245
5-24-84 JSD

DR-0079-5

DOE/PC/50041-30
(DE84008341)

Energy

F
O
S
S
I
L

THE WILSONVILLE ADVANCED COAL LIQUEFACTION
RESEARCH AND DEVELOPMENT FACILITY, WILSONVILLE,
ALABAMA

Topical Report No. 14: Catalyst Activity Trends in Two-Stage
Coal Liquefaction

February 1984
Date Published

Work Performed Under Contract No. AC22-82PC50041

Catalytic, Inc.
Wilsonville, Alabama

Technical Information Center
Office of Scientific and Technical Information
United States Department of Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Printed Copy A06
Microfiche A01

Codes are used for pricing all publications. The code is determined by the number of pages in the publication. Information pertaining to the pricing codes can be found in the current issues of the following publications, which are generally available in most libraries: *Energy Research Abstracts (ERA)*; *Government Reports Announcements and Index (GRA and I)*; *Scientific and Technical Abstract Reports (STAR)*; and publication NTIS-PR-360 available from NTIS at the above address.

THE WILSONVILLE
ADVANCED COAL LIQUEFACTION
RESEARCH AND DEVELOPMENT FACILITY
Wilsonville, Alabama

TOPICAL REPORT NO. 14
CATALYST ACTIVITY TRENDS IN TWO-STAGE COAL LIQUEFACTION

(Published: February 1984)

Prepared by
CATALYTIC, INC.
Wilsonville, Alabama 35186

Subcontractor to
SOUTHERN COMPANY SERVICES, INC.
Birmingham, Alabama 35202
Contract No. 43850

Prepared for
THE UNITED STATES DEPARTMENT OF ENERGY
Contract No. DE-AC22-82PC50041

and

ELECTRIC POWER RESEARCH INSTITUTE
Palo Alto, California 94303
Contract No. RP1234-1-2

THIS PAGE
WAS INTENTIONALLY
LEFT BLANK

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT.....	1
I. INTRODUCTION.....	2
A. Two-Stage Liquefaction Process Evolution	2
B. Modes of Integration.....	3
II. CATALYST COMPARISON STUDIES.....	4
A. Introduction.....	4
B. Physical and Chemical Properties.....	4
C. Screening Studies.....	5
III. PROCESS DATA ANALYSIS.....	8
A. Introduction.....	8
1. Data Base.....	8
2. Reactor Kinetics and Simulation.....	8
B. Effect of Coal Feedstock on Deactivation Rate.....	10
C. Activation Energy Study for SRC Hydrotreatment.....	14
1. SRC Conversion.....	14
2. Nitrogen and Sulfur Removal.....	16
D. Catalyst Deactivation Trends - ITSL Mode	18
1. Introduction.....	18
2. Discussion of Results.....	19
IV. SUPPORTING ANALYTICAL STUDIES.....	22
A. Catalyst Activity Comparison.....	22
1. Model Compound Work.....	22
2. Process Catalyst Activity.....	23
3. Catalyst Property Trends.....	24
B. Catalyst Fouling.....	24
1. Metal Deposition.....	24
2. Deposition of Carbonaceous Material..	26
C. Composition of Flashed Bottoms Product..	27
D. Catalyst Regeneration Studies.....	28

TABLE OF CONTENTS (Continued)

	<u>Page</u>
V. SUMMARIZED CONCLUSIONS AND RECOMMENDATIONS..	30
REFERENCES.....	33
APPENDIX.....	36
A. Changes in Chemical Composition of Flash Bottoms Product - Run 243.....	36
B. Miscellaneous Topics - Process Data Analysis.....	39
C. H/C Atomic Ratio of Carbonaceous Material on Aged Catalyst Samples.....	42
TABLES.....	43
FIGURES.....	64

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Pore Size Distribution Data for Fresh Catalysts (Armak-Ketjen, Shell 324M).....	43
2.	TSL Parameters Included in Data-Base.....	44
3.	Catalyst Deactivation Rate Data for SRC Conversion (NTSL Mode).....	45
4.	Activation Energy for SRC Conversion (Co-Mo Catalyst/NTSL Mode).....	46
5.	Temperature Corrected Deactivation Rate Data for SRC Conversion.....	48
6.	Activation Energy for SRC Conversion for Different Catalyst Types and Integration Modes.	59
7.	Catalyst Deactivation Rate Data for Nitrogen Removal.....	52
8.	Catalyst Deactivation Rate Data for Sulfur Removal.....	53
9.	Catalyst Deactivation Rate Data for SRC Conversion (ITSL Mode - Run 242).....	54
10.	Catalyst Deactivation Rate Data for SRC Conversion (ITSL Mode - Run 243(1)).....	55
11.	Catalyst Deactivation Rate Data for SRC Conversion (ITSL Mode - Run 243(2)).....	56
12.	Model Compound Catalyst Activity as a Function of Age.....	57
13.	Porosimetric Properties of Aged Catalyst Samples from Run 242.....	58
14.	Metals Concentration of Aged Catalyst Samples from Run 242.....	59
15.	Composition of Aged Catalyst Samples from Run 242.....	60
16.	Hydrogenation Activities of Aged Catalyst Samples (Run 242) in Powder and Pellet Form....	61
17.	Bulk and Pellet Densities of Aged Catalyst Samples from Run 242.....	62
18.	¹ H NMR Data for Flashed Bottoms Product Samples from Run 242.....	63

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Single -Stage (Thermal) SRC Unit.....	64
2.	Critical Solvent Deashing Unit.....	65
3.	H-Oil® Ebullated-Bed Reactor.....	66
4.	Hydrotreating Unit.....	67
5.	Non-Integrated Two-Stage Liquefaction Mode....	68
6.	Integrated Two-Stage Liquefaction Mode.....	69
7.	Partially-Integrated Two-Stage Liquefaction Mode.....	70
8.	Pore Size Distribution for Fresh Catalysts (Arnak-Ketjen, Shell 324M).....	71
9.	850°F+ Conversion in Heavy Oil Versus Catalyst Age, PDU Runs LCF-29, 30, 31, 32, 33, 34.....	72
10.	Percent Denitrogenation in Heavy Oil Versus Catalyst Age, PDU Runs LCF-29, 30, 31, 32, 33, 34.....	73
11.	Catalyst Deactivation Rate for Kentucky 9 Coal Feedstock (NTSL Mode).....	74
12.	Catalyst Deactivation Rate for Illinois 6 Coal Feedstock (NTSL Mode).....	75
13.	Activation Energy for SRC Conversion (Co-Mo Catalyst/NTSL Mode).....	76
14.	Temperature Corrected Catalyst Deactivation Feedstocks.....	77
15.	Effects of Catalyst Type and Integration Mode on Denitrogenation Rate Constant.....	78
16.	Effect of Catalyst Type and Integration Mode on Desulfurization Rate Constant.....	79
17.	Catalyst Activity Trends for SRC Conversion (ITSL Mode - Run 242)	80
18.	Catalyst Activity Trends for SRC Conversion (ITSL Mode - Run 243 (1)).....	81
19.	Catalyst Activity Trends for SRC Conversion (ITSL Mode - Run 243 (2)).....	82
20.	Catalyst Deactivation Rate for SRC Conversion for Batch Operation (ITSL Mode).....	83
21.	Comparison of Process and Model Compound Activity Trends.....	84
22.	Effect of Catalyst Age on Pore Volume and Average Pore Diameter for Aged Catalyst Samples from Run 242.....	85
23.	Extraneous Metals Concentration (Ti + Fe + Ca) of Aged Catalyst Samples from Run 242.....	86
24.	Comparison of Bulk and Surface Elemental Concentrations (Semi-Quantitative) by EDX.....	87
25.	Comparison of Bulk and Surface Extraneous Metal Concentrations (Semi-Quantitative) by EDX.....	88

LIST OF FIGURES (Continued)

<u>No.</u>	<u>Title</u>	<u>Page</u>
26.	Calcium and Titanium Line Profile Analysis (130 μ m) Across A Cleaved Pellet (Age - 583 LBS SRC/LB CAT).....	89
27.	Element Micrograph by EDX of a Cleaved Pellet (Age - 583 LBS SRC/LB CAT).....	90
28.	Effect of Catalyst Age on H/C Ratio of Carbonaceous Material on Aged Catalyst Samples from Run 242.....	91
29.	Comparison of the Hydrogenation Activities of Aged Catalyst Samples (Run 242) in Powder and Pellet Form.....	92
30.	Effect of Reactor Temperature and Catalyst Age on the Composition of HTR Flashed Bottoms Product.....	93
31.	Change in the Distribution of Aliphatic and Aromatic Hydrogen in Flashed Bottoms Product (Run 243).....	94

NOMENCLATURE

ABBREVIATIONS

CAT	Catalyst
C-E Lummus	Combustion-Engineering Lummus
Co-Mo	cobalt-molybdenum
CSD	Critical Solvent Deashing
DOE	Department of Energy
EDX	energy dispersive x-ray
EEI	Edison Electric Institute
EPRI	Electric Power Research Institute
ERDA	Energy Research and Development Administration
HDN	hydrodenitrogenation
HN	hydrogenation
¹ H NMR	proton nuclear magnetic resonance spectroscopy
HRI	Hydrocarbon Research Institute
HTR	hydrotreating
ITSL	integrated two-stage liquefaction
LCF	Lummus Cities Finer
Ni-Mo	nickel-molybdenum
Ni-W	nickel-tungsten
NTSL	non-integrated two-stage liquefaction
PDU	process development unit
PETC	Pittsburgh Energy Technology Center
PITSL	partially-integrated two-stage liquefaction
SCT	short contact time
SEM	scanning electron microscopy
SRC	solvent refined coal
THF	tetrahydrofuran
TSL	two-stage liquefaction
wt	weight

SYMBOL DEFINITIONS

a	pore diameter
A	frequency factor (Arrhenius equation)
°A	angstrom
Btu	British thermal units
Ca	calcium
cm	centimeter
C ₁ -C ₅	alkane gases, methane-pentanes
E	activation energy
Ed	activation energy for catalyst deactivation reactions
Fe	iron
ft	feet
gm	gram
hr	hour
H _{ARO}	aromatic hydrogen content

SYMBOL DEFINITIONS (continued)

HALIPH	aliphatic hydrogen content
H/C	hydrogen to carbon ratio
in	inch
KN	denitrogenation rate constant
K _o	intrinsic rate constant
K _s	desulfurization rate constant
K _{SRC}	SRC conversion rate constant
K _{SRC} ^a	temperature corrected SRC conversion rate constant
lbs	pounds
MHz	megahertz
N _F , N _p	nitrogen content in hydrotreater feed, product
R	universal gas constant
S _F , S _p	sulfur content in hydrotreater feed, product
t	process time (<700°F)/SRC processed per unit weight of catalyst
T	reactor temperature
Ti	titanium
V	pore volume
WHSV	weight-hourly space velocity
α	decay coefficient/catalyst deactivation parameter
ε	SRC conversion fraction
μm	micrometer

ABSTRACT

The Two Stage Coal Liquefaction process became operational at Wilsonville in May 1981, with the inclusion of an H-OIL® ebullated-bed catalytic reactor. The two stage process was initially operated in a nonintegrated mode and has recently been reconfigured to fully integrate the thermal and the catalytic stages. This report focuses on catalyst activity trends observed in both modes of operation.

A literature review of relevant catalyst screening studies in bench-scale and PDU units is presented. Existing kinetic and deactivation models were used to analyze process data over an extensive data base. Based on the analysis, three separate, application studies have been conducted. The first study seeks to elucidate the dependence of catalyst deactivation rate on type of coal feedstock used. A second study focuses on the significance of catalyst type and integration mode on SRC hydrotreatment. The third study presents characteristic deactivation trends observed in integrated operation with different first-stage thermal severities.

In-depth analytical work was conducted at different research laboratories on aged catalyst samples from Run 242. Model hydrogenation and denitrogenation activity trends are compared with process activity trends and with changes observed in catalyst porosimetric properties. The accumulation of metals and coke deposits with increasing catalyst age, as well as their distribution across a pellet cross-section, are discussed. The effect of catalyst age and reactor temperature on the chemical composition of flashed bottoms product is addressed. Results from regenerating spent catalysts are also presented.

I. INTRODUCTION

A. TWO-STAGE LIQUEFACTION PROCESS EVOLUTION

The Southern Company and the Edison Electric Institute (EEI) jointly initiated a coal liquefaction research and development program in March 1972. The program supported the construction of a 6 tpd thermal coal liquefaction facility at Wilsonville, Alabama. A Single-Stage thermal unit (Figure 1) was designed and installed by Catalytic, Inc., using technology initially developed in Germany (1932) and later refined by the Pittsburgh and Midway Coal Mining Co.

In April 1973, the Electric Power Research Institute acquired the program sponsorship role from EEI. The United States Department of Energy (DOE), originally known as the Energy Research and Development Administration (ERDA), has been a co-sponsor of the program since 1976. An improved solids separation system - the Critical Solvent Deashing Unit (Figure 2), designed by the Kerr-McGee Corporation, was installed in 1978. The primary product from the combined units was a solid, solvent refined coal (SRC). It was recognized then, that by the addition of a Second-Stage Catalytic Hydrotreating (HTR) unit, further upgrading of the SRC product could be achieved.

Hydrocarbon Research, Inc. provided the technology for the design of the H-OIL® ebullated-bed reactor (Figure 3). The HTR unit (Figure 4) was engineered and installed by Catalytic, Inc. and has been operational since May 1981. The inclusion of the HTR unit signalled the advent of the Two-Stage Liquefaction (TSL) Process at Wilsonville.

The past two years experience with TSL operation has effectively demonstrated the following achievements:

- SRC could be catalytically upgraded into a cleaner burning fuel by increasing its hydrogen content and reducing its sulfur and nitrogen levels. By employing a continuous SRC recycle, all the SRC may be converted to distillate products.
- Product slate flexibility could be improved (more liquid production and less gas-make) by independently varying the severities in the thermal and catalytic stages.
- Hydrogen could be effectively utilized by using a selective catalyst, i.e. a higher lb distillate per lb hydrogen efficiency could be obtained.

The TSL operation would be of relative economic advantage if the savings realized from the resulting process performance

improvements, outweighs the additional cost to be incurred for the HTR reactor and catalyst. Evidently, a catalyst with a higher activity for an extended period of time, would be preferable. This report seeks to analyze hydrotreater operating data and to present catalyst activity trends over the broad range of experimentation performed at Wilsonville.

B. MODES OF INTEGRATION

The inclusion of a hydrotreater enables two-stage operation in various modes of integration. Kerr-McGee Corporation has investigated six different integration modes, utilizing a TSL bench-scale unit (Ref. 1). At the Wilsonville facility, efforts were largely directed toward nonintegrated two-stage liquefaction (NTSL) operation and recently toward integrated two-stage liquefaction (ITSL) operation. The associated yield structures and relative merits for each of these operation modes has been discussed (Ref. 2).

