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PROJECT LIGNITE
PREMIUM FUELS FROM NORTHERN GREAT PLAINS LIGNITE

R & D REPORT NO. 106 - INTERIM REPORT NO. 3

LABORATORY STUDIES OF THE CONVERSION OF SOLVENT REFINED LIGNITE TO LIGHT LIQUID FUELS

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CONTENTS

Table 4 is large summarizing table.
Tables 5-10 arranged by Run number.

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I. SUMMARY

The first part of this interim report describes the results of characterization studies of solvent refined lignite (SRL) and solvent refined coal (SRC), and the second the results of SRL and SRC conversions to lighter materials.

The solubilities of SRL were determined in about forty organic solvents, several of which dissolved the SRL completely. The basic nitrogen and phenolic contents in the SRL were determined by potentiometric titrations. Some of the nitrogen in SRL comes from the solvent used in its preparation. From spectral studies, elemental analyses, and molecular weight determinations, some structural features of the average SRL molecule were deduced.

Approximately 90 hydrogenation experiments were conducted for SRL and SRC conversion to gas and distillable liquid products. In preliminary experiments, a standard set of reaction conditions was established for catalyst screening. Optimum conditions seemed to be 450°C with initial hydrogen pressures of 1800 psi for non-solvent reactions and 2500 psi with solvent. The best catalyst, in terms of overall conversion and denitrogenation, was presulfided Ni-Mo-Al_2O_3 which gave approximately 90 percent conversion of SRL to 10 percent gases and 80 percent distillable liquids. Almost equally high conversion was obtained with SRC using the same reaction conditions.

II. INTRODUCTION

A. BACKGROUND

Energy research has been pursued at the University of North Dakota for many years. The reason for the University's interest and activity was the presence of significant oil reserves and major lignite (low-rank, low-sulfur coal) resources in the Northern Great Plains. The latter amounts to 20 percent of the Nation's total coal resource. Because of coal's importance in the overall energy picture, coal research has increased dramatically in the last few years. The research programs of the University of North Dakota are addressed to several energy-related developments. They are: (1) the search for and characterization of lignite coal, (2) the utilization of lignite coal, (3) the environmental impact of lignite mining and utilization.

In the spring of 1972 the Engineering Experiment Station and the Chemical Engineering Department were awarded a five-year research and development contract, named "Project Lignite," by the U.S. Department of Interior, Office of Coal Research. The project was transferred to the Energy Research and Development Administration upon establishment of this agency for administration.

A major object has been upgrading of the Northern Great Plains Province Coals to premium fuels and chemical products. "Project Lignite" has as its ultimate goal the conceptual design of a pilot plant for an integrated lignite refinery for the production of liquid, solid, and gaseous products by a combination of new techniques developed during the course of the project and modifications of currently available technologies for coal and hydrocarbon processing. As part of the development of new techniques and processes necessary to bring this refinery concept to reality, the Chemical Engineering Department cooperated with the Chemistry Department in establishing a program of exploratory research into the basic chemistry necessary to develop economical products from lignite via "solvent refined lignite." The result was the "Committee on Fuel Research" which is an interdisciplinary group of chemists and chemical engineers formed in the spring of 1973 to attack the problems such as hydrogenation of SRL in a systematic and coordinated way. Under a subcontract from Project Lignite, the Department of Chemistry has been studying SRL hydrogenation, chemistry, and structure.

Primarily the work under the subcontract is to develop rapid techniques for characterizing SRL derived products, and to establish the background for a general coal research program in the Department of Chemistry.

This interim report covers in two parts the work done in the period of January 1973 through December 1975. The first part consists of the characterization of solvent refined materials (SRL and SRC), and the second of the SRL and SRC conversion studies.

The characterization work involved the analyses of SRL and its derivatives using instrumental techniques, including infrared (IR), mass spectrometer (MS), ultraviolet (UV), and nuclear magnetic resonance (NMR) in addition to chemical methods, and with all information interfaced by computer techniques. The usefulness of these analytical methods is well established, but because of the complex nature of SRL and SRC many of these methods were specially modified for coal research.

For SRL and SRC conversion studies, a research program was developed and carried out primarily to convert SRL to liquid products. The conversion was accomplished through catalytic reduction processes. This SRL conversion program consisted of baseline experiments, a survey of commercial catalysts previously developed primarily for petroleum refining, studies of catalyst pretreatment, and optimization of reaction conditions. Experiments were carried out on a bench scale using a one-liter batch reactor. Under relatively mild reaction conditions, 90 percent of the SRL has been converted to yield 80 percent liquids and 10 percent gases. Solvent refined coals (SRC) from Kansas City and Tacoma, Washington, have also been converted with equally high overall yields of liquid and gaseous products under reaction conditions similar to those developed for SRL conversion.

B. WORK ACCOMPLISHED

Experimental conditions have been established for converting 90 percent of the SRL to gaseous and liquid products, and recommendations have been made as to reaction conditions and catalysts for use in the Process Development Unit (PDU) of Project Lignite for converting the SRL to light liquid fuel components.

The hydrogenation experiments revealed several interesting results. One of these is the result of the solvent to SRL ratio studies. The initial ratio of solvent (tetralin) to SRL used influenced the overall conversion. Maximum conversion of 93 percent was obtained with a solvent to SRL ratio of 1:1. The conversion decreased slightly when the ratio was increased or decreased from 1:1. Catalyst conditioning in a hydrogen atmosphere before use promoted hydrogenation and increased overall conversion slightly. Also, it was demonstrated that SRC could be converted with almost equally high conversion under experimental conditions developed for SRL conversion.

The solubilities of SRL in about 40 organic solvents were determined during the characterization work. The solvents prossessing both polar and aromatic groupings resulted in higher solubilities.

From determinations of basic nitrogen, it was inferred that some of the nitrogen content of the SRL came from the solvent used in its preparation, and that, to produce SRL with the lowest nitrogen content, the solvent for SRL formation must also be low in nitrogen. Chemical and physical characteristics determined for SRL and SRC indicated some definite differences in chemical composition between them.

III. EXPERIMENTAL

A. SOLVENT REFINED LIGNITE (SRL)

The SRL for most of the hydrogenation experiments was obtained from the Pittsburg and Midway Coal Mining Company (P&M), in their Merriam, Kansas, laboratory (near Kansas City) and was produced from North Dakota lignite by solution-hydrogenation using chilled anthracene oil as the solvent at a solvent to coal ratio of 1.8:1 with a liquid hourly space velocity of 0.6 and a gaseous hourly space velocity of 100, using pure hydrogen. The dissolver temperature was 420°C and the pressure 1000 psi. The SRL was ground to 100-mesh before use.

The SRL-FS120 samples were prepared by the Project Lignite Laboratory in several batch autoclave runs using a petroleum derived solvent, Gulf FS120, at 2:1 weight ratio of solvent to MAF coal with a 1:1 molar ratio of CO to H_2 at 1000 psi initial pressure. The reaction period was 30 minutes at 400°C, and the maximum pressure was 3170 psi. Following reaction the product gas was removed at 205°C and the slurry was filtered at 205°C. The filtrate was distilled to remove solvent, leaving the SRL as vacuum bottoms. The conversions averaged 89 percent and the SRL yields 57 percent of the MAF coal.

The SRL-PDU samples were obtained from Run SDR-5 in the Process Development Unit of Project Lignite and deashed in the laboratory. The starting solvent for the PDU was Gulf FS120. The run was made at 1250 psi with a preheater outlet temperature of 722°F. Two dissolvers were used in series for a liquid hourly space velocity of 0.7 and a gas hourly space velocity of 116. The temperature through the first dissolver ranged from 741°F to 762°F, while the second was nearly constant at about 710°F. Conversion was about 74 percent and SRL yield 58 percent of the MAF coal. The deashed SRL-PDU contained about 16 percent by weight of the heavy ends of the original solvent. Elemental analyses of the SRL samples are listed in Table 1, Appendix B.

B. SOLVENT REFINED COAL (SRC)

The solvent refined coal from P&M (SRC-KC or SRC-CU-88) was prepared from a blend of Kentucky #9 and #14 coals, high-volatile bituminous B coals, in chilled anthracene oil using a continuous reaction system with a preheater temperature of 450°C and a dissolver temperature of 425°C at a pressure of 1500 psi and with a solvent to raw coal ratio of 2:1. Conversion was 90 percent and SRC yield 69 percent of the MAF coal.

The SRC-Tacoma was prepared at the SRC pilot plant of P&M near Tacoma, Washington, and was identified as: Sample Point, Bin A; Shipment, Sx No. 154; July 1, 1975. The coal used in this case was a blend of Kentucky #9 and #14. Elemental analyses of the SRC samples are included in Table 1, Appendix B.

C. CATALYSTS

Seven catalysts, Co-Mo-0401T, Co-Mo-0402T, Ni-4304E, Ni-4301E, Ni-1404P, Al-1404T, and HT-100E were purchased from Harshaw Chemical Company. Catalyst HZ-1 was supplied by Air Products and Chemicals, Houdry Division. Four Harshaw catalysts, Co-Mo-0402T, Ni-4301E, Ni-4303E, and HT-100E were presulfided. Stannous chloride was used both as the neat powder and impregnated on an alumina support. Table 2, Appendix B, summarizes information on these catalysts.

D. CATALYST PRESULFIDING PROCEDURE

The general catalyst presulfiding procedure was adapted from the method reported by Yavorsky and co-workers (1). Usually 37.5 grams of commercial catalyst was placed in the one-liter autoclave. The capped reactor was evacuated and filled with hydrogen sulfide gas to a pressure of 100 psig. Hydrogen was then added to a pressure of 600 psig. The reaction mixture was heated slowly with stirring to 260°C and was kept at this temperature for four hours. After reaction, the reactor was cooled slowly to room temperature. The reactor was depressurized by passing the gas through a sodium hydroxide solution trap for removing the excess H_2S. The reactor then was evacuated again using a water aspirator and filled either with air or nitrogen gas before the reactor top was opened.

In early hydrogenation runs, the catalyst was weighed in air and, on the average, the weight was about 40.5 g. In these experiments, the catalyst was prepared and used immediately unless specified otherwise.

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(1) Kawa, W., Friedman, S., Wu, W.R.K., Frank, L.V., and Yavorsky P.M., Amer. Chem. Soc., Division of Fuel Chem., Vol. 19, No.1, page 192 (1974).

E. HYDROGENATION EQUIPMENT AND PROCEDURES

1. Equipment

The hydrogenation reactor employed was a one-liter Hastelloy C, Magne-Drive batch autoclave purchased from Autoclave Engineers, Inc., Erie, Pennsylvania. The autoclave was connected to the gas manifold which in turn was connected to the gas cylinders and a hydraulic jack. The simplified diagram of this arrangement is illustrated in Figure 1, Appendix A.

2. General Description of Experiments

Table 3, Appendix B, tabulates the purpose of the various runs which were performed. In addition to those listed in the table, Runs 70, 73, and 74 were carried out in a one-gallon reactor at the Project Lignite laboratory for the purposes of hydrogenating larger quantities of SRL to obtain more of the gasoline and diesel fuel boiling range fractions (fractions 1_A and 1_B respectively). In Runs 80, 81, and 83-88 conversions of SRL-KC, SRL-PDU, SRC-KC and SRC-Tacoma were compared. A more detailed tabular summary of the experimental conditions, including the results and conclusions, is presented in Table 4, Appendix B.

3. General Experimental Procedures

a. Initial Hydrogenation Runs 1-6

In these preliminary experiments to establish an experimental baseline, 150 milliliters of tetrahydrofuran (THF) as the solvent, and 75 grams of solvent refined lignite (SRL) were placed in the one-liter autoclave. The reactor was purged of air, pressurized to 1000 psi with hydrogen, and stirred overnight. During the reaction, the reactor was continuously stirred and slowly heated to 375°C over a period of about one hour and kept at this temperature for two to four hours, followed by slowly cooling to room temperature. After transfer of the reaction mixture to a distillation flask, distillation was done first at atmospheric pressure to remove THF and then at a reduced pressure of one Torr up to 260°C. The residue (vacuum bottoms) boiling higher than 260°C at one Torr was considered as unconverted SRL. The percentage overall conversion is computed as 100 minus the percentage unconverted SRL.

b. Operating Variable Runs 7-17

In these runs, to establish standard reaction conditions with catalyst present, the experimental procedure was essentially as described above with specific differences being in the area of catalyst recovery. The specific amounts of catalyst used in each run are given in Table 4, Appendix B, and range from one to 75 percent based on 75 grams of SRL (i.e., 50 percent catalyst weight means that the weight of catalyst used was 50 percent of the weight of SRL).

The catalyst was not separated from the vacuum bottoms boiling higher than 260°C at one Torr in Runs 7-15 where the amount of catalyst used was 10 percent or less. The original weight of the catalyst used was subtracted from the vacuum bottoms mixture for the purpose of making conversion calculations. For Runs 16 and 17, the catalyst was decanted from the liquid and washed with four 10 milliliter portions of solvent. The extracts were combined with the original reaction liquid mixture. The catalyst was extracted with THF in a Soxhlet extractor until the THF was clear and colorless. The catalyst was then dried to a constant weight. The THF insoluble material left on the catalyst was considered as part of the unconverted SRL and usually amounted to one gram.

The liquid from the reaction mixture along with the solid catalyst for Runs 7-15 was distilled at atmospheric pressure to remove the lower boiling material when THF or benzene was used as the solvent, and then at a reduced pressure of one Torr to produce the following fractions: (1) IBP-87°C, (2) 87-139°C, (3) 139-200°C, (4) 200-260°C, and (5) residue above 260°C or vacuum bottoms. The overall percentage conversion was computed as 100 less the percentage vacuum bottoms. The percentage of vacuum bottoms was calculated based on the original 75 grams of SRL.

c. Catalyst Survey Runs 18-26

The general experimental procedure, described in Section b, was used for this series of experiments to survey available commercial catalysts. The standard reaction conditions were as follows: 75 grams SRL, 150 milliliters tetralin, 2500 psig initial hydrogen pressure, 37.5 grams (50 percent) of commercial catalyst, reaction temperature of 375°C, and reaction time of two hours.

For these experiments, the reaction gas was usually analyzed. After reaction, the reactor was cooled to 150°C and the reactor gas was passed through an acid trap, two 0°C traps, two -78°C traps, and was then collected in a 200-liter gas bag.

The ammonia absorbed in the acid trap was determined by back titration of the excess acid in the acid trap. The gas in the gas bag was immediately analyzed using a chromatograph to determine the amount and kinds of gases produced (Table 5, Appendix B).

d. Non-Solvent Runs 68-88

In those experiments where no solvent was used, the general reaction conditions and procedures were identical to those described in Section c except that an initial hydrogen pressure of 1800 psig and a reaction temperature of 450°C were used. The reaction mixture of liquid and solid was distilled to give fraction 1_A (IBP - 200°C/atm) and fraction 1_B (IBP - 87°C/1 Torr). The pot residue consisting of higher boiling liquids and catalyst was extracted with THF in a Soxhlet extractor. The extract was then distilled to remove the THF and the distillation continued at the reduced pressure of one Torr to give the following fractions: (2) 87-139°C, (3) 139-200°C, (4) 200-260°C, (5) residue above 260°C or vacuum bottoms.

F. REPRODUCIBILITY

In the hydrogenation experiments, products equivalent to more than 95 percent of the input materials were recovered when using lower reaction temperatures (375 and 425°C). However, at higher reaction temperature (450°C) the recovery was about 93 percent. The missing material may be caused by losses through handling and by errors in the absolute determination of the gas content. The gas analysis technique permits determination of the absolute quantities of only methane, ethane, nitrogen, and hydrogen gas in the gas bag. Errors because of this may be relatively small at lower reaction temperatures where little gas was produced; but at higher reaction temperatures when gas production was greater, noticeable discrepancies in material balance appear. Some of the experiments were repeated and the conversions were reproduced within one to two percent. For example, under similar conditions, the difference in conversion for Runs 19 and 20 was only 0.5 percent, for Runs 27 and 28, 2.0 percent, and for Runs 61 and 64, 0.8 percent. Typical material balances are given in Table 13, Appendix B.

G. PRODUCT CHARACTERIZATIONS

1. Gas Analyses

The gas mixture was analyzed for the kind and amount of gases at the Project Lignite Laboratory. The yield of ammonia and light amines was determined by passing the reaction gas through an acid trap, with the acid trap being back titrated. The light liquids trapped by the cold traps were combined and considered as part of fraction 1_A.

