

## BATCH AUTOCLAVE HYDROGENATION OF SOLVENT REFINED LIGNITE

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INTRODUCTION

A research program has been developed at the University of North Dakota (UND) for the upgrading of northern Great Plains Province Coals to premium fuels. The Department of Chemical Engineering with support of the Office of Coal Research and the Burlington Northern Railroad, has developed a process for solvent refining North Dakota lignite. The solid, low-melting product, solvent-refined lignite, (SRL) has considerable potential for use as a clean burning solid fuel. However, due to its high reactivity, high solubility, low ash, and low sulfur, it is also a reasonable starting material for catalytic hydrogenation to clean liquid fuels. Thus, the Department of Chemistry has been studying SRL hydrogenation, chemistry, and structure.

In this report a series of batch autoclave hydrogenation experiments on SRL are discussed. In these experiments the effect of variations in temperature, pressure, catalyst, and solvent medium are examined. The most important criterion has been the % conversion of SRL to distillable liquids plus gases. However, the SRL and liquid fractions have also been carefully examined by spectroscopic and analytical chemical methods. It is of interest that we can now readily convert SRL to distillable liquids and gases in over 90% conversion.

EXPERIMENTALSolvent Refined Lignite (SRL)

The SRL used in these hydrogenation experiments was prepared by the Pittsburg and Midway Coal Company, Kansas City, Mo., from North Dakota Lignite in chilled anthracene oil. The SRL was ground to 100 mesh. It has the following elemental analysis: C, 85.57; H, 5.62; O, 6.99; N, 1.41; S, 0.3; ash, 0.11. (2)

Catalysts

Six catalysts, Co-Mo-0401 T, Co-Mo-0402 T, Ni-4303 E, Ni-4301 E, Al-1404 T, HT-100 E were purchased from Harshaw chemical Company. Catalysts HZ-1 was supplied by Air Products and Chemicals, Houdry Division. Four Harshaw catalysts, Co-Mo-0402 T, Ni-4301 E, Ni-4303 E, and HT-100 E were presulfided by the procedure described by P.M. Yavorsky and co-workers (3). Stannous chloride was used as neat powder in run 25, and in run 26, it was impregnated on alumina support. The procedure for impregnation was also given in Yavorsky's paper (3). The presulfided catalysts were prepared and used immediately unless specified. Table I describes the catalysts in detail.

Hydrogenation Equipment and Procedures

The hydrogenation reactor employed is a 1-liter Hastelloy C, MagneDrive batch autoclave purchased from Autoclave Engineers, Inc. Erie, Pa.

In most of the experiments, the autoclave was charged with 75 g of SRL, 150 ml of solvent, a catalyst (1, 10, or 50% by weight based on 75 g of SRL) purged of air and pressurized with hydrogen (1000-2500 psi) from commercial cylinders (for pressure higher than 2,000 psi, a hydraulic jack from American Instruments was employed). The reaction mixture was normally stirred overnight,

heated slowly to the desired reaction temperature (375°, 425°, 450°C) in about 50-60 minutes and then held at this temperature for a period of 2 hours. The reactor was cooled slowly to about 150°C. It was then depressurized by passing the reaction gas mixture through an acid trap for ammonia removal, and then through two 0°C traps, two -78°C traps and was finally collected in a 200-liter gas bag.

The ammonia was determined by back titration of the excess acid in the acid trap. The gas in the gas bag was immediately analyzed by a dual-column gas chromatograph to determine the amounts of specific gases produced (Table II).

After removal of the gases, the liquid left in the reactor was separated from the catalyst by decantation. The catalyst, after being washed with 40 ml of solvent, was transferred to a Soxhlet extractor and extracted with THF until the solvent was colorless. The THF extract was then distilled up to 260°C at 1 mm. The non-distillable residue was considered as part of the unconverted SRL and added to the total unconverted SRL for conversion calculations.

The liquid fraction from the reaction mixture and the washing solvent were combined and then distilled first at atmospheric, then at reduced pressure (at 1 torr). When THF was used as a solvent, the reaction mixture was first distilled up to 135° at atm. pressure to remove the solvent, and then vacuum distilled up to 260°C at 1 torr. When tetralin was used as the solvent, the reaction mixture was distilled up to 200°C at atmospheric pressure and then continued at a pressure of 1 torr to yield the following fractions: initial boiling point (IBP)-89°, 89-139°, 139-200°, 200-260°C, and above 260°C (the vacuum bottom). The fraction with a boiling point higher than 260°C at 1 torr was considered to be unconverted SRL. Total conversions were calculated from the unconverted SRL. These distillation and conversion data are tabulated in Table III. We did not list the atmospheric and the first vacuum distillation fractions because they consisted of mainly solvents and a little of the lower boiling liquid which was derived from the cracking of either the SRL or the solvent or both.

In our hydrogenation experiments we have recovered better than 95% of the input material at lower reaction temperatures (375 and 425°C). However, at higher reaction temperature (450°C) the percent recovery was lower (about 93%). The missing material is due partly to the loss through handling and partly to error in the absolute determination of the gas content. By our gas analysis technique we can only determine the absolute amount of methane, ethane, nitrogen, and hydrogen gas in the gas bag. At lower reaction temperatures, little gas was produced, but at higher reaction temperatures the gas production was larger (Table IV).

