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DR-0381-6

DOE/OR/03054-31
(DE84014151)

Energy

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HYDROPROCESSING SRC

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Work Performed Under Contract No. AC05-78OR03054

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United States Department of Energy

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(DE84014151)
Distribution Category UC-89

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Office of Solvent-Refined Coal Products
under Contract DE-AC05-78-OR-03054

ABSTRACT

Catalyst activity and aging rate were studied in ICRC's process development unit (PDU) and at the Wilsonville Advanced Coal Liquefaction Facility under SRC-I Demonstration Plant hydroprocessing conditions. Similar studies using both high- and low-conversion modes were conducted by The Lummus Company. The studies determined variations in SRC conversion, hydrocarbon gas production, hydrogen consumption, and heteroatom removal. Samples of spent catalyst were analyzed to ascertain the reasons for catalyst deactivation. Finally, the ICRC PDU hydroprocessing results were compared with those generated at Lummus and Wilsonville pilot plants.

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EXECUTIVE SUMMARY

This topical report under Program Area 28.3, titled "LC-Finer Catalyst Testing," includes all SRC hydroprocessing results generated by both The Lummus Company and International Coal Refining Company (ICRC) R&D. Some of the SRC hydroprocessing data generated at the Wilsonville Pilot Plant are also included in the report for comparison.

Overall, the data showed that the design of the LC-Finer for the SRC-I Demonstration Plant is conservative for both high- and low-severity cases. More specific observations are discussed below.

The higher-than-expected gas yield and hydrogen consumption in the Lummus Process Development Unit (PDU) high-conversion run 2LCF-27 resulted from the high reactor temperature required to achieve the desired conversion. Experimental work conducted at ICRC R&D to determine the affect of reaction temperature 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 ratio of hydrocarbon gas to oil production and the ratio of hydrogen consumption to oil production increased sharply, indicating a sharp decline in selectivity for oil production. Heteroatom removal did not improve significantly by increasing the reaction temperature from 775 to 825°F.

The high reaction temperature in run 2LCF-27 also contributed to a high rate of catalyst deactivation, and decreasing recycle SRC reactivity. The high catalyst deactivation rate may be attributed to retrograde reactions producing coke precursors during operation. The formation of the coke precursors or insoluble organic material (IOM) in run 2LCF-27 due to the high reaction temperature was hypothesized to be the cause of reactor plugging.

The rapid deactivation and reactor plugging in Lummus' low-conversion run 2LCF-28 was also attributed to coking, as indicated by high IOM in the reactor product. However, low-conversion run 2LCF-29 was a success; gas yield and hydrogen consumption were consistent with the design basis, but on the high side of the range developed previously by Lummus.

Catalyst aging experiments conducted by ICRC R&D showed that SRC conversion, hydrocarbon gas and oil production, hydrogen consumption, and overall desulfurization, denitrogenation and deoxygenation, changed only slightly during the initial catalyst age of 246 lb SRC/lb catalyst at 775°F, but changed significantly after that. The catalyst aging experiment at 825°F experienced several operational problems, resulting in a much shorter period of constant catalyst activity than in the 775°F experiment. The decline in activity of Ni-Mo-Al catalyst observed in the ICRC PDU was comparable to that noted with Co-Mo-Al catalyst at Wilsonville in runs 235-3 and 4.

Analysis of spent catalyst from the ICRC PDU revealed a significant reduction in catalyst surface area, pore volume, and pore diameter, which resulted from coke and metal deposition. Additional analysis showed an unusually high level of sodium deposition, which was probably due to the presence of a high level of sodium in the feed. A mass balance around the system revealed that only 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.

The reduction in surface area and loss of pore structure from metal and coke deposition were hypothesized to be the main causes of the significant decline in catalyst activity. The decline in activity could also have been partly due to sodium deposition. However, it is not intended to add sodium carbonate to the SRC-I Demonstration Plant; therefore, sodium levels in the SRC feed to the demonstration plant hydrotreater should normally be lower.

INTRODUCTION

Production of distillate liquid by catalytic hydroprocessing of solvent- refined coal (SRC) is a major processing step in the SRC-I Demonstration Plant. One of the few commercially available hydroprocessing methods that can potentially handle SRC is the Lummus-Cities ebullated-bed hydrocracker or LC-Finer. 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 approximately 30% is recycle distillate diluent oil.

The LC-Finer was selected because of its proven capability in processing residual and heavy petroleum oils. The process employs a conventional hydroprocessing catalyst in an ebullated bed reactor in which the gaseous and liquid feeds are fed upwardly through an expanded bed of catalyst. The LC-Finer is well-suited to the processing needs of a refractory or very-high-molecular-weight feedstock because catalyst can be added or withdrawn from the reactor during operation. Because SRC comprises essentially high-molecular-weight asphaltenes and preasphaltenes, its composition may be the major contributor to rapid catalyst aging. In addition, the high metal content of SRC may contribute significantly to catalyst deactivation.

The demonstration plant LC-Finer has been designed around two different cases, each producing a different level of SRC conversion. SRC conversion is defined as the wt % or vol % of 850°F+ feed converted to 850°F- components. In the high-severity design case, approximately 80% of the net SRC feed is converted. Since the high-severity case involves substantial SRC recycle, the fresh SRC feed rate is only one-half that of the low-severity alternate design case in which no SRC is recycled and the conversion level is 46%. Since the higher conversion level of the high-severity case is compensated for by a lower net SRC feed rate, both high- and low-conversion modes produce roughly the same quantity of C_5-850°F distillate. However, the low-conversion design case yields a slightly greater amount of distillate while consuming less hydrogen and producing less hydrocarbon gas. These advantages are counterbalanced in the high-conversion case by a slight improvement in product properties (higher hydrogen content and lower heteroatom content). In addition, the lower net SRC feed rate in the high-conversion case makes SRC available for other end uses. The actual processing mode will be chosen during plant operation on the basis of both engineering and marketing considerations. Specific design data for the two severity cases are given in Table 1.

Because of the expected rapid catalyst deactivation rate, the cost of replacing catalyst will be a major consideration in hydroprocessing SRC. Besides the high cost of replacing catalyst in the LC-Finer, the other important aspect to consider is the variation of the yield structure with catalyst aging. In addition, it is important to know the true yield structure at the design catalyst replacement rate. Prior LC-Finer process studies by Lummus have indicated that a modified Shell 324 Ni-Mo-Al catalyst can provide the desired yield structure. SRC-I Demonstration Plant design support runs have also been carried out at the Wilsonville Advanced Coal Liquefaction Facility (runs 235-3 and -4) to confirm yield structure and catalyst activity data developed by Lummus. However, these studies were not run long enough to confirm yield structure and catalyst activity data at the design catalyst age.

Based on the uncertainties in the catalyst replacement rate and yield structure, ICRC initiated a research program to develop a data base that would increase confidence in the design basis. The program was specifically designed to demonstrate the yield structure and hydrogen consumption at the design catalyst replacement rate. The study was also designed to provide a basis for understanding quantitatively the effect of key process parameters such as space velocity, reaction temperature, concentration of SRC in the feed, source of SRC, and catalyst type on catalyst aging and yield structure. In addition, the research program was designed to study the nature and mechanism of catalyst deactivation.

This report describes and evaluates the results of the three PDU runs conducted by the Lummus Company to confirm the design and alternate design bases. It also describes the results of three additional runs conducted by ICRC R&D to confirm the design catalyst replacement rate. The information regarding LC-Finer runs was previously published by ICRC

Table 1

Expanded-Bed Hydrocracker Design Basis
(Nonproprietary Version)

1.

2.

Yield	Base design		Alternate design	
Feed	lb/hr	wt %	lb/hr	wt %
Fresh SRC				
Oil	3,766	1.83	7,514	3.56
SRC	70,068	34.13	140,153	66.44
Subtotal	73,834	35.96	147,667	70.00
Recycle				
Oil	78,784	36.91	63,286	30.00
SRC	55,703	27.13		
Subtotal	131,487	64.04	63,286	30.00
Total feed	205,322	100.00	210,953	100.00
Product distribution (wt % fresh SRC feed)				
H_2S	642	0.87	1,152	0.78
NH_3	1,270	1.72	1,167	0.79
H_2O	3,537	4.79	5,759	3.90
C_1-C_4	10,396	14.08	13,153	8.91
C5-400°F	12,345	16.72	13.703	9.28
400-500°F	13,984	18.94	10,721	7.26
500-650°F	9,074	12.29	12,212	8.27
650-850°F	11,274	15.27	13,792	9.34
SRC	14.981	20.29	79,696	53.97
H_2	- 3,692	- 5.00	- 3,692	- 2.50
Total	73,834	100.00	147,667	100.00

	Base design	Alternate design
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

and Lummus in several reports (1-5). The results of all experiments conducted by ICRC R&D were summarized by Garg (6). This report also includes available data generated at the Wilsonville Pilot Plant on hydroprocessing SRC in support of the SRC-I Demonstration Plant Project. Finally, a comparison of the data generated in all three laboratories is presented and compared to the design basis.

DISCUSSION OF CATALYST ACTIVITY ANALYSIS

The objective of the various SRC hydroprocessing runs conducted by the Lummus Company, ICRC R&D, and the Wilsonville Pilot Plant was to verify the activity and aging rate of the LC-Finer catalyst. Both the aging and activity concepts must be fully appreciated to understand the phenomenon of catalyst deactivation.

Catalyst activity provides a measure of the performance of a catalyst to effect a particular change. For example, if the catalyst improves the transformation of A to B, the conversion level of A would be the simplest measure of its activity. As a performance measure, conversion has the advantage of being directly observable by simply measuring the concentrations of A and B in the reactor effluent, and of measuring the most economically important variable, that is, the quantity of B produced. However, this performance measure has the disadvantage of being affected by process parameters such as reactor configuration, space velocity, temperature, and reactant concentration, which may vary from run to run and from reactor to reactor. To measure the performance of the catalyst in SRC hydroprocessing, ICRC has modeled the conversion of SRC to materials boiling below 850°F as a first-order reaction. Since the reactants and products are well mixed in the ebullated bed or fixed basket catalytic reactors, the conversion of SRC to materials boiling below 850°F is modeled assuming a first-order reaction for SRC conversion (k_{SRC}) in a completely mixed reactor (see Appendix A). This eliminates the contribution of factors such as space velocity and reactant concentration, and evaluates only the state of the catalyst at the system temperature. The model succeeds in focusing attention on the catalyst, but may be misleading if the founding assumptions are invalid. These assumptions are described in detail in Appendix A.

The second important concept, catalyst age, is reflected in a decline in catalyst activity with time. Catalyst age is normally determined by the total time on stream. This definition of catalyst age will be very misleading if a part of the experiment is carried out below the reaction conditions. Therefore, the total time on stream <u>at the reaction conditions</u> will be more appropriate to define the true catalyst age. If catalyst deactivation is caused by a poison in the feed, then the total quantity of that poison fed to the reactor per unit weight of catalyst will be a more appropriate measure of catalyst age. Suspected poisons include metals such as sodium, titanium, and boron, which are known to have deleterious effects on hydroprocessing catalysts. Since the composition of the feed SRC is approximately constant during a run, the total quantity of these poisons fed to the reactor will be proportional to the total quantity of SRC feed. Thus, a second useful measure of catalyst age is the total weight of SRC feed per unit weight of catalyst.

Yet a third measure of catalyst age will be appropriate if the catalyst deactivation is related to the "work" the catalyst has done, rather than the feed it has been contacted with. This measure of catalyst age, defined as the cumulative amount of SRC converted per unit amount of catalyst, can be used in comparing the catalyst aging in different reactor systems. This concept is very useful because it allows a direct evaluation of how much of the desired end product has been manufactured per unit amount of catalyst. Furthermore, this concept eliminates the differences in the measured catalyst age caused by the variations in the conversion levels and the use of different reactor configurations.

The different pilot plant hydroprocessing data bases discussed in this report involved batch aging of the catalyst. At any given time, all the catalyst in the reactor would have the same age. In contrast, the demonstration plant hydroprocessing unit will have continuous catalyst addition and withdrawal facilities. After startup on an initial batch, fresh catalyst will be continuously added, and used catalyst will be continuously withdrawn from the system. Because the reactor is well-mixed, the catalyst withdrawn from the system will have a distribution of ages and will include fresh catalyst as well as catalyst that is quite old. Similarly, the catalyst in the reactor will have a distribution of ages that is directly related to the degree of mixing in the reactor and the catalyst addition rate.

The average activity of the total catalyst charged to a well-mixed batch reactor can be determined by summing the products of the fraction of catalyst at a given age and the activity of the catalyst at that age. Because the ebullated-bed hydrocracker is a well-mixed system, the fraction of catalyst at a given age can be determined from the residence time distribution of an ideal stirred tank reactor. The activity of the catalyst at a given age can be determined through batch catalyst aging experiments, and can typically be described by the exponential decay function (see Appendix B). If the catalyst deactivation expression is available, the average catalyst activity in a continuously operating ebullated-bed hydrocracker can be derived by combining the expressions for catalyst deactivation and residence time distribution as shown in Appendix B. Consequently, if batch catalyst aging data are to be useful for design confirmation, catalyst decay must be accurately modeled. Furthermore, catalyst aging data must be available for an extended period in order to calculate a representative catalyst replacement rate.

The discussion that follows describes and evaluates all the experimental work conducted in support of the SRC-I Demonstration Plant LC-Finer design. The discussion is subdivided into four major sections. The first three sections cover the experimental work conducted by the three different organizations. In the fourth section, the data generated by these organizations are compared, and the impact of the generated data on the design basis is discussed.

THE LUMMUS COMPANY PDU RUNS

Three different LC-Finer PDU runs were carried out at The Lummus Company to provide data and information for both the high-conversion design and the low-conversion alternate design modes of LC-Finer operation. The high-conversion design mode run was scheduled for 45 days during which 500°F+ product was recycled with 35 vol % fresh SRC. The run was designed to yield a net conversion of 80 vol % of fresh feed SRC. The low-conversion alternate mode run was scheduled for 30 days during which 500-850°F product was recycled with 70 vol % fresh feed SRC. The low-conversion run was designed to obtain a 50 vol % conversion of fresh feed SRC. Table 2 summarizes the design operation and conversion specifications of high- and low-conversion LC-Finer runs.

The LC-Finer pilot plant consists of two expanded-bed catalytic reactors in series with ebullating liquid recycle for each reactor plus product recovery facilities. The detailed experimental program and run procedures can be found in a previous report published by ICRC (1).

For both high- and low-conversion runs, the reactors were charged with fresh catalyst, and then started up with creosote oil. Reactor temperatures were raised gradually to the desired temperature, at which point the feed was introduced; the desired flow rates were then established and held constant.

