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Heterogenous Catalysis of Solvent Refined Lignite to Obtain Chemical Feed Stocks

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HETEROGENOUS CATALYSIS OF SOLVENT REFINED LIGNITE
TO OBTAIN CHEMICAL FEED STOCKS

by

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Bachelor of Arts, Biology and Chemistry

Minot State College, 1976

A Thesis

Submitted to the Graduate Faculty

of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

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This Thesis submitted by John R. Rindt in partial fulfillment of the requirements for the Degree of Master of Science from the University of North Dakota is hereby approved by the Faculty Advisory Committee under whom the work has been done.

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This Thesis meets the standards for appearance and conforms to the style and format requirements of the Graduate School of the University of North Dakota, and is hereby approved.

William Johnson

Dean of the Graduate School

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Chemical Feed Stocks

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ABSTRACT

Continuous catalytic depolymerization of solvent refined lignite (SRL) was investigated by reacting it catalytically with hydrogen in a fixed bed trickle reactor, using tetralin as the solvent. At a reaction temperature of 450° C , a hydrogen atmosphere at 1,000 psi, and a liquid hourly space velocity of 1.0 to 1.5 hr⁻¹, 58 runs were made using eighteen different catalysts. Yields of light oil ranged from 0.010 to 0.211 grams of light oil produced per gram of SRL fed. Using a gas chromatograph-mass spectrophotometer, light oils were shown to contain toluene and ethyl benzene, in substantial quantities. Conversion of SRL, which ranged from 0.100 to 0.515 grams SRL converted per gram SRL fed, appeared to be related to the basic content of the catalyst surface.

CHAPTER I
INTRODUCTION

Aromatic chemicals, particularly benzene, toluene, and the xylenes (BTX), are important to the chemical industry. All three were among the top thirty chemical compounds produced in 1977; benzene ranked thirteenth, toluene seventeenth and xylene twenty-third. The amounts produced in 1977 were 11.25, 7.73, and 6.05 billion pounds, respectively (1). The annual rate of increase in production for BTX was 5-8% (2,3). BTX are used in the synthesis of plastics, rubber, rubber chemicals, surfactants, nylons, dyes, food additives, drugs and fungicides.

The sources of BTX include catalytic reforming and hydro-alkylation of virgin naphthas, olefin plant by-products, coal tars, cyclic hydrocarbon or naphthene-rich petroleum fractions, and light oils obtained by scrubbing coke oven gas with wash oil. Presently, aromatic petroleum fractions and coke oven light oils are the most important sources (4).

BTX, from petroleum distillable products, are obtained by catalytically reforming naphthenes present in petroleum products. An increase in aromatic content of 40% by volume is usual in catalytic reforming (5). Import petroleum prices have risen from \$3.39 per barrel in 1972 (6) to \$14.54 per barrel on April 1, 1979 (7) and are expected to increase significantly in the near future. The consequence is that

petroleum derived products, including BTX, will rise in cost at a similar pace.

Recently, refining techniques, including hydrodesulfurization and solvent extraction, have been applied to the processing of coke oven light oils to give greater quantities of aromatics. The principal products from the carbonization of one ton of coal in a slot-type oven at about 1100°C are listed in table 1. In light oil extraction processes, the benzene product will have a freezing point not higher than 4.8°C . Because the present benzene market requires a larger percentage of high quality product benzene having a freezing point of 5.3°C or higher, it is becoming increasingly difficult for those producers obtaining benzene from coke oven light oils, to meet present day requirements (8).

The demand for aromatic chemicals often exceeds the quantity that can be produced as a by-product of coke oven plants. As indicated, with BTX derived from petroleum distillation products and coal coking processes, current supplies of BTX face either raw material cost increases or production limitation. An abundant supply of raw material capable of providing sufficient product of desired purity is needed.

Considerable interest in lignite as a source of fuel and as a source of aromatic chemicals has recently been shown. Strip-mined lignite can be solvent refined to produce a product that is solid at room temperature and low in ash, nitrogen and sulfur. If shown to be feasible, solvent refined lignite (SRL) derived from a currently abundant natural reserve, represents a possible raw material source. This material, containing many naphthene and aromatic compounds, while

TABLE 1

PRINCIPAL PRODUCTS FROM THE CARBONIZATION OF
2,000 POUNDS OF COAL AT 1,100° C (9)

Amount(s)	Product(s)
1,520 lbs	coke and breeze
78 lbs	tar (10 gal)
20 lbs	ammonium sulfate
20 lbs	light oils (3 gal)
10,000 ft	gas

Typical analysis of coke oven light oils.

<u>Wt %</u>	<u>Product(s)</u>
5	forerunning compounds
65	benzene
15	toluene
10	xylenes, cumene, etc.
5	naphthalene, heavy oils, etc.

containing small amounts of unreactive impurities, such as sulfur and nitrogen, may be an excellent future source of aromatic chemical feedstocks.

In this study, a continuous, small-scale hydrocracking unit was designed and built to test the feasibility of obtaining aromatic feedstocks from SRL. Catalysts tested included those previously shown to yield aromatic products from several feed materials and under a variety of processing

conditions. Also tested were catalysts which theoretically resist nitrogen poisoning. Process conditions were selected following a review of aromatization processes.

CHAPTER II

LITERATURE REVIEW

A review of the literature established experimental parameters for the micro hydrocracking unit (MHU). Among these parameters were reaction temperature, reaction pressure, liquid hourly space velocity (LHSV), catalyst preparation and method of activation, and feed qualities. Many specific processes and several general guidelines were encountered which indicated values for experimental parameters that affected the degree of aromaticity of coal-derived liquid products. The processes that are described in this section deal with the conversion of coal to aromatic liquid products. Because conditions vary widely, a range of experimental parameters were found from which specific conditions were chosen for this study.

When attempting to increase aromatization in a gasoline-type product (light oil) derived from coal, Wu and Storch (10) reported that a pressure reduction from 8800 to 3700 psi may be completely compensated for by an increase of 0.3 to 3.0% by weight MoO_3 on MoO_3 - $\text{ZnO-Cr}_2\text{O}_3$ -synthetic Al_2O_3 - SiO_2 catalysts. At 8800 psi addition of 15% MoO_3 to $\text{MgO-MnO-Cr}_2\text{O}_3$ on Fullers earth increased the yield of gasoline but decreased the aromatic content. Addition of 5.0% MoO_3 made possible a reduction in reaction temperature from 500°C to 459°C , but resulted in a significant loss of aromatic content in the products. The catalyst used in early studies of aromatization was

53.5% MoO₃, 30% ZnO, and 16.5% MgO. It was used to aromatize middle oil (in the naphthalene boiling range) at 510° C and 2950 psi pressure in one stage. Prehydrogenation was necessary when the feed was middle oil from liquid phase hydrogenation of bituminous coal. Iron-tungsten catalysts, either 90% FeS- 10% WS₂, or 18% FeS- 2% WS₂ -80% active char, aromatized middle oil from hydrogenation of bituminous coal at 500° C and 3675 to 4410 psi following prehydrogenation. Prehydrogenation was not necessary, and high aromatic content was obtained, when a basic carrier plus a mild hydrogenating component consisting of 15% Cr₂O₃- 5% V₂O₃- 80% active char was used.

Donovan, Swarthmore and Weiss (11) and Brenner and Doelp (12) developed a two-step catalytic process for selectively hydrogenating and hydrocracking coke-oven light oil that contained 10 to 15% "primary oil". The first stage was operated at temperatures of 250° to 370° C in the presence of hydrogen at pressures of 135 to 1470 psi. Fresh feed rates, as measured by the LHSV varied from 0.5 to 5.0 hr⁻¹. A catalyst containing 10 to 20% by weight of the oxides of cobalt and molybdenum, with the MoO₃ content being from 3 to 5 times that of the CoO, was used in this first stage. Styrene, indene, and dicyclopentadienes, in addition to 50 to 80% of the ring sulfur compounds, were hydrogenated in the first stage. The second stage consisted of a hydroalkylation system operating under hydrogen atmosphere at a pressure of 450 to 1000 psi and temperatures of 590° to 630° C. The LHSVs were such that, under the reaction conditions, the nominal residence time of the reaction material was less than three minutes. The catalyst for this second stage was a

high activity chromia-alumina catalyst. Nonaromatic compounds were hydrocracked to light hydrocarbons and a substantial portion of alkyl aromatics were converted to benzene.

Stewart and Dyer (13) developed a process in which an aqueous slurry of pulverized coal was introduced into a reactor along with a mixture of supercritical water and hydrogen. The resultant mixture was retained in the reactor for sufficient time to insure efficient pyrolysis of the coal. This process converted the carbonaceous material to liquids, primarily arylalkanes, gaseous hydrocarbons and undissolved ash. The organic fraction provided a high yield of aromatic hydrocarbons and minimal formation of undesirable high molecular weight products such as asphaltenes. Conversions usually exceeded 25% by weight of the carbonaceous material charged.

Tarhan (14) developed a three-stage, high pressure-high temperature catalytic process to upgrade a coal tar feedstock containing largely polynuclear aromatic hydrocarbons. The first stage was operated at 3,000 psi and 450° C. The tar was hydrocracked over a sulfonated iron-molybdate-on-alumina catalyst using an hourly space velocity of 0.6 hr⁻¹ and a hydrogen to liquid feed volume ratio of 965 to 1. The product of this stage contained about 35% by weight of compounds boiling below 325° C. Products from the first stage reactor were reacted in the second stage, with hydrogen over a cobalt-molybdate on alumina catalyst at 400° C and about 3,000 psi. The LHSV of the second reactor was high, approximately 2.0 hr⁻¹. Oxygen-containing compounds, such as phenol, were hydrogenated to aromatics and saturated olefins such as styrene in this stage. A portion of the

product from stage two was treated catalytically over a chromia-alumina catalyst in the third stage. The reactor temperature was 610° C , the pressure was 800 psi and the LHSV was 0.5 hr⁻¹. A batch and once-through process resulted in about 30% recovery of one- and two-ring aromatics from coal tar or creosote. In a continuous, recycle process, recovery of one- and two-ring aromatics reached as high as 70 to 75% of the original feed. Reactor parameters for this process were variable: the LHSV may range from 0.1 to 2 hr⁻¹; the pressure from 1,000 to 10,000 psi; the temperature from 400° to 550° C ; and the hydrogen to feed volume ratio from 500 to 5,000. Various catalysts may also be used, with sulfonated nickel-molybdenum on alumina considered satisfactory.

Severson, Souby and Harris (15) reported gaseous and liquid product yields for a process in which lignite was continuously solvent refined at temperatures up to 510° C and a pressure of 2500 psi. Gas yields were 33.2 to 37.1% by weight, based on moisture and ash free (MAF) lignite. Liquid yields were 63.1 to 65.0%, by weight, on the same basis.

Wu and Storch (16) list several general rules for increasing the yield of aromatic products from coal-derived materials. Tar acids in the feed enhance aromatization. Under aromatization conditions, tar acids of the middle oil boiling range are converted to aromatic hydrocarbons of gasoline boiling range with little molecular-size reduction and, therefore, only slight gasification.

High pressure increases hydrogenation and decreases polymerization

but decreases the aromatic content of the product. Polymerization and condensation products, which form on the catalysts and reduce their activity, may be avoided at operating temperatures of 500° C.

Higher temperatures also give a favorable equilibrium ratio of aromatics to naphthenes and increase the rate of cracking hydroaromatics and isomerizing paraffins. Only a mild hydrogenating catalyst is required at higher temperatures.

In general, for efficient aromatization, the reaction temperature should be in the range of 200° to 500° C, pressure in the range of 440 to 8820 psi (with lower pressure favoring aromaticity), and a LHSV in the range of 0.5 to 5.0 hr⁻¹.

Aromaticity of the products may be favorably influenced by a variety of catalysts including support materials, such as alumina, silica, magnesium oxide, and active char, in combination with many active components including the oxides of nickel, cobalt, copper, vanadium, chromium, iron, molybden, zinc, tungsten, and the sulfides of tungsten and iron.

Several investigators suggest catalyst characteristics and activation procedures which affect aromatic yields.

Wu and Storch (17) indicated that aromatization catalysts should hydrogenate acids in the feed to aromatic hydrocarbons, not to naphthenes. Basic carriers, such as active char or active alumina, in combination with a mild hydrogenating component, such as vanadium or chromium oxide, hydrogenated tar acids to aromatic hydrocarbons but not to naphthenes. With acid carriers, such as silicates, these oxides failed to hydrogenate tar acids completely and also produced poly-

merization and condensation products. Increased hydrogenation and polymerization can be realized using a catalyst made of a strong hydrogenating component, such as molybdenum oxide, on an acid carrier. The resulting product is less aromatic than when a mild hydrogenating component on a basic carrier is used. An acid carrier used with a combination of weakly hydrogenating components, such as zinc, magnesium and chromium oxides, behaves the same as does a basic carrier.

Higginson (18) and Folkins and Miller (19) indicated that activation procedures are important in obtaining high activity and selectivity in a catalyst. During this step the surface area, average pore size, and active sites are developed or made accessible. The most common form of activation is calcination in air, nitrogen, or hydrogen at a temperature not lower than that at which the catalyst is to be used. Calcination is usually performed at a temperature in the range of 320° to 900° C. Catalysts prepared so that decomposable salts remain must be heated to at least the temperature at which the salts decompose. Thermal treatment in air results in a product with the highest possible surface area for a given material. Hydrogenation and dehydrogenation catalysts are usually activated in the presence of hydrogen. Nickel, cobalt, copper, and iron catalysts are activated by reducing their respective oxides to the metallic state; temperatures in the range of 300° to 500° C are suitable for these reductions. Varying steam content of the air plays a significant role in determining pore size and surface area.

Because several catalysts were not commercially available for use in this study, methods of catalyst synthesis were sought. Higginson (20),

and Folkins and Miller (21) outlined several methods for laboratory scale catalyst synthesis. These are detailed in the experimental procedures section.

CHAPTER III

EXPERIMENTAL PROCEDURES

The literature survey made it possible to assign major experimental parameters as follows: 1) a reaction temperature of 450° C ; 2) a reaction pressure of 1000 psi; 3) a hydrogen atmosphere; 4) either an acid carrier with weakly hydrogenating components, or a mild hydrogenating component on a basic carrier; and 5) for catalyst activation, a temperature of 400° C in a hydrogen atmosphere.

