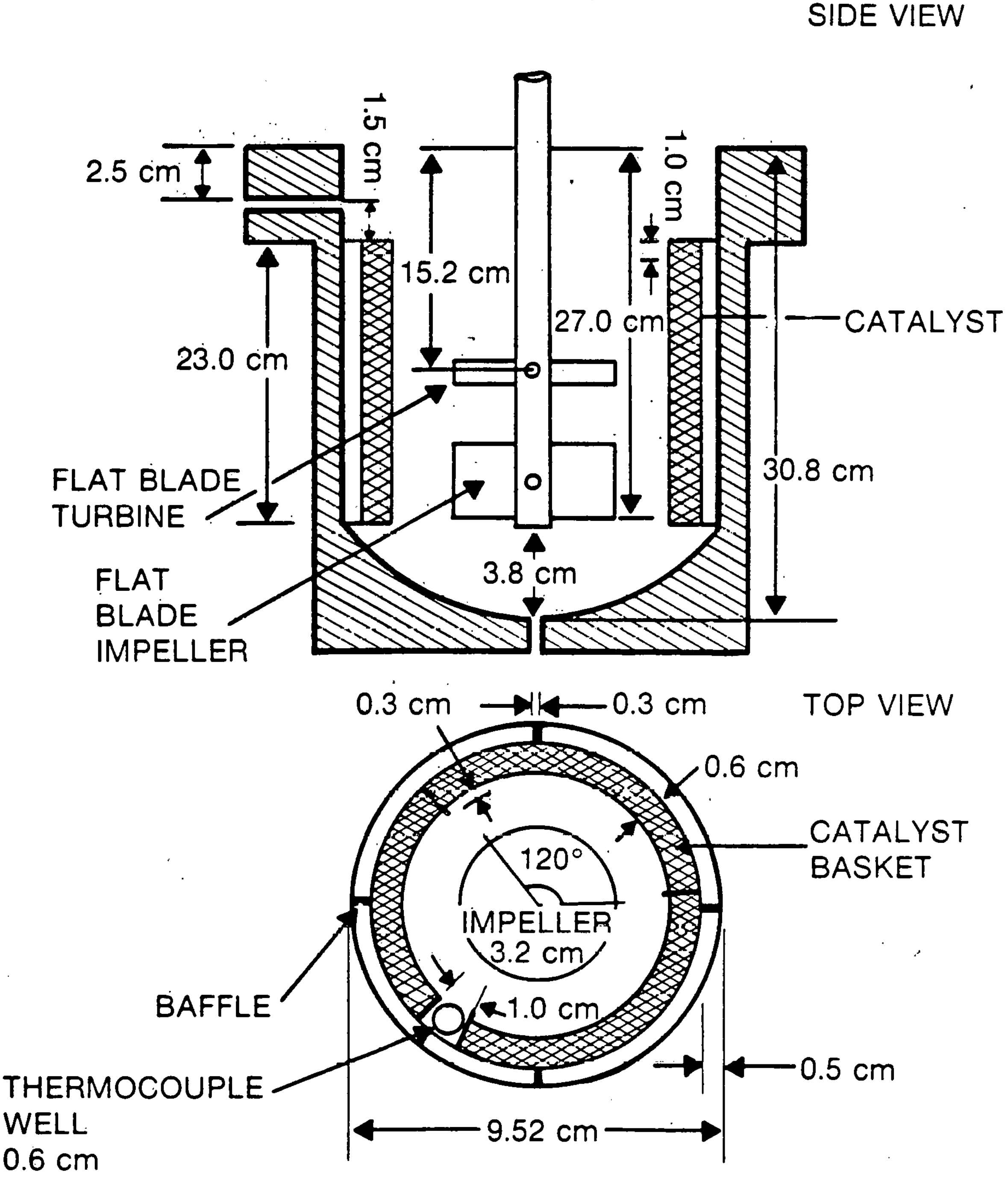

Table 4

Reactor Specifications

Reactor Dimensions

Inside diameter of the reactor = 9.52 cm

Total working volume of the reactor ≐ 1,835 mL

No. of thermocouple wells = 1

Effective height of the reactor = 30.8 cm

Hole at the bottom for feed inlet

Hole in the reactor side for product outlet

Basket Dimensions

Outside diameter = 8.5 cm

Inside diameter = 7.3 cm

Thickness = 0.6 cm

Screen size = 14 U.S. mesh with 0.14-cm openings

No. of segments in the basket = 3

No. of baffles inside the basket = 3

No. of baffles outside the basket = 4

Height of the basket = 23 cm

Catalyst

Catalyst size = 1/16-in. dia. extrudates

Maximum catalyst weight = 200 g

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by resistance heaters surrounding the reactor wall. The internal reactor temperature was controlled and measured by a thermocouple well immersed in the slurry phase.

Cold-Flow Experiments

A Plexiglas mockup of the reactor fitted with the catalyst basket was designed and fabricated to study mixing behavior and to determine gas holdup in the reactor. The experimental conditions for cold-flow studies were carefully chosen to simulate the actual mixing behavior at hydroprocessing reaction conditions, and are given below:

Reactor volume = 1,835 mL
Water flow rate = 200 g/hr
Air flow rate = 200 slph
Catalyst weight = 200 g
Stirring speed = 500-1,000 rpm

Mixing Behavior. Several different impeller configurations, e.g., marine propeller, and flat-blade and pitched-blade turbines, were tested to determine liquid mixing, gas dispersion, and gas/liquid/catalyst contact in the reactor. Gas/liquid/catalyst contact was qualitatively evaluated by observing the flow of gas and liquid through the fixed catalyst basket. However, liquid mixing was determined by dispersing a dye in the reactor.

Liquid mixing was excellent with almost all impeller configurations; less than 6 seconds were required to completely disperse the dye in the reactor. However, the flow of gas and liquid through the catalyst basket varied with impeller configuration and stirrer rpm. At a low impeller rate of 500 rpm, no flow of gas and liquid through the catalyst basket was observed; instead, the flow bypassed the basket, as depicted in Figure 2. Increasing the stirrer speed improved flow through the basket. However, the flow was not uniform, and was concentrated in the region close to the impellers, as shown in Figure 3. The catalyst in the regions marked by A, A', B, and B' was virtually isolated from the gas and liquid flow. A flat-bladed impeller encompassing the entire width of the basket (Figure 4) gave the best distri-

FIGURE 2

FLOW BY-PASSING THE FIXED CATALYST BASKET

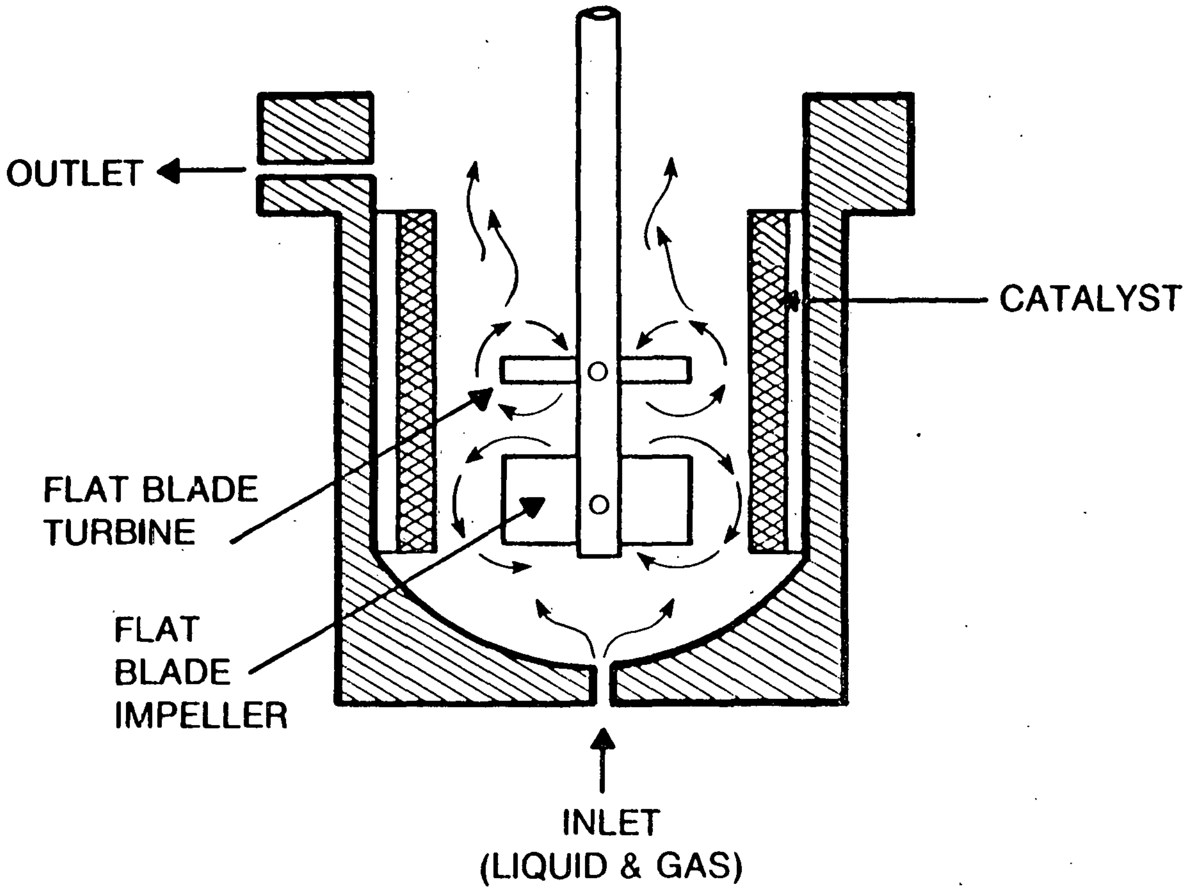


FIGURE 3

FLOW THROUGH THE FIXED CATALYST BASKET

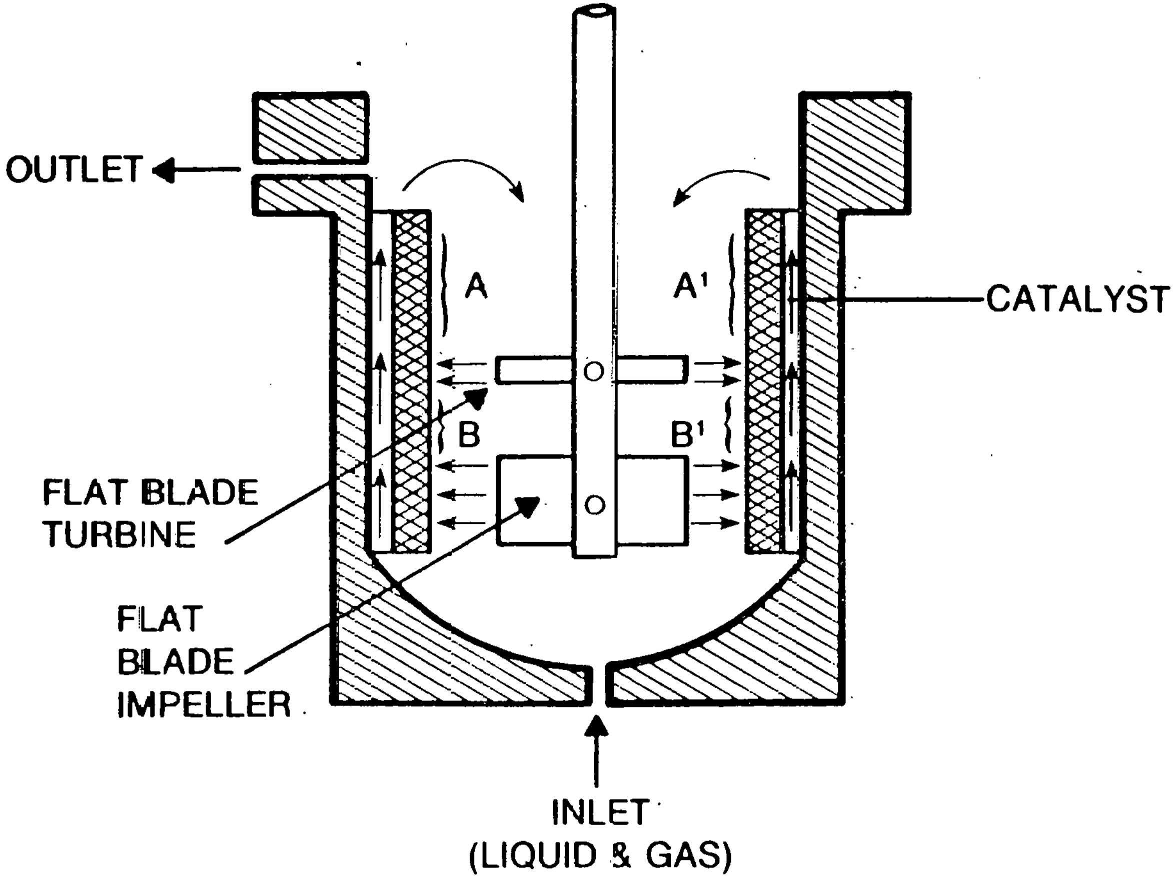
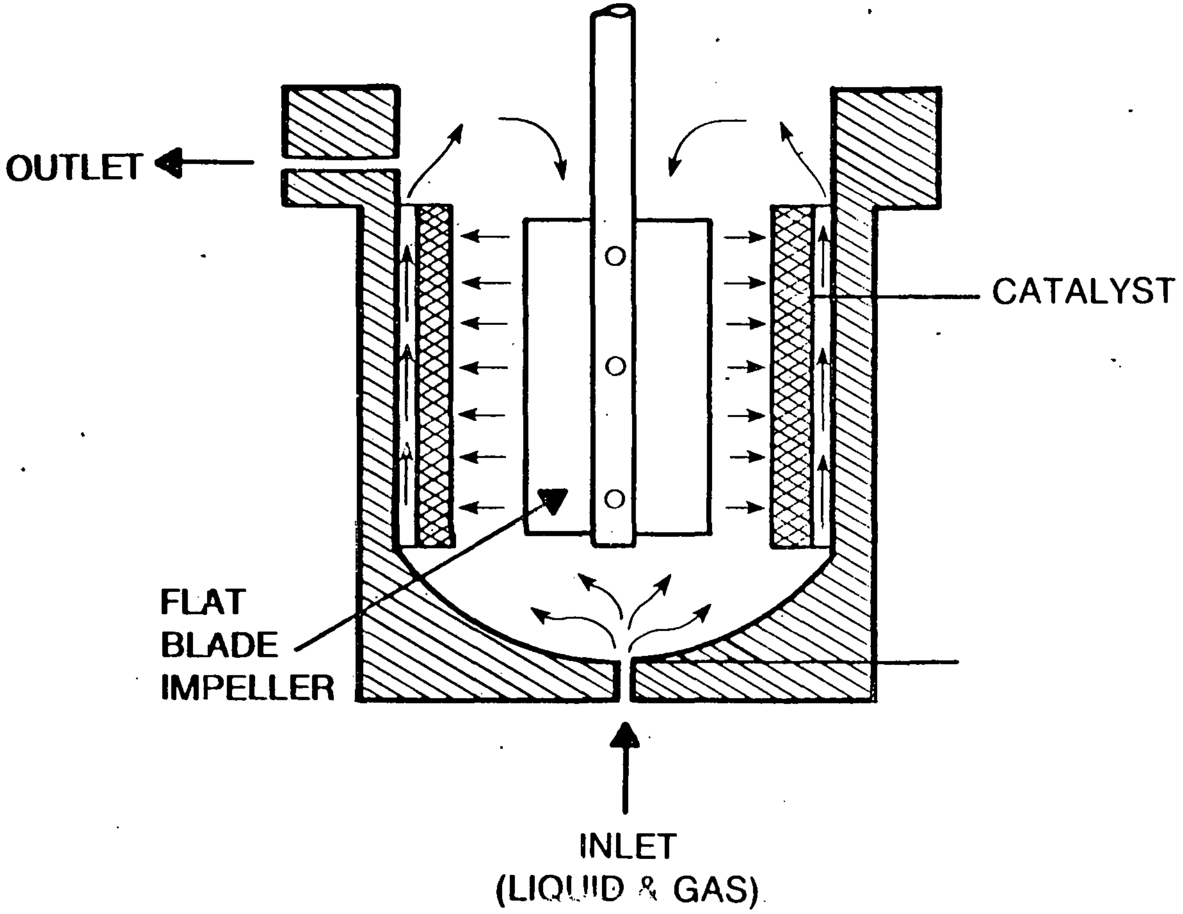


FIGURE 4

UNIFORM FLOW THROUGH FIXED CATALYST BASKET



bution of gas and liquid through the catalyst basket, and was selected for the hydroprocessing experiments.

Gas Holdup. Several simulated runs using the flat-bladed impeller were made to determine gas holdup. The experimental conditions were as follows:

Water flow rate = 200 g/hr
Air flow rate = 200 slph
Stirrer speed = 1,000 rpm

The measured low gas holdup of only 3.5 vol % would not significantly alter the nominal residence time of the liquid in the reactor. However, gas holdup increased considerably by increasing stirrer speed above 1,000 rpm. Because considerable slippage of the magnetic stirrer was observed at this higher speed, a stirrer speed of 1,000 rpm was selected for hydroprocessing runs to minimize slippage. An increase in gas holdup would normally decrease the effective liquid volume in the reactor, resulting in a reduction in nominal residence time. Such a reduction would decrease overall SRC conversion and concomitantly alter the product distribution. Since the factors controlling gas holdup are not understood, the change in the performance of the reactor due to scale-up is difficult to predict.

Process Development Unit (PDU) Operation

PDU Preparation. The basket was filled with a predetermined amount of catalyst and placed in the 2-liter autoclave. The autoclave was sealed and the entire PDU was pressure-checked to 2,000 psig for possible leaks using helium gas. When the unit was leak-tight, hydrogen gas flow was initiated to calibrate the hydrogen flow rate. After calibration was completed, creosote oil and hydrogen flow was started. At this time, the unit was checked for proper operation of all controllers.

Sulfiding the Catalyst. Reactor temperature was slowly raised from ambient to 600°F, while creosote oil and hydrogen gas passed through the unit. A sulfur compound such as ethane dithiol or ethyl disulfide was added to the creosote oil to sulfide the catalyst. The concentration of the sulfur compound in the feed was 3 wt %. Initially, no H_2S was detected by the on-line gas chromatograph (GC), but after a few hours, H_2S breakthrough occurred (indicating catalyst sulfiding), and H_2S concentration increased with sulfiding time. The creosote oil mixed with the sulfur compound was pumped for 6 more hours to ensure complete catalyst sulfiding; the amount of sulfur required for complete sulfiding was calculated to be 10.7 wt %.

Reaction Conditions. When catalyst sulfiding was completed, the pump was switched to begin pumping SRC feed material consisting of a 70 wt % HSRC/30 wt % hydrotreater process solvent mixture. Reactor temperature was raised from 600°F to the desired reaction temperature, and maintained at that level for a predetermined period. The reaction temperature was increased to a specified higher level, if desired during the course of the run. Several samples were taken for detailed analysis. A complete sample consisted of one 8-oz. total product liquid sample containing C_5^+ material, a light condensate sample, and a product gas sample. The light condensate sample was mainly water.

Product Work-Up

The feed and product liquid samples from a run were solvent-separated into pentane-soluble and -insoluble fractions. The pentane-soluble fraction was analyzed by encapsulated GC-simulated distillation to measure the 850°F- and 850°F+ fractions. Encapsulated GC-simulated distillation uses the standard ASTM D2887 procedure. A detailed description of the technique can be found in a report previously published by ICRC (14). The calculated value of 850°F+ was added to the weight percent pentane-insoluble fraction to determine the total amount of 850°F+ material in the total sample. Product distribution was calculated on the basis of 850°F+ conversion to gases and liquid (850°F+ material is defined in this report as SRC). SRC conversion was calculated using the following formula:

$$\text{Percent SRC conversion} = \frac{(850^\circ\text{F+ feed}) - (850^\circ\text{F+ product})}{(850^\circ\text{F+ feed})} \times 100$$

Total hydrogen consumption from gas represents the amount of hydrogen consumed from the gas phase during the hydroprocessing of SRC. At steady-state operation, during which the hydrogen content of the solvent does not change, this value will truly represent the net hydrogen consumption. However, the hydrogen content of the solvent changes somewhat in once-through or unsteady-state operation, resulting in either net consumption of hydrogen by the solvent or net transfer of hydrogen from the solvent. In hydroprocessing SRC, the total hydrogen consumption from gas is therefore adjusted by either adding the net hydrogen transferred out from the solvent or by subtracting the net hydrogen consumed by the solvent to calculate net hydrogen consumption (at steady state).

RESULTS AND DISCUSSION

Several SRC hydroprocessing runs were performed to determine the effect of process variables such as reaction temperature and reaction time on catalyst performance. The effect of variation in reactio temperature was evaluated in run CCL-50, while runs CCL-54 and CCL-6 were carried out to study catalyst aging at 775 and 825°F, respectively. The results of the hydroprocessing runs are described in detail below.

Process variables other than temperature, such as total pressure and hydrogen flow rate, were maintained constant during the operation of all three runs.

Effect of Reaction Temperature

Reaction temperature effects on catalyst performance were determined by using temperatures of 775, 800, and 825°F during run CCL-50. The initial reaction temperature of 775°F was raised in steps to 800 and 825°F. The results of run CCL-50 are summarized in Table 5.

The experimental data revealed that SRC conversion and hydrocarbon (HC) gas production were very sensitive to reaction temperature; both increased linearly, as shown in Table 5 and Figure 5. However, oil production did not change with temperature (Table 5). These results clearly indicate that the increase in SRC conversion with temperature resulted in increased HC gas rather than oil production. A similar interpretation can be derived by observing the significant increase in the selectivity for HC gases over oils with increased reaction temper-

Table 5

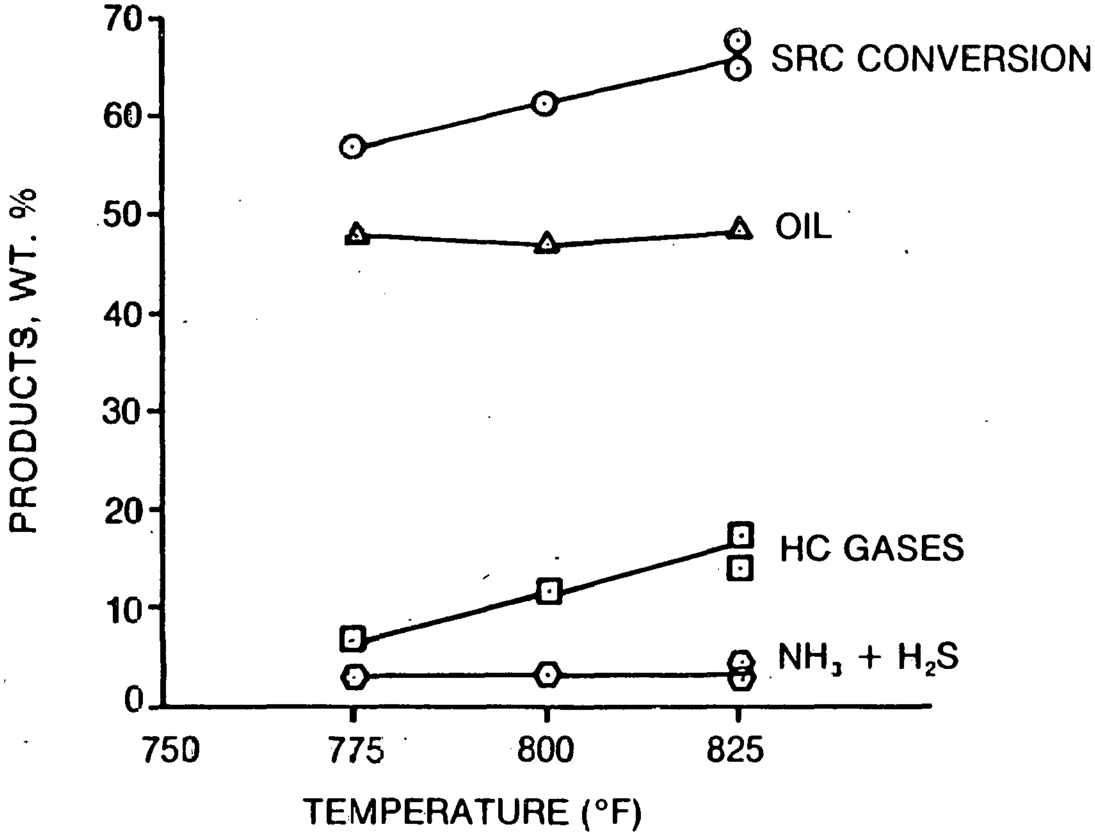
Variation of Product Distribution with Temperature

Sample no.	50-26	50-74	50-122	50-146	50-170
Time on stream (hr)	26	74	122	146	170
Catalyst age (g SRC/g catalyst)	16.1	45.5	74.7	89.0	102.8
Reaction temperature (°F)	775	800	825	825	775
Pressure (psig)	2,000	2,000	2,000	2,000	2,000
H_2 flow rate (scf/lb feed)	20.2	18.6	16.7	18.6	19.3
WHSV (g SRC feed/g catalyst-hr)	0.88	0.96	1.06	0.96	0.92
LHSV (mL feed/mL reactor-hr)	0.09	0.10	0.11	0.10	0.09
Product distribution (wt % SRC feed)					
HC	6.1	11.4	14.3	16.5	6.4
CO, CO_2	0.1	0.1	0.1	0.1	0.2
H_2S, NH_3	3.1	3.1	3.4	3.1	2.5
H_2O	4.1	4.5	4.4	4.4	3.7
Oil	47.8	46.6	48.0	48.0	43.1
SRC[a]	43.2	39.0	34.9	33.0	48.0
Conversion	56.8	61.0	65.1	67.0	52.0
H_2 consumption (wt % SRC feed)					
Total from gas	4.5	4.7	5.0	5.2	3.9
From solvent	(0.7)[b]	(0.5)	(0.4)	(0.4)	(0.6)
Net	3.8	4.2	4.6	4.8	3.3
Desulfurization (%)	86.1	89.8	93.2	90.6	80.1
Denitrogenation (%)	62.6	61.7	68.4	61.8	47.8
Deoxygenation (%)	71.6	77.4	76.3	76.3	65.1
Selectivity					
HC gases/oils	0.13	0.24	0.30	0.34	0.15
Oil/H_2 consumption	12.6	11.1	10.4	10.0	13.1
First-order rate constant for SRC conversion (hr^{-1})	1.16	1.50	2.00	1.94	1.00

[a] SRC is defined as the material boiling above 850°F.