A fundamental difference between integration modes lies in the recycle of HTR streams to the Thermal unit. In the NTSL mode (Figure 5), the Thermal, CSD, and the HTR units are combined sequentially without the recycle of any stream from the HTR unit to the Thermal unit. Hydrotreated SRC is withdrawn as a product and the hydrotreated solvent is recycled within the HTR unit. In the ITSL mode (Figure 6), both the hydrotreated SRC and solvent streams are combined and recycled to the Thermal unit. A few runs at Wilsonville investigated another process option: the partially integrated two-stage liquefaction (PITSL) mode (Figure 7), in which the hydrotreated solvent is recycled within the HTR unit (as in the case of the NTSL mode), but 30-50% of the product SRC is recycled to the Thermal unit.

The process configurational differences among integration modes result in differences in feedstock properties to the hydrotreater, which may affect catalyst deactivation rates. Hence, in this report, each integration mode will be treated separately, and comparisons will be drawn, only when applicable.

II. CATALYST COMPARISON STUDIES

A. INTRODUCTION

In the past two years of operation, four different types of catalyst have been used in the H-OIL® ebullated-bed reactor. The physical and chemical properties of the fresh catalyst are presented in this section. The effect of catalyst age on the properties of spent catalysts is discussed in a following chapter.

To meet specific product slate objectives, the reaction conditions employed at the hydrotreater had to be varied for different runs. Hence, a direct comparison of the activity and selectivity to form desired products is not attempted for the four catalysts. Screening studies for these catalysts have been pursued by other researchers. A review of their results are given in Section C.

B. PHYSICAL AND CHEMICAL PROPERTIES

The physical properties of the four catalysts used at Wilsonville are listed in the following table. HDS 1442A and HDS 1442B were provided by the American Cyanamid Company. Both HDS 1442A and HDS 1442B are cobalt-molybdenum catalysts, whereas Aramak-Ketjen and Shell 324M are nickel-molybdenum catalysts. The catalysts were of extrudate form and were of 1/32 inch and 1/16 inch pellet diameter.

Physical Properties of Fresh Catalysts

<u>Property</u>	<u>HDS 1442B</u>	<u>HDS 1442A</u>	<u>Armak-Ketjen</u>	<u>Shell 324</u>
Shape	Extrudate	Extrudate	Extrudate	Extrudate
Diameter (inch)	1/32	1/16	1/32	1/32
Compacted Bulk Density (lb/ft ³)	34	38	33	53
Surface Area (m ² /gm)	320	330	350	185
Pore Volume (cm ³ /gm)	0.83	0.72	0.70	0.45
Micro Pore Diameter (°A)	50	50	46	98
Macro Pore Diameter (°A)	2,200	1,500	1,500	None

With the exception of Shell 324M, the catalysts were of bi-modal pore distribution. Table 1 lists pore-size distribution data for Aramak-Ketjen and Shell 324M catalysts; the data has

been plotted in Figure 8. Armak-Ketjen catalyst has a larger total pore-volume than Shell 324M. A large percentage of this volume is, however, incorporated in the micropores ($\approx 45^\circ \text{A}$). Shell 324M, a unimodal catalyst, has most of its pore volume in the $80\text{--}115^\circ \text{A}$ region. A typical pore-size distribution for fresh HDS 1442A catalyst has been given (Ref. 3).

The chemical properties of the catalysts are listed below. Shell 324M has the highest metals loading (16.1 wt %) and therefore has a higher bulk density than the other catalysts used.

Chemical Properties of Fresh Catalysts

	<u>HDS 1442B</u>	<u>HDS 1442A</u>	<u>Armak-Ketjen</u>	<u>Shell 324M</u>
Metal Content (Wt %)				
Molybdenum	7.9	9.8	8.6	13.4
Nickel	-	-	3.7	2.7
Cobalt	2.5	2.7	-	-
HDS Activity Index	NA	35	NA	79

C. SCREENING STUDIES

A screening study, designed to evaluate six commercially available catalysts, has been performed at the Lummus PDU (Ref. 4). This work is of relevance to the Wilsonville program for the following reasons:

- The expanded bed LC-Finer used in the Lummus PDU resembles the ebullated-bed H-OIL[®] reactor used at Wilsonville;
- The solvent refined coal extract used as LC-Finer feedstock is similar to the SRC used as hydrotreater feedstock at Wilsonville;
- The reactor space velocity as well as the SRC/solvent ratio of the feed are comparable for both the units.

The solvent used in the study was a heavy fraction of a pre-hydrogenated Koppers Heavy Residue Creosote oil. The catalyst types investigated were: cobalt-molybdenum, nickel-tungsten and nickel-molybdenum. The reactor space velocity, pressure and SRC/solvent feed ratio were held constant for the runs, and the data obtained was normalized to a temperature of 810°F .

The conversion of SRC ($850^\circ \text{F}+$) and the percent denitrogenation obtained from these runs have been plotted against catalyst age in Figures 9 and 10. The following inferences were drawn from the trends observed in the figures as well as from elemental and fractionation analyses of the products.

- In general, nickel-molybdenum catalysts provide a greater conversion of 850°F+ SRC material to lighter products;
- Nickel-molybdenum catalysts produce more IBP-390°F and 390°F-500°F fractions;
- Nickel-molybdenum catalysts show a greater degree of hydrogenation, deoxygenation, and denitrogenation in all the heavy oil fractions.

Shell 324M was found to be superior to the Co-Mo, Ni-W and the other Ni-Mo catalysts with respect to 850°F+ conversion and denitrogenation.

Stiegel et al. have conducted bench-scale catalyst screening studies on nickel-molybdate catalysts of varying properties, using a 50 wt % mixture of SRC I in prehydrogenated creosote oil (Ref. 5,6). Their results are summarized below:

- Higher metals loading was found to be beneficial for hydrogenation, whereas both higher metals loading and larger pores result in increased denitrogenation;
- Bimodal catalysts accumulate more coke and metals than unimodal catalysts;
- Unimodal catalysts are capable of being restored to their original state upon regeneration (controlled oxidation), whereas bimodal catalysts suffer a small loss of surface area and pore volume.

Other investigators have conducted catalyst screening studies on bench-scale units in support of the H-Coal process (Ref. 3), where the catalyst contacts the feed coal. Some of the interesting observations were:

- Nickel-molybdenum, nickel-tungsten and tin-molybdenum catalysts were similar to cobalt-molybdenum catalyst with respect to liquefaction conversion, resid desulfurization, product viscosity and hydrogen content.
- A bimodal pore distribution was preferable with macro feeder pores of diameter ~1000Å, and micropore diameters in the 100-200Å range. Pores smaller than 50Å were found to be very susceptible to plugging by coke. Pores of about 100Å diameter appeared to be most effective for overall and distillate desulfurization.

Mitchell et al. have screened fresh and aged catalysts (Cyanamid 1442A, Cyanamid Ni-Mo, Armak Ni-Mo, Amocat 1A, and Amocat 1B), for hydrogenation, hydrocracking, isomerization, desulfurization, denitrogenation, and deoxygenation activities, using model compound mixtures (Ref. 7). The aged catalysts were obtained from aging tests that simulated the H-Coal process. The results indicated that the nickel-molybdenum catalysts were the most active for cracking, denitrogenation and deoxygenation reactions. They were comparable with Cyanamid 1442A (Co-Mo) and Amocat 1A (Co-Mo) for hydrogenation and desulfurization reactions. Amocat 1B (Mo) was found to be the least active catalyst from these model compound studies.

III. PROCESS DATA ANALYSIS

A. INTRODUCTION

This section of the report presents an analysis of hydro-treater unit operating data and discusses the results obtained from the analysis. Three separate studies have been performed, and will be described separately (Section B, C, and D) for the purpose of clarity.

1. DATA BASE

The data base examined in this work is fairly extensive, and includes HTR unit data from Runs 233-243. These runs cover a time span from August 1981 - June 1983, and represent approximately 93% of the process time since the HTR unit has been on-stream.

In a TSL operation (NTSL and ITSL), the heavy component of the feedstock to the HTR unit is processed in both the SRC and CSD units. A change in any operating parameter in these preceeding units could presumably affect HTR feedstock. A rigorous analysis of the HTR should not only investigate the effects of changes in HTR reactor parameters, but should also incorporate the above-mentioned changes in feedstock that might occur. Such an extensive analysis would be extremely complicated to conduct and could conceivably limit the inferences that may be drawn.

The important two-stage liquefaction parameters (qualitative and quantitative), that are believed to influence hydrotreater performance are listed in Table 2. The table indicates that the runs included in the data base cover a broad perspective of changes in each of the major TSL operating parameters. The effect of these parametric changes on catalyst activity and deactivation trends will be addressed in the following sections.

2. Reactor Kinetics and Simulation

A simplified three-lump, first-order, kinetic model has been developed for an ideal, stirred-tank reactor (Ref. 8). The model enables an SRC conversion rate constant (K_{SRC}) to be obtained in terms of SRC conversion (ϵ), and a weight-hourly space velocity (WHSV), as follows:

$$K_{SRC} = WHSV \frac{\epsilon}{1-\epsilon} \quad (1)$$

WHSV and ϵ are variables that are determined from process and laboratory measurements.

Conversion of SRC to lighter products has been shown to be due to both catalytic as well as thermal reactions (Ref. 9). The thermal baseline for SRC conversion is not available for the Wilsonville hydrotreater. For a given set of operating conditions, thermal conversion should, however, be independent of catalyst age and hence trends observed with the SRC conversion rate constant should be indicative of catalyst activity trends. Catalyst deactivation rate is monitored in terms of the decline of the conversion rate constant with age. Conversion of SRC to oils (pentane solubles) has been found to be strongly influenced in the presence of a catalyst; formation of oils from thermal reactions was shown to be insignificant (Ref. 9,10). Hence, conversion of SRC to oils might be a better indication of catalyst activity. However, oil formation as determined from a laboratory product fractionation analysis (Soxhlet extraction) would incorporate more error as compared with total SRC conversion (as determined by a modified ASTM vacuum-distillation), which has prompted the use of the latter for correlating purposes.

An activity decay model, proposed by Szepe and Levenspiel, has been used to describe the decay of the SRC conversion rate constant with catalyst age (Ref. 11):

$$K_{\text{SRC}} = K_0 e^{-\alpha t} \quad (2)$$

This model permits evaluation of two constants: K_0 , the intrinsic activity of the catalyst and α , the decay coefficient. The decay coefficient is a characteristic deactivation parameter and will be used to compare deactivation rates among different runs.

The classical Arrhenius equation has been used to relate the dependence of the rate constant on temperature:

$$K_{\text{SRC}} = A e^{\frac{-E}{RT}} \quad (3)$$

The activation energy for SRC conversion (E) may be evaluated from this expression from data for a reactor temperature change at a fixed catalyst age.

An overall reactor simulation program has been developed, based on the above models and certain heuristic correlations (Ref. 8). The program has been used to simulate reactor performance, i.e., SRC conversion, hydrogen consumption, product yield structure

and elemental content of the hydrotreated SRC, for all the runs included in the data-base (Ref. 8,12). The predicted values from simulation showed reasonably good agreement with the observed values obtained from process data computations. This result suggests that the kinetic and deactivation models used in the simulation were applicable for the data base investigated, and have been used as the basis in analyzing process data in the following studies.

B. EFFECT OF COAL FEEDSTOCK ON DEACTIVATION RATE

The feed coal at Wilsonville has been of bituminous rank ever since the HTR unit has been operational. The origin of the coal, however, has been changed from the Kentucky 9 Fies mine to the Illinois 6 Burning Star Mine. A previous report (Ref. 8), showed the dependence of deactivation rate on the feed coal processed, with the limited amount of data available at the time. This study aims at improving on the generality of that inference drawn, by including the maximum available amount of pertinent data. In order to study only feedstock effects and eliminate the effect of catalyst type and operation mode on the rate of deactivation, the runs selected for analysis employed a similar type of catalyst (Cobalt-Molybdenum), and had a similar mode of operation (NTSL).

The SRC conversion rate constant, K_{SRC} , can be easily computed from equation (1) if the SRC conversion (ϵ) and space velocity (WHSV) are known. This data has been obtained from previous quarterly/run reports. Table 3 summarizes deactivation rate data for Run 235 (Ref. 13), Run 236 (Ref. 14), and Run 240 (Ref. 15). Figure 11 is a semi-log plot of the SRC conversion rate constant versus process time for Kentucky 9 Fies coal feed (Run 235 at 780°F and 810°F). Figure 12 shows a similar plot for Illinois 6 coal (Run 236 at 780°F and Run 240 at 760°F). These plots are based on the exponential decay model described by equation (2). Hence, the intercept (at zero time) would correspond to the intrinsic rate constant, K_0 , while the slope of the line would yield the deactivation parameter, α . Least-square straight lines have been drawn through each set of data points in Figures 11 and 12.

An increase in reactor temperature by 30°F (Figure 11), results in a significant increase in the intrinsic rate constant. The deactivation parameters were, however, about the same at both temperatures. The dependence of the deactivation parameter on temperature has been shown on bench-scale units (Ref. 16,17). For the Wilsonville reactor, however, the deactivation parameter appears to be independent of reactor temperature over the range of temperature that has been investigated.

The runs examined in Figure 12, 236 and 240, have differences in not only reactor temperature, but also in catalyst extrudate size and first-stage severity. The effect of catalyst diameter on deactivation rate has been investigated, and it was found that deactivation rate decreased with an increase in catalyst diameter (Ref. 10). The cumulative effects of a lower reactor temperature, larger catalyst diameter and higher first-stage severity in Run 240 should have yielded a comparatively lower deactivation parameter than Run 236. However, the difference in the deactivation parameters for the two runs is statistically insignificant. Although these parameters should influence deactivation rate, the above observation suggests that the magnitudes of the changes in these parameters were not large enough to have appreciably affected the rate of deactivation.

A comparison of the catalyst deactivation rates for Kentucky 9 and Illinois 6 coal feedstocks would necessitate temperature correcting the data plotted in Figures 11 and 12. The SRC conversion rate constant is a function of reactor temperature and process time, and may be written as:

$$K_{SRC} = K_0' e^{-\alpha t} \cdot e^{-E/RT} \quad (4)$$

A temperature corrected rate constant, K_{SRC}'' , may be defined that is purely a function of process time:

$$K_{SRC}'' = \frac{K_{SRC}}{e^{-E/RT}} \quad (5)$$

The data required for determination of activation energies for accomplishing this correction is listed in Table 4. The activation energies were obtained from the slopes of the Arrhenius plots shown in Figure 13. Activation energies for the conversion of SRC derived from Kentucky 9 coal were about the same magnitude for feedstocks from both low and high first-stage severities (Runs 234 and 235, respectively). This result enabled the determination of an activation energy for SRC conversion for Illinois 6 coal from Runs 236 and 240, that were also at different first-stage severity levels. The activation energy for Illinois 6 coal was observed to be in the same range as that obtained with Kentucky 9 coal.