The micro hydrocracking unit (MHU) was designed with safety and ease of modification in mind. All portions of the MHU subjected to high pressure and/or high temperature were built behind a steel blow-out barricade. The area within the barricade was vented through a hood. Figure 1 is a flow sheet of the final MHU. In the following discussion, in instances where the same name may possibly have been applied to two or more different pieces of equipment, the equipment name was followed by a unique four or five digit identification number. The name, number, function and sources are listed by increasing identification number in appendix C.

Calibration of several pieces of experimental equipment was necessary. These included the gas chromatograph (GC), the high pressure slurry pump, the gas flow meter, and the distillation apparatus.

The gas chromatograph, GC-701, was calibrated using a solution of 91.4% by weight tetralin and 8.6% by weight naphthalene.

- CT cold trap
- CV check valve
- FI flow indicator
- GB gas bomb
- HT hydrogen tank
- P positive displacement pump
- PA product accumulator
- PI pressure indicator
- PR back pressure regulator
- R reactor
- RD rupture disk
- SA start up accumulator
- ST slurry tank
- TR temperature recorder
- V valve
- WT wet test meter

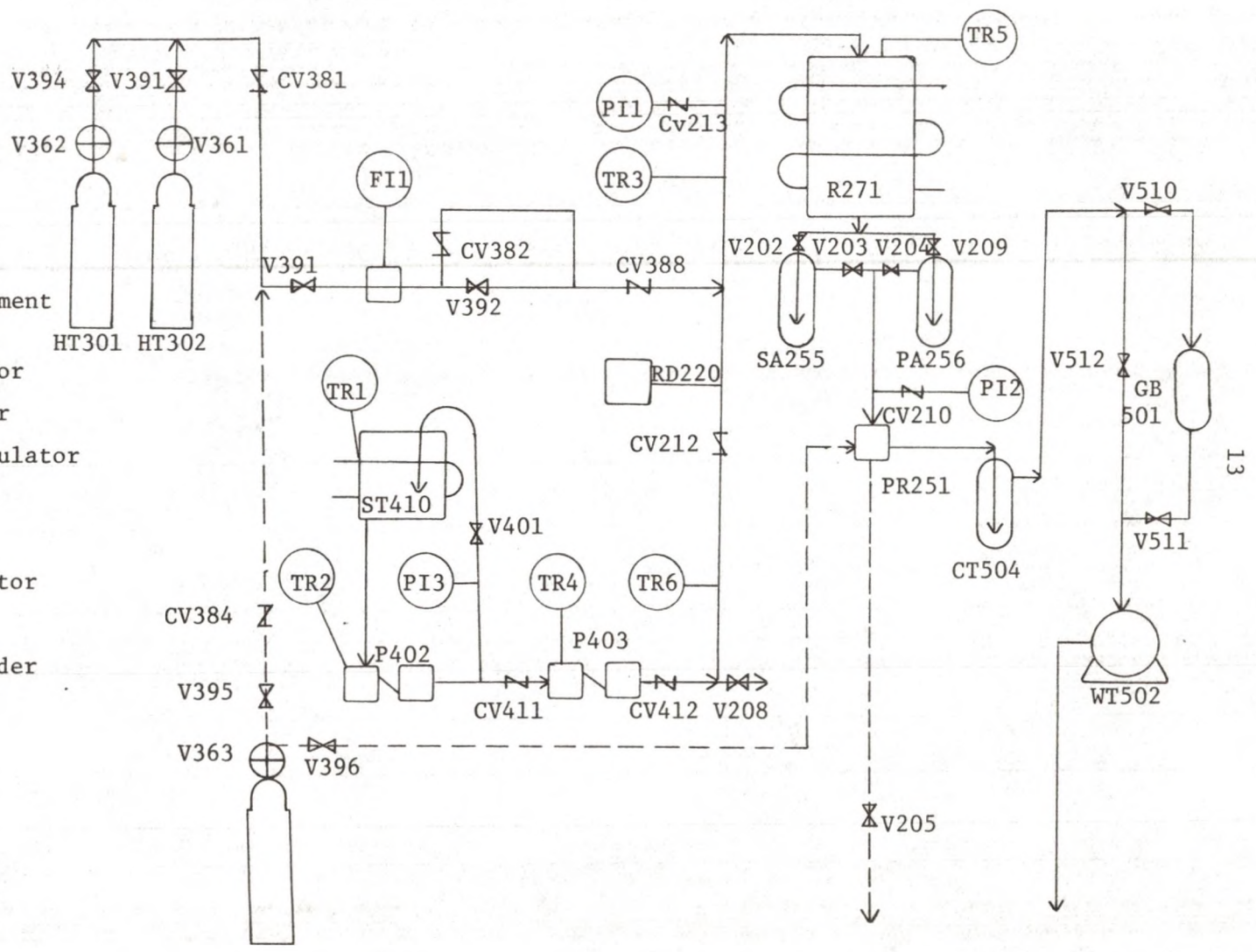


Fig. 1. Micro hydrocracking unit flow sheet.

GC analysis of this solution indicated a composition of 90.8% by weight tetralin, and 9.3% by weight naphthalene.

The high pressure slurry pump, P-403, was calibrated using tetralin. Tetralin was pumped for one hour at varying flow rates. A calibration curve of percent stroke versus volumetric flow rate in ml/hr was prepared and is shown in appendix 2, figure 5.

The flow meter, FI-101 was calibrated using hydrogen at a pressure of 1000 psi. The outlet hydrogen volume was measured, using a wet test meter, for varied flows. A calibration curve of percent flow versus volume rate of flow in ml of hydrogen per minute was determined and is presented in appendix 2, figure 6.

The distillation apparatus, DA-703, was calibrated using a slurry that was 49.2% by weight SRL and 50.8% by weight tetralin. Distillation indicated a slurry with a composition of 50.5% by weight SRL and 49.5% by weight tetralin.

Slurry preparation consisted of mixing equal weights of tetralin and SRL. The slurry was then heated to 65° C and hot-filtered on filtration apparatus FA-409 to remove insoluble particles. The resultant slurry was stored in one pint metal cans. Since the slurry was preheated prior to every run, small containers were needed to reduce repolymerization that results from repeated heating. One pint of slurry supplied approximately three runs. The SRL content of the feed slurry was determined using distillation apparatus DA-703. Feed slurry composition was reported as weight fraction SRL with the remainder assumed to be tetralin.

Several catalysts cited in the literature were available from commercial sources. A representative sample of these commercially available catalysts, as well as commercially available preformed support materials, are listed in table 2. These catalysts were used as a selection test. The results of this test were the basis for selecting catalysts which were expected to increase the yield of aromatic liquid product. The noncommercially available catalysts, whose compositions are listed in table 3, were manufactured as part of this study.

General methods of catalyst preparation include impregnation, precipitation, co-mixing or compounding, thermal fusion, leaching and evaporation. Thermal fusion, precipitation, leaching and evaporation methods were either not applicable or needed extensive laboratory equipment and were eliminated as possible methods of synthesis. Impregnation and co-mixing or compounding required only simple laboratory equipment and were selected as the synthesis methods, where appropriate.

Impregnation is used to incorporate an active component on a preformed support. The procedure includes: 1) contacting the support with a solution of a compound or salt, which upon heating will decompose to give the desired component; 2) removing excess solution; 3) drying; and 4) activating the material. Nondecomposable salts have been used in some cases, with the addition of a precipitation step used to deposit the active component on the support. Two types of impregnation are dipping or soaking and spraying. For the dipping method, the controllable variables are soak time and temperature and solution pH. After the support is soaked, it is drained, the anions (Cl^- , $\text{SO}_4^{=}$, etc.) are removed, and then it is dried. Drying laboratory catalysts is usually a simple procedure

TABLE 2

COMMERCIALY AVAILABLE CATALYSTS AND SUPPORTS

Name, supplier, and major active component for commercially available catalysts used as a screening test to determine good aromatization catalysts.

Name	Supplier	Major Active Component
Ni-4303	Harshaw	Nickel and tungsten
Ni-1601	Harshaw	Nickel, copper and Iron
Zn-0602	Harshaw	Zinc and chromium
V-0301	Harshaw	Vanadium
UOP-6-S	Universal oil products	Cobalt, nickel molybdenum
Al-0104	Harshaw	Alumina support material
Al-1404	Harshaw	Alumina support material
Mg-0601	Harshaw	Magnesia support material
G-32-H	Girdler	Charcoal support material

TABLE 3

CATALYSTS MANUFACTURED AS PART OF THIS STUDY

Name and weight percent metal oxide on catalyst surface for noncommercially available catalysts manufactured as part of this study.

Catalyst name	Weight percent metal oxide on catalyst surface.
1). NiO on Al-0104	0.3% MgO, 0.7% Fe ₂ O ₃ , 2.0% NiO
2). Fe ₂ O ₃ on Al-0104	0.5% NiO, 0.5% Fe ₂ O ₃
3). NiO on Mg-0601	14.3% NiO
4). Fe ₂ O ₃ on Mg-0601	47.6% Fe ₂ O ₃
5). NiO on G-32-H	2.03% NiO
6). Fe ₂ O ₃ on G-32-H	1.09% Fe ₂ O ₃
7). Cr ₂ O ₃ crush	10.0% Cr ₂ O ₃
8). NiO crush	0.00% NiO, 100% MgO
9). Fe ₂ O ₃ crush	14.3% Fe ₂ O ₃
10). CuO crush	10.0% CuO

carried out in air, or in drying ovens at about 110° C. The ability to control the final metal concentration is less certain in the dipping technique than it is in the drying technique. The significant difference between spraying and dipping is that in spraying the solution absorptivity of the support must be predetermined; then the support is sprayed with a fixed amount of metal solution.

Catalysts 1 through 6 in table 3 were manufactured using the dipping-impregnation method. The basic support, either Al-0104,

Mg-0601, or G-32-H, was dipped in a basic metal oxide (BMO) solution.

(22) The BMO solution was prepared by dissolving one gram of NiO or Fe_2O_3 in 50 ml of concentrated hydrochloric acid, and then diluting with 100 ml of distilled-deionized water. The BMO solution was absorbed into 100 grams of the basic metal support. The saturated support was then dried at 110°C . The dry BMO support was washed first with a 1 N NaOH solution and then with distilled water to remove the chloride. The resulting catalyst was dried and stored in a suitable container.

A co-mixed or compounded catalyst is one in which all the ingredients are mechanically mixed before the catalyst is formed into a pellet. Laboratory catalysts frequently are tested in the form of granules or pellets ranging in size from 8- to 20-mesh. Catalyst shape is determined mostly by the nature of the catalyst material. When forming catalyst supports, considerable attention must be given to pore size and structure. Large pores, those with average diameters in the range of 2000 A, can be introduced into catalysts by adding organic material that is later burned out. Five percent of starch or intensively shredded alphacellulose can be milled into a finely divided support, with or without the active catalyst. The mixture is then pelletized and dried. The resulting catalysts are oxidized to produce a catalyst with a bimodal pore size distribution.

Catalysts 7 through 10 of table 3 were manufactured using the co-mixing or compounding method. Five grams of starch were dissolved in 300 ml of boiling water. Five grams of BMO, either CuO, Cr_2O_3 , Fe_2O_3 , or NiO, were thoroughly mixed with forty-five grams of MgO. The

starch solution and BMO-MgO mixture were mixed together, and the resultant paste was allowed to dry to a powder. The dry powder was pelletized using a 1 1/4 -inch pellet press, with pelletizing pressures of 10,000 to 12,000 psi. The pellets were then crushed and screened to the Tyler equivalent mesh range 8 to 14. The catalysts were then dried and stored in individual containers.

In an effort to determine if catalyst preparation affected catalyst makeup, the surface characteristics of the catalysts manufactured as part of this study were compared with those of commercially available catalysts. One type of physical evaluation and three types of chemical evaluation were performed.

The physical evaluation consisted of observing the catalyst surface using a scanning electron microscope (SEM). Representative samples of each type of catalyst support material were photographed over a wide range of magnifications (10X to 10,000X) using the SEM.

One method of chemical evaluation was SEM analysis of the catalyst surface. The SEM was used to measure surface concentrations of metal oxides on the catalysts. Concentrations were reported as percent by weight of oxide. The two remaining methods of chemical analysis were the measurement of acidic or basic strength and the determination of acidic or basic content; both methods were suggested by Tanabe (23, 24).

To determine acidic or basic strength, a small sample of catalyst was placed in benzene. One of four indicator solutions was added to the benzene-catalyst solution, and the resultant color was recorded. This

process continued until the pK was bracketed. Thymol blue, bromothymol blue, methyl red, and bromo cresol blue indicators were used.

To determine basic content, 0.30 grams of basic catalyst, those with $pK > 7.0$, were placed in twenty ml of .1000 N hydrochloric acid. The reaction was allowed to proceed for five minutes at which time the mixture was vacuum filtered using filtration apparatus FA-277. The filtrate was titrated with .1004 N sodium hydroxide to a phenolphthalein endpoint.