[b] ( ) represents negative value.

FIGURE 5
VARIATION OF PRODUCT DISTRIBUTION
WITH TEMPERATURE



atures. (Selectivity is defined as the weight ratio of HC gas production to oil production). As expected, hydrogen consumption also increased with temperature (Table 5 and Figure 6). However, heteroatom gas production was not very sensitive to increasing temperature (see Table 5 and Figure 5). Likewise, minor variations in total desulfurization, denitrogenation, deoxygenation, and SRC sulfur content were noted with increasing temperature (Figures 7 and 8). The first-order rate constant for the conversion of SRC increased by a factor of two with an increase in the temperature from 775 to 825°F (refer to Appendix A, equation A-5).

The elemental analyses of pentane-soluble and -insoluble fractions of the actual feed for run CCL-50 and an analytical mixture of 70 wt % HSRC/30 wt % solvent are summarized in Table 6. Lower hydrogen and higher nitrogen and sulfur contents clearly indicated that the feed was somehow contaminated by a foreign material. Detailed analysis of the feed material by capillary GC indicated the presence of a small amount of creosote oil. However, this did not significantly affect the proportion of pentane solubles and insolubles and the 850°F- and 850°F+ fractions in the feed materials (Table 6).

Table 7 shows an increase in the hydrogen content of the pentane-soluble fraction of the total liquid product containing C_5^+ material at all three temperatures. The hydrogen content of the pentane-insoluble fraction of the product either remained constant or decreased compared with the feed material. However, the hydrogen contents of both fractions, decreased with increasing reaction temperature (Table 7). Although oxygen, nitrogen, and sulfur in the product fractions decreased considerably compared with the feed, they were not very sensitive to reaction temperature.

Since the reactor temperature was the same at the beginning and end of the run (775°F), the final activity of the catalyst was compared to its initial activity to evaluate the change. SRC conversion decreased from 57 to 52% after 170 hr of operation. Likewise, oil production, desulfurization, denitrogenation, deoxygenation, and hydrogen consumption decreased slightly with time on stream. The first-order rate constant for the conversion of SRC decreased from 1.2 to 1.0 hr^{-1} with time. All of these results indicate that the catalyst lost some of its

FIGURE 6
VARIATION OF HYDROGEN CONSUMPTION WITH TEMPERATURE

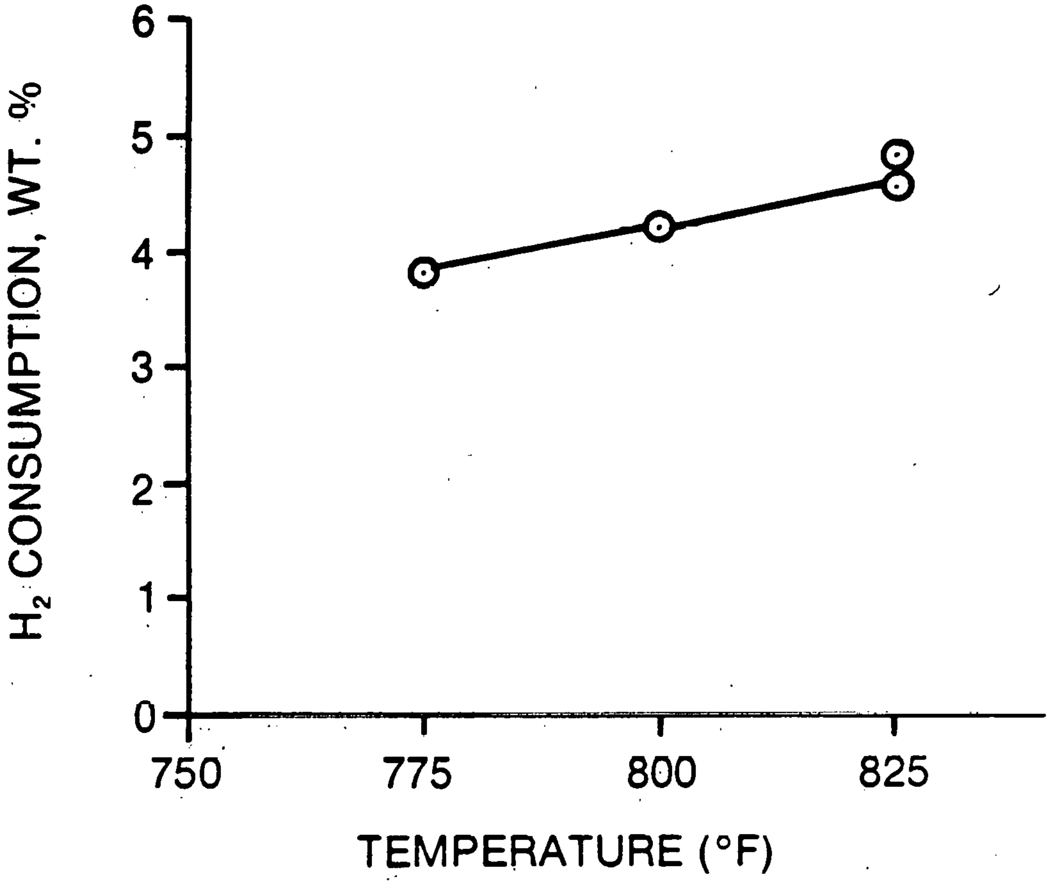


FIGURE 7
VARIATION OF HETEROATOM REMOVAL WITH TEMPERATURE

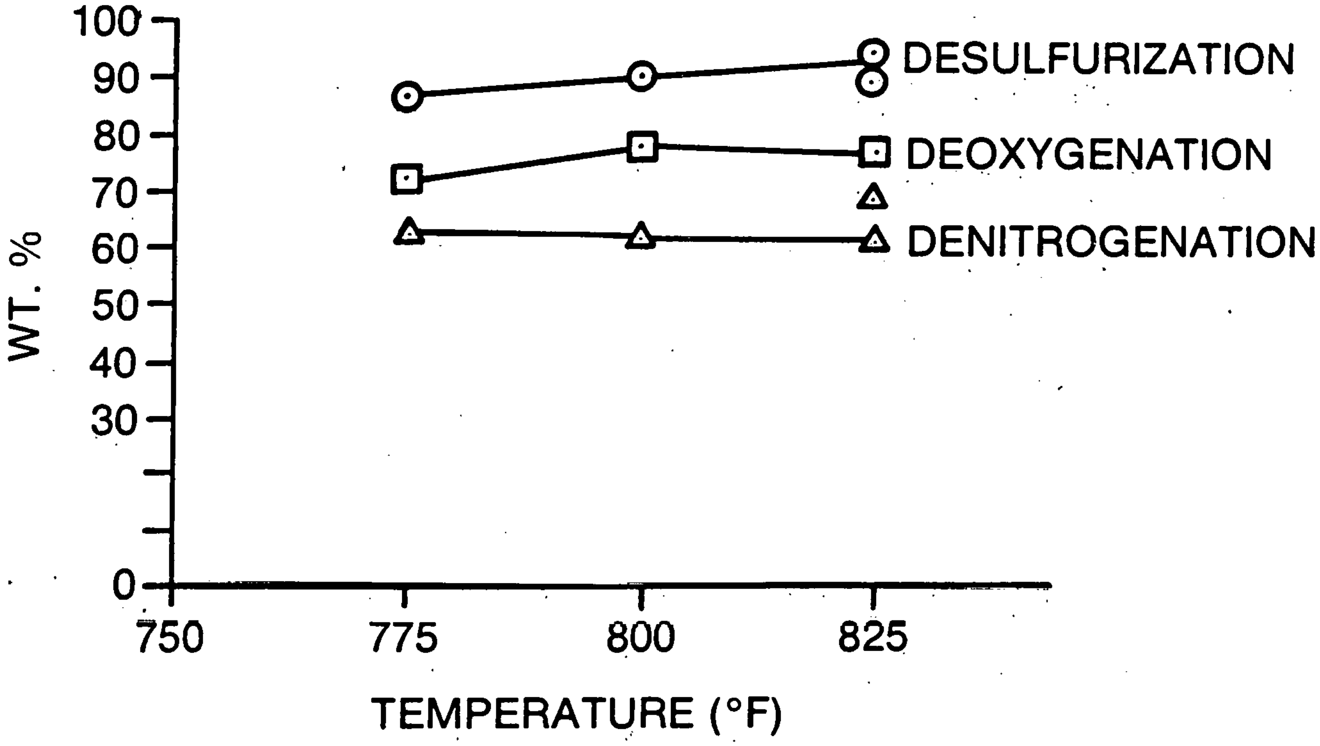


FIGURE 8
VARIATION OF SRC SULFUR WITH TEMPERATURE

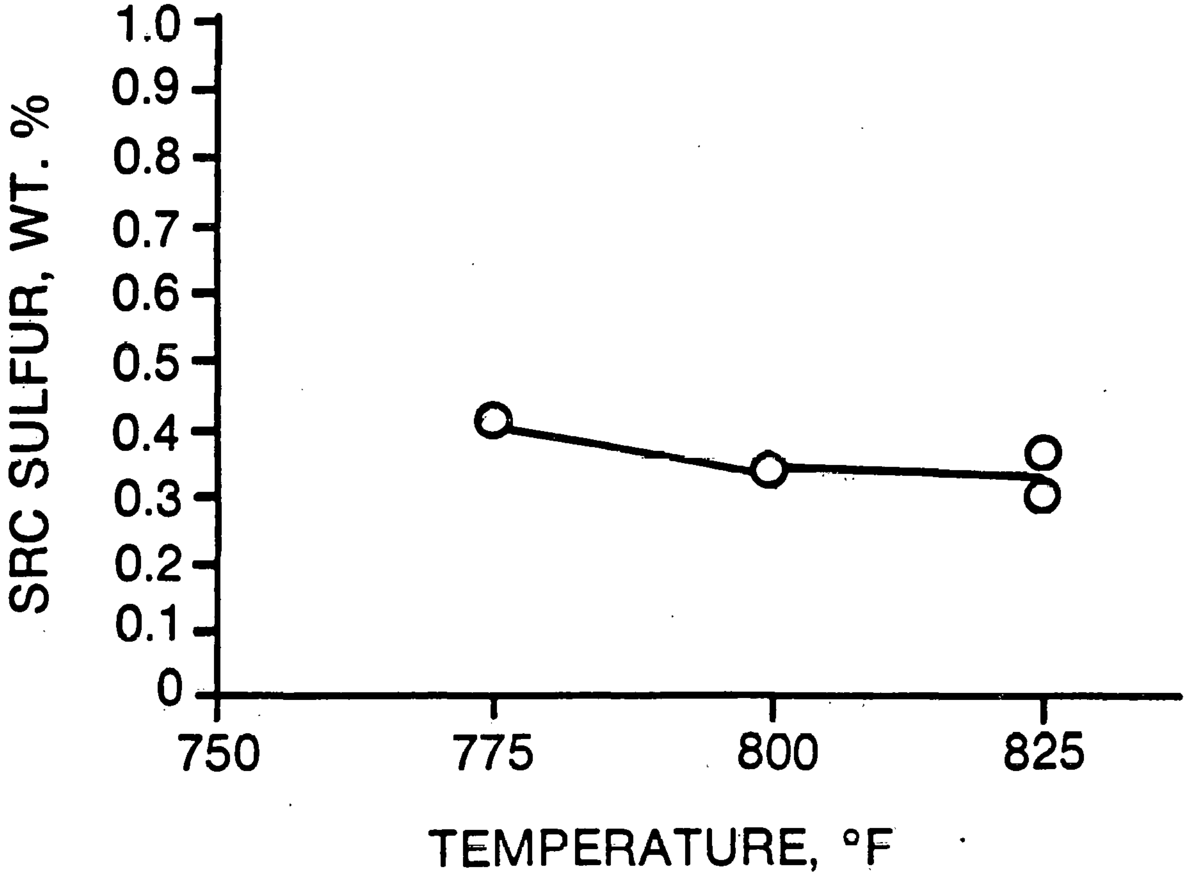


Table 6

Analysis of Feed Material

	Actual feed for run CCL-50	Analytical preparation of 70 wt % HSRC + 30 wt % solvent
Pentane solubles (wt %)	50.9	47.3
Pentane insolubles (wt %)	49.1	52.7
Pentane solubles: (wt %)		
C	89.2	88.8
H	8.1	9.2
O	1.3	1.4
N	1.1	0.7
S	0.4	0.1
Pentane insolubles: (wt %)		
C	85.6	85.1
H	5.5	5.6
O	5.3	5.8
N	2.5	2.3
S	0.9	0.9
Distillation fractions (wt %)		
850°F-	38.0	36.3
850°F+	62.0	63.7

Table 7

Distribution of Elements in the Feed and Product Liquid Samples

	Feed	Sample no.				
		50-26	50-74	50-122	50-146	50-170
Reaction temperature (°F)	--	775	800	825	825	775
Pentane solubles (wt %)	50.9	86.9	88.5	88.3	88.2	81.1
Pentane insolubles (wt %)	49.1	13.1	11.5	11.7	11.8	18.9
Pentane solubles: (wt %)						
C	89.2	89.3	89.8	89.7	89.8	89.4
H	8.1	9.2	8.8	8.7	8.7	9.0
O	1.3	0.7	0.6	0.6	0.7	0.8
N	1.1	0.5	0.6	0.4	0.6	0.6
S	0.4	<0.1	<0.1	<0.1	<0.1	<0.1
Pentane insolubles: (wt %)						
C	85.6	88.8	89.7	89.6	90.3	89.2
H	5.5	5.5	5.3	5.1	5.0	5.5
O	5.3	3.0	2.5	3.2	2.5	3.0
N	2.5	2.2	2.2	2.2	2.3	2.5
S	0.9	0.4	0.3	0.4	0.3	0.5

activity during the run, which was possibly due to several factors that will be discussed in detail in subsequent sections.

It can be concluded that SRC conversion, hydrocarbon gas production, and hydrogen consumption are very sensitive to reaction temperature. However, oil production does not change with increasing temperature from 775 to 825°F. An increase in hydrocarbon gas production along with hydrogen consumption results in a severe reduction in selectivity for oil production over both hydrogen consumption and hydrocarbon gas production. This observation suggests a very inefficient use of hydrogen at higher temperatures and emphasizes the benefits of using lower reaction temperatures. In addition, the data indicate no significant reduction in heteroatom removal by lowering the reaction temperature.

Effect of Residence Time

Residence time effects on catalyst performance were determined by using nominal residence times of 5 and 10 hr during runs CCL-50, 54, and 63. The residence time was varied at both 775 and 825°F by changing the internal volume of the reactor by placing a metal insert at the bottom of the autoclave. In effect, this decreased the nominal (void) residence time while keeping the catalyst residence time the same; this in effect left the feed pump rate to the reactor unchanged, and resulted in higher hydrocarbon gas formation and lower SRC conversion, as well as lower oil production (Table 8). The reduction in overall reactor residence time also considerably decreased heteroatom removal. With decreasing overall residence time, the selectivity for gas over oil increased and that for oil over hydrogen consumption decreased; the first-order rate constant for SRC conversion decreased slightly at 775°F, but decreased sharply at 825°F.

SRC hydroprocessing conceptually involves competing thermal and catalytic reactions. The proportion of thermal to catalytic reaction may vary due to variations in the residence times. If the reaction is predominantly catalytic, SRC conversion would remain unchanged with decreasing nominal (void) residence time. However, if thermal reaction predominates, conversion as well as the products from thermal reaction will diminish as residence time diminishes. At 775 and 825°F, the

Table 8

Variation of Product Distribution with Reaction Time

Sample no.	50-26	54-25	50-122	63-96
Reaction temperature (°F)	775	775	825	825
Reaction time (hr)	11	5	9	5
Pressure (psig)	2,000	2,000	2,000	2,000
H_2 flow rate (scf/lb feed)	20.2	17.0	16.7	17.7
WHSV (g SRC feed/g catalyst-hr)	0.88	1.20	1.06	0.97
Product distribution (wt % SRC feed)				
HC	6.1	6.6	14.3	22.3
CO CO_2	0.1	0.0	0.1	0.0
H_2S, NH_3	3.1	2.0	3.4	2.3
H_2O	4.1	4.5	4.4	5.0
Oil	47.8	32.8	48.0	27.4
SRC	43.2	57.4	34.9	47.6
Conversion	56.8	42.6	65.1	52.3
H_2 consumption (wt % SRC[a] feed)				
Total from gas	4.5	3.4	5.0	4.6
From solvent	(0.7)[b]	0.0	(0.4)	0.3
Net	3.8	3.4	4.6	4.9
Desulfurization (%)	86.1	78.0	93.2	81.1
Denitrogenation (%)	62.6	45.8	68.4	53.7
Deoxygenation (%)	71.6	68.6	76.3	76.6
Selectivity				
HC gas/oil	0.13	0.20	0.30	0.81
Oil/H_2 consumption	12.6	9.6	10.4	5.60
First-order rate constant for SRC conversion (hr^{-1})	1.16	0.88	2.00	1.07

[a] SRC is defined as the material boiling above 850°F.
[b] ( ) represents negative value.

conversion activity decreased as nominal (void) residence time decreased, indicating the preponderance of thermal reaction. The slight increase in gas yield at the lower residence times indicated that gases somewhat unexpectedly are derived via a catalytic reaction. Because the space velocity effect is so ill-defined by the data, conceivably the actual reaction mechanism may be reflected in an interaction of the thermal and catalytic steps. More work is needed to verify the variation and interaction of thermal and catalytic reactions with residence time to understand the true mechanism.

Catalyst Aging Studies

A mixture of HSRC and process solvent was hydroprocessed using the fixed catalyst basket reactor. Before the reactor was used for the catalyst aging study, one major modification was made to its design. The original design called for 0.1 liquid hourly space velocity (LHSV), which resulted in a nominal residence time of 10 hr. In order to reduce residence time, the reactor volume was reduced by placing a metal insert at the bottom of the autoclave; (see reference 1 for detailed information on changes in reactor design). The modification resulted in a LHSV of 0.2, which corresponded to a nominal residence time of approximately 5 hr.

Two runs were performed at constant temperatures of 775 and 825°F to determine the variation of SRC conversion and activity of the modified Shell Ni-Mo-Al catalyst with time. The results of these experiments are discussed below.

Catalyst Aging at 775°F. Catalyst activity and aging were determined at 775°F in run CCL-54. Utmost care was taken to maintain the operating conditions close to the desired values during the entire run. Several samples were collected during the course of the run to determine variations in SRC conversion and catalyst activity with time on stream.

Initial Catalyst Activity. Initially the Shell 324 Ni-Mo-Al catalyst yielded SRC conversions of 43 to 48% at 775°F (sample nos. 54-13 and 54-25; Table 9). Overall desulfurization, denitrogenation, and deoxygenation were 82.0, 47.5, and 68.3%, respectively. The sulfur content of unconverted SRC was 0.22 to 0.26%. Hydrogen consumption, determined by elemental hydrogen balance, was 3.2 to 3.4%. The first-

Table 9

SRC Hydroprocessing Product Distribution

	Sample no.										
	54-13	54-25	54-49	54-97	54-169	54-246	54-270	54-294	54-342	54-414	54-435
Time on stream (hr)	13	25	49	97	169	246	270	294	342	414	435
Reactor temperature (°F)	775	775	775	775	775	775	775	775	775	775	775
Pressure (psig)	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000	2,000
H_2 flow rate (scf/lb of feed)	14.2	17.0	19.6	16.7	15.3	14.9	14.7	14.4	15.0	15.2	15.5
WHSV (g of SRC feed/g of catalyst per hr)	1.34	1.20	1.03	1.20	1.28	1.21	1.23	1.26	1.21	1.22	1.24
Catalyst age (g of SRC feed/g of catalyst)	10.2	20.1	37.3	74.1	145.0	207.8	226.7	246.0	283.5	338.0	354.6
Product distribution (wt % SRC feed)											
HC	5.2	6.6	7.7	6.5	4.6	5.1	5.2	5.5	3.8	4.4	4.1
CO, CO_2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
H_2S, NH_3	2.1	2.0	2.2	2.1	1.8	1.7	1.6	1.5	1.0	0.7	0.6
H_2O	4.5	4.5	4.3	4.7	4.3	4.6	4.3	4.1	3.3	2.9	2.8
Oils	39.1	32.8	34.6	32.6	30.0	31.8	32.3	29.3	25.6	17.2	15.6
SRC	52.3	57.4	54.8	57.4	62.0	59.6	59.2	62.3	68.3	76.3	78.4
Conversion	47.7	42.6	45.2	42.5	38.0	40.4	40.8	37.7	31.7	23.7	21.6
H_2 consumption (wt % SRC feed)											
Total from gas	3.23	3.33	3.60	3.36	2.71	2.79	2.59	2.70	1.93	1.55	1.39
From solvent	0.01	0.06	0.05	0.06	(0.07)[a]	(0.02)	(0.09)	0.06	0.07	(0.01)	(0.09)
Net	3.24	3.39	3.65	3.42	2.64	2.77	2.50	2.76	2.00	1.54	1.30
Desulfurization (%)	82.0	78.0	84.2	78.8	74.4	70.3	75.2	70.1	48.8	34.0	34.5
Denitrogenation (%)	47.5	45.8	51.1	47.2	37.6	36.0	32.2	30.9	20.1	13.2	9.0
Deoxygenation (%)	68.3	68.6	65.8	70.7	65.0	70.2	65.4	62.1	49.9	44.8	42.2
SRC sulfur (%)	0.22	0.26	0.21	0.24	0.27	0.30	0.27	0.32	0.48	0.49	0.51
First-order rate constant for SRC conversion (hr^{-1})	1.22	0.88	0.85	0.88	0.78	0.82	0.85	0.76	0.56	0.38	0.34
Oils production/H_2 consumption	12.07	9.68	9.48	9.53	11.36	11.48	12.92	10.61	12.8	11.17	12.00

[a] Numbers in parentheses are negative values.

order rate constant for the conversion of SRC varied from 0.88 to 1.22 hr^{-1}. The distribution of elements in the pentane-soluble and -insoluble fractions of the total liquid product containing C_5^+ material (Table 10) showed no change in the hydrogen contents of the feed and product samples. However, the oxygen and sulfur contents in both fractions decreased significantly. Nitrogen content of the pentane-insoluble fraction, which represents unconverted SRC, changed only marginally relative to the feed.

Catalyst Aging. To evaluate catalyst performance with time, reaction temperature and other reaction conditions were held constant throughout run CCL-54. As seen in Table 9 and Figure 9, SRC conversion changed slightly during the first 294 hr (catalyst age = 246 g SRC/g catalyst), and then began to decrease gradually--from 38% at 294 hr to 21% at 435 hr. Similarly, oil and hydrocarbon gas production remained constant during the first 294 hr, and then started to decrease (see Table 9 and Figure 10). Although hydrogen consumption decreased gradually with time (Figure 11), the hydrogen contents of the pentane-soluble and -insoluble fractions did not vary significantly (Table 10). Figure 12 and Table 9 show that desulfurization, denitrogenation, and deoxygenation generally decreased slightly up to 294 hr, but decreased sharply thereafter. Likewise, SRC sulfur content did not change significantly up to 294 hr, but then increased sharply (Figure 13). The trend followed by the first-order rate constant (Figure 14) is similar to that noted for SRC conversion itself (Figure 9).

