Catalytic hydrogenation of PAMCO solvent-refined coal
by Lee Morgan Henton

A thesis submitted in partial fulfillment of the requirements for the degree of MASTER OF SCIENCE in Chemical Engineering
Montana State University
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Abstract:
Catalytic hydrogenation of Pittsburgh and Midway Coal Company's Solvent-Refined Coal was accomplished using commercial and lab-prepared catalysts.

Batch bomb tests indicated the relative activity of twenty-nine catalysts; five catalysts were used in the operation of a continuous reactor.

Liquid hydrogenation products were analyzed by ASTM distillation quartz tube method for sulfur content, and Macro Kjeldahl method for nitrogen content.

The Ketjen HC-5 catalyst (21% WO3 , 6.5% NiO on alumina) did the best desulfurization, 88%. The Harshaw HT-400 (15% MoO3 3% CoU on alumina) did the best denitrogenation, 64%.

Temperature, liquid hourly space velocity, and hydrogen-to-oil flow rates were studied with the continuous reactor; pressure and catalyst amount were held constant at 1000 psig and 70 ml, respectively As temperature increases, hydrocracking and heteroatom removal increase.

Optimum space velocity varied between 1 and 2, depending on the catalyst. Heteroatom removal decreased as space velocity increased,, A hydrogen-to-oil ratio of 10,000 SCF/bbl gave the best hydrocracking and heteroatom removal results at 445° C and liquid hourly space velocity equals 1.

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Date May 4, 1978

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Approved:

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ABSTRACT

Catalytic hydrogenation of Pittsburgh and Midway Coal Company's Solvent-Refined Coal was accomplished using commercial and lab-prepared catalysts.

Batch bomb tests indicated the relative activity of twenty-nine catalysts; five catalysts were used in the operation of a continuous reactor.

Liquid hydrogenation products were analyzed by ASTM distillation, quartz tube method for sulfur content, and Macro Kjeldahl method for nitrogen content.

The Ketjen HC-5 catalyst (21% WO_3, 6.5% NiO on alumina) did the best desulfurization, 88%. The Harshaw HT-400 (15% MoO_3, 3% CoO on alumina) did the best denitrogenation, 64%.

Temperature, liquid hourly space velocity, and hydrogen-to-oil flow rates were studied with the continuous reactor; pressure and catalyst amount were held constant at 1000 psig and 70 ml, respectively.

As temperature increases, hydrocracking and heteroatom removal increase.

Optimum space velocity varied between 1 and 2, depending on the catalyst. Heteroatom removal decreased as space velocity increased.

A hydrogen-to-oil ratio of 10,000 SCF/bbl gave the best hydrocracking and heteroatom removal results at 445°C and liquid hourly space velocity equals 1.

INTRODUCTION

As of 1974, petroleum and natural gas accounted for 75% of the total energy consumed in the United States (1). Since oil is a non-renewable resource and discovery of new reserves are lagging behind consumption, the end of affordable oil is approaching. Since exotic large scale resources like fusion are not expected to be commercial in the next fifty years, an interim source of energy is needed.

Coal is a viable choice. Proven reserves of coal in the United States hold 8 times as much energy as known domestic reserves of crude oil, natural gas, shale oils, and bitumens (2).

The nature of coal makes it unsuitable for many uses. Much transportation fuel must be liquid to fit existing systems; mineral ash accounts for up to 10% of coal. Many coals contain more sulfur and nitrogen than combustion fuels made from crude oil. Processing technology will therefore have to be developed in order to make distillate fuels from coal economically feasible.

Liquefaction of coal is not new. German liquified coal plants operated in the 1920's and 1930's. The Bureau of Mines operated a synthetic fuels demonstration plant from 1949 to 1953; Union Carbide operated a coal hydrogenation plant from 1952 to 1956. But coal-derived liquids were not economically competative in light of large crude oil discoveries (1, 3).

Coal liquids technology is again being developed to meet anticipated need: FMC COED pyrolysis oil, H-Coal, Synthoil, and Solvent-

Refined Coal are products of current technology. These still do not give large yields of high quality liquid fuel, however.

Therefore, the object of this research is to upgrade Pittsburgh and Midway Coal Company's SRC (Solvent-Refined Coal) into a clean distillate fuel.

RESEARCH OBJECTIVE

The object of this research is catalytic conversion of PAMCO's Solvent-Refined Coal (an upgraded coal product) to clean distillate fuels.

A number of commercial and lab-prepared catalysts were used to hydrotreat a solution of Solvent-Refined Coal (SRC) at high temperature and pressure. The product solution should have more low-boiling fractions than the feed solution; reduced sulfur and nitrogen product content is also desired.

The research plan included autoclave test screening of hydrotreating catalysts. Promising catalysts were employed in the operation of a continuous trickle-bed reactor. Effects of liquid hourly space velocity, hydrogen-to-oil ratio, and temperature were also studied in the continuous reactor.

BACKGROUND AND THEORY

Coal Liquifaction Processes

Different Types - Four types of liquefaction processes are being developed in the U.S.: pyrolysis, direct hydrogenation, Fischer-Trøpsch coal gas-to-liquid synthesis, and solvent hydrogenation.

Examples of the pyrolysis type are: FMC's COED process and Gulf Oil's coker distillate process. Products are a tar oil for hydrotreating and a char product (1).

Direct hydrogenation processes include Hydrocarbon Research Inc.'s H-COAL, Pittsburgh Energy Research Center's Synthoil, Conoco Coal Development Company's Zinc Chloride process and Institute of Gas Technology's Riser Cracking of coal. Types of contacting and catalysts vary widely. Coal slurry and hydrogen gas pass through an ebullating bed of catalyst in the H-COAL process; coal slurry and hydrogen pass turbulently through a fixed catalyst bed for Synthoil. Conoco passes reactants through a molten salt bed; residence time for pulverized coal particles is less than 10 seconds in the Riser Cracking tubular reactor.

Fischer-Tropach synthesis involves reacting steam and coal at high temperature to make CO and H_2 gas. The gas is first purified of sulfur and nitrogen compounds, then it reacts over a catalyst bed to make short chain alcohols and hydrocarbons (1).

Solution hydrogenation processes include PAMCO's Solvent-

Refined Coal (SRC), Consol's Cresap project, Exxon's donor solvent process, Morgantown Energy Research Center's "Two-Step," and the "Clean Fuels West" process sponsored by Southern California Edison, Mobil Oil, EPRI, and Conoco Coal. The method of hydrogen addition to the recycle solvent and/or coal solution varies according to the process (4).

SRC I - The SRC I process is the one of interest in this report. The solvent-refined coal major product is a solid at room temperature, with sulfur and ash content substantially reduced from the original coal. However, the original nitrogen of the coal remains in the product, and the hydrogen-to-coal ratio of the product is slightly less than that of the original coal. The upgrading of the solid solvent-refined coal product from SCR I is the object of this thesis research.

Figure 1 shows a simplified process schematic of Pittsburg and Midway Coal Company's Solvent-Refined Coal I process (5).

The process starts with pulverized coal being slurried with recycle solvent in a mix tank. Hydrogen and slurry are mixed, heated, and pumped to the high pressure dissolver. The product from the dissolver is flashed to separate the raw gases from the coal slurry. The raw gas is treated to remove impurities and hydrogen is recycled.

The coal slurry leaving the separator is at high temperature, as most of the coal matter is still liquid. Filtration separates the undissolved solids (ash and coal residue) from the hot liquid. The