#### Product Analyses

The elemental analyses of the distillation and the vacuum bottom fractions are recorded in Table V. The aromatic hydrogen to aliphatic hydrogen ratio was obtained by NMR spectroscopy, (Table V), and phenol and basic amine content (Table V) by titration. The carbon and hydrogen analyses were performed in our laboratory in semi-microscale (10-20 milligrams sample) in duplicate or triplicate. The analyses were periodically checked with standard samples (benzoic acid, and glucose). The NMR data were taken from a Varian A60 NMR spectrometer. For these spectra the SRL and vacuum bottom solids were normally dissolved in deuterated pyridine and the liquid samples in deuterated chloroform. For the solubility determinations of SRL and vacuum bottoms, a 0.15-2.0 g sample was stirred in 30 ml of benzene for 30 minutes, and then filtered. The filtrate was evaporated to dryness. The residue was weighed, and the solubility was calculated, Table V. The basic amines were titrated with 0.1 molar perchloric acid in a mixture of 50 ml of nitrobenzene and 5 ml of glacial acetic acid, and the end points were determined by potentiometric techniques (4). The phenols

were titrated potentiometrically with 0.1 molar tetrabutyl-ammonium hydroxide under nitrogen atmosphere in pyridine solvent (5).

The liquid product composition analyses were performed by Gulf Research and Development Company, Pittsburgh, PA (run 31 only). The results are present in Table VI.

## RESULTS AND DISCUSSION

A total of thirty-six batch autoclave hydrogenation experiments were performed to determine the effect of solvents, catalysts, temperature, and pressure on conversion of SRL to distillable liquid and gases. The NMR, elemental analysis, titration and solubility of vacuum bottoms data were obtained to give insight into the nature of the hydrogenation reactions.

### I. Solvent Studies

It is best if no solvent were to be used for the conversion of SRL into liquids. Practically the results illustrate that the yields are just too low when no solvents are used. Presumably the solvent has several roles during the hydrogenation which are helpful to the reductions. Most important it can function as a hydrogen carrier from the catalyst surface to the material to be reduced. It's secondary function is to cause the mixture to attain a fluid state at the reaction conditions.

In our initial hydrogenation experiments, tetrahydrofuran (THF) and tetralin were used as solvents. THF was employed because it dissolves both the SRL and hydrogenation product, and can be removed easily. Tetralin was used because of its well-known hydrogen donating ability (6) and its higher critical temperature. The conversion data of runs 1, 6 and 44 of Table III show that tetralin is a better solvent in terms of high conversion in the absence of a catalyst (tetralin, 40% and THF, 13-17.5%).

We have also compared naphthalene with tetralin in run 39 and 35, respectively. The conversion data again reveal that tetralin is a better starting solvent (tetralin, 88% and naphthalene, 66%). The ideal solvent is no solvent. However, this appears impractical as the experiments illustrate. The minimum solvent:SRL ratio was next to be established. Runs 41 and 42 were performed with presulfided Ni-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst at 450°C with a maximum pressure of 4150 psi, in the absence of a solvent. The conversions were 50%. Under similar conditions, with 150 ml of tetralin a conversion of 88% was found (run 35). In run 47 with 75 ml of tetralin the conversion was 93%. In run 48 in which the solvent volume was 37 ml, the conversion was 91%. Thus, tetralin is a better solvent than THF and naphthalene, probably due to a combination of its hydrogen donating character and higher critical temperature. The solvent to SRL ratio studies showed that the highest conversion was found when the solvent to SRL ratio was 1:1, but a relatively high conversion (91%) could be obtained with a ratio of 1:2. The lower conversion with larger solvent ratios suggests that the solvent is in competition with the SRL during the hydrocracking process.

### II. Catalyst Studies

In these studies, attention has been focussed on available catalysts both presulfided and not which had promise of effectiveness from previous reports. The objective was to obtain high conversions of SRL. In the initial catalyst:SRL ratio determination, all conditions were kept constant except for the amount of catalyst present. From runs 7 and 10 (Table III), the percent conversion of SRL did not change significantly on changing the catalyst concentration from 1 to 10%, i.e., 26 and 27%, respectively. However, there is a significant change from the absence of a catalyst to a 1% concentration, found in runs 1, 6, and 7 with THF as solvent, (i.e., from 12.5-17.5% to 25.7%).

With tetralin as the solvent the catalyst concentrations of 10% (run 15) and 50% (run 16) and an initial pressure of 2500 psi were made. This increase gave an increase in conversion of 41 to 48%. Though a 50% catalyst concentration may not be optimum, as compared to the continuous flow systems in which the catalyst to substrate ratio in the reactor is much higher, this percent ratio was maintained for the remainder of the experiments in order to evaluate the effectiveness of a given catalyst on the weight basis.