Operating Summary of PDU Runs

Shell 324 (nickel-molybdenum), 1/32-in.-extrudate catalyst was used in both high-conversion run 2LCF-27 and low-conversion run 2LCF-29, while American Cyanamid 1442B (cobalt-molybdenum) catalyst was used in the other low-conversion run, 2LCF-28. For the first 15 periods of once-through operation (24-hr period) for run 2LCF-27, the feed was a blend of 50 vol % SRC, a 850°F+ boiling material, and 50 vol % solvent, a blend of prehydrogenated and raw creosote oil. Solvent for subsequent periods was recycled LC-Finer 500°F+ product from the once-through operation or subsequent recycle passes. This solvent was prepared by distilling the accumulated total liquid product (TLP) to 500°F. For the feed blends, sufficient fresh SRC was added to the distilled 500°F+ fraction to effect a 1.45 ratio of fresh to unconverted SRC. The feed

Table 2

Expanded-Bed Hydrocracker Design and Alternate Design Bases for SRC-I Demonstration Plant

	High-conversion	Low-conversion
Feed blend		
Fresh SRC feed (vol %)	35	70
Recycle 500-850°F (vol %)	41	30
Recycle 850°F+ SRC (vol %)	24	0
Conversion specifications		
Hydrogen consumption		
wt % fresh SRC feed	5	2.5
scf/bbl	3,950	1,975
850°F+ conversion target (vol %)		
Per pass (total SRC)	45-50	45-50
Net (fresh SRC only)	75-80	--

for the two low-conversion runs, 2LCF-28 and 29, consisted of a blend of 70 vol % fresh 850°F+ SRC and 30 vol % prehydrogenated creosote oil for the first 12 days of once-through operation. For each subsequent period, the feed consisted of 30 vol % recycle solvent and 70 vol % fresh SRC. The solvent for the low-conversion runs was a 500-850°F product recovered by distilling the product from previous passes.

Several samples of feed and products were collected and analyzed during the course of all three runs, and the detailed information about the samples and analytical procedures can be found in a report published by ICRC (1-3).

High-Conversion Run 2LCF-27

Run 2LCF-27 was carried out for a total of 51 days. Fifteen of these days were once-through operation with fresh SRC and prehydrogenated creosote oil to prepare recycle material. Thirty days involved four recycle passes on solvent and unconverted SRC, and an additional six days of operation were performed to check catalyst activity and make sufficient product from the fourth recycle pass at a decreased feed rate. Conversions of SRC during the once-through operation increased from 24 to 52 vol % as the reactor temperature was increased. The highest net conversion of 81.0 vol % was noted during the first recycle pass. However, conversion decreased during subsequent periods because of catalyst deactivation, requiring adjustments in reactor temperatures and space velocities. The net conversion of SRC ranged from 63.7 to 81.9 vol % during the operation of run 2LCF-27. The highest net conversion of 81.9 vol % was noted at the end of the fourth recycle recycle pass. This increase in net conversion in spite of catalyst deactivation was due to the use of a significantly lower liquid hourly space velocity in the fourth recycle pass (0.16 hr^{-1}) compared with 0.32 hr^{-1} used in the first recycle pass. The predicted gas yield was significantly higher compared to the Lummus data base (Table 3). Furthermore, hydrogen consumption, both in run 2LCF-3 and that predicted based on 2LCF-27 data, was significantly higher than the design basis for the SRC-I Demonstration Plant (Table 2).

Table 3

Comparison of Yield-Structure from High-Conversion LC-Finer Runs

	Data base		Phase I prediction	
Data source	2LCF-3[a]		2LCF-27	
Coal source	Ky #9/14 Col.		Ky #9 Fies	
SRC separation technique	filtration		critical solvent deashing	
SRC source	-		Wilsonville run no. 209	
Pilot plant conditions				
Rel. space velocity	0.5		1-0.75	
Reactor temp (°F)	790		840	
850°F+ in feed (wt %)	50		55-68	
Recycle cut (nominal °F)	500+		500+	
No. batch recycle passes	6		4	
	Reactor feed	Net SRC	Reactor feed	Net SRC
Correlated yields (wt %)				
C_1-C_3	4.4	12.2	5.5	15.3
C_4	1.7	4.7	2.4	6.5
C_5-400°F	9.4	26.2	4.5	12.4
400-650°F	34.4	36.1	33.1	32.8
650-850°F	21.5	8.4	21.4	12.4
850°F+	28.0	10.9	32.6	19.0
Net 850°F+ conversion (vol %)	52.6	88.3	46.5	80.6
H_2 consumption (scf/bbl)	1,620	4,750	1,577	4,620
C_4+ product (°API)	2.1	19.7	2.6	16.0

[a] From Cities Service. 1982. Expanded bed hydroprocessing of solvent-refined coal (SRC) and short contact time (SCT) extracts. Prepared for U.S. DOE, FE-2038-43, April.

The operating conditions for 2LCF-27 were based on pilot plant run 2LCF-3 (Table 3), the only other LC-Finer PDU run in which unconverted SRC material was recycled. The relative space velocity in run 2LCF-3 was one-half that of run 2LCF-27, resulting in approximately 50°F lower reactor temperature to achieve the same conversion (Table 3). The lower reactor temperature may be the primary reason for the lower gas yield in run 2LCF-3 versus run 2LCF-27. This implies that gas production is temperature-sensitive. Furthermore, the gas yield in run 2LCF-27 is consistent with the SRC-I process gas yield/temperature relationship in the same temperature range, implying that gas yield is thermally rather than catalytically controlled.

The decrease in the rate of SRC conversion adjusted to constant space velocity and temperature was the same for both runs 2LCF-3 and -27 (Figures 1 and 2). Therefore, catalyst deactivation seemed not to be a strong function of reactor temperature or space velocity. The reaction rate decreased rapidly during runs 2LCF-3 and 27, both of which were operated for a catalyst age of 2.5 barrels of reactor feed per pound of catalyst. At this age, catalyst activity dropped to less than 50% of the initial value in both the runs.

The feed SRC was held at elevated temperatures in the absence of hydrogen in run 2LCF-27, which could cause retrograde reactions to form insoluble organic material (IOM) and other refractory materials. IOM and refractory materials could also be formed during the conversion of SRC, which would increase the coking tendency in the reactor. Analysis of products from run 2LCF-27 indicated an increase in IOM with each batch-recycle pass (Table 4). A cursory analysis of the spent catalyst revealed that some of the lost activity was due to hard coke deposits on the outer catalyst surface. The severe loss in conversion activity therefore could be due to both degradation of feed indicated by buildup of IOM and coking during the reaction.

Low-Conversion Run 2LCF-28

Like run 2LCF-27, SRC conversion during run 2LCF-28 decreased considerably with time on stream, requiring a continuous adjustment in operating conditions to maintain 50% conversion. The gas yield for run

FIGURE I

VARIATION OF RELATIVE SPACE VELOCITY AND TEMPERATURE WITH CATALYST AGE

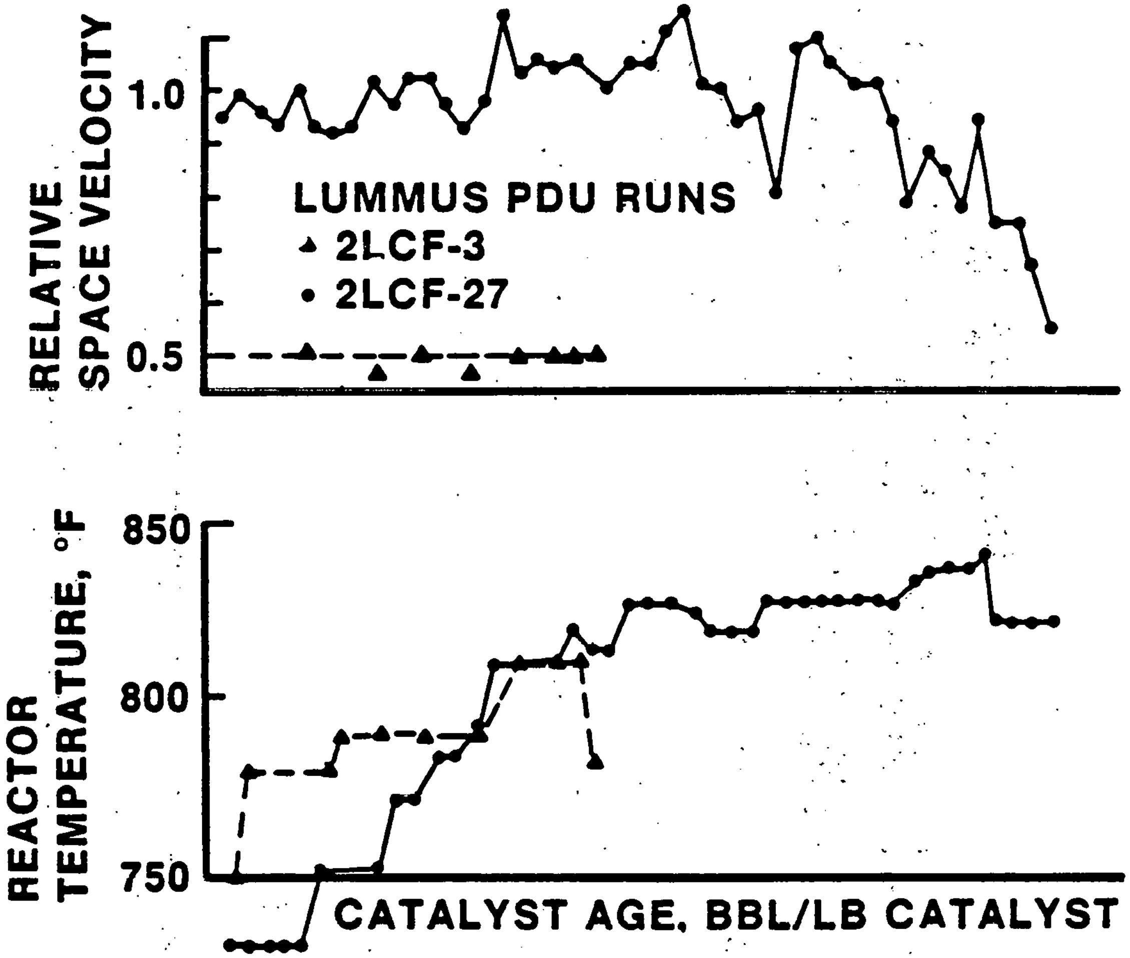

FIGURE 2
VARIATION OF RELATIVE ACTIVITY OF THE CATALYST WITH AGE

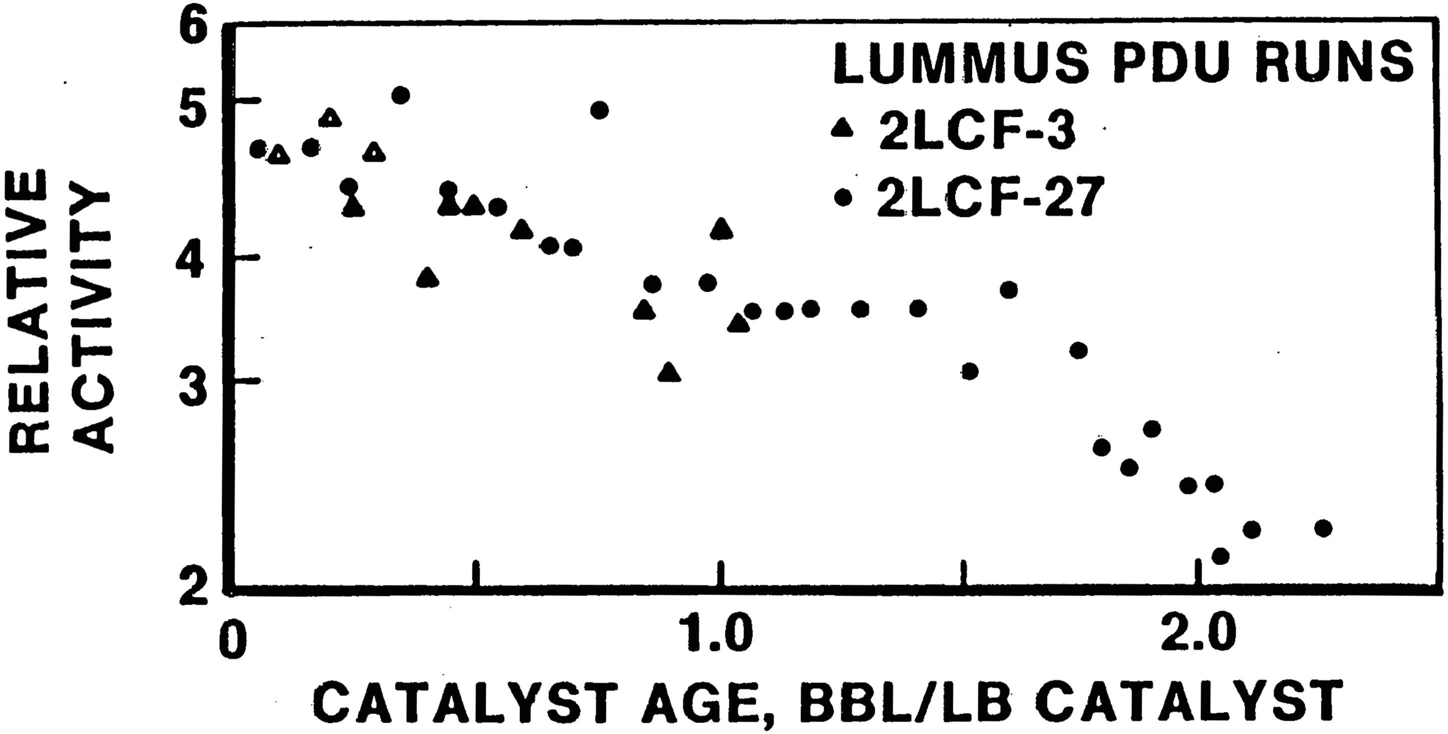

Table 4

Preliminary Analyses of Three PDU Runs for Total Liquid Product Insoluble Materials

PDU run	wt % total liquid product[a] IOM	wt % total liquid product[a] Ash
2LCF-27		
Once-through	0.0	0.0
1st batch recycle	0.2	0.1
2nd batch recycle	1.2	0.1
3rd batch recycle	3.8	0.0
2LCF-28		
Once-through	0.05	0.04
1st batch recycle	4.2	0.10
2LCF-29		
Once-through	0.1	0.03
1st batch recycle	0.04	0.02
2nd batch recycle	0.1	0.03
3rd batch recycle	0.12	0.06

[a] Oral communication--J. D. Potts, Cities Service, 6/10/81.