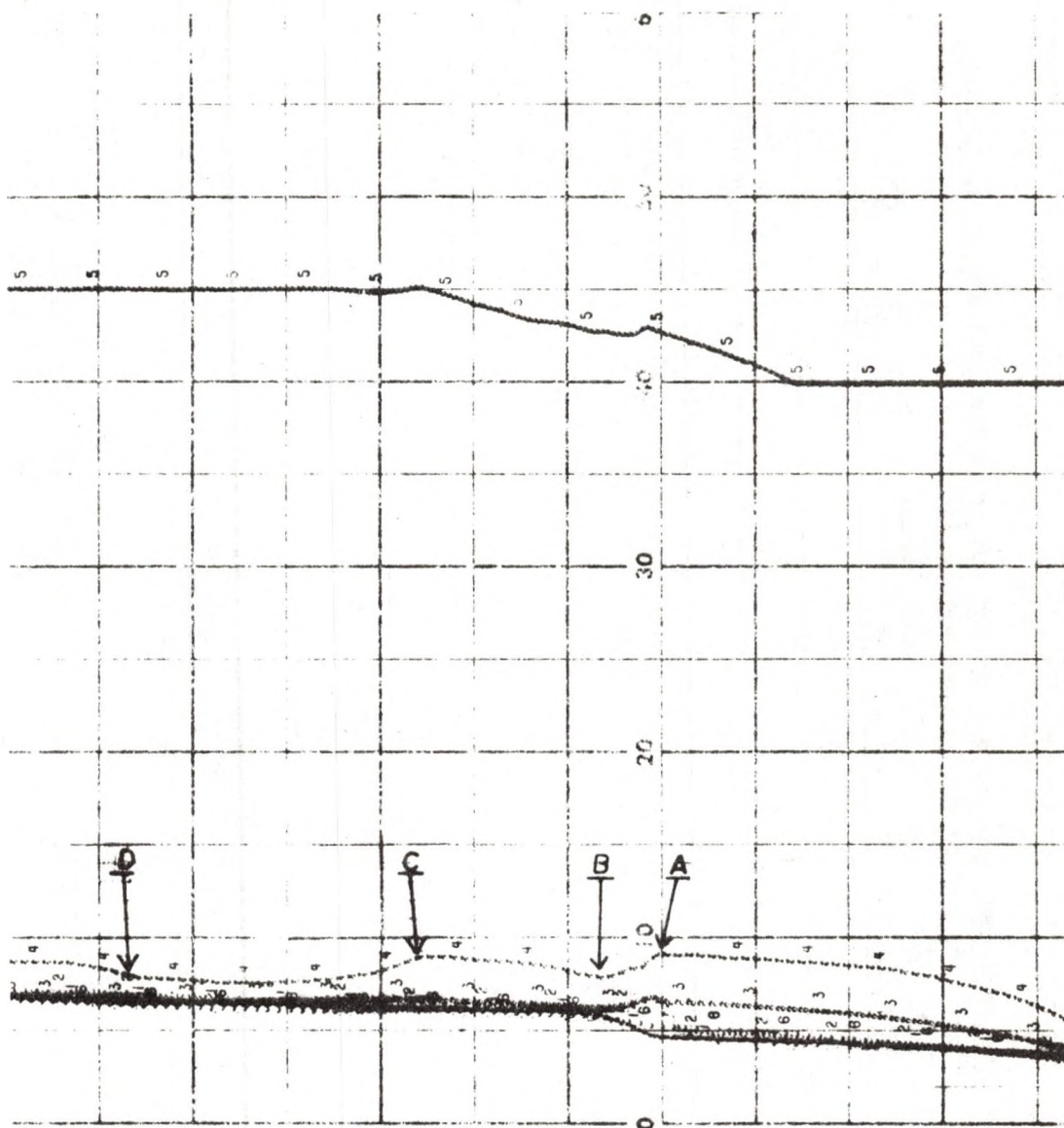
To determine acidic content, 0.30 grams of acidic catalyst, those with a $pK < 7.0$, were placed in twenty ml of .1004 N sodium hydroxide. The reaction was allowed to proceed for five minutes at which time the mixture was vacuum filtered. The filtrate was titrated with .1000 N hydrochloric acid to a pH less than 7.0. the resulting mixture was then titrated to a phenolphthalein end point with .1004 N sodium hydroxide.

Once prepared, 24.3 grams of catalyst was placed in reactor R-201 on top of 7.0 grams of inert packing P-272a or P-272b. The remaining reactor volume was filled with approximately 60 grams of packing. This sequence of packing allowed the slurry to be heated as it flowed through the packing so that it was at reaction temperature when it contacted the catalyst.

After the reactor was packed, the entire MHU was sealed and pressurized with nitrogen to 1000 psig. Any detectable leaks were stopped. The sealed system was left under pressure for 10 to 12 hours. If the pressure loss did not exceed 50 psi during this period, the run was started.

There were five periods per run; they were prestartup, catalyst activation, startup, run, and shutdown periods. During the prestart period the reactor heater was turned on, exhaust systems were started, and the temperature recorder was started. During the catalyst activation period the low pressure hydrogen flow was established, and a hydrogen flow check was made. The reactor was heated to catalyst activation temperature, and the slurry-line heaters were turned on. The startup period was completed when the MHU had achieved steady state. A reaction temperature of 450° C was achieved and maintained throughout the two hour startup and two hour run periods. The system was pressurized to 1000 psi with hydrogen and a flow of 700 ml per minute (STP) was maintained.

Because of the nature of the feed slurry, the high pressure slurry pump at times functioned improperly. Pump failure ranged from erratic output to total failure. After pump failure ruined many early runs (HC 4 to HC 21) some form of fluid flow indicator was sought. Figure 2 is the initial portion of the chart recorder used to record reaction temperatures. Coinciding with the start-up of the high pressure slurry pump, a sharp drop occurred in the pump head temperature. Point A on figure 2 represents this drop. The temperature of the pump head then slowly increased to an operating temperature which was always less than the original temperature (i.e. the temperature prior to point A) if the pump was functioning properly. The cause of the temperature deflection seen at the pump head was the result of the slurry flowing through the pump head. The original pump head temperature was set to be higher than the temperature of the slurry reservoir. The initial



- A.) High pressure slurry pump was started at 125% of stroke length setting
- B.) Flow reduced to 70% of stroke length.
- C.) Flow increased to 125% of stroke length as to check on pump function
- D.) Flow decreased to 70% of stroke length

Fig. 2. Micro hydrocracking unit start up temperature profile temperature chart from run HC-28. 10°C per unit in vertical direction, and 5 min. per unit horizontal direction increasing from right to left.

drop in pump head temperature is a result of the relatively cooler slurry flowing through the hotter pump head. As the run proceeded, the slurry and pump head approach an equilibrium temperature. With the use of the pump head temperature reading, pump operation was assessed and appropriate action taken.

If the high pressure pump was operating correctly, a cold trap for the approaching run period was prepared. The run period began after two hours of successful startup period. At the start of the run period, the product accumulator and cold trap were put on line and the following were recorded: the reactor temperature, percent hydrogen flow, wet test meter reading, inlet and outlet pressures, and time. During the run, pressure readings were recorded every 30 minutes. Time, percent flow, temperature, and wet test meter readings were recorded every 15 minutes. Temperature, pressure and percent flow were maintained at their established values. Two gas samples were taken during a run. One, a half hour after the start of a run, and the second one, a half hour before the end of a run.

The shut down period marked the end of a run. The product accumulator and cold trap were isolated and the reactor heat supply shut off. A nitrogen purge, at 1000 psi was established. The liquid product was removed, weighed, and placed in storage containers, and the weight recorded. Excess slurry was removed from the slurry tank. Tetralin was added to the slurry tank and pumped through the system for one hour. After one hour of cleaning pumps P-402 and P-403 and the slurry line heat tapes were shut off and the system depressurized. Tetralin was then pumped through valve V-208 immediately down stream

from pump P-403. When the exit tetralin appeared clean, the pumps and remaining heating tapes were shut off. Further clean up consisted of partial MHU disassembly followed by thorough cleaning with solvent. Air was passed through the system to evaporate and remove any remaining solvent.

Analysis of the exit gas stream was performed using gas chromatography. The gas chromatograph was standardized using two samples of a calibration gas. Gas samples were analyzed twice as a check for reproduceability. Analysis was reported in mole percent of individual component. Each analysis was normalized to one hundred percent.

Analysis of the liquid product entailed elemental analysis of the total liquid product sample, a simulated distillation using a gas chromatograph, and component identification of distillable products. Evaluation of elemental content consisted of nitrogen, sulfur, and carbon-hydrogen analysis performed following ASTM procedures (25). The liquid product was distilled in distillation apparatus DA-703 to separate the unreacted SRL from the distillable liquid product (DLP). An ASTM simulated distillation was performed on the DLP using gas chromatograph GC-701. The results were presented as the weight percent of DLP in a particular temperature range.

The DLP consisted of the clear liquid resulting from a distillation of the total liquid product. This distillation was run using distillation apparatus DA-703, at a temperature of approximately 150° C, and a pressure of 2 mm mercury (absolute). The resulting vapor was condensed using a dry ice-iso-propyl alcohol cold trap. The DLP was stored in 2 ml sealed glass ampules. Gas chromatography using gas

chromatograph GC-701, and gas chromatography-mass spectrophotometry (GCMS) using GC-707 were used for liquid component identification with the results reported as weight percent.

CHAPTER IV

RESULTS AND DISCUSSION

A total of fifty-eight hydrocracking runs were made. Of these, twenty-nine were at conditions established as standard operating conditions. Standard operating conditions were: reaction temperature of 450° C , reaction pressure of 1000 psi, and a liquid hourly space velocity (LHSV) of approximately one gram of slurry per gram of catalyst per hour.

The twenty-nine successful runs consisted of eighteen runs with the SRL-tetralin slurry and eleven blank runs using tetralin as the feed. Conditions for the eighteen runs are presented in Table 4.

Reproducibility of the operating conditions of the MHU was based on two runs with similar but non-standard experimental conditions. The catalyst was a magnesium oxide support material treated with iron oxide. This catalyst was not prepared in a manner similar to any other catalyst and resulted in a surface iron oxide concentration less than 0.1% by weight. The run duration, product yield, catalyst makeup, and liquid product analysis were in close agreement and, as such, is sufficient to support the assumption that data from individual runs may be reproduced if all conditions are held constant. A summary of the two runs is presented in table 5.

Material Balance and Yields

During the MHU shakedown period, the high pressure slurry

TABLE 4
 RUN CONDITIONS FOR THE SRL-TETRALIN SLURRY RUNS

Catalyst	H ₂ Flow (ml STP/min)	Pressure (psi)	Temperature (C°)	LHSV (hr ⁻¹)	Calculated Initial charge of slurry (grams)
1) Fe ₂ O ₃ on G-32-H	684.7	1005	450	1.2	61.4
2) NiO on G-32-H	729.7	1012	450	1.2	60.5
3) G-32-H	708.0	1025	450	1.3	65.3
4) Fe ₂ O ₃ on Al-0104	686.8	1005	450	1.3	65.2
5) NiO on Al-0104	693.6	1041	450	1.2	61.7
6) Al-0104	730.5	1034	450	1.4	67.2
7) Al-1404	695.5	1023	450		45.4
8) Mg-0601	708.4	1023	450	1.1	52.7
9) Fe ₂ O ₃ on Mg-0601	698.1	1000	450	1.2	61.0
10) NiO on Mg-0601	711.5	1025	450	1.3	64.5

TABLE 4--Continued

Catalyst	H ₂ Flow (ml STP/min)	Pressure (psi)	Temperature (C°)	LHSV (hr ⁻¹)	Calculated Initial charge of slurry (grams)
11) NiO on MgO crush	692.4	1025	450	1.6	79.3
12) Cr ₂ O ₃ on MgO crush	682.5	992	450	1.4	66.4
13) CuO on MgO crush	787.4	1005	450	1.1	55.6
14) Fe ₂ O ₃ on MgO crush	689.2	1025	450	1.2	59.6
15) Ni-4303	709.8	1033	450	1.3	63.5
16) Ni-1601	710.7	1020	450	1.2	56.5
17) Zn-0602	696.8	1043	450	1.4	66.9
18) UOP-6-5	707.5	1024	450	1.3	62.8

TABLE 5
ANALYSIS OF DISTILLABLE PRODUCT FOR TWO RUNS DISTILLED
AT 150° C. AND 2 MM HG

Time (hr)	Product (g)	Liquid Flow Rate (%)	Tetralin (Wt %)	Naphthalene (Wt %)	Light Oil (Wt %)
1.2	32.8	70	98.25	0.00	1.75
1.0	29.5	70	98.82	0.00	1.18

pump, P-403, successfully metered tetralin at a predictable rate. This is evident from the calibration curve in appendix 2, figure 5. The curve was also used to determine the amount of slurry charged during a run.

As the experimental portion of this study proceeded, problems with reproducible liquid yields became evident. As a check on the degree of success with which the high pressure slurry pump metered slurry, three runs were made using feed slurry and a pump setting of 70% stroke length, no catalyst, and other parameters at standard conditions. These runs yielded liquid products of 58.2, 59.9, and 64.2 grams, respectively. As indicated by these liquid yields, with all conditions held constant, a difference of at least 9% may be expected between any two runs. A check on the pump calibration curve in appendix 2 figure 5 yielded a flow rate of 50 ml per hour for a 70% stroke length setting. An estimated product yield resulting from this was 50 ml/hr times two hrs or 100 ml; quite different than what actually occurred. When a material balance was attempted, it was obvious that the error involved with the assumption that the pump was a constant metering de-

vice was too large to be acceptable. Due to the high variability of the metering pump the material balance was based on the assumption that the total material out equals the total material charged; that is, there was no accumulation or loss. The total amount of material leaving the process consists of the contents of the cold trap of the product accumulator, and the exit gas stream. Additional data needed to calculate a complete material balance included the results of the distillations of the feed slurry and total liquid product; the results of the ASTM simulated distillation of the DLP (26); and the GC analysis of the exit gas stream. These results are presented in Tables 6 and 7. The feed slurry composition ranged from 0.450 to 0.517 weight fraction SRL. Distillation of the total liquid product resulted in a composition ranging from 0.220 to 0.452 weight fraction residue. For this study it was assumed that the residue of this distillation was unreacted SRL and the distillate was the DLP. The results of the ASTM simulated distillation performed on the DLP could be separated into three fractions according to boiling point ranges. The temperature ranges for the three fractions were 22° C to 150° C ; 150° C to 210° C ; and 210° C to 250° C. The first fraction, defined as light oils, was suspected to contain the desired BTX compounds. The second cut was assigned to the solvent, and the third cut to naphthalene.

The flow rate of the exit gas stream ranged from 675 to 710.5 ml (STP) per minute, and its composition was in excess of 97 mole percent hydrogen in all cases. Three measurable hydrocarbon gases were present in most runs, those being methane, ethane, and propane. As expected, methane was highest in concentration while the propane concentration

TABLE 6

GAS PRODUCT FLOW RATE, MASS, AND COMPOSITION
FOR SUCCESSFUL RUNS

Catalyst	H ₂ Flow (ml STP/min)	Gaseous Product (grams)	Mole Fractions			
			H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈
Fe ₂ O ₃ on G-32-H	685.0	0.06	.9922	.0058	.0019	.0003
G-32-H	710.5	0.64	.9814	.0078	.0016	.0002
Fe ₂ O ₃ on Al-0104	693.1	0.54	.9892	.0065	.0013	.0003
Al-0104	704.4	0.78	.9898	.0095	.0018	.0005
Mg-0601	702.5	0.49	.9922	.0072	.0008	.0000
Fe ₂ O ₃ on Mg-0601	706.6	0.27	.9951	.0028	.0010	.0000
NiO on Mg-0601	685.2	0.36	.9894	.0041	.0012	.0001
NiO on MgO crush	681.2	0.22	.9959	.0021	.0010	.0000
Cr ₂ O ₃ on MgO crush	654.7	0.41	.9894	.0050	.0013	.0001
Fe ₂ O ₃ on Mg crush	675.6	0.94	.9800	.0119	.0020	.0010
Ni-1601	689.0	0.64	.9933	.0069	.0019	.0005
NiO on G-32-H	692.6	1.13	.9847	.0079	.0069	.0005
UOP-6-5	691.2	0.83	.9722	.0070	.0021	.0016
Al-1404	603.3	0.59	.9796	.0073	.0017	.0006

TABLE 6--Continued

Catalyst	H ₂ Flow (ml STP/min)	Gaseous Product (grams)	Mole Fractions			
			H ₂	CH ₄	C ₂ H ₆	C ₃ H ₈
Ni-4303	663.4	0.70	.9868	.0086	.0019	.0005
CuO on Mg crush	677.7	0.54	.9874	.0065	.0019	.0006
Zn-0602	695.3	0.64	.9839	.0038	.0021	.0014
NiO on Al-0104	657.3	0.53	.9909	.0066	.0015	.0003

was lowest. The total weight of gaseous product, calculated from the flow rate and gas composition ranged from 0.06 to 1.13 grams.