2. Carbon and Hydrogen Analyses

The H/C atomic ratios of distilled and vacuum bottom fractions are recorded in Table 6, Appendix B. The carbon and hydrogen analyses were generally performed in the Chemistry laboratory on a semi-microscale using 10 to 20 milligram samples in duplicate or triplicate. The analytical methods were periodically checked using standard samples of benzoic acid and glucose. The elemental analyses for Run 68 were done by Chemalytics Inc., Tempe, Arizona, and nitrogen and sulfur analyses for this run were performed by the Project Lignite Laboratory (Table 7, Appendix B). Some analyses were performed by DuPont, and by Spang Microanalytical Lab, Ann Arbor, Michigan.

3. Nuclear Magnetic Resonance Analyses (NMR)

The NMR data were obtained using a Varian A60 NMR spectrometer. SRL and vacuum bottoms solid samples were usually dissolved in deuterated pyridine and the liquid samples in deuterated chloroform. The results are reported as aromatic versus aliphatic hydrogen ratios, Ar-H/Al-H. The NMR spectra were usually taken with a sweep width of 1000 cycles so that the wide spreading aromatic peaks were completely included in the spectra. Aromatic and aliphatic proton peak areas were integrated two to three times and the average integration values were used to compute the Ar-H/Al-H ratios (Table 8, Appendix B).

4. Solubility Studies

Benzene was chosen as the solvent for the solubility determination of SRL and vacuum bottoms because SRL was only moderately (about 60 percent) soluble in benzene. In general, a 0.15 to 0.2 gram sample of either SRL or vacuum bottoms was stirred into 30 milliliters of benzene using a magnetic stirring bar for 30 minutes. The mixture was filtered and the filtrate was evaporated to dryness in a rotary evaporator. The evaporator was then evacuated using a vacuum pump for 30 minutes more. The residue was weighed, and the solubility calculated. Each determination was carried out in duplicate or triplicate, and the average percentage dissolution in benzene is reported in Table 9, Appendix B.

5. Titration Techniques

a. Determination of Basic Amines

The amount of basic nitrogen present in SRL or vacuum bottoms (VB) was determined largely by nonaqueous potentiometric titration. The SRL and VB sample (0.3 grams or larger) was dissolved in 50 milliliters of nitrobenzene and 5 milliliters of glacial acetic acid. The solution was titrated with 0.1 molar perchloric acid in dioxane. The end point was determined by potentiometric techniques using a pH meter equipped with calomel and standard glass electrodes. The titrations were carried out in duplicate or triplicate. The average values were expressed in milliequivalents/grams of SRL or VB (see Table 9, Appendix B).

b. Determination of Phenolic Acids

The amount of phenolic acids (phenols) present in the SRL or vacuum bottoms was similarly determined as described in Section a above. The SRL or VB sample of about 0.3 grams was dissolved in 50 milliliters of pyridine, and titrated under nitrogen atmosphere with 0.1 molar tetrabutylammonium hydroxide in dried benzene solution. The titration was monitored potentiometrically using a pH meter coupled with a standard glass electrode and a modified methanol-calomel sleeve-type electrode. The electrode modification was necessary because absolute dryness was required for the titration. The commercial pyridine used was pretested to determine the amount of acid present. The results are tabulated in Table 9, Appendix B, and are expressed as milliequivalents phenol/gram of VB.

6. Liquid Product Analyses

Two liquid products were analyzed for chemical composition by Gulf Research and Development Company, Pittsburgh, Pennsylvania. One set of analyses was done for each of the following fractions of Run 31: (1) IBP-200°C/Atm, (2) 87-139°C/1 Torr, (3) 139-200°C/1 Torr, and (4) 200-260°C/1 Torr. The fractions were first separated into saturates and aromatics and then the components were identified by mass spectrometry. Composition analyses for the fractions of Run 31 are listed in Table 10, Appendix B.

A similar set of analyses was done on the following fractions of Run 59: (1A) IBP-200°C/Atm; (1B) IBP-87°C/1 Torr; (2) 87 139°C/1 Torr; and (3) 139-200°C/1 Torr. The results of these analyses were particularly interesting because no solvent was used during hydrogenation, and thus all products were derived from SRL. The analyses are shown in Tables 11A and 11B, Appendix B.

Fractions 1_A, 1_B, 2, and 3 of Run 59 were also analyzed at the E.I. DuPont De Nemours & Company, Wilmington, Delaware. The analyses were done using a GC/MS combination. The fractions were chromatographed using an 8-foot column of 1/8-inch stainless steel tubing containing 10 percent SE-30 on Chromosorb ABS. The chromatograph was programmed from 65°C to 270°C at 6°C/minute. The collected sample for each peak was run through a DuPont 490 mass spectrometer and identified or tentatively identified by comparison of its mass spectrum with those of known materials. The composite chromatogram and peak identification of fractions 1A, 1B, 2 and 3 can be seen in Figure 2, Appendix A and Table 12, Appendix B.

IV. RESULTS AND DISCUSSION

A. CHARACTERIZATION WORK ON SRL

The purpose of the preliminary characterization of solvent refined lignite (SRL) was to better understand the structure and properties of SRL, the starting material for the hydrogenation reaction. The SRL characterization was done by spectral analyses, titration techniques, and solubility studies. The spectral methods used were nuclear magnetic resonance (NMR), infrared (IR), and ultraviolet (UV) spectroscopy. SRL samples vary somewhat in characteristics depending on the liquefaction solvent used in the first stage hydrogenation, i.e., in its preparation. Consequently, the following discussion must be interpreted considering this fact.

1. Spectral Studies

The IR spectra of SRL prepared using chilled anthracene oil (CAO) as solvent indicated that there was very little or no free carboxylic acid present (no IR absorption at the 1700 cm^{-1} region). A pretreatment of the SRL with aqueous hydrochloric acid followed by drying under nitrogen did not change the results. However, carboxylic acid absorption was found in the spectra of unprocessed lignite and air-oxidized SRL. Interestingly, the IR spectrum of the SRL is almost identical to that of bituminous coal.

While the IR spectral studies provided information on the functional groups in the SRL, they were not as informative as NMR data in revealing the chemical environments of the protons in SRL. The NMR spectrum of SRL in deuterated pyridine consists of three broad absorptions centered at $\delta 1.2$, 2.5, and 7.5. These represent aliphatic CH's, aliphatic CH's adjacent to a deshielding group such as a phenyl ring, etc., and aromatic CH's respectively. Analysis of the NMR spectrum showed that the ratio of aromatic to aliphatic protons is 0.78. Noteworthy is the fact that the comparable figure for bituminous coal of the same carbon content is 0.76. Deuterium exchange studies indicated there are about 2.5 milliequivalents of exchangeable protons per gram of SRL. UV analyses of SRL in 1,4-dioxane show considerable absorption in all of the near UV range indicating considerable conjugation in the material.

2. Titration Studies

Because phenols, carboxylic acid and amine groups could play roles in catalyst deactivation, the quantitative determinations of these functional groups was undertaken by potentiometric titration. The acidity and basicity of various samples of SRL are summarized in Table 14, Appendix B. The acidities of two samples of SRL prepared in the same solvent are nearly identical (cf.CAO Runs 504 and 505) and acidity did not change with time. The acidity of SRL prepared using different solvents varied from 0.7 to 2.5 meq/g. Additionally, the general appearance of the titration curve was very similar to that of phenol and markedly different from that of a mixture of phenol and benzoic acid, which suggest a low carboxylic acid content; this agrees with the IR spectrum results.

In general, the precision in the titrations for basic groups was not as good as for the acid titrations. However, considering the low basicity of SRL and the overall procedure, the precision is adequate. Values range from 0.161 to 0.624 meq/g, and about 1/4 the number of acid groups present per gram of SRL. Basicity varied when SRL was prepared using different solvents. Table 14, reporting the basicity of the solvents and the SRL prepared from them, indicates a trend relating the basicity of the SRL to that of the solvent used to produce the SRL. It appears that some of the nitrogen present in these samples of SRL came from the starting solvent used in its preparation.

There is also a general relationship between acidity and basicity; highly basic SRL is also highly acidic. The phenolic contents of the various reigning solvents have not been determined; however, the acidity of the solvent may effect the acidity of the SRL.

Some characterization work has been done on SRL-KC (Kansas City continuous flow) and on SRC-KC (Kansas City continuous flow) in terms of titrations, UV and NMR spectral analyses, elemental analyses, and molecular weight determinations. The results and interpretations of structural information derived from calculations and computer interfacing of the same data on a bank of model compounds are tabulated in Table 15, Appendix B.

3. Solubility Studies

The solubility of SRL, i.e., the percentage dissolved in a given weight of solvent, was investigated in order better to select a solvent for the second stage hydrogenation. Initial extensive studies of SRL prepared in chilled anthracene oil (CAO) were followed by more selective studies of other SRL samples. These data are summarized in Tables 16 and 17, Appendix B.

The solvents fall into three general classes: Class 1 is composed of those in which SRL has low solubility, Class 2 of those in which SRL is of intermediate solubility, and Class 3 of those in which all of the SRL dissolves. Nonpolar (hexane), highly polar (nitro-methane), and hydrogen-bonding (methanol) solvents of low molecular weight have low solvating ability for CAO-SRL (Table 16). Solvents which show some solvating ability for CAO-SRL have aromatic rings (PhOH, $PhCH_3$), polar groups and several aliphatic carbon atoms. CAO-SRL was most soluble in aromatic polar compounds ($PhNO_2$) which are acidic (phenol) or basic (anilines, pyridine). An aliphatic amine, $BuNH_2$, two cyclic ethers (dioxane, THF), and two relatively polar, high solvating, moderately basic solvents (DMSO, DMF) are also in this group. Noteworthy is the fact that most of the high-solvating solvents are either charge transfer donors or acceptors. More solvent studies should be done to determine whether charge-transfer is an important phenomenon in addition to hydrogen-bonding and polar effects. The latter two factors appear not to be sufficient by themselves to explain the solubility results. The average molecular weight for CAO-SRL was found to be 620 and there are 0.8 acidic functions (presumably phenolic) and 0.4 basic functions per average molecule considering that the sample has 1.34 meq of acidic functions and 0.534 meq of basic functions per gram of SRL. Thus, there are about twice as many acidic groups as basic ones, and a greater solubility in basic solvents would be expected. The high average molecular weight means that acidity is not the only important factor. The low H to C ratios of CAO-SRL (0.788) and the high aromatic to aliphatic hydrogen (0.78) ratio indicate both a high degree of aromaticity and a significant but smaller fraction of aliphatic structure in the average molecule of CAO-SRL. The insolubility of Class 1 solvents results from an inability to solvate the nonpolar part of the molecule in nitromethane and methanol. The insolubility of many highly aromatic materials in hexane is well known. However, in the case of the intermediate solvating Class 2 solvents, each has a benzene ring or several aliphatic carbons and a polar group.

Class 3 solvents, the highly solvating solvents, are composed of aromatic rings with polar acid or basic groups or aliphatic chains with basic groups. The exceptions apparently are dioxane and THF which together form a special high solvating subgroup consistent with their general solvating ability relative to, for example, diethyl ether.

4. Conclusions

The conclusions concerning an average molecule of CAO-SRL follow: The average molecule contains several aromatic rings, some condensed, an average of 0.8 acidic groups, mainly as phenols, and an average of 0.4 basic nitrogen atoms. Fixed in the non-acidic or non-basic structures are 1.8 atoms of oxygen and 0.37 atom of nitrogen per average molecule as determined by elemental analyses and titration data. In this matrix of aromatic rings, oxygen and nitrogen functions are connected by a smaller but significant number of aliphatic carbons.

B. SRL CONVERSION STUDIES

Nearly ninety batch autoclave hydrogenation experiments were performed to determine the effect of solvents, catalysts, temperature, and pressure on conversion of SRL to distillable liquids and gases. NMR, elemental analysis, titration and solubility of vacuum bottoms data were obtained to give insight into the nature of the hydrogenation reactions.

1. Preliminary Experiments (cf. Table 4, Appendix B)

The early experiments (Runs 1-6) were conducted in the absence of catalyst to establish baseline conditions. Tetrahydrofuran (THF) was used as the solvent; it was chosen because it dissolves SRL almost completely. The results from Runs 3 and 4 indicate that increasing the residence time decreased the overall conversion by 5 percent or more. Run 5 was carried out with THF and hydrogen only. The high recovery of THF (93 percent) in this run suggests that in the runs with SRL present, THF might be reacting with SRL to produce gas; the gas was not analyzed.

Runs 7 to 17 were carried out to establish standard reaction conditions for catalyst testing. Although each of the catalysts may not function optimally under a given set of conditions, a conservative set of reaction conditions must be established so that a large number of catalysts can be evaluated. Once the more promising catalysts are found, an optimization study of reaction conditions can be conducted for individual catalysts.

The data of Run 8 showed that the addition of one percent of cobalt-molybdate catalyst increased the overall conversion by more than 10 percent. When the catalyst concentration was increased to 10, 50, and 75 percent as in Runs 10, 22, 12, 13, 14, 15, 16, and 17, conversion did not respond sharply, though there were slight increases. Comparing the feed to catalyst ratio in commercial continuous flow units, 50 percent catalyst probably is reasonable, thus for catalyst comparison experiments 50 percent was used.

Results from Runs 8, 9, and 12 suggest that benzene and tetralin are better solvents than THF. Tetralin was used for catalyst testing because it has a higher critical temperature than the other solvents and also has the ability to donate hydrogen. When 150 ml of solvent was used, an initial hydrogen pressure of 2500 psi seemed best (discussed further under "Pressure Effect"). General conditions selected for catalyst testing were: 75 grams of SRL, 37.5 grams (50 percent) of catalyst, 150 milliliters of tetralin, initial hydrogen pressure of 2500 psi, reaction temperature of 375°C, and residence time of two hours.

2. Catalyst Screening (cf. Table 4, Appendix B)

A series of batch autoclave experiments was performed to evaluate six commercial catalysts: Ni-W-SiO_2-Al_2O_3, Ni-W-Al_2O_3, two varieties of Co-Mo-Al_2O_3 (Co-Mo-0401 and Co-Mo-0402), Al_2O_3, and Ni-Mo-Al_2O_3 (Table 2, Appendix B). In this series, (Runs 16, 18, 19, 20, 21, 22, and 24) the highest conversion of 54.4 percent was found in Run 24 with Ni-Mo-Al_2O_3. The lowest conversion of 45.6 percent was with Ni-W-SiO_2-Al_2O_3. The other catalysts gave conversions of 48 to 50 percent. The lower conversion might be because Ni-W-SiO_2-Al_2O_3 is relatively sensitive to nitrogen poisoning and the SRL contained 1.4 percent nitrogen. On the other hand, Ni-Mo-Al_2O_3 is less susceptible to nitrogen poisoning.

To determine the effect of presulfiding, three catalysts, Ni-W-Al_2O_3, Co-Mo-Al_2O_3 (Co-Mo-0402), and Ni-Mo-Al_2O_3, were presulfided and used immediately for hydrogenation. Of the three catalysts used at a reaction temperature of 375°C, presulfided Ni-Mo-Al_2O_3 gave the highest conversion, an increase of 7 percent over the non-sulfided run. For presulfided Ni-W-Al_2O_3 and Co-Mo-0402 (Runs 27, 28, and 29), there were increases of 11 and 10 percent, respectively, over the untreated catalysts. In Run 34, 7.5 g of acid-washed molecular sieve was added along with the presulfided Ni-Mo-Al_2O_3 catalyst, and the conversion was about the same as that of Ni-Mo-Al_2O_3 by itself in Run 31. In general, presulfiding the catalysts provided about a 10 percent increase in conversion. It is important to note that the volumes of lower boiling fractions (distillation fractions 2 and 3) were generally larger, and the last distillation fraction (fraction 4) was smaller than those from the non-sulfided catalyst runs. Figures 3, 4, and 5, Appendix A demonstrate that all three presulfided catalysts produced larger fractions of lighter distillate than the non-pretreated commercial catalyst at the same experimental conditions. Thus the distillation data indicate that the presulfided catalysts promote more extensive hydrogenation and cracking. Fraction 1 in Figures 3, 4, and 5, Appendix A was obtained by subtracting the sum of fractions 2, 3, and 4 from the total conversion. This fraction includes the gas yields, the 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 do not give a bias.