Figure 15 illustrates how selectivity varied with catalyst age. Interestingly, although SRC conversion decreased with catalyst age, selectivity was maintained at its initial value.

Catalyst Analysis. After run CCL-54, two samples of the spent catalyst, one from the upper and the other from the lower half of the basket, were recovered for detailed analysis. The spent catalyst samples were washed first with pyridine and then with pentane to remove any residual SRC from the surface, and then dried at room temperature under a continuous flow of nitrogen.

Table 11 summarizes the detailed analysis of fresh and spent catalysts. The data indicate that carbon was not deposited uniformly on the catalyst; that from the upper half of the basket contained more than

Table 10

Distribution of Elements in the Feed and Product Liquid Samples

	Sample no.											
	Feed	54-13	54-25	54-49	54-97	54-169	54-245	54-270	54-294	54-342	54-414	54-435
Pentane soluble (wt %)	47.3	82.7	79.4	82.6	80.2	78.8	77.9	76.9	73.6	65.5	61.4	61.5
Pentane insoluble (wt %)	52.7	17.3	20.6	17.4	19.8	21.2	22.1	23.1	26.4	34.5	38.6	38.5
Pentane solubles (wt %)												
C	88.8	89.4	89.4	89.8	90.1	89.7	89.5	89.9	89.6	89.9	89.6	89.4
H	9.2	9.2	9.3	9.3	9.3	9.1	9.1	9.0	9.3	9.3	9.2	9.0
O	1.4	0.8	0.7	1.0	0.7	0.9	0.7	0.8	0.8	1.0	1.3	1.2
N	0.7	0.6	0.6	0.5	0.6	0.7	0.7	0.8	0.7	0.7	0.7	0.8
S	0.1	0.04	0.04	0.01	0.04	0.05	0.07	0.05	0.05	0.11	0.22	0.19
H/C	1.24	1.24	1.24	1.24	1.24	1.21	1.23	1.21	1.24	1.24	1.23	1.21
Pentane insolubles (wt %)												
C	85.1	87.5	87.8	89.5	87.9	89.4	88.9	89.4	87.3	88.7	88.1	87.8
H	5.6	5.6	5.5	5.7	5.5	5.6	5.6	5.6	5.5	5.5	5.4	5.5
O	5.8	3.6	3.4	3.1	3.0	3.5	3.0	3.3	3.6	3.7	3.6	4.0
N	2.3	2.2	2.3	2.2	2.2	2.3	2.4	2.4	2.4	2.5	2.6	2.5
S	0.9	0.4	0.5	0.5	0.5	0.5	0.5	0.4	0.5	0.6	0.6	0.6
H/C	0.79	0.77	0.75	0.76	0.76	0.75	0.75	0.75	0.75	0.74	0.74	0.75

FIGURE 9
VARIATION OF SRC CONVERSION WITH TIME
(REACTION TEMPERATURE = 775°F)

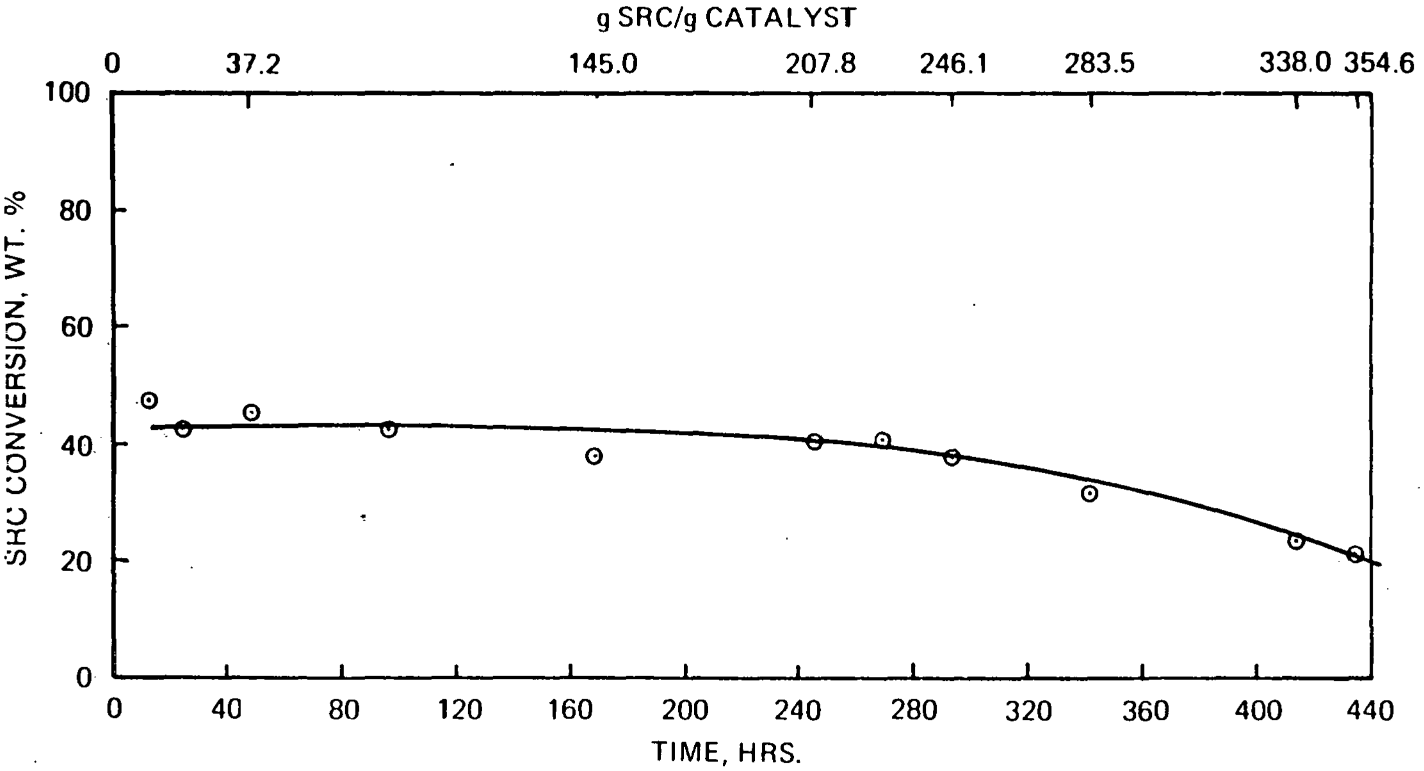


FIGURE 10
VARIATION OF OILS AND HYDROCARBON GASES PRODUCTION WITH TIME
(REACTION TEMPERATURE = 775°F)

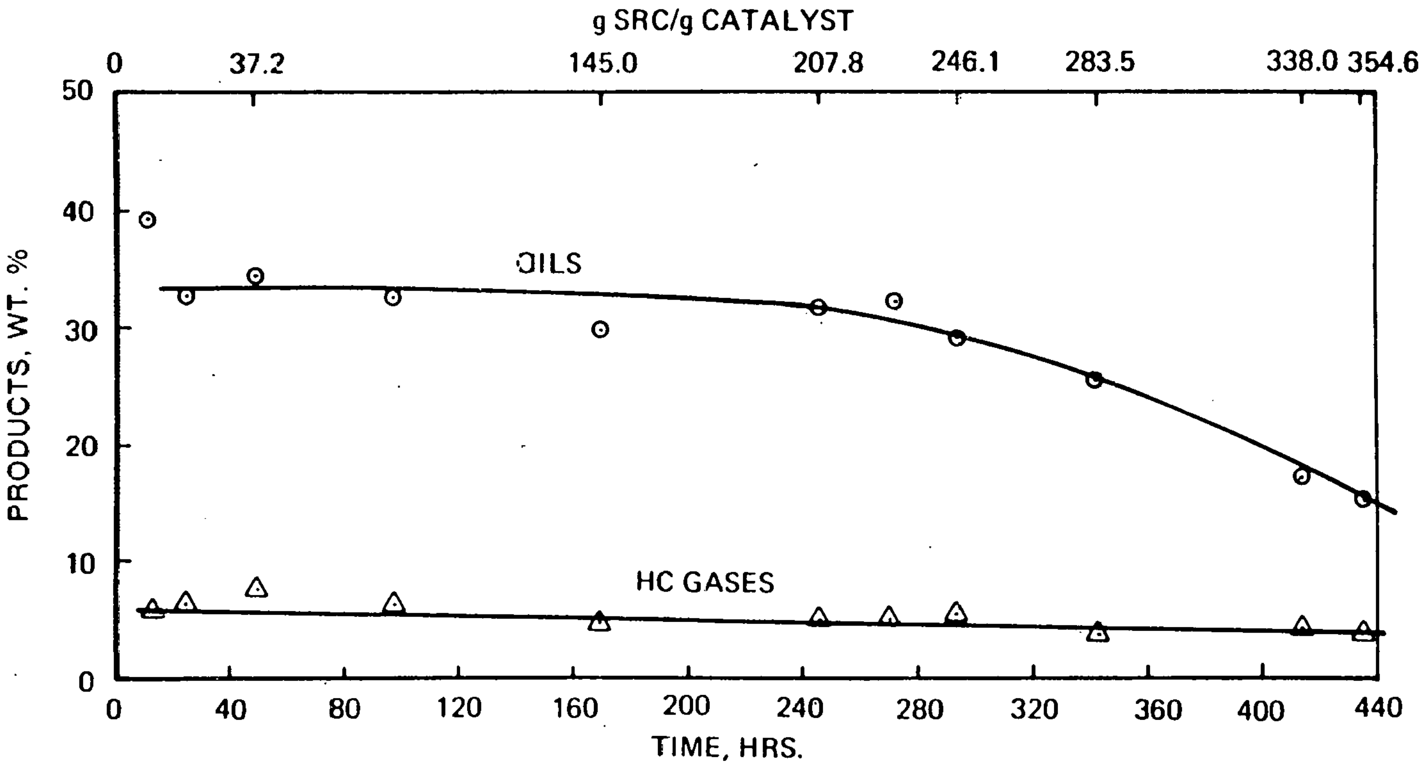


FIGURE 11
VARIATION OF H_2 CONSUMPTION WITH TIME
(REACTION TEMPERATURE = 775°F)

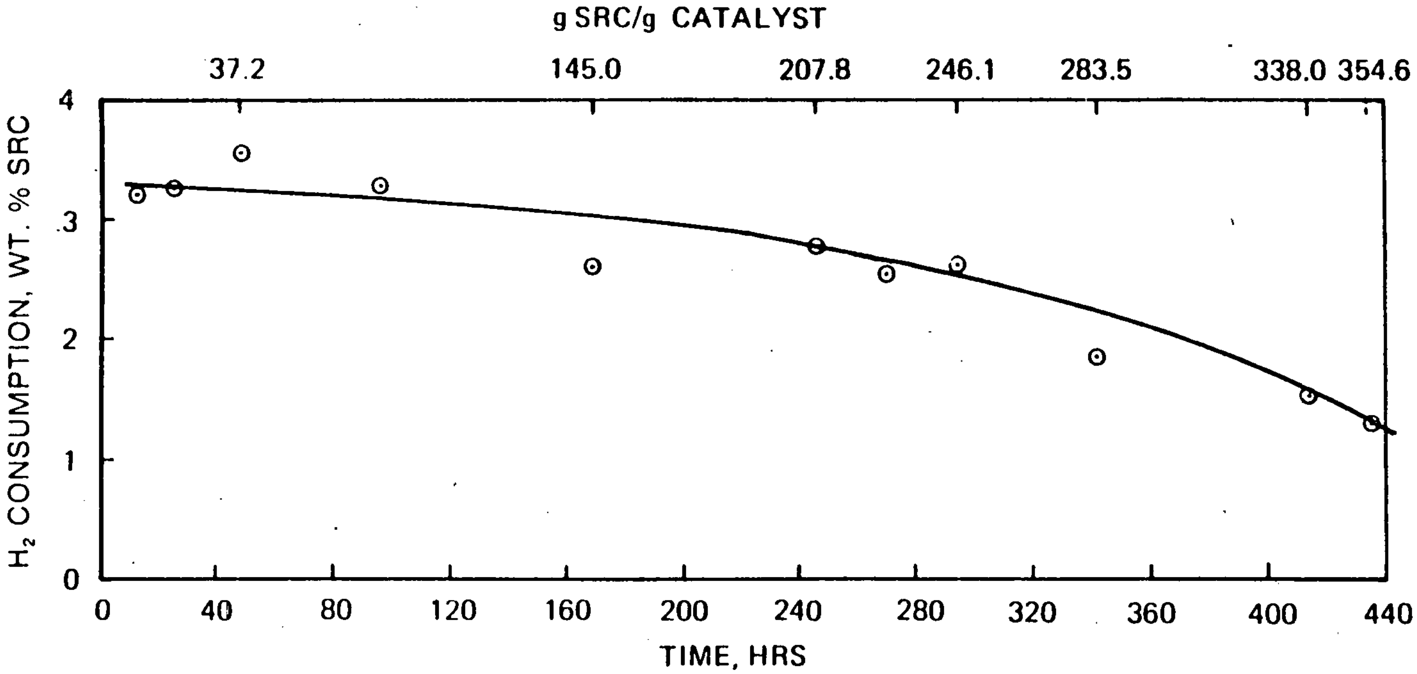


FIGURE 12
VARIATION OF HETEROATOMS REMOVAL
WITH TIME
(REACTION TEMPERATURE = 775°F)

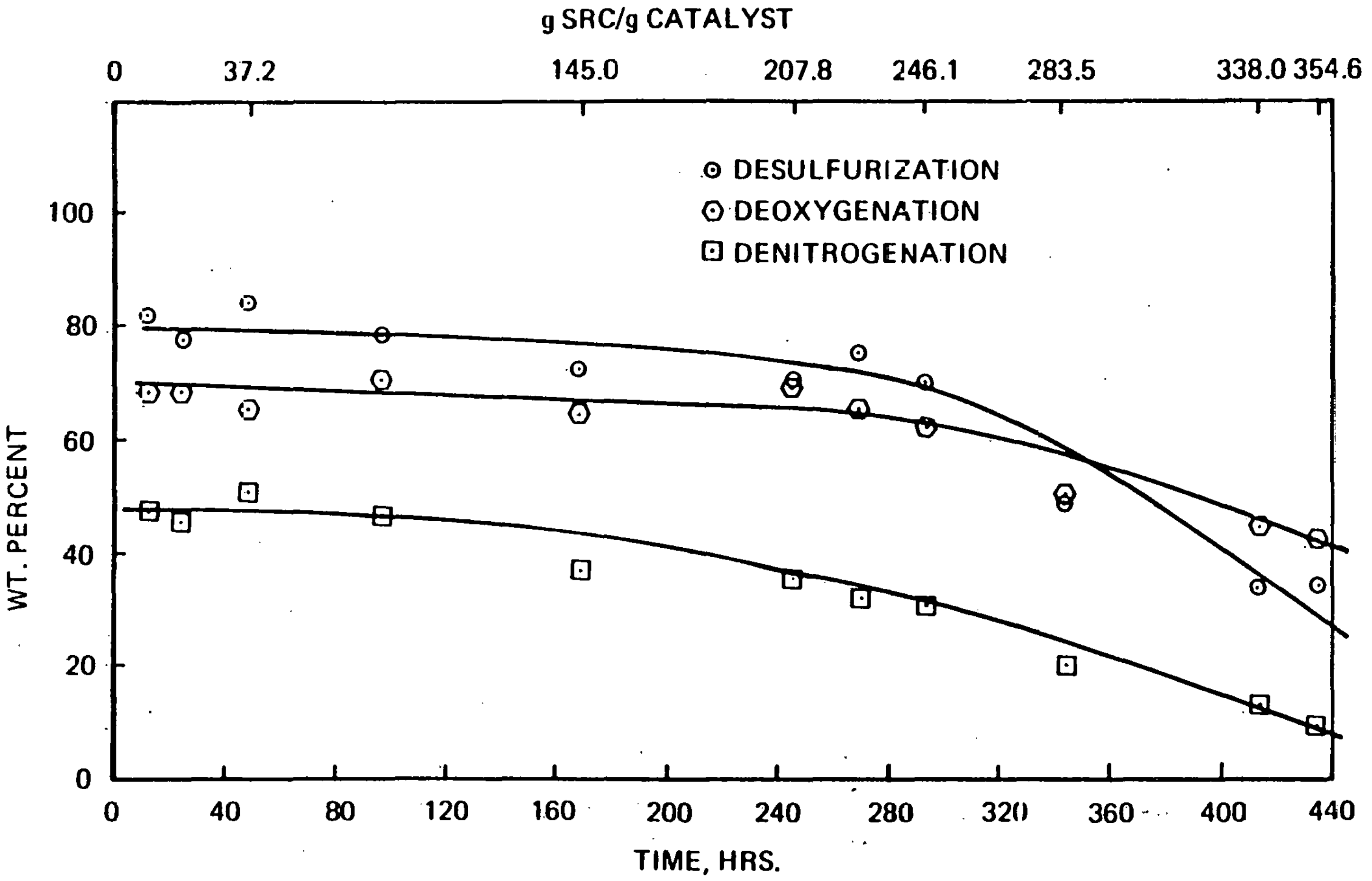


FIGURE 13
VARIATION OF SRC SULFUR WITH TIME
(REACTION TEMPERATURE = 775°F)

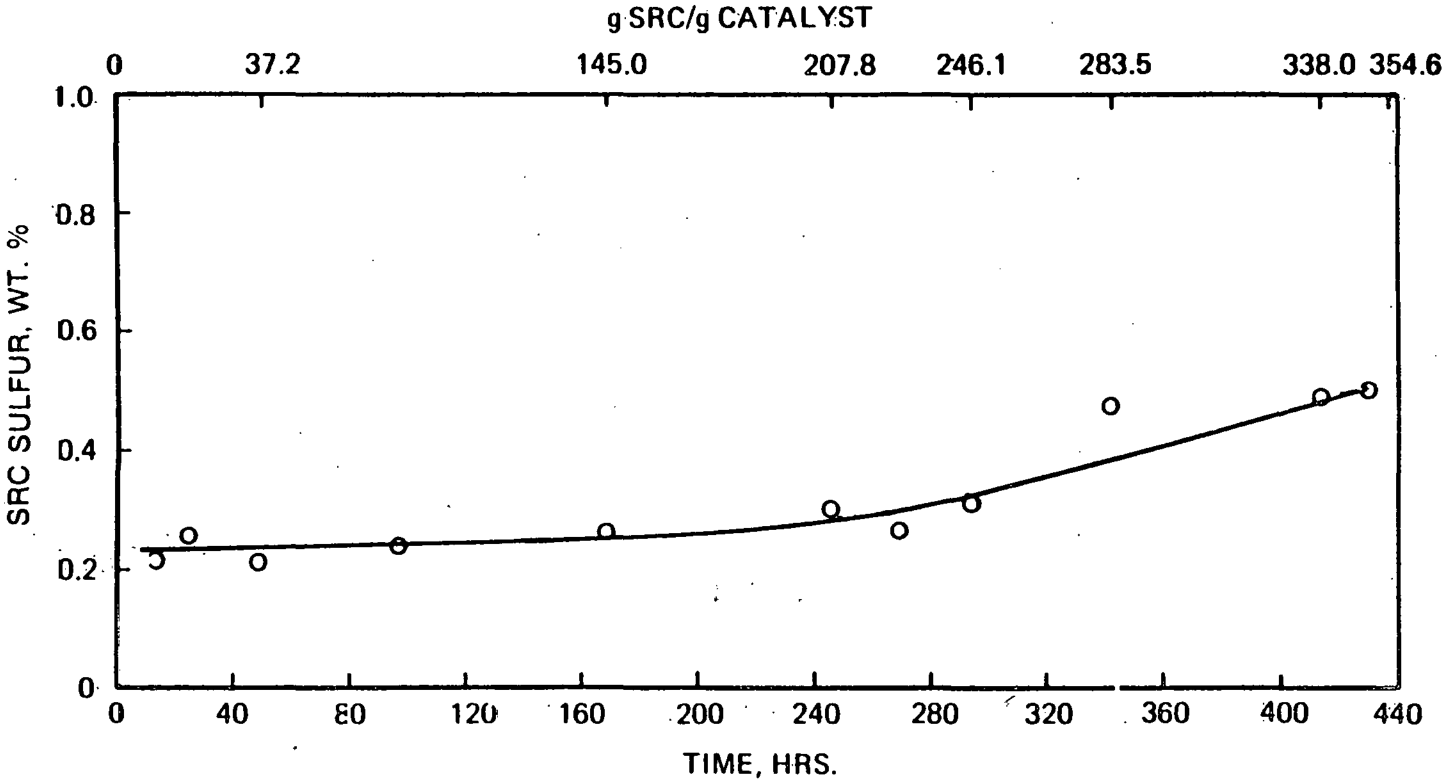


FIGURE 14
VARIATION OF FIRST-ORDER RATE CONSTANT FOR THE CONVERSION OF SRC WITH TIME (REACTION TEMPERATURE = 775°F)

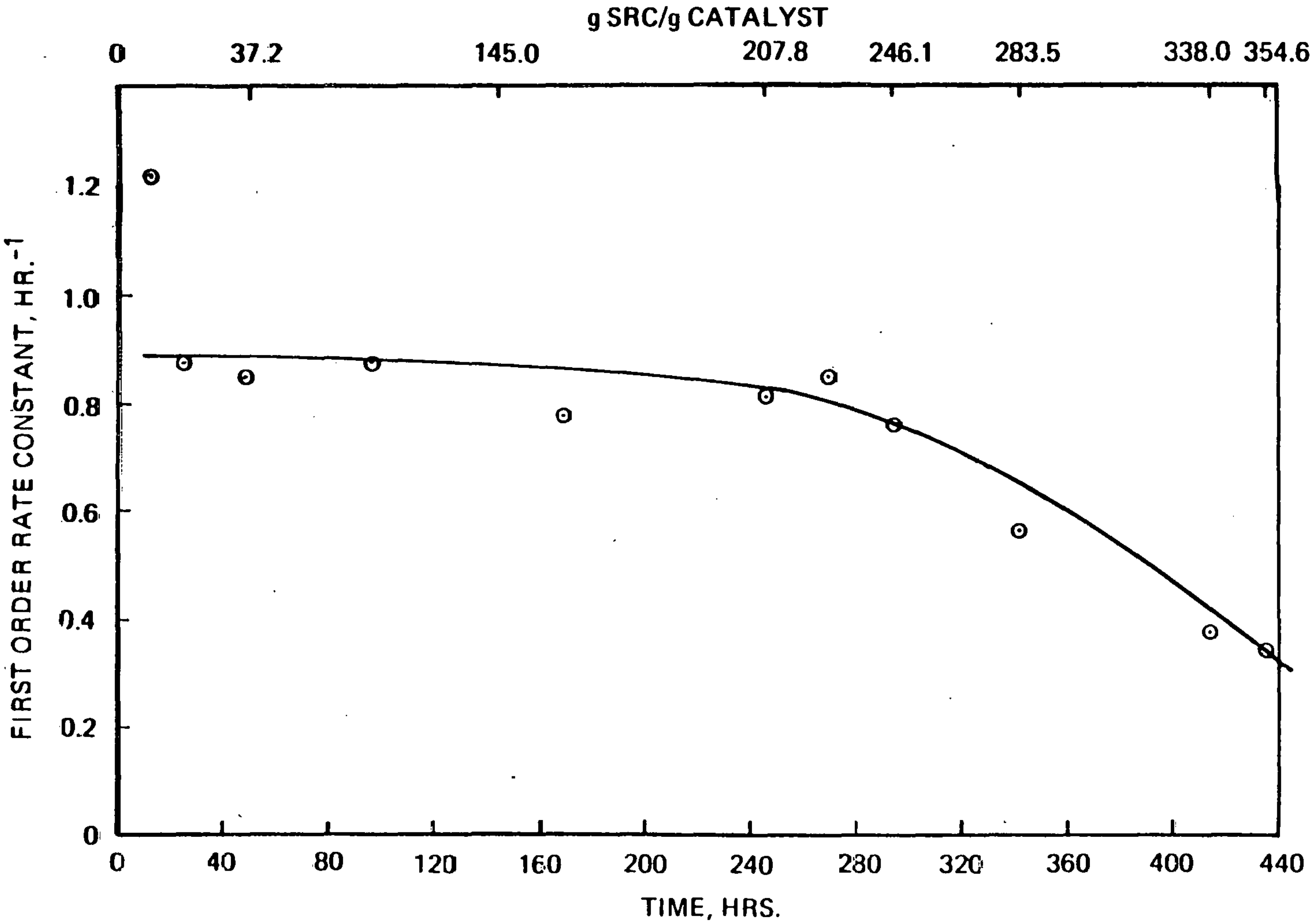


FIGURE 15
SELECTIVITY VARIATION WITH CATALYST AGE
(REACTION TEMPERATURE = 775°F)