Once a complete material balance was achieved, conversions of gaseous, liquid, and solid feed materials, and yields of gaseous, and liquid products were calculated. A summary of material balance calculations is presented in table 8.

Conversion of hydrogen, the gas feed material, is the difference between the hydrogen in the feed stream and the hydrogen in the exit stream, divided by the total hydrogen feed. Hydrogen consumption ranged from zero to 0.150 grams hydrogen consumed per gram hydrogen fed.

Conversion of tetralin, the liquid solvent feed material, was the difference between the tetralin in the feed and the tetralin in the liquid product divided by the tetralin in the feed. The solvent conversion ranged from -0.273 to 0.295 grams solvent converted per gram

TABLE 7

LIQUID PRODUCT MASS, SRL CONTENT, AND COMPOSITION FOR SUCCESSFUL RUNS

Catalyst	Liquid Product (grams)	Weight Fraction							SRL in Feed
		SRL in Liq. Product	Tetralin Prod. Blank	Napthalene Prod. Blank	Light Oil Prod.	Oil Blank			
Fe ₂ O ₃ on G-32-H	60.5	.353	.790	1*	.178	0	.032	0	0.450
G-32-H	63.8	.390	.787	1*	.147	0	.067	0	0.517
Fe ₂ O ₃ on Al-0104	64.4	.286	.865	1*	.115	0	.021	0	0.450
Al-0104	65.5	.452	.847	1*	.142	0	.011	0	0.517
Mg-0601	52.1	.436	.954	1*	0	0	.046	0	0.509
Fe ₂ O ₃ on Mg-0601	59.0	.343	.803	.945	.074	0	.123	.0555	0.450
NiO on Mg-0601	63.7	.427	.744	.967	.085	.033	.171	0	0.472
NiO on MgO crush	79.0	.308	.873	.792	.075	.273	.052	.0074	0.450
Cr ₂ O ₃ on MgO crush	65.0	.295	.796	.880	.112	.095	.092	.0248	0.480

TABLE 7--Continued

Catalyst	Liquid Product (grams)	Weight Fraction							SRL in Feed
		SRL in Liq. Product	Tetralin Prod. Blank	Napthalene Prod. Blank	Light Oil Prod. Blank				
Fe ₂ O ₃ on MgO crush	58.0	.222	.840	1*	.095	0	.066	0	0.450
Ni-1601	55.7	.279	.877	1*	.112	0	.011	0	0.509
NiO on G-32-H	58.6	.422	.901	.753	0	.229	.099	.019	0.493
UOP-6-5	60.0	.409	.622	.625	.282	.266	.089	.108	0.487
Al-1404	44.0	.390	.721	.995	.095	0	.184	.005	0.517
Ni-4303	62.2	.397	.811	.812	.103	.131	.086	.057	0.487
CuO on MgO crush	54.5	.264	.805	.943	.095	.057	.100	0	0.450
Zn-0602	65.0	.378	.779	.779	.067	.271	.154	0	0.487
NiO on Al-0104	59.8	.401	.730	.793	.126	.153	.145	.014	0.472

*No blanks run for these catalyst.

TABLE 8

RESULTS OF CALCULATED MATERIAL BALANCE

Catalyst	Conversion						
	SRL (gm lost) (gm fed)	Light Oil (Uncorr) (Corr) (gm light oil) (gm SRL fed)		Solvent (gm lost) (gm fed)	Naphthalene (Uncorr) (corr) (gm Naphthalene) (gm SRL fed)		H ₂ (gm H ₂ lost) (gm H ₂ fed)
Fe ₂ O ₃ on G-32-H	.227	.045	.045	.071	.252	.252	.007
G-32-H	.264	.077	.077	.016	.169	.169	.015
Fe ₂ O ₃ on Al-0104	.373	.033	.033	-.114	.180	.180	.002
Al-0104	.147	.012	.012	.051	.146	.146	.046
Mg-0601	.154	.051	.051	-.086	.000	.000	.016
Fe ₂ O ₃ on MgO crush	.520	.111	.111	-.169	.159	.159	.039
Ni-1601	.460	.015	.015	-.273	.156	.156	.037
NiO on G-32-H	.171	.112	.093	-.008	.000	-.235	.065
NiO on MgO crush	.319	.080	.071	-.096	.115	-.217	.020

TABLE 8--Continued

Catalyst	Conversion						
	SRL (gm lost) (gm fed)	Light Oil (Uncorr)(Corr) (gm light oil) (gm SRL fed)		Solvent (gm lost) (gm fed)	Naphthalene (Uncorr)(corr) (gm Naphthalene) (gm SRL fed)		H ₂ (gm H ₂ lost) (gm H ₂ fed)
Ni-4303	.201	.105	.099	.058	.125	-.013	.078
UOP-6-5	.197	.103	-.006	.295	.327	.061	.050
Cr ₂ O ₃ on MgO ³ crush	.394	.134	.107	-.073	.162	.059	.051
Al-1404	.270	.210	.206	.100	.109	.109	.150
NiO on Al-0104	.177	.178	.163	.179	.155	-.061	.061
Fe ₂ O ₃ on Mg-0601	.264	.174	.106	.045	.104	.104	-.007
CuO on MgO crush	.424	.160	.160	-.066	.153	.083	.150
Zn-0602	.245	.192	.192	-.081	.083	-.203	.017
NiO on Mg-0601	.107	.205	.205	.216	.101	.064	.027

solvent fed, with negative conversion indicating more tetralin in the liquid product than was present in the feed.

Conversion of SRL was defined as the grams of SRL initially charged minus the grams of residue from the distillation of the total liquid product, divided by the total grams of SRL charged. Conversions of SRL were from 0.100 to 0.515 grams SRL converted per gram of SRL fed.

Gas yield is shown by the mass ratio of hydrocarbon product gas to the feed slurry. Gas yields were in the range of 0.002 to 0.038 grams of gas per gram of SRL fed. This yield is quite low when compared to the gas yield resulting from the solvent refining of lignite; Severson, Souby and Harris (27) reported gas yields of 33.2 to 37.1 percent by weight of MAF lignite. For this gas yield, Severson, Souby and Harris (28) reported a liquid yield of 65% by weight (MAF lignite). This compares to a maximum of 0.2142 grams light oil per gram of SRL feed, reported in this study. This indicates that the relatively low production of gas may be because less reaction was taking place.

Catalysts which produced high gas yields for this study were Fe_2O_3 on MgO crush and NiO on G-32-H. The respective hydrocarbon gas product yields were 0.017 and 0.020 grams of gas per gram of slurry fed. Of the five support materials, alumina supports produced the largest gas yields. The gas yields for the support materials Al-1404, Al-0104, MgO crush, G-32-H, and Mg-0601 were 0.0104, 0.013, 0.013, 0.012, 0.010 and 0.010 grams per gram of slurry fed, respectively.

DLP Component Identification

Naphthalene and light oil yields were calculated using the mass ratios of the respective distillation cuts to the feed SRL. The major

desirable products for this study were aromatic chemicals. To determine if any BTX-type compounds were actually present in any of the distillation products, GCMS was used to identify individual components of the DLP. The DLPs were similar in nature, therefore only four representative samples were run. Table 9 is a summary of these results. In the DLP, there were ten peaks that were present in excess of 1%, in all four samples. These peaks had mass numbers of 91, 92, 105, 117, 118, 129, 130, 131, 132, and 133 respectively.


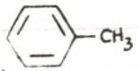
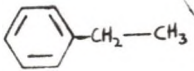
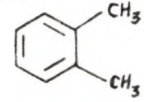
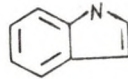
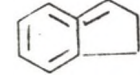
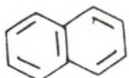
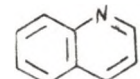
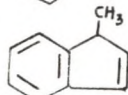
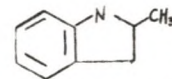
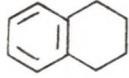
The major hydrogenation product from tetralin, mass 132, appeared to be naphthalene, mass 128. Tetralin has its parent or molecular ion peak and base peak, m , at 132, and a possible $m+1$ isotope peak at 133. The seven major peaks remaining could have been assigned to a variety of compounds. To limit the selection of possible products, a closer look at a model structure of coal was undertaken.

One proposed model of the chemical structure of coal is presented in figure 3 (29). As can be seen in figure 3, there are a large number of five- or six-membered ring compounds, both aromatic and naphthenic. Many contain nitrogen or oxygen as part of the ring structure. The possible depolymerization products from a substance such as this is still quite varied. With the aromatization conditions of this study, however, the products would tend to be aromatic or cyclic in nature as opposed to non-cyclic.

Because there was an interest in determining if any BTX compounds were present, possible peaks resulting from the presence of these compounds were examined. The BTX parent ion peaks should have appeared at mass numbers 78, 92, and 106, respectively. As seen in table 9, benzene,

TABLE 9

CHEMICAL AND MASS CHARACTERIZATION OF LIQUID PRODUCTS FOR 4 SUCCESSFUL RUNS

Mass Number	Suggested Compound or Fragment	Boiling Point C° 760 mm/Hg	Structure		Ni-1601	Content (%)		
			(30)	(31)		CuO Crush	Fe ₂ O ₃ Crush	Fe ₂ O ₃ on Mg-0601
78	Benzene	80.1			0.52	0.24	0.80	1.14
91	Toluene Fragment				8.87	9.43	9.38	8.78
92	Toluene	110.6			5.82	13.48	13.28	11.24
105	Ethyl Benzene	136.2			6.02	3.42	5.99	5.73
106	Xylene	139.1			0.68	0.24	0.47	0.51
117	Indole	254.0			5.16	3.74	5.10	4.88
118	Indane	178			2.27	1.02	1.77	1.78
128	Naphthalene	218			6.23	10.89	9.50	9.14
129	Quinoline	238.1			7.35	4.36	4.50	4.41
130	Methyl Indene	198.5			5.35	6.00	8.38	8.04
131	Methyl Indole	272			4.30	6.00	8.38	8.04
132	Tetralin	207.6			21.59	19.12	13.19	20.34
133	Tetralin Fragment				16.22	13.49	13.96	11.81

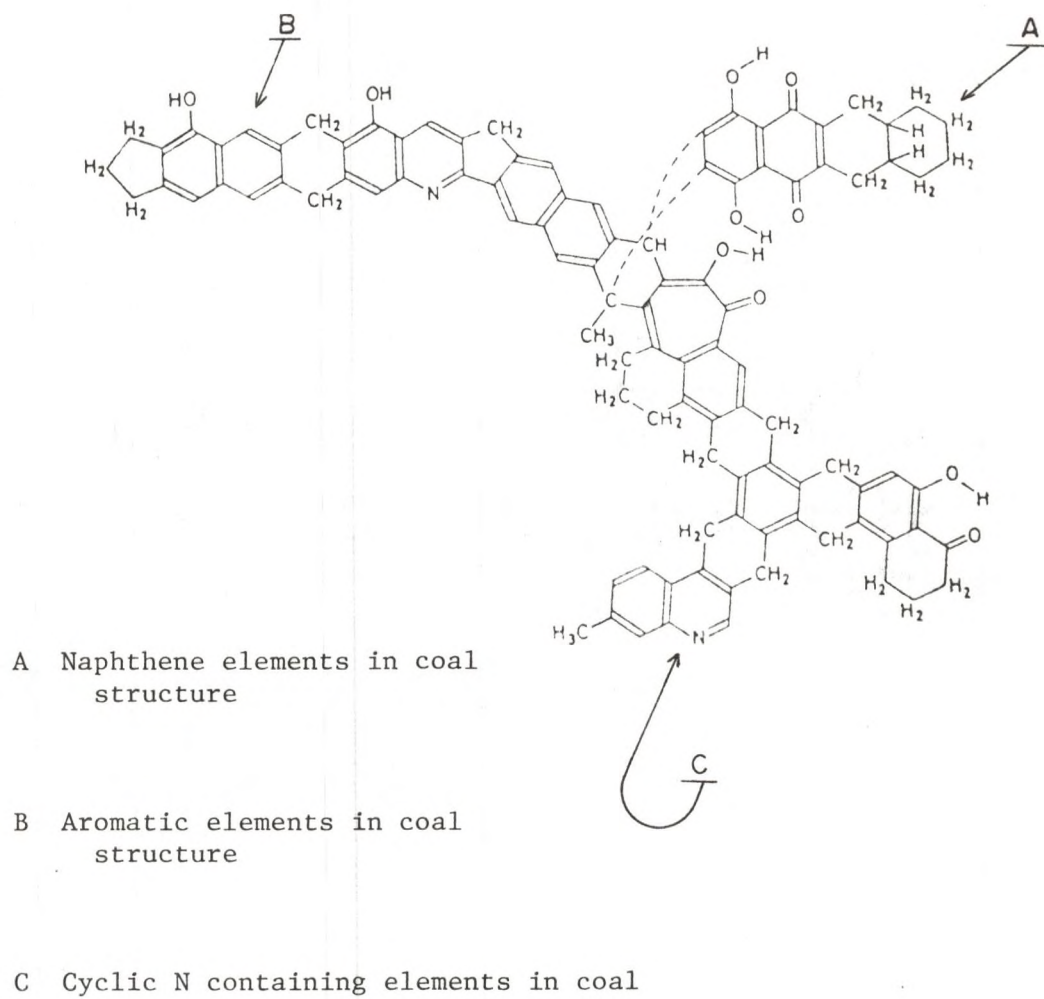
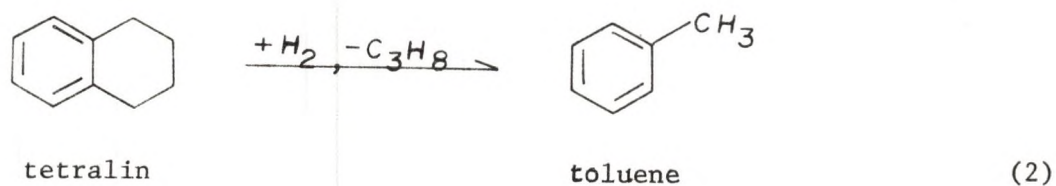
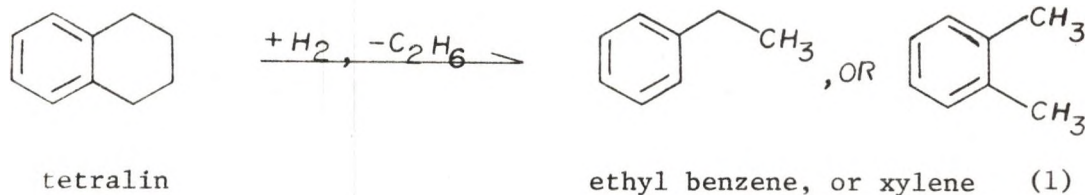
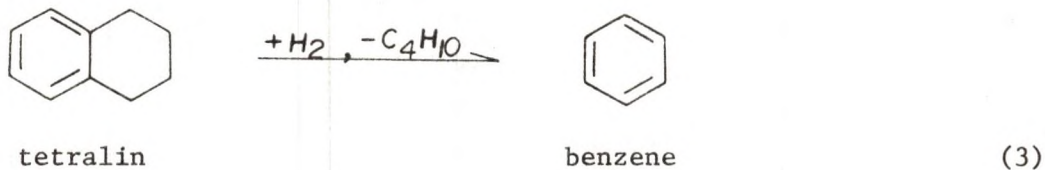