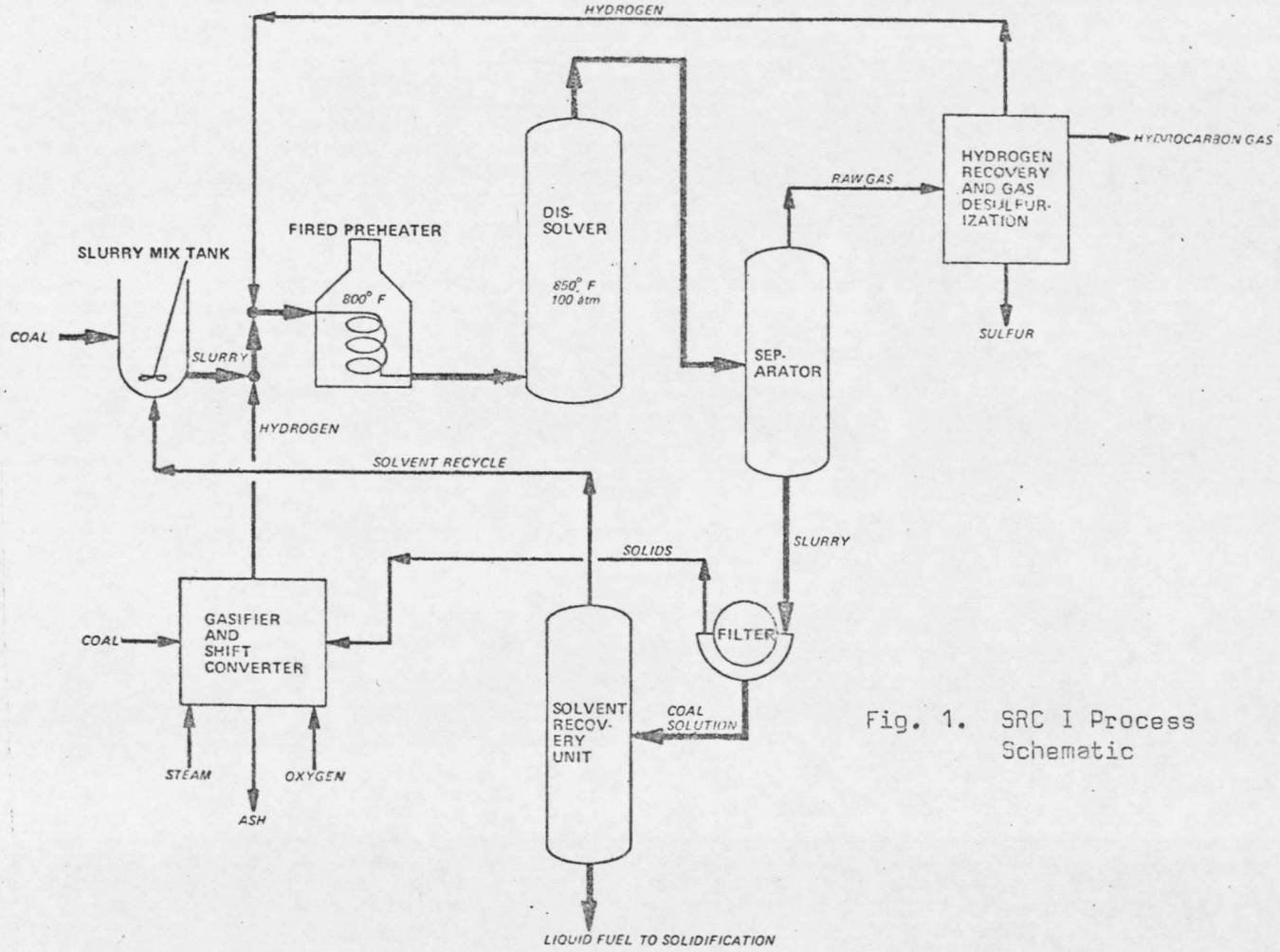


Fig. 1. SRC I Process Schematic

solid coal residue is reacted with steam and air to yield make-up hydrogen for the process.

The hot liquid from the filter enters a solvent recovery unit. The lower boiling material is separated from the recycle solvent. This lower boiling material yields a small amount of liquid product and a large amount of solid material at room temperature. The solid is "solvent-refined coal" (5, 6).

SRC II - More liquids and gases, with less solid product, can be made by a modified solvent-refined coal process called SRC II. The two main changes from the SRC I process are that: a) ash is not removed, but retained in the final solid product; b) it does not use a light "recycle solvent." Instead, some of the hot product stream is diverted for use as the process solvent (6).

If the SRC II liquid yields are high enough, upgrading the SRC II liquids may be more feasible than upgrading the ash-free solid from SRC I.

Factors in Liquefaction

A good many factors influence coal-to-liquid conversion. The rank of coal influences what products are possible. Coals vary in sulfur, nitrogen, oxygen, ash, and trace metal content. Some of those contaminants may be catalytic, but some inhibit catalysis by reacting with the catalyst or plugging heterogeneous catalyst pores.

A myriad of other factors influence coal conversion and types

of products. Length of processing time and type of process appear to be very important. The influence of solvent chemical and physical nature, solvent ratio, amount and type of reducing agents, pressure and temperature of solution and reaction, catalyst nature, and reactor configuration varies, depending on the time and type of processing.

Coal Structure and Composition - Figure 2 shows a representative structure for bituminous coal (7). Coal structure "consists of aromatic ring clusters of no larger than 6 or 7 rings tied together by bridge linkage" (8). Coal's H/C ratio is lower than most fuel materials derived from petroleum. The H/C ratio of Illinois No. 6 is 0.86, while residual heating oil No. 6's ratio is 1.55 and a refining naphtha fraction is 2.20 (9). Coal's low H/C ratio is another indication of the aromaticity of coal compared to petroleum.

Coal contains significant amounts of oxygen, sulfur and nitrogen. Compounds containing these impart undesirable qualities to fuel products, poison catalysts, or become combustion pollutants.

Removal of oxygen is least difficult because oxygen atoms are usually in phenol structures and not heterocyclic.

In uses of upgraded coal when the presence of oxygen is acceptable (low grade fuels), "it is desirable to remove only sulfur and nitrogen to minimize hydrogen consumption" (10).

Sulfur is less difficult than nitrogen to remove (10). Organic and inorganic sulfur are found in coal. Most inorganic sulfur is iron sulfide, FeS_2, and a small amount is present as sulfate ion.

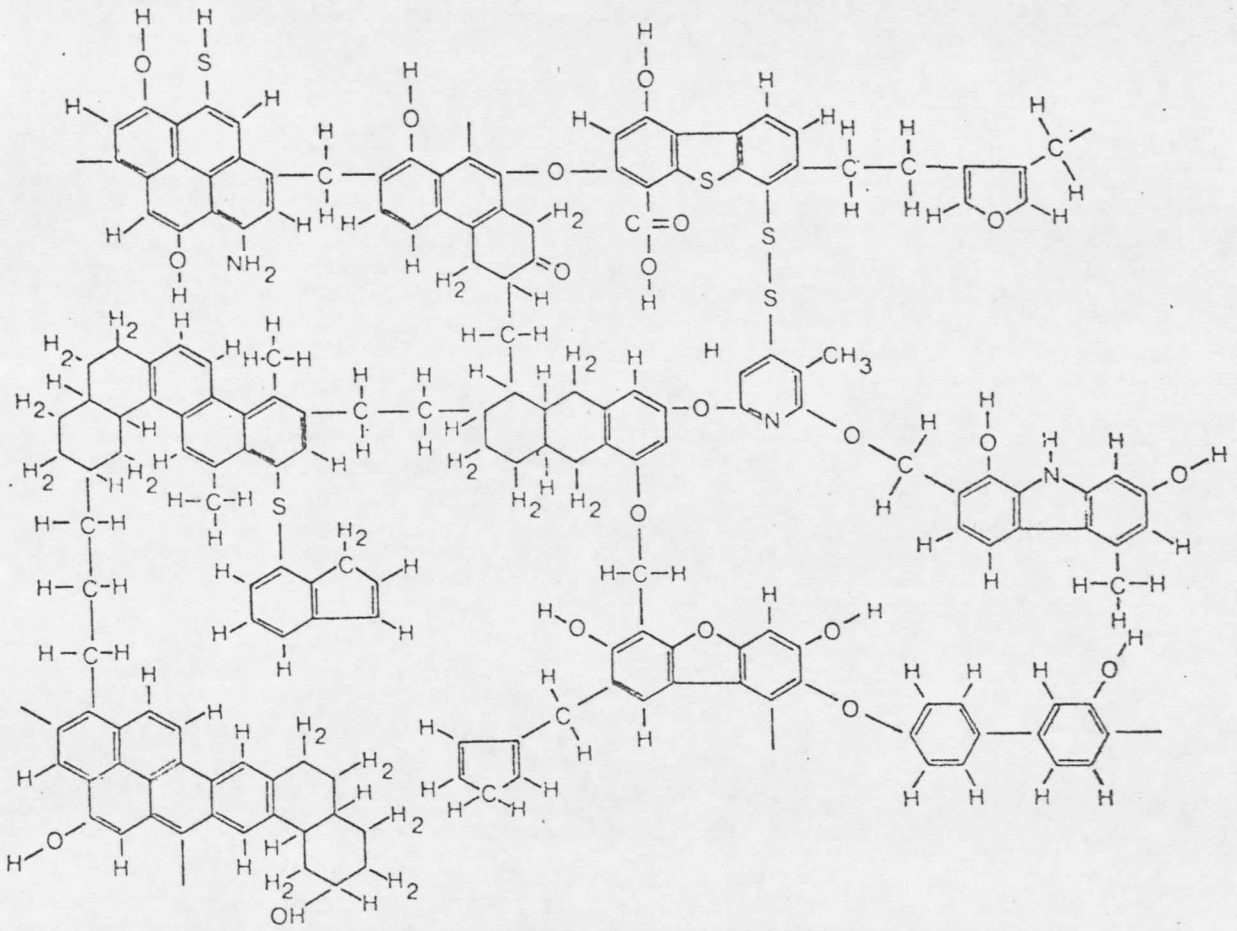


Fig. 2. A Representative of Bituminous Coal Structure (7)

Organic sulfur is mostly heterocyclic; total sulfur concentration in coals ranges from several percent to 10-15%. Nitrogen, like sulfur, is a catalyst poison and pollutant; it is present in concentrations of 1-2 weight percent in most coals (11).

An analysis of 100 coals "revealed the presence of well over half of the elements of the periodic table" (11). Table I shows average coal metal concentrations as compared to values in PAMCO's SRC I from Kentucky No. 9 coal. Trace metals may enhance or inhibit liquefaction catalysts and reactions. "Small amounts of TiO_2 on a silica or alumina support can cause a marked increase in surface acidity" (10). Aged catalyst pellets from the SYNTHOIL process were contaminated with ferrous sulfide, aluminum, and silicon; trace metals were variably distributed through the catalyst (12).