2LCF-28 was noted to be higher at the higher temperature than that of run 2LCF-27, supporting the hypothesis that gas is produced primarily from thermal reactions. The run had to be aborted after 22 days of operation due to plugging of the second reactor. The cause of the reactor bed plugging is not clear; however, based on the IOM concentration of the product (Table 4), it can be hypothesized that the plugging was caused by rapid coking. This run also experienced very rapid deactivation and reactor plugging during the period in which the IOM concentration was as high as in 2LCF-27.

The cause of the IOM buildup in 2LCF-28 cannot be the same as hypothesized for 2LCF-27, that is, buildup of IOM concentration due to batch recycle, because no unconverted SRC was recycled. More likely, coke precursors accumulated due to poor mixing in the reactor.

Low-Conversion Run 2LCF-29

Run 2LCF-29 was carried out for a total of 32 days. Twelve of these days were once-through operation with fresh SRC and prehydrogenated creosote oil to prepare the recycle solvent. Twenty days involved three recycle passes using this solvent. Gas yield and hydrogen consumption for this run were comparable to that reported in previous runs at comparable conditions (LCF-36 and 2LCF-18; Table 5). Previous run LCF-36 required an average reactor temperature of 800°F to achieve 64% SRC conversion at a relative space velocity of 0.5. Run 2LCF-18 required an average reactor temperature of 833°F to achieve 50% conversion at a relative space velocity of 1.1. However, gas yield and hydrogen consumption in run 2LCF-18 were 20% greater than in run LCF-36. These data indicated that gas yield and hydrogen consumption were strong functions of reactor temperature and space velocity. The relative space velocity in run 2LCF-29 was reduced to 0.75, and the reactor temperature was set to achieve the gas yield and hydrogen consumption equivalent to that of run LCF-36. The resultant reactor temperature and SRC conversion were 805°F and 45.6%, respectively.

Despite reaching an age of 1.28 barrels of SRC feed per pound of catalyst, no significant catalyst deactivation was observed in run 2LCF-29. This, coupled with the absence of IOM concentration in the

Table 5

Comparison of Yield Structure from Low-Conversion LC-Fining Runs

	Data base				Pilot plant data	
Data source	LCF-36[a]		2LCF-18[a]		2LCF-29	
Coal source	Ky #9/14 Col.		Ky #9 Pyro		Ky #9 Fies	
SRC separation technique	filtration		critical solvent deashing		critical solvent deashing	
SRC source	--		Wilsonville run no. 159		Wilsonville run no. 209	
Pilot plant conditions						
Rel. space velocity	0.5		1.1		0.75	
Reactor temp (°F)	800		833		805	
850°F+ in feed (wt %)	53		68.4		70-76	
Recycle cut (nominal °F)	500-850		500-850		500-850	
No. batch recycle passes	5		2		3	
	Reactor feed	Net SRC	Reactor feed	Net SRC	Reactor feed	Net SRC
Correlated yields (wt %)						
C_1-C_3	--	4.5	5.4	7.95	4.5	6.5
C_4	--	1.6	1.4	2.09	1.7	2.41
C_5-400°F	--	7.4	8.4	12.34	6.5	9.28
400-650°F	--	29.1	30.0	17.43	25.0	15.53
650-850°F	--	19.5	19.0	7.93	22.4	9.34
850°F+	--	35.9	34.5	50.50	37.8	53.97
850°F+ conversion (vol %)	--	64.2	50.0	50.0	45.5	45.6
H_2 consumption (scf/bbl)	--	2,025	1,700	2,419	1,322	1,980
C_4+ product (°API)	--	-1.8	1.7	-0.3	0.3	-2.1

[a] From Cities Service. 1982. Expanded bed hydroprocessing of solvent-refined coal (SRC) and short contact time (SCT) extracts. Prepared for U.S. DOE, FE-2038-43, April.

products (Table 4), is further evidence that the retrograde reactions (measured by the increasing IOM) in run 2LCF-27 contributed to the loss of conversion activity.

Summary of Lummus PDU Runs

The higher-than-expected gas yield and hydrogen consumption in high-conversion run 2LCF-27 were the result of the high reactor temperature required to achieve the desired conversion. Several factors contributed to the high reactor temperature: high space velocity, high rate of catalyst deactivation, and decreasing recycle SRC reactivity. The high catalyst deactivation rate may be attributed to retrograde reactions, producing coke precursors during operation. It is hypothesized that the formation of IOM resulted in reactor plugging.

The rapid deactivation and reactor plugging in low-conversion run 2LCF-28 was also attributed to coking, indicated by high IOM in the reactor product probably caused by poor reactor mixing and high temperatures. In the successful low-conversion run 2LCF-29, the gas yield and hydrogen consumption were consistent with the Lummus data base. Likewise, coking did not occur in this run.

Finally, the batch recycle operation of the PDU is not sufficient to simulate the yield structure for continuous SRC recycle in a commercial LC-Finer due to buildup of IOM and refractory materials.

ICRC R&D PDU RUNS

Three different SRC hydroprocessing runs were performed by ICRC R&D to develop catalyst aging data and to determine the effect of process variables like reaction temperature using modified Shell 324 Ni-Mo-Al catalyst.

PDU Run Procedure

The hydroprocessing of SRC was carried out using a novel fixed-bed catalyst basket reactor. The detailed design of the reactor was discussed in a report previously published by ICRC (6). The catalyst basket was filled with a predetermined amount of modified Shell 324 Ni-Mo-Al catalyst (1/16-in. extrudates) and placed in the 2-L autoclave. The autoclave was sealed, and the entire PDU was checked for proper operation of all controllers and also pressure-tested for possible leaks as discussed previously (6). The catalyst was sulfided at 600°F using creosote oil mixed with ethyl disulfide. The sulfiding procedure was identical to that discussed previously (6). After sulfiding the catalyst, SRC feed material consisting of 70 wt % SRC/30 wt % hydrotreater solvent was pumped through the reactor. The reactor temperature was then slowly increased to the desired reaction temperature and maintained there for the entire run. Typical reaction conditions used in the experiments were as follows: hydrogen pressure - 2,000 psig, H_2 feed rate - 8,000 scf/bbl total feed, and weight hourly space velocity (WHSV) - 1.0 g feed/g catalyst/hr.

The feed and product liquid samples were solvent-separated and analyzed by encapsulated gas chromatographic simulated distillation, as discussed previously (6), to determine 850°F- and 850°F+ fractions. Overall product distribution was calculated on the basis of conversion of 850°F+ material to gases and liquid.

Effect of Reaction Temperature

Reaction temperature effects on catalyst performance were determined by using temperatures of 775, 800, and 825°F in the fixed-basket catalytic reactor. SRC conversion and hydrocarbon (HC) gas production were noted to be very sensitive to reaction temperature; both increased linearly with increasing reaction temperature, as shown in Figure 3. Oil production, however, did not change with temperature. 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 temperature (Table 6). As expected, hydrogen consumption increased with temperature (Table 6). However, heteroatom gas production was not very sensitive to increasing temperature (Table 6 and Figure 3). Likewise, minor variations in total desulfurization, denitrogenation, and deoxygenation were noted with increasing temperature. The first-order rate constant for the conversion of SRC also increased with increasing temperature. (Refer to Appendix A, equation A-5.)

It can be concluded that SRC conversion, hydrocarbon gas production, and hydrogen consumption are very sensitive to reaction temperature. 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, suggesting an inefficient use of hydrogen at higher temperatures. In addition, the data indicate no significant loss in heteroatom removal activity of the catalyst 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 by changing the internal volume of the reactor through placement of a metal insert at the bottom of the autoclave. In effect, this decreased the nominal (void) residence time, both at 775 and 825°F, while keeping the catalyst residence time the same. This 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 7). Heteroatom removal also decreased considerably with reduced overall reactor residence time, while the selectivity for gas over oil increased and that for oil over hydrogen consumption decreased. The first-order rate constant for SRC

FIGURE 3
VARIATION OF PRODUCT DISTRIBUTION
WITH TEMPERATURE

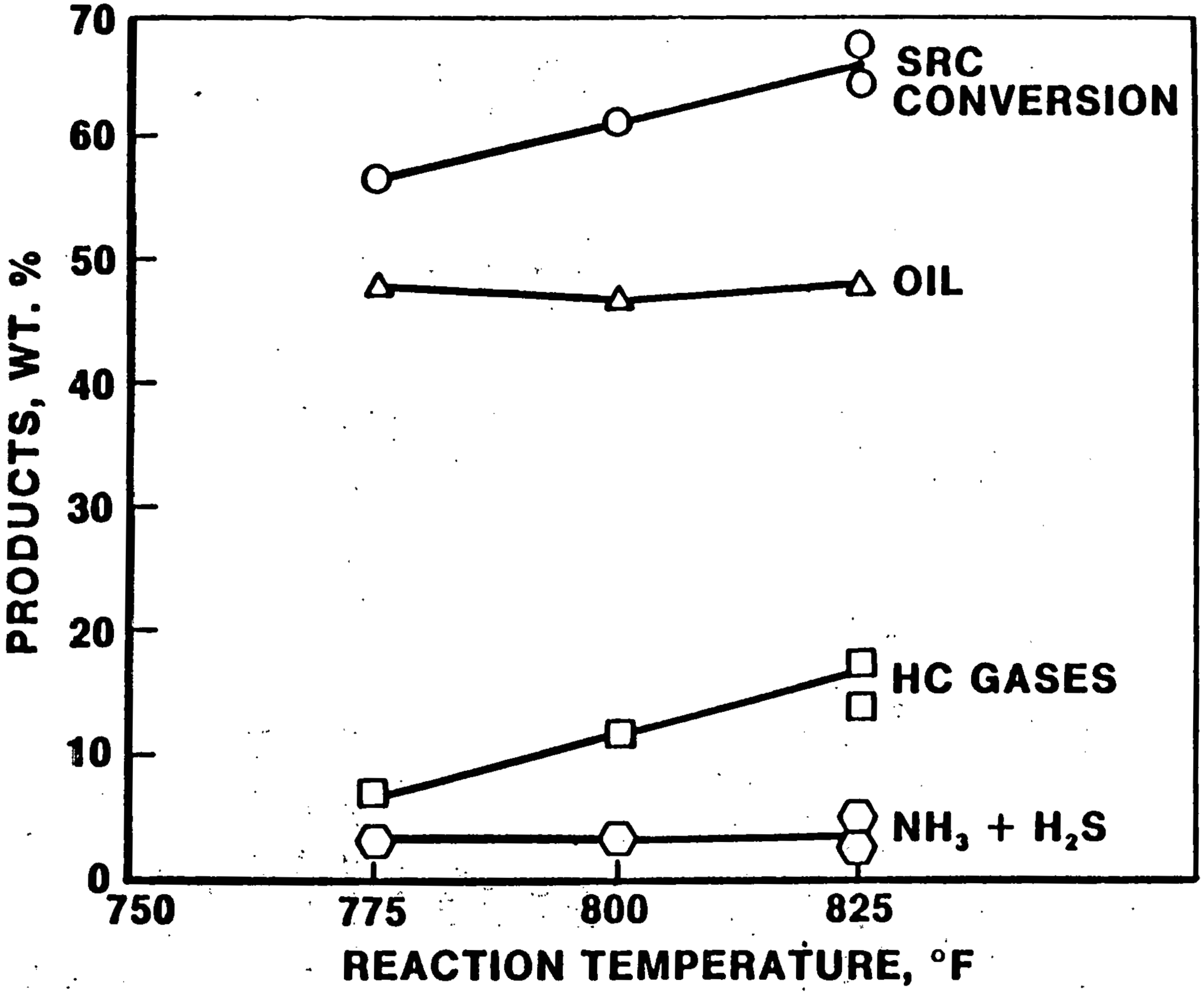

Table 6

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 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 % 850°F+ material)					
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 % 850°F+ material)					
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 gas/oil	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.

Table 7

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 % 850°F+ material)[a]				
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 % 850°F+ material)				
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

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

conversion decreased slightly at 775°F, but decreased sharply at 825°F with decreasing residence time.

The hydroprocessing of SRC conceptually involves competing thermal and catalytic reactions. The proportion of thermal to catalytic reaction may vary by varying the residence times. If the reaction is predominantly catalytic, SRC conversion will remain unchanged with decreasing void residence time. However, if the thermal reaction predominates, conversion as well as the products from the thermal reaction will diminish as residence time diminishes. At 775 and 825°F, conversion activity decreased as void residence time decreased, indicating a preponderance of thermal reactions. The slight increase in the 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

Catalyst activity and aging were studied at 775 and 825°F in two different ICRC PDU runs, CCL-54 and CCL-63, using modified Shell 324 Ni-Mo-Al catalyst. As expected, the initial conversion of SRC and the rate constant at 825°F were higher than at 775°F (Figures 4 and 5); 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 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 6 and 7. On the contrary, oil production was lower at higher temperatures (Figure 6). Finally, the selectivity for oil over hydrogen consumption was considerably lower at 825 than at 775°F (Figure 8).