The next series of batch autoclave experiments were performed to evaluate several proven commercial catalysts with SRL. The six commercial catalysts are the following: Ni-W-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Ni-W-Al<sub>2</sub>O<sub>3</sub>, Co-Mo-Al<sub>2</sub>O<sub>3</sub>-0401 T and -0402 T, Al<sub>2</sub>O<sub>3</sub>, Ni-Mo-Al<sub>2</sub>O<sub>3</sub>. Their compositions are given in Table I. In this series, (runs 16, 18, 19, 20, 21, 22, and 24) the highest conversion (54.5%) was found in run 24 with Ni-Mo-Al<sub>2</sub>O<sub>3</sub>. The lowest conversion (45.6%) was with Ni-W-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. The others are about 48 to 50% conversions. The lower conversion might be due to the fact that Ni-W-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is relatively sensitive to nitrogen poisoning (1.4% of N in SRL), while on the other hand, Ni-Mo-Al<sub>2</sub>O<sub>3</sub> is less sensitive to nitrogen poisoning (7%).

To determine the effect of presulfiding, three of the above catalysts (Ni-W-Al<sub>2</sub>O<sub>3</sub>, Co-Mo-Al<sub>2</sub>O<sub>3</sub>-0402 T, and Ni-Mo-Al<sub>2</sub>O<sub>3</sub>) were presulfided and immediately used for hydrogenation. Among the three catalysts used at reaction temperature of 375°C, presulfided Ni-Mo-Al<sub>2</sub>O<sub>3</sub>, the best under non-presulfided conditions, allowed the highest conversion of SRL (62.1%, run 32). This is a difference of 7% from the non-presulfided run. For the presulfided Ni-W-Al<sub>2</sub>O<sub>3</sub> and Co-Mo-Al<sub>2</sub>O<sub>3</sub>-0402 T catalysts (runs 27, 28, and 29), there was an increase of 11% and 10% respectively. In run 34, 7.5 g of acid-washed molecular sieves was added along with the presulfided Ni-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst, and the conversion was about the same as that of Ni-Mo-Al<sub>2</sub>O<sub>3</sub> by itself (run 31). In general, the presulfided catalysts provided a 10% increase in conversion. Importantly the volume of lower boiling fractions (distillation fraction 1, 2, and 3 in Table III) were generally larger and the last distillation fraction (fraction 4 in Table III) was smaller than those from the non-presulfided catalyst runs. Figures 1, 2, and 3 demonstrate the fact that all three presulfided catalysts produced greater amounts of lighter distillate than the regular commercial catalyst at the same experimental conditions. Thus the distillation data indicate that the presulfided catalysts promote a more extensive hydrogenation and cracking. Fraction 1 in the graphs of Figures 1, 2, and 3 was obtained by subtracting the sum of fraction 2, 3, and 4 from the total conversion. This fraction includes the gas yields, mechanical loss and products that boil lower than 89°C at 1 torr. Mechanical losses are probably the same for both the presulfided and regular catalyst runs, and therefore for comparison purposes, they are constants.

At higher reaction temperatures (425°C and 450°C) the presulfided Ni-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst (runs 31, 35) and Ni-W-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (runs 33, 43, 46) catalyst (which is known as a dual-function hydrocracking catalyst) has been tested. The distillation data show that the presulfided Ni-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst of runs 31 and 35 at both temperatures gave higher conversions than the presulfided Ni-W-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst of runs 33 and 46 at 425°C, 76% vs 68.5% and at 450°C, 88% vs 84%. In run 45, with reaction temperature of 450°C and with no catalyst, the conversion was only 60%, and therefore a difference of more than 25% was due to the effect of the catalyst (run 35 and 46). Thus, presulfiding the catalysts and a reaction temperature of 450°C are necessary for high conversions.

Zinc chloride is another catalyst which has an interesting activity for both hydrogenation and cracking, and it is of special interest since it appears to be less sensitive to nitrogen poisoning (8). Two runs were carried out at 375°C with this catalyst; run 25 as neat ZnCl<sub>2</sub> (10%) powder, and the other, run 26, 6.4% ZnCl<sub>2</sub> impregnated on alumina (Harshaw Al-1404 T). Run 25, with neat ZnCl<sub>2</sub> powder, gave a 53.5% conversion which is as high as that of Ni-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst. The impregnated

ZnCl<sub>2</sub> catalyst yielded a lower conversion (47% from run 26). This smaller conversion is perhaps due to a smaller amount of ZnCl<sub>2</sub> that was used. Work was discontinued with this catalyst due to anticipated catalyst recovery problems.

A cracking catalyst, HZ-1, from Houdry Catalysts was also tested at 425°C with SRL. The conversion was not as high (52.5%) as those with presulfided catalysts in general (run 36).

Thus far, the presulfided Ni-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst is the best catalyst in terms of high conversion of SRL to gaseous and liquid products, and that the presulfided catalysts generally give a higher yield of lower boiling fractions than the non-presulfided type.