Ultimate analyses of solvent-refined coal and its source coal, Kentucky No. 9 are given in the Materials section tables.

SRC Structure and Composition - Although no compound breakdown of solvent-refined coal has been published in the literature, characterization by solubility fraction is practiced by several people (see Materials section).

The sulfur and ash levels of SRC are much less than its parent coal, but the nitrogen level is not reduced. Desulfurization is about 80% and de-ashing about 97%.

Table I

Mean analytical values for chemical elements in coal (11)

Constituent	Mean, ppm	Std. dev.	Value in ash-free, solvent-refined Kentucky No. 9 coal[a]
As	14.02	17.70	1
B	102.21	54.65	
Be	1.61	0.82	
Br	15.42	5.92	6.2
Cd	2.52	7.60	
Co	9.57	7.26	0.8
Cr	13.75	7.26	
Cu	15.16	8.12	
F	60.94	20.99	
Ga	3.12	1.06	
Ge	6.59	6.71	
Hg	0.20	0.20	
Mn	49.40	40.15	1.7
Mo	7.54	5.96	
Ni	21.07	12.35	
P	71.10	72.81	
Pb	34.78	43.69	
Sb	1.26	1.32	
Se	2.08	1.10	
Sn	4.79	6.15	
V	32.71	12.03	2.8
Zn	272.29	694.23	
Zr	72.46	57.78	
Al	12 900	4500	65
Ca	7700	5500	
Cl	1400	1400	167
Fe	19 200	7900	
K	1600	600	
Mg	500	400	196
Na	500	400	2.6
Si	24 900	8000	
Ti	700	200	96
moisture	9.05%	5.05%	0.00%
ash	11.44%	2.89%	0.051%

Source: Illinois State Geological Survey [a] Data obtained by Manahan's research group, primarily by neutron activation analysis.

The H/C atom ratio of SRC is lower than the parent coal, 0.769 vs. 0.837, even though hydrogen is consumed in the process. Apparently hydrogen from the coal goes to desulfurization (making H_2S) and making hydrocarbon gases.

A gradient elution chromatographic analysis of SRC, SYNTHOIL, and H-COAL products was performed by a Mobil Oil team (13). The analysis consisted of separating the liquids into thirteen different solubility fractions.

Solvent-refined coal has much more asphaltene content than do SYNTHOIL, H-COAL, or petroleum residuum. Eighty-one weight percent SRC is asphaltene, while 12 weight percent Light Arabian Residuum is asphaltene (13).

Several general trends were learned from characterizing each of the thirteen fractions themselves: a) The polar, heavy fractions are more aromatic than the light fractions. b) The molecular weights (and therefore sizes) of coal liquid components are significantly smaller than petroleum residua components of the same fraction. (c) Nitrogen and oxygen content of SRC is highest in the asphaltene fractions, but sulfur content is nearly constant in all fractions (13).

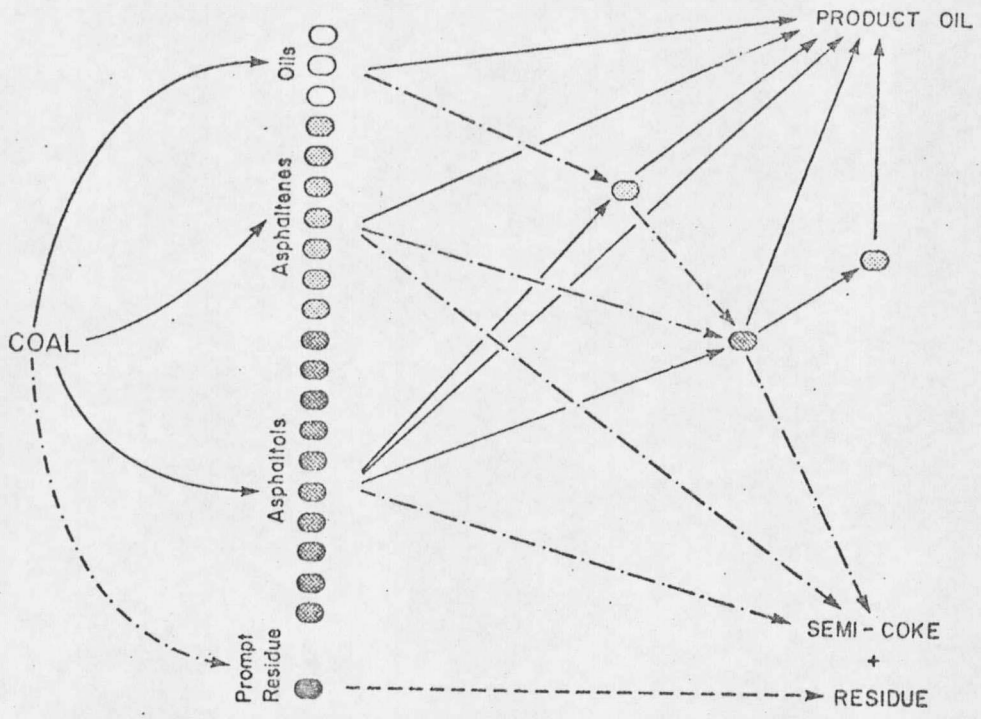
Dissolution of Coal - According to Weller's traditional model of solvent coal liquefaction, oils appear last in a sequence of reactions: coal ⟶ asphaltene ⟶ oil (4). It is known that "depolymerization of coal takes place at high temperatures (up to 420°C and 80 atmosphere initially in an autoclave) in the presence of solvents" (14). The slowest reaction is from asphaltene ⟶ oil, with the coal ⟶ asphaltene being 25 times as fast (8).

However, recent studies show that coal can sometimes be converted to oil very quickly, without going through the very slow asphaltene to oil step. Rapid heating and short residence time experiments have led to a new model for coal-to-oil conversion. Figure 3 displays the new model (4).

When coal is heated in a solvent to 400°C, the easily-broken bonds between ring clusters are rapidly broken. Four types of prompt intermediates appear: a) oils, soluble in pentane; b) asphaltenes, soluble in benzene but not pentane; c) asphaltols, soluble in pyridine but not benzene; and d) residue, not including ash.

The first three types of species then proceed with relatively slow progressive (toward oil) and regressive (to semi-coke) reactions. Semi-coke and residue do not react progressively (4).

Reaction to "Prompt" Intermediates - Time is the important factor in the first coal reaction, break-up into the four species of "prompt" intermediates. Only with rapid heating and quenching are the



A working model of reaction paths in donor solvent liquefaction of a bituminous vitrinite. The curved lines at the left represent rapid cleavage of scissile bonds to yield prompt liquefaction intermediates. These comprise a large number of distinct species forming a hierarchy of increasing polarity toward the bottom of the figure, and also a prompt residue. Relatively slow progressive reactions, indicated by solid lines, convert the prompt intermediates to oil. The progressive reactions compete with relatively slow regressive reactions, indicated by dot-dash lines, that lead to semi-coke.

Fig. 3. Coal Dissolution and Reaction Model (4).

"prompt" intermediates noticed.

The rapid reactions are thermal; they do not depend on: a) the presence or absence of hydrogen; b) the presence or absence of a solid catalyst; c) hydrogen donor properties of the solvent (4).

Mobil Oil data on short reaction time yielded several additional facts. "The initial molecular weight distribution is bimodal, with some fragments having weights greater than 2050, and the remaining fragments are between 300 and 900" (4). The molecular weight of most coals vary from 2000 to 12,000; tars and residual oils have molecular weights ranging up to the millions (15).

Forty percent of the oxygen and sulfur in coal is removed quickly, using hydrogen only from the coal.

"Early dissolution products are more aromatic than the original coal"; since the coal's hydrogen is consumed in heteroatom removal, the increase in aromaticity makes sense (4).

"Prompt liquefaction intermediates contain relatively few polycyclic aromatic structures" (4).

Slower Progressive and Regressive Reactions - Several generalizations can be made about the products from slow reactions of the prompt intermediates.

"At longer times, the aromatic content (of the product) increases, as does also the number of polycondensed aromatic rings"(4). Higher temperatures also increase those two values.

The H/C ratio decreases as reaction time and severity increase. Though much hydrogen can be consumed, it goes mostly for the production of gas and re-hydrogenating hydroaromatic structures (recycle solvent). Little hydrogen goes to heteroatom removal (4).

Asphaltols are the main source of semi-coke. "Coke formation results if thermal cracking 'gets ahead' of hydrogenation of coaly(sic) matter by hydrogen transfer from the donor solvent" (4).

The hydrogen donor capability of the solvent is most important during the slow reactions. Regressive reactions predominate if a hydrogen donor solvent is not used. A donor solvent apparently suppresses the regressive reactions leading to coke. Figure 4 illustrates the point (4).

