A Study of Deactivation and Regeneration of Catalysts Used in the LC-Fining of Solvent Refined Coal

C. W. Curtis, J. A. Guin, R. Nalitham, A. Mohsin, and A. R. Tarrer

Department of Chemical Engineering, Auburn University,
Auburn University, AL 36849

J. D. Potts and K. E. Hastings

Cities Service Research and Development Company,
P.O. Box 3908, Tulsa, OK 74102

Introduction

Lummus Cities-Fining (LC-Fining) was developed by Cities Service over the past twenty years and is licensed by the CE Lummus Company. The technology has been successfully applied to the upgrading of low quality petroleum crudes and refinery residues. LC-Fining is currently being applied to the upgrading of coal extracts.

The cost of commercial cobalt molybdenum and nickel molybdenum catalysts has escalated by a factor of four over the last five years. This has produced a strong economic incentive to regenerate used LC-Fining catalysts. The Auburn University research program was undertaken to obtain detailed information on the effect of various solvent and SRC types on the deactivation of a commercial Shell 324 nickel-molybdenum catalyst, to understand the mechanism of catalyst deactivation in catalytic upgrading of coal extracts and to develop effective regeneration methods.

Experimental

Materials. The solvents used in this study were Koppers heavy residue creosote oil, hydrogenated to 7.0%, 7.5% and 8.0% hydrogen and labeled for this study as "solvent D," "solvent C," and "solvent AB," respectively. The solvent refined coals (SRC) used in this study were from (1) Pyro Kentucky #9 coal processed at the Wilsonville SRC Pilot Plant using Kerr McGee critical solvent deashing as the solids separation method and labeled as SRC I-A (Wilsonville Run 161 and 163); (2) Kentucky #9 coal processed at the Fort Lewis, Washington SRC Pilot Plant and labeled as SRC I-B; and (3) Fies coal processed at the Wilsonville SRC Pilot Plant also using Kerr McGee deashing and designated as Fies SRC (Wilsonville Run 209). The catalyst used was Shell 324 nickel-molybdenum, 1/32 inch extrudate. The catalyst was presulfided according to the manufacturer's suggested procedure before use. Spent catalysts were obtained from the CE Lummus LC-Fining PDU (Process Development Unit) operation in New Brunswick, New Jersey. Spent catalyst A was obtained after processing a 70/30 volume blend of SRC I-A/solvent AB for 28 days, and spent catalyst B was obtained after processing a 50/50 volume blend of SRC I-B/solvent AB for 24 days. Elemental analyses of the solvents and SRC's are given in Table I. Naphthalene (Fisher, scintanalyzed) and hexadecane (Pfaltz and Bauer) were used in the model compound hydrogenation reactions.

Equipment and Analysis. Batch catalyst deactivation experiments and naphthalene hydrogenation reactions were performed in tubing bomb reactors of volumes of 46 cc and 17.5 cc, respectively. The tubing bomb was immersed in a fluidized sand bath maintained at 430° ± 2°C and was agitated at 860 CPM. Hydrogen was charged to the tubing bomb through a Nupro fine metering valve.

Products from the naphthalene hydrogenation reactions were analyzed by gas chromatography using a Varian Model 3700 equipped with a SP2250 column (2.4 m x 0.3 m O.D.), FID detection and temperature programming from 60° to 165°C at 5°C/min. Surface area measurements of the catalysts were obtained by nitrogen adsorption. Catalyst

pellets were regenerated by low, medium and high temperature ashing. A four chamber L.F.E. Model 504 low temperature asher (LTA) operated at 0.5 mm Hg oxygen and 250 watts was used for the LTA experiments.

Reaction Procedures. The batch catalyst deactivation study was performed in a 46cc tubing bomb at 430°C and 1250 psig initial hydrogen pressure charged at 25°C. A 70/30 SRC/solvent charge (weight basis) was used with an initial fresh catalyst weight of 1.25 g. Four deactivation cycles were performed; each cycle was followed by a separate hydrogenation reaction on a catalyst aliquot using a 10 wt.% naphthalene in hexadecane solution reacted in a 17.5 cc tubing bomb at the reaction conditions of 410°C and 1250 psig.