Fig. 3. P. H. Given's (31) proposed model for the chemical structure of coal.

toluene, and xylene were present in measurable quantities. No compound could be readily assigned to the remaining major peak, that of mass 91. However, according to Silverstein, Bassler, and Morril (32), toluene has a parent ion peak at mass 92, and an m-1 or base peak at mass number 91. All but one of the remaining peaks were assigned to aromatic compounds, assuming the peaks represented parent ion peaks. They were ethylbenzene, indole, indane, quinoline, and methyl indene at mass numbers 105, 117, 118, 129, and 130, respectively. SRL was considered to be the parent material for compounds containing nitrogen, or of a structure not easily derived from tetralin or its main derivative, naphthalene.

It may be possible to produce benzene, ethyl benzene, toluene, and xylene by reaction similar to those presented in reaction 1, 2, and 3 (33). For the reactions in equations in 1 through 3 tetralin was chosen as the reactant. There are many tetralin-like substances containing aromatic and naphthene type elements present in coal and coal-derived substances. The reactions of hydrogen with aromatic and naphthene-type elements present in the SRL feed material are also to be represented by equations 1 through 3.





Analysis of the product gas, shown in table 6, indicated measurable quantities of methane, CH_4 , ethane, C_2H_6 , and propane, C_3H_8 . Possible gas phase products of equations 1 and 2 are ethane and propane. The gas product analysis did not contain butane, a possible gas phase product of equation 3. This accounts for the possible appearance of toluene, ethyl benzene and xylene as reaction products, and may account for the relatively small amounts of benzene in the light oil. The small amount of the liquid product of equation 1, o-xylene, can not be explained by the data which resulted from this study. The relatively high amounts of toluene and ethyl benzene in the light oil, may be due to conditions which favor the kinetics of reactions 1 and 2.

Light Oil Yield

As indicated by GCMS analysis, the DLP does contain toluene. In a distillation, toluene would be in the cut boiling from 100° to 150° C, its boiling point at atmospheric pressure is 110.6° C (34). This cut was defined as light oils. The light oil cut of the DLP for the four representative samples analyzed by GCMS contained an average of 20.1 % by weight toluene. This value is higher than the coke oven light oil toluene content of 15 percent, listed in table 1. Toluene recovered from the coke oven light oils is a major source of toluene. Therefore, the light oils produced under the conditions of this study contain processable quantities of toluene. Because the light oils contain the desired aromatic compound, the yield of light oils was the basis for catalyst performance evaluation.

Catalysts one through seven of table 2 were rejected because of low yields of light oils; no blank runs were made for those catalysts. Blank runs, using tetralin as the feed material, were performed with the remaining eleven catalysts at reaction conditions. The results of these runs were used to determine the solvent contribution to the yield of light oils. The yield of light oils in which the contribution from the solvent has been accounted for is designated corrected yield of light oils in table 8.

Catalysts 12 through 18 of table 8 are the most promising catalysts based on the corrected yield of light oils. The range of corrected light oil yields was from 0.002 to 0.210 grams of light oil per gram of SRL fed. The commercially available alumina catalyst, Al-1404 was best, with NiO impregnated on MgO support material Mg-0601 second. Corrected light oils, as expected, are all less than their corresponding light oil yield. The difference ranged from 0 to 0.11. Corrected yields are, on the average, 0.023 less than the uncorrected yield of light oil. This indicates that, in most cases more light oil was produced from a SRL-tetralin slurry than from a pure tetralin feed, suggesting that the light oils originated from the SRL.

The basic metal oxides, Fe_2O_3 and NiO, impregnated upon and/or co-mixed with the three support materials Al-0104, G-32-H and Mg-0601 produced improved yields of liquid oil, relative to the support material alone, in all but one case.

The one case in which the addition of a basic metal oxide to a support material decreased the production of light oils was the addition of the metal oxide, Fe_2O_3 , on the support G-32-H. The combina-

tion of Fe_2O_3 on G-32-H decreased the light oil yield from .078 for G-32-H, to .045 for the Fe_2O_3 impregnated G-32-H support material. In all other cases, the addition of a basic metal oxide to one of the three support materials produced a higher light oil yield than the support material alone. From the data of table 10 it was apparent that NiO produced the largest increase in yield when added by impregnation to all three support materials. The support G-32-H appeared to be the poorest support material for the purposes of this study.

Analysis of several non-standard and standard runs showed that the yield of light oils, in general, decreased with increasing flow rate of reactants as measured by the liquid hourly space velocity (LHSV).

Standard and non-standard runs listed in table 11 compare five catalysts, all run at two LHSV values, and SRL to tetralin ratios of about 0.50 and 0.25. The distillable liquid product contained only trace amounts of light oils for high LHSV and low feed slurry SRL content. For runs with low LHSV and high feed slurry content, however, naphthalene and light oils composed at least 4% by weight of the DLP. Analysis of these runs indicates that the time the SRL is in contact with the catalyst was important in the yields of light oils and naphthalene. In all of these instances, when the catalyst was in contact with larger amounts of SRL for longer times, an increase in the production of light oils and naphthalene was noted.

Elemental Analysis

A summary of elemental analysis of the total liquid product is presented in table 12. Inherent inaccuracies in the test procedures

TABLE 10

YIELD OF LIGHT OILS FOR NON-COMMERCIALY AVAILABLE CATALYSTS

Active Component	Al	G-32-H	Mg-0601	MgO Crush
-	.0117	.0780	.0509	.0796
Ni	.1821	.1135	.2068	—
Fe	.0331	.0452	.1796	.1118
Cr ₂ O ₃	—*	—*	—*	.1349
CuO	—*	—*	—*	.1612

*Insoluble-unable to mount on support.

TABLE 11

EFFECTS OF LHSV ON DISTILLABLE LIQUID PRODUCT YIELDS

Catalyst	% SRL Fed	LHSV (g slurry) (g catalyst)	Analysis of Distillable Liquid Product		
			Wt % Tetralin	Wt % Naphthalene	Wt % Light Oils
Mg-0601	.260	5.4	100.00	0.00	0.00*
Mg-0601	.509	1.1	95.36	0.00	4.64
UOP-6-5	.260	3.0	100.00	0.00	0.00
UOP-6-5	.487	1.3	62.10	28.20	8.89
Ni-1601	.260	5.4	100.00	0.00	0.00
Ni-1601	.509	1.2	87.70	11.20	1.10
V-0301	.260	5.7	100.00	0.00	0.00
V-0301	.509	1.4	94.72	0.00	5.28
Zn-0602	.260	5.6	100.00	0.00	0.00
Zn-0602	.487	1.4	77.88	6.68	15.44

*Trace amounts present.

TABLE 12

ELEMENTAL ANALYSIS OF LIQUID PRODUCTS AND FEED
SLURRY FOR SUCCESSFUL RUNS

Catalyst	Wt % C	Wt % H	C/H	Wt % N	Wt % S	Slurry*
Fe ₂ O ₃ on G-32-H	88.59	7.26	12.20	0.27	0.24	1
NiO on G-32-H	86.62	7.45	11.63	0.33	0.25	1
G-32-H	87.43	7.57	11.55	0.26	0.36	1
Fe ₂ O ₃ on A1-0104	90.18	8.17	11.04	0.22	0.25	1
NiO on A1-0104	86.90	7.68	11.32	0.26	0.25	1
A1-0104	82.95	5.46	15.19	0.30	0.06	1
A1-1404	84.88	8.79	9.66	0.20	0.19	1
Mg-0601	88.89	7.79	11.41	0.39	0.26	3
Fe ₂ O ₃ on Mg-0601	87.78	8.23	10.67	0.34	0.26	1
NiO on Mg-0601	85.37	7.60	11.23	0.31	0.27	1
NiO on MgO Crush	83.67	7.81	10.71	0.27	0.35	1
Cr ₂ O ₃ on MgO Crush	90.45	8.13	11.13	0.26	0.24	1
CuO on MgO Crush	88.10	8.32	10.58	0.24	0.11	1
Fe ₂ O ₃ on MgO Crush	84.59	7.36	11.49	0.21	0.19	1

TABLE 12--Continued

Catalyst	Wt % C	Wt % H	C/H	Wt % N	Wt % S	Slurry*
NiO-4303	89.08	8.64	10.31	0.25	0.27	2
Ni-1601	90.72	9.50	9.55	0.29	0.14	3
Zn-0602	88.20	7.63	11.56	0.25	0.24	2
UOP-6-S	89.25	7.96	11.21	0.24	0.12	2

* SLURRY ELEMENTAL ANALYSIS

<u>Slurry</u>	<u>% C</u>	<u>% H</u>	<u>% N</u>	<u>% S</u>	<u>C/H</u>
1	90.04	8.84	0.43	0.32	10.19
2	88.77	8.71	0.40	0.28	10.19
3	91.84	8.48	0.48	0.30**	10.83

**Average of above 2

used to determine the elemental content of the varying process streams were large in comparison to the changes indicated by these tests. As a result, conclusions drawn solely from this data could not be considered conclusive. A reduction in nitrogen content was observed in every case. However, there appeared to be no relationship between nitrogen reduction and yields. Liquid product nitrogen content reductions were in the range of 0.10 to 0.16 weight percent, or from a nominal percentage of .40 to a range of .30 to .24 weight percentage nitrogen. A nitrogen balance was calculated to determine if the loss of nitrogen could be determined. In most cases, the gas product contained measurable nitrogen and was included in the cal-

culated nitrogen balance. The results of the nitrogen balance, tabulated in table 13, shows that nitrogen in the gas product in most cases accounts for the loss of nitrogen in the liquid feed. This may have indicated that denitrification occurred during the process.

In most cases the reduction in sulfur content was in the range of 0.02 to 0.06 weight percent sulfur. There does not appear to be any relationship between sulfur reduction and any measurable experimental parameter. However, due to the strong odor of H_2S during occasional gas production, it is assumed that the loss of sulfur is due to the production of H_2S gas.

The carbon to hydrogen (C/H) mass ratio indicates some success at aromatization. The degree of aromatization may increase with increasing C/H ratio as may be seen when comparing the C/H ratio of methane, a hydrocarbon, to the C/H ratio of benzene, an aromatic compound. The C/H ratio of methane is 3.0, while for benzene it is 12.0. Weight percent carbon to weight percent hydrogen ratios increased for all but two runs, Ni-1601, and Al-0104. Overall, the C/H ratios increased from a nominal feed slurry value of 10.2 to a range of 10.6 to 12.2, indicating some increase in aromatic character of the liquid product.

Catalyst Evaluation

The results from analyses performed on various catalysts are presented in table 14. Analysis of pK range suggests that a possible failure to remove anions, such as Cl^- , during the catalyst manufacturing procedure existed. The presence of Cl^- ions on the surface of the

TABLE 13
RESULTS OF NITROGEN BALANCE

Catalyst	Nitrogen in Liquid Feed (grams N ₂)	Nitrogen in Liquid Product (grams N ₂)	Nitrogen in Gas Product (grams N ₂)	Nitrogen Balance Product-Feed (grams N ₂)
Fe ₂ O ₃ on G-32-H	.264	.163	.319	.218
NiO on G-32-H	.260	.193	.548	.481
G-32-H	.281	.166	.818	.703
Fe ₂ O ₃ on Al-0104	.280	.142	.278	.140
NiO on Al-0104	.265	.155	1.239	1.129
Al-0104	.289	.197	.724	.631
Al-1404	.195	.088	.679	.571
Mg-0601	.253	.203	.000*	-.500
Fe ₂ O ₃ on Mg-0601	.262	.201	1.708	1.646
NiO on Mg-0601	.278	.197	.534	.454
NiO on MgO crush	.341	.213	.104	-.024
Cr ₂ O ₃ on MgO crush	.285	.170	.441	.325

TABLE 13--Continued

Catalyst	Nitrogen in Liquid Feed (grams N ₂)	Nitrogen in Liquid Product (grams N ₂)	Nitrogen in Gas Product (grams N ₂)	Nitrogen Balance Product-Feed (grams N ₂)
CuO on MgO crush	.239	.131	.449	.341
Fe ₂ O ₃ on MgO crush	.256	.122	.538	.403
Ni-4303	.254	.156	.405	.307
Ni-1601	.271	.162	.000*	-0.110
Zn-0602	.268	.163	1.192	1.087
UOP-6-S	.251	.144	1.837	1.730

*Air leak in gas sample cylinder.