### III. Pressure Effect

Runs 10, 11, 12, 13, 14, and 15 were performed to study the effect of pressure on conversion of SRL to distillate liquids and gases. In runs 10 and 11, an increase of initial pressure from 1000 to 1800 psi, with THF as solvent, did give an increase in conversion of 27.3% to 38%. However, in the case of tetralin as solvent, there was no significant effect on conversion with an increase in initial hydrogen pressure from 1750, 2060 to 2500 psi (40%, 43%, and 40.9% respectively).

### IV. Temperature Studies

Several experiments were carried out to determine the ideal reaction temperature with a relatively high conversion. Runs 32, 31, and 35 were carried out at reaction temperatures of 375°, 425°, and 450° respectively while all other conditions remained constant. The percent conversions increased linearly with reaction temperature as illustrated in Figure 4. The percent conversions are 62% for 375°C, 76% for 425°C, and 88% for 450°C. These results suggest that hydrocracking does not proceed readily until the reaction temperature reaches 450°C.

As the reaction temperature increased, gas production also increased rapidly. The total yields of methane and ethane for reactions at 375°, 425°, and 450°C were 0.40 g, 1.78 g, and 5.48 g, respectively (run 32, 31, 35, Table II). The ideal reaction temperature is that where gas production is at a minimum and the total conversion is at a maximum. Perhaps, the ideal case may not be obtainable, but the gas production of 5.48 g is still tolerable, and therefore the reaction temperature of 450°C appears to be most favorable.

### V. Analytical Methods for Monitoring Reaction Products

Besides using percent conversion as our guideline to determine the effect of solvents, temperature, pressure, and catalysts on the hydrogenation of SRL, we also used and developed other analytical methods to monitor the extent of these hydrogenations. These methods consist of carbon and hydrogen analyses (Table V), NMR data (Table V), basic amine and phenol determinations (Table V), and gas production (Table II).

The atomic H/C ratios were calculated from hydrogen and carbon elemental analyses. These ratios did not vary too much until run 27 (the presulfided catalyst run) and they appeared to be higher for all the runs with presulfided catalysts (e.g., regular commercial catalyst run, 26, fraction (2) 1.22 (3) 1.00, (4) 0.97 (5) 0.90, and for the presulfided catalyst run 27, fraction (2) 1.45, (3) 1.26, (4) 1.15, and (5) 0.96). Runs 27 to 33 gave the typical high atomic H/C ratios.

We have also analyzed the distillation fractions by NMR spectroscopy. The aromatic to aliphatic ratios reveal the same general trend as found in the atomic H/C ratio studies, that is, the aromatic to aliphatic hydrogen ratios are high for earlier runs (up to run 26) and are low from run 27 to run 34. These data suggest that the presulfided catalysts promote the hydrogenation of the aromatic system in the SRL to a greater extent than the non-presulfided catalysts (e.g.,

run 18, with the regular commercial catalyst, fraction (2) 0.56, (3) 1.00, (4) 1.15, and run 27 with a presulfided catalyst (2) 0.19, (3) 0.21, (4) 0.24). These results indicate that there is more aliphatic hydrogen in the distillation fractions of the presulfided catalyst runs.

The gas analysis data are tabulated in Table II. The higher reaction temperatures tend to yield a larger amount of gases. This is demonstrated in run 32 at 375°, 21 at 425°, and 35 at 450°C with the total methane and ethane yields of 0.40 g, 1.78 g, and 5.48 g respectively. Our aim was to minimize the gas yield and maximize the liquid yield, and thus the reaction temperature should probably not be much higher than 450°C.

In general, nitrogen compounds are known as catalyst poisoning agents, and therefore we are naturally concerned with the basic nitrogen content in the SRL and in the hydrogenation products. We are also interested in the denitrogenation capability of the catalysts. We have adopted the non-aqueous potentiometric titration method for the determination of the basic nitrogen. The titration data are listed in Table V. Most of the vacuum bottoms were analyzed for basic amines and in some cases, some of the distillation fractions were also analyzed in this way.

In general, titration data indicate that the basic amines in the vacuum bottoms of regular commercial catalyst runs were either about the same as in the original SRL (0.54 meq/g SRL) or slightly below. For the presulfided catalyst runs of Ni-4303 E Co-Mo-0402 T and Ni-4301 E, the titratable amine content remained about the same as the original SRL, but that of the presulfided HT-100 E (Ni-Mo-Al<sub>2</sub>O<sub>3</sub>) was reduced by 50% or more (run 31, 32, and 34, Table V). Thus, this suggests that NiS-MoS<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is a better denitrogenation catalyst than NiS-WS<sub>2</sub>-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and CoS-MoS<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>.

The phenolic content of the SRL and its hydrogenated products were also determined by non-aqueous potentiometric titrations. In most cases, the vacuum bottom was titrated for phenols so that the phenolic content could be compared with that of SRL (1.34 meq/g SRL). In general, the phenolic content in the vacuum bottom was much lower than that of the SRL (Table V). It is also interesting to note that the runs with a high conversion usually produced a vacuum bottom with a lower phenolic content.

The compositional analysis for the four distillation fractions from run 31 was carried out by the Gulf Research and Development Company. The results are shown in Table VI. The higher boiling fraction appear to have greater amounts (by weight) of fused aromatic systems. Thus, further reduction is needed.