The temperature corrected rate constant data for both coal feedstocks is listed in Table 5, and is plotted as a function of process time in Figure 14. Least square straight lines have been drawn through both sets of data points, to provide a direct comparison of the deactivation rates for the two feed coals. The results obtained from the least square analysis are the following:

	α	$K_0'(\text{HR}^{-1} \times 10^{-8})$	Corr. Coeff.
Kentucky 9 Coal	0.00145	1.30	-0.83
Illinois 6 Coal	0.00034	1.25	-0.72

It is interesting to observe that the temperature corrected data yields approximately similar intrinsic rate constants for both coal feedstocks. However, the deactivation parameter for Kentucky 9 coal is about 4 times the magnitude of the deactivation parameter for Illinois 6 coal. This result strongly suggests that the rate of catalyst deactivation for SRC derived from Kentucky 9 coal was significantly higher in comparison to that derived from Illinois 6 coal.

As explained later in this report, catalyst deactivation is caused by deposition of carbonaceous materials, extraneous metal deposition and adsorption of nitrogen compounds (poisons). The carbon and nitrogen contents for aged catalyst for both coals is shown below:

	Kentucky 9 Coal		Illinois 6 Coal	
	Run 3-235	Run 4-235	Run 236	Run 240
Process Time (hrs)	431	272	430	760
Wt % Carbon	22.14	13.61	11.95	11.56
Wt % Nitrogen	0.43	0.26	0.68	0.69

The above data clearly indicate that for comparable catalyst age (process time), the carbon content on an aged catalyst is much higher for Kentucky 9 coal. This observation is consistent with and could explain the higher deactivation parameter

obtained for Kentucky 9 coal. The nitrogen content is, surprisingly, higher for Illinois 6 coal feedstock, but the differences are marginal and might not have had a major influence on deactivation rate.

In order to identify the cause for the comparatively higher carbon content for Kentucky 9 coal feed, the chemical properties of the HTR feed (CSD-SRC and solvent) need to be investigated. The data in the following table has been derived from special product work-up periods in each of the runs.

	Kentucky 9 Coal		Illinois 6 Coal	
	Run 3-235	Run 4-235	Run 236	Run 240
First Stage Severity	High	High	Low	High
CSD-SRC				
Wt % Preasphaltenes	18.9±4.1	17.7±4.0	23.2±1.9	17.1±4.3
H/C Atomic Ratio	0.83±0.02	0.84±0.02	0.86±0.01	0.84±0.03
HTR Solvent				
Wt Fraction (>650°F)	0.64	0.64	0.67	0.64
H/C Atomic Ratio	1.35±0.03	1.34±0.03	1.37±0.02	1.34±0.04
Kinetic Activity	78.0±2.6	75.3±3.6	77.8±1.1	73.7±3.4
Equilibrium Activity	81.4±2.3	82.0±2.2	80.8±0.5	80.1±1.8

For constant reactor temperature and pressure, coke formation would be enhanced by a higher preasphaltenic content and a corresponding lower H/C ratio in the CSD-SRC feed (Ref. 16). A heavy solvent with a low H/C ratio and high kinetic and equilibrium activity should inhibit coking reactions from occurring (Ref. 21).

In light of what has been stated above, the trends in the preceding data are not in accordance with the observation of a higher carbon content on the catalyst for Kentucky 9 coal feedstock. The differences in H/C ratios, kinetic and equilibrium activities for the two feedstocks, are statistically irrelevant. The comparatively higher preasphaltenic content of CSD-SRC and marginally heavier HTR solvent in Run 236 could be a result of the low first-stage severity employed.

In summary, it is difficult to isolate the cause of the seeming dependence of deactivation rate and carbon deposition on the type of coal processed. The available data of macroscopic chemical properties of aged catalyst and feedstock does not provide any clue to explain the observed findings. ¹H-NMR analysis (proton-types) and Mass-spectrometry analysis (types of compounds, chain-linkages etc.) of the feed would provide 'microscopic' insight, and might better explain the effect of coal feedstock on catalyst deactivation rate.

C. ACTIVATION ENERGY STUDY FOR SRC HYDROTREATMENT

Since the HTR unit has been on stream, the operation mode has evolved from NTSL to ITSL, via a PITSL mode. Catalyst type has been changed from a Cobalt-Molybdenum (Co-Mo) to a Nickel-Molybdenum (Ni-Mo) based catalyst. This study was aimed at evaluating the significance of the changes in type of catalyst and integration mode on the hydrotreatment of SRC. The hydrotreatment process would include the following classes of reactions, which have been examined in this study:

1. SRC Conversion

Activation energies for SRC conversion have been obtained from runs that employed different combinations of catalyst type and integration modes. The data for activation energy determination is listed in Tables 4 and 6, and the results are summarized below:

<u>Run No.</u>	<u>Catalyst</u>	<u>Integration Mode</u>	<u>Activation Energy</u> (Btu/lb mole)
234	HDS-1442B (Co-Mo)	NTSL	45,600
238,239	HDS-1442B (Co-Mo)	PITSL	37,100
241	Armak-Ketjen (Ni-Mo)	NTSL	27,700
242	Shell 324M (Ni-Mo)	ITSL	28,400

From the above data, it may be inferred that Ni-Mo catalysts result in lower activation energies than Co-Mo catalyst, irrespective of integration mode. This suggests that the Ni-Mo catalysts used are preferable for SRC conversion reactions. Work done at the C-E Lummus PDU appears to verify this finding (Ref. 4). Also, Shell 324M catalyst (Ni-Mo) has been recognized for its superior hydrogen uptake and nitrogen removal capability as compared with its Co-Mo counterpart (Ref. 25).

Comparison of Runs 238-239 with Run 234 indicates a lower activation energy for the partially-integrated operation mode, the catalysts used in both cases being identical. The finding that an integrated mode of operation appears to lower activation energy would prompt expectation that Run 242 (ITSL) should have yielded a lower activation energy than Run 241 (NTSL). The data, however, indicates otherwise. The apparent anomaly could be explained if Armak-Ketjen catalyst (Run 241) were a stronger catalyst for SRC conversion than Shell 324M (Run 242). A stronger Ketjen catalyst would tend to decrease the activation energy, and hence compensate for a higher activation energy to be expected for the NTSL operation mode.

To investigate the validity of this hypothesis, a micro-autoclave study was performed to compare the two catalysts (on a weight basis). The results were as follows:

<u>Catalyst</u>	<u>SRC Conversion (%)</u>
Shell 324M	40.0
Armak-Ketjen	52.0

Ketjen catalyst resulted in a higher conversion of SRC to oils (pentane solubles) compared with Shell 324M, confirming the suspected difference in the two catalysts.

The summarized observations thus far indicate that Ni-Mo catalysts and an integrated mode of operation appear to favor SRC hydrotreatment. These findings were based on the computation of activation energy for SRC conversion, which is a sensitive parameter to scatter in the data as well as to the catalyst age at which it is determined. Hence, confirmation was sought by analyzing other independent data to substantiate these findings.

2. Nitrogen and Sulfur Removal

In this section, a study of the trends of denitrogenation and desulfurization rate constants as a function of process time has been attempted for runs that employed different catalysts and integration modes. It was shown earlier that the decay of a rate constant appears to be dependent on the type of coal feedstock used. Hence, in the study, the runs examined used a similar feed coal (Illinois 6).

The denitrogenation and desulfurization rate constants may be obtained from process and laboratory data and have been previously defined (Ref. 8) as:

$$K_N = \text{WHSV} \left\{ \left(\frac{N_F}{N_P(1-\epsilon)} \right) - 1 \right\} \quad (6)$$

$$K_S = \text{WHSV} \left\{ \left(\frac{S_F}{S_P(1-\epsilon)} \right) - 1 \right\} \quad (7)$$

where

K_N, K_S - denitrogenation and desulfurization rate constants
 N_F, S_F - nitrogen and sulfur weight fraction in feed
 N_P, S_P - nitrogen and sulfur weight fraction in product

Tables 7 and 8 lists the denitrogenation and desulfurization rate data for Runs 236, 239 and 241. Figures 15 and 16 show the decay of the these rate constants with process time. Least-square straight lines have been drawn through each set of data points, and the results are presented below:

General Equations: $K_N = K_{N0} e^{-\alpha_N t}$; $K_S = K_{S0} e^{-\alpha_S t}$

K_{N0}, K_{S0} - intrinsic denitrogenation and desulfurization activity
 α_N, α_S - decay coefficient for denitrogenation and desulfurization reactions

	Run 236 (NTSL, Co-Mo)	Run 239 (PITSL, Cu-Mo)	Run 241 (NTSL, Ni-Mo)
K_{N0}	2.81	4.27	4.24
α_N	0.0034	0.0020	0.0022
Corr Coeff	-0.83	-0.81	-0.93
K_{S0}	7.02	13.03	13.17
α_S	0.0029	0.0022	0.0024
Corr Coeff	-0.98	-0.93	-0.91

It is to be noted that the reactor temperature (780°F) was the same for the above three runs. From the Arrhenius equation (3), it may be inferred that for a constant reactor temperature, a comparatively higher rate constant at any given process time would imply a lower activation energy, assuming the frequency factor to be constant for a similar class of reactions. Utilizing this rationale, it is evident from Figures 15 and 16, or from the above data, that Ni-Mo catalyst (Run 241) and the partially-integrated mode of operation (Run 239) result in a lower activation energy for heteroatom removal compared with Run 236 (Co-Mo catalyst, NTSL mode).

These comparative trends are in close agreement with those observed from SRC conversion data and serve to strengthen the inference that SRC hydrotreatment is favored by Ni-Mo catalyst and an integrated mode of operation.

Hydrotreatment of coal-derived material has been recognized to be strongly influenced by the presence of a catalyst. It is understandable, therefore, that a change in catalyst from Co-Mo to an apparently stronger Ni-Mo catalyst should result in an improvement in SRC conversion and in heteroatom removal. It would be interesting if an explanation could be afforded as to why integrating the mode of operation would likewise influence SRC hydrotreatment.

A comparison of feedstock properties to the hydrotreater for different integration modes is shown below. Data from Runs 236 and 239 are comparable since they both employed similar first-stage severity and hydrotreater temperature conditions. Run 242 was not performed under equivalent conditions and the data has been included only to indicate trends.

	Run 236 (NTSL)	Run 239 (PITSL)	Run 242 (ITSL)
<u>CSD-SRC</u>			
Preasphaltenes (wt %)	24.00	9.30	10.25
Asphaltenes (wt %)	49.00	50.85	44.00
Oils (wt %)	27.00	39.85	45.75
Wt % H	5.95	6.55	6.65
C/H Ratio	14.15	13.20	13.10
S (wt %)	1.01	0.81	0.50
N (wt %)	1.35	1.50	1.02
<u>Solvent</u>			
>650°F	2	2	3.55
<650°F	1	1	1
Activity (long test)	81	81	85

Integrating the units results in a lighter CSD-SRC feed to the hydrotreater, evident from the lower preasphaltenic and higher oil content. The lighter CSD-SRC feed has an expectedly higher hydrogen content and a lower heteroatomic content. The reduction in preasphaltenic content to the hydrotreater by integration would imply a lower rate of deposition of carbonaceous material, which in turn would signify a higher aged catalyst activity. This could be a plausible explanation for the lower activation energy for SRC conversion that results from integrating the mode of operation.

The identical solvent properties (boiling fraction distribution and activity) for the NTSL and PITSL modes is possibly a consequence of the continuous recycle of the solvent within the HTR unit (Figures 5 and 7), employed in both of these modes that used similar Co-Mo catalyst. In the ITSL mode (Figure 6), where a Ni-Mo catalyst was used, the recycle of flash bottoms to the Thermal unit appears to result in a much heavier hydrotreater feed solvent of a marginally higher activity.

The donor reactivities/stabilities for different homologous ring series have been studied (Ref. 26), and the following results were obtained and are listed according to reactivity ranking:

Aromatics

Pyrene > Phenanthrene > Anthracene > Naphthalene > Acenaphthylene > Indene

Hydroaromatics

1,2,3,6,7,8 - Hexahydropyrene > 9,10 - Dihydrophenanthrene > 9,10 - Dihydroanthracene >

1,2 - Dihydronaphthalene > Tetralin > Acenaphthene > Indan

These results clearly indicate that larger ring aromatic and hydroaromatic compounds have a higher reactivity to donate and shuttle hydrogen. The heavier solvent that results from integrated operation would be of a reactive nature, and may presumably aid in reducing the activation energy for SRC conversion. The improved SRC hydrotreatment in the integrated mode of operation may be attributed to these identifiable changes in hydrotreater feedstock (CSD-SRC and solvent) properties.

D. CATALYST DEACTIVATION TRENDS - ITSL MODE

1. Introduction

This section discusses trends in the decay of the SRC conversion rate constant with catalyst age for Runs 242, 243(1) and 243(2), which employed the fully-integrated operation mode. Step increases were made in the hydrotreater temperature during the course of each of these runs to comply with specific product-slate objectives. In general, the temperature range investigated,

630-750°F, was lower than the temperature employed (725-830°F) in previous runs (228-241). Due to the differences in reactor temperature, catalyst type, first-stage severity and integration mode, a direct comparison of deactivation trends between the fully-integrated runs and any of the previous runs would not be of much significance. Hence, deactivation trends of the fully-integrated runs will be discussed separately.

Tables 9, 10 and 11 list catalyst deactivation rate data for SRC conversion for Runs 242, 243(1) and 243(2) respectively. The SRC conversion rate constant has been plotted versus catalyst age in Figures 17, 18 and 19, on semi-log coordinates, in accordance with equation (2). A mere inspection of the plots reveals a fair amount of scatter in the data, especially at the lower temperatures (630-690°F). This scatter is not believed to reflect an inadequacy of the deactivation model used; rather, it appears to be caused by either one or both of the following:

- Continuous change in chemical composition of the recycle stream in the integrated operation, due to hydrotreater temperature increases to compensate for catalyst aging, and changes in thermal dissolver conditions (See Appendix A);
- The magnified effect of process and laboratory measurement errors at low conversion levels.

It should be noted that for the earlier runs which employed the NTSL operation mode and constant hydrotreater temperatures in excess of 750°F (high conversion levels), the same model yielded much better correlation coefficients (Ref. 8,12).