Tested at higher reaction tempratures, 425 and 450°C, were the presulfided Ni-Mo-Al_2O_3 catalyst (Runs 31, 35) and the Ni-W-SiO_2-Al_2O_3 catalyst (Runs 33, 43, and 46). (The Ni-W-SiO_2-Al_2O_3 is known as a dual-function hydrocracking catalyst.) The distillation data (Table 4, Appendix B) show that the presulfided Ni-Mo-Al_2O_3 catalyst in Runs 31 and 35 at each temperature gave a higher conversion than the presulfided Ni-W-SiO_2-Al_2O_3 catalyst in Runs 33 and 46. The comparison at 425°C being 76 versus 68.5 percent and at 450°C, 88 versus 84 percent. In Run 45, at a reaction temperature of 450°C but without catalyst, the conversion was only 60 percent; therefore a difference of more than 25 percent was due to the catalyst (Runs 35 and 46). Thus, presulfiding the catalysts and a reaction temperature of 450°C appear optimum for high conversions for the conditions investigated.

Stannous chloride is a catalyst which has interesting activities for both hydrogenation and cracking and is of special interest since it appears to be less sensitive to nitrogen poisoning. Two runs were carried out at 375°C with this catalyst; Run 25 using 10 percent of neat $SnCl_2$ powder gave 54 percent conversion, and Run 26 using 6.4 percent of $SnCl_2$ impregnated on alumina (Harshaw Al-1404-T) gave a lower conversion of 47 percent, likely because a smaller amount of $SnCl_2$ was used. Little nitrogen was removed as ammonia. Work with this catalyst was discontinued because of the low denitrogenation activity and because problems in catalyst recovery were anticipated.

A cracking catalyst, HZ-1, from Houdry Catalysts was used at 425°C with SRL. The conversion was not as high, being only 52.5 percent in Run 36, as with presulfided catalysts in general.

Combinations of catalysts were tested using the optimum reaction conditions developed for the presulfided $Ni\text{-}Mo\text{-}Al_2O_3$ catalyst in the absence of solvent. In Run 71, a high-nickel catalyst was tested; it was not presulfided. The overall conversion of 84 percent was slightly lower than that of 87 percent obtained using the presulfided $Ni\text{-}Mo\text{-}Al_2O_3$ catalyst in Run 68.

Tungsten disulfide was noted as a good hydrogenation and hydrocracking catalyst. In Run 75, this catalyst (50 percent as a neat powder) was used. The overall conversion was only 76.2 percent. Yields of the lower boiling fractions, 1_A and 1_B, were much lower than usual, only about 5 percent versus 20 percent for the $Ni\text{-}MO\text{-}Al_2O_3$ run, but the yields of the two higher boiling fractions, 3 and 4, were larger than usual. Water (1.5 g) and ammonia (0.47 g) yields were lower than in other tests. Hydrogen uptake was only 600 psi instead of 1000 psi in the $Ni\text{-}Mo\text{-}Al_2O_3$ run. These results suggest that the hydrogenation was not extensive and consequently cracking was not fully promoted. Both factors contribute to the lower yields of ammonia and water, and reduced overall conversion.

In Run 72, a combination of WS_2 (10 percent) and $Ni\text{-}Mo\text{-}Al_2O_3$ (50 percent) was used. The addition of WS_2 to the catalyst did not provide a significant advantage. The conversion was 87.7 percent compared with 87.0 percent for Run 68 in which presulfided $Ni\text{-}Mo\text{-}Al_2O_3$ was used alone. The liquid product distribution was similar to that obtained when using presulfided $Ni\text{-}Mo\text{-}Al_2O_3$ catalyst alone.

A combination of a cracking catalyst, HZ-1, and presulfided $Ni\text{-}Mo\text{-}Al_2O_3$ was tested in Run 84. Adding cracking catalyst had a deleterious effect on conversion resulting in 83.2 percent conversion instead of the usual 87 percent. The NMR data from this run are quite different from those usually obtained. The aromatic-aliphatic ratios are unusually high. The unusually high aromatic concentration may be due to the effect of the cracking catalyst. The saturated alkyl groups that are usually attached to the aromatic systems were probably cleaved to produce gases and leaving liquids which are primarily aromatics.

Thus far presulfided Ni-Mo-Al_2O_3 catalyst is the best catalyst in terms of high conversion of SRL to gaseous and liquid products, and the presulfided catalysts generally give a higher yield of lower boiling fractions than the non-presulfided catalysts.

3. Catalyst Conditioning (cf. Table 4, Appendix B)

Runs 57, 59, 61, 62, 63, 77 and 79 were conducted to investigate the effect of catalyst conditioning. In previous runs, presulfided catalyst was exposed to air during the catalyst weighing and SRL loading. It was noted that the presulfided catalyst was spontaneously warmed, perhaps because of air oxidation, so a series of experiments was performed to study the effect of catalyst conditioning.

In Run 61, the presulfided catalyst was air-exposed during the normal weighing period. The conversion, yields, and the NMR analyses for Run 61 appeared normal. In Runs 57 and 59, the presulfided catalyst was stored in a hydrogen atomsphere for 24 hours and then was exposed to air during SRL addition. Again the catalyst heated spontaneously. The results from these two runs were not greatly different from those runs in which the catalyst was exposed to air immediately. In Run 62, the catalyst was not conditioned and not exposed to air, either during catalyst weighing or SRL addition; the conversion was 90.4 percent, slightly higher than was observed in Runs 57, 59, or 61. In Run 63, the catalyst was conditioned in a hydrogen atmosphere and not exposed to air at any time, and the conversion was 89.2 percent. The small increases of two to three percent in conversion in Runs 62 and 63 may not be significant. These experiments were repeated in Runs 77 and 79, but this time the conversions were 87 to 88 percent - the same as when the catalyst was unconditioned and exposed to air during weighing and addition of SRL. It is worth noting that the catalysts in these four experiments which were not exposed to air did not heat. Thus, catalyst conditioning in a hydrogen atmosphere had essentially no effect in terms of conversion, and the normal extent of air-exposure did not influence conversion.

4. Pressure Effect (cf. Table 4, Appendix B)

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 12, an increase of initial pressure from 1000 to 1750 psi, with THF as solvent, resulted in an increase in conversion from 27 to 41 percent. However, further increases in pressure from 1750 to 2500 psig, with tetralin as solvent, had no significant effect on conversion:

Run No.	10	12	13	14	15
Solvent	←THF→		←Tetralin→		
Initial H_2 Press, psig	1000	1750	1750	2060	2500
Conversion, Wt%	27.3	41.3	40.1	42.7	40.9

5. Temperature Studies (df. Table 4, Appendix B)

Several experiments were carried out to determine the optimum reaction temperature for relatively high conversions. Summarized below are the results of three runs at different reaction temperatures, with other conditions constant:

Run No.	32	31	35
Temperature, °C	375	425	450
Conversion, Wt%	62.1	75.7	88.3
Methane plus Ethane, grams	0.40	1.78	5.48

The percentage conversion increases almost linearly with reaction temperature as is illustrated in Figure 6, Appendix A. As the reaction temperature increased, gas production also increased, as indicated by the total yield of methane plus ethane. This suggest that hydrocracking does not proceed readily until reaction temperature approaches or exceeds 450°C. The ideal reaction temperature would be the temperature at which gas production is a minimum and total conversion is a maximum. Perhaps the ideal may not be obtainable, but gas production of 5.48 grams is tolerable. Therefore, a reaction temperature of 450°C appears to be most favorable.

6. Solvent Studies (cf. Table 4, Appendix B)

The most economical conversion of SRL would be if no solvent were required for the conversion of liquids. However, the solvent has several roles during hydrogenation which are helpful. First, the solvent functions as a hydrogen carrier from the catalyst surface to the material being reduced. Additionally, the presence of solvent reduces the viscosity of the reaction mixture which facilitates diffusion. Several hydrogenation experiments were performed to find out: (1) the best solvent for hydrogenation and (2) the best solvent:SRL ratio.

In the initial hydrogenation experiments, tetrahydrofuran (THF) and tetralin were used a solvents. THF was employed because it dissolves both SRL and the hydrogenation products, and it can be readily recovered. Tetralin was used because of its well-known hydrogen donating ability and its higher critical temperature. Naphthalene also was compared with tetralin in the presence of a catalyst:

Run No.	1	44	45	35	39
Temperature, °F	375	375	450	450	450
Solvent	THF	← Tetralin →			Naphthalene
Catalyst	← None →			Ni-Mo-Al_2O_3	
Conversion, Wt%	16.9	40.0	60.0	88.3	65.6

Tetralin is a much better solvent than tetrahydrofuran in the absence of a catalyst probably because of ita hydrogen donor properties. Tetralin is also a much better solvent than naphthalene when catalyst is present.

The ideal solvent for study would be a SRL - or lignite - derived solvent, but for this work such a solvent was not available. However, under similar reaction conditions, a petroleum derived solvent, carbon black feedstock FS-120, has been compared with tetralin. The conversion results showed that FS-120 is almost as good as tetralin in terms of high conversion (91 percent for tetralin in Run 48 and 89 percent for FS-120 in Run 49).

It is important to determine the minimum amount of solvent needed to sustain a reasonably high conversion of SRL to light liquid products. A series of experiments was conducted with tetralin solvent to SRL ratios of 2, 1, 0.5, 0.25, 0.2, 0.1, and zero (without solvent). The results are shown below:

Solvent:SRL Ratio	Run Numbers	Average Conversion
2	35, 78, 82	87.0
1	47, 66	91.8
0.5	48, 49	90.2
0.25	65, 69	88.9
0.2	54, 55	87.0
0.1	56	89.6
0 (No solvent)	57, 59, 61-64 66, 68	88.1

For the solvent to SRL ratio of 2, four experiments were carried out. In one of them, Run 76, failure of the stirrer resulted in the reaction being carried out without mixing, and the conversion was only 59.7 percent, much lower than in the other runs. This illustrates the importance of stirring the reaction mixture during the reaction period. The overall conversions realized in Runs 35, 78, and 82 range from 85 to 88 percent, even though the runs were carried out over a six month interval. Thus, the conversion results appear to be relatively reproducible.

For a solvent to SRL ratio of 1, the highest conversion of the series, 92.6 percent, was obtained in Run 47, and replicate Run 66 gave a conversion of 91.0 percent. When the ratio was decreased to 0.5, the conversion was 91.2 percent (Run 48). A conversion of 92.8 was obtained using a tetralin:SRL ratio of 0.5 in Run 50; the SRL was prepared, using FS-120 as the liquefaction solvent, in a batch autoclave.

When the tetralin to SRL ratio was further reduced, the overall conversions decreased slightly. With a ratio of 0.25, conversions of 88.8 and 89.0 percent were obtained in Runs 65 and 69, respectively. Runs 54 and 55 were carried out with a 0.2 ratio and resulted in conversions of 86.0 and 88.0 percent, respectively. Run 56, performed with a solvent to SRL ratio of 0.1, gave a conversion of 89.6 percent.

Several hydrogenation experiments were carried out using no solvent at all. Relatively high conversions were obtained in Runs 57, 59, 61-64, 66 and 68. This demonstrated that a relatively high conversion of SRL to gaseous and liquid products could be accomplished without the aid of the solvent in a batch process. The first two runs without solvent were made using a stirrer which gave very poor mixing. The conversions were only 50.6 percent in Run 41 and 49.5 percent in Run 42. These two experiments confirmed the importance of thorough mixing in the reactor. The stirrer was modified after these two runs, and the result was higher conversions in succeeding experiments.

The conversion results from the solvent (tetralin) to SRL ratio studies indicate that the maximum conversion of 92.6 percent was attained with a solvent to SRL ratio of 1, and that the conversions decreased only slightly with either a decrease or an increase in solvent ratio. Finally, when no solvent was used, a relatively high conversion of 88.1 percent was still attained. This is shown more clearly in Figure 7, Appendix A.

An interesting observation is noted from NMR analyses of the liquid fractions obtained from the series of experiments on the solvent to SRL ratio studies. The analyses were usually carried out on fractions 2, 3, and 4. The aromatic to aliphatic proton ratios were calculated from the NMR spectra for each of the distillation fractions. The ratios for fractions 2, 3, and 4 are plotted versus the volume of solvent used as the hydrogenation medium (Figure 8, Appendix A). The aromatic to aliphatic proton ratio increases linearly in each of the fractions as the ratio of solvent to SRL decreases in each run. When no solvent was used, the aromatic contents were the highest.

7. Conversions of SRC and SRL (cf. Table 4, Appendix B)

The catalytic conversion process was intensively studied using SRL prepared by Pittsburgh and Midway Coal Mining Company's continuous flow unit. However, it is also intersting to see whether this process is applicable to SRC and SRL prepared by other processes (such as in a batch autoclave or in other continuous flow systems). Samples of SRC from P & M at Kansas City were examined. SRL samples from the Process Development Unit (PDU) and from batch autoclave work were also available from Project Lignite. Thus, the conversion of SRL and SRC samples from five different sources or processes has been investigated as follows:

Run No.	Type	Sources
64, 68	SRL-KC	P&M Continuous Unit Kansas City
85, 87	SRL-PDU	Project Lignite PDU
	SRL-FS-120	Project Lignite Laboratory prepared with FS-120
80, 81, 83	SRC-KC	P&M Continuous Unit at Kansas City
86, 88	SRC-Tacoma	P&M Pilot Plant at Tacoma, WA.

The highest conversions, (90.7 and 93.1 percent) were obtained with SRL from the PDU. This may be partially explained by the fact that this SRL contained about 16 percent of the liquefaction solvent which should be more readily converted than SRL. The lowest, 83.7 to 86.1 percent, were found with the SRC from Kansas City. The difference between the SRL and the SRC from Kansas City averages only 3 percent, which may not be significant.

Other results were similar in terms of liquid distributions, aromatic versus aliphatic hydrogen ratios (NMR data), and hydrogen uptake during reaction. The 30 percent yield of the first distillation fraction (1_A) obtained from SRC-KC was a little higher than the 20 to 25 percent realized with the others. In general, the ammonia produced was higher for SRC than for SRL; the lowest was found with the SRL-PDU. This might be due to the lower nitrogen content of about 2 percent for SRC and 1.5 percent for SRL-KC.

The conversions obtained in Run 51 when using SRL-FS120 indicated this material is converted at least as well as SRL-KC. When the ratio of tetralin to SRL was 0.5 the conversion of SRL-KC was 90.2 percent and of SRL-FS120 92.8 percent. The liquid product distributions were also similar.

Thus, from the batch autoclave experimental results, it can be concluded that solvent refined coals, regardless of their source can be converted to gases and distillable liquids under the reaction conditions developed primarily for SRL-KC conversion.

8. Analytical Methods for Monitoring Reaction Products

Besides using percentage conversion of solvent refined lignite as a guideline to determine the effect of the various process parameters, other analytical methods were developed and used to monitor the extent of these hydrogenations. These methods consist of carbon and hydrogen analyses (Table 6), NMR data (Table 8), basic amine and phenol determinations (Table 9), and gas production (Table 5).

The atomic H/C ratios were calculated from hydrogen and carbon elemental analyses. These ratios did not vary appreciably until Run 27 (the presulfided catalyst run) and they appeared to be higher for all runs with presulfided catalysts:

Run No.	26	27
Catalyst Treatment	None	Presulfided
H/C Ratios of Fraction		
2	1.22	1.45
3	1.00	1.26
4	0.97	1.15
5	0.90	0.96

Run 27 gave typical high atomic H/C ratios.

The distillation fractions were also analyzed 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 the earlier runs through Run 26 and are low from Run 27 to Run 34. Runs 18 and 27 are representative:

Run No.	18	27
Catalyst Treatment	None	Presulfided
Ar- H/Al-H Ratios of Fraction		
2	0.56	0.19
3	1.00	0.21
4	1.15	0.24

These results indicate that there is more aliphatic hydrogen in the distillation fractions of the presulfided catalyst runs.

The weights of the evolved gases are tabulated in Table 5. Higher reaction temperatures tend to promote larger gas yields as indicated:

Run No.	32	21	35
Reaction Temp., ^{o}C	375	425	450
Methane plus Ethane, grams	0.40	1.78	5.48

Liquid yields should be high. Consequently, reaction temperature should probably not be much higher than 450^{o}C in order that gas yields do not become excessive.

In general, nitrogen compounds are known as catalyst poisoning agents, and therefore the basic nitrogen contents of the SRL and of the hydrogenation products were of concern, as was the denitrogenation capability of the catalysts. A non-aqueous potentiometric titration method was adopted for the determination of the basic nitrogen. Most of the vacuum bottoms and some of the distillate fractions were analyzed for basic amines.