From the benzene dissolution data, no noticeable trend is found as in other analytical methods. One thing worth noting is that the vacuum bottoms are normally more soluble than the original SRL (62.2% for SRL).

The production of water is not too predictable although it seems in general to be higher for the later runs (from run 26 on). The difference in water yield is small and the fluctuation is large. Thus, no constructive conclusion can be drawn.

Thus, to sum up, a series of batch autoclave hydrogenation experiments were performed for converting solvent refined lignite (SRL) to premium liquid fuels. A total of thirty-six experiments were performed to accomplish the following: (1) establish the general conditions for the hydrogenation, (2) survey suitable commercial catalysts, (3) investigate the influence of presulfided catalysts, and (4) study the effect of the reaction temperature and solvent. From the initial runs, we have established the general conditions for the catalyst comparison,

that is, an initial hydrogen pressure of 2500 psi, 50% catalyst by weight, 150 ml tetralin, and 375°C for reaction temperature. For these conditions, a total of eight catalysts were tested with SRL. The best two of these runs are Ni-Mo-Al<sub>2</sub>O<sub>3</sub> (Harshaw HT-100) and stannous chloride catalysts for high conversion of SRL to products. The next series of batch autoclave experiments utilized presulfided catalysts. Result showed that Ni-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst still gave the highest conversion. The reaction temperature studies demonstrated that the percent conversion of SRL to distillable liquid and gases increases linearly with the increase of reaction temperature, with a high of 88% conversion at 450°C. From the solvent experiments, tetralin is shown to be necessary for the high conversion. Thus, the experimental conditions for the highest conversion, thus far attained, are the following: initial hydrogen pressure of 2500 psi, 75 g of SRL, tetralin, presulfided HT-100 catalyst, at 450°C for 2 hours.

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TABLE I

Catalysts Used in SRL Hydrogenation

Catalyst	Supplier	Trade Name	Composition Wt. pct.	Pore Vol. cc/g	SA m <sup>2</sup> /g	Shape
Co-Mo-Al <sub>2</sub> O <sub>3</sub>	Harshaw	Co-Mo-0401 T	3 CoO, 9 MoO <sub>3</sub>	0.40	160	1/8" tablets
Co-Mo-Al <sub>2</sub> O <sub>3</sub>	Harshaw	Co-Mo-0402 T	3 CoO, 15 MoO <sub>3</sub>	0.40	200	1/8" tablets
Ni-W-Al <sub>2</sub> O <sub>3</sub>	Harshaw	Ni-4303 E	6 Ni, 19 W	0.54	152	1/12" extrudates
Ni-W-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Harshaw	Ni-4301 E	6 Ni, 19 W	0.37	228	1/12" extrudates
Al <sub>2</sub> O <sub>3</sub>	Harshaw	Al-1404 T	97 Al <sub>2</sub> O <sub>3</sub>	0.42	180	1/8" tablets
Ni-Mo-Al <sub>2</sub> O <sub>3</sub>	Harshaw	HT-100 E	3.8 Ni, 16.8 Mo	0.54	190	1/16" extrudates
Zeolite	Houdry	HZ-1	45 Al <sub>2</sub> O <sub>3</sub> , 53SiO <sub>2</sub>	--	100-150	0.2" pellets

TABLE II

Gas and Water Production

Run	Methane, g	Ethane, g	Ammonia, g	Water, g
16	0.27	0.09	--	1.6
18	0.19	0.13	--	1.6
19	--	--	--	1.8
20	0.21	0.08	--	1.7
21	0.13	0.04	0.01	1.7
22	--	--	0.01	1.6
24	--	--	0.24	1.4
25	--	--	0.01	1.7
26	0.28	0.18	0.08	2.1
27	0.22	0.20	0.33	4.9
28	--	--	0.35	--
29	0.17	0.07	0.19	2.5
30	--	--	0.36	1.9
31	1.10	0.68	0.45	1.2
32	0.27	0.13	0.41	1.4
33	1.27	0.64	0.26	1.5
34	0.81	1.04	0.56	2.1
35	2.14	3.34	0.59	3.3
41			0.30	3.0
43			0.27	2.0
46			0.32	2.5