2. Discussion of Results

An initial period of rapid deactivation, possibly due to carbonaceous material deposition, may be observed for Runs 242 and 243(2). The reactor temperature during this period (680°F), was identical for both runs. The starting, presulfided catalysts for these two runs indicated similar elemental analyses and model compound hydrogenation activities as shown below:

	S(wt %)	C(wt %)	N(wt %)	Hydrogenation Activity, mg moles (Ref. 38)
Run 242 catalyst	6.44	5.12	0.89	175
Run 243(2) catalyst	5.96	5.56	0.91	178

Run (243(2)), however, indicated an appreciably lower intrinsic rate constant and a higher deactivation rate, as illustrated below:

Run 242: $K_o = 0.373$, $\alpha = 0.0032$, $\text{Corr} = -0.906$

Run 243(2): $K_o = 0.243$, $\alpha = 0.0050$, $\text{Corr} = -0.817$

The different model parameters obtained could be a consequence of any one or a combination of the following differences between the two runs:

- The WHSV during this period was higher for Run 243(2);
- A short contact time first stage (dissolver bypassed) was used in Run 242; the dissolver was in service for Run 243(2);
- In Run 242 the hydrotreater was started-up with feedstock prepared during an NTSL run, whereas in Run 243(2), ITSL material was used as feedstock.

During the initial period of Run 243(1), the hydrotreater temperature and hence conversion were significantly lower than the above two runs, and the data does not indicate a clear trend of decline in catalyst activity.

An increase in reactor temperature to 720°F shows reasonably similar deactivation behavior for all three runs, as indicated below by the deactivation model parameters:

Run	242	243(1)	243(2)
* K_o	0.413	0.370	0.338
α	0.00086	0.00035	0.00034

* K_o was obtained by a least square analysis extrapolation of the data, for comparison purposes. Ideally, the initial period of rapid activity decline should be included.

The difference in deactivation parameters between Run 242 and Runs 243(1), 243(2) may be attributed to the different first stage severities employed. The SCT first stage (dissolver bypassed) used in Run 242 had a comparatively lower thermal severity and resulted in a heavier feedstock to the hydrotreater, which could understandably increase the catalyst deactivation rate. Since a fair amount of scatter exists in the data, this difference may not be statistically significant. Figure 20 is a plot of the deactivation data obtained from the three runs for a reactor temperature of 720°F. The close proximity of the deactivation curves is readily evident. A band has been drawn, enclosing a region that includes a maximum amount of batch deactivation points.

The defined region of interest is being currently used to determine the rate of catalyst addition and withdrawal for a continuous mode of operation. It may also be utilized for design and scale-up purposes.

At the present time, there is a paucity of ITSL deactivation data for extended time periods for reactor temperatures in excess of 720°F. The hydrotreater was operated at 730°F and 750°F for brief periods of time during Runs 242 and 243(2) respectively. The effect of reactor temperature on the deactivation parameter for ITSL operation is discussed in Appendix B. Also included in the appendix is a study of the effect of temperature and catalyst age on activation energy for SRC conversion.

V. SUPPORTING ANALYTICAL STUDIES

Aged catalyst samples were withdrawn from the hydrotreater on a regular basis for Runs 242, 243(1) and 243(2). Extensive analytical studies have been conducted at Wilsonville and in external research facilities on Run 242 catalyst samples, and the results will be discussed in this section. Model compound hydrogenation activities have been determined for Run 243(1) catalyst samples (Ref. 28); other work on these samples is ongoing.

A. CATALYST ACTIVITY COMPARISON

1. Model Compound Work

Hydrogenation and hydrodenitrogenation model compound tests have been performed on aged catalysts samples to provide an indication of relative catalyst activity, independent from process measurements.

Naphthalene was used as the model compound for the hydrogenation (HN) study. Tetralin as well as the decalin isomers are the defined reaction products:

Quinoline was the chosen model compound for the hydrodenitrogenation (HDN) study. Quinoline is first hydrogenated to intermediate compounds and then denitrogenated to hydrocarbons, which are the defined reaction products:

H-C (Reaction Products): Benzene, Toluene, Isopropylbenzene, Cyclohexane, etc.

The concentrations of the reaction products is determined by gas chromatographic analysis, from which the stoichiometric hydrogen requirement can be computed. A relative catalyst activity may then be defined as follows:

$$\text{Activity (HN, HDN)} = \frac{\text{Hydrogen addition rate with aged pellets, } \frac{\text{mg moles}}{\text{min. cm}^3 \text{ pellet}}}{\text{Hydrogen addition rate with presulfided pellets, } \frac{\text{mg moles}}{\text{min. cm}^3 \text{ pellet}}}$$

A description of the microautoclave reactor, experimental set-up and typical reaction conditions used, has been reported (Ref. 28). The results of the model compound study are listed in Table 12, and the data is plotted in Figure 21. Since the HN as well as HDN activities showed similar declining trends, they were plotted on the same coordinate axes. The results will be discussed in conjunction with process catalyst activity trends.

2. Process Catalyst Activity

The SRC conversion rate constant, derived from process data, provides a measure of catalyst activity. Figure 17 is a plot of the rate constant as a function of catalyst age over the range of temperature investigated. The rate constants have been corrected for differences in reactor temperature by utilizing the procedure described previously (Section B), and the activation energy obtained in Table 6.

The temperature corrected rate constants have also been plotted as a function of catalyst age in Figure 21, to provide a comparison of the trends in the decay of model compound activity with process data activity. Three distinct regimes may be observed from both curves:

- An initial period of rapid decline in activity which appears to be dependent on catalyst age rather than reactor temperature. (It is of interest to note that in the NTSL mode of operation and at the higher reactor temperature employed, an initial rapid decline in activity has not been observed);
- An intermediate region that reveals a fairly low deactivation rate. This region has been consistently observed for the ITSL mode of operation and at a reactor temperature of 720°F;
- A third region that indicates a higher deactivation rate at a reactor temperature of 750°F. However, the replacement of 25% catalyst inventory by unsulfided catalyst during this period,

should have had an impact on the deactivation rate and precludes the drawing of any accurate inferences.

The good agreement between model compound activity and activity monitored from the process is evident from the similar deactivation curves obtained in Figure 21. The activity of a catalyst is widely believed to be related to its characteristic properties, i.e., pore volume, pore size distribution, and surface area. For this reason, it was sought to examine the influence of catalyst age on the above catalyst properties and compare any observable trends with the activity trends that were already established.

3. Catalyst Property Trends

The aged catalyst samples withdrawn from the reactor were extracted with THF and characterized by mercury porosimetry. Table 13 lists pore volume and average pore diameter data for the aged catalyst samples. These properties have been plotted as a function of catalyst age in Figure 22.

The declining trends exhibited by these catalyst properties with age and reactor temperature are in accordance with the activity trends observed in Figure 21. The addition of fresh, unsulfided catalyst at an age of about 600 $\frac{\text{lbs SRC}}{\text{lb Cat}}$ results in an expected increase in average pore diameter and pore volume. The process catalyst activity, however, does not reflect a corresponding increase, because the fresh pore volume does not include active, sulfided sites.

Overall, the results clearly indicate that both model compound activity as well as porosimetric analyses of a spent catalyst sample correlates well with its process activity. In the event of a process upset or instrumentation failure, these laboratory tests would be useful in providing a more reliable measure of catalyst activity, compared with a process-derived quantity.

B. CATALYST FOULING

Among the recognized deactivation mechanisms, fouling is suspected to be a prime cause of catalyst deactivation in the H-OIL® reactor. Fouling is due to the deposition of extraneous metals present in the feedstock as well as the deposition of carbonaceous material from regressive reactions.

1. Metal Deposition

The concentrations of active and extraneous metals on aged catalyst samples (extracted with THF) from Run 242 are presented in Table 14. The total extraneous metals content

(titanium, iron and calcium), has been plotted as a function of age in Figure 23. The figure clearly shows that the metals accumulate on the catalyst with increasing age. Toward the end of the run, the metals concentration appears to have leveled-off, but the addition of a large batch of fresh, uncontaminated catalyst clouds the data to some extent. It can be concluded from the data in Table 14 that nickel concentration remains constant throughout the run duration. The molybdenum concentration, however, appears to decrease initially and levels off at about 10 wt %. To provide insight into the metals deposition profile across the aged catalyst pellets, the samples were analyzed by scanning electron microscopy (SEM).

Elemental concentrations of twelve aged catalyst samples (prior to addition of fresh catalyst batch), were obtained using the SEM's energy dispersive x-ray (EDX) analyzer. The bulk concentrations (for a crushed pellet), and surface concentrations (for a whole pellet) have been plotted as a function of catalyst age in Figure 24, for the elements aluminium, sulfur, phosphorous, and nickel, which are present in the parent catalyst. Although the results are semi-quantitative in nature, they allow a comparison of bulk and surface concentrations for any given element, and reveal their trends with catalyst age.

It is evident from Figure 24 that surface concentrations of the parent elements decrease at a faster rate than the bulk concentrations. This behavior is believed to be due to the dilution effect caused by the deposition of extraneous elements on the pellet surface, rather than the migration of the parent elements towards the pellet core. Figure 25 is a similar plot of extraneous metals concentrations as a function of catalyst age. Surface concentrations increase at a faster rate than bulk concentrations for the extraneous metals, clearly indicating that metal deposition is surface enriched.

This inference is further strengthened by the results of a line profile analysis of an aged, cleaved pellet, shown in Figure 26. A line profile analysis is an elemental x-ray count intensity as a function of position along the radius of the pellet. As shown in the figure, the recorder signal indicates a very high concentration of calcium and titanium at the outer edge of the pellet in a 10 μ m thick "egg-shell" layer (2.5% of catalyst diameter). The concentrations of these elements declines rapidly with distance toward the center of the pellet.

Element micrographs (dot-maps) are shown in Figure 27 for a cleaved pellet of the same age. Again, calcium is resident

on the outer edge as an 'egg-shell' covering, whereas, the active species, Ni and Mo appear to be uniformly distributed across the cross-section of the pellet.

2. Deposition of Carbonaceous Material

The THF-extracted catalyst samples have been analyzed for carbon, hydrogen, nitrogen and sulfur using microanalytic techniques. The results are presented in Table 15. Carbon content increases rapidly and reaches an equilibrium content of about 9.0 wt %. The hydrogen content appears to decrease with increasing catalyst age and consequently, results in a decline in the H/C ratio of the carbonaceous material as illustrated in Figure 28.

From the figure, it would appear that this H/C ratio would approach a steady-state value of about 1.10-1.15. This ratio would still be higher than the H/C ratio of the feed SRC to the hydrotreater (0.90-0.94). The unexpectedly high H/C ratios for "coke" have been previously observed for SRC hydrotreating at Wilsonville and at the Lummus PDU (Ref. 20). This suggests that the carbonaceous material deposited during SRC hydrotreating is by a different mechanism than the carbonaceous material deposited in the H-Coal operation, where a much lower H/C ratio compared with feed has been reported. Efforts are now being directed at explaining these differences.

The nitrogen content (Table 15), appears to remain fairly constant throughout the run and probably does not appreciably affect catalyst activity. The sulfur level increases initially and levels-off at about 7.0 wt % on an aged basis.

To determine the distribution of the carbonaceous material across the pellet surface, an indirect approach has been used, since the EDX analyzer does not detect carbon. THF extracted catalyst pellets and powder (-325 mesh) were tested for their hydrogenation activities by the naphthalene test, described earlier. The activities are presented in Table 16 and the data has been plotted as a function of catalyst age in Figure 29. As may be expected, the activities of catalyst powder are consistently higher than corresponding pellet activities. Crushing of a pellet into fine powder did not, however, result in a recovery of intrinsic activity, and the rate of decline of activity with age is about the same for both pellet and powder forms. The rate of decline of activity, i.e., increase in diffusional resistance with time, is caused by catalyst fouling. Clearly then, overall fouling must have penetrated the pellet in order to impose diffusional limitations on the fine powder generated. Since metal deposition has been shown to be surface enriched, it may be deduced that deposition of carbonaceous material (the other fouling mechanism) must have penetrated the pellet. The rapid decline in initial activity may be attributed to rapid deposition of carbonaceous material at an early catalyst age.

The effect of fouling on some of the physical properties of the catalyst (pore volume, average pore diameter) has been discussed. The deposition of metals and coke on the catalyst also results in a significant increase in the bulk and pellet densities of the catalyst as evident from the data presented in Table 17. For this reason, catalyst sample size was chosen on a volume basis for the analytical work performed, rather than the conventional weight basis.

C. COMPOSITION OF FLASHED BOTTOM PRODUCT

During Run 242, hydrotreater feed (V-1064) and product bottoms (V-1067) were sampled periodically to coincide with catalyst withdrawals. Certain compositional parameters of the feed samples were found to be fairly constant, as compared with the product, over the run duration. The response of product composition to changes in reactor temperature and catalyst aging may then be determined.

The pentane-soluble fraction of the product bottoms samples were analyzed by Gas Chromatography - Mass Spectrometry, and 80 compounds were individually identified. The concentrations of a specific group of hydroaromatics, represented by 26 unequivocally identified compounds, were measured for each sample. Table 18 lists the total concentration of the hydroaromatic group in each sample and the data has been plotted versus catalyst age in Figure 30.

The product bottoms samples were also analyzed for hydrogen distribution on a 200 MHz Bruker Spectrometer. The ratio of the hydrogen resident on large multi-nuclear aromatics (condensed aromatics) to the hydrogen on single aromatic rings (non-condensed aromatics) has been determined. This ratio has also been listed in Table 18 and plotted versus catalyst age in Figure 30.

The reactor temperature ($<720^{\circ}\text{F}$) during the early stages of Run 242 appears to be sufficiently low to cause an increase in the concentration of condensed rings and a consequent decrease in the hydroaromatic content. At a constant reactor temperature of 720°F , the hydroaromatic content appears to be fairly constant, but the ring size appears to marginally decrease. After a catalyst age of about 500 lbs SRC/lb catalyst, the concentration of hydroaromatics shows a definite declining trend. This may be attributed to the increase in reactor temperature to 750°F as well as to the addition of a large batch of unsulfided catalyst. It has been shown that the ITSL pasting solvent in the Lummus PDU decreases in hydroaromatic content for a second-stage hydrogenation temperatures in excess of 750°F (Ref. 32). An increase in reactor temperature should expectedly have resulted in a decrease in the ratio of condensed to non-condensed aromatic

compounds. However, the data indicates a substantial increase in ring-size, and the change in slope observed is significantly more than the estimated error of 0.2%. It is difficult to assign any one cause to this change, but the following arguments could explain the observed trends:

- The decline in process and model compound catalyst activity, and the decrease in pore volume and average pore diameter that was shown earlier, suggest rapid catalyst deactivation rate during this period. The loss in catalyst activity coupled with the addition of unsulfided catalyst might have rendered the catalyst incapable of cracking condensed rings, even at the elevated temperature of 750°F;
- The increase in reactor temperature to 750°F was accompanied by a significant increase in C₁-C₅ gas production, i.e., from 1.3% to 2.7% of feed SRC. This suggests that thermal conversion reactions could have gained prominence at this elevated temperature. Thermal reactions have a poor selectivity for distillate (non-condensed aromatic) production and could conceivably cause an increase in the ratio of condensed to non-condensed aromatic compounds.