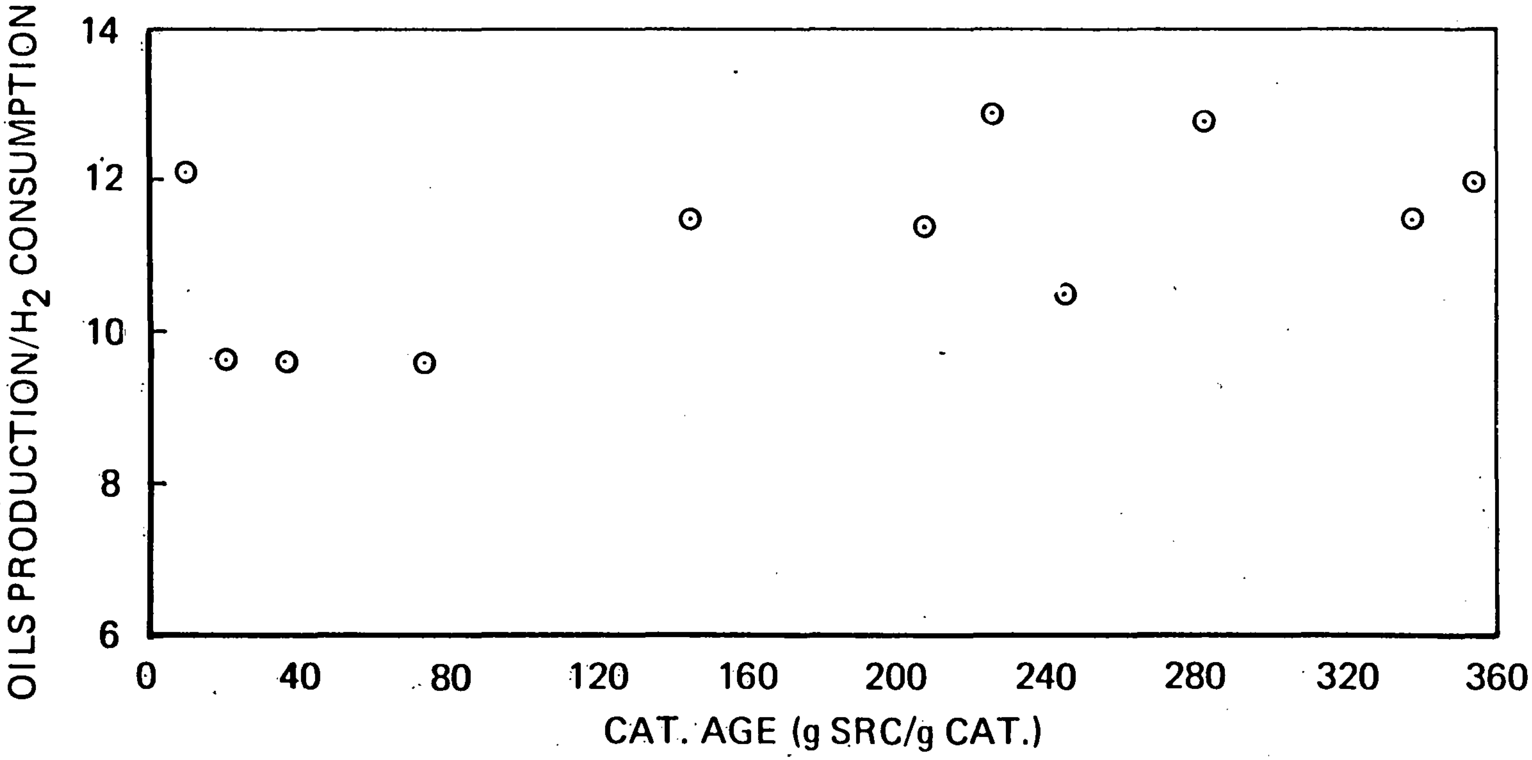


Table 11

Detailed Analysis of Fresh and Spent Catalysts from Run CCL-54

	Wt %		
		Spent catalyst	
	Fresh catalyst	Upper half of basket	Lower half of basket
C		18.4	8.1
H		1.7	1.4
N		0.6	0.3
S		6.3	7.0
Ni	2.7	2.0	1.9
Mo	15.9	10.1	10.0
Fe		0.2	0.3
Ti		0.3	0.4
Ca		0.1	0.1
Na		4.2	4.3
Surface area (m^2/g)	152	89	72
Median pore diameter (Å)	96	49	39
Median pore volume (mL/g)	0.38	0.14	0.10

twice as much carbon. However, the level of metals deposited on both samples was comparable. Deposition of metals and carbon on catalysts is known to reduce the surface area, pore volume, and catalyst activity, and the data in Table 11 substantiate this--surface area and pore diameter and volume of both catalyst samples were significantly reduced. Decreased surface area and pore volume probably reduced catalyst activity.

Whether the reduced activity was due to carbon or metal deposition, or both, is currently unknown. The level of metals and carbon deposited was normal, except for an unusually high level of sodium (Table 11), which probably resulted from a high sodium level in the feed SRC (Table 12), due to Na_2CO_3 addition during the initial coal liquefaction step. A mass balance around the reactor revealed that only minor portions of the iron and titanium in the feed SRC were deposited on the catalyst, whereas most of the sodium was retained by the catalyst (Table 12). Because sodium has been reported to severely deactivate cracking as well as desulfurization catalysts (4 and 5), the unusually high level of sodium deposited on the catalyst may be one of the reasons for catalyst deactivation. More work is needed to confirm this observation.

Catalyst Aging at 825°F. The activity and aging of the modified Shell 324 Ni-Mo-Al catalyst was determined at 825°F in run CCL-63. As mentioned earlier, the mixture of HSRC and process solvent was pumped along with hydrogen to the reactor immediately after the catalyst was sulfided. The reactor temperature was increased from 600 to 825°F, where it remained for the entire run. PDU operation was smooth for the first 138 hr on stream (including 102 hr at 825°F), after which the feed pump failed and the unit was shut down; the reactor temperature was reduced to 550°F to prevent catalyst deactivation during shutdown. Operation was resumed after 216 hr. The unit was shut down one more time at 241 hr (127 hr on stream at 825°F) due to a hydrogen leak, and the reactor temperature was again reduced to 550°F. Operation was resumed at 318 hr and continued until 356 hr. Overall, the unit was on stream at 825°F for a total of 165 hr, during which several samples were taken for detailed analysis.

Table 12

Metal Distribution in the Feed (Weight of Fresh Catalyst, 280 g; Calculated Weight of Spent Catalyst, 416 g)

	Amount of metals (g)		
	In the feed (1)	Deposited on catalyst (2)	In the product (1) - (2)
Iron	14.9	1.0	13.9
Sodium	19.8	17.7	2.1
Titanium	11.9	1.5	10.4

Initial Catalyst Activity. The Shell 324 Ni-Mo-Al catalyst initially showed an SRC conversion of 54%, which was significantly lower than that noted in run CCL-50 (sample no. 63-34; Table 13). Oil and hydrocarbon gas production were 31 and 20%, respectively. Both these values were again significantly different from those noted in run CCL-50. Overall desulfurization, denitrogenation, and deoxygenation were 93, 60, and 76%. Hydrogen consumption, determined by elemental hydrogen balance, was 5%. The distribution of elements in the pentane-soluble and -insoluble product fractions of the total liquid product containing C_5^+ material (Table 14) showed a significant decrease in hydrogen, oxygen, and sulfur contents compared with the feed liquid. The decrease in hydrogen content was probably due to the preponderance of thermal over catalytic reaction at 825°F, as discussed earlier. SRC sulfur content decreased from 1.0 to 0.1 wt %; however, the nitrogen content of the pentane-insoluble fraction, which represents unconverted SRC, changed only marginally relative to the feed. The first-order rate constant for the conversion of SRC was calculated to be 1.12 hr^{-1}, which was also considerably lower than that noted in run CCL-50. The reasons for the marked differences in the results of runs CCL-63 and CCL-50 were already discussed in detail in the section titled "Effect of Residence Time."

Catalyst Aging. SRC conversion changed slightly during the first 96 hr at 825°F (catalyst age = 59 g SRC/g catalyst), but decreased considerably thereafter; this decrease in conversion after 96 hr could have been due to catalyst deactivation during the 3-day shutdown (Table 13 and Figure 16). Similarly, oil and hydrocarbon gas production remained constant during the first 96 hr, but decreased thereafter (see Table 13 and Figure 17). Hydrogen consumption decreased slightly during the initial 96 hr, but decreased significantly when the unit was restarted after the 3-day shutdown (Figure 18); however, no significant variations in the hydrogen contents of the pentane-soluble and -insoluble fractions were noted (Table 14). Selectivity for oil production over hydrogen consumption decreased slightly with catalyst age (Table 13), even after the shutdown.

Table 13

SRC Hydroprocessing Product Distribution

	Sample no.					
	63-24	63-48	63-72	63-96	63-151	63-165
Time on stream (hr)	24	48	72	96	151	165
Reactor temperature (°F)	825	825	825	825	825	825
Pressure (psig)	2,000	2,000	2,000	2,000	2,000	2,000
H_2 flow rate (scf/lb of feed)	16.0	18.7	18.5	17.7	12.4	14.6
WHSV (g of SRC feed/g of catalyst per hr)	0.93	0.87	0.97	0.97	1.24	1.06
Catalyst age (g of SRC feed/g of catalyst	16.0	29.5	44.0	58.5	99.1	108.4
Product distribution (wt % SRC[a] feed)						
HC	20.37	21.28	17.64	22.31	14.77	15.40
CO, CO_2	0.00	0.00	0.00	0.00	0.00	0.00
H_2S, NH_3	2.57	2.32	2.18	2.28	1.13	1.28
H_2O	5.04	5.29	4.92	5.04	4.18	4.21
Oils	31.44	27.64	32.17	27.35	18.05	13.40
SRC	45.33	47.95	46.98	47.65	64.37	68.16
Conversion	54.67	52.05	53.02	52.35	35.63	31.84
H_2 consumption (wt % SRC[a] feed)						
Total from gas	4.75	4.48	3.90	4.64	2.50	2.48
From solvent	0.22	0.26	0.30	0.27	0.42	0.42
Net	4.97	4.74	4.20	4.91	2.92	2.90
Desulfurization (%)	93.39	88.24	84.23	81.08	63.02	62.20
Denitrogenation (%)	59.89	52.81	49.29	53.67	20.06	25.35
Deoxygenation (%)	76.60	80.36	74.79	76.60	63.43	63.95
SRC sulfur (%)	0.10	0.18	0.23	0.23	0.38	0.38
First-order rate constant SRC conversion (hr-1)	1.12	0.94	1.09	1.07	0.69	0.50
Oil production/H_2 consumption	6.33	5.83	7.66	5.57	6.18	4.62

[a] SRC is defined as the material boiling above 850°F.

Table 14

Distribution of Elements in Feed and Product Liquid Samples

		Sample no.					
	Feed	63-24	63-48	63-72	63-96	63-151	63-165
Pentane soluble (wt %)							
	47.3	86.5	82.7	81.5	82.0	67.8	66.5
Pentane insoluble (wt %)							
	52.7	13.5	17.3	18.5	18.0	32.2	33.5
Pentane solubles (wt %)							
C	88.8	89.9	90.4	90.3	90.0	90.1	90.2
H	9.2	8.8	8.7	8.7	8.7	8.5	8.5
O	1.4	0.6	0.6	0.7	0.7	0.9	0.9
N	0.7	0.6	0.6	0.6	0.6	0.9	0.7
S	0.1	0.01	0.01	0.02	0.05	0.07	0.07
H/C	1.24	1.18	1.15	1.16	1.16	1.13	1.13
Pentane insolubles (wt %)							
C	85.1	89.9	90.2	90.0	90.4	89.6	89.6
H	5.6	5.1	5.0	5.0	4.9	5.0	4.9
O	5.8	3.7	2.5	2.8	2.6	2.9	2.8
N	2.3	2.0	2.2	2.3	2.2	2.6	2.5
S	0.9	0.2	0.4	0.4	0.4	0.5	0.5
H/C	0.79	0.68	0.66	0.67	0.65	0.67	0.66

FIGURE 16
VARIATION OF SRC CONVERSION WITH TIME
(REACTION TEMPERATURE = 825°F)

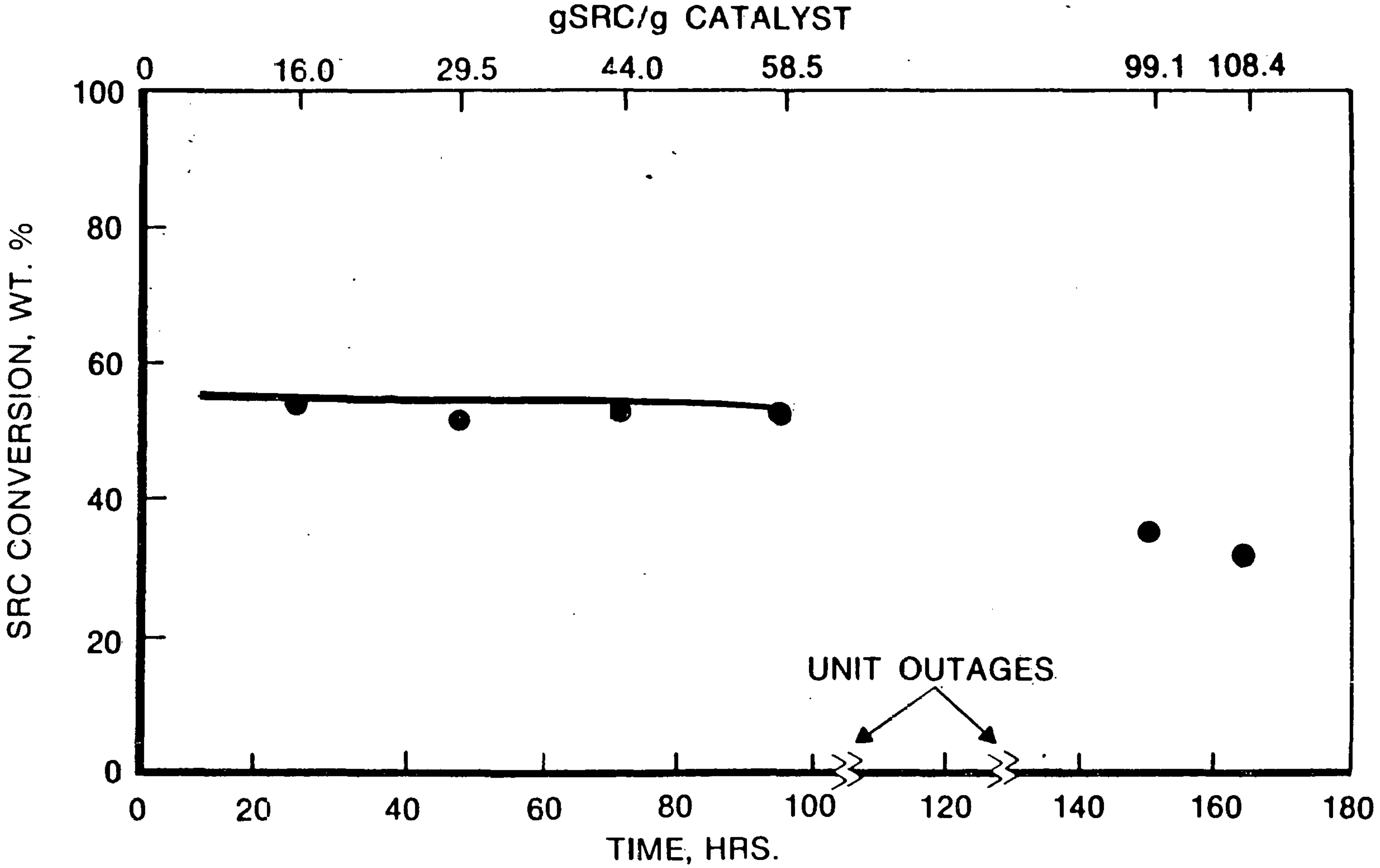


FIGURE 17
VARIATION OF PRODUCTION OF OILS AND HYDROCARBON GAS WITH TIME
(REACTION TEMPERATURE = 825°F)

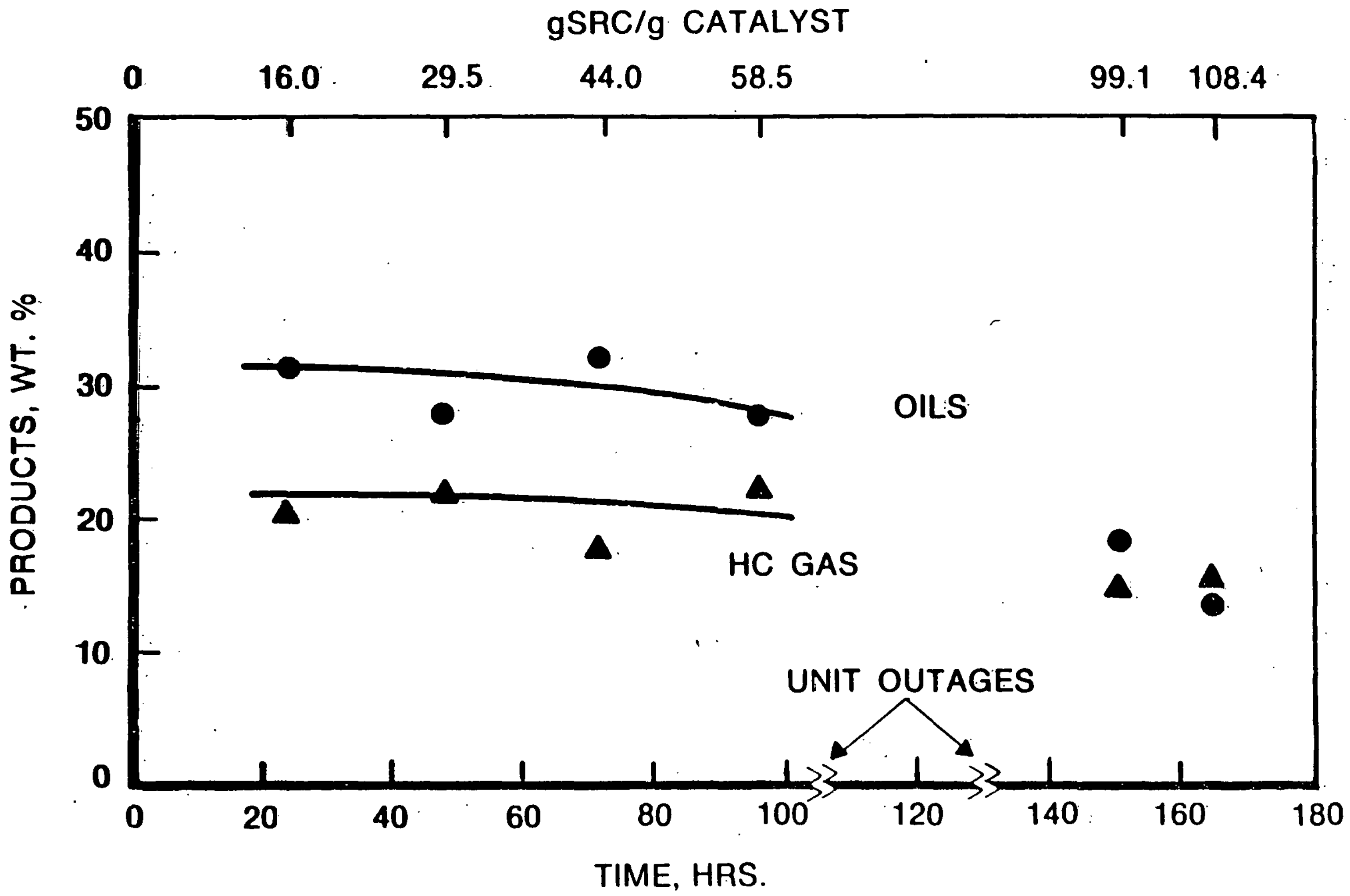
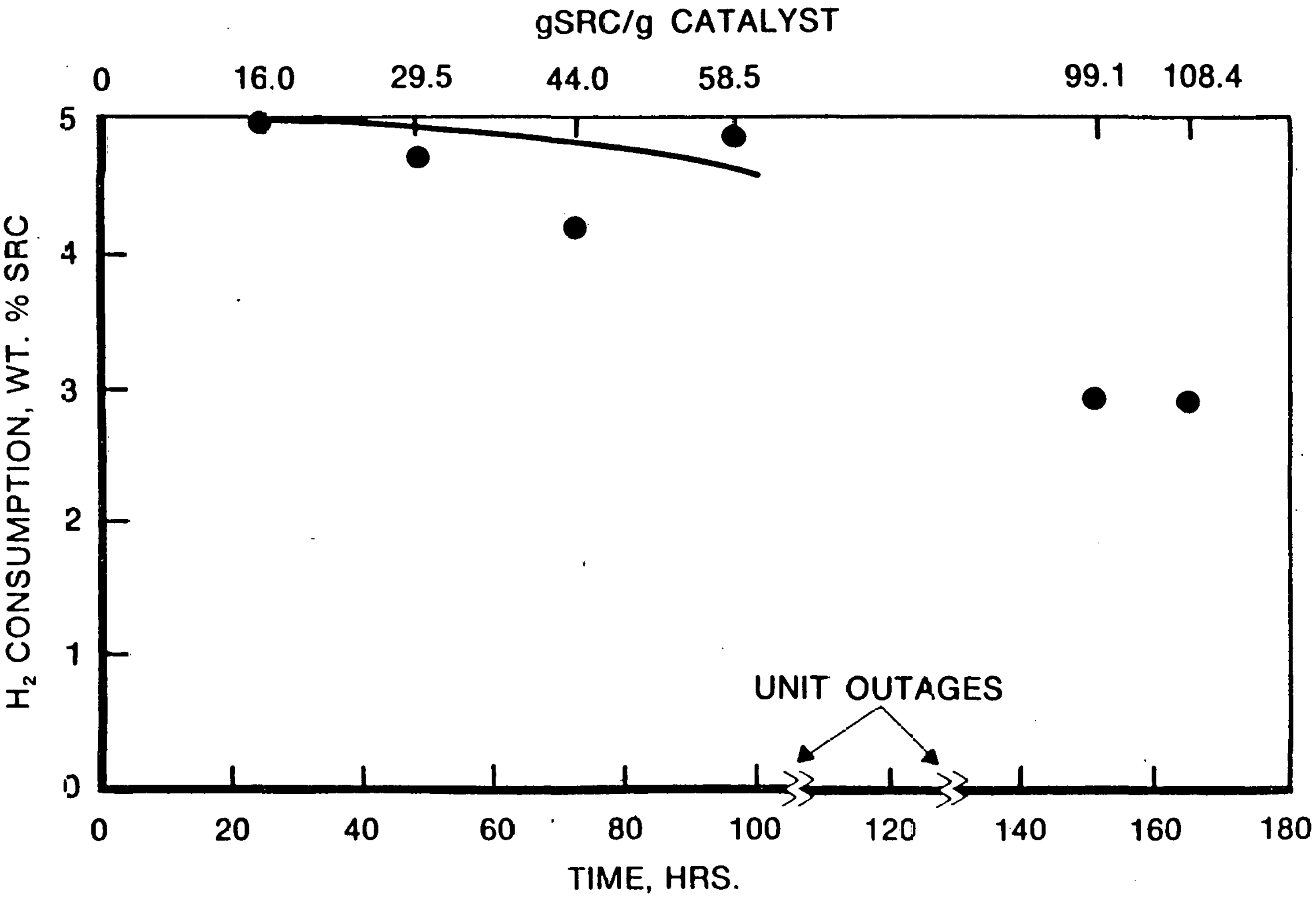


FIGURE 18
VARIATION OF H_2 CONSUMPTION WITH TIME
(REACTION TEMPERATURE = 825°F)



Desulfurization decreased gradually (Figure 19), while the sulfur content of SRC in the reactor products increased gradually (Table 13). Denitrogenation and deoxygenation decreased slightly up to 96 hr, but decreased sharply when the unit was restarted after the 3-day shutdown (Figure 19). The first-order rate constant for the conversion of SRC showed the same trend noted for SRC conversion (Figure 20). The severe decline in catalyst activity after 96 hr could have been due to the problems encountered during the operation of run CCL-63. These problems could have prematurely deactivated the catalyst. The data at 825°F also showed a very high gas yield, which could have been due to maldistribution of gas and liquid through the catalyst basket. Because these results seem to be out of line with those obtained both in run CCL-50 and at Wilsonville, the data obtained at 825°F in run CCL-63 are questionable and should be used with caution.

Catalyst Analysis. A sample of the spent catalyst was recovered after run CCL-63 for detailed analysis. The sample was first washed with pyridine and then with pentane to remove any residual SRC from the surface. The washed sample was then dried at room temperature under a continuous flow of nitrogen.