TABLE 14
 CATALYST CHARACTERISTICS FOR CATALYSTS USED DURING SUCCESSFUL RUNS

<u>Catalyst</u>	<u>Pk_{a/b}</u>	<u>Range</u>	<u>Acidic or Basic Content</u> mmoles/gr catalyst	<u>Physical Dimensions</u>	<u>Surface Composition</u>
Fe ₂ O ₃ on G-32-H	2.8-4.8		.116(acidic)	8-16 mesh	98.91% Carbon 1.09% Fe ₂ O ₃
NiO on G-32-H	2.8-4.8		.271(acidic)	8-16 mesh	97.97% Carbon 2.03% NiO
G-32-H	>9.0		.318 (basic)	8-16 mesh	100% Carbon
Fe ₂ O ₃ on Al-0104	<1.2		.179 (acidic)	1/8" pellets	99.0% Al ₂ O ₃ .5% Fe ₂ O ₃ .5% NiO
NiO on Al-0104	<1.2		.221(acidic)	1/8" pellets	97.0% Al ₂ O ₃ .3% MgO .7% Fe ₂ O ₃ 2.0% NiO
Al-0104	6.8-7.2		.247(acidic)	1/8" pellets	99.0% Al ₂ O ₃
Al-1404	6.8-7.2		.210(acidic)	1/8" pellets	97% Al ₂ O ₃
Mg-0601	>9.0		.451(basic)	1/8" pellets	99% MgO

TABLE 14--Continued

<u>Catalyst</u>	<u>Pk_a/b</u>	<u>Range</u>	<u>Acidic or Basic Content</u> mmoles/gr	<u>Physical Dimensions</u>	<u>Surface Composition</u>
Fe ₂ O ₃ on Mg-0601	>9.0		.479(basic)	1/8" pellets	52.4% MgO 47.6% Fe ₂ O ₃
NiO on Mg-0601	>9.0		.440(basic)	1/8" pellets	85.7% MgO 14.3% NiO
NiO on MgO crush	>9.0		.715(basic)	4-10 mesh	100% MgO
Cr ₂ O ₃ on MgO crush	>9.0		2.147(basic)	4-10 mesh	90% MgO 10% Cr ₂ O ₃
CuO on MgO crush	>9.0		1.505(basic)	4-10 mesh	90% MgO 10% CuO
Fe ₂ O ₃ on MgO crush	>9.0		2.520(basic)	4-10 mesh	85.3% MgO 14.7 Fe ₂ O ₃
Ni-4303	2.8-4.8		0.231(acidic)	1/8" pellets	6.0% NiO 19% WO Al ₂ O ₃

TABLE 14--Continued

Catalyst	$\text{P}k_{\text{a/b}}$	Range	Acidic or Basic Content mmoles/gr catalyst	Physical Dimensions	Surface Composition
Ni-1601	2.8-4.8		0.208(acidic)	1/8" pellets	3-4% NiO, CuO, Fe ₂ O ₃ Remain Al ₂ O ₃
Zn-0600	2.8-4.8		0.175(acidic)	1/8" pellets	10% ZnO 10% Cr ₂ O ₃ Remain Al ₂ O ₃
UOP-6-S	2.8-4.8		0.549(acidic)	1/16" beads	CO, Ni, NO, Al ₂ O ₃

catalyst markedly effected the surface pK, the measure of surface acidity or basicity. On both the alumina and the charcoal catalyst supports, the pK decreased after impregnation of the basic metal oxides. This is an interesting anomaly as the addition of basic material to basic, or mildly acidic, material should not increase acidic content. In cases where this occurs, it was assumed that Cl^- was not removed during the preparation or activation procedures.

Acidic content of catalyst surfaces ranged from 0.116 to 0.549 millimoles of acid per gram of catalyst. Because the reported range of acidic content was small in comparison to experimental error produced in the analysis procedure used to obtain acidic content, any effort to relate it to yield or conversion properties would not be statistically valid. Basic content, however, with a range of 0.318 to 2.52 millimoles of base per gram of catalyst does represent a much larger range of values. It has been suggested that there may be a relationship between increasing catalytic acidic or basic content and increasing catalytic activity (35). Basic content plotted against conversion of SRL in figure 4 suggests the conversion of SRL increases with increasing basic strength. The catalysts which were prepared by co-mixing had the largest basic content, and the highest conversion of SRL. NiO , Cr_2O_3 , CuO , and Fe_2O_3 crush had basic contents of 0.715, 2.147, 1.505 and 2.520 millimoles base per gram of catalyst, respectively. This high basic content may have been due to the bi-modal pore structure developed during activation procedures (36). Bi-modal pore structure is characterized by high surface area. The high surface area allowed a high degree of contact between the acidic solution and the basic active

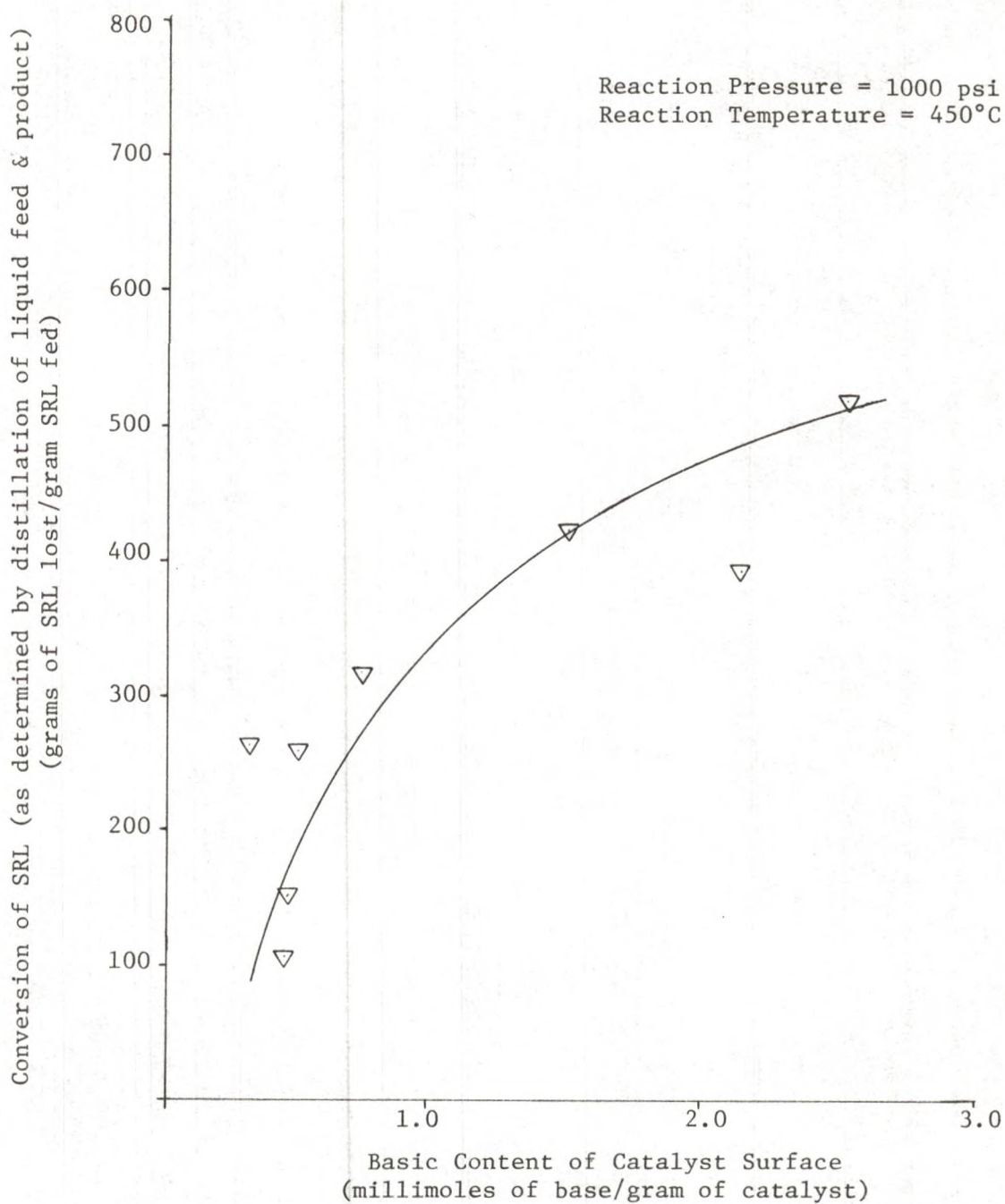


Fig. 4. Conversion of SRL vs. the basic content of the catalyst surface.

sites resulting in a high basic content. No equipment was available during the course of this study to measure catalyst surface area.

CHAPTER V

CONCLUSIONS

The following conclusions were drawn from data and experience developed during this study.

1. The conversion of SRL, which is the overall decrease in the SRL content of the liquid feed and liquid product, tends to increase with basic strength of the catalysts for the conditions of this study.

2. The best overall catalysts, based on the yield of light oils are Al-0104, NiO on Mg-0601, Zn-0602, and NiO on Al-0104.

3. The addition of metal oxides, NiO, Fe_2O_3 , CuO and Cr_2O_3 to various support materials, in most cases increased the yield of light oil from a tetralin-SRL feed. The largest increase in light oil yield was produced with the addition of NiO.

4. Light oils obtained from SRL-tetralin slurry at the reaction conditions of this study contain toluene in processible quantities.

5. The yield of light oils increased with decreasing LHSV and increasing SRL feed content.

6. Gas production for conditions of this study was low compared to the gas production reported for the solvent refining of lignite.

7. Generally, the concentrations of nitrogen and sulfur in the liquid phases were reduced due to the production of N_2 and H_2S gas.

8. Aromatic content of the liquid product was increased relative to the feed material, as evidenced by an increased carbon to hydrogen

mass ratio.

9. The method of catalyst manufacture affects the basic or acidic surface content of the catalyst.

10. For purposes of this study, the micro hydrocracking unit runs were reproducible.

CHAPTER VI

SUGGESTIONS FOR FUTURE WORK

The goal of this study was to produce aromatic chemicals from SRL with minimal production of gas. Because toluene was produced in separable quantities with minimal production of gas, most future work would be on improving yields.

Parameters which would affect the yields of aromatic chemicals, and as such, warrant future consideration for active research, include the LHSV, catalyst makeup and reaction temperature. A decrease in LHSV and an increase in temperature should increase the yield of aromatic chemicals. A closer look at the relationship between acid or base content of the catalyst and conversion of SRL is warranted. This would entail the development of a series of catalysts which produce a wide range of acidic and basic content. Also necessary is the development of a feed system with which a known amount of slurry may be fed with more accuracy and reliability than was exhibited during this study.

Several catalysts show enough potential to indicate further research is warranted. Included in these are NiO, Fe₂O₃, Al₂O₃ and MgO. Varying concentrations of NiO on a variety of supports may produce significant improvements.

APPENDIX I

MICRO HYDROCRACKING UNIT OPERATIONS CHECKLIST

CHECKLIST

I. Pre-Startup

1. Set reactor heater varac at 120
2. Start exhaust fan
3. Hook up pressure relief line
4. Start condenser H₂O
5. Bypass cold trap
6. Hook up wet test meter discharge line
7. Put ice in temperature recorder cold junction and start temperature recorder
8. Isolate product accumulator by closing both inlet and outlet valves
9. Put startup accumulator on line by opening both inlet and outlet valves
10. Open back pressure regulator outlet valve
11. Put ~600 ml tetralin in slurry tank
12. Open slurry recycle valve

II. Catalyst Activation

- _____ 1. Run pump at 125% setting for ~30 seconds (slurry pumps at ~35 psig)
- _____ 2. Establish low pressure hydrogen flow:
- _____ a. Open low pressure H₂ tank valve
- _____ b. Adjust low pressure H₂ tank pressure regulating valve to 25-50 psig
- _____ c. Open low pressure H₂ tank shutoff valve
- _____ d. Adjust inlet gas metering valve to give an H₂ flow of about 70%
- _____ 3. Establish catalyst activation temperature:
- _____ a. When reactor temperature reaches 400° C. adjust variac to maintain this temperature (usually variac setting will range from 75 to 85)
- _____ 4. Maintain temperature at 400° C. and hydrogen flow at ~70% for 2 hours
- _____ 5. Heat up slurry system to at least 70° C. Typical variac settings and resultant temperatures are:
- | Location | Variac Setting | Temp (°C.) |
|------------------------|----------------|------------|
| Slurry Tank | 28 | 75 |
| Outside Line | 42 | 80 |
| Upstream Inside Line | 22 | 100 |
| Downstream Inside Line | 22 | 80 |
- _____ 6. During catalyst activation period make an H₂ flow check:
- _____ a. Adjust inlet gas metering valve to give an H₂ flow of 73%
- _____ b. Measure the time for 0.10 ft³ of gas to flow through the wet test meter
- _____ c. Record: (1) Flow meter reading, (2) Wet test meter temperature, (3) Barometric pressure
- _____ d. Calculate the H₂ flow in ml/min and then correct to standard conditions

III. Startup

1. Establish reaction temperature:
 - _____ a. Set reactor heater variac at 120
 - _____ b. When reactor temperature reaches 450° C. adjust variac to maintain this temperature (usually the variac setting will range from 75 to 85)

N.B.