D. CATALYST REGENERATION STUDIES

The results from the previous sections showed a significant effect of deactivation on catalyst activity and properties during Run 242. Some of the aged catalyst samples retained only 30% of intrinsic activity, while the pore volume and pore diameter decreased by about 55%, compared with the initial, unsulfided sample. This was attributed to the increase in the content of carbonaceous material and extraneous metals (the chief causes of deactivation) with catalyst age, which has also been discussed.

The presulfided catalyst sample and four aged samples have been regenerated via controlled oxidation, and the results are shown below:

^ΔProperties of Regenerated Catalysts (Run 242)

Catalyst Age (lb SRC/lb Cat)	Bulk Density (gm/cm ³)	Pellet Density (gm/cm ³)	Pore Volume (cm ³ /gm)	Average Pore Diameter (°A)
Fresh unsulfided	0.786	1.38	0.430	115
1 (Presulfided)	-	1.44	0.383	106
278	0.799	1.45	0.397	113
467	0.830	1.46	0.383	104
546	0.817	1.47	0.377	106
685	0.820	1.48	0.371	100

^ΔSource: (Ref. 29)

The above data shows that burn-off of carbonaceous material by regeneration restores about 85-90% of initial pore volume and pore diameter. The metal deposits, that are not removed by oxidation, would account for the difference between regenerated and original catalyst properties.

The importance in the restoration of intrinsic catalyst properties by regeneration can be judged from model compound activity tests. Aged catalyst samples from Run 242 have been fully regenerated by sulfiding, after controlled oxidation, and were then tested for model compound hydrogenation and hydrodenitrogenation activities (Ref. 9). The results indicated a 98% recovery of intrinsic hydrogenation activity and about 90% recovery of hydrodenitrogenation (cracking) activity. Similar regeneration work using model compounds tests on H-Coal spent catalysts showed agreeable results (Ref. 33). It was found that carbonaceous material had the greatest effect on hydrogenation and cracking activity, and by regeneration, these activities could almost completely be restored. The hydrodesulfurization activity, (influenced by metal deposition) could, however, be only partially restored.

V. SUMMARIZED CONCLUSIONS AND RECOMMENDATIONS

The following conclusions were drawn from the various studies that have been presented in this report:

Process Data Analysis

- SRC derived from Kentucky 9 coal caused a higher rate of catalyst deactivation, with respect to SRC conversion activity, in comparison to Illinois 6 coal. Consistent with this observation, the carbon content of the catalyst was found to be higher for Kentucky 9 coal feedstock.
- SRC conversion and heteroatom removal reactions appeared to be favored by nickel-molybdenum catalysts as compared with cobalt-molybdenum catalysts. Results from catalyst screening studies using SRC as feedstock are in accordance with this observation.
- An integrated mode of operation favored SRC hydro-treatment as compared with non-integrated operation. Integrating the mode of operation was observed to cause a reduction in the preasphaltenic content of the CSD-SRC feed, as well as to result in a heavier solvent fraction to the hydrotreater. Both these identifiable changes in feedstock properties, as a result of integration, would be beneficial for SRC hydrotreatment.
- An initial period of rapid deactivation was observed for ITSL operation, whereas NTSL operation exhibited a relatively constant deactivation rate.
- Fairly good reproducibility was obtained for batch deactivation data in the ITSL operation mode at a reactor temperature of 720°F. The range of catalyst age investigated was 200-1000 lbs SRC/lb catalyst.
- Catalyst deactivation rate appeared to be independent of reactor temperature (760-810°F) for NTSL operation (Co-Mo catalyst). In the ITSL operation, (Ni-Mo catalyst), the deactivation rate was seemingly dependent on temperature, over the range (720-750°F) investigated.

Supporting Analytical Studies

- Hydrogenation and hydrodenitrogenation catalyst activities, derived from model compound tests, revealed similar trends as obtained from process catalyst activity measurements. The pore volume and average pore diameter of the catalyst declined in a corresponding manner with catalyst activity.

- The deposition of extraneous metals on the catalyst showed a gradual build-up with increasing catalyst age. The metals largely resided on the outer periphery of a catalyst pellet.
- The deposition of carbonaceous material was much more rapid in comparison with metal deposition and appeared to reach an equilibrium content. The H/C ratio of the carbonaceous material on the catalyst decreased with age and also tends to an equilibrium value that was higher than the H/C ratio of the feed SRC. Unlike metal deposition, carbonaceous deposits appeared to have uniformly penetrated the pellet.
- The concentrations of hydroaromatics and multi-nuclear aromatics in the hydrotreater bottoms product were sensitive to reactor temperature changes as well as to the age of the catalyst. A favorable level of hydroaromatics was maintained at a reactor temperature of 720°F. Temperatures in excess of 750°F would be detrimental in producing a desirable chemical composition for the recycle stream that is used in the direct liquefaction of feed coal.
- Regeneration of aged catalysts caused a 85-90% recovery of initial pore volume and pore diameter. The regenerated catalyst samples showed a 98% recovery of intrinsic hydrogenation activity and about 90% recovery of hydrodenitrogenation activity. This indicated that deposition of carbonaceous material was a primary cause of catalyst deactivation.

RECOMMENDATIONS

The following recommendations for future work are proposed, based on the results of this work:

- The existing deactivation model may be made more sophisticated by determining and incorporating, (a) the dependence of the deactivation parameter on reactor temperature, and (b) activation energy dependence on catalyst age.
- Improvements in the existing kinetic model could be accomplished by pursuing the following studies:
 - determination/verification of the reaction order for the SRC conversion reaction, by studying the effect of WHSV on SRC conversion over a wide range of WHSV.
 - incorporation of a new parameter to describe feed quality (chemical composition), which appears to be changing with time for integrated operation.

- A thermal baseline needs to be established at different reactor temperature levels, to identify the thermal contribution to SRC conversion reactions.
- The conversion of asphaltenes to oils (lighter fractions of SRC) involve predominantly catalytic reactions, and should provide a better indication of process catalyst activity.
- The model compounds chosen for catalyst activity tests represent an oversimplification of the SRC/solvent feed to the hydrotreater. A composite model solvent, that includes heteroaromatic and multi-ring aromatic compounds, e.g., Mobil synthetic solvent, might be a better and more justifiable choice for analytical tests.

REFERENCES

1. Janka, R. C., and Paranjape, A. S., Investigation of Various Process Options in Two-Stage Liquefaction - Bench Scale Results. Proceedings of the Eighth Annual EPRI Contractors' Conference on Coal Liquefaction, May (1983).
2. Rao, A. K., Pillai, R.S., Lee, J.M., and Johnson, T. W., Recent Advances in Two-Stage Coal Liquefaction at Wilsonville. Proceedings of the Eighth Annual EPRI Contractors' Conference on Coal Liquefaction, May (1983).
3. Bertolacini, R. J., Gutberlet, L. C., Kim, D. K., and Robinson, K. K., Catalyst Development for Coal Liquefaction. EPRI Report AF-1084 under Project 408-1, June (1979).
4. Potts, J. D., Chillingworth, R. S., and Unger, H., U.S. DOE Report ET-10135-T1, April (1982).
5. Stiegel, G. J., Tischer, R. E., and Polinski, L. M., Ind. Eng. Chem. Process Des. Dev. to be published, September (1983).
6. Stiegel, G. J., Tisher, R. E., and Polinski, L. M., U.S. DOE Report PETC/TR-82/7.
7. Mitchell, T. O., Whitehurst, D. D., Farcasiu, M., Dickert, J. J. Jr., Heady, B. O., and Oderfer, G. A., Response of Product and Solvent Composition to Catalyst Deactivation During Coal Liquefaction. Proceedings of the Fourth Annual EPRI Contractors' Conference on Coal Liquefaction, May (1979).
8. Catalytic, Inc., Topical Report No. 4, Catalytic Hydrogenation Unit Studies, DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. FE-10154-118, November (1982).
9. Nalitham, R. V., Ph.D. Thesis, Auburn University, Auburn, AL (1983).
10. Stiegel, G. J., Polinski, L. M., and Tischer, R. E., Ind. Eng. Chem. Process Des. Dev., 21, 477 (1982).
11. Levenspiel, O. Chemical Reaction Engineering, 2nd Ed., J. Wiley & Sons, (1972).
12. Moniz, M. J., Davies, O. L., and Cantrell, C. E., Catalytic Upgrading of SRC Product in Two-Stage Coal Liquefaction. Proceedings of the Eighth Annual EPRI Contractors' Conference on Coal Liquefaction May (1983).

REFERENCES (Continued)

13. Catalytic, Inc., Annual Technical Report - 1981, DOE Contract No. DE-AC22-76ET10154, EPRI Contract No. RP1234-1-2, Document No. DOE-ET-10154-120, April (1983).
14. Catalytic, Inc., Quarterly Technical Progress Report (January - March 1982), DOE Contract No. DE-AC22-76ET10154, EPRI Contract No. RP1234-1-2, Document No. DOE-ET-10154-122, April (1983).
15. Catalytic, Inc., Technical Progress Report, Run 240 with Illinois 6 Coal, DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE-PC-50041-11, December (1982).
16. Nalitham, R. V., Tarrer, A. R., Curtis, C. W., and Guin, J. A., Ind. Eng. Chem. Process Des. Dev., to be published, October (1983).
17. Kim, D. K., Bertolacini, R. J., Forgac, J. M., Pellet, R. J., and Robinson, K. K., Catalyst Development for Coal Liquefaction. EPRI Report AF-1233 under Project 408-1,-2, November (1979).
18. Catalytic, Inc., Quarterly Technical Progress Report (July - September 1981), DOE Contract No. DE-AC22-76ET10154, EPRI Contract No. RP-1234-1-2, Document No. FE-10154-110, August (1982).
19. Bronfenbrenner, J., International Coal Refining Company, personal communication, March (1982).
20. Znaimer, S., International Coal Refining Company, personal communication, April (1983).
21. Moniz, M.J., M.S. Thesis, Auburn University, Auburn, AL (1982).
22. Catalytic, Inc., Technical Progress Report, Runs 238 and 239 with Illinois 6 Coal, DOE Contract No. DE-AC22-82PC50041, EPRI contract No. RP1234-1-2, Document No. FE-10154-117, November (1982).
23. Catalytic, Inc., Technical Progress Report, Run 241 with Illinois 6 Coal, DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE-PC-50041-14, February (1983).
24. Catalytic, Inc., Technical Progress Report, Run 242 with Illinois 6 Coal, DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, Document No. DOE-PC-50041-19, July (1983).

REFERENCES (Continued)

25. Kellet, T. F., Sartor, A. F., and Trevino, C. A., Hydrotreating Catalyst Selection. Presented at the NPRA Annual Meeting, New Orleans, Louisiana, March (1930).
26. Curtis, C. W., Guin, J. A., and Kwon, K. C., Coal Solvolysis in a Series of Model Compound Systems. Presented at the AIChE Annual Meeting, Los Angeles, California, November (1982).
27. Catalytic, Inc., Technical Progress Report, Run 243 with Illinois 6 Coal, DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, to be published (1983).
28. Catalytic, Inc., Topical Report No. 9, Utilization of the Hydrogen Microautoclave in Support of the Coal Liquefaction Process, DOE Contract No. DE-AC22-82PC50041, EPRI Contract No. RP1234-1-2, to be published (1983).
29. Stiegel, G. J., Tischer, R. E., and Cillo, D. L., Catalyst Testing for Two-Stage Liquefaction. Proceedings of the Eighth Annual EPRI Contractors' Conference on Coal Liquefaction, May (1983).
30. Freeman, G. B., IMMR, University of Kentucky, personal communication, March (1983).
31. Schweighardt, F. K., International Coal Refining Company, letter to A. Rao, Catalytic, Inc., March 16 (1983).
32. Winschel, R. A., and Burke, F. P., Process and Product Oil Characterization in Two Stage Coal Liquefaction. Proceedings of the Eighth Annual EPRI Contractors' Conference, May (1983).
33. Cable, T. L., Massoth, F. E., and Thomas, M. G., Fuel Proc. Tech., 4, 265 (1981).
34. Schweighardt, F. K., Air Products and Chemical, Inc., letter to A. Rao, Catalytic, Inc., August 5 (1983).
35. Shah, Y. T., Reaction Engineering in Direct Coal Liquefaction, Addison-Wesley Publishing Co., (1981).

APPENDIX A

Changes in Chemical Composition of Flash Bottoms Product - Run 243

A. BACKGROUND

In the NTSL mode of operation (fuel oil product slate), the HTR reactor was normally operated at a fixed temperature ($>750^{\circ}\text{F}$) for the duration of the run. Catalyst deactivation with increasing age would result in a higher SRC yield. In the ITSL mode of operation, however, a history of step-increases in HTR reactor temperature has to be made for the following reasons:

- A reduced temperature ($\leq 680^{\circ}\text{F}$) is required at the start of the run to prevent excess conversion of the SRC with the fresh, presulfided catalyst. Temperature is subsequently increased in steps to desired conditions.
- To maintain an all distillate product slate (SRC conversion 21-25%), reactor temperature has to be increased to compensate for catalyst deactivation.

The chemical properties of ITSL pasting solvent have been shown to be dependent on reactor temperature (Ref. 32). The increases in HTR reactor temperature should then be expected to change the chemical composition of the recycle stream, which in turn would have an effect on the composition of the HTR feed solvent. During Run 243(1 & 2), the dissolver reaction conditions, i.e. temperature, pressure and space velocity, were also varied during the course of the run. Again, the composition of the HTR feed as well as recycle bottoms would be consequently affected.

The intent of the following study is to demonstrate the significant changes in chemical composition of flash bottoms product that occurred during Run 243.

B. RESULTS AND DISCUSSION

Five product bottoms samples were withdrawn over a time period (February - June 1983) covering the duration of Run 243. The sample descriptions are as follows:

Sample No	Withdrawal Date	Run No	Catalyst Batch	HTR Reactor Temp ($^{\circ}\text{F}$)
1	February 24	243(1)	12-243	630
2	March 6	243(1)	12-243	690
3	March 24	243(1)	12-243	720
4	May 18	+ 243(2)	13-243	720
5	June 01	+ 243(2)	13-243	720

*In this run, dissolver volume was decreased by 50%, and temperature was increased from 800°F to 810°F

The samples were batch-distilled using a modified-ASTM method, and separated into distillate (-850°F) and residue ($+850^{\circ}\text{F}$) fractions. A gas chromatographic simulated distillation and an elemental analysis (H content) were performed on each of the distillate samples. The weight fraction (%) of heavy distillate boiling in the $650\text{--}750^{\circ}\text{F}$ range was determined. The results are presented below:

<u>Sample No.</u>	1D	2D	3D	4D	5D
<u>H content (wt %)</u>	5.68	9.88	10.16	10.25	10.74
<u>$\Delta\text{Wt \%}$ (650-750°F)</u>	23.7	22.4	21.4	20.8	19.50

ΔSource : (Ref. 34)

The data indicates a substantial decrease in the percent of heavy distillate material, as the run progressed. This was accompanied by a significant increase in hydrogen content of the distillate samples. These results suggest that reactor temperature increases and catalyst change-out have a substantial impact on recycle stream distillate composition.