Titration data (Table 9, Appendix B) indicate that the concentration of basic amines in the vacuum bottoms, resulting when regular commercial catalysts were used, were about the same or slightly lower than in the original SRL (0.54 meq/g SRL). For the presulfided catalyst runs using Ni-4303, Co-Mo-0402 and Ni-4301, the titrable amine content remained about the same as in the original SRL, but for the presulfided HT-100-E (Ni-Mo-Al_2O_3), titrable amine content was reduced by 50 percent or more (Runs 31, 32 and 34, Table 9). Thus, it appears that $NiS\text{-}MoS_2\text{-}Al_2O_3$ is a better denitrogenation catalyst than $NiS\text{-}WS_2\text{-}SiO_2\text{-}Al_2O_3$ or $CoS\text{-}MoS_2\text{-}Al_2O_3$.

The phenolic content of the SRL and its hydrogenated products were also determined by non-aqueous potentiometric titrations. In most runs, the vacuum bottoms sample was titrated for phenols so that the phenolic content could be compared with the 1.34 meq/g in the SRL. In general, the phenolic contents of the vacuum bottoms were much lower than that of the SRL (Table 9). It is also interesting to note that the runs with a high conversion usually produced vacuum bottoms with lower phenolic contents.

Three total chemical compositional analyses were carried out (two by Gulf Research and Development Company and one by DuPont). The analyses done by Gulf were on the distillation fractions obtained from Runs 31 and 59. The one by DuPont was for Run 59 only. The methods of analyses by the two companies were different. However, the results were very interesting. In Run 31, tetralin was used as a solvent, while in Run 59, no solvent was used. The results from Runs 31 and 59 are shown in Tables 10 and 11, Appendix B, respectively.

The analyses of the samples from Run 31 show a wider spectrum of compounds or compound types than those from Run 59. The latter, especially in fraction 1_A, revealed two main aromatic compound types - benzenes and tetralins. Fraction 1_A from Run 59 also was higher in total aromatics, 43 versus 24 percent for Run 31. Fractions 1_B, 2, and 3 are highly aromatic; thus, these coal liquids may be excellent chemical feedstocks for BTX production.

The analyses by DuPont on Run 59 were done differently. In these analyses, the saturates were not separated from the aromatics before they were identified. A composition gas chromatogram is quite complex. However, it is apparent that the fractions contained a large amount of aromatics as was found by Gulf analyses. The results are in Figure 2, Appendix A, and Table 12, Appendix B.

Fraction 1_A, the fraction in the gasoline boiling range, had a clear research octane number of 72 (CRON) as determined by Gulf Research and Development Company. Fraction 1_B, in the diesel oil boiling range, was not obtained in sufficient quantity for a cetane number determination.

The results of elemental analyses of the liquid fractions from the different laboratories appeared to have some minor differences, but overall, it appears that nitrogen and sulfur contents of each sample are less than 0.1 weight percent.

The benzene dissolution data revealed no obvious trends. However, the vacuum bottoms samples are normally more soluble than the original SRL, which is 62.2 weight percent soluble in benzene.

The production of water is somewhat erratic, although it seems in general to be higher for runs after Run 25.

9. Conclusions

The following general conditions were established for the catalyst comparisons: an initial hydrogen pressure of 2500 psi, 50 percent catalyst by weight, 150 ml tetralin solvent, and 375°C reaction temperature. Under these conditions, a total of eight catalysts were tested with SRL. Studies were also conducted of the effects of catalyst pretreatment, temperature, pressure, type and amount of solvent, and of the hydrogenation of solvent refined lignites and solvent refined coals from various sources.

The conclusions drawn from this work are as follows:

a) The catalysts Ni-Mo-Al_2O_3 (Harshaw HT-100) and $SnCl_2$ gave the highest conversions of SRL to distillable liquid products, though the $SnCl_2$ removed little nitrogen as ammonia.

b) Presulfided catalysts gave generally high conversions. Presulfided Ni-Mo-Al_2O_3 was more effective in removing heteroatoms of nitrogen and oxygen in addition to giving a high conversion, and was judged the best catalyst overall of those tested.

c) The conversion of SRL to gases and distillable liquids increased almost linearly with reaction temperature over the range studied and reached 88 percent at 450°C.

d) The conversion of SRL increased as the initial reactor pressure was increased from 1000 psi to 1750 psig, but further increases to 2500 psig were not beneficial.

e) Tetralin is a good solvent for SRL conversion, but a relatively high conversion is obtained in the absence of solvent.

f) Solvent refined coals, regardless of their sources, were converted to gases and distillable liquids in relatively high yields using reactor conditions developed for SRL-KC conversion.

g) The experimental conditions for most effective conversion are: initial hydrogen pressure of 2500 psig, 75g of SRL, tetralin solvent with a solvent to SRL ratio of unity, presulfided HT-100 catalyst, 450°C, and two hours reaction time.

APPENDIX A - FIGURES

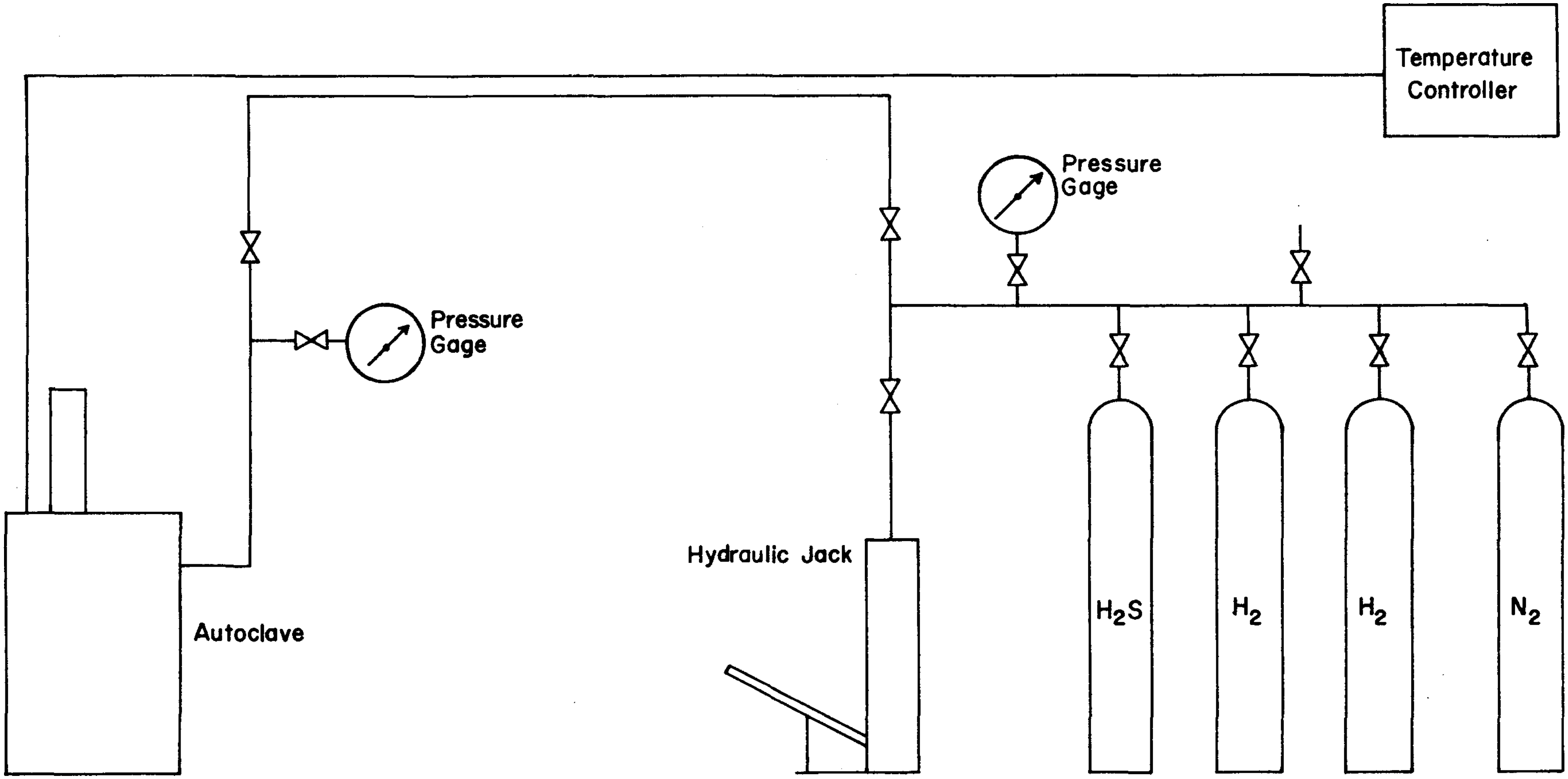

FIGURE I - HIGH PRESSURE REACTION SYSTEM

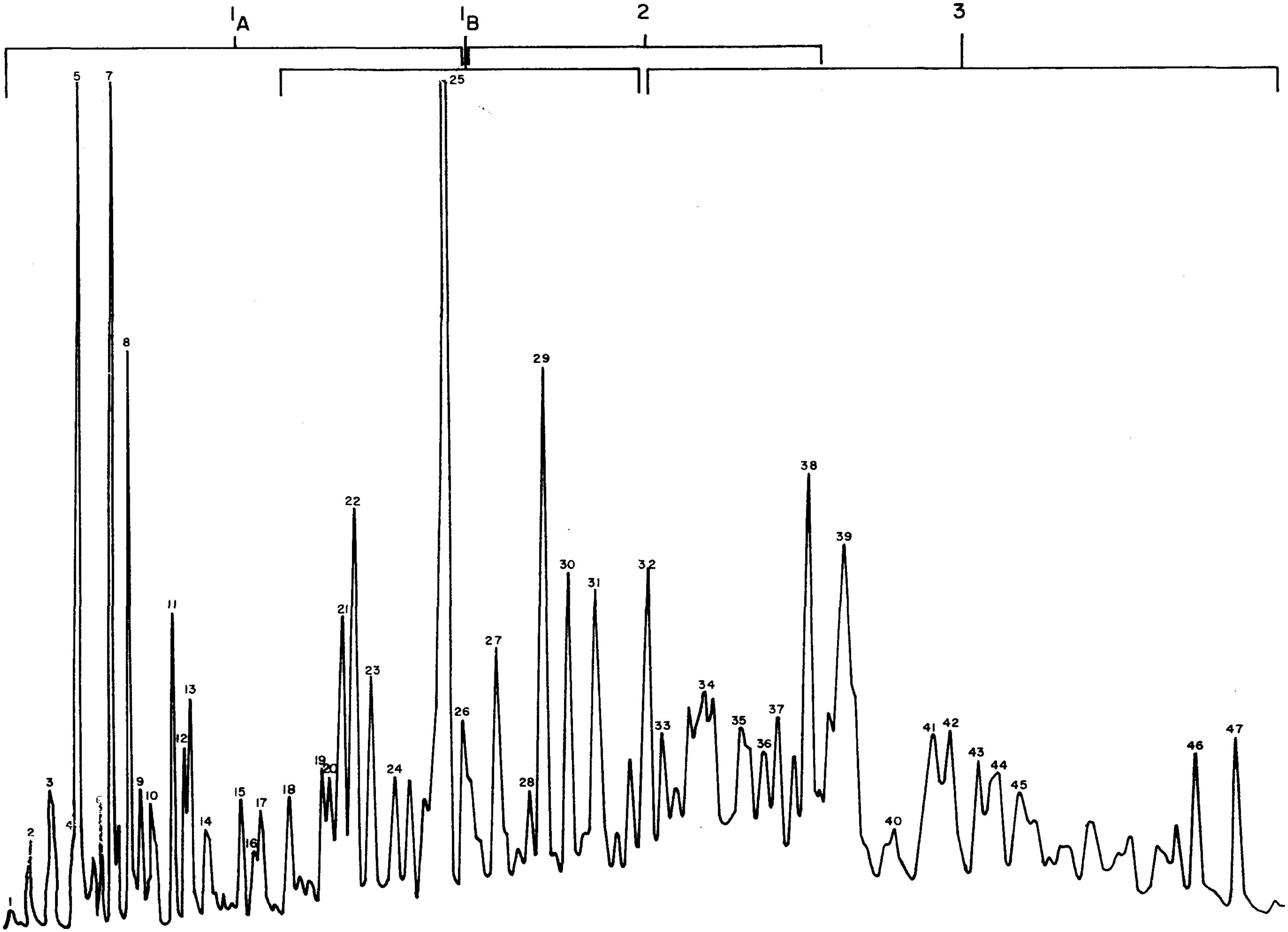

FIGURE 2 - GAS CHROMATOGRAM OF LIGNITE DERIVED LIQUIDS
Composite of Liquids I_A, I_B, 2 and 3