About 90% of a bituminous coal was converted to pyridine-solubles when heated rapidly in either tetralin or naphthalene. That 5 minute period is the regime of rapid reaction to "prompt" intermediates. After the first 5 minutes, the slower progressing and regressive reactions compete. In this second time regime, pyridine-solubles markedly decreased in naphthalene, while remaining stable in the hydrogen donor solvent tetralin. Progressive reactions to lighter products continued in tetralin, but coke was formed in naphthalene (4).

Desulfurization Reaction Steps - hydro desulfurization (HDS) occurs at less severe conditions than hydrodenitrogenation (HDN). Several investigators have tested model compounds to determine step

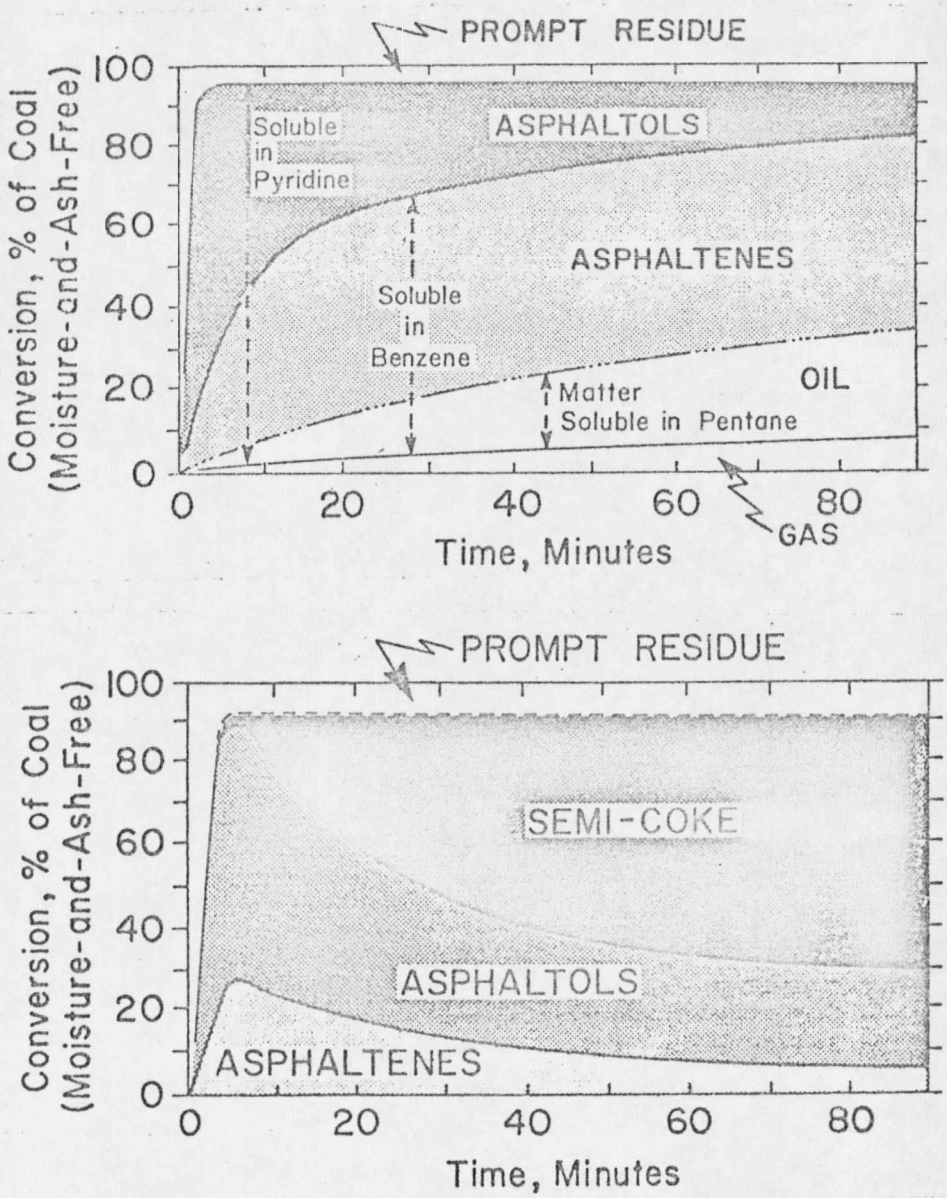


Fig. 4. Conversion of Bituminous Coal with Rapid Heating at 400°C.

Top - in Tetralin
Bottom - in Naphthalene

sequences in sulfur removal from aromatics; they conclude aromatic ring saturation is not necessary for C-S bond breaking (10, 16).

Some thermal removal of sulfur occurs. Desulfurization was observed for coal oils passed over inert support beds from 316-427°C, though no nitrogen removal occurred (17,18).

Denitrogenation Reaction Steps - Aromatic nitrogen is removed in three steps:

1) Equilibrium hydrogenation of the nitrogen-containing ring to hydroaromatic structure.

2) Cracking of ring, with nitrogen becoming an $-NH_2$.

3) Elimination of amine group as ammonia, NH_3.

The second step, breaking the hydroaromatic ring, is the rate-determining step (10,19).

Difficulty of nitrogen removal increases as the number of rings in a compound increases. University of Delaware found denitrogenation of 3-ring compounds was slow compared to quinoline, though hydrogenation of the outer rings was still rapid (19). Oklahoma State University researchers likewise found "real" liquefied coals much harder to treat than a model raw anthracene oil (18).

Cracking Reactions - The goal of coal hydrocracking is to selectively crack the coal structure with a minimum consumptiom of hydrogen. Hydrogen generation is an expensive part of current coal liquid technology. "The function of hydrogen is to 'heal' those carbon

bonds involved in a C-C bond scission and also to form NH_3 and H_2S for heteroatom removal" (10).

Polynuclear compounds are cracked by first hydrogenating one of the rings, then cracking it. "The hydroaromatic structure most favorable for hydrocracking rather than hydrogenation is that in which the nonaromatic ring is fully saturated and in which hydrogenation causes loss of an aromatic ring. Least favored is a nonaromatic ring which has a double bond" (20, 10).

By thermodynamics, cracked products are more favored than hydrogenation products at temperatures above 350°C. But the rates for hydrogenation products are greater. Activation energies of the hydrogenation step are very low, but activation energies for cracking steps are between 20 and 35 kcl/mole (19,20).

Coking occurs when cracked products react irreversibly to high molecular weight, unreactive solid compounds. Coking is undesirable since it reduces liquid product yield and plugs or deactivates catalyst.

Hydrogen-to-carbon ratios of cokes are lower than of the coke precursors. "Pyrolysis coking reactions are not simple polymerizations, as hydrogen is eliminated" (10). Also, activation energy of condensation reactions is usually larger than for cracking reactions. Two possible approaches may avoid coking: using low temperatures to minimize thermal free radicals; and quenching the radicals formed by hydrogen donor or supercritical catalysis (10).

Other structure and composition factors influence coking. Unsubstituted aromatics coke less than substituted ones, possibly because "Thermal free-radicals are involved in the coking-condensation reaction" (10).

Substitution of a nitrogen atom in a polynuclear aromatic increased the coking rate by 10 times in thermal pyrolysis. Also position of the nitrogen in the ring affects the rate.

Gas and liquid phase reactions differ also (10). Anthracene pyrolyzes more easily in liquid phase than vapor. Phenyl radicals act differently too. In solution, phenyl radicals add to aromatics, leading to coking; in gas they capture a hydrogen atom from a substituted methyl group.

Effects of Variables on Conversion and Sulfur-Nitrogen Removal

Solvent - "The use of condensed compounds having aromatic and hydroaromatic or hydroaromatic and phenol rings increases the liquefaction of coal" (8). The Pott-Broche solvent extraction of coal process was operated in Germany during the 1930's and 1940's; the solvent was 20% cresol - 80% tetralin, at a 2:1 solvent-to-coal ratio. The solution theory was that coal depolymerizes under the influence of cresol and heat; the loosely bound hydrogens from the tetralin (1,2,3,4 tetrahydronaphthalene) are easily given up to stabilize the polymer radicals. Most current coal solvent-refining and liquid phase hydrogenation processes use middle fractions from the process as a recycle solvent. Recycle solvent composition is both similar to coal fragments and cheaper than tetralin.

Solvent nature affects liquid coal conversion and product distribution. Though coal rapidly breaks into fragment molecules regardless of the nature of the solvent, subsequent slower stabilization reactions depend on solvent nature (4). Some factors correlate with coal dissolution activity:

- relative ease of reaction with a typical free radical, CCl_3 (20)
- non-polar solubility parameter of the solvent (21)
- penetration of coal fragments by solvent (20).

Conversion, product distribution, and diffusion resistances vary with solvent-to-coal ratio. University of North Dakota researchers found hydrotreatment of solvent-refined lignite gave highest conversions

in a 1:1 ratio with tetralin. Conversion decreased for an increase or decrease from that ratio. By NMR analysis, the aromatic/aliphatic proton ratio of products increased as solvent ratio decreased; product in which no solvent was used had the highest aromatic/aliphatic ratio (22).

Viscosity of a SRC-solvent solution is very dependent on the SRC concentration in the 30-50% range. Kinematic viscosisty varies from 4 to 20 to 150 centistokes for concentrations of 30, 40, and 50%, respectively (23).