The distillate and residue fractions have also been analyzed by ^1H -NMR (200 MHz). The hydrogen contents of each of the samples and their absolute distribution are listed below:

$\Delta^1\text{H}$ -NMR Hydrogen Distribution Data

<u>Sample No.</u>	<u>Distillate</u>			<u>Sample No.</u>	<u>Residue</u>		
	<u>H Content (wt %)</u>	<u>HARO (wt %)</u>	<u>HALIPH (wt %)</u>		<u>H Content (wt %)</u>	<u>HARO (wt %)</u>	<u>HALIPH (wt %)</u>
1D	9.68	1.44	8.24	1R	6.50	1.98	4.52
2D	9.88	1.48	8.40	2R	7.04	1.96	5.08
3D	10.16	1.41	8.72	3R	7.09	1.92	5.17
4D	10.25	1.23	9.02	4R	7.29	1.84	5.45
5D	10.74	1.12	9.62	5R	7.61	1.62	5.99

ΔSource : (Ref. 34)

The aromatic hydrogen content has been plotted versus aliphatic hydrogen content in Figure 31, for the distillate and residue fractions. The plots clearly indicate an increase in the content of aliphatic hydrogen and a concurrent decrease in the aromatic hydrogen, with process time. These results compliment the observation made from the GC-simulated distillation data.

Clearly, the changes in HTR and dissolver operating parameters during the course of the run directionally increased the degree of hydrogenation of the flashed bottoms product. A slight perturbation of any stream in an integrated operation

should affect downstream reactor performance. For this reason, the significant change in chemical composition of the flash bottoms recycle stream could conceivably have caused the scatter in catalyst deactivation data.

APPENDIX B

Miscellaneous Topics - Process Data Analysis

A. INTRODUCTION

As a result of the process data studies presented in Chapter III, certain interesting comparative trends have come to light.

- An initial period of rapid deactivation has been observed for ITSL operation (Figures 17, 19 and 21). Operation in the NTSL mode does not exhibit this behavior (Figures 11 and 12). It is to be noted that the reactor temperatures were lower during the ITSL operation for the initial period. Also, the catalysts used were different for both operations.
- The rate of catalyst deactivation appears to be independent of reactor temperature for NTSL operation (Figure 11 and 12). The limited data available for ITSL operation suggests a deactivation rate dependency on reactor temperature (Figures 17 and 21). Again, it is to be noted that the temperature range investigated was higher for NTSL operation (760-810°F), as compared with ITSL operation (720-750°F);
- In the ITSL operation, reactor temperature was increased in steps to compensate for loss in catalyst activity. Activation energies for SRC conversion were determined and were found to increase with catalyst age;
- High temperature operation appears to require a higher activation energy for SRC conversion, for both NTSL and ITSL operation modes. This could possibly be due to the increase in thermal conversion reactions at the higher temperatures.

The above inferences have been based on trends obtained from the limited data base available at the present time. The expansion of the data base with time would serve to improve on the generality of the inferences drawn.

B. DISCUSSION

From the deactivation model (2) and the Arrhenius equation (3), the reaction velocity constant for SRC conversion may be written as follows:

$$K_{\text{SRC}} = K_0' e^{-\alpha t} e^{-E/RT} \quad (4)$$

The inferences in the previous section for integrated operation seem to suggest that:

$$\alpha = \alpha(t, T) \quad (8)$$

$$E = E(T, t) \quad (9)$$

The deactivation parameter (α) appears to be a discrete function of catalyst age/process time (t) during the initial period of deactivation. A close examination of the deactivation trends in Figures 17, 19 and 21 would lead one to suspect that:

$$\begin{aligned} \alpha &= \alpha_1(T) & 100 > t > 0 \\ \alpha &= \alpha_2(T) & t > 200 \end{aligned} \quad (10)$$

The available data does not clearly define the exact catalyst age at which the deactivation rate changes. The change occurs in the age interval of 100-200 lbs SRC/lb catalyst. After a catalyst age of 200 lbs SRC/lb catalyst, the deactivation parameter appears to be uniquely dependent on reactor temperature (Figures 17, 19 and 21). Recent data from Run 244 confirms this belief.

The influence of reactor temperature on activation energy for SRC conversion is apparent only at reactor temperatures below 680°F. Arrhenius plots prepared for Runs 233-234 and 243(1) indicate a substantially lower activation energy for temperatures in the 630-680°F range. However, this inference tends to be speculative, owing to the scatter in the data ($\pm 3\%$) for the reduced SRC conversions (4-12%) at these temperatures. It may be of interest that the dependence of activation energy on reactor temperature has also been observed in the hydrotreatment of COED oil with a Ni-Mo catalyst (Ref. 35). In all likelihood, future hydrotreater operation will be at temperatures of 680 F and above. The dependence of activation energy on reactor temperature would hence be inconsequential.

The increase in activation energy with catalyst age is to be expected since the resulting continuous loss in catalyst activity would imply a gradual shift in emphasis, from catalytic to thermal SRC conversion. Activation energies for SRC conversion have been determined at different catalyst ages by extrapolating the least square lines in Runs 242 and 243(2).

The results are presented below:

Run No	Catalyst Age, <u>Lbs SRC</u> <u>Lb Cat</u>	<u>Btu</u> <u>E, lb mole</u>
242	250	28400
242	500	50900
243(2)	550	66500
Δ244	1180	84000

ΔThe same catalyst batch from Run 243(2) was used in Run 244.

The above data clearly demonstrates the dependence of activation energy on catalyst age. Future efforts should be directed at obtaining additional process data so that an empirical correlation may be developed to describe this dependence. Laboratory experiments with an autoclave reactor could then be used to provide a reliable confirmation of the results.

It is also important to focus on obtaining deactivation data at different temperatures levels for extended time periods. The dependence of the deactivation parameter on reactor temperature may be expressed as (Ref. 16):

$$\alpha = \alpha_0 e^{-E_d/RT} \quad (9)$$

E_d - Activation energy for deactivating reactions
(deposition of carbonaceous materials).

Based on the above discussion, a more accurate estimate of the rate constant for SRC conversion would be obtained from:

$$K_{SRC} = K_0' e^{- (T) \times t} \times e^{\frac{-E(t)}{RT}} \quad (10)$$

APPENDIX C

H/C Atomic Ratio of Carbonaceous Material on Aged Catalyst Samples

It has been consistently observed that the carbonaceous material on the catalyst has a higher H/C ratio than the feed SRC to the HTR unit, irrespective of the type of catalyst or mode of integration employed. The H/C ratio of the feed SRC in NTSL operation ranged from 0.80-0.90, and about 0.90-0.94 for ITSL operation. The following table lists H/C atomic ratios for aged catalysts from Wilsonville Runs 228-242. The aged catalyst samples have been analyzed at various laboratories using different work-up procedures. The average H/C ratio was found to be 1.20.

<u>Run No.</u>	<u>Catalyst Type</u>	<u>Catalyst Age (lb SRC/lb Cat)</u>	<u>C (wt %)</u>	<u>H (wt %)</u>	<u>H/C (Atomic Ratio)</u>	<u>Work-Up Procedure (Laboratory)</u>
228-229	HDS-14428	683	13.89	1.35	1.16	THF Extraction (Galbraith)
3-235	HDS-1442B	501	22.14	2.47	1.33	Toluene Extraction (Galbraith)
4-235	HDS-1442B	332	13.61	1.09	0.95	Toluene Extraction (Galbraith)
236	HDS-1442B	279	8.43	1.53	1.52	Toluene Extraction (Galbraith)
236	HDS-1442B	390	11.95	1.14	1.14	Toluene Extraction (Galbraith)
238	HDS-1442B	278	12.00	1.28	1.28	Toluene Extraction (Galbraith)
239	HDS-1442B	783	7.12	0.69	1.15	Toluene Extraction (Galbraith)
240	HDS-1442A	454	12.59	1.27	1.20	Toluene Extraction (HRI)
241	Armak-Ketjen	129	13.60	1.09	0.95	Toluene Extraction (Wilsonville)
241	Armak-Ketien	550	12.22	1.21	1.18	Toluene Extraction (HRI)
242	Shell 324M	527	9.72	0.98	1.20	Toluene Extraction (HRI)
242	Shell 324M	527	9.17	0.92	1.20	THF Extracted (PETC))

Table 1
Pore Size Distribution Data for Fresh Catalysts (Arnak-Ketjen, Shell 324M)

Arnak-Ketjen				Shell 324M			
Pore volume, V $\frac{(\text{cm}^3)}{(\text{gm})}$	Pore diam., a (°A)	$\log a$	$\frac{dV}{d(\log a)}$	Pore Volume, V $\frac{(\text{cm}^3)}{(\text{gm})}$	Pore diam., a (°A)	$\log a$	$\frac{dV}{d(\log a)}$
0.0	10000	4.000	0.000	0.0	3000	3.477	0.000
0.004	8750	3.942	0.069	0.007	2000	3.301	0.040
0.009	5800	3.763	0.028	0.007	1500	3.176	0.000
0.019	4000	3.602	0.062	0.007	800	2.903	0.000
0.029	3000	3.477	0.080	0.013	600	2.778	0.048
0.054	2000	3.301	0.142	0.013	500	2.699	0.000
0.078	1500	3.176	0.192	0.013	350	2.544	0.000
0.137	800	2.903	0.216	0.026	250	2.398	0.089
0.162	600	2.778	0.200	0.033	175	2.243	0.045
0.172	500	2.699	0.127	0.059	115	2.061	0.143
0.196	350	2.544	0.155	0.270	100	2.000	3.459
0.211	250	2.398	0.103	0.388	70	1.845	0.761
0.231	175	2.243	0.129	0.421	60	1.778	0.493
0.251	115	2.061	0.110	0.434	50	1.699	0.165
0.260	100	2.000	0.148	0.447	45	1.653	0.283
0.320	70	1.845	0.387	0.454	35	1.544	0.064
0.418	60	1.778	1.463	0.454	30	1.477	0.000
0.512	50	1.699	1.190				
0.600	45	1.653	1.913				
0.684	35	1.544	0.771				
0.699	30	1.477	0.224				

Table 2
TSL Parameters Included in Data-base

Runs Included: 233-243
Time Period: August 1981 - June 1983

<u>Parameter</u>	<u>Parameter type</u>
Catalyst	HDS 1442A (Co-Mo) HDS 1442B (Co-Mo) Armak-Ketjen (Ni-Mo) Shell 324M (Ni-Mo)
Feed Coal	Kentucky 9 Fies Illinois 6 Burning Star
Operation Mode	NTSL ITSL (partially and fully integrated)
First Stage Severity	High Severity (with dissolver) Low Severity (with dissolver) Short Contact Time (without dissolver)
HTR Reactor Temperature	Range: 630°F-830°F

Table 3
Catalyst Deactivation Rate Data for SRC Conversion (NTSL Mode)

Kentucky 9 Fies Coal				Illinois 6 Burning Star Coal			
Run 3-235 (HTR Temp - 780°F)		Run 4-235 (HTR Temp - 810°F)		Run 5-236 (HTR Temp - 780°F)		Run 8-240 (HTR Temp - 760°F)	
*Process Time (hrs)	SRC Conv. Rate Const(K) hr ⁻¹	*Process Time (hrs)	SRC Conv. Rate Const(K) hr ⁻¹	*Process Time (hrs)	SRC Conv. Rate Const(K) hr ⁻¹	*Process Time (hrs)	SRC Conv. Rate Const(K) hr ⁻¹
10.5	1.16	27.0	1.85	37.0	1.05	58.0	0.98
30.0	1.13	51.0	1.86	71.0	1.14	82.0	0.79
54.0	0.98	75.0	1.77	108.0	1.11	106.0	0.78
78.0	0.91	129.5	1.68	156.0	1.10	130.0	0.75
126.0	0.99	137.0	1.47	180.0	1.13	154.0	0.78
150.0	0.94	161.0	1.57	204.0	1.06	178.0	0.79
222.0	0.72	185.0	1.68	228.0	1.11	226.0	0.75
246.0	0.82	209.0	1.31	252.0	1.10	250.0	0.77
270.0	0.74	233.0	1.40	276.0	1.08	274.0	0.72
294.0	0.70			332.0	1.03	298.0	0.62
342.0	0.60			356.0	0.95	322.0	0.69
366.0	0.80			380.0	1.03	340.0	0.69
390.0	0.89					370.0	0.78
414.0	0.57					396.0	0.72
						418.0	0.74
						442.0	0.72
						466.0	0.64
						490.0	0.69
						511.0	0.71
						535.0	0.78
						583.0	0.64
						607.0	

*Process time was computed by correcting the clock-time for (a) plant shut-down time, and (b) time when reactor temperature was below 700°F.

Table 4
Activation Energy for SRC Conversion (Co-Mo Catalyst/NTSL Mode)

Run. 234

Basis: Data for activation energy determination should ideally be obtained at a fixed catalyst age. In this run, frequent changes were made in reactor temperature and hence deactivation trends were not observed. Material balance data (special product work-up periods) has therefore been utilized (Ref. 18):

<u>MB Period</u>	<u>T(°F)</u>	<u>WHSV</u>	<u>ε</u>	<u>K_{SRC}</u>	<u>$\frac{1}{T} (^{\circ}\text{R}^{-1} \times 10^3)$</u>	<u>ln K_{SRC}</u>
234A	725	1.30	0.225	0.377	0.8440	-0.974
234B	783	1.37	0.397	0.901	0.8045	-0.103
234C	830	1.68	0.526	1.864	0.7750	0.623

Equation: $K_{\text{SRC}} = A e^{-E/RT}$

$E = 45800 \frac{\text{Btu}}{\text{lb mol}}$ $A = 1.1 \times 10^8 \text{ hr}^{-1}$ Corr Coeff = -0.9995.

Table 4. (continued)
Activation Energy for SRC Conversion (Co-Mo Catalyst/NTSL Mode)

Runs 3-235, 4-235

Basis: In these runs, a separate batch of catalyst was used at each temperature level. Data was obtained from material balance periods at a catalyst age of approximately 250 $\frac{\text{lb SRC}}{\text{lb Cat}}$. Intrinsic rate constant data has not been used because of the possible errors that could result from, (a) differences in initial catalyst activities (presulfided S contents) and, (b) transients in feed concentration, inventory levels etc., until the unit has 'lined-out'.