As shown in Table 15, a significant amount of carbon was deposited on the catalyst; moderate amounts of metal deposition other than sodium were also noted. (Similar results were noted in the catalyst aging run at 775°F.) Metal and carbon deposition caused a significant reduction in the surface area and pore volume of the catalyst; in fact, the pore volume analysis of the spent catalyst revealed an almost total disappearance of pore structure. The reduction in the surface area and the loss of pore structure are the main reasons for the significant reduction in catalyst activity.

Heavy sodium deposition on the catalyst was due to the presence of a high level of sodium in the feed SRC (Table 2); as mentioned earlier, this resulted from Na_2CO_3 addition in the initial coal liquefaction step. A mass balance around the reactor revealed that minor portions of iron and titanium in the feed SRC were deposited on the catalyst, whereas a major portion of sodium in the feed SRC was retained by the catalyst (Table 16). Similar results were noted in the SRC hydroprocessing run at 775°F. The amount of sodium deposited on the catalyst

FIGURE 19
VARIATION OF HETEROATOMS REMOVAL WITH TIME
(REACTION TEMPERATURE = 825°F)

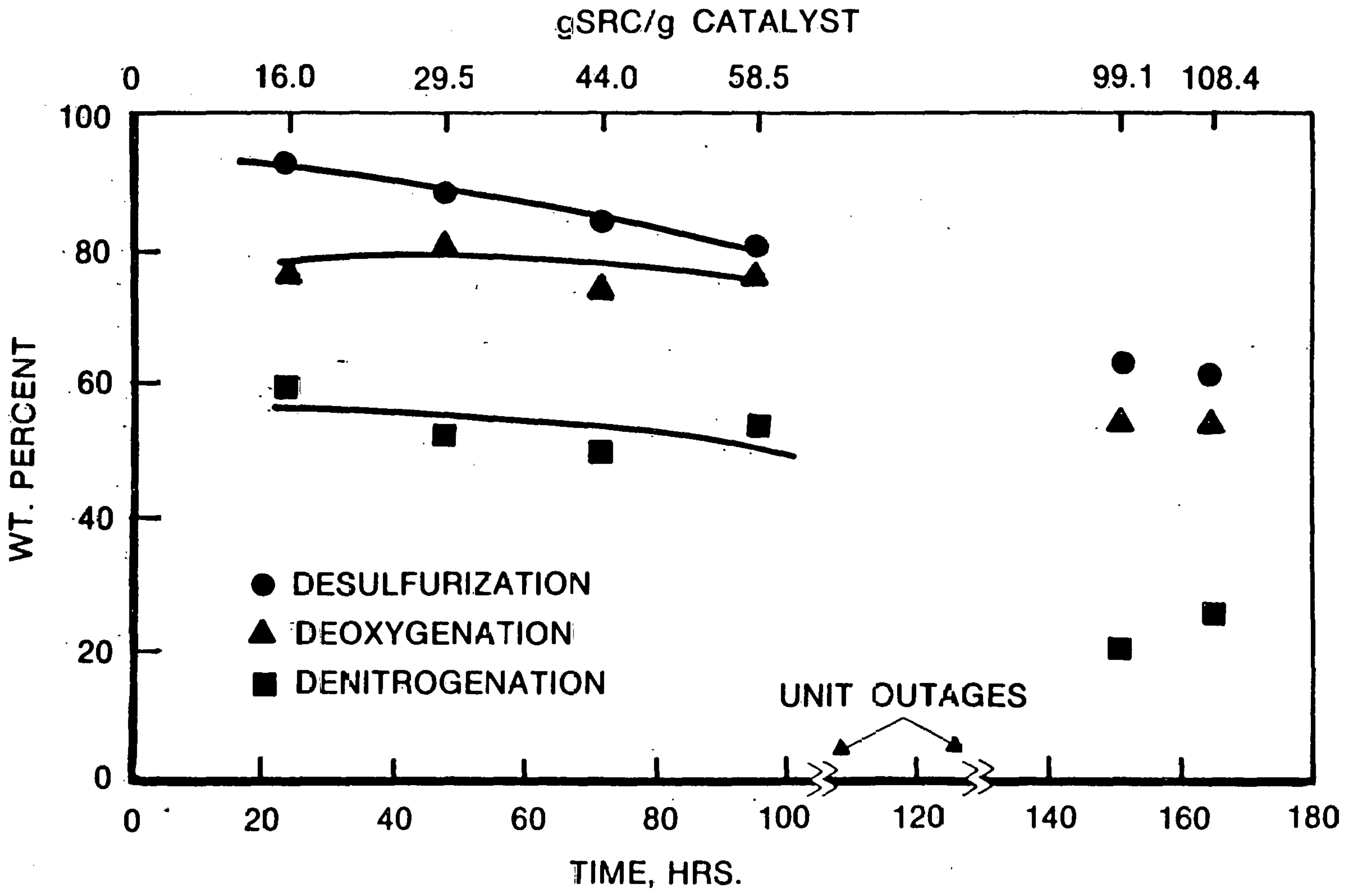


FIGURE 20
VARIATION OF FIRST-ORDER RATE CONSTANT FOR SRC CONVERSION WITH TIME
(REACTION TEMPERATURE = 825°F)

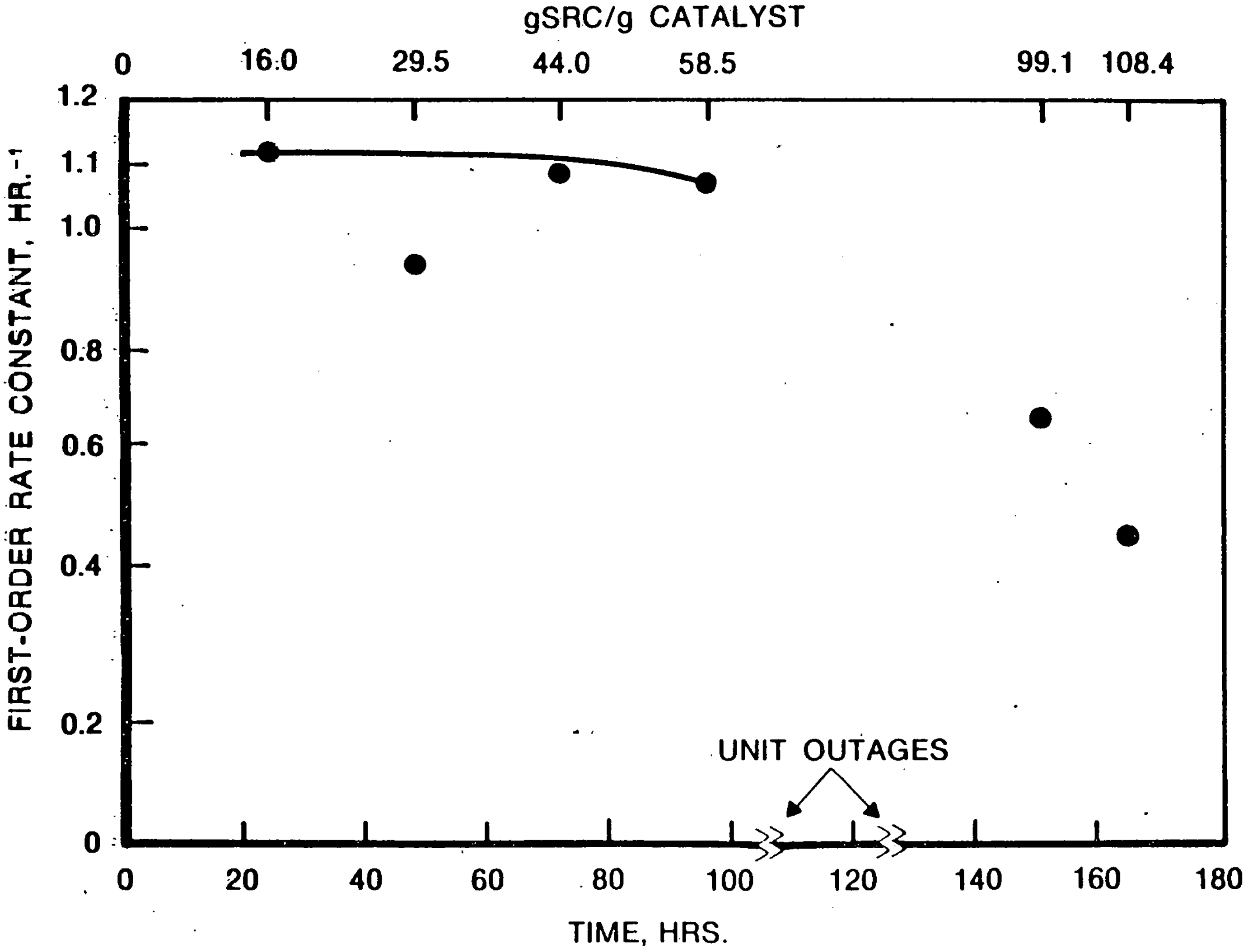


Table 15

Detailed Analysis of the Fresh and Spent Catalysts from Run CCL-63

	Fresh catalyst (wt %)	Spent catalyst (wt %)
C	--	22.9
H	--	1.4
N	--	0.6
S	--	6.7
Ni	2.7	1.8
Mo	15.9	6.6
Fe	--	0.1
Ti	--	0.1
Ca	--	0.002
Na	--	2.0
Surface area (m^2/g)	152	22.3
Medium pore diameter (Å)	96	--
Median pore volume (mL/g)	0.38	<0.05

Table 16

Metal Distribution in the Feed and Spent Catalyst from Run CCL-63 (Weight of Fresh Catalyst, 300 g; Calculated Weight of Spent Catalyst, 450 g)

	Amount of metals (g)		
	In the feed (1)	Deposited on catalyst (2)	In the product (1) - (2)
Iron	6.6	0.5	6.1
Sodium	8.6	9.0	--
Titanium	5.2	0.5	4.7

(Table 16) was higher than that present in the feed SRC because the amount of SRC hydroprocessed below 825°F was not included in the total amount of feed SRC. The heavy sodium deposition may also be one of the reasons for the severe catalyst deactivation.

Comparison of Catalyst Aging at 775 and 825°F. Catalyst activity and aging data discussed earlier are compared in this section to determine relative catalyst activity and aging at 775 and 825°F. As expected, the initial conversion of SRC and the rate constant at 825°F were higher than at 775°F (Figures 21 and 22); SRC conversion was 54% at 825°F as opposed to 43-48% at 775°F. Heteroatom removal activity of the catalyst was also higher at 825°F than at 775°F during the first few hours of operation. Hydrocarbon gas production and hydrogen consumption were considerably higher at 825°F than at 775°F, as shown in Figures 23 and 24. On the contrary, oil production was lower at the higher temperature (Figure 23). Finally, the selectivity for oil production over hydrogen consumption was considerably lower at 825°F that at 775°F (Figure 25).

Catalyst activity remained constant during the first several hours of operation at both temperatures, but then declined sharply. At 775°F, SRC conversion changed slightly during the initial catalyst aging period of 246 g SRC/g catalyst, and then began to decrease gradually from 38% at a catalyst age of 246 to 21% at a catalyst age of 357 g SRC/g catalyst (Figure 21). Similar results were noted for the first-order conversion rate constant, oil and hydrocarbon gas production, and hydrogen consumption (see Figures 22 to 24). Although SRC conversion decreased with catalyst age at 775°F, selectivity was maintained at its initial value (Figure 25).

Catalyst activity at 825°F also changed slightly during the initial catalyst aging period of 59 g SRC/g catalyst, but then decreased sharply; SRC conversion decreased from 52 to 31%, as shown in Figure 21. Similar results were noted for oil and hydrocarbon gas production, first-order rate constant, and hydrogen consumption (Figures 22 to 24). However, selectivity decreased slightly with catalyst age at 825°F (Figure 25). As discussed earlier, the sharp decline in catalyst activity at 825°F, as well as shorter catalyst life compared with that at 775°F could have been due to several problems encountered during the operation of run CCL-63.