The use of supercritical solvent media for coal dissolution and reaction is an attractive alternate to traditional polyaromatic solvents. Supercritical fluids are characterized by high solvating power, high heat capacities, higher diffusivities than liquids, and high heat transfer properties (10).

Stanford Research Institute (20) conducted supercritical coal dissolution using a variety of common liquids. Thermal and chemical changes of the coal were observed, not a dissolution of unchanged coal. That agrees with the model of coal dissolution Squires proposed (4).

Nearly all the supercritical fluids gave a thermal effect--some of the coal was changed from pyridine-insoluble material to pyridine-soluble. Secondary alcohols gave a chemical effect over and above the thermal effect, similar to tetralin--significantly more coal product was changed to pyridine-soluble material. Isopropyl alcohol and tetralin each converted about 50% of the coal to pyridine-

solubles in reaction at 335°C, 90 minutes, and 1000 psig of either N_2 or H_2.

The best conversion was obtained when a catalytic amount of potassium isopropoxide was added to isopropyl alcohol. The coal product was 97% soluble in pyridine; sulfur content was reduced from 2.2% to 0.4% (20). Neither methanol nor t-butanol exhibited the same effects as isopropyl alcohol or secondary butanol. It is postulated that "some chemical action by the solvent, such as hydride donation, is increasing the dissolution capacity"(20).

Important to note is that experiments showed the thermal change effect was not dependent on attaining the supercritical state. Also, though pyridine solubility of the coal is affected, "no major fraction of the coal is extracted by supercritical isopropanol, benzene, or methanol under (the reaction) conditions" (20).

Hydrogen Effects - Although the presence of H_2 is not needed for the rapid thermal first-step reactions in Squires model (4), hydrogen is useful in the second-step slower reactions. Solvent-refined coal processes find "solvation (of coal) increases under hydrogen pressure due to partial hydrogenation" (8). PAMCO's solvent-refined coal bench-scale work found that "solvent efficiency declined as it was reused in the absence of H_2 ... (the decline) was attributed to a transfer of H_2 from the solvent to the coal during the solution process" (8). Several other solvent processes hydrogenate the solvent separately from

the solution process, but "satisfactory results are obtained by adding H_2 directly to the dissolver" (8).

In hydrotreating SRC filtrate under severe conditions, deRosset found hydrogen consumption was 2500-3000 SCF/bbl (23). He also concluded from his data that hydrogenation was equilibrium limited, but cracking was kinetically limited (24). During Consolidated Coal's 1963-1968 work with coal liquefaction in molten salts, rate constants for convertible fractions of coal were independent of pressure (26). Also, variation in H_2 flow rates may have little effect. Rate changes from 8 to 12 MSCF/bbl during hydrogenation of COED tar over a fixed bed had no significant effect (27).

Presence of gaseous hydrogen enhances desulfurization and denitrogenation of coal liquids (10, 18). During denitrogenation of quinoline, a model compound for nitrogen removal from coal studies, hydrogenation steps exhibited a positive order with respect to H_2 pressure; cracking steps show a negative or zero order for H_2 pressure (16).

Hydrogen gas generated in situ is more active for some coal forms than others. ERDA's COSTEAM process makes hydrogen during liquefaction by reaction of carbon monoxide and water; the COSTEAM process works better with lignite and low rank materials than with bituminous coal.

Temperature Effects - Temperature affects gas production, coking, heteroatom removal, and cracking in coal liquefaction

processes. In PAMCO's SRC process, "degree of solution is primarily dependent on temperature and liquid residence time" (8). In addition, coke formation was observed above 440°C.

Generally, an increase in temperature at a given pressure will increase the gas fraction of total conversion products (28). In lignite liquefaction, total conversion increases approximately linearly with temperature from 375°-450°C, but the gas fraction increases much more than the liquid (22). At a given pressure, gas formation was 50% less at 400°C than at 450°C for hydrogenation of solvent-refined lignite. More middle oils and heavy ends were formed at 400°C: "Heavy liquids are favored at the expense of the gases" (29). Hiteshue (28) notes liquid conversion is usually not increased above 450°C.

Nitrogen removal from coal liquids usually requires higher temperatures than sulfur removal. Denitrogenation of the model compound quinoline increased more from 342 to 363°C than from 325-342°C (19). Both sulfur and nitrogen removal usually increase with temperature of reaction.

Pressure Effects - An increase in pressure at a given temperature will generally not change the gas conversion, but the liquid conversion usually increases (28,29). However, batch hydrogenation of solvent-refined lignite on Harshaw HT-400 cobalt molybdate was found to yield more liquid product at 1750 psig initial cold pressure than at 2500 psig or 1000 psig (29).

The highest pressures at a given temperature were found to yield the lowest amounts of vacuum bottoms for hydrogenation of solvent-refined lignite (29).

Heteroatom removal increased for coal model compounds or mixtures as pressure increased. Sulfur and nitrogen removal increased with pressure for raw anthracene oil at 700°F and low space velocities over catalyst (30). Nitrogen removal from quinoline increased with pressure up to 1500 psig, above which removal leveled off (31).

Hydrogen Sulfide and Other Effects - The presence of small amounts of H_2S promotes denitrogenation of coal liquids; in addition it does not inhibit hydrodesulfurization until it reaches 2-3% mole concentration. H_2S enhances hydrodenitrogenation (HDN) over a heterogeneous metal catalyst in two ways:

1) Sulfided metal catalysts are more active than the oxide form for HDN.
2) H_2S helps the hydrocracking activity of the catalyst (10).

Since sulfur is removed as H_2S, sulfur in a feedstock doesn't inhibit HDN; however, high nitrogen concentration in a feed inhibits hydrodesulfurization (10, 18).

Both sulfur and nitrogen removal reactions proceed by first-order kinectics with the concentration of each type of compound (16, 17).

The lowest liquid hourly space velocities, LHSV, generally give the best reported liquid conversions and HDN. Best results were obtained by deRosset for SRC at the most severe conditions: 450°C,

LHSV=$\frac{1}{4}$, and 3000 psig H_2 over 200 ml of catalyst (24). Raw anthracene oil showed increased nitrogen removal as LHSV decreased at appropriate temperatures (18).

Coal rank influences liquefaction results. In the German plants, the types of coal used determined the severity of the operating conditions. Brown coal could be hydrogenated at much lower pressure than harder coal (3).

Finally, beneficiation of coal affects catalytic coal conversions (32). Unbeneficiated coal reacts best: this is probably due to catalytic FeS in the rock and ash mixed with the coal.

CATALYSIS

Catalysts are important in coal hydrotreating. Catalysts work by allowing alternate mechanism paths for hydrocracking, hydrogenation, and heteroatom removal reactions; the alternate paths have lower activation energies than uncatalyzed paths, so catalysts increase reaction rates.

Hydrocracking catalysts must be dual functional. They must both crack high molecular weight hydrocarbons and hydrogenate the unsaturates (coke precursor) formed (33,35).

Factors in Catalyst Activity, Selectivity, and Activity Maintenance - Heterogeneous catalysts, most often used in hydrotreating, are affected by support type and structure, metal loading, surface acidity, surface area, pore size, plugging, and poisons.

Alumina or silica-alumina with or without alkaline and rare earth promoters are often used for hydrocracking catalyst supports. Supports often determine cracking, and loaded metals affect hydrogenation (31). Typical catalyst metals used for hydrogenolysis are listed in Table II (10).

Table II. Typical Hydrogenolysis Metals

Breaking of Bond Type	Metal						
C-C	Group VIII	Re	W	Mo			
C-N	"	"	"	"	"	Cu	
C-O	"	"	"	"	"	"	Ag
C-S	"	"	"	"	"	"	"

Heterogeneous catalysts are usually sulfided (treated with H_2S) to be most active. Sulfides of tungsten, molybdenum, cobalt, and nickel are more active on supports than their oxides. This is fortunate since most metal catalysts go to sulfides in a 1% sulfur reactant concentration (10).

Surface acidity of a catalyst is important. Catalyst work done in Germany "led to the conclusion catalysts on basic supports were suitable for ... prehydrogenation reactions, while those with acidic support are preferred as splitting catalysts" (34). It has been recently found that preferred center ring cracking of phenanthrene is possible with a Cr_2O_3 - Al_2O_3 catalyst with low acidic strength. "Therefore, controlled acidity may be an approach to enhancing the selectivity of center ring cracking reactions" (10).

Strongly acidic catalysts for the petroleum industry are "extremely sensitive to nitrogenous poisons; therefore, it appears desirable to provide a support that contains a large number of only moderately acidic sites" (35). Studies in upgrading SRC found that acidity of the catalyst surface also affected carbon deposition (10). Desulfurization activity is influenced by acidity also -- "hydrogenation reactions occur on strongly electrophilic sites, while desulfurization occurs on weakly electrophilic sites" (10).

High surface area is important to coal product catalysts, as found by Montana State University (36), and University of North Dakota (37). In a series of in-house catalyst supports impregnated with Ni-Mo

at the University of North Dakota, activities per unit of surface area were highest for catalysts containing TiO_2 (α and β); but a commercial Ni-Mo catalyst on alumina had much higher surface area and better overall activity (37).