The reaction temperature may be reached while establishing high pressure H₂ flow (see 8 below) - continually check to make sure the reaction temperature has not been exceeded.
- _____ 2. Close low press H₂ tank valve
- _____ 3. Open inlet gas metering valve
- _____ 4. Open low pressure H₂ tank pressure regulating valve
- _____ 5. Close low pressure H₂ tank shutoff valve
- _____ 6. Close inlet gas metering valve
7. Priming pump:
 - _____ a. Remove tetralin from slurry tank by soaking it up with tissues
 - _____ b. Pour about 600 ml of SRL slurry into slurry tank and start recycle pump. (adjust pressure to ~35 psig)
 - _____ c. Run pump at 125% for less than 30 seconds (including time in step 6)
 - _____ d. Shut off both pumps
8. Back-pressurize with N₂ to ~1000 psig
 - _____ a. Close back pressure regulator inlet and outlet valves
 - _____ b. Open N₂ tank valve
 - _____ c. Adjust N₂ tank pressure regulating valve to 1000 psig
 - _____ d. Open back pressure regulator inlet valve

III. Startup--Continued

9. Establish high pressure hydrogen flow:
- _____ a. Close inlet gas metering valve
 - _____ b. Open high pressure H₂ tank valve
 - _____ c. Adjust high pressure H₂ tank pressure regulating valve to ~1100 psig
 - _____ d. Open high pressure hydrogen tank shutoff valve
 - _____ e. Open inlet gas metering valve until H₂ flow is about 70%
 - _____ f. Disconnect flow meter and open inlet gas metering valve about 1 full turn
 - _____ g. After system pressure reaches about 900 psig, open product accumulator outlet valve
 - _____ h. After system pressure reaches 975 psig, close inlet gas metering valve about 1 1/2 turns and connect flow meter
 - _____ i. Adjust inlet gas metering valve to give an H₂ flow of 90-100% until the back pressure regulator opens as indicated by flow through the wet test meter
 - _____ j. Adjust the N₂ tank pressure regulating valve to bring the system to the desired pressure
 - _____ k. Shut the product accumulator outlet valve
 - _____ l. Adjust inlet gas metering valve to give an H₂ flow of 73%
10. Establish slurry flow:
- _____ a. Run pump at 125% setting for 15 minutes (slurry pump at about 34 psig)
 - _____ b. Check T.R. to see if pump is working
 - _____ c. Reduce pump setting to 70%
 - _____ d. Recheck T.R. for pump performance
 - _____ e. Feed slurry for 2 hours
- _____ 11. During startup prepare the dry ice-isopropyl alcohol cold trap

IV. Run

1. At start of run period:
 - _____ a. Open product accumulator inlet and outlet valves
 - _____ b. Close startup accumulator inlet and outlet valves
 - _____ c. Connect cold trap
 - _____ d. Record:
 - Time
 - Wet test meter reading (ft³)
 - Reactor temperature (°C.)
 - Inlet pressure gauge reading (psig)
 - Outlet pressure gauge reading (psig)
- _____ 2. Adjust reactor heater variac and inlet gas metering valve as necessary to maintain desired operating conditions
- _____ 3. Every 15 minutes record time, wet test meter reading, and reactor temperature; in addition, every 30 minutes record inlet and outlet pressure gauge readings
4. Gas samples
 - _____ a. 1st sample - start collecting sample 30 minutes after the run begins
 - _____ b. 2nd sample - start collecting sample 60 minutes before the run ends
 - _____ c. Sampling procedure:
 - (1) Evacuate the gas sample cylinder using a vacuum pump
 - (2) Install the gas sample cylinder in the sampling system leaving the top Swagelok fitting about 2 turns from being tight

IV. Run--Continued

- (3) Open the gas sample outlet shutoff valve
 - (4) Simultaneously close the gas sample bypass valve and open the gas sample inlet shutoff valve
 - (5) Purge the inlet line to the gas sample cylinder for about 3-4 seconds and tighten the top Swagelok fitting
 - (6) Open the inlet gas sample cylinder valve
 - (7) After 25 seconds, open the outlet gas sample cylinder valve
- _____ 5. Make at least one H₂ flow check following the procedure outline in catalyst activation - item 6

V. Shutdown

1. At end of run period:
 - _____ a. Open startup accumulator inlet and outlet valves
 - _____ b. Close product accumulator inlet and outlet valves
 - _____ c. Disconnect cold trap
2. Establish nitrogen purge:
 - _____ a. Close back pressure regulator inlet valve
 - _____ b. Close inlet gas metering valve
 - _____ c. Close high pressure H₂ tank valve
 - _____ d. Open high pressure H₂ tank pressure regulating valve; this bleeds H₂ from the line between the high pressure H₂ tank and the inlet gas metering valve
 - _____ e. Close high pressure H₂ tank shutoff valve
 - _____ f. Adjust N₂ tank pressure regulating valve to 1100 psig
 - _____ g. Open N₂ tank shutoff valve
 - _____ h. Open inlet gas metering valve until N₂ flow is 70%
3. Establish cleaning solvent flow:
 - _____ a. Turn off pump
 - _____ b. Remove SRL slurry from slurry tank by soaking it up with tissues
 - _____ c. Clean recycle stream thoroughly
 - _____ d. Pour about 175 ml of tetralin into slurry tank
 - _____ e. Start pump and run at 125% setting
4. After 60 minutes of cleaning:
 - _____ a. Turn off pumps
 - _____ b. Open slurry recycle valve
 - _____ c. Turn off all heaters except pump head

5. Depressurize the system:

- _____ a. Increase nitrogen flow to 90-95% using the inlet gas metering valve
- _____ b. Open product accumulator outlet valve
- _____ c. Start decreasing system pressure by carefully opening back pressure regulator outlet valve

N.B.

The rate of pressure decrease can best be controlled by observing the wet test meter - adjust the back pressure regulator outlet valve so that the wet test meter turns as fast as possible without blowing the water out of the manometer

- _____ d. Adjust the inlet gas metering valve as necessary to maintain N_2 flow at 90-95%

6. After the system has been depressurized:

- _____ a. Close product accumulator outlet valve
- _____ b. Close inlet gas metering valve
- _____ c. Close N_2 tank valve
- _____ d. Open N_2 tank pressure regulating valve
- _____ e. Close N_2 tank shutoff valve
- _____ f. Close cooling water shutoff valve
- _____ g. Turn off temperature recorder
- _____ h. Break line at inside check valve
- _____ i. Pump clean tetralin through pump until exit stream is clear
- _____ j. Turn off heat to pump head

APPENDIX II
CALIBRATION CURVES

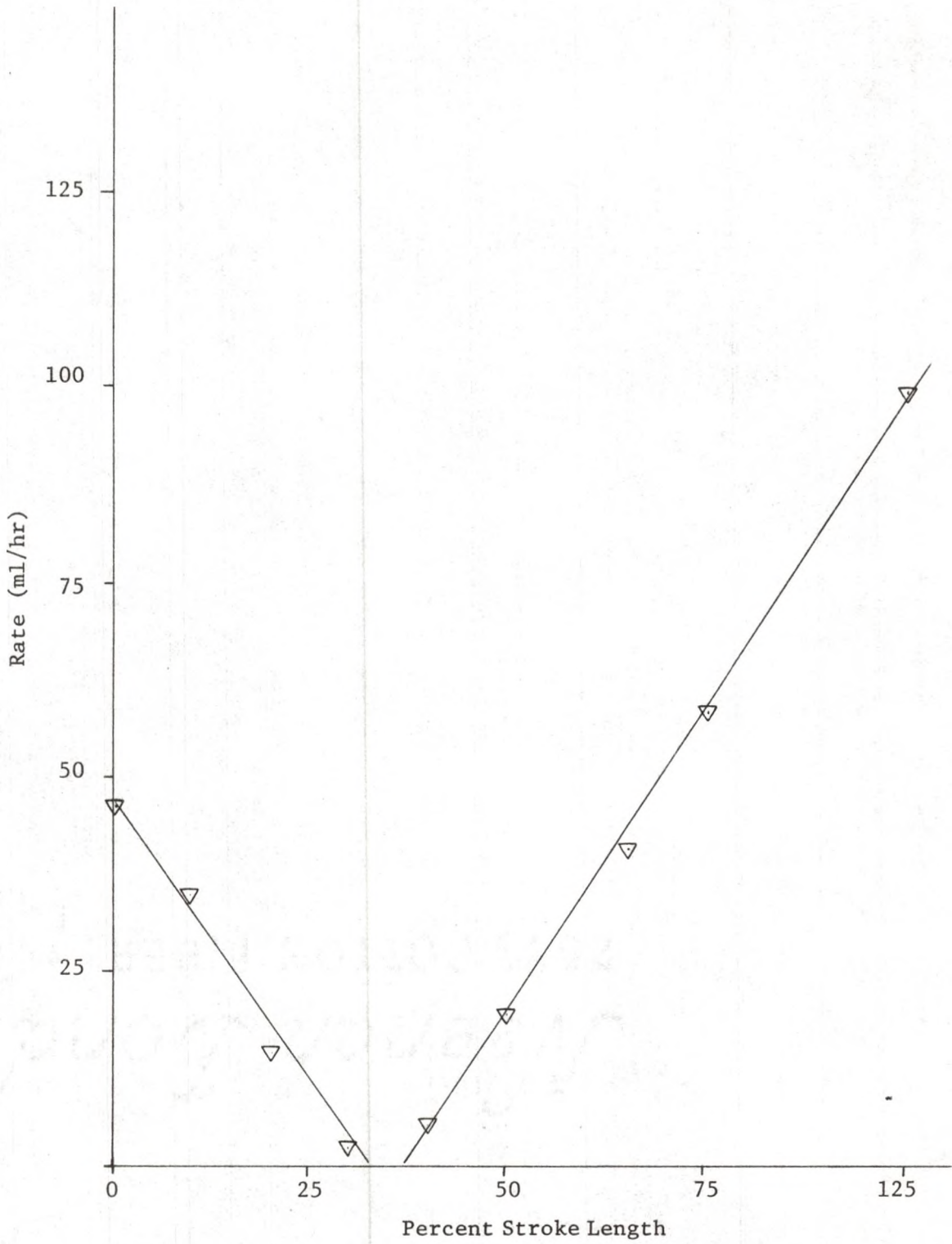


Fig. 5. High pressure slurry pump calibration curve

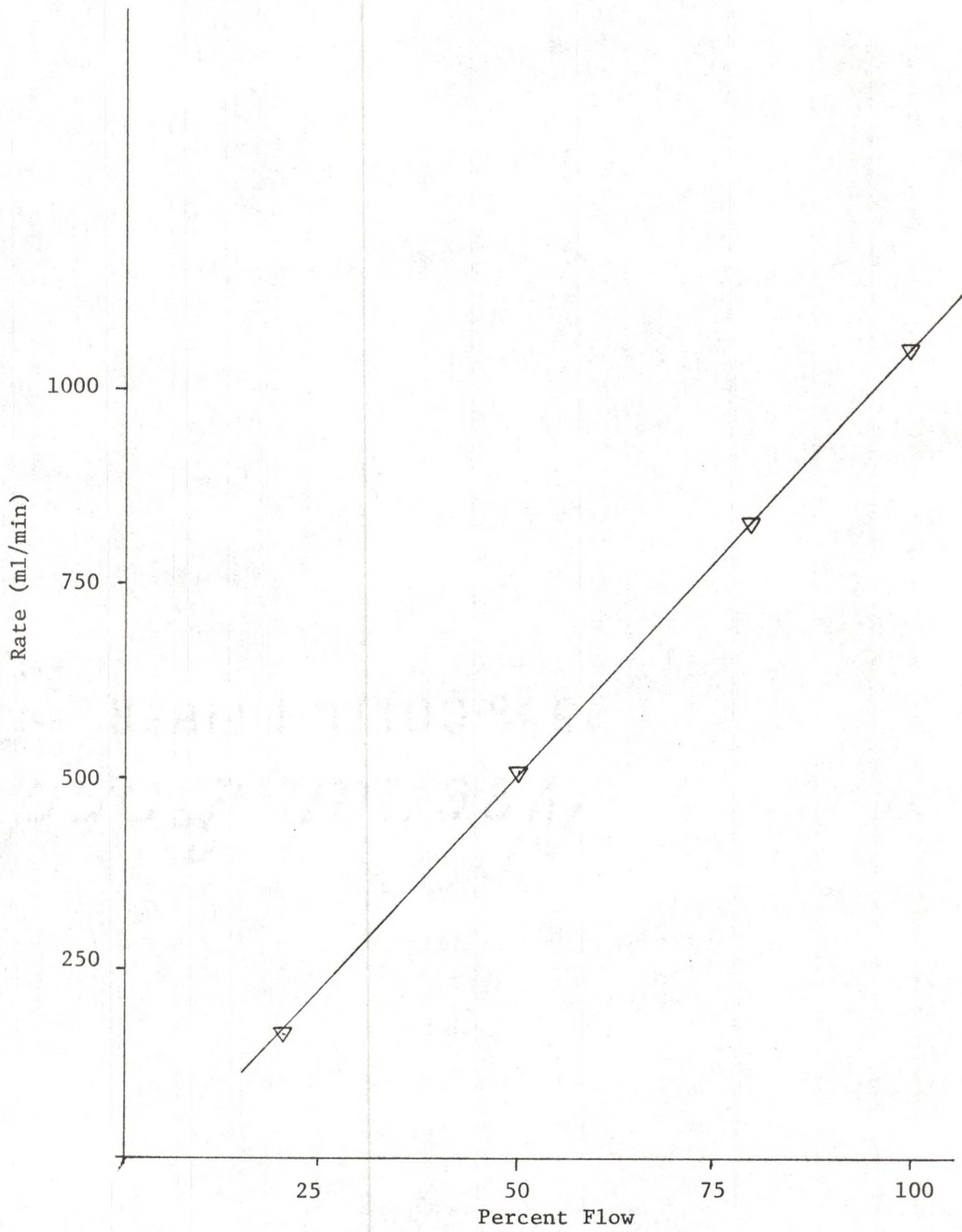


Fig. 6. Inlet gas flow meter calibration curve

APPENDIX III

LIST OF EQUIPMENT AND SUPPLIES

Equipment and Supply List

- H-101 Hood- ventilation of reaction area. Manufactured at UND Chemical engineering dept.
- VT-201 Pressure relief line- emergency ventilation of line. Three inch flexible metal tubing- exits into main exhaust system for lab.
- V-202 Start-up accumulator inlet valve- control inlet flow to start-up accumulator. Whitey valve SS-3TS4, Whitey Company, Oakland, California.
- V-203 Start-up accumulator outlet valve- control outlet gas flow from start-up accumulator. Whitey valve number SS-3TS4, Whitey Company, Oakland, California.
- V-204 Product accumulator outlet valve- control outlet gas flow from product accumulator. Whitey valve SS-3TS4, Whitey Company, Oakland, California.
- V-205 Back pressure regulator vent valve- vent gas used as pressure regulator. System depressurization. Fine metering valve SS-21RS4, Whitey Company, Oakland, California.
- V-206 Product accumulator outlet valve- liquid product removal. P.D. series straight through plug valve, SS4PDMH-FA, Whitey Company, Oakland, California.
- V-207 Start-up accumulator outlet valve- start-up liquid removal. Plug valve SS4PDMH-FA, Whitey Company, Oakland, California.
- V-208 Slurry flow indication valve, indicates if high pressure slurry pump, P-403, is operational; also used for cleaning pump system. Valve SS-3TS4, Whitey Company, Oakland, California.
- V-209 Product accumulator outlet valve- control of gas flow from product accumulator. Valve SS-3TS4, Whitey Company, Oakland, California.
- CV-210 Outlet pressure guage surge check valve- prevent damage to outlet pressure guage. Ball check valve SWK-4402, Autoclave Engineers, Inc., Erie, Pa.
- CV-212 Hydrogen check valve, prevent H₂ from flowing into and through pump. Ball check valve SWK-4402, Autoclave Engineers, Inc., Erie, Pa.