FIGURE 21
VARIATION OF SRC CONVERSION WITH CATALYST AGE

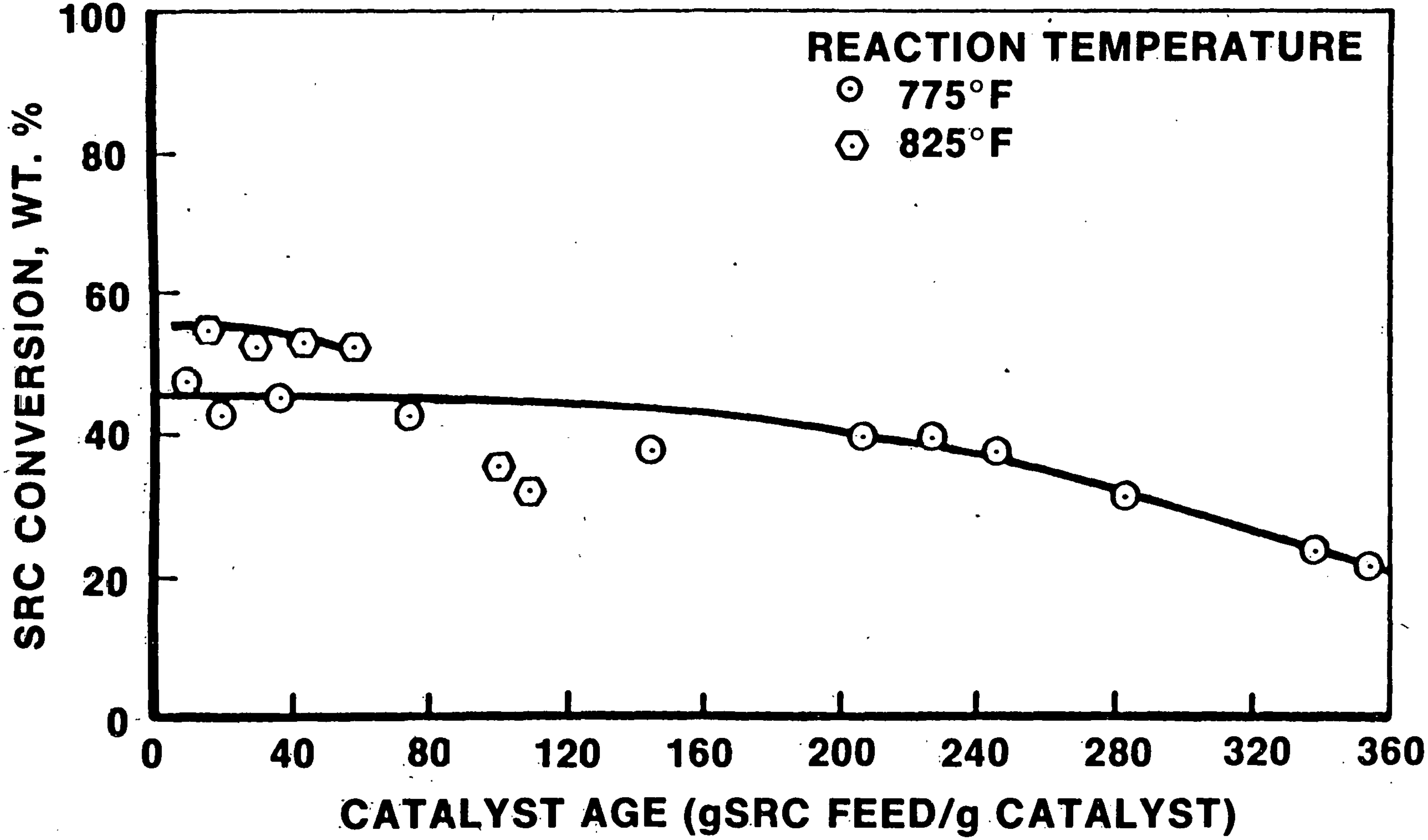


FIGURE 22
VARIATION OF RATE CONSTANT WITH CATALYST AGE

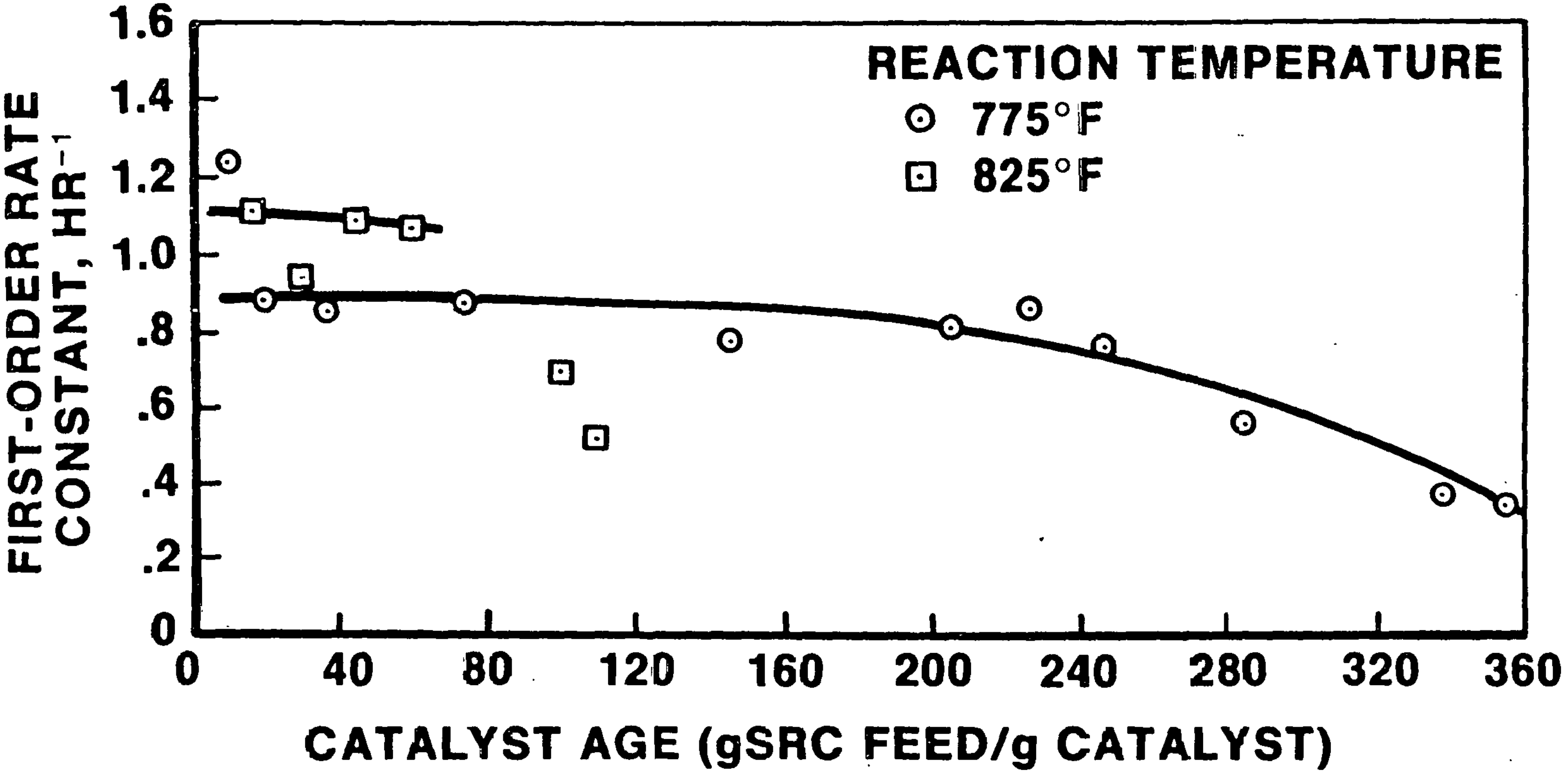


FIGURE 23
VARIATION OF OIL AND HC GAS PRODUCTION WITH CATALYST AGE

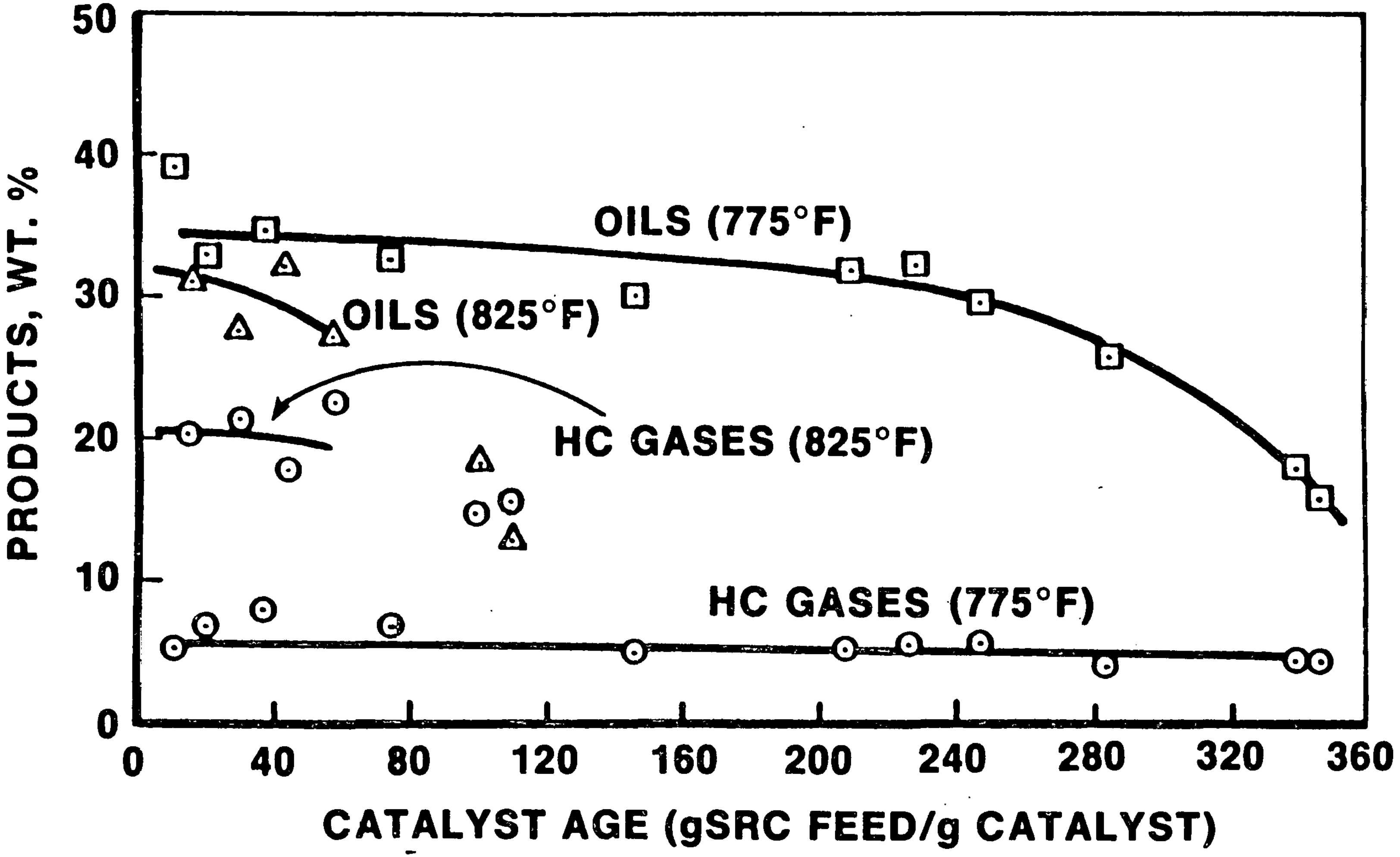


FIGURE 24
VARIATION OF HYDROGEN CONSUMPTION
WITH CATALYST AGE

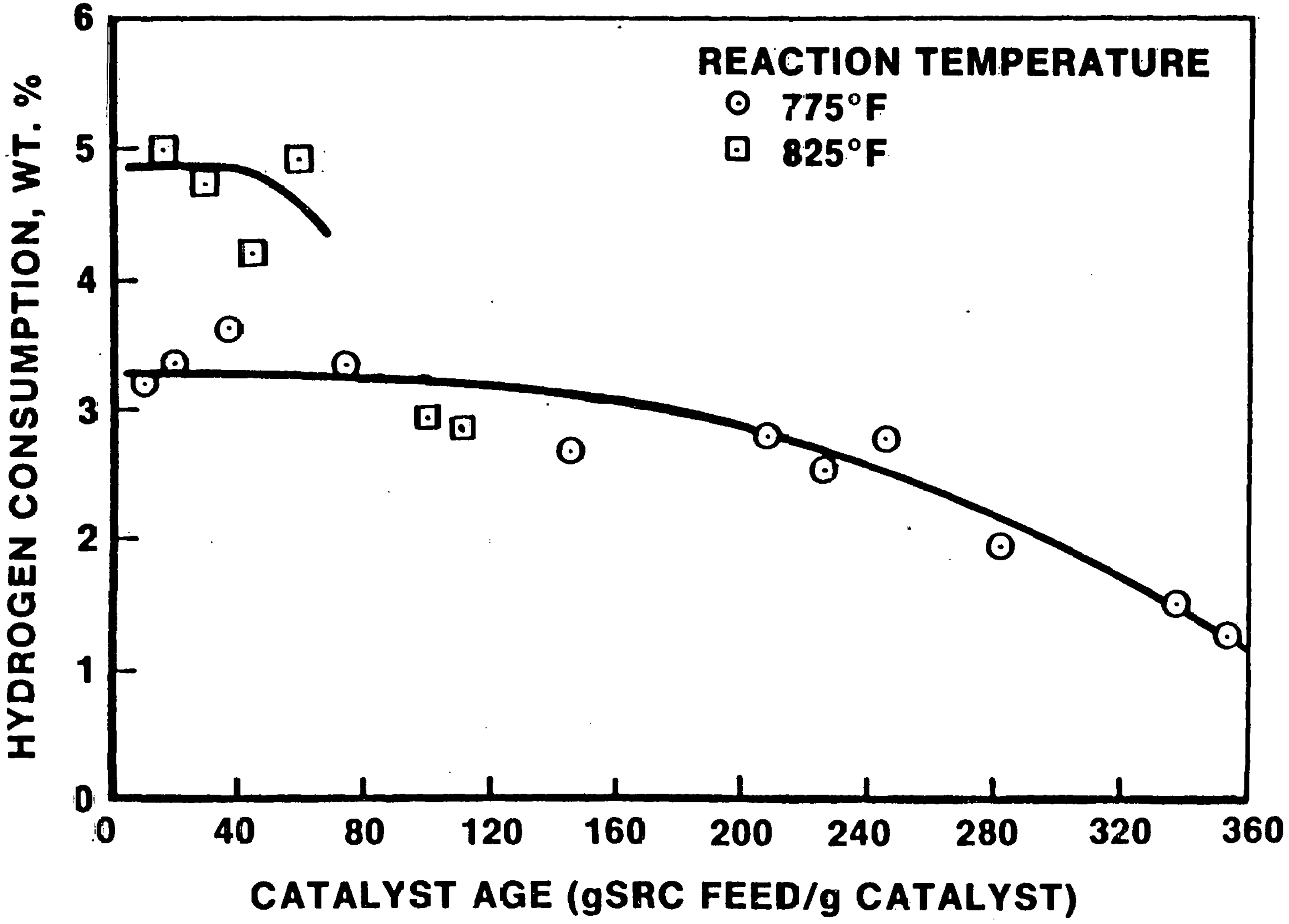
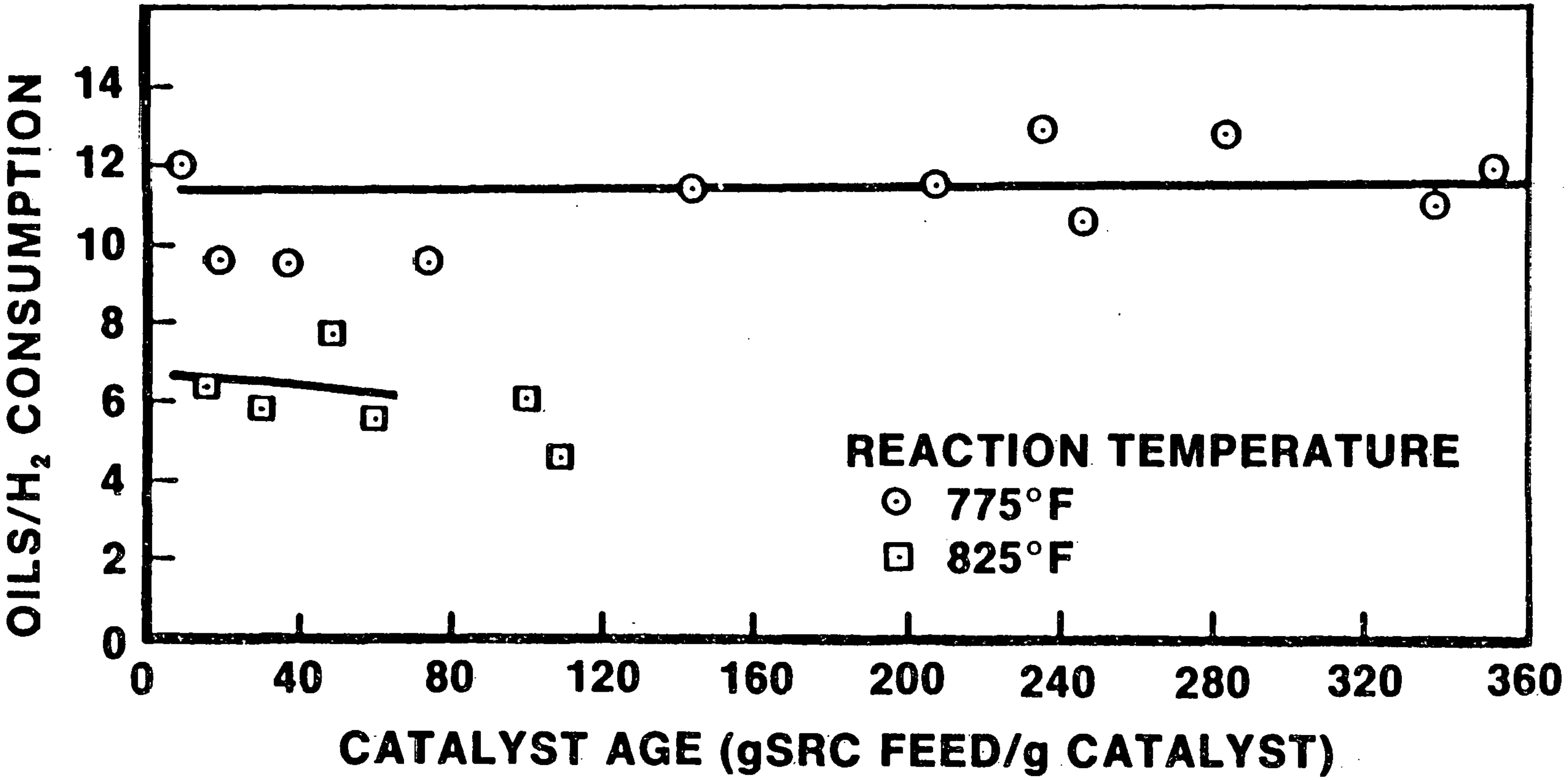


FIGURE 25
VARIATION OF SELECTIVITY WITH CATALYST AGE



CONCLUSIONS

Overall, the design of the LC-Finer for the SRC-I Demonstration Plant is conservative for both the high- and low-severity conversion cases. Careful analysis of the experimental data lead to the following additional conclusions.

- ICRC PDU data were comparable with those of Wilsonville and better than those of Lummus in terms of overall conversion and yield structure.
- Catalyst deactivation in the ICRC PDU was higher than that at Wilsonville, but the ages at which activity started to decline were similar in the two units.
- The decline in catalyst activity was probably mainly related to coke and metal deposition, which severely reduced surface area and pore volume.
- The presence of large amounts of sodium in the feed and its significant retention by the catalyst could also have contributed to catalyst deactivation.
- Initial catalyst deactivation rate was comparable at 775 and 825°F; catalyst activity remained constant during the initial part of the run and then declined dramatically.
- SRC conversion, hydrocarbon gas production, and hydrogen consumption increased with increasing reaction temperature.
- Increasing SRC conversion resulted in a net increase in hydrocarbon gas, but did not increase oil production.
- Greater hydrocarbon gas production together with higher hydrogen consumption with increasing temperature resulted in a severe decline in the selectivities for oil production over both hydrocarbon gas production and hydrogen consumption.
- Heteroatom removal did not improve significantly by increasing reaction temperature.

RECOMMENDATIONS

In this program, several factors critical to the development of SRC hydroprocessing technology were identified. However, the following work is needed to fully understand their role in developing this technology:

- Investigate the effect of sources of SRC, such as different coals.
- Investigate the effect of coal liquefaction reaction severity.
- Develop data on long-term catalyst deactivation.
- Investigate the effect of reaction conditions on catalyst activity and aging.
- Investigate the effect of metal and coke deposition on catalyst deactivation.
- Investigate the effect of sodium on catalyst activity and aging.
- Investigate the effect of concentration of SRC on catalyst activity and aging.
- Investigate the effect of catalyst type on catalyst aging and yield structure.

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NOMENCLATURE

a - Reaction rate with catalyst at age t relative to rate with fresh catalyst

C_A - Weight concentration of component A in product, lb A/lb product

C_{A_o} - Weight concentration of component A in feed, lb A/lb feed

E - Fractional conversion of component A by weight

F - Liquid feed rate at STP, lb/hr

k_A - Rate constant for disappearance of A at time t, hr^{-1}

k_{A_o} - Rate constant for disappearance of A at time $t = 0$, hr^{-1}

k_d - Rate constant for loss of catalyst activity, hr^{-1}

r_A - Rate of disappearance of A at time t, lb/hr

r_{A_o} - Rate of disappearance of A at time $t = 0$, lb/hr

t - Catalyst age in representative units (i.e., lb SRC feed/lb catalyst or lb SRC converted/lb catalyst)

W - Weight of catalyst charged to reactor, lb

WHSV - Weight hourly space velocity, lb feed/hr-lb catalyst

t - Nominal catalyst residence time (W/F), hr

T - Average catalyst addition rate, lb SRC/lb catalyst

T' - Reaction temperature, °F

APPENDIX A

Modeling of SRC Hydroprocessing Reaction

The reactions being considered are:

$$A \xrightarrow{k_A} B + C$$

$$B \xrightarrow{k_B} C$$

where A is SRC (850°F+ material),
B is distillate (C_6 - 850°F), and
C is gas (C_1-C_5).

Modeling of SRC Conversion

The disappearance of A can be modeled as an irreversible reaction that is first-order in concentration of A:

$$-r_A = k_A C_A \qquad \frac{\text{lb/hr A converted}}{\text{lb catalyst}} \qquad \text{(Eqn. A-1)}$$

where k_A is the first-order rate constant for the conversion of SRC at catalyst age t (hr^{-1})

and C_A is the concentration of SRC (lb/lb product)

Assuming the reactor is completely mixed, then a material balance for A can be written as[1]:

$$\frac{C_{A_o}}{C_A} = 1 + k_A \tau \qquad \text{(Eqn. A-2)}$$

---

[1] Levenspiel, O. 1972. Chemical reaction engineering. John Wiley and Sons, Inc., pp. 545-546.

where τ is nominal residence time and is approximated by the equation:

$$\tau = W/F = \frac{1}{WHSV} \quad \frac{\text{lb catalyst}}{\text{lb/hr feed}} \qquad \text{(Eqn. A-3)}$$

where W is the weight of the catalyst in lb, F is liquid feed in lb/hr, and WHSV is weight hourly space velocity in lb/hr/feed over lb/catalyst.

The conversion of A can be defined by:

$$E = 1 - \frac{C_A}{C_{A_o}} \qquad \text{(Eqn. A-4)}$$

Equations A-2 and A-4 can be combined to give the rate constant for the conversion of A:

$$k_A = \text{WHSV} \left(\frac{E}{1-E}\right) \qquad \text{(Eqn. A-5)}$$

In a case in which the reactor system is composed of two well-mixed reactors in series, the value of the rate constant can be calculated by the following expression:

$$k_A = 2\ \text{WHSV} \ [(\frac{1}{1-E})^{\frac{1}{2}} - 1] \qquad \text{(Eqn. A-5.1)}$$

Since the catalyst deactivates with time, the calculated k_A is a function of time and can be defined as:

$$k_A = k_{A_o} a \qquad \text{(Eqn. A-6)}$$

where

$$a = \frac{-r_A}{-r_{A_o}} \qquad \text{(Eqn. A-7)}$$

r_A = rate of reaction at time t, and
r_{A_o} = rate of reaction at time zero.

Substituting Eqn. A-6 in Eqn. A-5, we get

$$k_{A_o} a = \mathrm{WHSV} \left(\frac{E}{1-E} \right) \qquad \text{(Eqn. A-8)}$$

Assuming a first-order catalyst deactivation mechanism, the deactivation rate can be calculated by the following equation[1]:

$$\frac{da}{dt} = - k_d a \qquad \text{(Eqn. A-9)}$$

where k_d is the deactivation rate constant in lb catalyst/lb SRC.

Integrating Eqn. A-9 gives

$$a = e^{-k_d t} \qquad \text{(Eqn. A-10)}$$

where t is batch catalyst age in lb SRC/lb catalyst.

Substituting Eqn. A-10 in Eqn. A-8

$$k_{A_o} e^{-k_d t} = \mathrm{WHSV} \left(\frac{E}{1-E} \right) \qquad \text{(Eqn. A-11)}$$

Substituting Eqn. A-10 in Eqn. A-6, we get

$$k_A = k_{A_o} e^{-k_d t} \qquad \text{(Eqn. A-12)}$$

Taking the natural logarithm of Eqn. A-12 results in

$$\ln k_A = -k_d t + \ln k_{A_o} \qquad \text{(Eqn. A-13)}$$

Plotting the value of $\ln k_A$ (as measured) vs. batch catalyst age (t) produces a line with a slope equal to the deactivation rate constant (k_d) and an intercept equal to the conversion rate constant at time zero (k_{A_o}).

---

[1] Levenspiel, O. 1972. Chemical reaction engineering. John Wiley and Sons, Inc., pp. 544-546.

Further, for any batch catalyst age (t), the rate constant for conversion of SRC can be modeled by a standard Arrhenius expression:

$$k = A e^{-\Delta E/RT'} \qquad \text{(Eqn. A-14)}$$

where ΔE is the activation energy, A is the frequency factor or pre-exponential factor (theoretically the rate constant that would be observed at infinite temperature), and T' is the reaction temperature.

Assumptions

A number of assumptions are inherent in the above derivations. If any of these assumptions are invalid, the validity of the model will be greatly reduced.

The reaction is modeled as being first-order in the concentration of SRC only. It is assumed that solvent concentration and hydrogen partial pressure do not influence the kinetics, and that the effect of SRC concentration is accurately reflected by the first-order expression. Because all of the experimental pilot plant programs operated at total pressures of 2,000-2,800 psia with hydrogen partial pressure in the range of 1,600-2,300 psia, this parameter was not varied sufficiently to determine its effect on the reaction mechanism. This is especially true because each pilot plant maintained essentially constant hydrogen partial pressures throughout its runs. However, because the pilot plants operated in the pressure range specified in the SRC-I Demonstration Plant hydroprocessing design, all the experimental data should be valid with respect to the effect of hydrogen partial pressure. In a similar way, except for minor variations, each of the pilot plants operated at one space velocity and SRC concentration. Because the validity of the first-order expression is assessed by considering the accuracy of Equation A-2 for various times and initial concentrations while simultaneously accounting for the masking effects of experimental uncertainty and catalyst deactivation time, these assumptions have not been verified.

Solvent concentration will have a significant effect on reaction modeling and experimental design. If the solvent concentration is too low, the hydrogen transfer from solvent to SRC becomes rate-limiting, or the proportion of cracking of solvent to gas becomes appreciable relative to the gas produced by SRC conversion. It is believed that the system does not become solvent-starved until a solvent concentration level well below the 30% used in the current studies and in the Lummus design. The proportion of gas produced by solvent cracking is not known. Since Wilsonville carried out the hydroprocessing experiments using 50% solvent in the feed as opposed to 30% in the design basis, solvent cracking may be responsible for incremental gas production.

The residence time, τ, should reflect the time that the reactants are in the reaction zone. As this is catalytic hydrocracking, the residence time should reflect the time that the feed is in contact with the catalyst. Purely thermal cracking will also be occurring, but this set of reactions can be subsumed by the expression for catalytic cracking if most of the cracking is catalytic or if the proportion of catalytic cracking to thermal cracking is fixed. There is no doubt that catalytic cracking predominates at lower temperatures. At higher temperatures, the onset of thermal cracking is signaled by a large increase in hydrocarbon gas production. In addition, the proportion of thermal to catalytic cracking will be fixed if the ratio of thermal residence time to catalytic residence time is fixed. While this is true for a given reactor, it is not true in comparing different reactor systems. As discussed in the text, the variation of thermal residence time between reactors is probably responsible for some of the disparity between experimental results from different reactor systems.

The catalytic residence time will be properly reflected by the reciprocal of the weight hourly space velocity only if a constant proportion of the feed is vaporized. The degree of feed vaporization is affected by such factors as total pressure, gas-to-feed ratio, SRC concentration in the feed slurry, and temperature. In evaluating the results from a single reactor system, the most significant effect will be that of temperature. Since more solvent vaporizes at higher temperatures, the true residence time increases as the temperature rises.

Although the magnitude of this effect is not known, vapor/liquid equilibrium and gas and liquid holdup correlations indicate the effect will be minor.

Finally, it should be emphasized that the weight hourly space velocity (WHSV) should be based on the total liquid feed to the reactor, including both solvent and SRC. In recycle operation, the kinetic rate constant should be calculated on the basis of per-pass space velocities and conversions per pass.

A well-mixed reactor has been assumed in the derivations. This hypothesis has been confirmed by cold-flow modelling and tracer studies in the various reactor systems.

APPENDIX B

Derivation of Expression for Average Catalyst Activity in Continuous Operation

A continuous SRC hydroprocessing process relies on the addition of fresh catalyst and withdrawal of spent catalyst to maintain process performance. In order to determine the catalyst requirements of a continuous process, accurate batch catalyst deactivation is required. The batch catalyst deactivation data can be fitted with a typical catalyst deactivation expression of the form:

$$k_A = k_{A_o} e^{-k_d t} \qquad \text{(Eqn. B-1)}$$

where: k_A = first order rate constant for conversion of SRC at age t (in hr^{-1}),

k_{A_o} = initial rate constant for conversion of SRC (in hr^{-1}),

k_d = exponential deactivation rate constant (in lb cat/lb SRC), and

t = batch catalyst age (in lb SRC/lb cat). (See Appendix A.)

The average catalyst activity in a hydrotreater operating with the continuous addition and withdrawal of catalyst can be calculated by summing the products of the fraction of catalyst in the reactor at a given age and the activity of the catalyst at that age. Because the hydrotreater is a well-mixed system, the fraction of catalyst at a given age can be determined from the established residence time distribution expression for an ideal stirred tank reactor. The catalyst activity and residence time expressions can then be combined to calculate the average activity of the catalyst. A rigorous mathematical derivation of the average catalyst activity follows:

$$\begin{array}{l}\text{Average} \\ \text{Activity}\end{array} = \sum_{t=0}^{\infty} \left[\begin{array}{c}\text{Activity of Catalyst} \\ \text{at Age t}\end{array}\right] \left[\begin{array}{c}\text{Fraction of Catalyst} \\ \text{at Age t}\end{array}\right]$$

$$= \int_0^{\infty} \left\{k_{A_o}{}^{-k_d t}\right\} \left\{\frac{1}{T} \; e^{-t/T}\right\} dt$$

$$= k_{A_o}/T\ (k_d + 1/T)$$

$$\text{Average } k_A = k_{A_o}/\ (k_d T + 1) \qquad \text{(Eqn. B-2)}$$

where: T = average catalyst addition rate lb SRC/lb catalyst

To determine the batch catalyst age equivalent to a given catalyst replacement rate, equate Equations B-1 and B-2. Therefore,

$$k_{A_o}/k_d T + 1) = k_{A_o} e^{-k_d t}$$

or $$t = \frac{\ln\ (k_d T + 1)}{k_d} \qquad \text{(Eqn. B-3)}$$

APPENDIX C

Comparison of LC-Finer Design Basis with Wilsonville and ICRC Pilot Plant Data

The catalyst activity and aging data obtained at The Lummus Company, Wilsonville Pilot Plant, and ICRC PDU were compared to the LC-Finer Design basis to verify the design catalyst activity and replacement rate. Before the data are discussed, it is important to compare the history of SRC samples used at the three facilities in addition to the design and performance of the three reactors.

History of SRC Samples

The SRC sample used in Lummus PDU runs 2LCF-27, 28, and 29 was obtained from the Wilsonville Pilot Plant. The sample was generated from Kentucky #9 Fies mine coal during the operation of run 209. Since the coal contained less than 0.1% chlorine, no sodium carbonate was added during the run. The SRC sample used both for the operation of the Wilsonville hydrotreater and the ICRC PDU was also generated from Kentucky #9 Fies mine coal, but during the operation of run 235. The batch of Kentucky #9 coal used in run 235 contained more than 0.1% chlorine, requiring Na_2CO_3 addition in the initial liquefaction step to prevent chlorine corrosion.

The feed SRC at Lummus was held at elevated temperatures in the presence of air, which could have resulted in retrograde reactions forming insoluble organic material (IOM) and other refractory materials. The feed SRC for the operation of the ICRC PDU was held at elevated temperatures, but in the presence of nitrogen to minimize any retrograde reactions. In the Wilsonville Pilot Plant, fresh SRC recovered from the Kerr-McGee deashing unit was mixed with the solvent and fed to the hydrotreater, avoiding prolonged exposure of the SRC to elevated temperatures, and thereby minimizing any retrograde reactions. Therefore, it is possible that the feed SRC was subjected to different degrees of retrograde reactions at the three facilities. No attempt was made to quantify the extent of these reactions.

The degradation of feed SRC due to retrograde reactions may have an effect on catalyst activity and aging. The exposure of feed SRC to different degrees of such reactions at the three facilities further complicates the comparison of catalyst activity and aging. In addition, the presence of different amounts of sodium in the feed SRC due to the addition of Na_2CO_3 in the liquefaction step affects catalyst activity and aging. Since it is rather difficult to determine the effect of both retrograde reactions and sodium content on catalyst activity and aging, no attempt is made in this report to quantify them.

Reactor Design

Fundamental differences between the reactors used at The Lummus Company, Wilsonville Pilot Plant, and at ICRC R&D are summarized in Table C-1. The simplified flow sketches of the facilities are shown in Figures C-1 and C-2. Both Lummus and Wilsonville used ebullated-bed reactors for hydroprocessing SRC. In contrast, a fixed catalyst basket reactor was designed to simulate the operation of an ebullated-bed reactor and used by ICRC R&D in the PDU runs. This reactor was essentially an annular fixed catalyst basket fitted into a 2-liter stirred autoclave. In the reactor both liquid and gases are forced outward through the catalyst basket by a flat blade impeller to provide efficient contact between catalyst, liquid, and gases. Resistance heaters surrounding the wall were used to provide heating, while the temperature inside was measured and controlled by multiple thermocouples well immersed in the slurry phase. The detailed description and design of the reactor is discussed in a previous report by ICRC (6). The catalyst size used both at Lummus and Wilsonville is smaller than that used in the PDU.