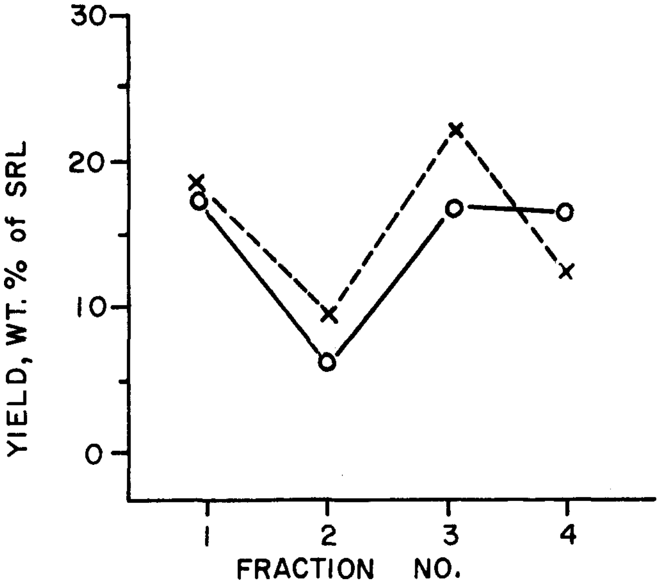

FIGURE 3 - YIELDS OF DISTILLATION FRACTIONS WITH Ni-Mo-Al_2O_3 CATALYST

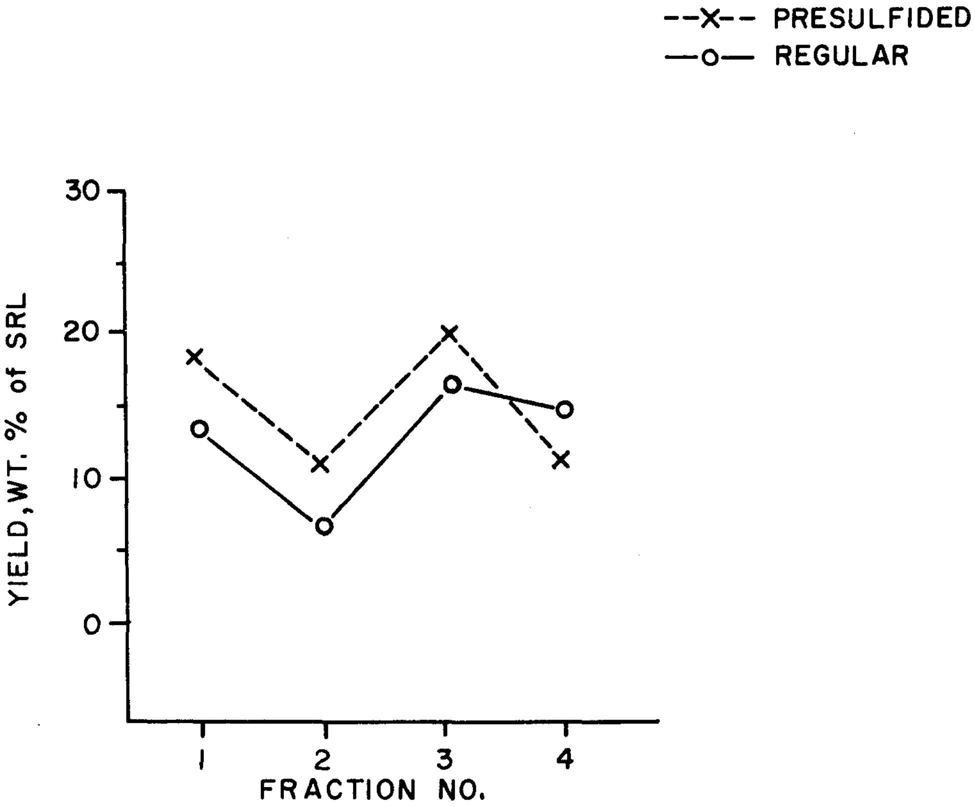

FIGURE 4 - YIELDS OF DISTILLATION FRACTIONS WITH Co-Mo-Al_2O_3 CATALYST

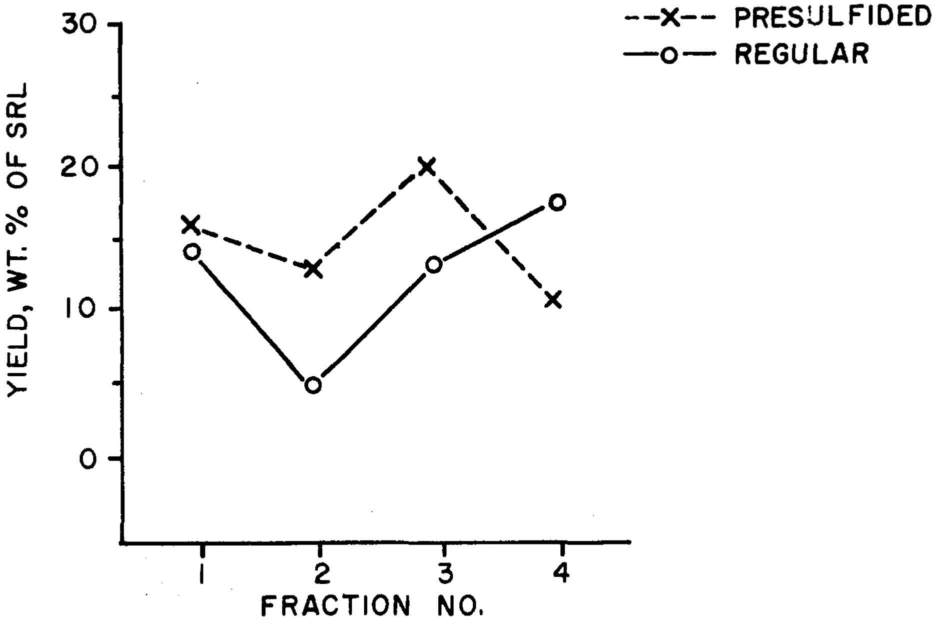

FIGURE 5 - YIELDS OF DISTILLATION FRACTIONS WITH $Ni-W-Al_2O_3$ CATALYST

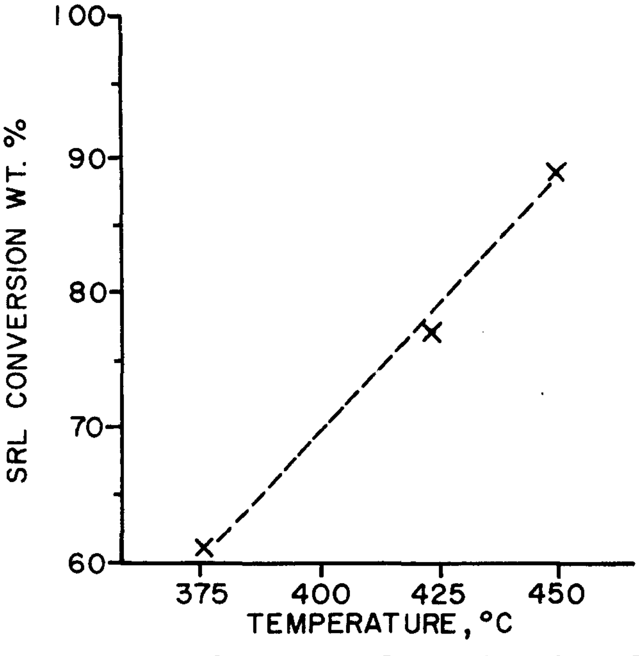

FIGURE 6 - SRL CONVERSION VERSUS REACTION TEMPERATURE FOR PRESULFIDED HT-100 CATALYST

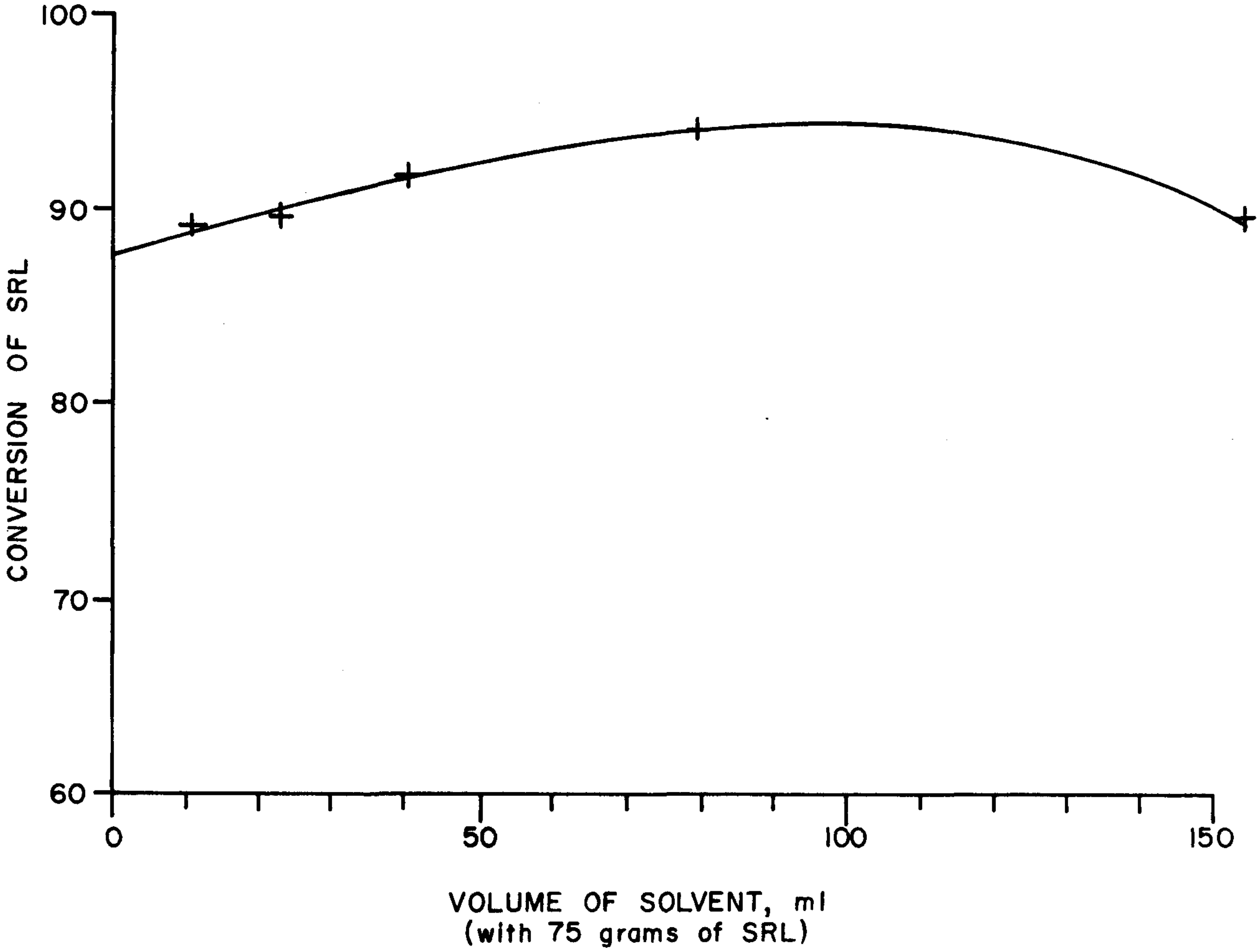

FIGURE 7 - SRL CONVERSION VERSUS VOLUME OF SOLVENT

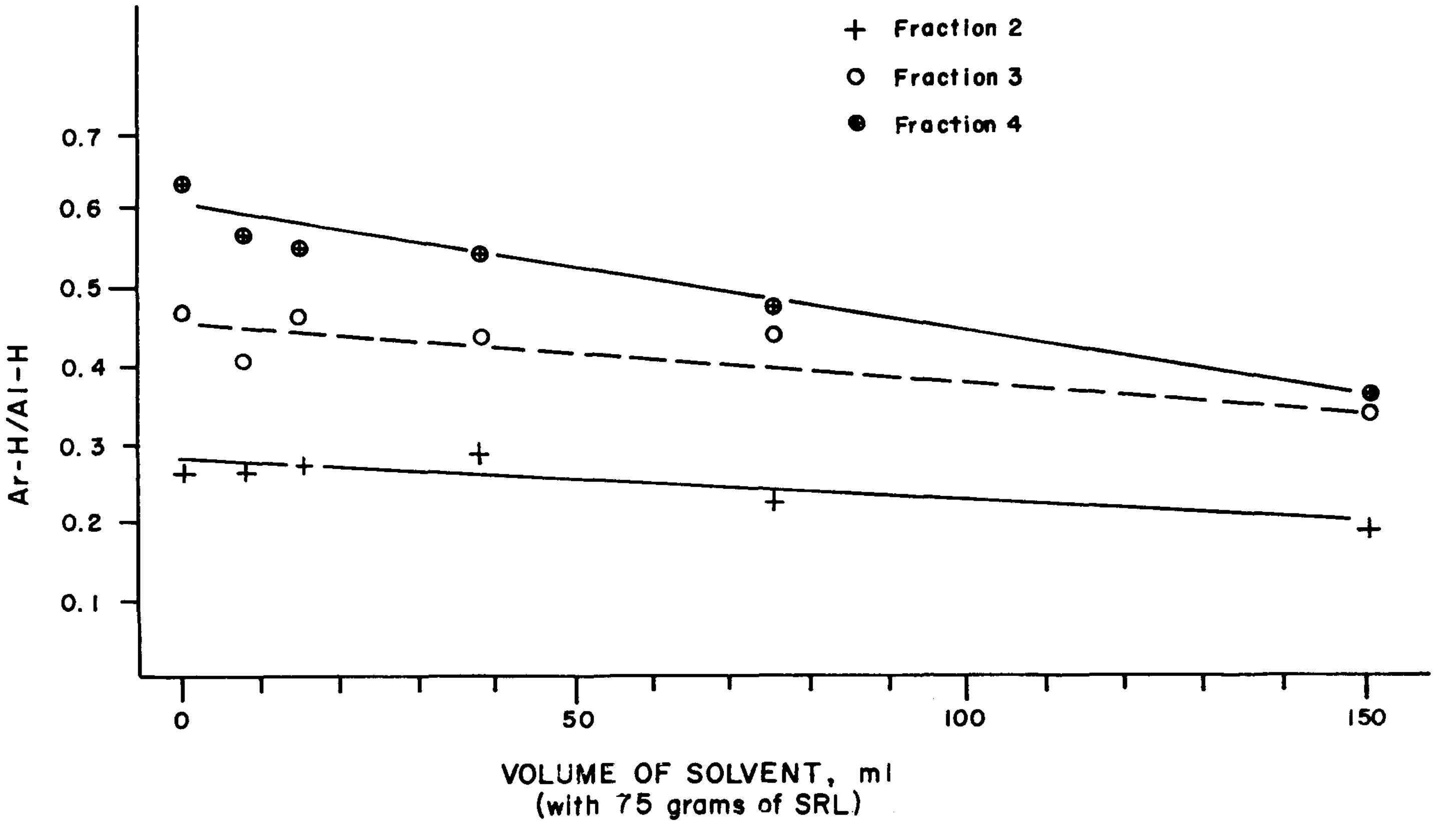

FIGURE 8—Ar-H/Al-H RATIOS VERSUS VOLUME OF SOLVENT FOR DISTILLATE FRACTIONS

APPENDIX B - TABLES

Table 4 is large summarizing table.
Tables 5-10 arranged by Run number.

Table 1

Elemental Analyses of Solvent Refined Coal and Lignite

	SRL-FS-120	SRL-KC	SRL-PDU	SRC-Tacoma	SRC-KC **
C	84.79	85.57	81.10	87.23	87.58
H	6.02	5.62	6.42	6.01	5.38
N	1.22	1.41	0.86	0.65	2.11
S	0.51	0.3	1.35	1.43	0.68
Ash	0.19	0.11	.00	0.55	0.07
O*	7.27	6.99	10.17	4.13	4.18
Used in Runs	50,51	All Others	85,87	86,88	80,81 83

* Obtained by difference

** Identified as SRC-CU-88 in Table 4

TABLE 2

Catalysts Used in SRL Hydrogenation

Catalyst	Supplier	Trade Name	Composition, Wt. pct.	Pore Vol. cc/g	Surface Area m^2/g	Shape
Co-Mo-Al_2O_3	Harshaw	Co-Mo-0401-T	3 CoO, 9 MoO_3	0.40	160	1/8" tablets
Co-Mo-Al_2O_3	Harshaw	Co-Mo-0402-T	3 CoO, 15 MoO_3	0.40	200	1/8" tablets
Ni-W-Al_2O_3	Harshaw	Ni-4303-E	6 Ni, 19 W	0.54	152	1/12" extrudates
Ni-W-SiO_2-Al_2O_3	Harshaw	Ni-4301-E	6 Ni, 19 W	0.37	228	1/12" extrudates
Al_2O_3	Harshaw	Al-1404-T	97 Al_2O_3	0.42	180	1/8" tablets
Ni-Mo-Al_2O_3	Harshaw	HT-100-E	3.8 Ni, 16.8 Mo	0.54	190	1/16" extrudates
Zeolite	Houdry	HZ-1	45 Al_2O_3, 53 SiO_2	---	100-150	0.2" pellets
Nickel	Harshaw	Ni-1404-P	68% Ni	---	115	powder
WS_2	Alfa Inorganics		neat			powder
$SnCl_2$						
$SnCl_2$-Al_2O_3						

Table 3

Classification of Experiments

Purpose of the Experiments	Run Number
Establishing an experimental baseline	1 to 6
Extablishing a set of standard reaction conditions for catalyst	7 - 17
Survey	
Commerical Catalyst Testing	18 - 26
Presulfided Catalyst Testing	27 to 29
Reaction Condition Optimization experiments for the presulfided Ni-Mo-Al_2O_3 catalyst	30 to 46
Solvent:SRL ratio studies	46 to 56
Catalyst Conditioning	57 to 64, 72, 75, 84
Checking the reproducibility of earlier experiments in the area of solvent:SRL ratio studies and catalyst conditioning	65 to 69, 76 to 79, and 82

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C H- (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia, g produced	Water g produced	Benzene solubility Vac. Bottom	Milliequiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic/g
(1) 1	75 g SRL(KC), 150 ml THF, 900 psi H_2 initial, 375° C, 2 hrs.	iB → 90° atm											
		90 → 250°/1mm	25.3		1.17								
		Vac. bottom	82.5	0.74								0.50	0.72
3	75 g SRL(KC), 150 ml THF 1000 psi H_2 initial, 375° 4 hrs., max. press. 2600 psi	iB → 126°atm											
		126 → 250/1 mm	18.6		0.72								
		Vac. Bottom	94.5									0.38	0.83
4	Same as in Run 3 max. press. 2750 psi	iB → 130/atm			0.65								
		130 → 250/1mm	17.6										
		Vac. Bottom	93.7									0.39	0.62
6	same as in Run 3 except 2 hrs., max. press. 2800 psi	iB → 130/atm											
		130 → 250/1mm	27.3		0.76								
		Vac. Bottom	87.5									0.42	0.75
8	75 g SRL (KC) 150 ml THF, 1000 psi H_2 initial, 375° 2 hrs, 1% Co-Mo catalyst (Co-Mo-0401-T-1/8), max. press. 2450 psi	iB → 130°/atm											
		130 → 200°/atm	1.2		0.11								
		iB → 97°/1mm	0.4		0.44								
		97 → 139°/1mm	4.0		0.73								
		139 → 265°/1mm	34.0		1.43								
		Vac. Bottom	65.5									0.56 (0.54)	1.07 (1.14)

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
9	Same as in	iB →130°/atm								trace			
	Run 8 except	130 →200/atm	0.7		0.28								
	150 ml benzene	iB →87/1mm	0.9		0.67								
	instead of	87 →139/1mm	7.7		1.51								
	THF, max press	139 →240/1mm	20.9		2.41								
	2500 psi	Vac. Bottom	60.5									0.54	1.09
	<u>Conclusions</u>												
	(a) Even 1% catalyst is better than none (b) THF and benzene comparable as solvents												