Results and Discussion

Catalyst Deactivation. Deactivation of Shell 324 Ni/Mo catalyst used in the upgrading of SRC was examined in four cycle batch deactivation experiments using various SRC/solvent feed blends. The loss of catalyst hydrogenation activity after the SRC reaction was measured by the degree of naphthalene hydrogenation after each cycle. As shown in Table 2, the catalyst showed deactivation in each SRC/solvent system as measured by a decrease in naphthalene conversion. A comparison of the activity level of the fresh presulfided Ni/Mo catalyst is also given. Of the various combinations of SRC and solvent employed, the SRC I-A/solvent C and SRC I-B/solvent C systems appear to have the least catalyst deactivation after four reaction cycles.

When solvent and catalyst with no SRC present are reacted in a similar set of experiments, essentially no catalyst deactivation was observed as measured by changes in naphthalene conversion. However, comparisons of the entire product distributions between the fresh presulfided catalyst and the solvent treated catalysts showed a definite difference as illustrated in Table 3. Less decalin formation and more tetralin formation of the solvent treated catalyst represents a decrease in the hydrogenation activity of the catalyst after contact with the solvent.

Tailoring of the solvent and SRC/solvent combination for maximal SRC upgrading and minimal catalyst deactivation may be an important factor in catalytic upgrading according to preliminary evidence. This certainly warrants further investigation. A comparison of the five different SRC/solvent combinations using catalyst prepared in the same batch indicates that solvent AB in concert with the SRC's used may have a more pronounced deactivating effect than that of solvent C. The deactivation behavior plotted in terms of the naphthalene conversion after each cycle is given in Figure 1.

Since coking occurs at high carbon loadings, elevated reaction temperatures and conditions of hydrogen starvation, experiments were performed to investigate the effect of each of these parameters on catalyst deactivation at the SRC/solvent reaction temperature. Deactivation data has been obtained with a range of SRC loadings in two cycle hydroprocessing reactions. The effect of increased SRC loading on catalyst activity is evident after one cycle and becomes more pronounced after two. Catalyst activity definitely decreases with increased SRC loadings (Figure 2). Experiments were also performed at constant SRC loading at elevated temperatures and at conditions involving both excess and limited hydrogen. Experiments using SRC I-A and SRC I-B with solvent AB and fresh presulfided catalysts show high levels of activity at 430°C after one cycle which rapidly dropped off to essentially no activity at 500°C (Table 4). Hydroprocessing reactions were performed using 1250 psig hydrogen and no hydrogen at 500°C. The catalysts used were both the spent catalysts from the LC-Fining PDU operation and fresh presulfided catalyst. A 45% increase was observed in the hydrogenation activity level of the fresh sulfided catalyst with hydrogen present as opposed to no hydrogen being present. No difference in catalyst activity was observed for the spent catalyst regardless of hydrogen

presence. A more substantial effect of the hydrogen presence would most likely be observable at lower processing temperatures.

Deactivation Mechanism. Regeneration of spent catalysts from the LC-Fining PDU operation was attempted using controlled oxidation at three temperature levels: low, ∿150°C in an excited oxygen atmosphere; medium, 370°C with an air atmosphere; and high, 950°C also with air atmosphere. A histogram of the regeneration levels achieved after oxidation or grinding are shown in Figure 3. The hydrogenation activity of both spent catalyst A and B is low before oxidative treatment, with catalyst A showing greater deactivation (PDU run at 70/30 SRC/solvent ratio). Spent catalyst B can be essentially regenerated to its original activity level as based on naphthalene conversion by a combination of medium temperature ashing followed by presulfiding. Presulfiding alone provides significant regeneration for spent catalyst B and a definite increase in activity of spent catalyst A. Presulfiding of the spent catalyst pellets apparently increased the catalyst activity by activating or sulfiding sites which had lost their activity during the coal extract upgrading reaction and removal of hydrocarbon deposits. Grinding the spent catalyst pellets to -200 mesh provides increased activity for both spent catalysts possibly by exposing fresh active sites. Both high temperature and low temperature ashing show slight increases in the activity of spent catalyst B, but none for spent catalyst A.