Pore size constraints limit heterogeneous catalysts. Asphaltene molecules are reported to be 40-50 A^o, big enough to plug small pores (10). Engelhard Industries (35) is testing catalysts on 100 A^o supports; Weller found 200 A^o pore size to be optimum in his coal treatment work (38); Exxon got the best asphaltene removal with catalysts in the 200-350 A^o range, as compared with 60-80 A^o and 40 A^o (39). Although zeolites held hope as catalysts because of their superior resistance to NH_3 and H_2S (10), their pore size of 5-13 A^o (33) is probably too small.

Heterogenous catalysts suffer activity degradation from both poisoning and fouling. Sulfur and nitrogen poison some catalysts when present above part per million concentrations; sulfur usually hurts hydrogenation components and nitrogen hurts the cracking components (33). Catalyst deactivation has been noted for processing SRC, Synthoil, and COED tar, all which contain sulfur and nitrogen at about 1% concentration.

Easily sulfur-poisoned catalysts include platinum and palladium; sulfur-resistant catalysts are molybdenum, tungsten, iron, nickel-molybdenum, and nickel-tungsten (40). Nitrogen also causes irreversible activity loss for platinum on silica-alumina (33).

Alkali salts and titanium compounds are poisons in coal processing. For example, sodium ions cause irreversible surface area loss during catalyst regeneration; TiO_2 deposition on silica-alumina increases surface acidity (10).

Fouling results from either coke formation or trace contaminants covering catalyst reaction surfaces. Metals, ash, and asphaltenes may all contribute to catalyst degradation as observed in SRC upgrading (10,24).

Homogeneous catalysts, molten salts, and supercritical catalysis are suggested as more effective in avoiding mass transfer limitations of three-phase heterogeneous catalysis.

Lewis acid-type compounds are usually good homogeneous catalysts: these include metal halides, especially chlorides. Zinc chloride is being used for coal liquefaction research in both small and large coal-to-catalyst ratios. Catalyst recovery and corrosive properties of chlorides are two restraining factors in metal chloride use. Zinc chloride reacts with H_2S and NH_3 during liquefaction reactions, but current processes have been developed for 99.9% catalyst recovery (3, 8, 26).

Much work is continuing in heterogeneous and homogeneous catalysis of coal conversion. Good sources include Rapoport (40), Stanford Research Institute (20), University of North Dakota (29), Conoco Coal Development (26), Hiteshue (28), Englehard Industries (35), Montana State University (36), and patents by Mobil Oil (41), Exxon (39),

Universal Oil Products (42), and Atlantic Richfield (43).

Given any one particular catalyst system, diffusion processes may be rate-determining. The paths for reaction using heterogeneous catalysts are as follows:

1. Diffusion of reactants to catalyst exterior
2. Diffusion of reactants in pores
3. Adsorption on catalyst surface
4. Reaction
5. Desorption of products
6. Diffusion out of pores
7. Diffusion away from catalyst exterior.

Film diffusion resistance can be decreased by increasing the reactant mass flow rate past the catalyst particle; pore diffusion resistance is decreased by using smaller catalyst particles having less pore length.

Film diffusion is tested by making two series of runs, each at a different constant weight, W, of catalyst. The liquid feed rate, F, is varied in each series of runs. Conversion is plotted versus W/F. If the curves coincide, film diffusion is not rate-controlling.

Pore diffusion is tested by making two runs at the same catalyst charge, but using different size pellets. The same conversion at a constant weight of catalyst/feed rate ratio, W/F, means pore diffusion is not rate controlling. If pore resistance is controlling, then the conversion will increase with decreasing pellet size (44).

MATERIALS, EQUIPMENT, AND PROCEDURES

Coal Composition

Two 10-gallon cans of solid Solvent-Refined Coal were received from Pittsburgh and Midway Mining Company's Ft. Lewis pilot plant. It is Sample 110, taken June 13, 1975.

The coal type used to make the SRC was Kentucky #9 from the Colonial Mine. The coal is washed and sized at the mine; the size used is $\frac{3}{4}$" x 0 dried to $< 1\%$ moisture before use. The 1975 yearly average proximate and ultimate analyses as received are listed in Table 3.

Table 3. Coal Analyses to SRC Process

Proximate wt. percent as received		
Moisture	2.25	
Ash	10.50	
Volatiles	36.75	
Fixed Carbon	50.50	
Ultimate wt. percent as received		
Moisture	2.25	
C	70.10	
H	4.89	
N	1.37	
S	3.51	
Cl	0.04	
Ash	10.50	
O	7.34	by difference

SRC Composition

The ultimate analysis of the SRC sample as reported by PAMCO is given below in Table 4 .

Table 4. SRC Ultimate Analysis

C	87.33%
H	5.60%
N	2.28%
S	0.68%
O	4.11%
Ash	0.33%

No complete compound analysis is available in the literature for Solvent-Refined Coal.

Coal-derived liquids are known for their large number of compounds present, none of which usually exceeds 2% concentration. Table 5 lists compounds in the product from Union Carbide coal hydrogenation process of the 1940's and 1950's.

Most current coal products are characterized by types of solubility fractions. A.J. de Rosset of UOP characterized an SRC sample as follows (25):

C_7 insol.	89.4%
Benzene insol.	34.7%
DMF/Xylene insol.	0.15%
Ash content	0.11%

Table 5. Typical Compounds in a Coal-Derived Liquid (13)

Aromatic Indane and Hydroaromatic:
- Tetrahydronaphthalene
- Naphthalene
- 1-Methylnaphthalene
- 2-Methylnaphthalene
- 2,3-Dimethylnaphthalene
- 2,6-Dimethylnaphthalene
- 2,7-Dimethylnaphthalene
- Acenaphthene
- Diphenyl
- Fluorene
- 9,10-Dihydroanthracene
- Anthracene
- Phenanthrene

and the following bases:
- Pyrrole
- Pyridine
- 2-Methylpyridine
- 3-Methylpyridine
- 4-Methylpyridine
- 2-Ethylpyridine
- 3-Ethylpyridine
- 4-Ethylpyridine
- 2-Methyl-6-ethylpyridine
- 3-Methyl-6-ethylpyridine
- 4-Methyl-2-ethylpyridine
- 2,3,4-Trimethylpyridine
- 2,3,5-Trimethylpyridine
- 2,3,6-Trimethylpyridine
- 2,4,5-Trimethylpyridine
- 2,4,6-Trimethylpyridine
- Aniline
- 2-Methylaniline
- 3-Methylaniline
- 4-Methylaniline
- 2-Ethylaniline
- 2,3-Dimethylaniline
- 2,4-Dimethylaniline

Aromatic and Hydroaromatic continued:
- Chrysene
- Perylene
- Picene

Aliphatic:
- n-Undecane
- n-Dodecane
- n-Tridecane
- n-Heptadecane

Heterocyclic:
- Dibenzofuran
- Benzothiophene
- Dibenzothiophene
- 2,3-Dimethylpyridine
- 2,4-Dimethylpyridine
- 2,5-Dimethylpyridine
- 2,6-Dimethylpyridine
- 3,4-Dimethylpyridine
- 3,5-Dimethylpyridine
- 2-n-Propylpyridine
- 2-Methyl-4-ethylpyridine
- 2,5-Dimethylaniline
- 3,4-Dimethylaniline
- 3,5-Dimethylaniline
- 1-Naphthylamine
- 2-Naphthylamine
- Indole
- 2-Methylindole
- 3-Methylindole
- Carbazole
- Quinoline
- 2-Methylquinoline
- 7-Methylquinoline
- Isoquinoline
- 1-Methylisoquinoline
- 3-Methylisoquinoline

Mobil Oil(13) used gradient elution chromotography to characterize SRC into 13 different fractions. Table 7 gives and explains a characterization of a Wilsonville, Alabama SRC.

Solvent Composition

The solvent used in the project is one formerly used by Mobil Oil researchers (4). The composition was chosen due to its approximation of a recycle solvent which would be used in an SRC process.

Table 6. Solvent Composition (4)

43% tetralin
38% methyl naphthalene
17% m-p Cresol
2% gamma picoline

Contains .36% S and .59% N

Feed to the Continuous Reactor

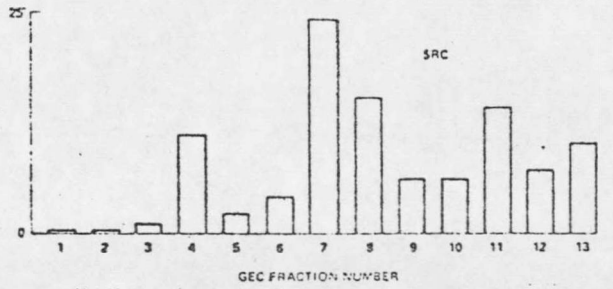
The SRC solution feed to the continuous reactor was prepared by pressure-temperature treatment in batch autoclaves. A 1.5:1 solvent-to-SRC charge was pressured to 2000 psig H_2 initially, heated to 400^{o}C and held there for one-half hour. The bomb was air cooled for 8 hours, depressurized and emptied of solution.