<u>MB Period</u>	<u>T(°F)</u>	<u>WHSV</u>	<u>ϵ</u>	<u>K_{SRC}</u>	<u>$\frac{1}{T(^{\circ}\text{R}^{-1} \times 10^3)}$</u>	<u>ln K_{SRC}</u>
3-235AB	782	1.96	0.33	0.965	0.8052	-0.03524
4-235D	809	1.90	0.42	1.376	0.7880	0.3191

$$E = 41150 \frac{\text{Btu}}{\text{lb mol}}$$

$$A = 1.7 \times 10^7 \text{ hr}^{-1}$$

Runs 236, 240

<u>MB Period</u>	<u>T(°F)</u>	<u>WHSV</u>	<u>ϵ</u>	<u>K_{SRC}</u>	<u>$\frac{1}{T(^{\circ}\text{R}^{-1} \times 10^3)}$</u>	<u>ln K_{SRC}</u>
236-2, 236-A	780	1.15	0.48	1.061	0.8065	0.0592
240-5	761	1.13	0.419	0.815	0.819	-0.2047

$$E = 41900 \frac{\text{Btu}}{\text{lb mol}}$$

$$A = 2.6 \times 10^7 \text{ hr}^{-1}$$

Table 5
Temperature Corrected Deactivation Rate Data for SRC Conversion

Kentucky 9 Fies Coal

*Equation (5): $K_{SRC}'' = \frac{K_{SRC}}{e^{-E/RT}}$

Run 3-235			Run 4-235		
Process Time (hrs)	K_{SRC}, hr^{-1}	$K_{SRC}'', \text{hr}^{-1} (\times 10^{-8})$	Process Time (hrs)	K_{SRC}, hr^{-1}	$K_{SRC}'', \text{hr}^{-1} (\times 10^{-8})$
10.5	1.16	1.28	27.0	1.85	1.31
30.0	1.13	1.24	51.0	1.86	1.32
54.0	0.98	1.08	75.0	1.77	1.25
78.0	0.91	1.00	129.5	1.68	1.19
126.0	0.99	1.09	137.0	1.47	1.04
150.0	0.94	1.03	161.0	1.57	1.12
222.0	0.72	0.77	185.0	1.68	1.19
246.0	0.82	0.90	209.0	1.31	0.93
270.0	0.74	0.81	233.0	1.40	0.99
294.0	0.70	0.77			
342.0	0.60	0.66			
366.0	0.80	0.88			
390.0	0.89	0.98			
414.0	0.57	0.63			

Table 5 (continued)
Temperature Corrected Deactivation Rate Data for SRC Conversion

Illinois 6 Burning Star Coal

*Equation (5): $K_{SRC}'' = \frac{K_{SRC}}{e^{-E/RT}}$

Run 236			Run 240		
Process Time (hrs)	K_{SRC}, hr^{-1}	$K_{SRC}'', \text{hr}^{-1} (\times 10^{-8})$	Process Time (hrs)	K_{SRC}, hr^{-1}	$K_{SRC}'', \text{hr}^{-1} (\times 10^{-8})$
37.0	1.05	1.16	82.0	0.79	1.18
71.0	1.14	1.25	106.0	0.82	1.22
108.0	1.11	1.22	130.0	0.78	1.16
156.0	1.10	1.21	154.0	0.75	1.12
180.0	1.13	1.24	178.0	0.78	1.09
204.0	1.06	1.17	226.0	0.79	1.18
228.0	1.11	1.22	250.0	0.75	1.12
252.0	1.10	1.21	274.0	0.77	1.15
276.0	1.08	1.19	298.0	0.72	1.07
332.0	1.03	1.13	322.0	0.62	0.92
356.0	0.95	1.05	346.0	0.69	1.03
380.0	1.03	1.13	370.0	0.69	1.03
			396.0	0.78	1.16
			410.0	0.72	1.07
			442.0	0.74	1.10
			466.0	0.72	1.07
			490.0	0.69	1.03
			535.0	0.71	1.06
			583.0	0.78	1.16
			607.0	0.64	0.95

Btu

*The activation energy used in computing the above data was 45600 Btu/lb mole. This value is in close agreement with the results obtained in Table 3, and also with an activation energy computed by ICRC from Wilsonville data from Runs 228-235 (Ref. 19).

Table 6
Activation Energy for SRC Conversion for Different Catalyst Types
and Integration Modes

Runs 238, 239

Basis: A separate batch of catalyst was used in each of these runs. Data was obtained at a catalyst age of about $250 \frac{\text{lbs SRC}}{\text{lb Cat}}$ (180 lbs process time) in Run 238. Since the WHSV was relatively high for Run 239, data was obtained at a similar process time (Ref. 22).

<u>Date (1982)</u>	<u>T(°F)</u>	<u>WHSV</u>	<u>ϵ</u>	<u>K_{SRC}</u>	<u>$\frac{1}{T} (^{\circ}\text{R} \times 10^{-3})$</u>	<u>ln K_{SRC}</u>
April 19 (238)	750	2.44	0.207	0.637	0.8264	-0.451
May 12 (239)	784	2.91	0.250	0.969	0.8039	-0.031

$$E = 37100 \frac{\text{Btu}}{\text{lb mole}} \quad A = 3.2 \times 10^6 \text{ hr}^{-1}$$

Run 241

Basis: In this run, a separate batch of catalyst was used at each temperature level. Data for Run 10-241 was obtained at a catalyst age of about $250 \frac{\text{lbs SRC}}{\text{lb Cat}}$. Run 9-241 was terminated at an age of $150 \frac{\text{lbs SRC}}{\text{lb Cat}}$; data was obtained prior to termination (Ref. 23).

<u>Date (1982)</u>	<u>T(°F)</u>	<u>WHSV</u>	<u>ϵ</u>	<u>K_{SRC}</u>	<u>$\frac{1}{T} (^{\circ}\text{R} \times 10^{-3})$</u>	<u>ln K_{SRC}</u>
August 9 (9-241)	750	1.26	0.355	0.693	0.8264	-0.366
Sept 12 (10-241)	777	1.13	0.441	0.892	0.8084	-0.115

$$E = 27700 \frac{\text{Btu}}{\text{lb mole}} \quad A = 7.0 \times 10^4 \text{ hr}^{-1}$$

Table 6 (continued)
Activation Energy for SRC Conversion for Different Catalysts
and Integration Modes

Run 242

Basis: At a catalyst age of about $250 \frac{\text{lbs SRC}}{\text{lb Cat}}$, the reactor temperature was increased from 680°F to 700°F and then to 720°F (Ref. 24). Since the increases were accomplished in a short interval of time (9 days), the effect of catalyst deactivation can be justifiably neglected. Average rate constants have been used in the determination, owing to scatter in the data.

<u>Date (1982)</u>	<u>T(°F)</u>	<u>ϵ</u>	<u>WHSV</u>	<u>K</u>
December 11	680	0.174	1.04	0.22
December 12	678	0.170	1.12	0.23
December 13	680	0.147	1.09	0.188
December 15	699	0.222	0.99	0.282
December 16	701	0.236	1.13	0.350
December 17	704	0.233	1.10	0.334
December 18	721	0.260	0.88	0.310
December 19	720	0.251	1.02	0.341
December 20	719	0.251	0.97	0.325
	<u>T(°F)</u>	<u>$\bar{K}$</u>	<u>$\frac{1}{\bar{T}}(^{\circ}\text{R} \times 10^{-3})$</u>	<u>$\ln K_{\text{SRC}}$</u>
	680	0.213	0.8772	-1.547
	700	0.322	0.8621	-1.1332
	720	0.325	0.8475	-1.124

$$E = 28400 \frac{\text{Btu}}{\text{lb mole}} \quad A = 6.6 \times 10^4 \text{ hr}^{-1} \quad \text{Corr} = -0.88$$

Table 7
Catalyst Deactivation Rate Data for Nitrogen Removal

SRC Conversion %	WHSV, lb/hr feed lb catalyst	*Nitrogen, wt % Feed/Product	Hydrodenitrogenation Rate const, K_N^{-1} , hr ⁻¹	*Process time, hr
Run 236 (Ref. 14)				
0.45	1.41	1.53/1.20	1.86	108
0.51	1.44	1.06/0.96	1.80	156
0.51	1.24	1.17/1.17	1.29	180
0.48	1.25	1.74/1.49	1.56	204
0.53	1.08	1.34/1.24	1.40	276
0.39	1.29	1.50/1.52	0.80	308
Run 239 (Ref. 22)				
0.36	4.16	1.56/0.97	4.16	65
0.32	2.95	1.84/1.32	2.95	89
0.24	3.88	1.31/0.72	3.88	174
0.25	2.33	0.01/0.62	2.33	222
0.25	3.68	1.06/0.76	2.68	246
0.18	2.25	1.40/1.01	2.25	270
0.17	2.46	1.40/0.93	2.46	338
0.18	1.96	1.29/0.90	1.96	362
Run 241 (Ref. 23)				
0.44	1.13	1.91/1.11	2.35	235
0.48	1.14	2.21/1.47	2.16	283
0.44	1.12	1.92/1.12	2.30	307
0.42	1.31	1.93/1.40	1.81	403
0.45	1.20	1.41/1.18	1.41	427
0.46	1.18	1.56/1.27	1.49	451
0.46	1.18	2.16/1.67	1.64	499
0.40	1.23	1.69/1.35	1.35	571
0.40	1.16	1.70/1.22	1.52	595
0.43	1.16	2.12/1.80	1.25	643
0.36	1.12	1.99/1.81	0.70	715
0.38	1.14	1.84/1.72	0.78	739
0.32	1.18	1.70/1.54	0.74	763

*The above table includes only reliable daily nitrogen analysis data.

*Process time implies actual operating time when reactor temperature was about 700°F.

Table 8
Catalyst Deactivation Rate Data for Sulfur Removal

SRC conversion, ε	WHSV, lb/hr feed lb catalyst	*Sulfur, wt % Feed/Product	Hydrodesulfurization, Rate constant, K_S , hr ⁻¹	*Process time, hr
Run 236 (Ref. 14)				
0.42	1.43	0.45/0.15	6.13	37
0.46	1.30	0.57/0.20	5.56	71
0.48	1.27	0.58/0.20	5.81	91
0.51	1.44	0.44/0.23	4.18	156
0.50	1.12	0.44/0.20	3.76	252
0.51	1.08	0.53/0.26	3.49	276
0.39	1.29	0.39/0.21	2.64	308
0.57	1.21	0.49/0.41	1.15	404
Run 239 (Ref. 22)				
0.36	2.75	0.69/0.20	12.07	65
0.32	2.81	0.71/0.22	10.53	89
0.33	2.70	0.63/0.22	8.84	113
0.25	3.11	0.73/0.23	10.05	198
0.25	2.91	0.67/0.24	7.92	222
0.17	3.02	0.73/0.30	5.83	338
0.18	2.62	0.80/0.29	6.14	362
Run 241 (Ref. 23)				
0.44	1.12	0.67/0.11	6.75	331
0.41	1.15	0.89/0.29	4.83	355
0.40	1.18	0.82/0.31	4.04	547
0.40	1.23	0.71/0.30	3.65	571
0.39	1.16	0.68/0.35	2.57	595
0.40	1.25	0.68/0.39	2.38	619
0.43	1.16	0.72/0.30	3.74	643
0.32	1.30	0.87/0.47	2.25	691
0.36	1.12	0.84/0.44	2.24	715
0.38	1.14	0.76/0.42	2.20	739

*The above table includes only reliable daily sulfur analysis data.

*Process time implies actual operating time when reactor temperature was above 700°F.

Table 9
 Δ Catalyst Deactivation Rate Data for SRC Conversion (ITSL Mode - Run 242)

<u>Date, 1982-83</u>	<u>Reactor Temp. °F</u>	<u>WHSV, lb/hr feed lb catalyst</u>	<u>ϵ</u>	<u>KSRC, hr⁻¹</u>	<u>Catalyst Age lbs SRC/lb Catalyst</u>
November 23	706	1.00	0.350	0.385*	17
27	666	0.94	0.233	0.350*	34
29	689	0.80	0.288	0.284*	54
30	669	0.78	0.268	0.330*	63
December 01	681	0.79	0.268	0.290	72
03	679	0.90	0.238	0.280	91
08	681	1.07	0.200	0.268	131
09	680	1.04	0.174	0.220	142
10	680	1.08	0.171	0.220	155
11	680	1.04	0.174	0.220	167
12	678	1.12	0.170	0.230	179
13	680	1.09	0.147	0.188	192
14	685	1.02	0.190	0.240	204
15	699	0.99	0.222	0.282	216
16	701	1.13	0.236	0.350	229
17	704	1.10	0.233	0.334	242
18	721	0.88	0.260	0.310	253
19	720	1.02	0.251	0.341	266
20	719	0.97	0.251	0.325	278
21	720	0.96	0.272	0.359	290
22	720	0.95	0.235	0.290	303
23	720	0.97	0.218	0.270	315
25	721	1.05	0.238	0.330	344
26	720	0.94	0.236	0.290	356
28	719	0.91	0.263	0.330	379
29	720	0.95	0.264	0.341	391
30	721	1.04	0.238	0.325	405
January 01	718	1.09	0.201	0.270	429
04	719	0.97	0.215	0.260	467
05	720	0.96	0.225	0.279	479
06	719	0.98	0.203	0.250	492
07	735	1.07	0.232	0.320	506
08	749	1.08	0.249	0.358	520
09	749	1.05	0.291	0.430	534
10	749	0.99	0.302	0.428	546
11	746	0.99	0.305	0.430	559
12	748	0.94	0.277	0.410	571
13	745	1.01	0.277	0.387	584
14	748	1.03	0.251	0.345	598
15	749	1.04	0.261	0.370	611
17	748	1.02	0.263	0.360	639
18	749	0.96	0.253	0.325	651
19	750	0.81	0.311	0.860	662
20	745	0.91	0.243	0.290	673
21	750	0.90	0.284	0.357	685

Δ Source: (Ref. 24).

*These rate constants have been corrected for a reactor temperature of 680°F.

+105 lbs of fresh, unsulfided catalyst added to reactor, and equivalent amount withdrawn.