Catalyst activity remained constant during the first several hours of operation at both temperatures, and then declined sharply. At 775°F, SRC conversion changed slightly during the initial catalyst aging period

FIGURE 4
VARIATION OF SRC CONVERSION WITH CATALYST AGE

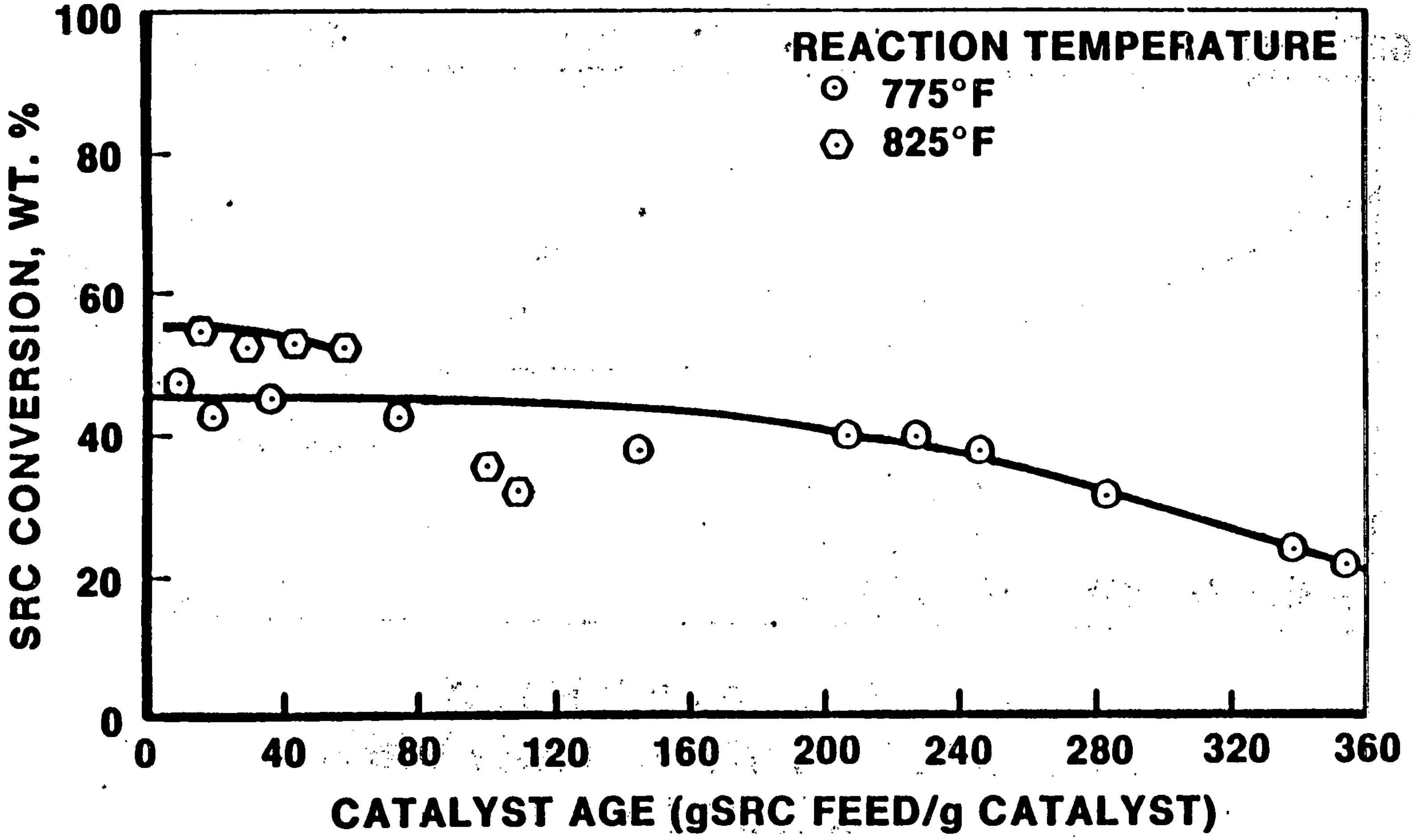


FIGURE 5
VARIATION OF RATE CONSTANT
WITH CATALYST AGE

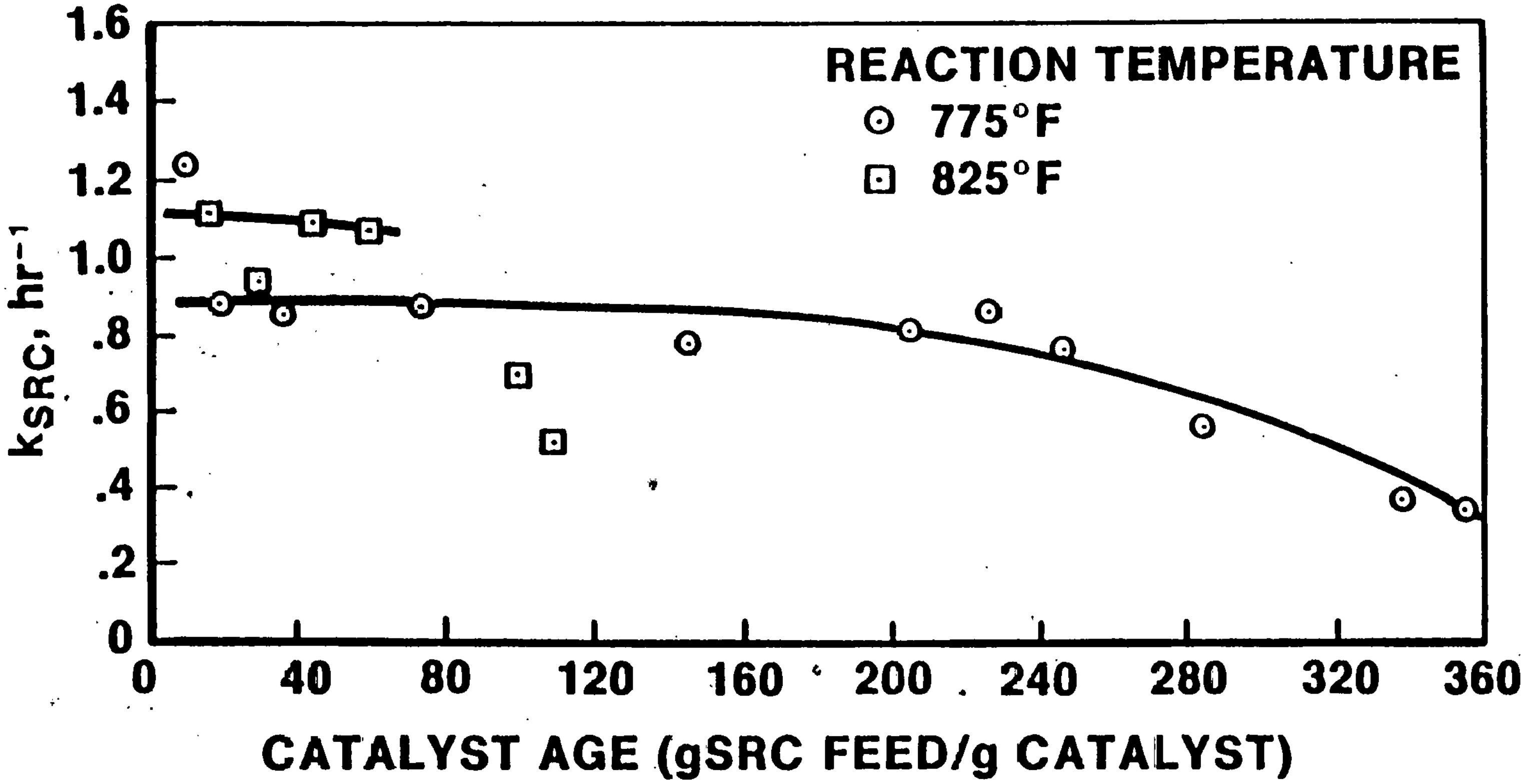


FIGURE 6
VARIATION OF OIL AND HC GAS PRODUCTION WITH CATALYST AGE

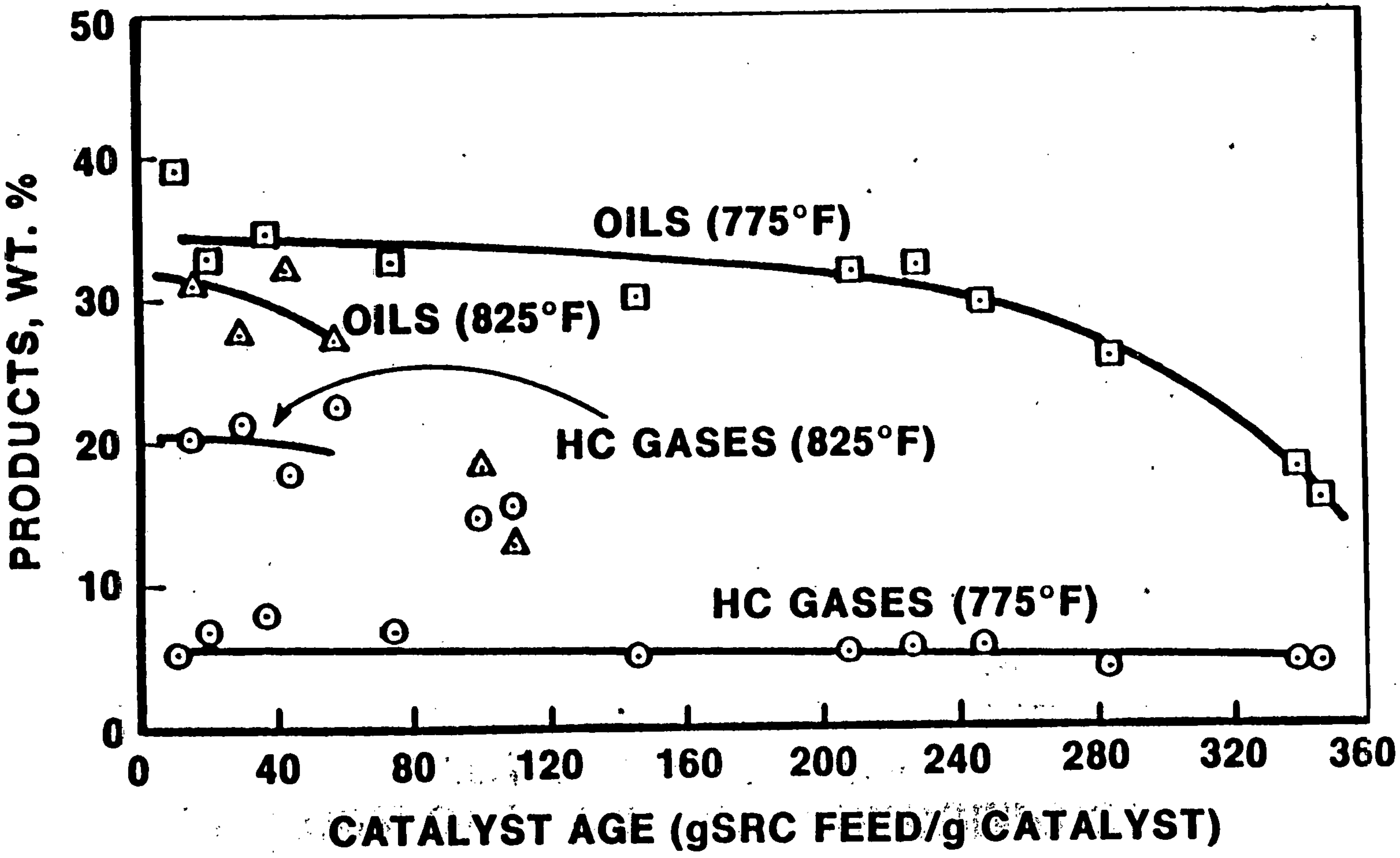


FIGURE 7
VARIATION OF HYDROGEN CONSUMPTION WITH CATALYST AGE

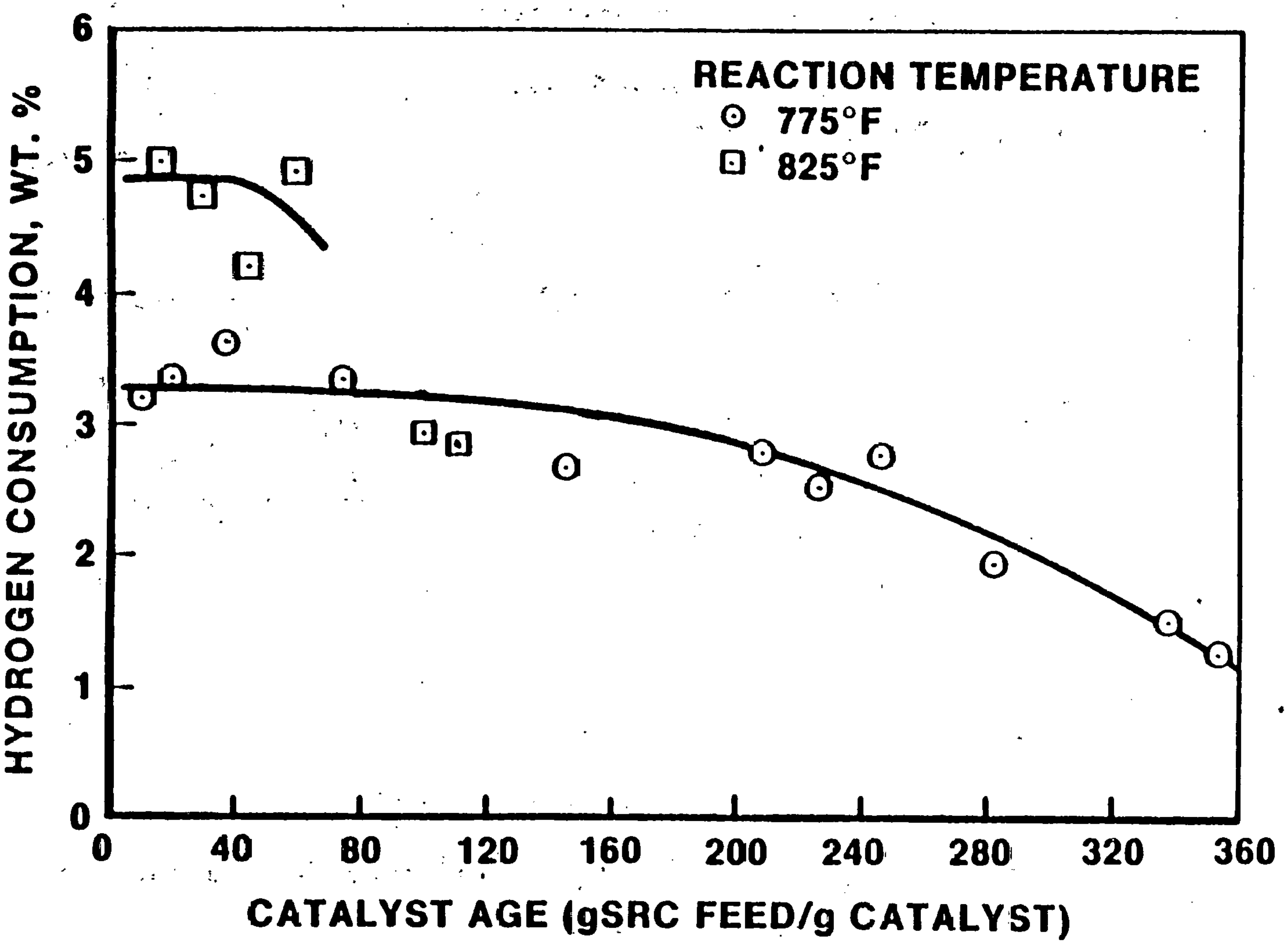
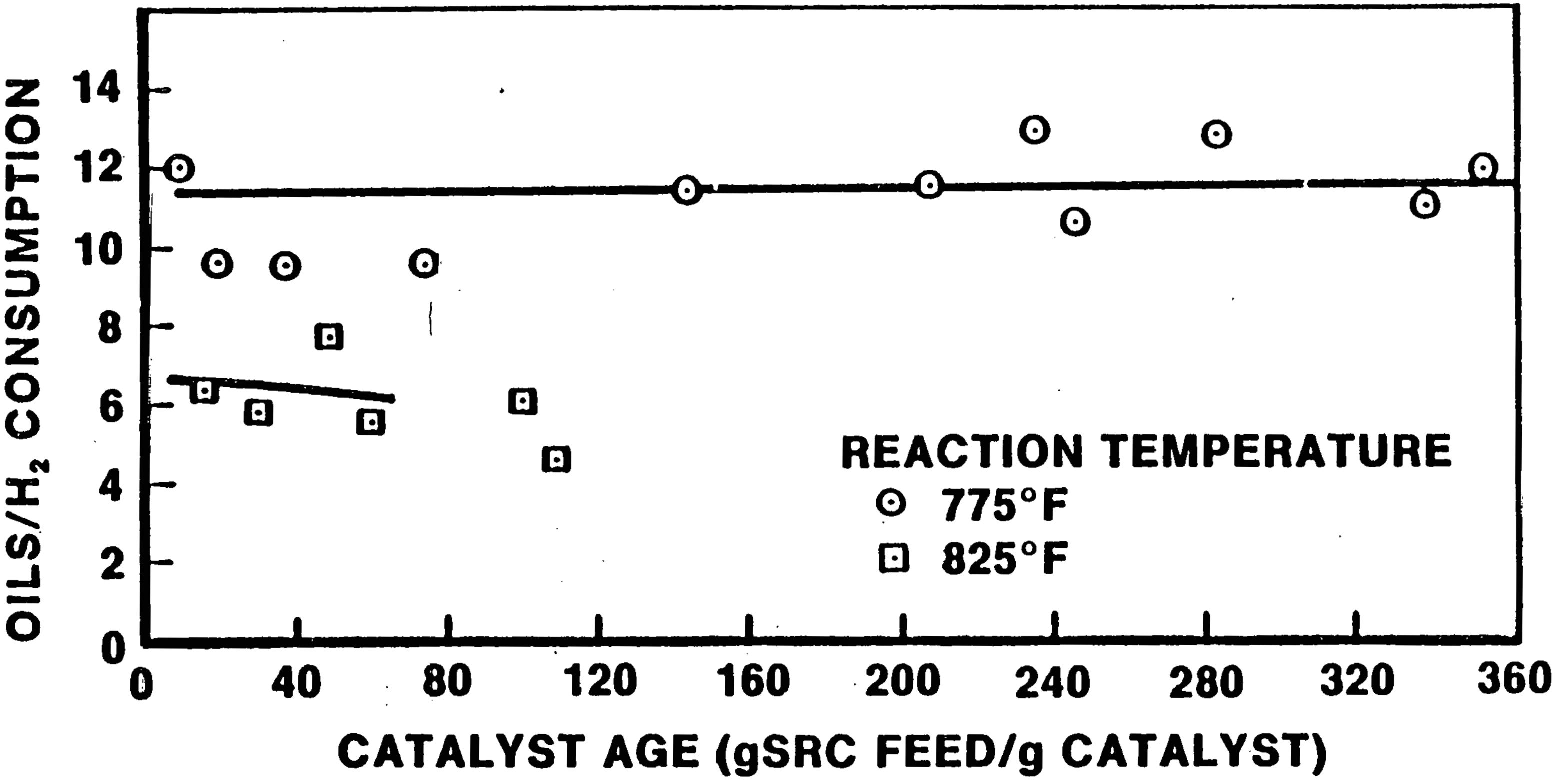