TABLE III  
Tabulation of Hydrogenation Data

Run	Reaction Conditions		Solvent 150 ml.	Catalyst <sup>2</sup>	Reaction °C	Distillation of Fractions			Total Conversion Wt. %			
	H <sub>2</sub> , psi initial	Press., psi max.				1	2	3		4	5	
1	900	2600	THF	none	375		→	→	25.3	82.5	17.5	
6	1000	2800	THF	none	375		→	→	27.3	87.5	12.5	
7	1000	2450	THF	1% Co-Mo-0401 T	375		→	→	32.0	74.3	25.7	
10	1000	2600	THF	10% Co-Mo-0401 T	375		→	→	25.5	72.7	27.3	
11	1800	2850	THF	10% Co-Mo-0401 T	375		2.0	→	35.6	62.0	38.0	
12	1750	2800	Tetralin	10% Co-Mo-0401 T	375		3.3	→	28.8	58.7	41.3	
13	1750	2800	Tetralin	10% Co-Mo-0401 T	375		2.0	→	32.8	59.7	40.1	
14	2060	3300	Tetralin	10% Co-Mo-0401 T	375		2.1	19.6	12.0	57.3	42.7	
15	2500	4100	Tetralin	10% Co-Mo-0401 T	375		2.1	20.5	11.3	59.1	40.9	
16	2500	4210	Tetralin	10% Co-Mo-0401 T	375		7.5	19.5	11.7	52.1	47.9	
18	2500	4300	Tetralin	Ni-4303 E	375		14.6	4.5	12.8	16.8	51.3	48.7
19	2500	3650	Tetralin	Co-Mo-0402 T	375		13.8	5.5	16.4	14.3	50.0	50.0
20	2500	4100	Tetralin	Co-Mo-0402 T	375		5.5	16.7	14.3	50.5	49.5	49.5
21	2500	4400	Tetralin	Ni-4301 E	375		4.4	14.0	16.8	54.4	45.6	45.6
22	2500	4500	Tetralin	Al-1404 T	375		4.1	13.5	15.2	50.8	49.2	49.2
24	2500	4160	Tetralin	HT-100 E	375		17.8	5.6	17.6	15.5	45.5	54.5
25	2500	3950	Tetralin	10% SnCl <sub>2</sub>	375		5.2	20.7	9.3	46.5	53.5	53.5
26	2500	4150	Tetralin	6.4% SnCl <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	375		5.7	18.8	14.9	53.1	46.9	46.9
27	2500	4150	Tetralin	Ni-4303 E <sup>4</sup>	375		15.8	3.3	20.0	10.7	36.1	59.8
28	2500	4100	Tetralin	Ni-4303 E <sup>4</sup>	375		9.9	19.1	12.7	36.8	57.8	57.8
29	2500	4050	Tetralin	Co-Mo-0402 T <sup>4</sup>	375		18.3	10.5	19.5	11.3	40.4	59.6
31	2500	4200	Tetralin	HT-100 E <sup>4</sup>	425		14.0	21.3	11.5	24.3	75.7	75.7

TABLE III (continued)

Run	Reaction Conditions		Solvent 150 ml.	Catalyst <sup>2</sup>	Reaction °C	Distillation of Fractions					Total Conversion Wt. %
	H <sub>2</sub> , psi initial	psi max.				1	2	3	4	5	
32	2500	4100	Tetralin	HT-100 E <sup>4</sup>	375	18.3	9.6	22.1	12.1	37.9	62.1
33	2500	4300	Tetralin	Ni-4301 E <sup>4</sup>	425		10.1	21.5	10.4	31.5	68.5
34	2500	4100	Tetralin	HT-100 E <sup>4,5</sup>	425		18.0	17.5	8.4	23.1	76.9
35	2500	4300	Tetralin	Ni-4301 E <sup>4</sup>	450		17.1	15.2	6.8	11.7	88.3
36	2500	4160	Tetralin	HZ-1	425		4.1	18.0	17.1	47.5	52.5
39	2500	3900	Naphthalene	HT-100 E <sup>4</sup>	450		5.6	19.0	14.0	34.4	65.6
41	1750	4000	none	HT-100 E <sup>4</sup>	450		3.7	+	5.4	50.0	50.0
42	1700	4000	none	HT-100 E <sup>4</sup>	450		4.4	+	4.7	50.5	49.5
43	2500	4550	Tetralin	Ni-4301 E <sup>4,6</sup>	450		17.8	13.0	8.0	20.4	79.6
44	1000	1800	Tetralin	none	375		+	+	38.2	60.0	40.0
45	2000	4150	Tetralin	none	450		6.8	22.6	17.3	40.0	60.0
46	2500	4650	Tetralin	Ni-4301 E <sup>4</sup>	450		12.0	17.0	16.5	16.3	83.7
47	2500	4500	75 ml Tetralin	HT-100 E <sup>4</sup>	450		18.1	14.4	4.1	7.4	92.6
48	2100	4500	37 ml Tetralin	HT-100 E <sup>4</sup>	450		12.3	14.0	5.3	8.8	91.2

1 In every hydrogenation experiment, 75 g of SRL was used, and the reactions were kept at the reaction temperature of two hours.

2 The catalyst used was 50% by weight of 75 g SRL unless specified.

3 Fraction 1 in this table was calculated by subtracting the sum of fraction 2, 3, and 4 from the total conversion. Thus, fraction 1 includes mechanical losses, gaseous products, and light distillates.