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs.* SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Milliequiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(2) 15	75g SRL(KC), 150 ml tetralin, 2500 psi H_2 initial, 375°, 2hrs., 10% Co-Mo catalyst (Co-Mo-0401-T-1/8), max press. 4100 psi	iB → 87°/1mm			0.49	0.0				3.2			0.24
		87 → 139/1mm	2.1		0.67	27.32							0.64
		139 → 210/1mm	20.5	0.94	1.08	163.2							0.64
		210 → 260/1mm	11.3	0.88	1.19	225.0							0.72
		Vac. Bottom	59.1	0.81								0.58	0.80
16	same as in Run 15 except 50% catalyst, max. press. 4210	iB → 87°/1mm			0.54	0.0	0.27	0.09		3.2	69.8		
		87 → 139/1mm	7.5	1.22	0.53	16.49							
		139 → 210/1mm	19.5	1.03	0.98	146.0							
		210 → 260/1mm	11.7	1.03	1.09	125.0							
		Vac. Bottom	52.1	0.92								0.57	0.87
17	same as in Run 15 except 75% catalyst, max. press. 4320	iB → 87°/1mm			0.52	---	0.24	0.08		3.9	74.8		
		87 → 139/1mm	6.9	1.22	0.51	7.00							
		139 → 200/1mm	18.9	1.03	0.78	134.2							
		200 → 260/1mm	12.1	0.94	0.89	57.95							
		Vac. Bottom	50.0	0.81								0.64	0.86
	<u>Conclusions</u> 50% catalyst loading appears most satisfactory												

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/Aliphatic C-H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(3) 16	75g SRL(KC), 150 ml Tetralin, 2500 psi H_2 initial, 375°C, 2 hrs., 50% Co-Mo catalyst (Co-Mo-0401-T-1/8), max. press. 4210 psi	iB → 87°/1mm			0.54	0.0	0.27	0.09		3.2			
		87 → 139/1mm	7.5	1.22	0.53	16.49							
		139 → 210/1mm	19.5	1.03	0.98	146.0							
		210 → 260/1mm	11.7	1.03	1.09	125.0							
		Vac. Bottom	52.1	0.92							69.8%	0.57	0.87
18	same as in Run 16 except 50% Ni-W catalyst (Ni-4303 E 1/2 Lot 8), max. press. 4300 psi	iB → 87°/1mm			0.50	---	0.19	0.13		1.5			
		87 → 139/1mm	4.5	1.12	0.56	2.6							
		139 → 200/1mm	12.8	0.97	1.00	134.4							
		200 → 260/1mm	16.8	0.93	1.15	325.6							
		Vac. Bottom	51.3	0.88							73.5%	0.52	0.97
19	same as in Run 16 except 50% Co-Mo catalyst (Co-Mo-0402-T-1/8), max. press. 3650 psi	iB → 87°/1mm			---	---	---	---		1.8			
		87 → 139/1mm	5.5	1.11	0.56	27.6							
		139 → 200/1mm	16.4	0.99	0.88	137.1							
		200 → 260/1mm	14.3	0.91	0.96	320.0							
		Vac. Bottom	50.0	0.78							65.5%	0.55	0.91

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL <u>vs</u>. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Milliequiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
20	Repeat of Run 19, max. press 4100 psi	iB → 87°/1mm			0.50	---	0.21	0.08		1.7			
		87 → 139/1mm	5.5	1.14	0.50	19.20							
		139 → 200/1mm	16.7	1.13	0.82	129.3							
		200 → 260/1mm	14.3	0.98	0.91	301.7							
		Vac. Bottom	50.5	0.81							71.1%	0.56	0.73
21	same as in Run 16 except 50% Ni-W catalyst (Ni-4301 E1/12 Lot 129), max. press. 4400 psi	iB → 87°/1mm			0.49	---	0.13	0.04	0.01	1.7			
		87 → 139/1mm	4.4	1.16	0.65	3.13							
		139 → 200/1mm	14.0	1.03	1.21	210.5							
		200 → 260/1mm	16.8	0.91	0.90	334.2							
		Vac. Bottom	54.4	0.86							62.4%	0.48	1.32
22	same as in Run 16 except 50% Alumina catalyst (Al-1404-T-1/8 Lot 141), max press. 4500 psi	iB → 87°/1mm			0.50	---			0.01	1.6			
		87 → 139/1mm	4.1	1.02	1.05	59.39							
		139 → 200/1mm	13.5	0.84	1.93	240.9							
		200 → 260/1mm	15.2	0.82	2.01	343.1							
		Vac. Bottom	50.8	0.85							55.1%	0.54	1.12
23	same as in Run 16 except 50% Ni-Mo catalyst (HT-100 E 1/16 Lot 21 Drum 36), max. press. 4300 psi	iB → 87°/1mm			0.50	---	0.18	0.13	0.20	2.8			
		87 → 139/1mm	4.8	1.21	0.42	10.31							
		139 → 200/1mm	17.9	1.02	0.68	92.42							
		200 → 260/1mm	14.4	1.03	0.73	236.7							
		Vac. Bottom	49.9	0.91							78.2%	0.41	0.52

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs.* SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
24	Repeat of Run 23, max. press 4160 psi	iB → 87°/1mm			0.48		---	---	0.24	1.4			
		87 → 139/1mm	5.6	1.20	0.44	14.02							
		139 → 200/1mm	17.6	1.07	0.67	125.0							
		200 → 260/1mm	15.5	0.96	0.76	263.0							
		Vac. Bottom	45.5	0.91							78.4%	0.45	0.52
25	75g SRL(KC), 150 ml Tetralin, 2500 psi H_2 initial, 375°, 2 hrs., 10% by wt. pure $SnCl_2$ catalyst, max press. 3950 psi	iB → 87°/1mm			0.50		---	---	0.01	1.7			
		87 → 139/1mm	5.2	1.24	0.42	14.81							0.44
		139 → 200/1mm	20.7	1.31	0.76	92.73							0.40
		200 → 260/1mm	9.3	1.04	0.80	155.26							0.54
		Vac. Bottom	46.5	-							82.9	0.46	0.66
26	same as in Run 25 except 4.8g $SnCl_2$ on 29g Alumina catalyst (Al-1404 T 1/8 Lot 141), max press. 4150 psi	iB → 87°/1mm			0.50	---	0.28	0.18	0.08	2.1			
		87 → 139/1mm	5.7	1.22	0.48	18.16							
		139 → 200/1mm	18.8	1.00	0.81	115.1							
		200 → 260/1mm	14.9	0.96	0.88	227.3							
		Vac. Bottom	53.1	0.90							94.9	0.36	0.66

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL vs. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
	Conclusions Based on total conversion (small vac. Bottom) the Ni-Mo and $SnCl_2$ catalysts looked best. Also, solubility and low N and phenols in vac. Bottom supported this. Since catalyst recovery problems with the $SnCl_2$ system were anticipated, Ni-Mo looked best from this set of experiments.												

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL vs. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(4) 27	75g SRL(KC), 150 ml tetralin, 2500 psi H_2 initial, 375°C, 2 hrs., 43.1g presulfided Ni-W catalyst (Ni-4303), max. press. 4150 psi	iB → 87°/1mm					2.2	0.20	0.33	4.9			
		87 → 139/1mm	13.3	1.46	0.19	5.59							0.04
		139 → 200/1mm	20.0	1.26	0.21	46.94							0.06
		200 → 260/1mm	10.7	1.15	0.24	98.89							0.13
		Vac. Bottom	40.2	0.96							85.3%	0.41	0.47
28	same as Run 27 except 41.3g presulfided Ni-W catalyst (Ni-4303), max. press. 4000 psi	iB → 95°/1mm					---	---	0.35	---			
		95 → 139/1mm	9.9	1.42	0.16	10.89							0.06
		139 → 200/1mm	19.1	1.25	0.23	44.07							0.12
		200 → 260/1mm	12.7	1.16	0.27	106.1							0.14
		Vac. Bottom	42.2	0.92							81.9	0.49	0.45
29	same as Run 27 except 40.3g presulfided Co-Mo catalyst (Co Mo-0402), max. press. 4050 psi	iB → 87°/1mm					0.17	0.07	0.19	2.5		0.005	
		87 → 139/1mm	10.5	1.40	0.21	4.76						0.19	0.08
		139 → 200/1mm	19.5	1.17	0.32	76.12						0.21	0.16
		200 → 260/1mm	11.3	1.06	0.42	148.8						0.25	0.24
		Vac. Bottom	40.4	0.87							67.9	0.53	0.79

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL vs. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
32	same as Run 27 except 40.5g presulfided NiMo catalyst (HT-100), max. press. 4100 psi Conclusions Presulfiding improves overall conversion and yields of light liquids with all three catalysts tested. NiMo is best both presulfided and non-presulfided in terms of overall conversion, light oil, hydrogen uptake, lower aromaticity, NH_3 production solubility of vac bottom, and lowest basic N and phenol in the Vac. Bottom	iB →87°/1mm					0.27	0.13	0.41	1.4		0.004	
		87 →139/1mm	9.6	1.40	0.14	2.4						0.06	
		139 →200/1mm	22.1	1.32	0.18	30.6						0.09	
		200 →260/1mm	12.1	1.17	0.23	78.6						0.13	
		Vac. Bottom	37.9	1.01	0.20						86.4	0.23	0.22

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs.* SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(5) 57	75g SRL(KC), No solvent, 40g presulfided NiMo catalyst (HT-100), 450°C, 2 hrs., 1800 psi H_2 initial, max press. 3600 psi, catalyst conditioned in H_2 for 24 hrs., not weighed	iB → 200°/atm	43.8		0.08								
		iB → 89°/1mm			0.25								
		89 → 139/1mm	10.8		0.24								
		139 → 200/1mm	20.5		0.38								
		200 → 260/1mm	0.7		0.80								
		Vac. Bottom	12.3										
59	same as Run 57, but catalyst conditioned in H_2 and H_2S-not weighed	iB → 200°/atm	40.8		0.13								
		iB → 89°/1mm			0.23								
		89 → 139/1mm	9.5		0.23								
		139 → 200/1mm	20.6		0.46								
		200 → 260/1mm	0.4		0.76								
		Vac. Bottom	11.9										
61	same as Run 57, but catalyst taken out and weighed in air after presulfiding (some air oxidation took place), no H_2 conditioning.	iB → 89°/1mm	40.0		0.26								
		89 → 139/1mm	13.2		0.26								
		139 → 200/1mm	11.4		0.46								
		200 → 260/1mm	1.7		0.64								
		Vac. Bottom	12.1										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL <u>vs</u>. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
62	same as Run 61, but SRL loaded with fresh presulfided catalyst under N_2	iB → 200°/atm	46.0		0.06								
		iB → 89°/1mm			0.28								
		89 → 139/1mm	13.5		0.25								
		139 → 200/1mm	16.4		0.34								
		200 → 260/1mm	2.1		0.58								
		Vac. Bottom	9.6										
63	same as Run 57 (presulfided catalyst conditioned 24 hrs., under H_2 at 400 psi), catalyst not weighed and SRL loaded under N_2	iB → 200°/atm	46.7		0.07								
		iB → 89°/1mm			0.24								
		89 → 139/1mm	14.7		0.23								
		139 → 200/1mm	14.8		0.34								
		200 → 260/1mm	2.7		0.61								
		Vac. Bottom	10.8										

<u>Conclusions</u>

H_2 and/or H_2S conditioning of the presulfided catalyst for 24 hrs has no beneficial effect. Air exposure of presulfided catalyst has a detrimental effect. Best to use fresh presulfided catalyst immediately (do not weigh), and load SRL under N_2

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL vs. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Milliequiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(6) 1	75g SRL(KC), 150 ml THF, 900 psi H_2 initial, 375°C, 2hrs.	iB → 90°/atm											
		90 → 250/1mm	25.3		1.17								
		Vac. Bottom	82.5	0.74								0.50	0.72
6	75g SRL(KC), 150 ml THF, 1000 psi H_2 initial, 375° C, 2 hrs., max. press. 2800 psi	iB → 130/atm											
		130 → 250/1mm	27.3		0.76								
		Vac. Bottom	87.5									0.42	0.75
44	75g SRL(KC), 150 ml tetralin, 375°, 2 hrs., max. press. 1800 psi, 1000 psi H_2 initial.	iB → 87°/1mm											
		87 → 260/1mm	38.2										
		Vac. Bottom	60.0										
35	75g SRL(KC), 150 ml tetralin, 450°, 2hrs., 2500 psi H_2 initial, 40.6g presulfided NiMo catalyst (HT-100), max. press. 4160	iB → 200°/atm					2.1	3.3	0.6	3.3			
		iB → 87°/1mm											
		87 → 139/1mm	17.1		0.19								
		139 → 200/1mm	15.2		0.36								
		200 → 260/1mm	6.8		0.39								
		Vac. Bottom	11.7										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
39	75 g SRL, 150 g naphthalene 425°C, 2 hrs. 40.3 g presulfided NiMo Catalyst (HT-100), max. press. 3900 psi	iB → 200°/atm											
		iB → 87°/1mm											
		87 → 139/1mm	5.6										
		139 → 200/1mm	19.2										
		200 → 260/1mm	14.0										
		Vac. Bottom	34.4										
48	75g SRL(KC), 37ml tetralin, 2100 psi H_2 initial, 450° 2 hrs., 40g presulfided NiMo cat. (HT-100) max. press. 4550 psi	iB → 87°/1mm											
		87 → 139°/1mm	12.3		0.29								
		139 → 200/1mm	14.4		0.43								
		200 → 260°/1mm	5.1		0.53								
		Vac. Bottom	8.8										
49	same as Run 48 except 37 ml FS-120 solvent used, max. press. 4600 psi	iB → 87°/1mm											
		87 → 139°/1mm	12.1										
		139 → 200°/1mm	9.2										
		200 → 260°/1mm	3.5										
		Vac. Bottom	10.7										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
	Conclusions Tetralin best solvent both with and without catalyst FS-120 essentially just as good as tetralin.												

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(7) 35	75g SRL(KC), 150 ml tetralin, 2500 psi H_2 initial, 450°C, 2 hrs., 40 g presulfided Ni Mo. cat (HT-100), max. press. 4160	iB → 87°/1mm											
		87 → 139°/1mm	17.1		0.19								
		139 → 200/1mm	15.2		0.36								
		200 → 260/1mm	6.8		0.39								
		Vac. Bottom	11.7										
82	same as Run 35	iB → 87°/1mm			0.11				0.85				
		87 → 139°/1mm	11.5		0.30								
		139 → 200°/1mm	21.2		0.45								
		200 → 260°/1mm	24.3		0.56								
		Vac. Bottom	12.5										
78	same as Run 35	iB → 200°/atm			0.29				0.79				
		iB → 87°/1mm			0.48								
		87 → 139/1mm	16.0		1.41								
		139 → 200/1mm	23.7		1.42								
		200 → 260/1mm	9.3		1.49								
		Vac. Bottom	14.9										
47	same as Run 35 except 75 ml tetralin, max. press. 4550 psi	iB → 87°/1mm											
		87 → 139/1mm	18.0		0.22								
		139 → 200/1mm	14.4		0.43								
		200 → 260/1mm	4.1		0.43								
		Vac. Bottom	7.4										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs.* SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
66	same as Run 47	iB → 200°/atm			0.15								
		iB → 87°/1mm	46.8		0.24								
		87 → 139/1mm	13.8		0.24								
		139 → 200/1mm	15.7		0.34								
		200 → 260/1mm	7.7		0.39								
		Vac. Bottom	9.0										
48	same as Run 47 except 37 ml tetralin, 2100 psi H_2 initial, max. press. 4550 psi	iB → 87°/1mm											
		87 → 139/1mm	12.3		0.29								
		139 → 200/1mm	14.4		0.43								
		200 → 260/1mm	5.1		0.53								
		Vac. Bottom	8.8										
65	75g SRL(KC), 19 ml tetralin, 40g presulfided NiMo cat (HT-100) 1800 psi H_2 initial, 450, 2 hrs., max. press. 3600 psi	iB → 200°/atm			0.09								
		iB → 89°/1mm			0.22								
		89 → 139/1mm	15.3		0.22								
		139 → 200/1mm	12.2		0.37								
		200 → 260/1mm	1.9		0.53								
		Vac. Bottom	11.2										
69	same as Run 65	iB → 89°/1mm											
		89 → 139/1mm	8.6										
		139 → 200/1mm	10.4										
		200 → 260/1mm	0.7										
		Vac. Bottom	11.0										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs.* SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/Aliphatic C-H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
54	75g SRL(KC), 15 ml tetralin, 1800 psi H_2 initial, 450°C, 2 hrs. 40g presulfided NiMo cat. (HT-100), max. press. 3300 psi	iB → 87°/1mm											
		87 → 139/1mm	24.5		0.26								
		139 → 200/1mm	15.0		0.46								
		200 → 260/1mm	4.5		0.55								
		Vac. Bottom	14.0										
55	same as Run 54 except 2000 psi H_2, initial, max press. 3800 psi	iB → 87°/1mm											
		87 → 139/1mm	10.1										
		139 → 200/1mm	19.9										
		200 → 260/1mm											
		Vac. Bottom	12.0										
56	same as Run 54 except 7.5 ml tetralin, 1800 psi H_2 initial, max. press. 3800 psi	iB → 87°/1mm											
		87 → 139/1mm	11.3		0.26								
		139 → 200/1mm	8.7		0.40								
		200 → 260/1mm	4.1		0.56								
		Vac. Bottom	10.4										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs.* SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
61	75g SRL(KC), no solvent, 40 g presulfided NiMo cat. (HT-100) weighed in air, 450°, 2 hrs., 1800 psi H_2 initial max. press. 3600 psi	iB → 89°/1mm	40.0		0.26								
		89 → 139°/1mm	13.2		0.26								
		139 → 200°/1mm	11.4		0.46								
		200 → 260/1mm	1.7		0.64								
		Vac. Bottom	12.1										
64	same as Run 61	iB → 200°/atm	23.6		0.08								
		iB → 89°/1mm	24.5		0.23								
		89 → 139/1mm	17.7		0.26								
		139 → 200/1mm	8.7		0.48								
		200 → 260/1mm	1.7		0.61								
		Vac. Bottom	12.9										
68	same as Run 61	iB → 200/atm	25.4		0.14				0.99				
		iB → 89°/1mm	21.0		0.19								
		89 → 139/1mm	10.9		0.26								
		139 → 200/1mm	8.8		0.49								
		200 → 260/1mm	2.3		0.59								
		Vac. Bottom	13.0										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SPC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
	<u>Conclusions</u> <u>Slight</u> improvements in conversion and in hydrogen richness (<u>cf</u>.NMR) are observed as amount of solvent increases to about 75 ml. However, the amount of solvent is not critical overall.												