FIGURE 8
VARIATION OF SELECTIVITY WITH CATALYST AGE



of 240 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 4). Similar results were noted for the first-order conversion rate constant, oil and hydrocarbon gas production, and hydrogen consumption (see Figures 5 to 7). Although SRC conversion decreased with catalyst age at 775°F, selectivity was maintained at its initial value (Figure 8).

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 4. Similar results were noted for oil and hydrocarbon gas production, first-order rate constant and hydrogen consumption (Figures 5 to 7). However, selectivity decreased slightly with catalyst age at 825°F (Figure 8).

The sharp decline in catalyst activity at 825°F, as well as shorter catalyst life compared to that at 775°F could be due to several 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. In addition, the results at 825°F seemed to be out of line with those obtained both at The Lummus Company and at Wilsonville. Because of these discrepancies, the data obtained at 825°F in run CCL-63 are questionable and should be used with caution.

Catalyst Analysis

Samples of spent catalyst were recovered after runs CCL-54 and 63 and analyzed to determine the causes of catalyst deactivation.

The analysis of spent catalyst (Table 8) indicated that carbon was not deposited uniformly on the catalyst in run CCL-54: the catalyst from the upper half of the basket contained more than twice as much carbon. The deposition of carbon on catalyst in run CCL-63 at 825°F was substantially higher than in run CCL-54. As expected, the level of metals deposited on catalyst samples was higher in run CCL-54 than in CCL-63, since the level of metals deposition is a function of catalyst age. Deposition of metals and carbon on catalysts is known to reduce

Table 8

Detailed Analysis of Fresh and Spent Catalyst

	Fresh catalyst	Weight % spent catalyst		
		CCL-54		CCL-63
		Upper half of basket	Lower half of basket	
C	-	18.4	8.1	22.9
H	-	1.7	1.4	1.4
N	-	0.6	0.3	0.6
S	-	6.3	7.0	6.7
Ni	2.7	2.0	1.9	1.8
Mo	15.9	10.1	10.0	6.6
Fe	-	0.2	0.3	0.1
Ti	-	0.3	0.4	0.1
Ca	-	0.1	0.1	0.002
Na	-	4.2	4.3	2.0
Surface area (m^2/g)	152	89	72	22.3
Median pore diameter (A°)	96	49	39	-
Median pore volume (m^2/g)	0.30	0.14	0.10	<0.05

surface area, pore volume, and catalyst activity, as substantiated by the data in Table 8. In fact, the pore volume analysis of the spent catalyst from run CCL-63 revealed an almost total disappearance of pore structure. Therefore, the reduction in the surface area and pore volume probably are the main reasons for the significant reduction in catalyst activity.

Whether the reduced catalyst activity was due to carbon or metal deposition, or both, is currently unknown. The level of metals and carbon deposited on the catalyst was normal, except for an unusually high level of sodium (Table 8), which probably resulted from the presence of a high sodium level in the feed SRC (Table 9), 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 9). Because sodium has been reported to severely deactivate cracking as well as desulfurization catalysts (7 and 8), the unusually high level of sodium deposited on the catalyst may be one of the prime reasons for catalyst deactivation.

Table 9

Metal Distribution in the Feed and Spent Catalyst

	Amount of metals (g)		
	In the feed (1)	Deposited on catalyst (2)	In the product (1) - (2)
Run CCL-54 at 775°F			
Iron	14.9	1.0	13.9
Sodium	19.8	17.7	2.1
Titanium	11.9	1.5	10.4
Run CCl-63 at 825°F			
Iron	6.6	0.5	6.1
Sodium	8.6	9.0	-
Titanium	5.2	0.5	4.7

THE WILSONVILLE PILOT PLANT RUNS

Several SRC hydroprocessing runs were performed at the Wilsonville Pilot Plant to study the activity and aging of American Cyanamid 1442B Co-Mo-Al catalyst. Wilsonville run 235 was carried out at design demonstration plant conditions (low-conversion mode) using Kentucky #9 coal in the dissolver section. The product SRC from run 235 was hydroprocessed in the Wilsonville ebullated-bed hydrotreater to verify the design activity and aging of the catalyst (9 and 10). While the dissolver conditions were maintained constant, the hydroprocessing operation during run 235 was divided into two sub-runs, numbers 3 and 4. The first, hydrotreater run 3, was carried out for 581 hr (500 lb total SRC feed/lb catalyst) at from 775-780°F, whereas run 4 was carried out for 386 hr (332 lb total SRC feed/lb catalyst) at the slightly higher temperature of 810°F.

Pilot Plant Procedure

SRC was hydroprocessed using an ebullated-bed reactor designed by Hydrocarbon Research Institute and 1/32-in. Co-Mo-Al catalyst. As in the ICRC PDU runs, the catalyst was first sulfided in creosote oil before SRC was processed in the unit. The feed material to the hydrotreater consisted of 50 wt % SRC/50 wt % solvent, which was pumped through the reactor. The reactor temperature was slowly raised and maintained at the desired level for the entire run. The detailed reaction conditions used for runs 3 and 4 are summarized in Table 10. In addition to using different reaction temperatures, sodium carbonate was added to the liquefaction stage feed slurry during the operation of both runs 3 and 4.

Discussion

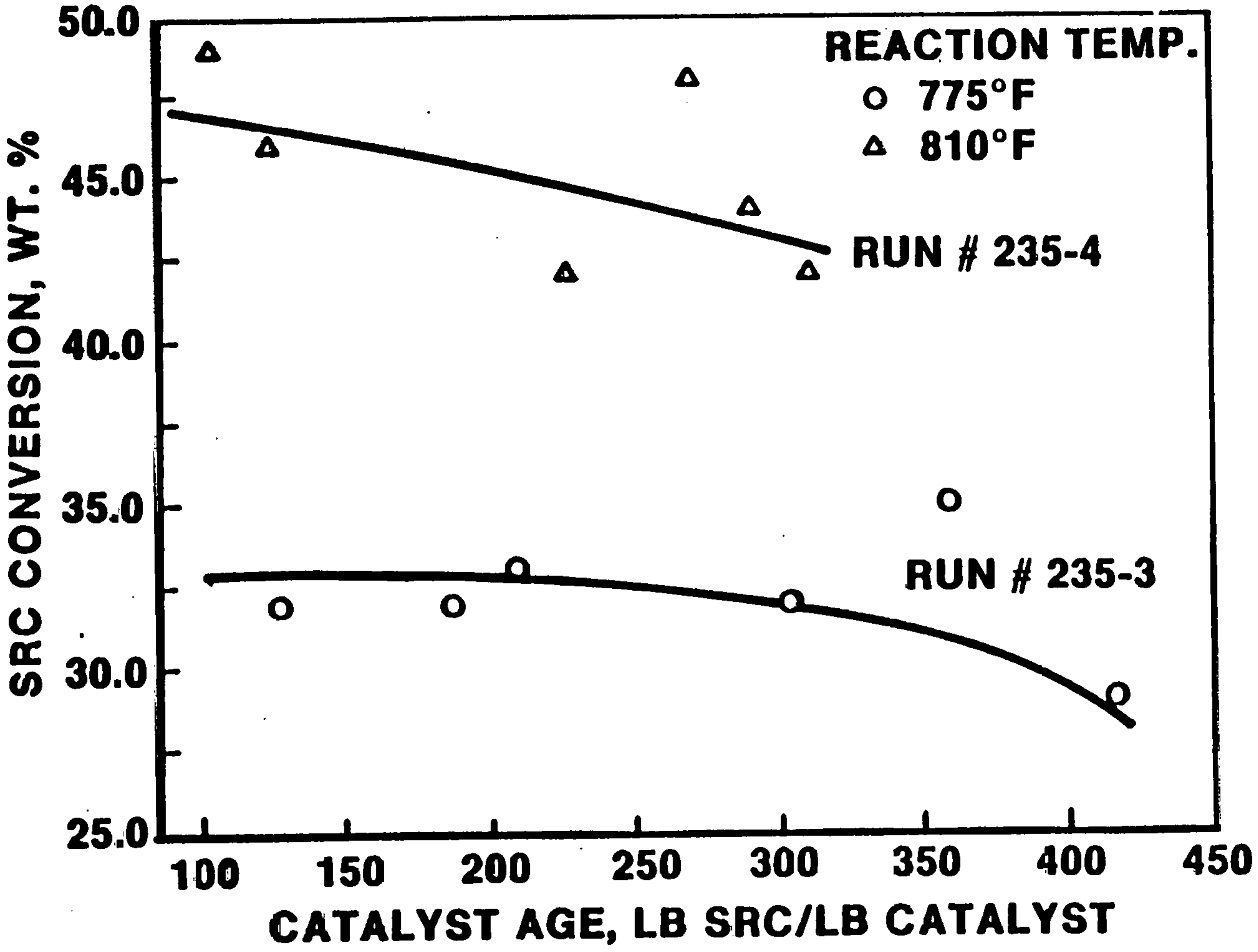
The conversion of SRC in run 3 plotted against catalyst age in Figure 9 showed no decline in conversion level up to an extended catalyst age of 350 lb SRC/lb catalyst. Thereafter, conversion decreased rapidly from 32 to 25%, beginning with an age of about 350 lb SRC/lb catalyst. The value of the first-order rate constant for run 3 also

Table 10

Nominal Process Conditions for Wilsonville Hydrotreater Runs

	Run 235-3	Run 235-4
Temperature (°F)	780	810
WHSV (hr^{-1})	2.0	1.8
SRC concentration (wt %)	46	47
Inlet H_2 partial pressure (psia)	2,400	2,350
Catalyst	American Cyanamid 1442B Co-Mo-Al	American Cyanamid 1442B Co-Mo-Al

FIGURE 9
SRC CONVERSION VERSUS CATALYST AGE FOR WILSONVILLE RUNS



remained nearly constant during the initial part of the run (up to an age of 320 lb SRC/lb catalyst), and then decreased (Figure 10); the initial value of the rate constant was about 1.0 hr^{-1}, and the run was terminated when it reached about 75% of this initial value at a catalyst age of 500 lb SRC/lb catalyst. However, in run 4, the conversion level seemed to decrease continuously with catalyst age, and first-order rate constant decreased only slightly with catalyst age from an initial value of 2.0 hr^{-1}. The run was terminated when the value decreased to 75% of its initial value at the age of 332 lb SRC/lb catalyst.

The lengths of the two runs were significantly different: run 3 exceeded run 4 by 170 lb SRC processed/lb catalyst. However, this difference existed only if catalyst life was measured as pounds of SRC processed per pound of catalyst. When catalyst age was measured as pounds of SRC converted per pound of catalyst to account for the actual "work" performed by the catalyst, the above difference in catalyst age dramatically disappeared (Figure 11). Catalyst activity was almost constant until an age of about 100 lb of SRC converted/lb catalyst in run 3 was reached, but declined rapidly thereafter. However, catalyst activity declined gradually in run 4.