- CV-213 Inlet pressure guage surge check valve- prevent damages to inlet pressure guage. Ball check valve SWK-4402. Autoclave Engineers, Inc., Eric, Pa.
- RD-220 Rupture disk- protect system from excessive pressure build-up. Safety clamp SS4600, Autoclave Engineering, Inc., Eric, Pa. Fike rupture disc psig 2208 at 72°. Fike, Blue Springs, Mo.
- HT-223 Heat tapes- heat slurry feed system. A) Briskheat number BIH-N 1/2, at N= feet in length. 115 volts, 288 watts. B) Glass-Col apparatus, 140 watts, 115 volts.
- PR-251 Back pressure regulator- regulate system pressure. Grove number S-91XW, Range 100-3000 pounds/in². Grove Valve and Regulator Company, California.
- SA-255 Start-up accumulator- accumulate liquid during startup period (300 ml). High pressure monel double ended sampling cylinder, 4HDM300, 3500 psi. Hoke Distributor, Minneapolis, Mn.
- PA-256 Product accumulator-accumulate liquid product during run period (1000 ml). High pressure monel double ended sampling cylinder 4HDY1000, 3500 psi. Hoke Distributors, Minneapolis, Mn.
- R-271 Reactor- reaction vessel consists of tubular reactor, heating element and control. Length =18 in., OD=.750 in., ID=.655 in., Vol=72.7 cc., Rest time= 87.2 min., Operation temperature= 450° C., LHSV= 1.23 per hour. Tubular fixed bed reactor- steel tube in an aluminum jacket. Jacket fitted with clamp on heating element. Entire unit is surrounded by 4 inch asbestos steam pipe insulation. Unit manufactured by Mr. T. Hamerling, Master Machinist, Chemical Engineering Dept., UND, Grand Forks, ND.
Heating element-Chromolox number HB2 230B, 120 volts, 800 watts. Control-powerstat variable transformer number 3WP, 120 volt input, 140 volt output, 10 amps.
- C-274 Condensor- coal reactor outlet stream. Assembled from steal tubing and various swaglok fittings. Crawford Fittings Company, Solon 39, Ohio.
- ST-275 Leak detector- detection of leaks in system when under pressure. Snoopy leak detector, functional temperature range 0° - 100° C. Nupro Company, Willoughby, Ohio.
- FA-271 Catalyst filtration apparatus- separation of catalyst and liquid used to qualify catalyst. 9 cm. beuchner funnel, 1000 ml suction flask and vacuum pump.

- B-299 Product storage bottle- safe storage of a highly volatile liquid product. Brown small mouth 500 ml glass bottle w/ poly-seal #31 caps. Curtin-Matheson Scientific Inc., Maryland Hts, Mo.
- HT-301 High pressure H₂ tank- supply of H₂ to system during run period. H.E. Everson, Grand Forks, ND.
- HT-302 Low pressure H₂ tank- supply H₂ to system during catalysts-activation period. H.E. Everson, Grand Forks, ND.
- NT-303 Nitrogen tank- supplies N₂ for depressurization and is used in backpressure regulator as regulation gas.
- V-361 High pressure H₂ tank pressure regulating valve-control pressure of H₂ from high pressure
- V-362 Low pressure H₂ tank pressure regulating valve-control of H₂ pressure during catalyst activation period. H1710-540 Series Regulator, 0 to 150 psig Smith Welding Equipment Div., Tescom Corp. Minneapolis, Minnesota
- V-363 High pressure N₂ tank pressure regulating valve-control of N₂ pressure during pressurization (startup and Run periods). H800 Series Regulator, 0 to 4000 psig. Smith Welding Equipment Division, Tescom Corp., Minneapolis, Minnesota
- CV-381 Hydrogen check valve- prevents flow of gas back into H₂ tanks. Ball check valve SWB 4400. Autoclave engineers Inc., Erie, Pa.
- CV-382 Surge check valve- seals H₂ inlet line in the event of down stream line rupture. Ball check valve SWK-4402. Autoclave Engineers, Inc., Erie, Pa.
- CV-383 Slurry check valve- prevents slurry from entering inlet H₂ line. Ball check valve SWB-4400. Autoclave Engineers, Inc., Erie, Pa.
- CV-384 Nitrogen check valve- prevents flow of gas back into N₂ tank. Ball check valve SWB-4400. Autoclave Engineers Inc., Erie, Pa.
- V-391 Inlet gas metering valve- controls flow rate of inlet gas. Fine metering valve SS-22RS4 Whitey Company, Oakland, California
- V-392 Surge check bypass valve- release pressure on surge check valve to reestablish flow of gas. Valve SS-3TS4. Whitey Company, Oakland, California

- V-393 High pressure H₂ shut off valve- controls flow of inlet H₂ during Run period. Valve SS-3TS4.
Whitey Company, Oakland, California
- V-394 Low pressure H₂ shut off valve- controls flow of inlet H₂ during catalyst activation period. Valve SS-3TS4.
Whitey Company, Oakland, California
- V-395 N₂ shut off valve- controls flow of inlet N₂ into reaction system-during shut down period. Valve SS-3TS4.
Whitey Company, Oakland, California
- V-396 Back pressure regulation inlet valve- control N₂ to back pressure regulation. Valve SS-3TS4.
Whitey Company, Oakland, California
- V-401 Slurry recycle valve- control of pressure on line to high pressure slurry pump. Valve SS-3TS4.
Whitey Company Oakland, California
- P-402 Slurry recycle pump- mixes slurry and feed slurry ends pressure and high pressure slurry pump. Bronze Rotary gear pump 4271 K21 1.5 gal/min @ 100 psi and 1725 RPM motor, 1/4 hp, 1725 RPM, 118 volts, 3.61
- P-403 High pressure slurry pump- feeds slurry to pressurized system meters feed rates. Milroy D Controlled voluum pump HDB-1-30 Variable Capacity, reciprocity plunger, positive displacement pump rated pressure = 30, motor, 1/4 hp @ 1725 RPM, 115 Volts 3.8 Amps. Milton Ray Company, Phila., Pa.
- FA-409 Slurry filtration apparatus- remove undissolved particles from SRL-tetralin slurry. Heated 40 cm Buichner funnel w/tared cold trap. (150° C.) Chemical Engineer Stockroom UND, Grand Forks, ND
- ST-410 Slurry tank- stores feed slurry during run. Stainless Steel 800 ml beaker fitted with 5/8 fence pipe fitting. Adapted by Tony Flannerly Master Machanic UND Chemical Engineering Dept. Grand Forks, ND
- CV-411 Slurry feed check valve- eliminate back flow from high pressure slurry pump during run and startup period. Spring loaded check valve SS-4C-25 Nu PRO Co.
- GB-501 Gas sampling banks- samples product gas during run period, High pressure monel double ended sample cylinder. Hoke DOT 3B 400.
- WT-502 Wet test meter- measure fr³ of exit gas during Run period and Calibration of flow meter. Precision Scientific Company

- H-503 Hood- safety ventilation for system. 3 x 5 ft stainless steel hood. Eight inch ventilation ducting. Adapted for use by Mr. Tony Hammerly Master Mechanic Chemical Engineering Dept. UND, Grand Forks, ND.
- CT-504 Cold trap- remove vapor of exit gas stream during Run period. Tared 200 ml pyrex test tube and stopper.
- V-510 Gas sample inlet shut off valve- control of gas flow into gas sampling valve during Run period. Valve SS-35T4. Whitey Company, Oakland, California.
- V-511 Gas sampling outlet shut off valve- control of gas flow out of gas sampling valve. Valve SS-35T4. Whitey Company, Oakland, California.
- DA-703 Micro Distillation Apparatus- distillation of liquid product. Distillation unit was designed and built by Mr. Dave Hassit, Chemist, UND.
- GC-707 Gas chromatograph-mass spectrophotometer- analysis of liquid product. Available at G.F. E.T.C. operator Dave Miller.
- SEM-709 Scanning electron microscope- analysis of catalyst surface. Available at G.F. E.T.C. operator Diane K. Rindt and George Montgomery.
- WC-785 Wasli Contami- contain most of liquid waste material. Used 5 gallon drums-various supplies.
- P-979 Pellet pressure and mold- formation of catalysts. Mold assembly # 20-2112. Buchler Ltd, Evanston, Ill.
- S-998 Solvent Refined Lignite- coal related feed stock-obtained from Project Lignite UND, Grand Forks. PDU Run # M-11A. 0% ash, 100% pyridene extractable.
- T-999 Tetralin (1, 2, 3, 4 tetrahydronaphthalene)-process solvent. Fisher Scientific Company.
- F11 Percent flow meter- monitors gas flow into system-Brooks Thermal Mass Flow Meter System Sensor # 5810-1-A Indicator H 5820-1-1A.
- P11 Pressure guage (inlet)-indicates pressure upstream from reactor- Maximum safety pressure guage. Range= 0-3000 psig.

APPENDIX IV

BASIC COMPUTER PROGRAM USED TO OBTAIN THE
CALCULATED MATERIAL BALANCE

Z1 Run #
 Z Blank #
 C1 Run Charge grams
 C2 Run product liquid grams
 C3 Run gas product grams
 F1 Run H₂ flow STP ml/min
 F2 Initial H₂ flow STP ml/min
 P1 Run feed fraction SRL
 P2 Run product fraction SRL
 P3 Run liquid product fraction tetralin (wt)
 P4 Run liquid product fraction naphthalene (wt)
 P5 Run liquid product fraction light oils (wt)
 D1 Run gas product fraction CH₄ (mole)
 D2 Run gas product fraction C₂H₆ (mole)
 D3 Run gas product fraction C₃H₈ (mole)
 D4 Run gas product fraction W₂ (mole)
 P6 Run gas product fraction H₂ (mole)
 X1 Yield light oil (gram light oils/gram SRL)
 X2 Yield naphthalene (gram naphthalene/gram SRL)
 Y1 Tetralin in Run charge (gram)
 Y2 Blank liquid product fraction naphthalene
 Y3 Blank liquid product fraction light oil
 Y4 Blank liquid product fraction tetralin
 A2 Yield naphthalene-blank (gram naphthalene/gram tetralin)
 A3 Yield light oil blank (gram light oil/gram tetralin)
 A4 Yield of light oil Run (corrected)
 C1 Conversion of SRL based on % Distribution of Run feed and product
 A5 Yield of naphthalene (corrected)
 H1 Conversion of H₂
 E1 Run yield of H₂ grams
 E2 Yield of CH₄ gas
 E3 Run yield of C₂H₆ gas
 E4 Run yield of C₃H₈ gas
 E5 Run yield of N₂ gas
 P7 Run yield of gas (grams)
 P8 Blank yield of gas (grams)
 P9 Blank grams gas/gram tetralin
 I1 Blank yield of H₂ (grams)
 I2 Blank yield of CH₄ (grams)
 I3 Blank yield of C₂H₆ (grams)
 I4 Blank yield of C₃H₈ (grams)
 F3 Initial Blank H₂ flow STP ml/min
 F4 Blank H₂ flow STP ml/min
 J1 Blank gas product fraction H₂ (mole)
 J2 Blank gas product fraction CH₄ (mole)
 J3 Blank gas product fraction C₂H₆ (mole)
 J4 Blank gas product fraction C₃H₈ (mole)
 G4 Blank liquid product yield (grams)
 G5 Blank liquid feed (grams)
 B9 Grams SRL charged

B1 Run liquid feed fraction N (wt)
B2 Run liquid feed fraction S (wt)
B3 Run liquid feed fraction H (wt)
B4 Run liquid feed fraction C (wt)
B5 Run gas product fraction N (wt)
B6 Run gas product fraction S (wt)
B7 Run gas product fraction H (wt)
B8 Run gas product fraction C (wt)
K1 Grams of nitrogen feed
K2 Grams of nitrogen recovered in liquid (Run)
K4 Grams of nitrogen out total
K5 ΔN
K6 C/H Ratio

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INPUT Z1,Z,G2,F1,F2,P1,P2,P3,P4,P5,D1,D2,D3,D4
INPUT P6,Y2,Y3,Y4,F3,F4,J1,J2,J3,J4,G4,B1,B2,B3
INPUT B4,B5,B6,B7,B8
E1=2.016*P6*F1*5.357*10-3
E2=16.04*D1*F1*5.357*10-3
E3=30.04*D2*F1*5.357*10-3
E4=44.10*D3*F1*5.357*10-3
E5=28.02*D4*F1*5.357*10-3
P7=E2+E3+E4+E5
G1=G2+P7
X1=(P5*G2*(1-P2))/(P1*G1)
X2=(P4*G2*(1-P2))/(P1*G1)
Y1=G1*(1-P1)
I1=2.016*J1*5.357*10-3*F4
I2=16.04*J2*5.357*10-3*F4
I3=30.04*J3*5.357*10-3*F4
I4=44.10*J4*5.357*10-3*F4
P8=I2+I3+I4
P9=P8/(G4+P8)
G5=P8+G4
A2=((G4)*Y2)/G5
A5=((G2*P4)*(1-P2)-(((Y2*G4)/G5)*Y1))/(G1*P1)
A3=(Y3*G4)/G5
A4=((G2*(1-P2)*P5)-((A3*G1*(1-P1))))/(P1*G1)
C1=((P1*G1)-(P2*G2))/(P1*G1)
B9=G1*(1-P2)
H1=(F2-(F1*P6))/F2
K1=G1*B1
K2=G2*B5
K4=E5+K2
K5=K1-K4
K6=B8/B7
PRI "RUN"; Z1
PRI "BLANK"; Z
PRI "RUN CHARGE (GRAMS)"; G1
PRI "RUN FEED WT FR SRL"; P1
PRI "CONVERSION OF SRL"; C1
PRI "YIELD OF LIGHT OILS"; X1
PRI "YIELD OF LIGHT OILS (COR)"; A4
PRI "YIELD OF NAP"; X2
PRI "YIELD OF NAP (COR)"; A5
PRI "CONVERSION OF H2 GAS"; H1
PRI "GRAMS N2 FEED"; K1
PRI "GRAMS N2 RECOVERED (LIQ)"; K2
PRI "GRAMS N2 RECOVERED (GAS)"; E5
PRI "DELTA NITROGEN"; K5
PRI "RUN YIELD OF HC GAS"; P7/G1
PRI "BLANK YIELD OF HC GAS"; P9
PRI "C/H RATIO"; K6

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