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL vs. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(8) 32	75g SRL, 150 ml tetralin, 375°C, 2 hrs, 40.5g presulfided NiMo catalyst (HT-100), max. press. 4100	iB → 87°/1mm					0.27	0.13	0.41	1.4		0.004	
		87 → 139/1mm	9.6	1.40	0.14	2.40						0.06	
		139 → 200/1mm	22.1	1.32	0.18	30.6						0.09	
		200 → 260/1mm	12.1	1.17	0.23	78.6						0.13	
		Vac. Bottom	37.9	1.01	0.20						86.4	0.23	0.22
31	same as Run 32 except 425°C, max. press. 4200	iB → 200/atm					1.10	0.68	0.45	1.2			
		iB → 87/1mm	14.0	1.37	0.18	9.10							
		87 → 139/1mm	21.3	1.25	0.30	102.3							
		139 → 200/1mm	11.5	1.14	0.37	218.6							0.04
		200 → 260/1mm	24.3	1.02	0.45								0.12
		Vac. Bottom									87.6	0.20	0.32
35	same as Run 32 except 450°C. max. press. 4160	iB → 200°/atm					2.14	3.34	0.59	3.3			
		iB → 87°/1mm											
		87 → 139/1mm	17.1		0.19								
		139 → 200/1mm	15.2		0.36								
		200 → 260/1mm	6.8		0.39								
		Vac. Bottom	11.7										
	<u>Conclusions</u> Much better conversion at 450°C; much more gas formed but liquid yield still good.												

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Milliequiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(9)10	75g SRL(KC), 150 ml THF, 1000 psi H_2 initial, 375°C, 2 hrs., 10% CoMo catalyst (Co-Mo-0401-T-1/8), max. press. 2600 psi	iB → 130°/atm											
		130 → 140/atm	11.0	1.36	0.46								
		iB → 139/1mm	25.5	0.96	1.81								
		139 → 250/1mm		0.81	2.82								
		Vac. Bottom	72.7	0.41								0.09	0.05
11	same as Run 10 except 1800 psi H_2 initial, max. press. 2850 psi	iB → 130/atm											
		130 → 200/atm	0.9		0.12	0.0							
		iB → 87°/1mm	1.1		0.51	0.56							
		87 → 139/1mm	2.0		0.83	25.2							
		139 → 260/1mm	33.6		1.69	52.5							
		Vac. Bottom	62.0									0.47	0.73
12	75g SRL(KC), 150 ml tetralin, 1750 psi H_2 initial, 375°C, 2 hrs., 10% Co-Mo catalyst (Co-Mo-0401-T-1/8), max. press. 2800 psi	iB → 200/atm			0.45	0.0				0.0			
		iB → 87°/1mm			0.52	0.0							
		87 → 139/1mm	3.3		0.96	29.6							
		139 → 260°/1mm	28.8	0.84	1.58	271.2							
		Vac. Bottom	58.7	0.78								0.51	1.09

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs.* SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
13	Repeat of Run 12, max. press 2800 psi	iB → 87°/1mm			0.50	0.0							
		87 → 139/1mm	2.0		0.69	32.56							
		139 → 260/1mm	32.8		1.19	153.6							
		Vac. Bottom	59.9		---							0.53	0.96
14	same as Run 12 except 2060 psi H_2 initial, max. press. 3300 psi	iB → 87/1mm			0.49	0.0							
		87 → 139/1mm	2.1		0.65	69.9							
		139 → 210/1mm	19.6		1.05	162.8							
		210 → 260/1mm	12.0		1.12	126.5							
		Vac. Bottom	57.3									0.57	0.87
15	same as Run 12 except 2500 psi H_2 initial, max. press. 4100 psi	iB → 87/1mm			0.49	0.0							
		87 → 139/1mm	2.1		0.67	27.32							
		139 → 210/1mm	20.5	0.94	1.08	163.2							
		210 → 260/1mm	11.3	0.88	1.19	225.0							
		Vac. Bottom	59.1	0.81								0.58	0.80
	<u>Conclusions</u> With ether THF or tetralin as solvent, as initial pressure increases slight improvements in conversions and oil production were observed.												

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(10) 61	75g SRL(KC), no solvent, 40g presulfided NiMo catalyst (HT-100), 450°C, 2hrs., 1800 psi H_2 initial, max. press. 3600 psi	iB → 89°/1mm	40.0		0.26								
		89 → 139/1mm	13.2		0.26								
		139 → 200/1mm	11.4		0.46								
		200 → 250/1mm	1.7		0.64								
		Vac. Bottom	12.1										
64	same as Run 61	iB → 180°/atm	23.6		0.08								
		iB → 89°/1mm	24.5		0.23								
		89 → 139/1mm	17.7		0.26								
		139 → 200/1mm	8.7		0.48								
		200 → 235°/1mm	1.7		0.61								
		Vac. Bottom	12.9										
68	same as Run 61	iB → 180/atm	25.4		0.14				0.99				
		iB → 89/1mm	21.0		0.19								
		89 → 139/1mm	10.9		0.26								
		139 → 200/1mm	8.8		0.49								
		200 → 235/1mm	2.3		0.59								
		Vac. Bottom	13.0										
81	75g SRC-CU-88, other conditions same as Run 61	iB → 200°/atm	26.0		---				1.4	4.0			
		iB → 87°/1mm	7.5	1.37	0.32								
		87 → 139/1mm	4.9	1.25	0.35								
		139 → 200/1mm	8.9	1.12	0.52								
		200 → 235/1mm	6.5	0.96	0.74								
		Vac. Bottom	16.3										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs.* SRC (11) Misc.

RUN #	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
83	same as Run 81 (also see Run 80 - next page)	Same	20.2 1.5 5.9 13.7 5.9 16.0	1.39 1.35 1.16 0.96 0.76	0.12 0.26 0.27 0.43 0.62				1.6	4.0			
85	75g SRL-PDU, other conditions same as in Run 61	Same	25.3 8.8 13.2 14.5 0.1 9.3		0.08 0.18 0.20 0.36 0.63				0.31				
87	same as Run 85	Same	20.1 5.7 13.2 16.1 4.2 6.9		0.10 0.20 0.17 0.28 0.47				0.42				
86	75g SRC-Tacoma, other conditions same as Run 61	Same	19.6 5.9 8.9 12.4 5.1 13.2		0.15 0.22 0.27 0.45 0.55								

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL vs. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
88	same as Run 86	iB → 200/atm	18.7		0.10				>1.0				
		iB → 87°/1mm	7.6		0.22								
		87 → 139/1mm	8.9		0.26								
		139 → 200/1mm	12.0		0.35								
		200 → 235/1mm	6.0		0.51								
		Vac. Bottom	11.3										
80	same as Run 81 and 83	iB → 200°/atm	29.1		0.08				>1.0	4.0			
		iB → 87°/1mm	7.5	1.41	0.25								
		87 → 139/1mm	7.7	1.39	0.35								
		139 → 200/1mm	15.2	1.20	0.52								
		200 → 235/1mm	7.1	1.01	0.74								
		Vac. Bottom	13.9	0.76									
	<u>Conclusions</u> All SRL and SRC samples behaved very similarly. However, SRC-CU-88 gave the poorest overall conversions.												

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL vs. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
(11) 30	75g SRL(KC), 150 ml tetralin, 40.2 g presulfided NiMo catalyst (HT-100), 425°C, 2 hrs., 2200 psi H_2 initial, max. press. 3300 psi	iB → 87°/1mm							0.36	1.9			
		87 → 139/1mm	10.5	1.34	0.40	8.0							
		139 → 200/1mm	20.0	1.17	0.39	84.9							
		200→260/1mm	14.0	1.03	0.54	212.2							
		Vac. Bottom	21.8	0.90	0.65						93.1%	0.16	0.33
33	75g SRL(KC), 150 ml tetralin, 40.1g presulfided Ni-4301 catalyst, 425°C, 2 hrs., 2500 psi H_2 initial, max. press. 4300 psi	iB → 87°/1mm					1.3	0.64	0.26	1.5			
		87 → 139/1mm	10.1	1.37	0.20	11.3							
		139 → 200/1mm	21.5	1.22	0.34	100.8							
		200 → 260/1mm	10.4	1.12	0.49	185.5							
		Vac. Bottom	31.5	0.81	0.72							0.50	0.74

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
34	75g SRL(KC), 150 ml tetralin, 40.7g presulfided NiMo catalyst (HT-100), 7.5 g acid washed Mol. sieves 5Å, 2500 psi H_2 initial, 425°C, 2 hrs., max. press. 4100 psi	iB → 200°/atm					0.81	1.0	0.56	2.1			
		iB → 87°/1mm											
		87 → 155/1mm	18.0		0.19	13.8							
		155 → 200/1mm	17.5		0.33	108.8							
		200 → 260/1mm	8.4		0.34	119.2							
		Vac. Bottom	23.1									0.28	0.27
36	75g SRL(KC), 150 ml tetralin, 50% HZ-1 catalyst, 425°C, 2 hrs, 2500 psi H_2 initial, max. press. 4160 psi	iB → 87°/1mm											
		87 → 139/1mm	4.1										
		139 → 200/1mm	18.0										
		200 → 260/1mm	17.1										
		Vac. Bottom	47.5										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
38	75g SRL(KC), 150 ml tetralin, 40.4 g presulfided NiMo catalyst (HT-100), 450°C, 1 hr., 2500 psi H_2 initial, max. press. 4150 psi	iB → 200°/atm											
		iB → 87°/1mm	37.7										
		87 → 139/1mm	5.1										
		139 → 200/1mm	9.5										
		200 → 260/1mm	6.2										
		Vac. Bottom	23.0										
75	75g SRL(KC), no solvent, 50% WS_2 catalyst, 450°C, 2 hrs., 1800 psi H_2 initial	iB → 200/atm	5.3		0.14					1.5			
		iB → 70°/0.4mm	4.7	1.30	0.52								
		70 → 110/0.4mm	7.5	1.25	0.53								
		110 → 180/0.4mm	26.2	1.01	0.83								
		180 → 235/0.4mm	11.3	0.93	0.88								
		Vac. Bottom	23.8	0.75									
76	75g SRL(KC), 150 ml tetralin, 40.5 g presulfided NiMo catalyst, (HT-100), 450°C, 2 hrs., 2500 psi H_2 initial, max. press. 2900 psi (No stirring).	iB → 200°/atm			0.67				0.78				
		iB → 70°/0.4mm			0.18								
		70 → 110/0.4mm	28.3	0.88	3.34								
		110 → 180/0.4mm	18.4	0.84	2.16								
		180 → 235/0.4mm	2.0	0.85	2.34								
		Vac. Bottom	40.3	0.77									

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Milliegiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
77	75g SRL(KC), no solvent, 40.5g presulfided NiMo catalyst (HT-100), 450°C, 2 hrs., 1800 psi H_2 initial, max. press. 3300 psi-catalyst under H_2 four days before SRL added.	iB → 200°/atm	13.5		0.05				0.75				
		iB → 70°/0.4mm	4.3		0.38								
		70 → 110/0.4mm	8.5	1.24	0.38								
		110 → 180/0.4mm	17.9	1.02	0.70								
		180 → 235/0.4mm	5.7	0.94	0.86								
		Vac. Bottom	12.7	0.71									
84	75g SRL(KC), no solvent 40.5g presulfided NiMo catalyst (HT-100) and 18.5 g cracking catalyst (HZ), 450°C, 2 hrs, 1800 psi H_2 initial	iB → 200°/atm	17.9		0.13				0.65	3.0			
		iB → 70°/0.4mm	5.9	1.27	0.47								
		70 → 110°/0.4mm	10.3	1.14	0.60								
		110 → 180/0.4mm	12.4	0.95	1.03								
		180 → 235/0.4mm	3.5	0.91	1.10								
		Vac. Bottom	16.8	0.73									

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
50	75g SRL-FS-120, 37ml tetralin, 40g presulfided NiMo catalyst (HT-100), 450° 2 hrs, 2100 psi H_2 initial max. press. 4600 psi	iB → 87°/1mm											
		87 → 139/1mm	13.1										
		139 → 200/1mm	11.1										
		200 → 260/1mm	3.1										
		Vac. Bottom	7.2										
51	same as Run 50 except Ni-W-NiO_2 (Ni-4301) catalyst used.												
			8.7										
			12.7										
			7.1										
			11.1										
52	150g SRL(KC), 37ml tetralin, 80g presulfided NiMo catalyst (HT-100), 450°, 2hrs, 2100 psi H_2 initial, max. press. 4000 psi	iB → 87°/1mm											
		87 → 139/1mm	11.7										
		139 → 200/1mm	18.2										
		200 → 260/1mm	6.6										
		Vac. Bottom	19.0										

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
70	One gallan autoclave - relative amounts and conditions same, i.e. 450°C, 2 hrs, 1800 psi H_2 initial, 50% presulfided NiMo catalyst (HT-100), max press. about 3600 psi (3.78 times the amount of SRL (KC) and catalyst), no solvent	iB → 87°/1mm 87 → 139/1mm 139 → 200/1mm 200 → 260/1mm Vac. Bottom	24.9 13.4 10.2 1.6 4.3		0.12 0.17 0.25 0.53 0.53								
73	same as Run 70	iB → 200°/atm iB → 87°/1mm 87 → 139/1mm 139 → 200/1mm 200 → 260/1mm Vac. Bottom	14.1 12.9 13.1 10.4 1.9 7.2				10.5	12.9 (C_3H_8 24.4 g)		19.0			

Table 4 Collection of Data on SRL Hydrogenation Classified in Type of Experiments

(1) Preliminary (2) Amount of Catalyst 1%, 10%, 50%, 75% (3) Catalyst Survey as Received (4) Catalyst Survey Presulfided (5) Catalyst conditioning (6) Type of Solvent to Use (7) Amount of Solvent to Use and No-Solvent Runs (8) Temperature Study (9) Pressure Effects (10) SRL *vs*. SRC (11) Misc.