Reactor Performance

Table C-2 shows that at 775°F the ICRC PDU experienced either equivalent or higher SRC conversion than did the Lummus and Wilsonville units, which had comparable conversion levels (the data from PDU Run CCL-63 are excluded in this comparison). However, SRC conversion was noted to be significantly higher in the ICRC PDU than it was in the Lummus and Wilsonville units, both at 800 and 825°F. The higher SRC

Table C-1

Description of Reactors

	Lummus	Wilsonville	PDU
Catalyst	Ni-Mo-Al	Co-Mo-Al	Ni-Mo-Al
Catalyst size (in.)	1/32	1/32	1/16
H_2 pressure (psig)		2,300	2,000
H_2 feed rate (scf/lb feed)		16.0	16-20
WHSV (g feed/g catalyst-hr)		2.0	1.0
Relative residence time (hr)		1	2.5-5
Reactor type	ebullated bed	ebullated bed	fixed basket

FIGURE C-1
ICRC PDU SCHEMATIC FLOW SHEET

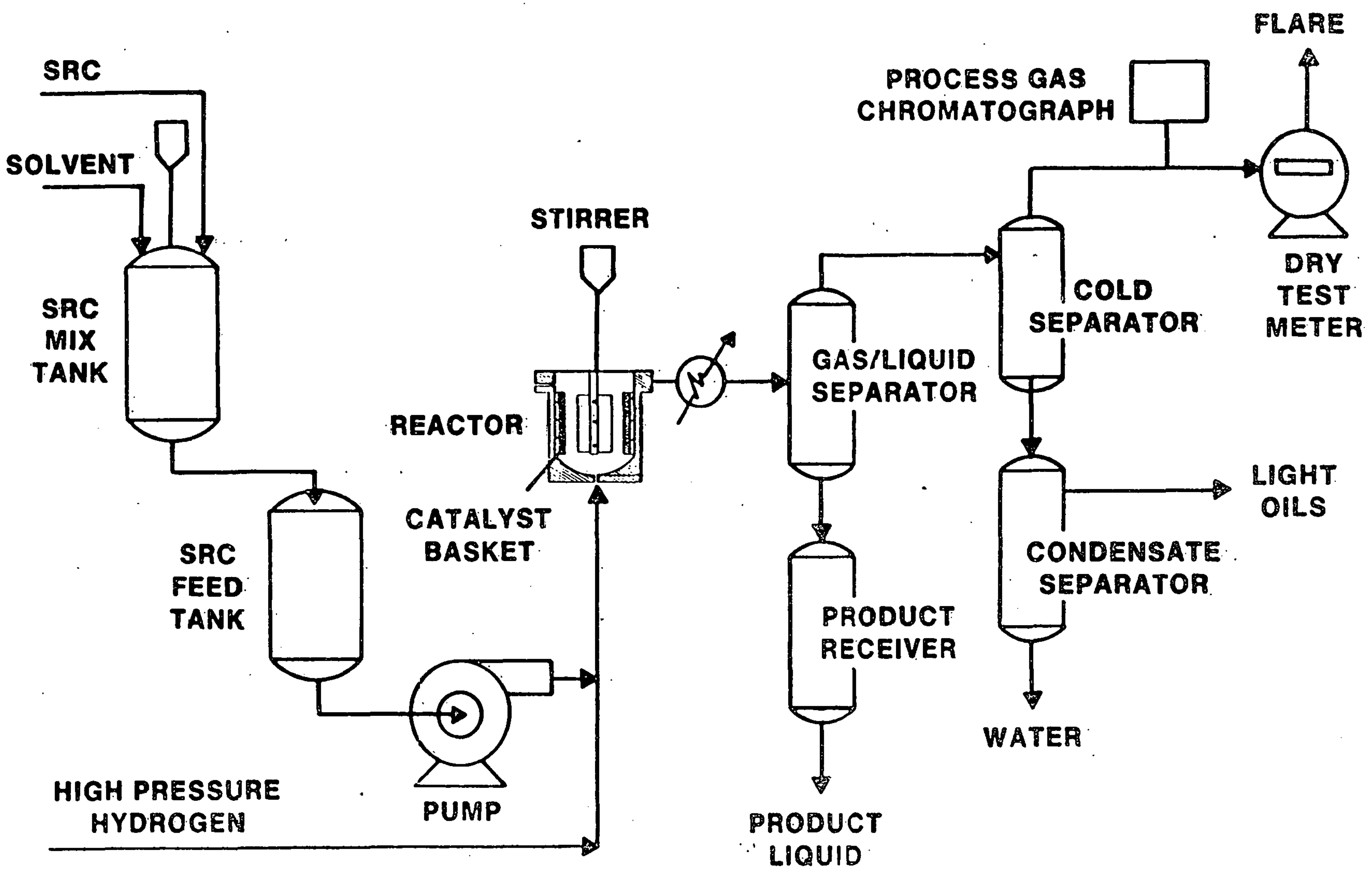


FIGURE C-2
WILSONVILLE PILOT PLANT
SCHEMATIC FLOW SHEET

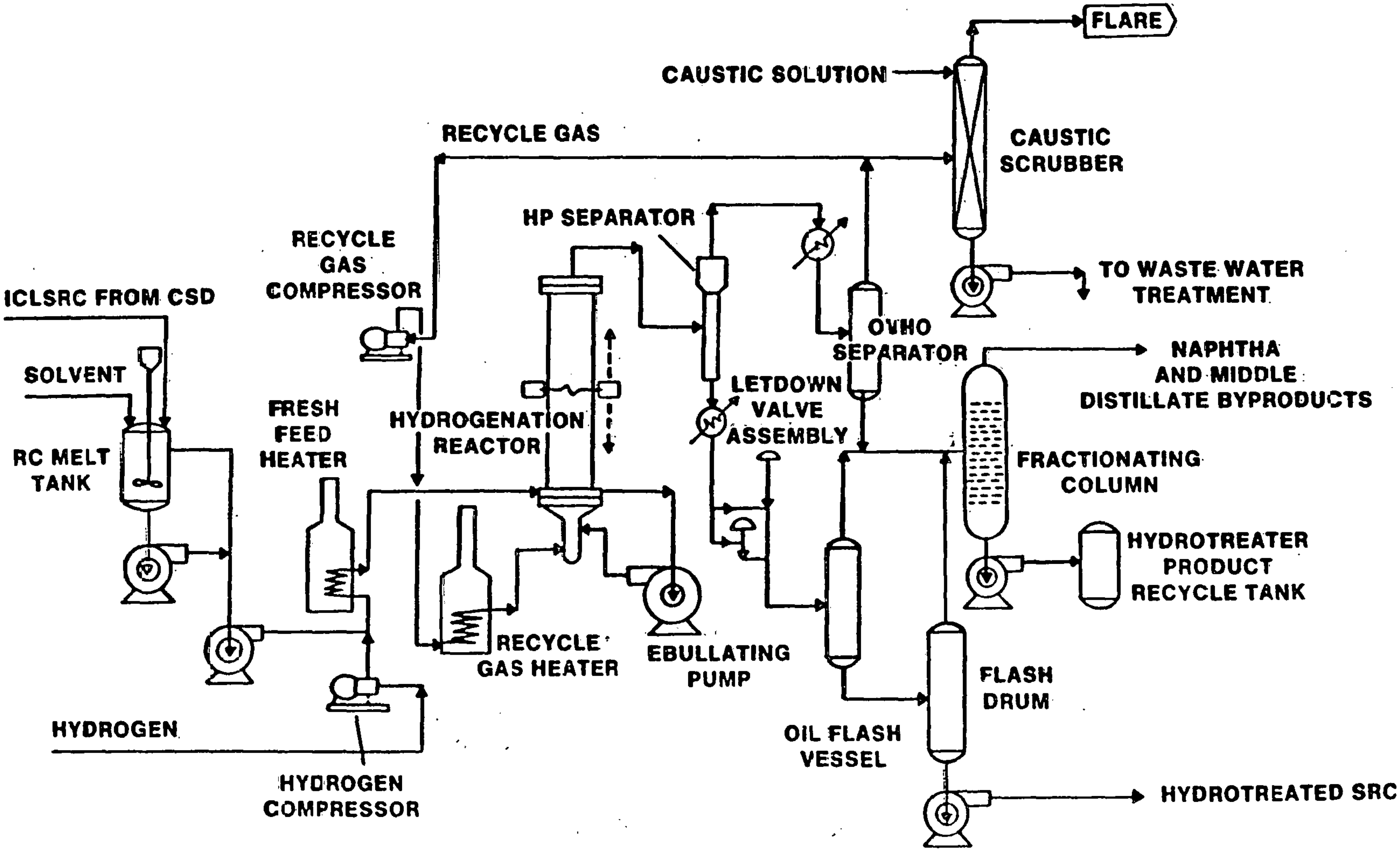


Table C-2

Comparison of SRC Conversion, Catalyst Age, and First-Order Rate Constant

	Lummus			Wilsonville			PDU		
Temperature (°F)	SRC conversion (wt %)	Catalyst age (lb SRC/ lb catalyst)	Rate constant (hr^{-1})	SRC conversion (wt %)	Catalyst age (lb SRC/ lb catalyst)	Rate constant (hr^{-1})	SRC conversion (wt %)	Catalyst age (lb SRC/ lb/catalyst)	Rate constant (hr^{-1})
775	35	-		35	274	1.0	38-57	10-246	0.8-1.2
800	52	-		45	65	1.6	61	45	1.5
825	-	-		53	-	2.1	67	89	1.9

conversion level in the ICRC PDU could have been due to either longer residence time or lower catalyst age. The first-order rate constants for conversion of SRC in the ICRC PDU were nearly equivalent to Wilsonville at all three temperatures and were higher than Lummus.

The product distributions of the three reactors at 800°F are compared and summarized in Table C-3. The significantly higher SRC conversion observed in the ICRC PDU was complemented by higher oil production. As mentioned earlier, the higher SRC conversion level in the ICRC PDU could have been due to lower catalyst age and longer residence time. However, the first-order rate constant, which normalizes the differences in the residence time, was similar to that of Wilsonville, but was considerably higher than that of Lummus. The production of heteroatoms and HC gases in the ICRC PDU was comparable to Lummus, but higher than Wilsonville. Hydrogen consumption in the ICRC PDU was significantly higher than that of Wilsonville, but was lower than that of Lummus. However, hydrogen consumption per unit SRC conversion in the ICRC PDU was similar to that of Wilsonville, but was considerably lower than that of Lummus.

The most desirable aspects of any SRC hydroprocessing reactor design are high conversion with low HC gas production and low hydrogen consumption. Based solely on these factors, the performance of the fixed catalyst basket reactor was equivalent to that of Lummus' reactor, but inferior to that of Wilsonville. However, based on first-order rate constant and hydrogen consumption per unit SRC conversion, the performance of the fixed catalyst basket reactor was comparable to that of Wilsonville, but better than that of the Lummus ebullated-bed reactor.

Comparison of Catalyst Aging Data

Based on the results of three LC-Finer Pilot Plant runs, 2LCF-27, 28 and 29, the Lummus Company developed kinetic correlations for use in the SRC-I Demonstration Plant LC-Finer design. These correlations included three key kinetic parameters: the activation energy for the SRC conversion (ΔE), the pre-exponential factor (A), and the exponential rate constant for catalyst deactivation (k_d). The calculated values of these parameters are summarized in Table C-4. The derivation of the kinetic model and the underlying assumptions are presented in Appendices A and B.

Table C-3

Comparison of Yields at 800°F[a]

	Lummus	Wilsonville	PDU
Relative liquid residence time (hr)		1	5
Catalyst age (lb SRC/lb catalyst)	-	65.0	45.0
Product distribution (wt % SRC)			
$NH_3 + H_2S$	3.2	1.5	3.1
H_2O	4.0	6.6	4.5
C_1-C_5	10.4	6.0	11.4
Oil (850°F-)	36.0	39.3	46.6
SRC (850°F+)	52.2	50.7	41.1
SRC conversion (%)	48.8	49.0	60.9
H_2 consumption (wt % SRC)	5.6	4.1	5.2
Rate constant (hr^{-1})	—	1.6	1.5
$\frac{H_2 \text{ consumption}}{\text{SRC conversion}}$	—	0.084	0.085

[a] It should be noted that differences in product distribution and SRC conversion could be attributed to differences in residence time.

Table C-4

Kinetic Constants for Conversion of SRC

Runs	WE (kCal/g-mole)	A (hr^{-1})	k_d (hr^{-1})
Lummus			
2LCF-27 and -29			
Wilsonville			
235-3	26.9	3.25×10^8	0.0008
235-4	26.9	3.25×10^8	0.0011

The activity of the catalyst at any age can be calculated by the following equation (see Appendix A):

$$a = \frac{k_{SRC}}{k_{SRC_0}} = e^{-k_d t}$$

where t is batch catalyst age in lb SRC/lb catalyst.

The Wilsonville Pilot Plant data were also subjected to similar kinetic analysis to determine the values of kinetic parameters and to compare them to the design values. The values of the various kinetic parameters are summarized in Table C-4, along with LC-Finer design values. Interestingly, the rate of catalyst deactivation, both at Wilsonville and Lummus, were very similar. However, the activation energy and pre-exponential factors at Wilsonville were considerably higher than at Lummus. This information revealed that the rate of SRC conversion (catalyst activity) demonstrated at the Wilsonville Pilot Plant on ACCO 1442B (Co-Mo-Al) catalyst was higher than that of the Lummus design basis for Shell 324 (Ni-Mo-Al) catalyst (see Figure C-3). Furthermore, in spite of higher rates of SRC conversion at Wilsonville, the rate of catalyst deactivation was similar to that noted at Lummus.

There could be two possible explanations of the above differences: that the Co-Mo-Al catalyst is a superior catalyst to Ni-Mo-Al for hydroprocessing SRC or that the kinetic data obtained in the LC-Finer Pilot Plant are not representative of what would be observed in a large-scale plant such as Wilsonville. However, Lummus had demonstrated in runs 2LCF-28 and -29 that the activity of ACCO 1442 B (Co-Mo-Al) catalyst was nearly the same as that of Shell 324 (Ni-Mo-Al) catalyst. This information tends to support the hypothesis that data obtained from the LC-Finer Pilot Plant are not representative of a large-scale plant.

The data in Table C-4 show that the catalyst deactivation rates are equivalent for Wilsonville runs 3 and 4 over the catalyst life tested. Similar results are reported by Wilsonville in the EPRI Conference (see

FIGURE C-3
COMPARISON OF SHELL 324 AND ACCO 1442B CATALYST ACTIVITY

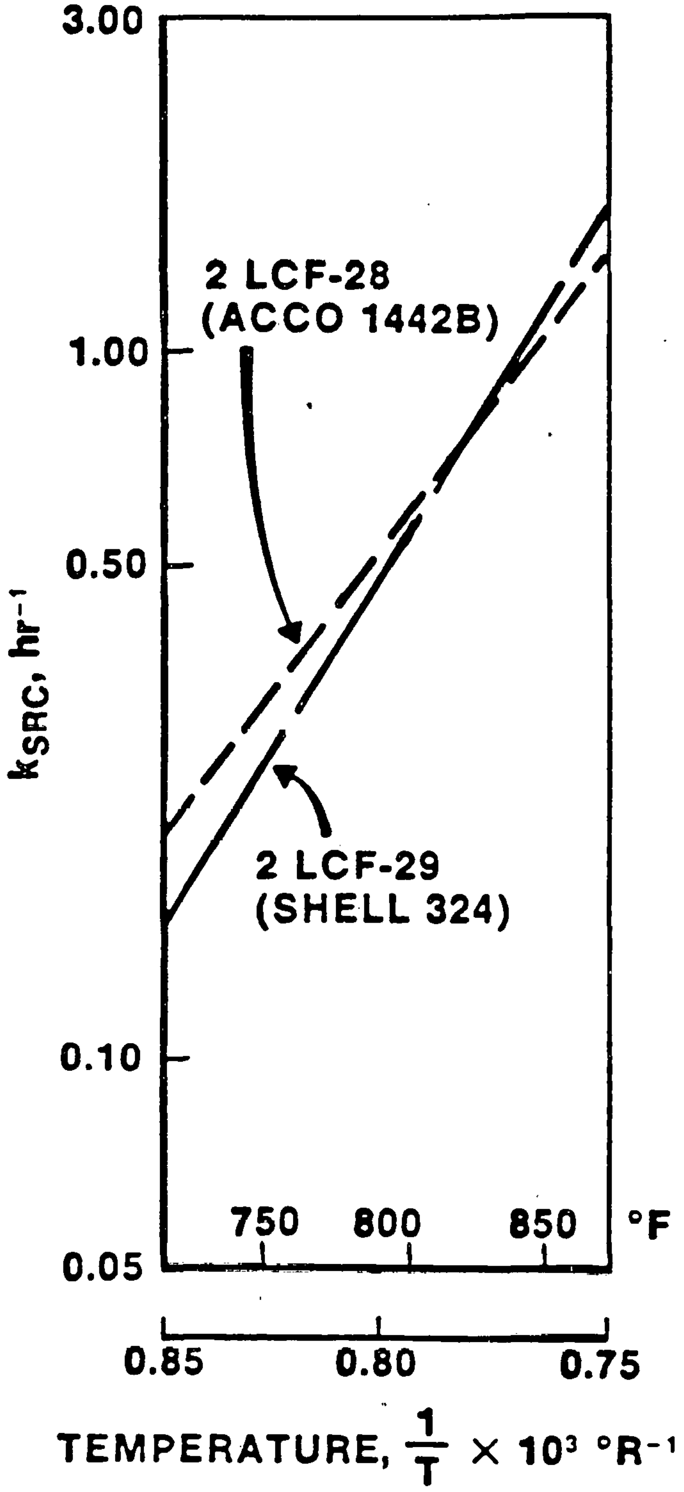


Figure C-4 and Reference 11). Based on this information and on the data in Table C-4, the Wilsonville catalyst activity was calculated as a function of temperature and plotted in Figure C-5. The data clearly indicate that the catalyst activity noted at Wilsonville is much higher than that noted at the Lummus Pilot Plant. The ICRC PDU data in Figure C-4 correspond well to the Wilsonville data, further supporting the fact that there is little difference between the activity of ACCO 1442 B (Co-Mo-Al) and Shell 324 (Ni-Mo-Al) catalysts for the conversion of SRC. Therefore, it can be reasonably concluded that the data generated in the LC-Finer Pilot Plant are not representative of the large-scale plant.

The rate of catalyst deactivation is as important as the initial activity of the catalyst. The adjusted rate constants data for conversion of SRC generated at Lummus, Wilsonville, and ICRC R&D are plotted in Figure C-6 as a function of catalyst age. The basis for the calculation of these data is derived and discussed in Appendices A and B. The catalyst deactivation rates for Wilsonville runs 3 and 4 were shown earlier to be equivalent, and therefore are represented by one line. The initial data generated at Wilsonville agree well with ICRC R&D data, but differ dramatically from the Lummus data. The data generated at Wilsonville and at ICRC R&D showed unequivocally higher catalyst activity than those from Lummus. However, the data generated both at Wilsonville and ICRC R&D fall short of a catalyst age equal to the Lummus design catalyst batch age. The longest Wilsonville run was just over 500 lb SRC/lb catalyst. Therefore, it is difficult to say anything about the activity of the catalyst beyond an age of 500 lb SRC/lb catalyst. Similarly, the longest run conducted by Lummus reached an age which is once again shorter than the design catalyst age. Clearly, the design catalyst performance values for the demonstration plant LC-Finer were obtained by extrapolating the data.

An obvious problem with extrapolating any data is the possibility that the extrapolated values may be unrealistic. The catalyst aging data obtained by ICRC R&D (Figure C-6) showed a more rapid decline in catalyst activity than observed at Wilsonville. Interestingly, the ICRC R&D data showed that after a lengthy stable period of operation, catal-