The rate of carbonaceous material removal from the spent catalysts during medium temperature oxidation is shown in Figure 4. After forty hours of oxidation, spent catalyst B pellets and pellets of both spent catalyst A and B ground to -200 mesh reached constant weight. However, ninety hours are required for spent catalyst A to reach constant weight. These results indicate that spent catalyst A obtained from a higher SRC loading in PDU feed may have more carbonaceous material blocking the pores. The carbonaceous material may also be more refractory.

Surface area analyses were performed using both spent catalysts A and B and catalysts A and B regenerated by medium temperature oxidation followed by sulfiding. The surface areas before and after treatment and the naphthalene conversions obtained are given in Table 5. A direct correlation between surface area and hydrogenation activity of the catalyst is observed and is shown in Figure 5.

Spent catalysts obtained after four batch reaction cycles of SRC I-B/solvent AB and Fies SRC/Solvent D were regenerated in the same manner as the spent catalysts obtained from the PDU operation. By medium temperature ashing followed by presulfiding, the batch deactivated catalysts are regenerated to essentially their original activity level. Medium temperature oxidation alone of the batch deactivated catalysts gives partial but not complete catalyst regeneration.

To determine the effect of metals deposition on catalyst deactivation, ash obtained from Kentucky #9 coal was added to solvent C and batch deactivation experiments were performed. The degree of catalyst deactivation at varying ash concentrations is shown in Figure 6.

Summary. Batch experiments as well as results from LC-Fining catalytic upgrading of coal extracts indicate deactivation of the Shell 324 Ni/Mo catalyst in the presence of SRC. At increased levels of SRC loading, deactivation increases. The chief cause of catalyst deactivation appears to be coking. The Shell 324 catalyst can be substantially regenerated after the upgrading reaction by medium temperature ashing followed by presulfiding.

Acknowledgement

Auburn University gratefully acknowledges the support of Cities Service Research and Development Company for this work.

Table 1

Analysis of Solvents and SRC

	Solvent A/B	Solvent C	Solvent D	SRC I-A	SRC I-B	Fies SRC
Elemental content, wt%						
Carbon	91.48	91.6	91.28	90.3±0.1	87±0.2	87.6±0.2
Hydrogen	8.01	7.5	7.03	6.4±0.2	6.2±0.1	6.2±0.1
Oxygen	<0.5	<0.5	0.88	-	-	-
Nitrogen	0.29	0.36	0.69	2.1±0.2	2.1±0.3	2.0±0.2
Sulfur	0.03	0.19	0.27	-	-	-
Ash, wt%				0.2	0.6	-
Distillation, °F						
276.8	0.0	0.0	0.0			
336.2	0.4	0.9	1.1			
395.6	1.4	3.9	1.8			
435.2	2.3	6.8	2.5			
464.0	3.3	9.6	3.0			
500.0	6.3	15.8	4.4			
582.8	21.6	34.6	12.6			
647.6	25.9	47.5	17.9			
674.6	35.8	57.5	24.5			
746.6	64.0	81.9	52.6			
820.4	100.0	99.9	99.9			

Table 2

Batch Catalyst Deactivation Tests With SRC and Solvent

Feed Blend	Presulfided Catalyst Batch Number	Naphthalene Conversion	Naphthalene Conversion in Activity Test Reaction With Deactivated Catalyst From: 1st Cycle	2nd Cycle	3rd Cycle	4th Cycle
Fresh Pre-	1	94				
sulfided	2	90				
Catalyst	3	99.5				
SRC I-A/	1&2		83±5	44±3	33	32
Solvent AB	3		84	60		
SRC I-B/	1&2		86±4	66±5	40	34
Solvent AB	3		83±7	71±7	59	48
SRC I-A/ Solvent C	3		86	74	67	-
SRC I-B/	3		86	73	68	64
Solvent C	3		85	70	-	-
Fies SRC/	3		92	80	43	22
Solvent D	3		84	75	64	35
Fies SRC/ Solvent D	3		73	68	59	39