RUN # ↓	Conditions	Distillation Temperature Ranges	% of SRL	H/C Ratio	Aromatic/ Aliphatic C -H (NMR)	Ultra Violet 320 nm	Methane g produced	Ethane g produced	Ammonia g produced	Water g produced	Benzene solubility Vac. Bottom	Millieqiv. Basic Amine /g vac. bottom	Milliequiv. Phenolic /g
74	same as Run 70	iB → 200°/atm iB → 87°/1mm 87 → 139/1mm 139 → 200/1mm 200 → 260/1mm Vac. Bottom	16.1 13.0 8.4 11.5 2.0 6.2				7.7	17.4 (C_3H_8 24.4g)		17.0			

TABLE 5

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
43			0.27	2.0
46			0.32	2.5

Table 6

Tabulation of H/C Atomic Ratios

	Distillate Fractions*			
Run	2	3	4	5
SRL				0.75
10	1.375	0.963	0.813	0.413
12	---	---	0.844	0.779
16	1.22	1.03	1.03	0.91
18	1.12	0.97	0.93	0.88
19	1.11	0.98	0.91	0.78
20	1.14	1.13	0.98	0.81
21	1.16	1.03	0.91	0.86
22	1.02	0.84	0.82	0.85
24	1.20	1.07	0.96	0.91
25	1.24	1.31	1.04	---
26	1.22	1.00	0.96	0.90
27	1.46	1.26	1.15	0.96
28	1.42	1.25	1.16	0.92
29	1.40	1.17	1.06	0.87
30	1.34	1.17	1.03	0.90
31	1.37	1.25	1.14	1.02
32	1.40	1.32	1.17	1.01

* Boiling ranges of the distillate fractions:

1_A	IBP-200°C/atm
1_B	IBP-87°C/1 Torr
2	87-139°C/1 Torr
3	139-200°C/1 Torr
4	200-260°C/1 Torr
5	260°C + Bottoms/1 Torr

Table 7

Elemental Analyses for Run 68

Distillate Fractions*	Weight Percent C	H	N	S
1A	84.84	12.05	0.2	<0.1%
1B	88.96	10.35	0.14	<0.1%
2	90.30	9.54	<0.1%	<0.1%
3	92.59	8.17	<0.1%	<0.1%
4	92.87	7.49	<0.1%	<0.1%
5	92.88	6.98	0.13	<0.1%

* Boiling ranges of the distillate fractions

1_A	IBP-200°C/atm
1_B	IBP-87°C/1 Torr
2	87-139°C/1 Torr
3	139-200°C/1 Torr
4	200-260°C/1 Torr
5	260°C + Bottoms/1 Torr

Table 8

NMR Analyses, Ar-H/Al-H Ratios of Distillate Fractions

	Distillation Fractions*				
Run	1_A	1_B	2	3	4
8			0.44	0.73	1.43
9			0.67	1.51	2.41
10			0.46	1.81	2.82
11			0.51	0.81	1.69
12			0.52	0.96	1.58
13			0.69	---	1.19
14			0.65	1.05	1.12
15			0.67	1.08	1.19
16			0.53	0.98	1.09
17			0.51	0.78	0.89
18			0.56	1.00	1.15
19			0.56	0.88	0.96
20			0.50	0.82	0.92
21			0.65	1.21	0.92
22			1.05	1.93	2.01
23			0.42	0.68	0.73
24			0.44	0.67	0.76
25			0.42	0.76	0.80
26			0.476	0.81	0.88
27			0.185	0.213	0.24
28			0.16	0.23	0.27
29			0.21	0.32	0.42
30			0.40	0.39	0.54
31			0.18	0.30	0.37

Run	1_A	1_B	2	3	4
32			0.14	0.18	0.23
33			0.19	0.33	0.34
34			0.19	0.33	0.34
35			0.19	0.36	0.39
47			0.22	0.43	0.43
48			0.29	0.43	0.53
53			0.75	1.09	1.05
54			0.26	0.46	0.55
56			0.26	0.40	0.56
57	0.08	0.25	0.24	0.38	0.80
58	0.11	0.23	0.23	0.34	---
59	0.13	0.23	0.23	0.46	0.76
61	---	0.26	0.26	0.46	0.64
62	0.06	0.28	0.25	0.34	0.58
63	0.07	0.24	0.23	0.34	0.61
64	0.08	0.23	0.26	0.48	0.61
65	0.09	0.22	0.22	0.37	0.53
66	0.15	0.24	0.24	0.34	0.39
67	0.11	0.15	0.12	0.12	0.22
68	0.14	0.19	0.26	0.49	0.59
70	0.12	0.17	0.25	0.53	0.53
71	0.01	0.39	0.46	0.73	0.83
72	0.14	0.28	0.32	0.48	0.64
74	0.12	0.23	0.30	0.525	.62
75	0.14	0.516	0.537	0.829	0.88
76	0.67	0.18	3.34	2.16	2.34
77	0.05	0.38	0.38	0.70	0.86

Run	1_A	1_B	2	3	4
78	0.29	0.48	1.41	1.42	1.49
79	0.09	0.23	0.25	0.39	0.65
80	0.08	0.25	0.25	0.40	0.60
81	---	0.32	0.35	0.52	0.74
82	0.105	---	0.30	0.45	0.56
83	0.124	0.264	0.27	0.43	0.62
84	0.13	0.47	0.60	1.03	1.10
85	0.08	0.18	0.20	0.36	0.63
86	0.15	0.22	0.27	0.45	0.55
87	0.10	0.20	0.17	0.28	0.47
88	0.10	0.22	0.26	0.35	0.51

* Boiling ranges of the distillation fractions:

1_A	IBP-200°C/atm
1_B	IBP-87°C/1 Torr
2	87-139°C/1 Torr
3	139-200°C/1 Torr
4	200-260°C/1 Torr
5	260°C + Bottoms/1 Torr

Table 9

Characterization of Vacuum Bottoms

Run	% Dissolution in Benzene	meq Basic Amine / g. of Vac. Bot.	meq Phenol / g. of Vac. Bot.
SRL	62.2	0.543	1.34
10	---	0.537	1.09
11	---	0.091	0.055
12	---	0.511	1.09
13	---	0.534	0.963
14	---	0.577	0.874
15	---	0.575	0.804
16	69.8	0.566	0.869
17	74.8	0.641	0.863
18	73.5	0.520	0.970
19	65.5	0.549	0.913
20	71.1	0.549	0.913
21	62.4	0.482	1.32
22	55.1	0.544	1.12
23	78.2	0.409	0.520
24	78.4	0.447	0.518
25	82.9	0.457	0.657
26	94.9	0.363	0.661
27	85.3	0.467	0.469
28	81.9	0.485	0.447
29	67.9	0.53	0.79
30	---	0.16	0.33
31	87.6	0.20	0.32
32	86.4	0.23	0.23
34	---	0.28	0.27

Table 10

CHARACTERIZATION OF HYDROGENATED SOLVATED LIGNITE PRODUCTS FROM RUN 31

Sample	31-1 IBP-200°C/atm (IBP-392°F)	31-2 87-139°C/1Torr (189-282°F)	31-3 139-300°C/1 Torr (292-392°F)	31-4 200-260°C/1 Torr (392-500°F)
Saturates				
Wt.% of Sample	73.5	12.5	8.6	3.6
Paraffins	0.0	0.4	1.9	1.5
Non Condensed Cycloparaffins	56.8	3.5	0.9	0.8
Condensed Dicycloparaffins	16.7	3.8	2.9	0.7
Condensed Tricycloparaffins	0.0	4.2	2.9	0.6
Aromatics				
Wt.% of Sample	24.0	86.5	90.6	96.2
Alkylbenzenes	6.8	1.1	0.7	2.0
Indanes/Tetralins	16.0	16.6	4.1	3.2
Naphthalenes	0.5	4.9	2.3	1.7
Phenanthrenes	0.0	0.9	0.9	0.0
Hydrophenanthrenes	0.0	30.3	23.6	4.9
Pyrenes	0.0	1.6	9.1	20.0
Hydropyrenes	0.0	16.2	40.0	36.1
Acenaphthenes/Biphenyls	0.0	1.4	0.0	0.0
Chrysenes	0.0	1.4	3.9	12.6
Benzopyrenes	0.0	0.2	1.9	6.4
Naphthols	0.0	2.5	1.0	1.6
Resorcinols	0.1	3.6	0.4	0.6
Phenols	0.6	6.2	2.6	5.1

TABLE 11A: FIA SEPARATION DATA ON DISTILLATE FRACTION From Run 59

Sample	% Saturates	% Olefins	% Aromatics
1A	57.0	0.0	43.0
1B	13.7	10.3	76.0
2	0.0	7.0	93.0
3	0.0	0.0	100.0

TABLE 11B: Mass Spectrometric Group Type Analysis of Aromatic Fractions from Run 59

		Percent in Fraction			
Z No.	Group Type	1A	1B	2	3
-28	Benzopyrenes	0.0	0.0	0.0	0.4
-24	Chrysenes	0.0	0.0	0.1	1.7
-12	Decahydropyrenes	0.1	0.1	0.4	4.0
-16	Hexahydropyrenes	0.3	0.5	1.5	15.3
-18	Tetrahydrofluoranthenes	0.1	0.1	0.2	2.7
-22	Pyrenes/Fluoranthenes	0.0	0.2	0.8	7.4
-20	Dihydropyrenes	0.0	0.2	0.9	4.6
-10	Octahydroanthracenes	0.0	0.8	7.4	15.3
-12	Hexahydrophenanthrenes	0.0	0.0	0.1	0.0
-14	Tetrahydroanthracenes	0.3	0.6	3.5	16.5
-18	Phenanthrenes	0.0	0.1	0.6	2.6
-16	Fluorenes/Dihydroanthracenes	0.0	0.1	2.1	1.7
-14	Acenaphthenes/Biphenyls	0.0	0.6	5.0	0.6
-8	Tetralins	47.5	70.5	40.7	11.5
-10	Tetrahydroacenaphthenes	0.0	3.2	11.7	4.3
-12	Naphthalenes	0.8	6.1	8.5	3.2
-6	Benzenes	46.3	12.3	3.5	1.5
	Naphthol	0.2	1.5	6.3	2.3
	Dihydroxybenzenes	0.9	1.0	2.4	1.4
	Phenol	3.5	2.2	4.2	3.1

Table 12

Composition of Composite Sample
(1_A, 1_B, 2, 3)

Peak	Compound	Mass.
1	Methyl pentane	(86)
2	N-Hexane	(86)
3	Methyl cyclopentane	(84)
4	Benzene	(78)
5	Heptane	(84)
6	Heptane	(100)
7	Methyl cyclohexane	(98)
8	Toluene	(92)
9	Dimethyl cyclohexane	(112)
10	Dimethyl cyclohexane	(112)
11	Dimethyl cyclohexane	(112)
12	Xylene or ethyl benzene	(106)
13	Xylene (meta or para)	(106)
14	Xylene (ortho ?)	(106)
15	Isopropyl cyclohexane	(126)
16	N-propyl benzene	(120)
17	Cumene	(120)
18	Trimethyl benzene	(120)
19	Indane	(118)
20	Isobutyl cyclohexane	(140)
21	N-butyl benzene	(134)
22	Decalin	(138)
23	Methyl indane	(132)
24	Decalin ?	(138)

Table 12 (cont'd)

Peak	Compound	Mass.
25	1,2,3,4-Tetrahydronaphthalene	(132)
26	Naphthalene	(128)
27	2-Methyl-tetrahydroanphthalene	(146)
28	Methyl-tetrahydronaphthalene	(146)
29	Methyl-tetrahydronaphthalene	(146)
30	Methyl naphthalene plus dimethyl tetrahydronaphthalene	(142) (160)
31	Dimethyl tetrahydronaphthalene	(160)
32	Tetrahydroacenaphthalene	(158)
33	Trimethyl tetrahydronaphthalene	(174)
34	Mixture of trimethyl tetrahydronaphthalene and unknown	(174) (190)
35	Mixture of unknown and unknown	(168) (192)
36	Mixture of unknown and unknown	(188) (192)
37	Unknown	(172)
38	N-butyl tetrahydronaphthalene	(188)
39	2-N-butyl naphthalene and 2-methyl biphenyl	(184) (168)
40	Pentamethyl dihydronaphthalene	(200)
41	Tetramethyl dihydronaphthalene and hexamethyl dihydronaphthalene	(186) (214)
42	Tetramethyl dihydronaphthalene and hexamethyl dihydronaphthalene and hexamethyl tetrahydronaphthalene	(186) (214) (216)
43	Hexamethyl dihydronaphthalene and hexamethyl tetrahydronaphthalene and unknown	(214) (216)

Table 12 (cont'd)

Peak	Compound	Mass.
44	(Anthracene (Dimethyl tetrahydroanthracene and (Trimethyl tetrahydronaphthalene	(178) (210) (216)
45	Hexamethyl naphthalene and dimethyl tetrahydroanthracene dimethyl dihydroanthracene	(212) (210) (208)
46	Dibenzoheptafulvene	204
47	Dihydrodibenzoheptafulvene	206

Table 13 Material Balance Calculations

Input, grams	Run No. 27	31	35
SRL	75.0	75.0	75.0
Tetralin	145.5	145.5	145.5
Catalyst	43.1	40.5	40.6
H_2	10.8	10.8	10.8
Tetralin wash	38.8	38.8	38.8
Total	313.2	310.6	310.7
Output, grams			
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 14

Comparison of Phenolic and Basic Nitrogen Contents of SRL

Liquefaction Solvent	project lignite Run No.	Phenol, meq/g of SRL	Basic Nitrogen, meq/g of SRL	Basic Nitrogen, meq/g of solvent
CAO 1/	504	2.18	0.614	0.314
CAO	505	2.10	0.624	0.399
CAO 2/	---	1.34	0.534	---
Tar S2	509	1.49	0.288	0.022
FS-120	514	1.53	0.300	0.024
Exxon HAN	519	2.48	0.452	0.008
Fuel Oil No. 5	513	0.69	0.161	0.0056

1/ Chilled Anthracene oil.

2/ Prepared in a continous flow apparatus in Kansas City using North Dakota Lignite.

Table 15

Characterization Data

	SRL (batch)	SRL (continuous)	SRC (continuous)
Mol. Formula	$C_{44.2}H_{34.6}O_{2.71}N_{0.62}S_{0.06}$	$C_{29.1}H_{21.6}O_{1.23}N_{0.42}S_{0.07}$	$C_{41.1}H_{30.1}O_{1.48}N_{0.85}S_{0.12}$
Avg. Mol. Wt.	620	440	563
UV $E^{320}_{pyridine}$	31,900	19,750	32,700
Phenolic O-H, eq/mol	1.35	0.54	0.46
RO-H, eq/mol	0.20	0.69	0.27
R-O-R, eq/mol	1.16		
Basic N, eq/mol	0.38	0.21	0.46
Non-basic N, eq/mol	0.24	0.21	0.39
$C_{Aromatic}$	34.2	25.7	33.8
F_A	0.773	0.88	0.82
σ	0.35	0.22	0.33
H_a/C_a	0.65	0.74	0.69
Aromatic	$C_{34}H_{14}$	$C_{26}H_{19}$	$C_{34}H_{10}$
Aliphatic	$C_{10}H_{20}$	C_3H_6	$C_{10}H_{30}$
Avg. Chain Length, atoms	2.24	1.36	1.41

Table 16. Solubilities of SRL (CAO, Run 504) in Organic Solvents

Solvent	% Dissolved	Solvent	% Dissolved
<u>Class 3</u>			
Aniline	100	Anisole	77.1
Dimethyl aniline	100	Chloroform	75.7
n-Butyl amine	100	Nitroethane	
n-Hexylamine	100	1-Nitropropane	69.9
Methyl formamide	100	Acetone	69.8
Dimethyl sulfoxide	100	Dichloromethane	69.7
Phenol (50°C)	100	Phenyl acetate	66.6
Nitorbenzene	100	Amyl Alcohol	62.5
Pyridine	100	Toluene	58.5
Dioxane	99.8	Benzene	61.9
Acetophenone	100	Butanoic Acid	59.3
Tetrahydrofuran	100	Propanoic Acid	59.3
Methyl benzoate	98	Diethyl ether	54.5
<u>Class 2</u>		Mesitylene	52.6
Ethyl acetate	84	1-Butanol	52
Methyl ethyl ketone	80.5	1-Propanol	50.8
1,2-Dimethoxyethane	80.0	Ethanol	47.0
		Acetic Acid	47.0
		<u>Class 1</u>	
		Nitromethane	6.3
		Methanol	3.3
		Pentane	6.8
		Hexane	11.6
		Heptane	7.9
		Carbon tetrachloride	20.2
		Formic Acid	25.3

Table 17. Solubilities of SRL (FS-120, Run 514) in Organic Solvent

Solvent	% Dissolved
Pyridine	100
Phenol (50°C)	100
Nitrobenzene	100
n-Butyl Amine	100
Benzene	67.6
n-Butanol	63.5
Methanol	34.0