It is generally accepted that catalyst aging and activity depend heavily on reaction temperature. It is also believed that increasing the temperature will increase catalyst activity, but will also serve to accelerate catalyst aging. However, the data presented above partly contradict these theories. At higher temperatures, catalyst activity was higher, as expected, but the deactivation rate was lower. Although the feed to the dissolver was kept constant throughout run 235, detailed analysis of the data indicates that the composition of the feed SRC to runs 3 and 4 varies in several ways. For example, the feed to the hydrotreater in run 3 contained significantly higher amounts of sodium compared with the feed in run 4. It is a known fact that the presence of sodium will limit catalyst activity and cause excessive catalyst deactivation. In addition to variations in sodium content, there were unquantified differences in the composition of feed to runs 3 and 4. The mere existence of these differences raises severe doubts about the

FIGURE 10
RATE CONSTANT VERSUS CATALYST AGE FOR WILSONVILLE RUNS

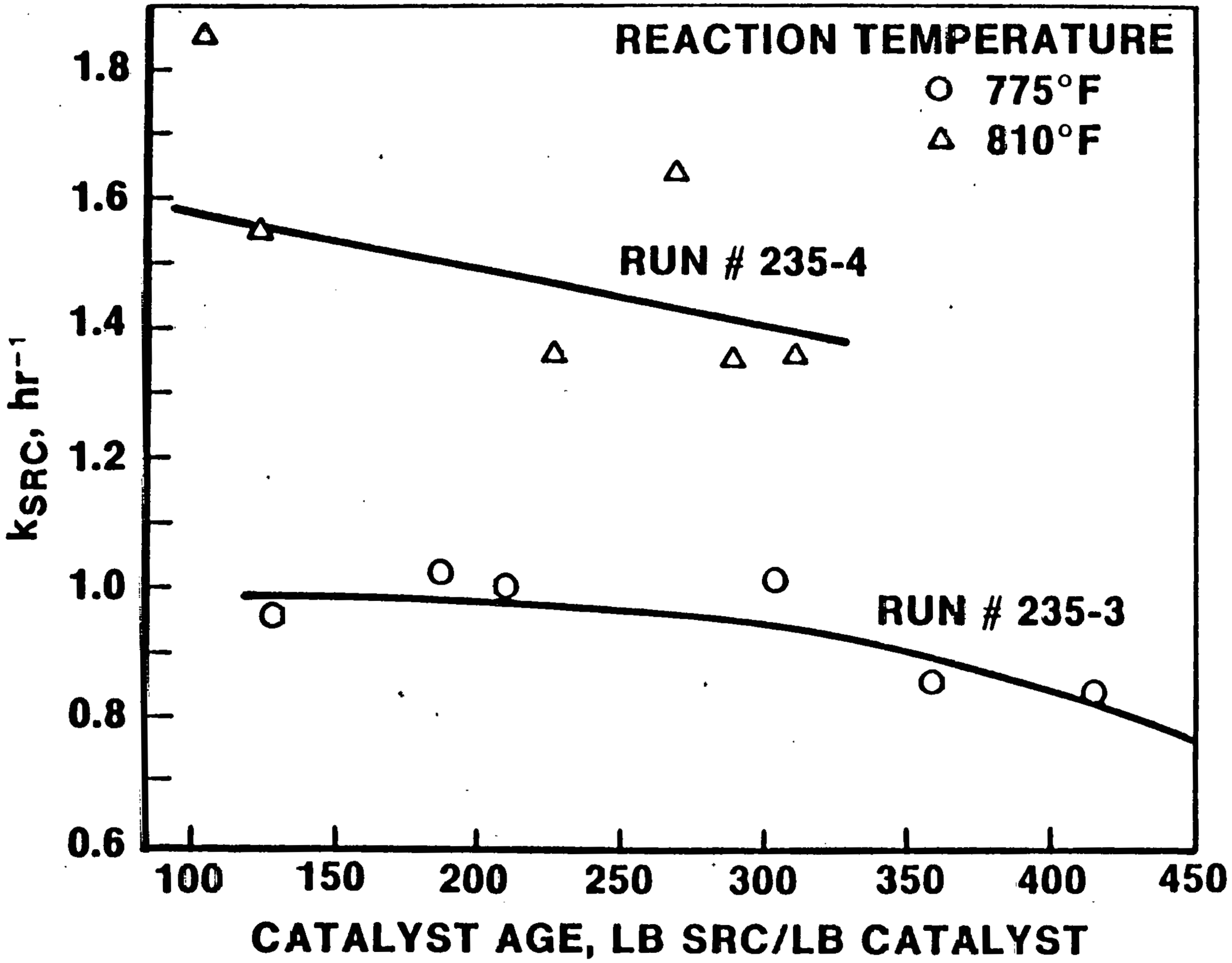
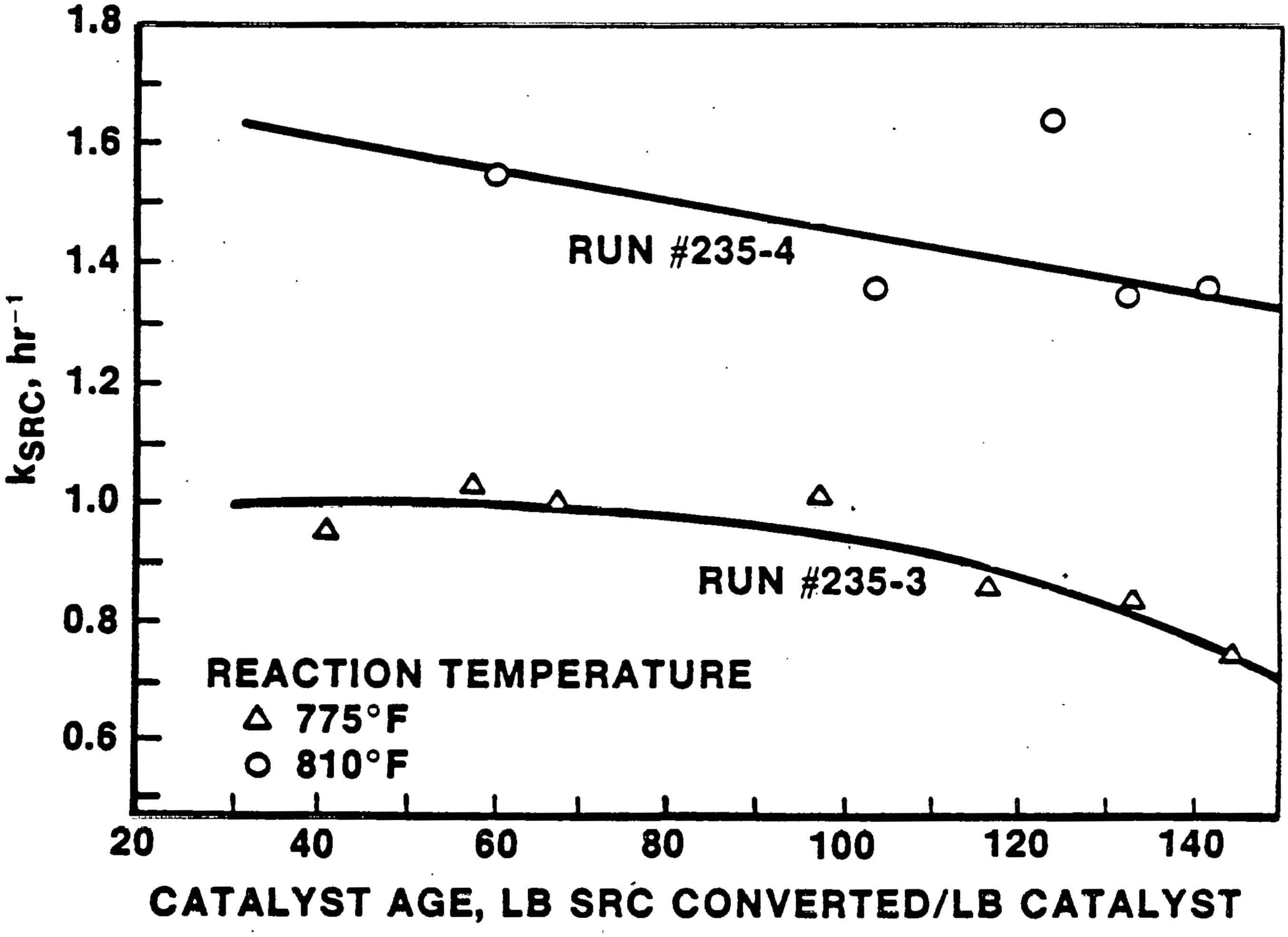


FIGURE 11
RATE CONSTANT VERSUS LBS SRC CONVERTED/LB CATALYST FOR WILSONVILLE RUNS



validity of the earlier observations that at higher temperatures, catalyst activity was higher, but that the deactivation rate was lower. Therefore, it would be unfair to say that catalyst activity is higher at higher temperatures, as well as that the catalyst deactivates more slowly at higher temperatures. More work with controlled composition of the feedstock is needed to confirm catalyst activity and aging at both low and high temperatures.

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.
- Catalyst deactivation rate was comparable at 775 and 825°F temperatures; 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 $t = o$, 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 $t = o$, 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

τ - 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]:

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

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[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:

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

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:

$$k_A = 2\ WHSV\ [(\frac{1}{1-E})^{½} - 1] \qquad \text{(Eqn. A-5.1)}$$

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

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

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

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

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}).

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[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:

$$\text{Average Activity} = \sum_{t=0}^{\infty} \begin{bmatrix}\text{Activity of Catalyst}\\ \text{at Age t}\end{bmatrix} \begin{bmatrix}\text{Fraction of Catalyst}\\ \text{at Age t}\end{bmatrix}$$