Table 3

Comparison of Product Distribution Before and After Solvent Aging

	Base Activity With Fresh Presulfided Catalyst	Solvent AB		Solvent C	
		1st Cycle	2nd Cycle	1st Cycle	2nd Cycle
Naphthalene conversion	99.5	98.9	98.9	98.9	98.9
Conversion to:					
Trans-decalin	74	34	28	40	29
Cis-decalin	19	11	10	13	11
Tetralin	6	46	58	39	54

Table 4

Effect of Elevated Temperature and Hydrogen Starvation on Catalyst Activity

Hydroprocessing Reaction Temperature, °C (initial H_2 pressure = 1250 psi)	Feed Blend	% Naphthalene Conversion in Activity Test
430	SRC I-A/Solvent AB	84
460	SRC I-A/Solvent AB	51
500	SRC I-A/Solvent AB	17
430	SRC I-B/Solvent AB	84
460	SRC I-B/Solvent AB	40
500	SRC I-B/Solvent AB	10

Catalyst	Feed Blend	Hydrogen Pressure psig (reaction temperature = 500°C)	Naphthalene Conversion in Activity Test
Spent Catalyst A	SRC I-A/Solvent AB	1250	6
Spent Catalyst A	SRC I-A/Solvent AB	0	5
Spent Catalyst B	SRC I-B/Solvent AB	1250	6
Spent Catalyst B	SRC I-B/Solvent AB	0	5
Fresh Presulfided Catalyst	SRC I-A/Solvent AB	1250	17
Fresh Presulfided Catalyst	SRC I-B/Solvent AB	0	12

Table 5

Surface Area and the Hydrogenation Activity of Different Catalysts

Catalyst	Surface Area m^2/g	% Naphthalene Conversion In Activity Test
Spent Catalyst A	2	34
Spent Catalyst B	87	73
Spent Catalyst A-oxidized at 370°C and presulfided	141	92
Fresh presulfided catalyst	188	99
Spent Catalyst B-oxidized at 370°C and presulfided	225	100