Table 7. Description, Concentration, and Makeup of Mobil's GEC Fraction Analysis of SRC

GEC fraction	Description
1. Saturates	Colorless oil or white wax, melting slightly above room temperature. Very soluble in paraffinic solvents.
2. MNA–DNA oil	Very light yellow heavy oil, sometimes with waxy solids, easily melted. Very soluble in aromatic solvents.
3. PNA oil	Bright yellow-orange oil.
4. PNA soft resin	Usually a tacky orange-red semisolid, slow to turn fluid at elevated temperature, but pours readily at 200 °F.
5. Hard resin	Red-brown powders which turn tacky slightly above 100 °F. Extremely viscous liquids at 240 °F.
6. Polar resin	
7. Eluted asphaltenes	Dark brown powder. Behavior intermediate between resins and polar asphaltenes. Very soluble in methylene chloride.
8–12. Polar asphaltenes	Black powder, very friable. Very high softening point. Poorly soluble in methylene chloride, very soluble in THF.
13. Noneluted	Among others, can be strongly acidic components (carboxylic acids), inorganic solids (carbon, catalysts fines, etc.).

	Concn in GEC fraction (wt %)			
Hydrocarbon type	Satu-rate	MNA–DNA	PNA oils	PNA soft resin
Paraffins	37.9	0.0	0.0	0.0
Olefins	*a*	*b*	*b*	*b*
Naphthenes	61.0	0.0	0.0	0.0
Monoaromatics	1.1	44.7	7.7	9.6
Diaromatics	0.0	25.4	59.8	11.4
Triaromatics	0.0	9.1	15.5	15.7
Tetraaromatics	0.0	0.5	8.3	27.1
Pentaaromatics	0.0	7.2	4.2	18.2
Aromatic sulfur compounds	0.0	5.5	2.6	9.8
Unidentified aromatics	0.0	7.6	1.9	8.2
Total	100.0	100.0	100.0	100.0

a Insufficient sample. *b* Analysis not applicable.



Presulfiding Reactor

Commerical catalysts are dried at 100°C for a day, then sulfided. Sulfiding the catalysts increases cracking and denitrogenation activity.

The sulfiding reactor is a two foot long one inch I.D. steel pipe, with a quarter inch thermowell extending a foot into it.

The pipe is loaded with one-fourth inch inert alumina support spheres, then catalyst, then more inert spheres.

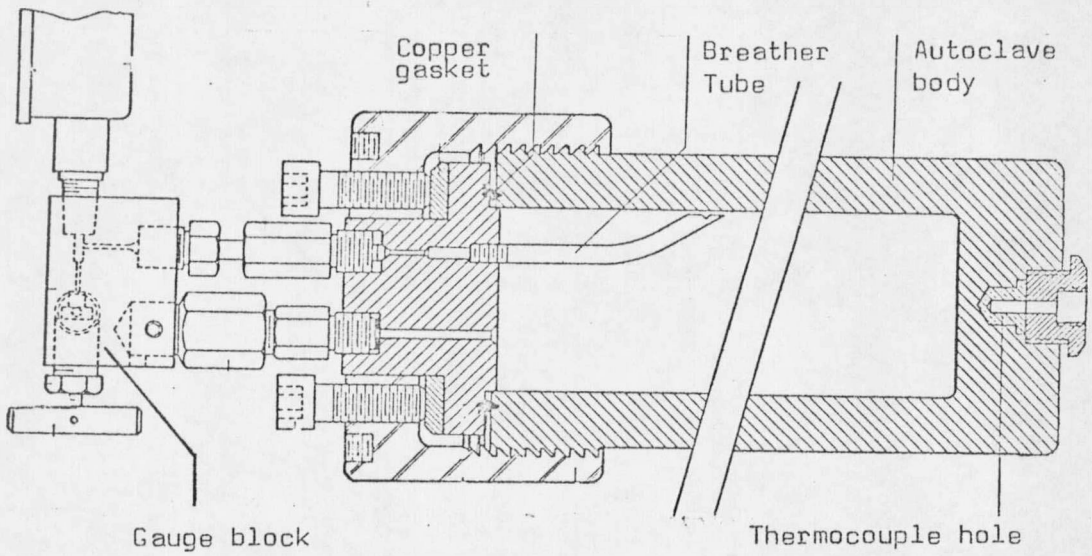
A mixture of hydrogen and 5-10% hydrogen sulfide flows through the reactor for twelve hours at 350°C and atmospheric pressure. The outgas is scrubbed with water and sodium hydroxide. The temperature is maintained with a controller and electric pipe heater. The catalyst is cooled with continued gas flow. Sulfided catalysts are stored in sealed jars to prevent exposure to air and water.

Rocking Bomb Reactor

A Parr series 4000 pressure reaction apparatus was used to make batch runs (46). Details of the heater and bomb are shown in Figure 5.

The Parr bomb was charged with solvent, solid SRC, and catalyst. Twenty ml. of heterogeneous catalyst or 10 ml. of powders and salts were used.

A pressure head and copper gasket fit on the top of the bomb. An eight-bolt screw cap secured the head; a pressure gauge block was connected to the head.



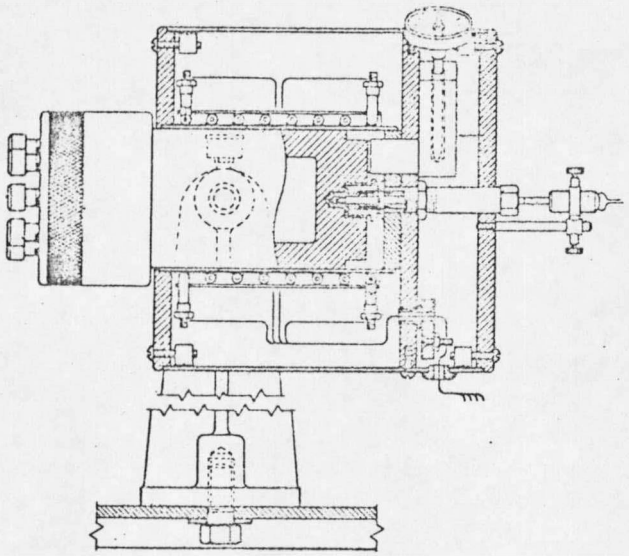


Figure 5. Autoclave and Heater

The bomb was pressurized with hydrogen to about 2000 psig with a Haskel gas compressor (47). If no leaks appeared in five minutes, the bomb was placed in the rocker-heater. A bolt screwed through the heater base and into the bomb bottom secured it. An iron-constantan thermocouple was inserted into a hole of the securing bolt.

The electric drive rocker was started; heat input was controlled with a Powerstat variable transformer; temperature was graphed by a Honeywell temperature recorder.

Initial runs were conducted for one-half hour at 415-420^{o}C. Subsequent runs were at 435-445^{o}C since no coking was observed. About 50 minutes heat-up were required to reach run temperature.

After the run, the bomb cooled in air to room temperature. Gas pressure was bled off gradually over 10 minutes to minimize loss of liquid product. Products were stored in glass bottles until analyses were performed.

Continuous Reactor

The reactor system is shown in Figure 6.

The reactor is a one-inch O.D. three-foot long Inconel pipe. It is packed with a section of inert Norton Denstone support in the top section; the mid section holds a 50-50 mix of active catalyst and inert support; the bottom section is filled with inert support. A 1/4" stainless steel thermowell extends from the top down through the packed catalyst and support.