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

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

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

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

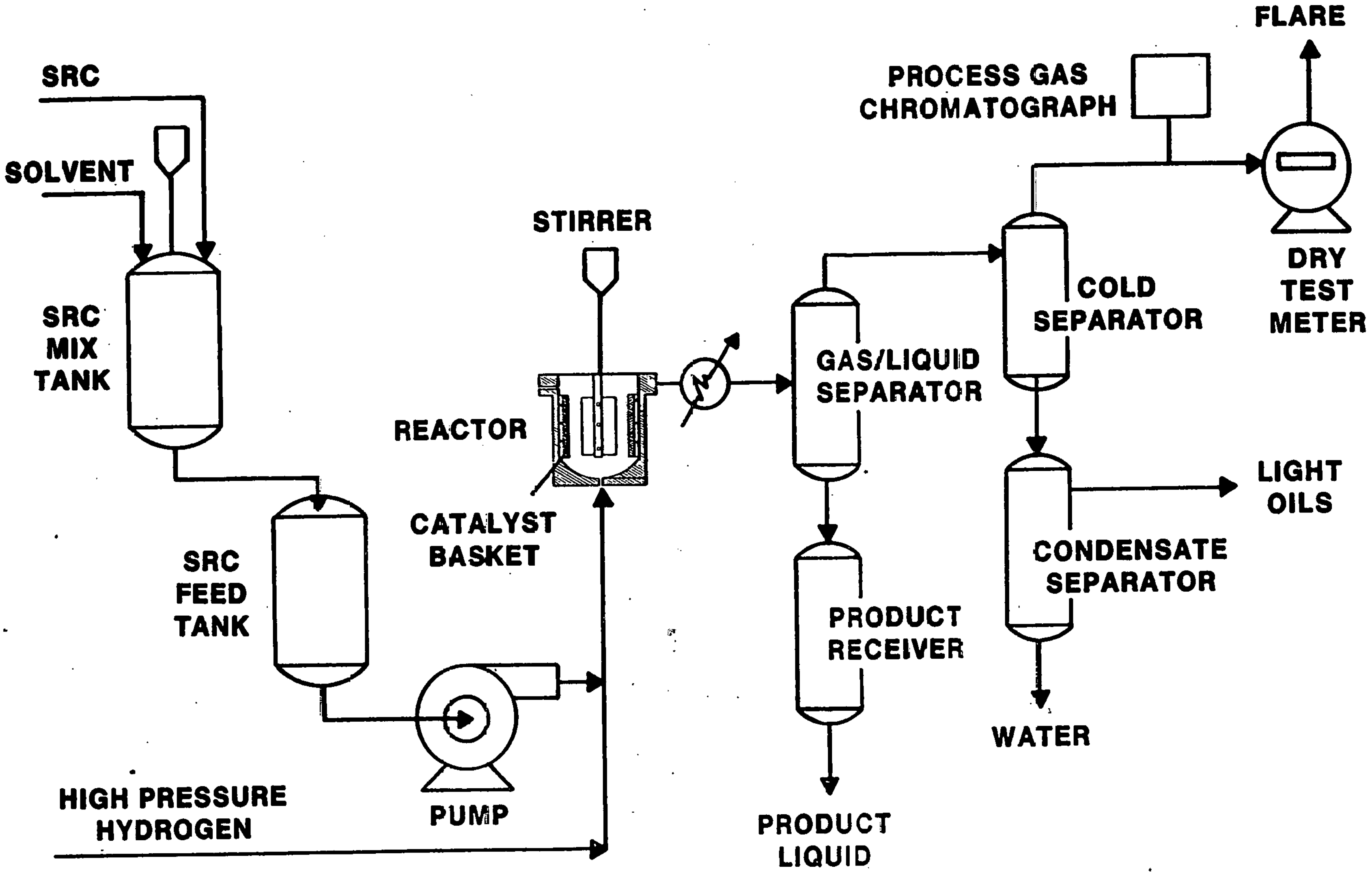


FIGURE C-2
WILSONVILLE PILOT PLANT SCHEMATIC FLOW SHEET

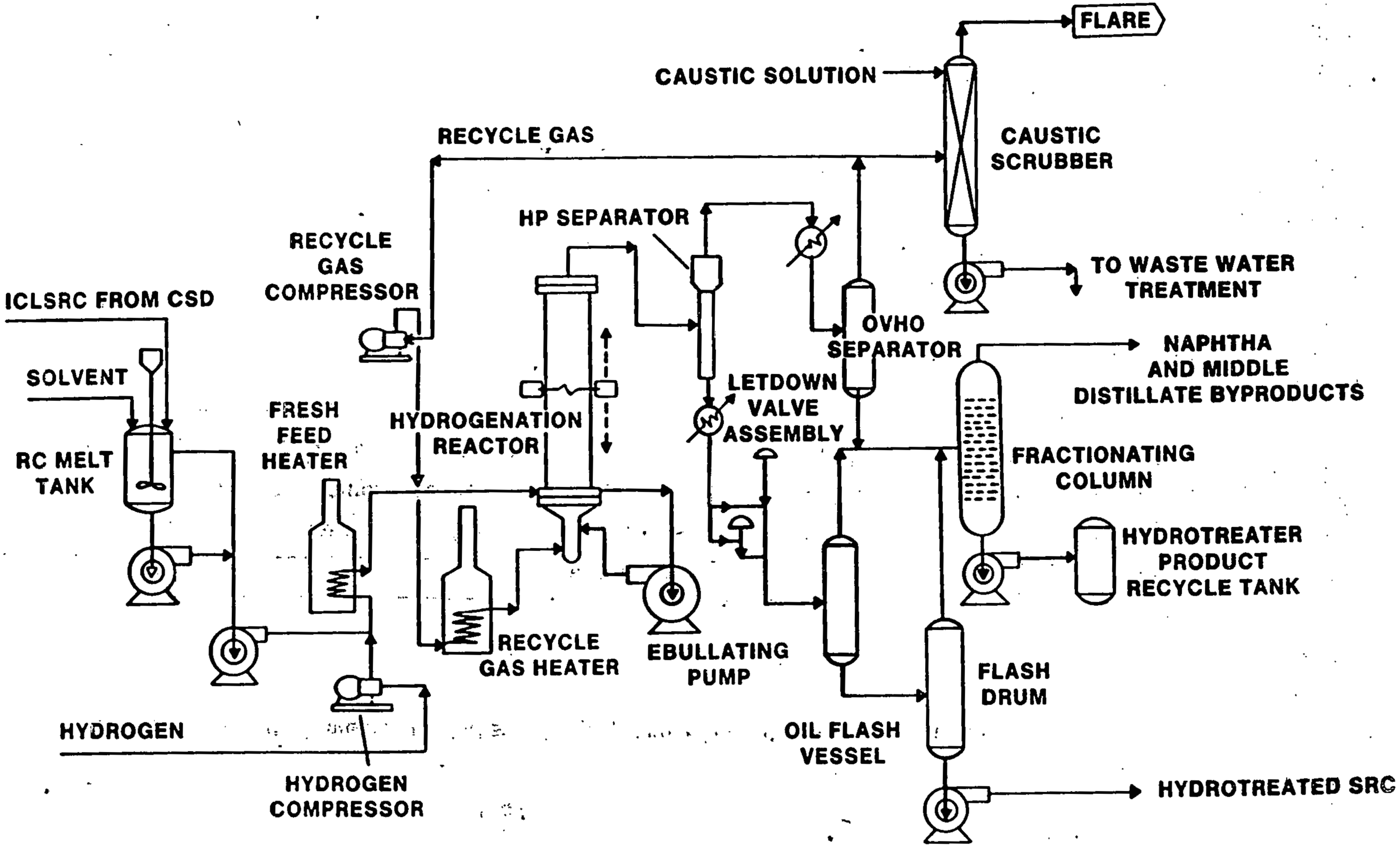


Table C-2

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

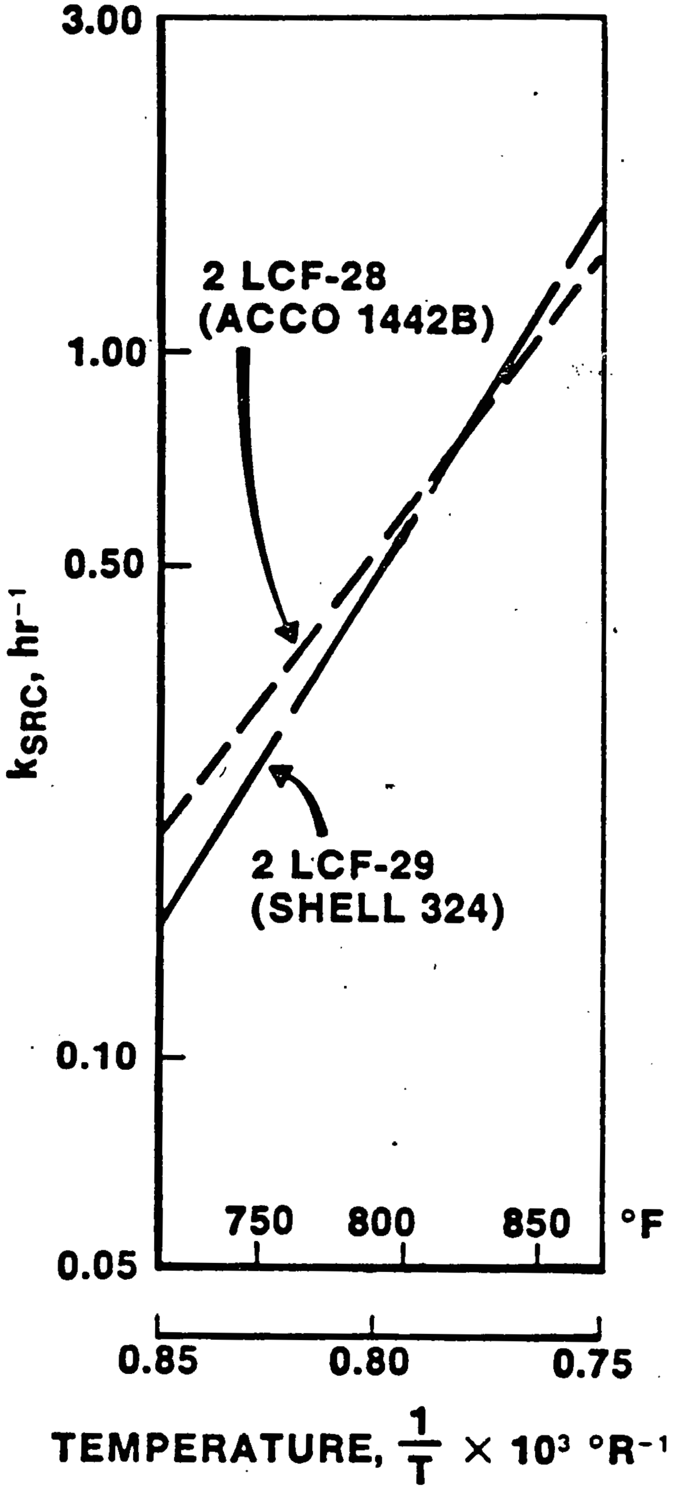


Figure C-4 and Reference 11). Based on this information and on the data in Table C-4, the Wilsonville catalyst activity was calculated as a function of temperature and plotted in Figure C-5. The data clearly indicate that the catalyst activity noted at Wilsonville is much higher than that noted at the 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

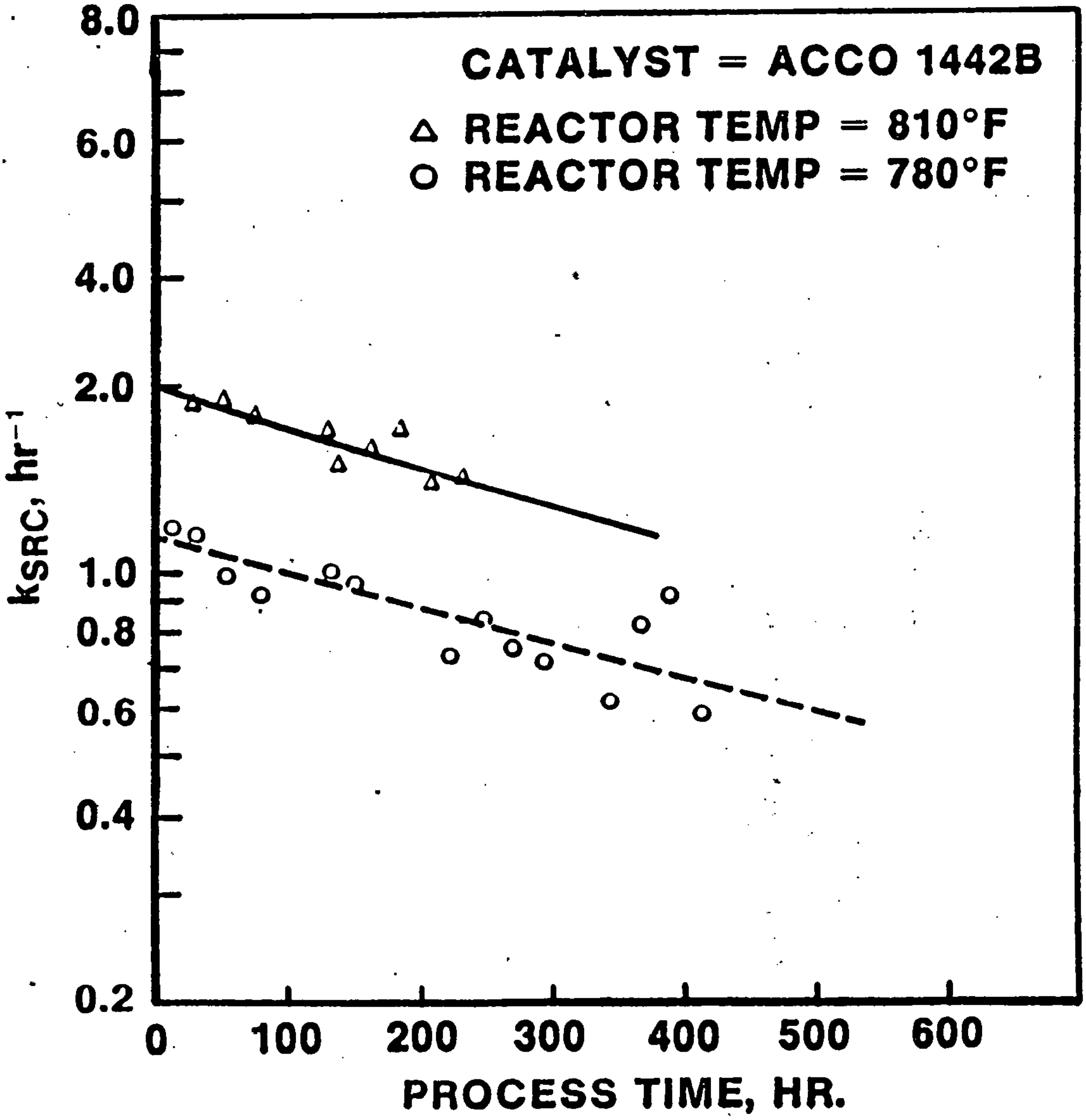


FIGURE C-5
RATE CONSTANT FOR SRC CONVERSION VERSUS REACTOR TEMPERATURE

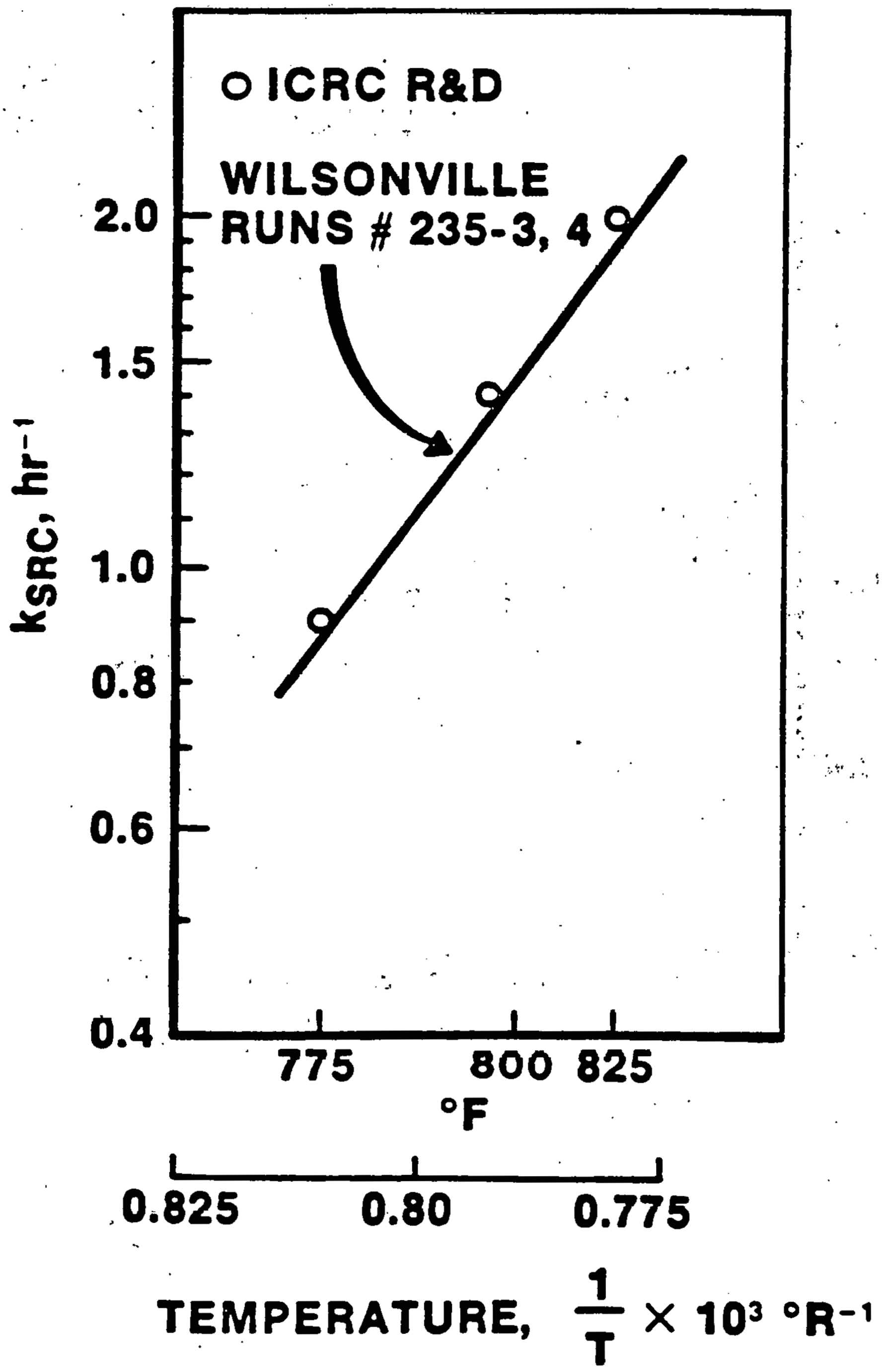
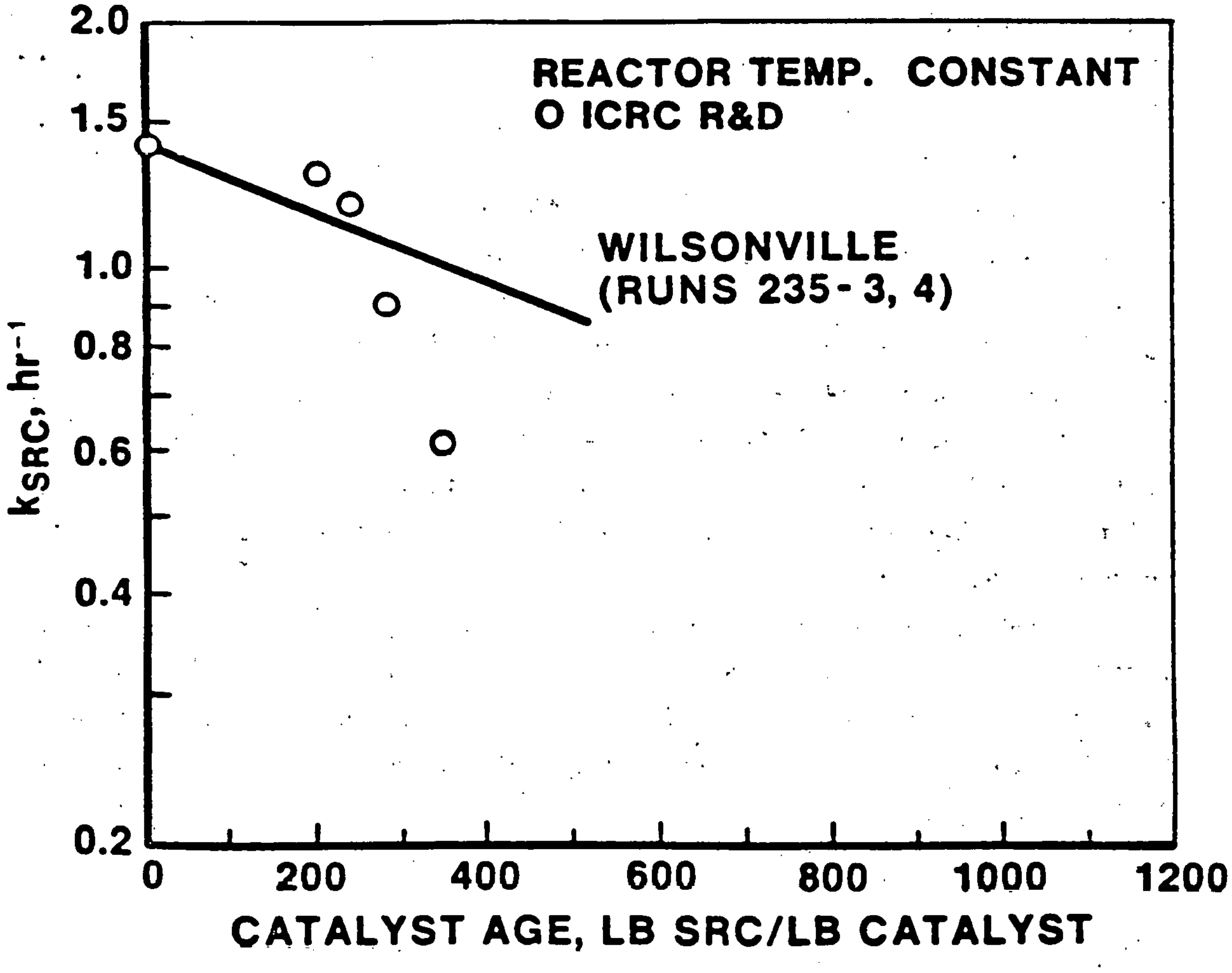