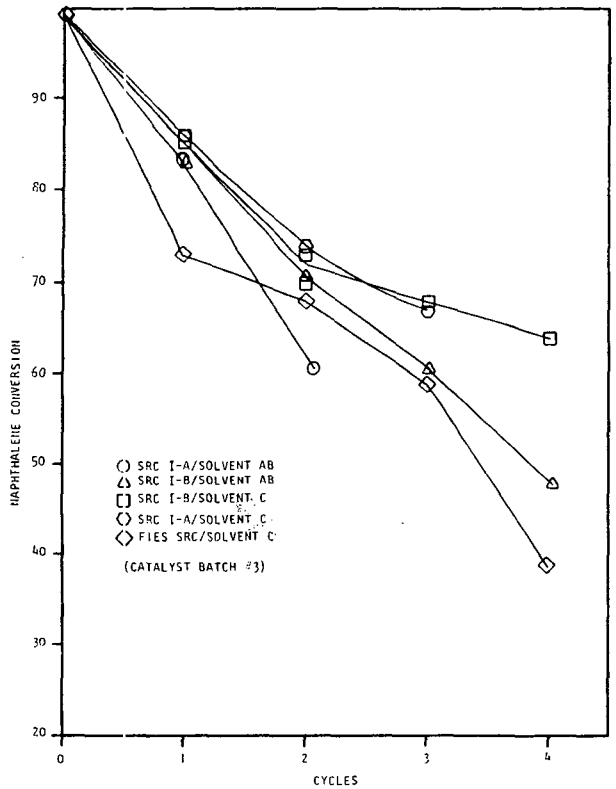


FIGURE 1. PERFORMANCE COMPARISON OF SRC I-A, SRC I-B, AND FIES SRC IN SOLVENT AB AND SOLVENT C

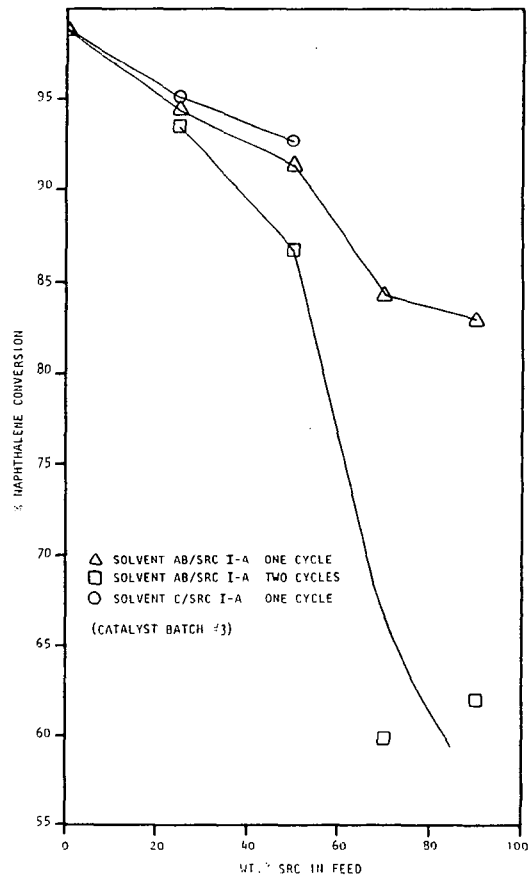
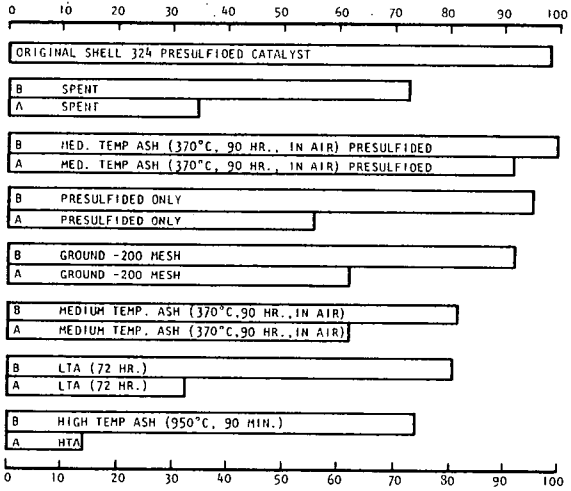