Table 10
 Δ Catalyst Deactivation Rate Data for SRC Conversion (ITSL Mode - Run 243(1))

Date, 1983	Reactor Temp, °F	WHSV, lb/hr feed lb catalyst	ϵ	K _{SRC} , hr ⁻¹	Catalyst Age, lbs SRC/lb catalyst
February	10	631	0.92	0.081	33
	13	630	1.00	0.095	60
	15	630	0.77	0.059	79
	16	627	0.88	0.095	90
	17	630	1.07	0.047	104
	18	631	1.12	0.047	118
	20	630	1.14	0.065	147
	21	628	1.16	0.034	161
	22	629	1.15	0.041	176
	23	630	1.17	0.056	191
	24	634	1.15	0.055	205
	25	658	1.12	0.080	220
	26	657	1.14	0.055	234
	27	657	1.17	0.077	249
March	01	659	1.13	0.066	279
	02	659	1.02	0.037	292
	03	659	1.04	0.075	306
	04	659	1.12	0.054	320
	05	689	1.19	0.150	351
	07	689	1.23	0.107	366
	08	688	1.20	0.095	381
	09	687	1.19	0.094	397
	10	688	1.18	0.121	412
	11	715	1.27	0.201	428
	12	719	1.32	0.235	445
	13	719	1.32	0.203	462
	14	720	1.31	0.214	478
	15	719	1.21	0.190	494
	16	718	1.22	0.211	509
	18	720	1.41	0.165	538
	19	719	1.23	0.193	553
	20	716	1.33	0.220	570
	21	717	1.27	0.192	587
	22	716	1.27	0.191	603
	23	718	1.27	0.178	619
	24	718	1.24	0.171	634
	25	718	1.26	0.190	650
	26	717	1.23	0.155	666
	27	718	1.21	0.179	682
	28	716	1.21	0.144	698
	29	719	1.25	0.196	715
	30	719	1.26	0.188	731
	31	719	1.31	0.216	748
April	01	718	1.38	0.166	766
	02	720	1.30	0.157	782
	03	720	1.28	0.179	798
	*04	720	1.27	0.175	815
	*24	690	0.98	0.147	855
	25	691	1.11	0.157	869
	26	690	1.24	0.084	885
	27	705	1.16	0.145	899
	28	719	1.20	0.195	914
	29	718	1.25	0.180	930
	30	719	1.30	0.180	946
May	01	719	1.30	0.179	963
	02	719	1.26	0.184	979

Δ Source: (Ref. 27).

*Transfer-line from preheater to dissolver (first-stage) was modified and replaced in the period, April 5-23. Dissolver conditions changed from 50% to 25% volume usage.

Table 11
 Δ Catalyst Deactivation Rate Data for SRC Conversion (ITSL Mode - Run 243(2))

<u>Date, 1983</u>	<u>Reactor Temp, °F</u>	<u>WHSV, lb/hr feed lb catalyst</u>	<u>ϵ</u>	<u>K_{SRC} hr⁻¹</u>	<u>Catalyst Age, lbs SRC/lb Catalyst</u>
May 05	680	1.14	0.144	0.190	24
06	677	1.12	0.173	0.235	38
08	680	1.21	0.48	0.162	69
09	676	1.18	0.135	0.184	83
10	679	1.11	0.110	0.137	97
11	678	1.07	0.115	0.139	111
19	720	1.22	0.201	0.308	210
20	718	1.20	0.209	0.317	226
21	719	1.19	0.179	0.259	242
22	718	1.20	0.158	0.226	257
23	718	1.20	0.222	0.342	273
25	716	1.22	0.244	0.393	301
*26	720	1.12	0.208	0.294	316
27	719	0.96	0.274	0.364	328
28	718	1.01	0.246	0.330	341
29	719	1.05	0.228	0.311	354
30	719	1.01	0.226	0.295	367
31	718	0.95	0.225	0.276	380
June 01	720	0.98	0.236	0.301	392
04	720	1.00	0.258	0.346	418
05	719	0.97	0.212	0.260	430
06	719	0.95	0.235	0.292	442
07	719	0.95	0.235	0.291	454
08	719	1.01	0.247	0.330	467
09	719	1.03	0.236	0.317	480
10	720	1.01	0.226	0.295	492
11	718	0.99	0.196	0.240	505
12	719	0.97	0.188	0.224	517
13	719	0.97	0.219	0.271	529
14	719	0.97	0.237	0.301	541
16	729	1.10	0.242	0.352	568
17	729	1.06	0.271	0.395	581
18	728	1.08	0.243	0.345	595
19	728	1.07	0.273	0.400	608
20	727	1.13	0.228	0.334	623
21	729	1.09	0.247	0.358	637
22	728	1.05	0.257	0.363	650
23	718	1.05	0.218	0.293	663
24	717	1.06	0.228	0.313	677
25	716	0.99	0.242	0.315	689
26	717	1.01	0.241	0.320	702
27	717	1.10	0.202	0.278	716

Δ Source: (Ref. 27)

*Coal feed rate dropped from 250 lb/hr to 200 lb/hr.

Table 12
 *Model Compound Catalyst Activity as a Function of Age

<u>Catalyst Age, lbs SRC lb Cat</u>	<u>ΔRelative HN Activity, %</u>	<u>Relative HDN Activity, %</u>
1	100.0	100.0
43	87.1	71.0
88	64.0	59.0
133	62.7	51.0
182	51.5	54.0
233	50.3	53.0
272	54.0	60.0
381	42.0	-
415	53.0	50.0
498	37.0	-
527	39.0	-
583	34.0	29.0
607	28.0	-

*This data has been obtained from Auburn University (Ref. 9), where the model compound work was performed.

Δ Some of the HN activity tests were conducted in triplicate. The mean values are reported. A standard deviation of $\pm 2.5\%$ is representative for the above data.

Table 13
*Porosimetric Properties of Aged Catalyst Samples from Run 242

<u>Catalyst Age,</u> <u>lbs SRC</u> <u>lb Cat</u>	<u>Pore Volume,</u> <u>cm³/gm</u>	<u>Average Pore</u> <u>Diameter, °A</u>
Fresh (unsulfided)	0.430	115
1	0.297	86
43	0.257	78
88	0.248	74
133	0.236	73
182	0.237	72
233	0.235	72
272	0.233	74
300	0.236	72
315	0.233	68
381	0.230	66
415	0.237	71
498	0.210	64
527	0.203	48
583	0.197	52
607	0.229	68
672	0.237	64

*Source: (Ref. 29)

Table 14
*Metals Concentration on Aged Catalyst Samples from Run 242

<u>Catalyst Age, lbs SRC/lb CAT</u>	<u>Titanium (wt %)</u>	<u>Iron (wt %)</u>	<u>Calcium (wt %)</u>	<u>Nickel (wt %)</u>	<u>Molybdenum (wt %)</u>
1	<0.1	0.1	<0.1	2.0	12.0
43	0.2	0.2	0.1	2.1	11.2
88	0.2	0.3	0.1	2.1	11.0
133	0.3	0.4	0.1	2.1	11.9
182	0.6	0.5	0.2	2.0	10.2
233	0.7	0.7	0.2	2.3	10.1
272	0.5	0.5	0.2	2.1	10.0
300	0.5	0.6	0.2	2.1	10.1
315	0.6	0.6	0.2	2.0	10.5
381	0.6	0.7	0.2	2.1	10.5
415	0.7	0.8	0.2	2.0	10.1
498	0.8	1.1	0.2	2.4	9.9
527	0.7	0.8	0.2	1.9	10.3
533	0.9	0.9	0.2	2.2	9.6
607	0.8	1.0	0.2	2.1	10.0
672	0.9	0.8	0.2	2.4	10.7

*Source: (Ref. 29).

Table 15
*Composition of Aged Catalyst Samples from Run 242

<u>Catalyst Age</u> <u>lbs SRC/lb CAT</u>	<u>Carbon</u> <u>(wt %)</u>	<u>Hydrogen</u> <u>(wt %)</u>	<u>Nitrogen</u> <u>(wt %)</u>	<u>Sulfur</u> <u>(wt %)</u>	<u>H/C Atomic</u> <u>ratio</u>
1	7.94	1.15	0.5	5.8	1.74
43	8.80	1.20	0.4	7.3	1.62
88	9.79	1.22	0.5	7.5	1.48
133	9.99	1.26	0.5	7.6	1.50
182	8.45	1.04	0.5	6.9	1.47
233	8.72	0.99	0.4	6.7	1.35
272	8.50	0.93	0.5	6.9	1.30
300	9.04	0.99	0.5	6.5	1.30
315	8.71	0.93	0.4	7.0	1.27
381	8.85	0.92	0.5	7.1	1.24
415	7.74	0.89	0.4	7.0	1.37
498	9.34	0.94	0.5	6.7	1.20
527	9.17	0.92	0.4	7.2	1.20
583	8.85	0.86	0.4	7.2	1.16
607	8.17	0.85	0.4	7.0	1.24
672	8.39	0.85	0.4	5.9	1.21

*Source: (Ref. 29).

Table 16
⁺Hydrogenation Activities of Aged Catalyst Samples
 (Run 242) in Powder and Pellet Form

<u>Catalyst Age, lbs SRC/lb Cat</u>	<u>Δ Relative Hydrogenation Activity, %</u>	
	<u>Catalyst Pellet</u>	<u>Catalyst Powder</u>
88	64.0	80.0
133	62.7	79.0
182	51.5	72.0
233	50.3	71.0
272	54.0	75.0
381	42.0	66.0
415	53.0	73.0
498	37.0	53.0
527	39.0	57.0
583	34.0	52.0
607	28.0	-

⁺Source: (Ref. 9)

ΔHydrogenation activities are relative to the respective
 presulfided catalyst pellet and powder state.

Table 17
 Δ Bulk and Pellet Densities of Aged Catalyst Samples⁺ from
 Run 242

<u>Catalyst Age (lb SRC/lb Cat)</u>	<u>Bulk Density (gm/cm³)</u>	<u>Pellet Density (gm/cm³)</u>
Unsulphided	0.786	1.38
1	0.898	1.54
43	0.863	1.60
88	0.863	1.62
133	0.927	1.67
182	0.913	1.65
233	0.948	1.59
272	0.940	1.70
300	0.913	1.65
315	0.894	1.68
381	0.919	1.68
415	0.932	1.68
498	0.938	1.68
527	0.936	1.72
583	0.942	1.71
607	0.965	1.67
672	0.929	1.67

[^]Source: (Ref. 29)

⁺Catalyst Samples were THF extracted

Table 18
 $\Delta^1\text{H}$ NMR Data for Flashed Bottoms Product Samples from Run 242

<u>Catalyst Age</u> <u>(Lbs SRC/lb Cat)</u>	<u>Condensed</u> <u>Non condensed</u> (Aromatic Ratio)	<u>% Hydroaromatics</u> <u>(Pentane Soluble Fraction)</u>
133	2.87	1.73
182	2.60	2.25
233	2.10	2.10
272	2.25	2.45
300	2.40	2.85
415	2.42	2.50
498	2.17	-
527	2.45	1.84
583	2.10	-
607	1.63	3.33
672	1.24	4.85

Δ Source: (Ref. 31)

FIGURE 1. SINGLE STAGE (THERMAL) SRC UNIT

FIGURE 2. CRITICAL SOLVENT DEASHING UNIT

FIGURE 3. H-OIL[®] EBULLATED-BED REACTOR

FIGURE 4. HYDROTREATING UNIT

FIGURE 5. NON-INTEGRATED TWO-STAGE LIQUEFACTION MODE

FIGURE 6. INTEGRATED TWO-STAGE LIQUEFACTION MODE

FIGURE 7. PARTIALLY-INTEGRATED TWO-STAGE LIQUEFACTION MODE

FIGURE 8. PORE SIZE DISTRIBUTION FOR FRESH CATALYST (ARMAX-KETJEN, SHELL 324 M)

FIGURE 9. 850°F CONVERSION IN HEAVY OIL VERSUS CATALYST AGE
PDU RUNS LCF-29, 30, 31, 32, 33, 34 (REF 3)

FIGURE 10. PERCENT DENITROGENATION IN HEAVY OIL VERSUS CATALYST AGE
PDU RUNS LCF-29, 30, 31, 32, 33, 34 (REF. 3)

FIGURE II. CATALYST DEACTIVATION RATE FOR KENTUCKY 9 COAL FEEDSTOCK (NTSL MODE)

FIGURE 12. CATALYST DEACTIVATION RATE FOR ILLINOIS 6 COAL FEEDSTOCK (NTSL MODE)

FIGURE 13. ACTIVATION ENERGY FOR SRC CONVERSION
 (CO-MO CATALYST / NTSL MODE)

FIGURE 14. TEMPERATURE CORRECTED CATALYST DEACTIVATION RATES FOR KENTUCKY 9 AND ILLINOIS 6 COAL FEEDSTOCKS

FIGURE 15. EFFECT OF CATALYST TYPE AND INTEGRATION MODE ON DENITROGENATION RATE CONSTANT

FIGURE 16. EFFECT OF CATALYST TYPE AND INTEGRATION MODE ON DESULFURIZATION RATE CONSTANT

FIGURE 17. CATALYST ACTIVITY TRENDS FOR SRC CONVERSION
(ITSL MODE - RUN 242)

FIGURE 18 CATALYST ACTIVITY TRENDS FOR SRC CONVERSION (ITSL MODE - RUN 243(1))

FIGURE 19. CATALYST ACTIVITY TRENDS FOR SRC CONVERSION
(ITSL MODE - RUN 243(2))

FIGURE 20. CATALYST DEACTIVATION RATE FOR SRC CONVERSION FOR BATCH OPERATION (ITSL MODE)

FIGURE 21. COMPARISON OF PROCESS AND MODEL COMPOUND ACTIVITY TRENDS

FIGURE 22. EFFECT OF CATALYST AGE ON PORE VOLUME AND AVERAGE PORE DIAMETER FOR AGED CATALYST SAMPLES FROM RUN 242 (REF. 29)

FIGURE 23. EXTRANEOUS METALS CONCENTRATION (TI+FE+CA) ON AGED CATALYST FROM RUN 242 (REF. 29)

FIGURE 24. COMPARISON OF BULK AND SURFACE ELEMENTAL CONCENTRATIONS (SEMI-QUANTITATIVE) BY EDX (REF 30)

FIGURE 25. COMPARISON OF BULK AND SURFACE EXTRANEIOUS METAL CONCENTRATIONS (SEMI-QUANTITATIVE) BY EDX (REF 30)

FIGURE 26. CALCIUM AND TITANIUM LINE PROFILE ANALYSES (130 μm) ACROSS A CLEAVED PELLET (AGE-583 LBS SRC/LB CAT)

CLEAVED PELLET SURFACE

CALCIUM

MOLYBDENUM

NICKEL

FIGURE 27. ELEMENT MICROGRAPH BY EDX OF A CLEAVED PELLET
(AGE - 583 LBS SRC/LB CAT)

FIGURE 28. EFFECT OF CATALYST AGE ON H/C RATIO OF CARBONACEOUS MATERIAL ON AGED CATALYST SAMPLES FROM RUN 242 (REF 29)

FIGURE 29. COMPARISON OF THE HYDROGENATION ACTIVITIES OF AGED CATALYST SAMPLES (RUN 242) IN POWDER AND PELLET FORM

FIGURE 30. EFFECT OF REACTOR TEMPERATURE AND CATALYST AGE ON THE COMPOSITION OF HTR FLASHED BOTTOM PRODUCT

FIGURE 31. CHANGE IN THE DISTRIBUTION OF ALIPHATIC AND AROMATIC HYDROGEN IN FLASHED BOTTOMS PRODUCT (RUN 243)