FIGURE C-4
VARIATION OF CATALYST DEACTIVATION WITH TEMPERATURE

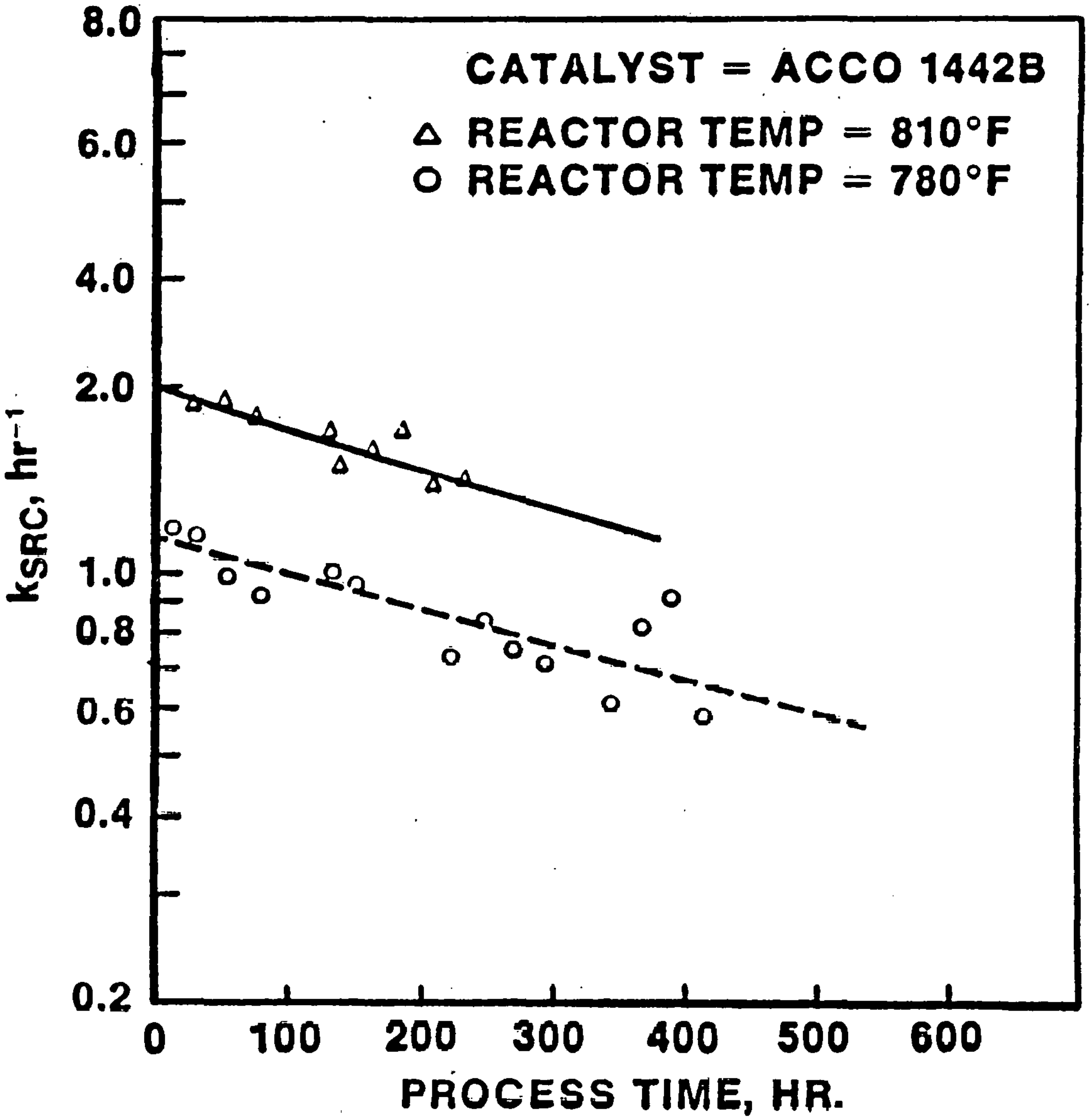


FIGURE C-5
RATE CONSTANT FOR SRC CONVERSION VERSUS REACTOR TEMPERATURE

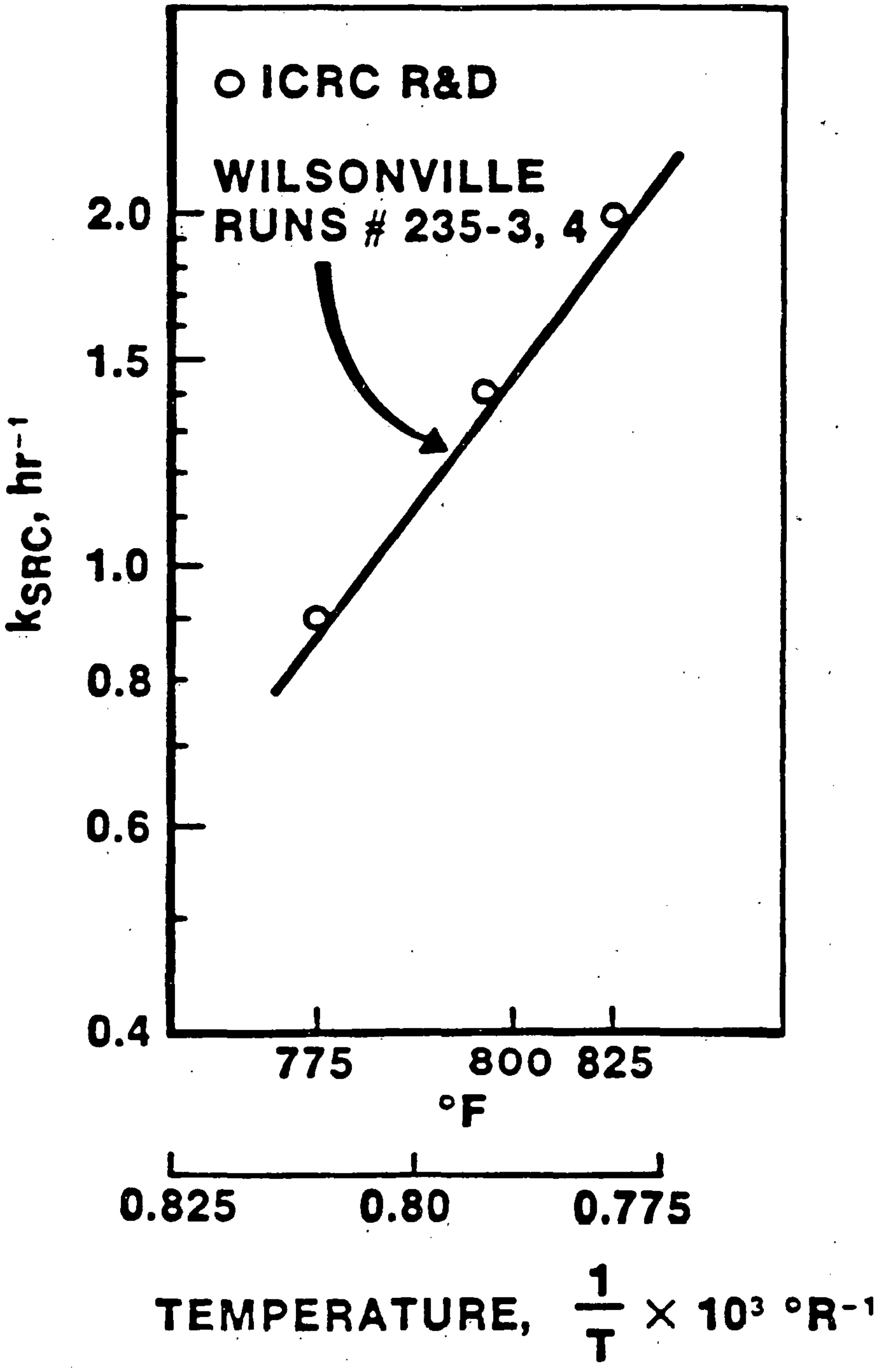
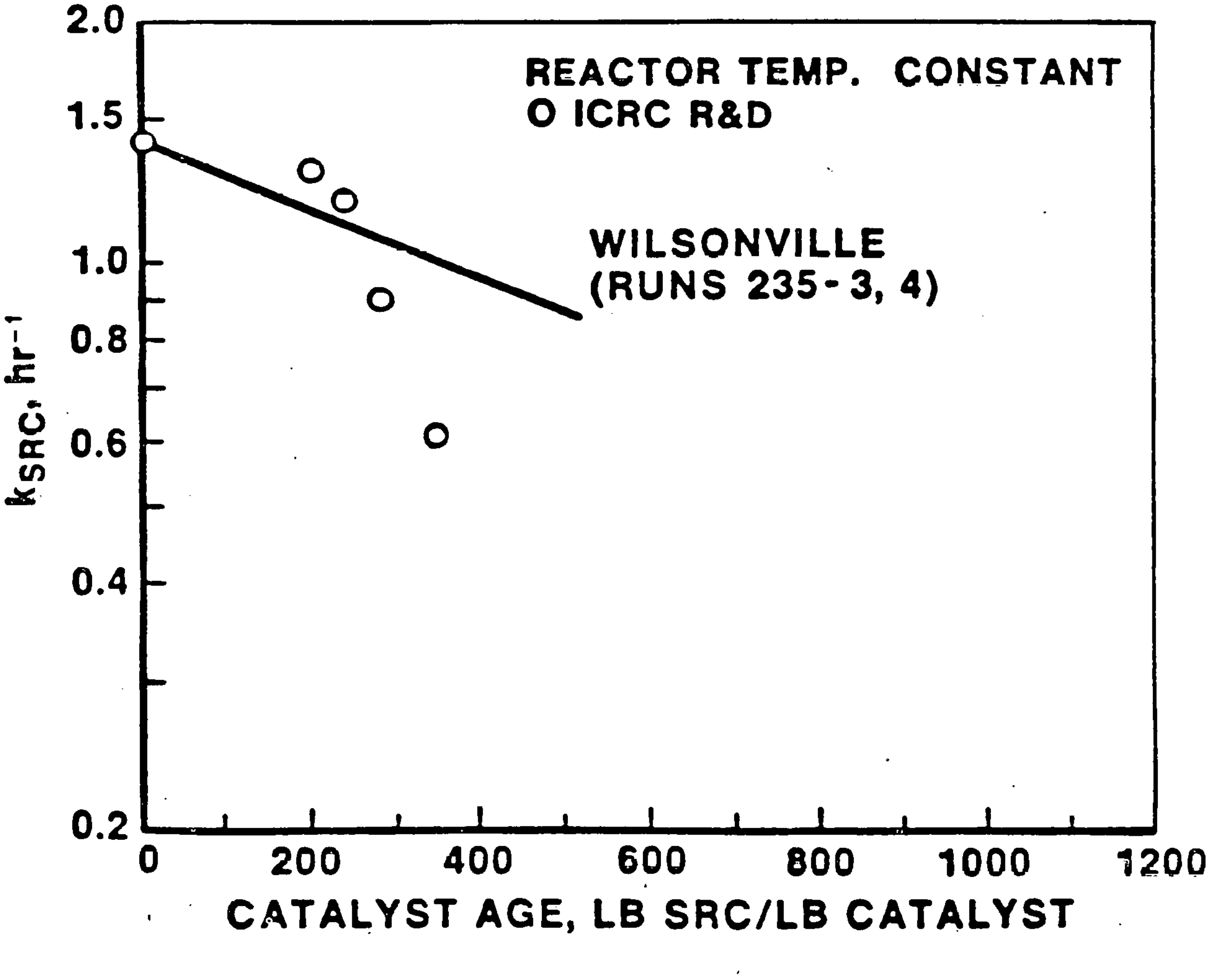


FIGURE C-6
RATE OF CATALYST DEACTIVATION VERSUS SRC FEED RATE



yst activity decreased sharply, demonstrating the danger of basing a design on extrapolated data.

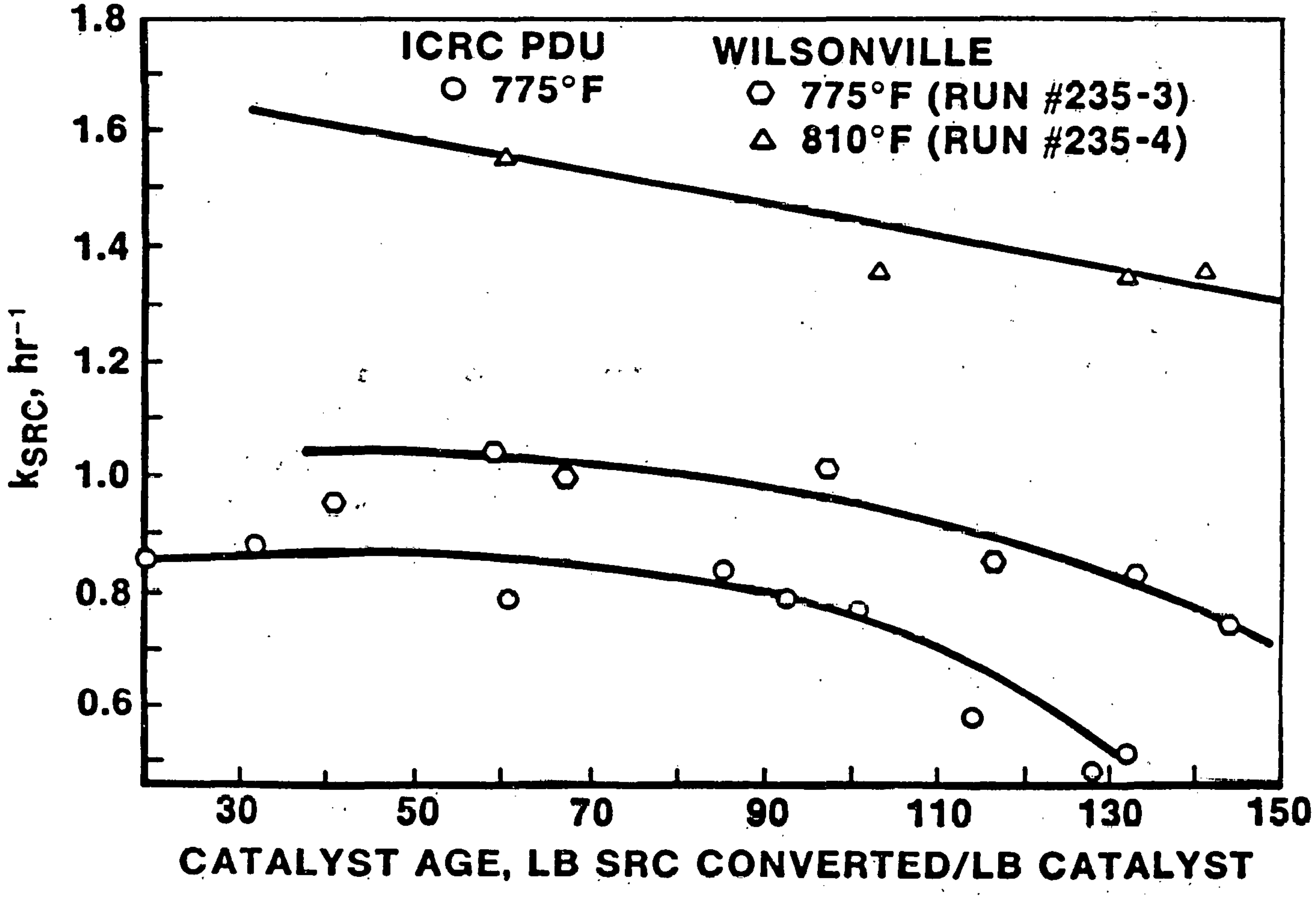
Another interesting point was noted when the catalyst age data were evaluated not as a function of lb SRC processed per lb catalyst, but as a function of actual "work" performed by the catalyst (i.e., SRC converted). This approach tends to eliminate all the variations due to changes in SRC conversion and provides a better measure of catalyst age. The catalyst activity data, when plotted in Figure C-7 as a function of the above-defined catalyst age for the ICRC PDU and Wilsonville runs 3 and 4, show that the catalyst activity began to decline both in the ICRC PDU and Wilsonville run 3 at almost the same age (100 lb SRC converted/lb of catalyst). However, the activity declined more sharply in the ICRC PDU than in run 3. The less severe decline in run 3 could have been due to an increase in reaction temperature from 775 to 782°F after approximately 100 lb of SRC converted/lb of catalyst. It is well known that an increase in temperature will increase SRC conversion, and will therefore mask the decline in conversion due to catalyst deactivation. It is conceivable that a sharp decline in catalyst activity in run 3 would have resulted had the run been carried out for a longer period (catalyst age greater than 150 lb SRC converted/lb of catalyst). This information further points out the danger of extrapolating the data beyond actual experience.

Extrapolation of data beyond actual experience is commonly practiced in various industries. However, the value of the extrapolated data greatly depends on the quality of the input data. When the data from Wilsonville runs 3 and 4 were fitted to the exponential catalyst deactivation model described in Appendix B, the following values of deactivation constants were obtained:

Run number	k_d	Correlation coefficient
235-3	0.00081	0.69
235-4	0.00106	0.51

The extremely low values of the correlation coefficients clearly indicate that the catalyst deactivation rate could not be modeled by a

FIGURE C-7
VARIATION OF RATE CONSTANT VERSUS LBS. SRC CONVERTED/LB CATALYST FOR ICRC PDU AND WILSONVILLE RUNS



simple first-order catalyst deactivation equation, making any extrapolated data from this model of limited value.

Based on the above discussion it appears that the LC-Finer design basis for the demonstration plant is quite conservative. Therefore, as designed, the SRC-I Demonstration Plant LC-Finer will likely have enough catalyst and reactor capacity to process all of the SRC generated at the design conversion rate, not just two-thirds of the SRC as specified in the alternate design basis. Furthermore, it appears that the catalyst replacement rate will be more than adequate to maintain the conversion specified in the alternate design basis.

Effect of Catalyst Age on Product Quality

The above discussion has concentrated mainly on the conversion of SRC to 850°F- product. However, it is important to point out that there are several other key design parameters that have to be met, such as selectivity (distillate rather than hydrocarbon gas), hydrogen consumption, and heteroatom removal, in order to completely verify the SRC-I Demonstration Plant LC-Finer design basis, since such parameters could vary with catalyst age. ICRC PDU run CCL-54 clearly showed a decrease in heteroatom removal activity of the catalyst with age. Wilsonville data also indicated a rapid decline in the desulfurization activity of the catalyst with age. Therefore, it is conceivable that product quality parameters such as hydrogen and sulfur contents may be significantly different at the design catalyst age than the design basis. However, at this time, insufficient data are available to further elaborate on this point.

The selectivities of products, defined as the ratio of distillate oil to hydrocarbon gas and distillate oil to hydrogen consumption, are key factors that can vary with catalyst age. The data generated at ICRC R&D showed that the selectivities did not depend on catalyst age, provided the reaction temperature was held constant. When the reaction temperature was raised, the selectivities dropped considerably. In LC-Finer runs 2LCF-27 and -29, the reaction temperature was raised continuously to maintain the desired SRC conversion, which suggests that in those runs the conversion was maintained at the expense of product selectivity. Certainly, such practice in the demonstration plant will result in significantly higher hydrogen consumption than the design basis, which will alter the economics of the entire plant.

Like selectivity, the quality of distillate oil is an important variable in LC-Finer operation. The data generated at Wilsonville seemed to indicate that distillate product quality did not vary with either conversion or catalyst age, as shown in Figures C-8 and C-9. The hydrogen content and specific gravity of a specific boiling range of total distillate oils (IBP-850°F) were very similar at different SRC conversion levels, implying that the quality of the distillate oil would not vary with conversion and catalyst age. However, it is known that as overall SRC conversion changes with catalyst age, the absolute quantity of distillate oil will change.

Effect of Feed SRC

The design of the SRC-I Demonstration Plant LC-Finer was based on data generated by hydroprocessing SRC from Kentucky #9 coal. All experiments conducted by Lummus and ICRC R&D to verify the design basis were also carried out using SRC from Kentucky #9 coal. In practice, the design of a commercial plant should be independent of a particular coal type and should be able to handle similar feedstock from other sources. Therefore, another run was carried out at Wilsonville (run 240; HTR run 8) using an Illinois #6 coal. The coal was again liquefied in the dissolver using demonstration plant reaction conditions to generate SRC. The product SRC was then hydroprocessed at a reaction temperature of 760°F and a WHSV of 1.2 lb total SRC feed/lb catalyst using American Cyanamid 1442 B (Co-Mo-Al) catalyst, and a reaction mixture of 50% SRC and 50% solvent. The SRC conversion level attained was 40%, and the run was carried out for a catalyst age of 454 lb SRC/lb catalyst.

Surprisingly, Wilsonville run 8 on SRC from Illinois #6 coal had a very low catalyst deactivation rate compared with that obtained with SRC from Kentucky #9 coal. Furthermore, the first-order rate constant for the conversion of SRC during the initial period of run 8 agreed well with that observed with SRC from Kentucky #9 coal. Considering these facts, the catalyst replacement rate for hydroprocessing SRC from

FIGURE C-8
COMPARISON OF DISTILLATE QUALITY AT DIFFERENT SRC CONVERSIONS WILSONVILLE HYDROTREATER

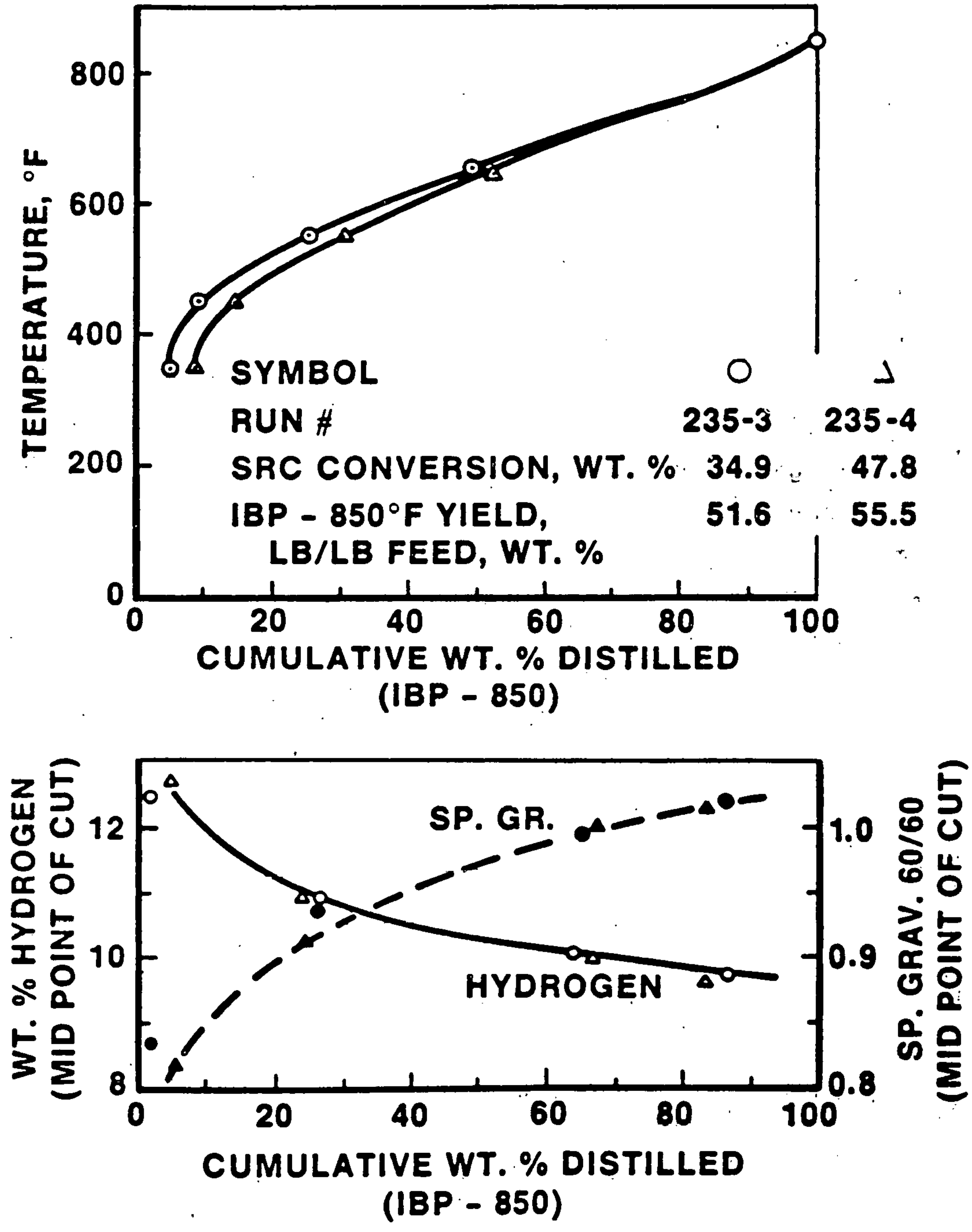
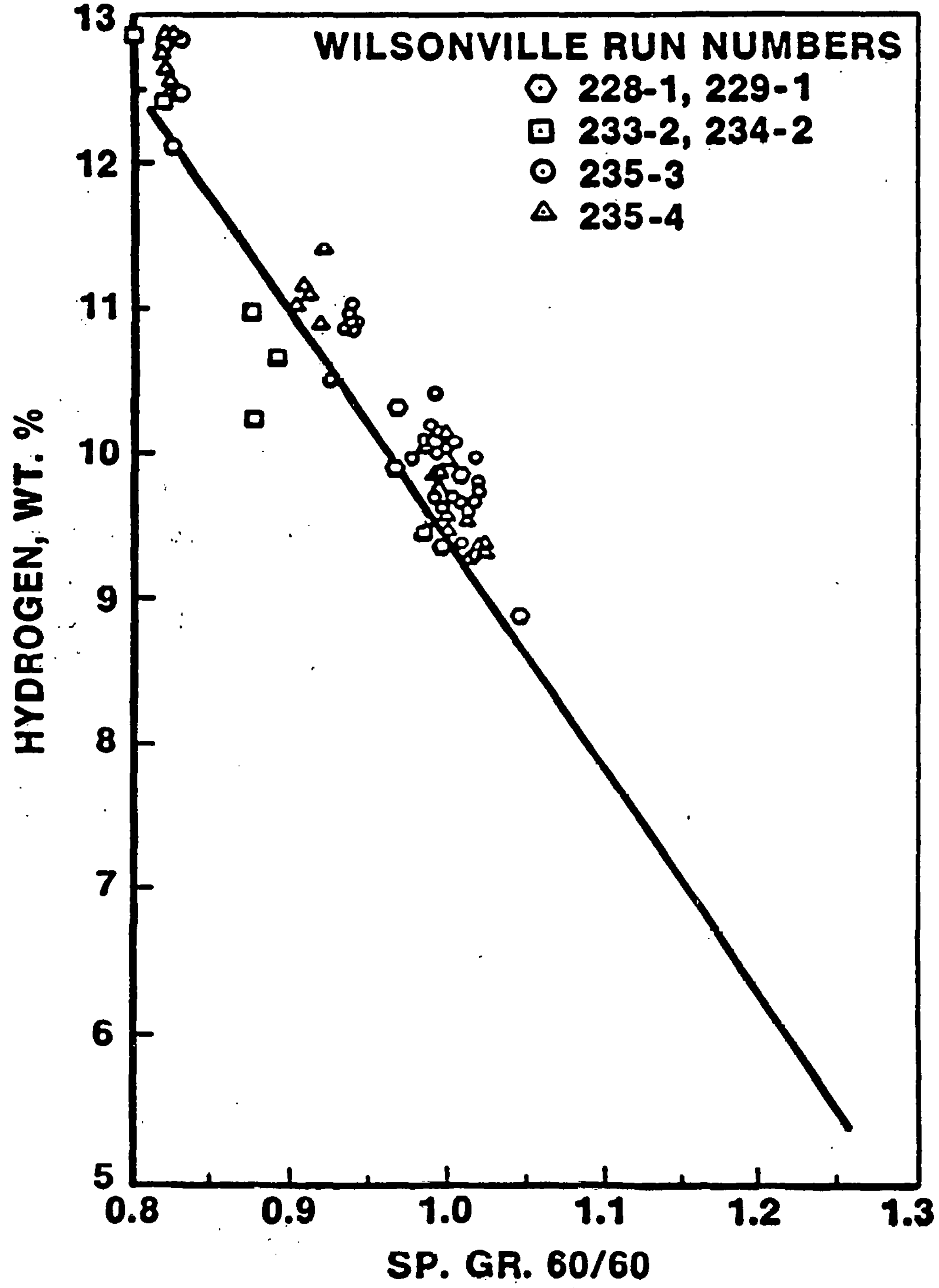


FIGURE C-9
VARIATION OF HYDROGEN CONTENT VERSUS SPECIFIC GRAVITY OF DISTILLATE OILS



Illinois #6 coal would be much lower than that with SRC from Kentucky #9 coal. Therefore, the source of SRC represents an important factor in the LC-Finer design. The catalyst activity and aging data on SRC from Illinois #6 coal further strengthens the conclusion made earlier that the SRC-I Demonstration Plant LC-Finer design is very conservative.

Discussion On Catalyst Deactivation

Analysis of the spent catalysts from Wilsonville runs 3 and 4 and from the ICRC PDU runs showed significant deposition of coke and metals on the spent catalysts. The analyses of feed and hydrotreated SRC interestingly revealed that during the initial part of the Wilsonville runs, most of the metals such as sodium and titanium were retained by the catalyst. The data also indicated that the catalyst eventually became saturated with these metals and no further deposition occurred. The analyses of Wilsonville data discussed earlier showed that catalyst activity started to decline after a certain time on stream, which surprisingly coincided with the time on stream at which the catalyst apparently became saturated with metals. This coincidence suggests that catalyst activity depends largely on metals deposition. Initially, a high catalyst activity level is maintained because of the availability of an excessive number of reactive sites or large surface area due to the presence of an excess amount of catalyst. However, continued operation of the unit causes a significant reduction in the surface area of the catalyst, as well as the number of active sites, which results in a severe reduction in catalyst activity.

The above explanation is a simplistic description of a rather complicated system. Many factors other than reduction in surface area and number of active sites may occur at the same time and affect catalyst activity. For example, pore size of the catalyst will decrease with metal and coke deposition. Pore mouth plugging and reduction in pore size will not allow reactants such as SRC to diffuse through the pores, resulting in inaccessibility of internal active sites of the catalyst to SRC molecules. Therefore, diffusional problems also play an important part in catalyst activity.

The results from the ICRC PDU operation also tend to support the above explanation concerning the deactivation of catalyst by coke and metals deposition. Analysis of the spent catalyst showed not only a significant level of metal deposition, but also a significant reduction in both surface area and pore size. However, more work is needed to quantify the reduction in catalyst activity by metals and coke deposition.

The effect of metals deposition on catalyst activity was indirectly studied in Wilsonville run 8. Since the Illinois #6 coal used in this run contained a lower concentration of chlorine, sodium carbonate was not added to the initial coal liquefaction step. This resulted in significantly less sodium in the feed SRC to the hydrotreater compared to run 3. The concentrations of iron and titanium, however, were similar to those contained in the feed SRC for run 3. The results from run 8 (discussed earlier) showed only a marginal decline in catalyst activity over the entire period of operation. In addition, the first-order rate constant for the conversion of SRC was similar to that for feed SRC from Kentucky #9 coal. Analysis of feed SRC and product from run 8 revealed a retention of titanium by the catalyst, but very little sodium retention. This information indicated that either SRC from Illinois #6 coal is more reactive than that from Kentucky #9 coal or sodium has a severe detrimental effect on the activity of the catalyst. This is a very general statement because the reactivity of SRC may very well depend on the reaction conditions or severity used to generate it.

Comparison of the results from the PDU and Wilsonville runs 3 and 8 raises several important questions: Why was the SRC from Illinois #6 coal more reactive than SRC from Kentucky #9 coal? Why didn't catalyst activity decline during processing SRC from Illinois #6 coal? What is the true mechanism of catalyst deactivation? What is the impact of metals and coke deposition on catalyst activity? What is the effect of sodium on catalyst activity? These questions are very important and should be answered to ensure the successful operation of the SRC-I Demonstration Plant LC-Finer.

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