FIGURE 2. FEED BLEND SRC CONTENT EFFECT ON CATALYST DEACTIVATION



LTA = LOW TEMP ASH HTA = HIGH TEMP ASH

FIGURE 3. SPENT CATALYSTS A AND B REGENERATION

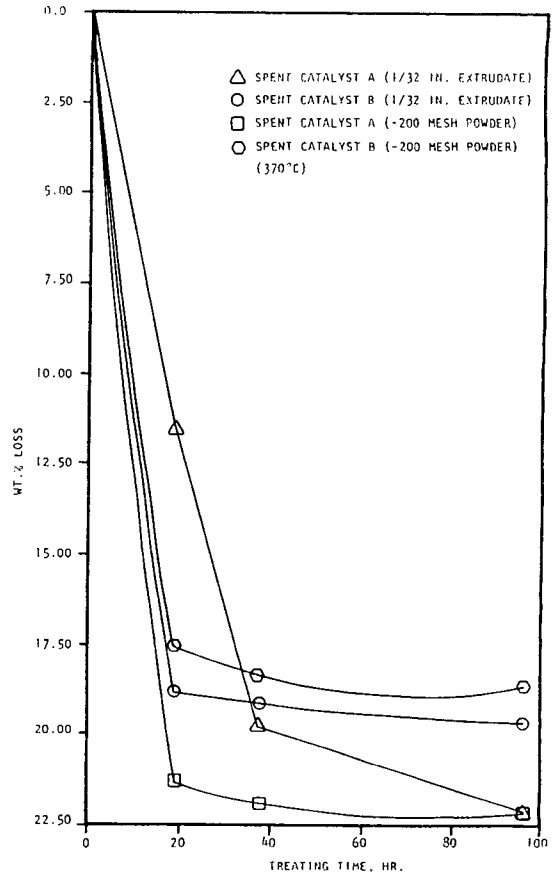


FIGURE 4. SPENT CATALYSTS OXIDATION WEIGHT LOSS CURVES

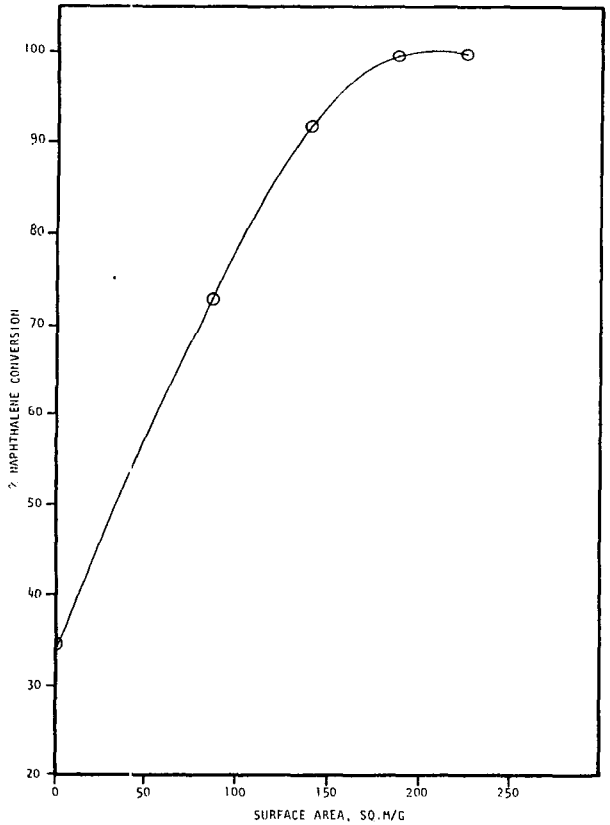


FIGURE 5. SURFACE AREA AND CATALYST ACTIVITY RELATIONSHIP

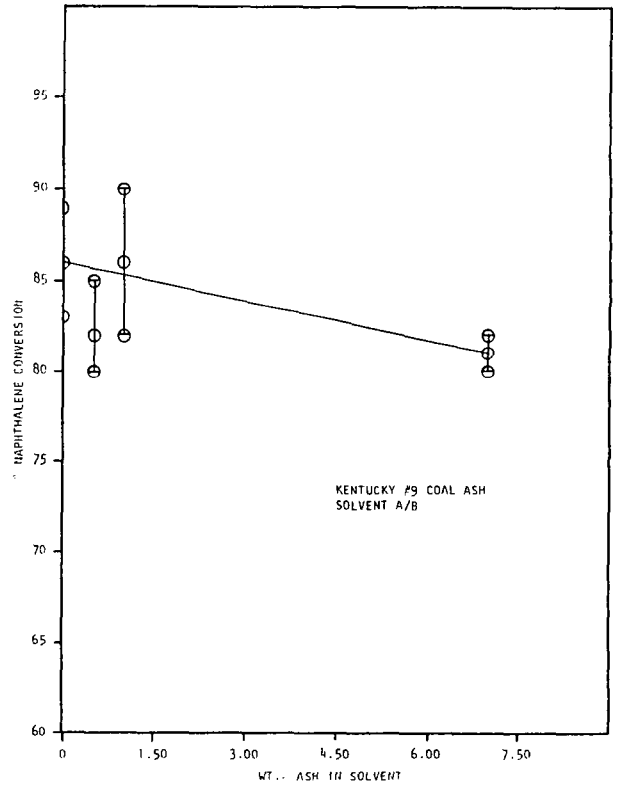


FIGURE 6. CATALYST DEACTIVATION WITH VARYING ASH CONCENTRATION