FIGURE C-6
RATE OF CATALYST DEACTIVATION VERSUS SRC FEED RATE



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

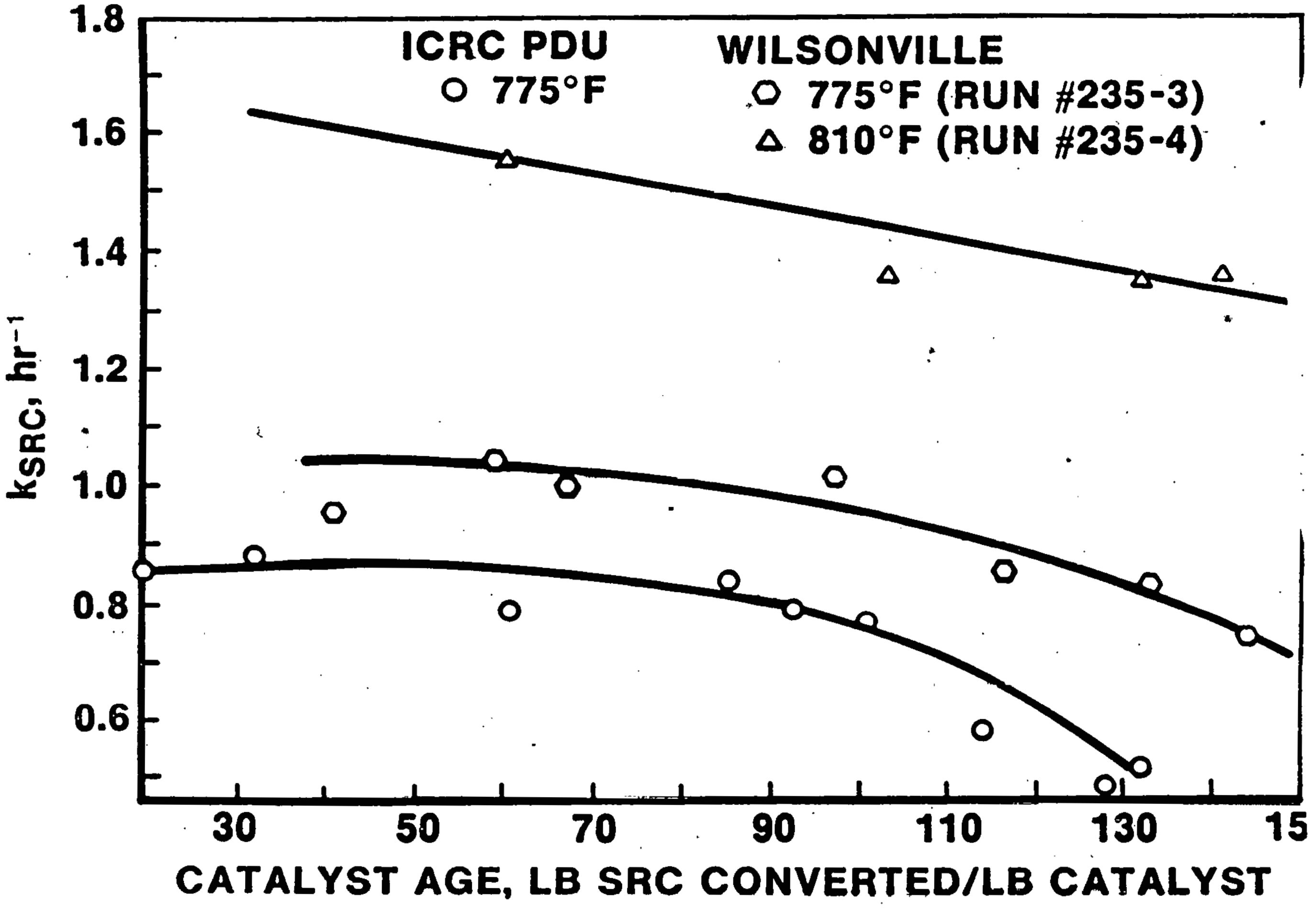
Another interesting point was noted when the catalyst age data were evaluated not as a function of lb SRC processed per lb catalyst, but as a function of actual "work" performed by the catalyst (i.e., SRC converted). This approach tends to eliminate all the variations due to changes in SRC conversion 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

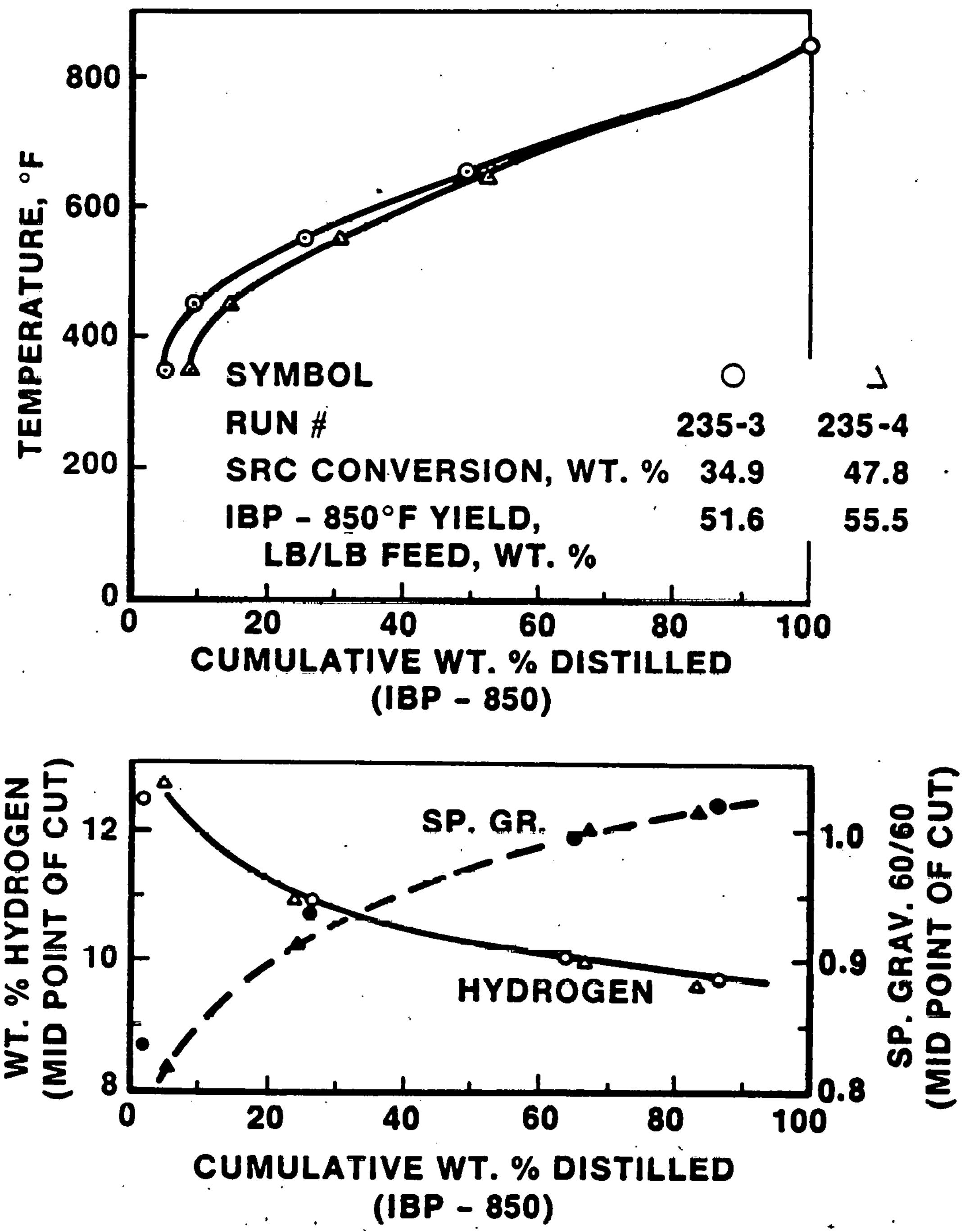
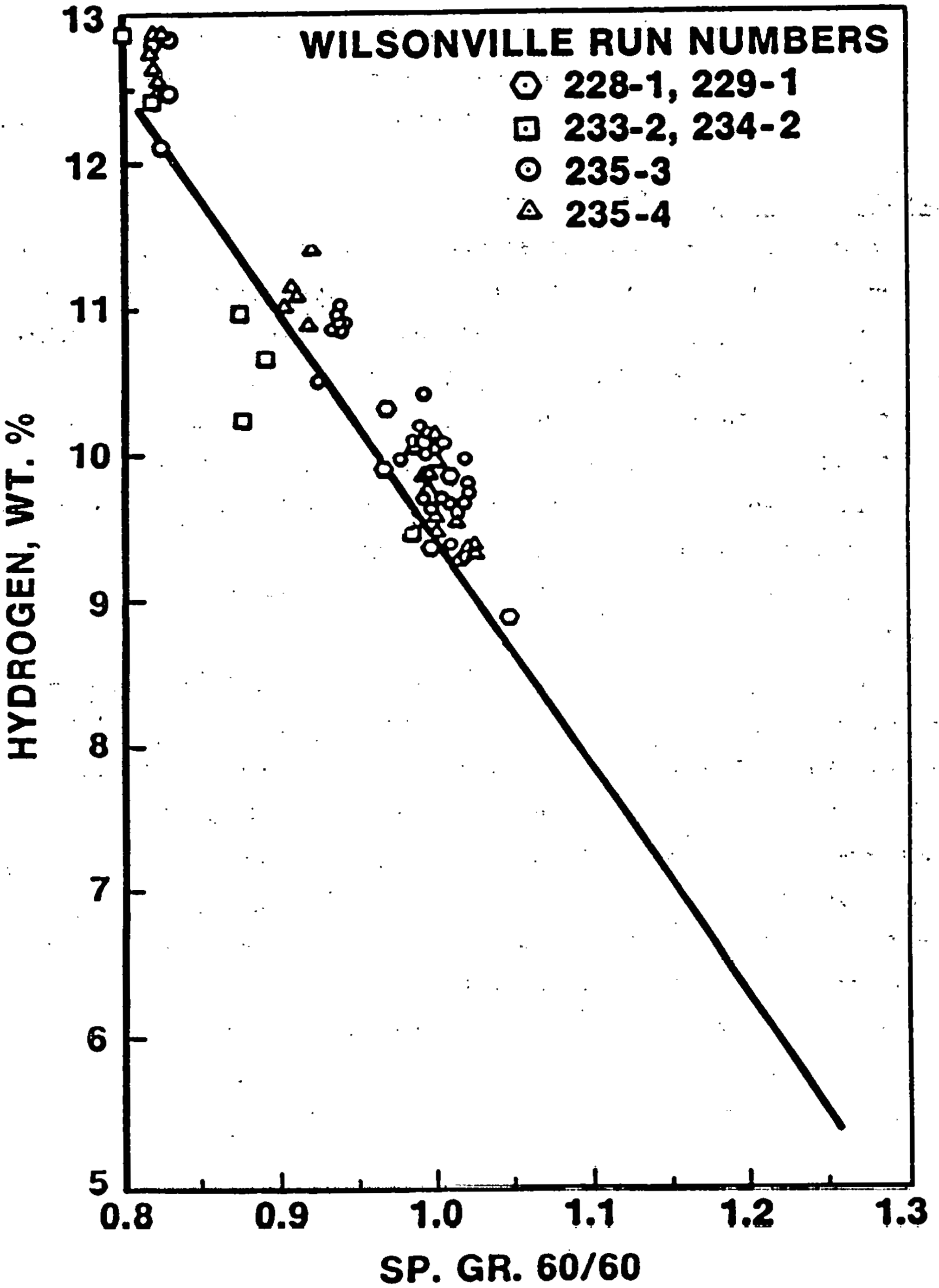


FIGURE C-9
VARIATION OF HYDROGEN CONTENT VERSUS SPECIFIC GRAVITY OF DISTILLATE OILS



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.