4 The catalyst was presulfided before used.

5 Acid washed Molecular Sieves 5A (7.5 g) was added.

6 This presulfided catalyst was 4 days old.

TABLE IV. Mass Calculations

		Calculation of input and output of the hydrogenation autoclave		
		Run 27	Run 31	Run 35
<u>Input:</u>	SRL	75.0	75.0	75.0
	Tetralin	145.5	145.5	145.5
	Catalyst	43.1	40.5	40.6
	H <sub>2</sub>	10.8	10.8	10.8
	Tetralin wash	38.8	38.8	38.8
	Total	313.2	310.6	310.7
<u>Output:</u>	Raw Material (hydrogenation products)	228.6	233.4	210.1
	Catalyst	64.0	62.8	60.3
	Autoclave cold traps	1.1	0.0	3.3
	Adhere to autoclave	1.0	1.2	1.0
	Gases from reaction	7.1	7.5	14.5
	Total	301.8	304.9	288.2
% recovery		96.4%	98.2%	92.7%

TABLE V

Tabulation of H/C Ratio, Aromatic to Aliphatic Hydrogen Ratio, and Titration Data

Run	Fraction	H/C Ratio	$\frac{\text{Ar-H}}{\text{Al-H}}$	Amines <sup>1</sup>	Phenols <sup>1</sup>	Benzene Dissolution, %
SRL		0.75	2.57	0.54	1.34	62.2
10	2	1.357	1.81			
	3	0.963				
	4	0.813	2.82			
	5	0.413		0.09	0.055	---
11	2	---	0.81			
	3	---				
	4	---	1.69			
	5	---	---	0.47	0.73	---
12	2	---	.96			
	3	---				
	4	0.844	1.58			
	5	0.779		0.51	1.09	---
13	2	---	0.69			
	3	---				
	4	---	1.19			
	5	---		0.53	0.96	---
14	2		0.65			
	3	---	1.05			
	4		1.12			
	5			0.58	0.87	---
16	2	1.22	0.53			
	3	1.03	0.98			
	4	1.03	1.09			
	5	0.91		0.57	0.87	69.8

TABLE V Continued

Run	Fraction	H/C Ratio	$\frac{\text{Ar-H}}{\text{Al-H}}$	Amines <sup>1</sup>	Phenols <sup>1</sup>	Benzene Dissolution, %
18	2	1.12	0.56			
	3	0.97	1.00			
	4	0.93	1.15			
	5	0.88		0.52	0.97	
19	2	1.11	0.56			
	3	0.98	0.88			
	4	0.91	0.96			
	5	0.78		0.55	0.91	
20	2	1.14	0.50			
	3	1.13	0.82			
	4	0.98	0.91			
	5	0.81		0.56	0.73	71.1
21	2	1.16	0.647			
	3	1.03	1.21			
	4	0.91	0.90			
	5	0.86		0.48	1.32	
22	2	1.02	1.05			
	3	0.84	1.93			
	4	0.82	2.01			
	5	0.85		0.54	1.12	55.1
24	2	1.20	0.44			
	3	1.07	0.67			
	4	0.96	0.76			
	5	0.91		0.45	0.52	78.4

TABLE V Continued

Run	Fraction	H/C Ratio	Ar-H Al-H	Amines <sup>1</sup>	Phenols <sup>1</sup>	Benzene Dissolution, %
25	2	1.24	0.42			
	3	1.31	0.76			
	4	1.04	0.80			
	5			0.46	0.66	82.9
26	2	1.22	0.48			
	3	1.00	0.81			
	4	0.96	0.88			
	5	0.90		0.36	0.66	94.9
27	2	1.46	0.19			
	3	1.26	0.21			
	4	1.15	0.24			
	5	0.96		0.41	0.47	85.3
28	2	1.42	0.16			
	3	1.25	0.23			
	4	1.16	0.27			
	5	0.92		0.49	0.45	81.9
29	2	1.40	0.21	0.19	0.08	
	3	1.17	0.32	0.21	0.16	
	4	1.06	0.42	0.25	0.24	
	5	0.87		0.53	0.79	67.9
30	2	1.34	0.40			
	3	1.17	0.39			
	4	1.03	0.54			
	5	0.90	0.65	0.16	0.33	

TABLE V Continued

Run	Fraction	H/C Ratio	$\frac{Ar-H}{Al-H}$	Amines <sup>1</sup>	Phenols <sup>1</sup>	Benzene Dissolution, %
31	2	1.37	0.18			
	3	1.25	0.30			
	4	1.14	0.37			
	5	1.02	0.45	0.20	0.32	87.6
32	2	1.40	0.14			
	3	1.32	0.18			
	4	1.17	0.23			
	5	1.01	0.2	0.23	0.23	86.4
34	2		0.19			
	3		0.33			
	4		0.34			
	5			0.28	0.27	

<sup>1</sup> The basic amines and Phenols are expressed as meq. per gram of SRL or other distillation fractions.

TABLE VI

## CHARACTERIZATION OF HYDROGENATED SOLVATED LIGNITE PRODUCTS

Boiling Range	Run 31-2		Run 31-3		Run 31-4		Run 31-1
	87°C (189°F)- 139°C (282°F)	139°C (282°F)- 200°C (392°F)	139°C (282°F)- 200°C (392°F)	200°C (392°F)- 260°C (500°F)	200°C (392°F)- 260°C (500°F)	200°C (392°F)- 260°C (500°F)	IBP- 200°C (392°F)
	Saturates						
Wt% of Sample	12.5	8.6	8.6	3.6	3.6	73.5	
Paraffins	0.4	1.9	1.9	1.5	1.5	0.0	
Non Condensed Cycloparaffins	3.5	0.9	0.9	0.8	0.8	56.8	
Condensed Dicycloparaffins	3.8	2.9	2.9	0.7	0.7	16.7	
Condensed Tricycloparaffins	4.2	2.9	2.9	0.6	0.6	0.0	
	Aromatics						
Wt % of Sample	86.5	90.6	90.6	96.2	96.2	24.0	
Alkylbenzenes	1.1	0.7	0.7	2.0	2.0	6.8	
Indanes/Tetralins	16.6	4.1	4.1	3.2	3.2	16.0	
Naphthalenes	4.9	2.3	2.3	1.7	1.7	0.5	
Phenanthrenes	0.9	0.9	0.9	0.0	0.0	0.0	
Hydrophenanthrenes	30.3	23.6	23.6	4.9	4.9	0.0	
Pyrenes	1.6	9.1	9.1	20.0	20.0	0.0	
Hydropyrenes	16.2	40.0	40.0	36.1	36.1	0.0	
Acenaphthenes/Biphenyls	1.4	0.0	0.0	0.0	0.0	0.0	
Chrysenes	1.4	3.9	3.9	12.6	12.6	0.0	
Benzopyrenes	0.2	1.9	1.9	6.4	6.4	0.0	
Naphthols	2.5	1.0	1.0	1.6	1.6	0.0	
Resorcinols	3.6	0.4	0.4	0.6	0.6	0.1	
Phenols	6.2	2.6	2.6	5.1	5.1	0.6	

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<sup>1</sup> Fractions s, 3, and 4 were distilled at 1 torr, and fraction 1 was at atmospheric.

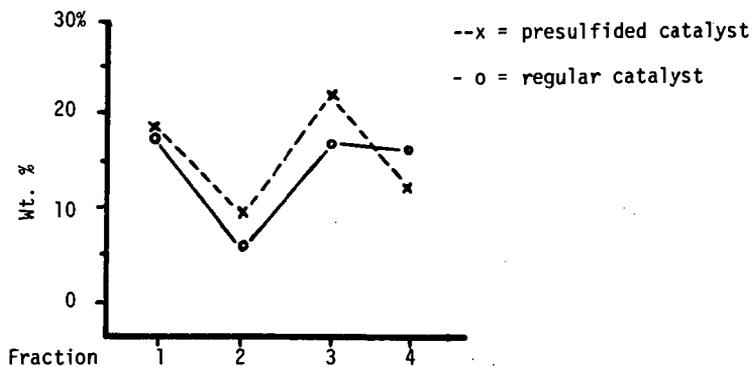


Figure 1. Comparison of distillation fractions from Ni-Mo-Al<sub>2</sub>O<sub>3</sub> catalyst.

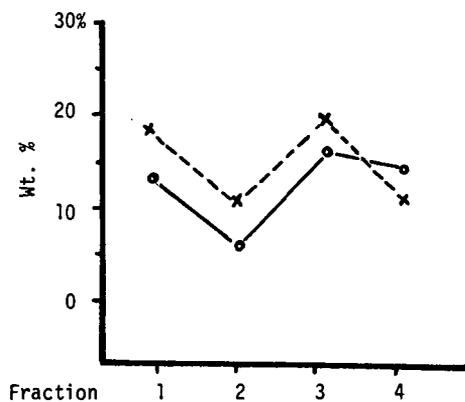


Figure 2. Comparison of distillation fractions from Co-Mo-Al<sub>2</sub>O<sub>3</sub>-0402 T catalyst.

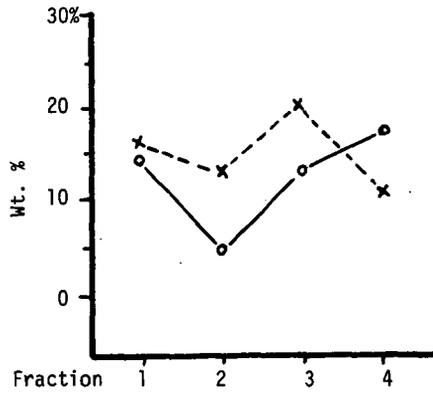


Figure 3. Comparison of distillation fractions from Ni-W-Al<sub>2</sub>O<sub>3</sub> catalyst.

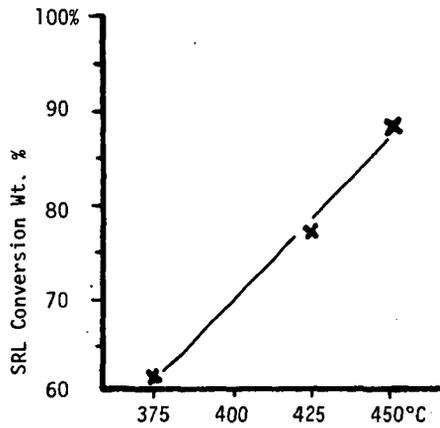


Figure 4. Percent Conversion vs. Reaction Temperature For Presulfided HT-100 Catalyst.

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