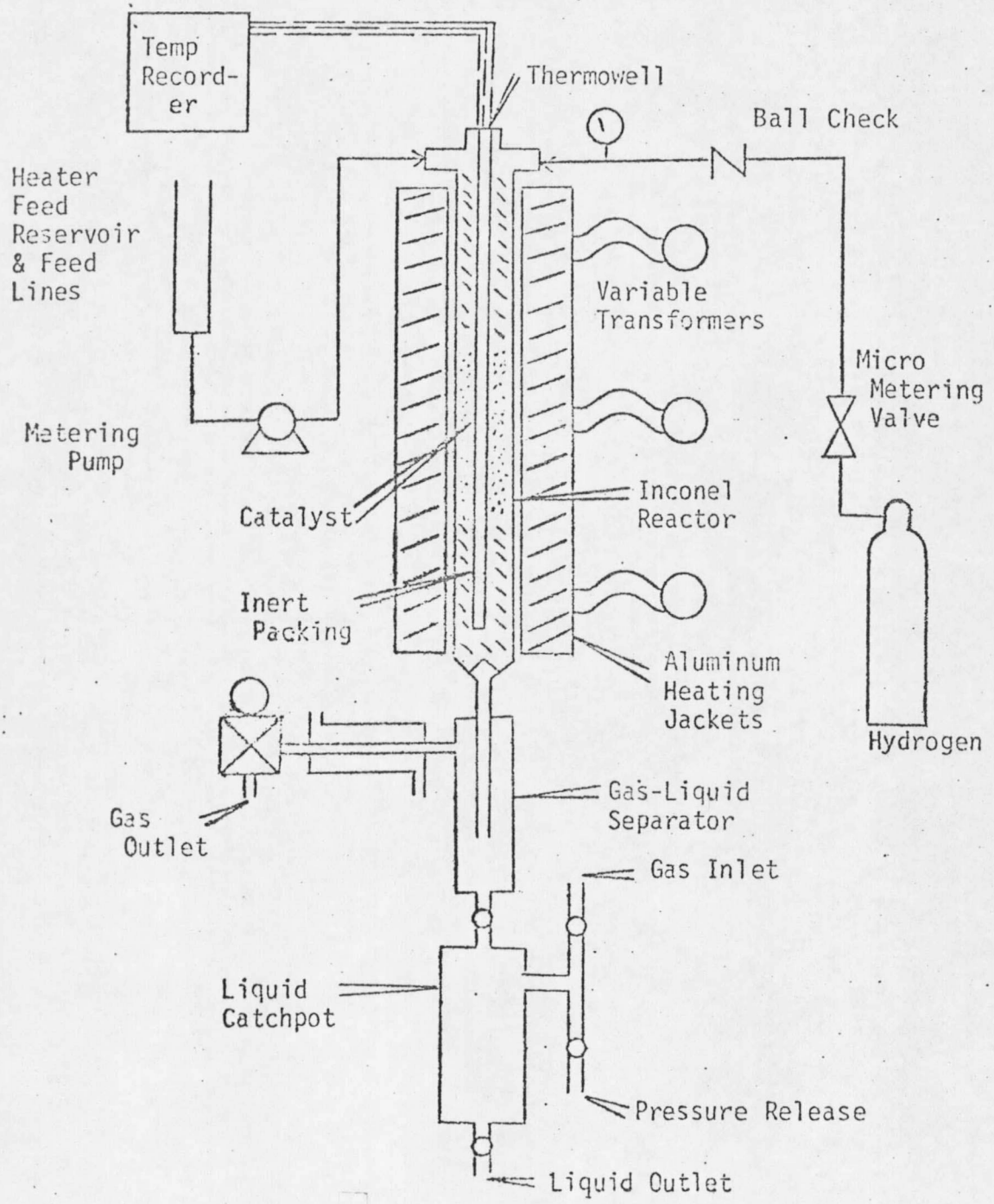


FIGURE 6. Continuous Reactor

The reactor pipe fits in an aluminum block, which facilitates isothermal operation. Three nichrome heating wires wrapped around the block are controlled by manual variable transformers. A sheet metal container with zonolite insulation inside encloses the aluminum block.

Three chrome-alumel thermocouples in the thermowell monitor the top, middle, and bottom parts of the active catalyst section; the thermocouples are connected to a Leeds and Northrup temperature recorder.

Technical grade hydrogen flows through a Nupro metering valve, a ball check valve, and past a pressure gauge into the top of the reactor.

A solution of solvent-refined coal is pumped from a glass reservoir through 1/8" stainless steel tubing and into the reactor by a Hills-McCanna chemical proportioning pump. The reservoir, tubing, and pump are all electrically heated to prevent the feedstock from plugging lines or pump check valves.

The SRC solution and hydrogen flow downward through the catalyst bed and into the gas-liquid separator. Gases pass through the Grove back-pressure regulator, are scrubbed, and vented into a hood. Liquids drop down into the liquid catchpot.

To empty the catchpot, the valve between the gas-liquid separator and catchpot is closed. Pressure is let down through the pressure release valve and product is collected from the bottom of the

catchpot. After the product dump, the catchpot is re-pressurized with nitrogen through the gas inlet valve. The valve between the separator and the catchpot is re-opened, with no disruption of system pressure. The cycle is repeated for ecery liquid sample.

Continuous Runs

The following describes the best procedure developed during the project. One preliminary run had minor differences in catalyst amount and thermocouple placement, but the rest of the continuous runs were conducted as outlined here.

A rule of thumb is that 100 ml. of small pellets fill 9½-10" of reactor with the thermowell in place. The reactor was filled as follows:

1/4" spheres inert Norton Denstone support	15 ml.	13.5" preheat section
1/8" extrusions inert Norton Denstone support	120 ml.	
50-50 mix of catalyst and inert Denstone (70 ml. active catalyst)	140 ml.	14" reaction section
1/8" inert Denstone	80 ml.	8"
Rest was filled with 1/4" spheres and steel screen to hold packing material in place		

Thermocouples were placed in the thermowell to measure temperatures in three parts of the reactor. The first was 10¾" into

the packed material (near the bottom of the preheat section). The second was 20 1/4" into the bed (center of the reaction section). The third was 28 1/4" into the bed (just below end of reaction section).

The reactor was placed in the aluminum block. Feed lines and product separation and collection pieces were connected; the whole system was pressurized and tested for leaks.

The reactor was heated to steady state temperature in about 8 hours. Power input was manually controlled with three Powerstat variable transformers and indicated by three ampmeters. The Leeds and Northrup temperature recorder printed bed temperatures during a four-minute cycle.

Hydrogen flow to the reactor was controlled by a micro-metering valve. Experience showed that calibration of the micro-metering valve is unreliable. A chromatographic analysis attempt of off-gases from similar reactors at Montana State University found the off-gas to be overwhelmingly hydrogen. Therefore, a wet test meter was connected after the off-gas scrubber to measure the hydrogen flow rate.

After the hydrogen rate was set, pumping of the SRC solution was begun. Flow was measured by the level in a graduated glass reservoir. Hydrogen and liquid flow rates were checked every 20 minutes since both tended to fluctuate. Flows could usually be controlled to $\pm$ 10% of the desired hydrogen-to-oil ratio.

Once both flow rates and temperature were steadied out, the reactor was operated at constant conditions for at least 90 minutes before the first sample period began.

When operating parameters were changed, a 60 minute transition period at constant conditions was allowed. Transition period products were cleared from catchpot before sample period collection began. Each sample product was about 80 to 100 ml.

Potential plugging of the reactor system required continuous monitoring; runs lasted from twelve to twenty hours, with four to nine sample products per run.

After the run, feedstock solution, hydrogen, and power input were halted. Motor oil was pumped through the system to help clean lines and loosen reactor packing.

The feed lines and bottom collection pieces were disconnected from the reactor; the reactor was removed from the block while still hot. The thermowell must be pulled while the reactor is hot, otherwise it and the packing usually become stuck and the pipe must be drilled out.

Acetone is pumped through the reservoir and lines to clear them. All pieces from the reservoir to the outlet side of the pump are dismantled and cleaned if necessary. The reactor pipe, separator, and catchpot are cleaned with acetone; the back pressure regulator is dismantled and cleaned.

Analytical Procedures

Products from the batch and continuous runs were analyzed to determine the degree of cracking, denitrogenation, and desulfurization.

Water in the sample interfered with the distillation analysis, so Drierite (anhyhdrous $CaSO_4$) was used. The only effective method was to directly add $\frac{1}{2}$ teaspoon of Drierite to 100 ml. samples in sealed jars.

An indication of cracking was determined by ASTM atmospheric distillation method D-86 (48). This method determines the amounts of distillables at temperatures between 70 and 700°F. Comparison of feed and product distillation curves of percent distilled vs. temperature allows calculation of cracking.

Weight percent sulfur in the samples is determined by the quartz-tube combustion method, ASTM method D1551 (49, 50). Samples from metal chloride catalyst runs had hydrogen chloride interference of titration measurement in ASTM D1551. A gravimetric procedure which precipitated the sulfate using barium chloride was used for those samples (51).

Weight percent nitrogen in samples was determined by the Macro Kjeldahl method, ASTM E 258 (52, 53).

Chromatographic analysis of continuous reactor off-gas has not been successfully done.

RESULTS AND DISCUSSION

The object of the experiments was to catalytically convert PAMCO's Solvent-Refined Coal (SRC) to clean distillate fuels. Available commercial catalysts were first tested, then catalysts prepared here at Montana State University.

Liquid conversion was measured by distillation of products up to 700°F; sulfur content of the products was determined by the quartz tube combustion method; nitrogen content was determined by the Macro Kjeldahl method.

Twenty-eight catalysts were used in thirty-two batch runs; five catalysts were used in five continuous runs. The effects of temperature, residence time (in terms of liquid hourly space velocity), and hydrogen-to-oil ratio were investigated in the continuous runs of the trickle bed reactor.

Metal loading, support, surface area, and pore volume data available on the catalysts tested are listed in Appendix A. Conversion, heteroatom removal, and run conditions for each batch test are listed in Appendix B. Appendix C contains conversions, heteroatom removal, and run conditions for all continuous runs.

Preliminary Runs

Feed Solution - PAMCO's Solvent-Refined Coal is a dark, shiny solid at room temperature; only 3% of it will boil off up to 650°F (13). Such a solid couldn't be easily pumped into a continuous reactor, so a solvent vehicle was used.

A suitable solvent for coal work was suggested at the 1975 ERDA University Contractors Conference. It is described in Materials, Equipment and Procedures.

The use of as little solvent as possible made elevated temperatures necessary. To retain the nitrogen compound characteristics of a coal oil solvent, the solvent could not be heated past 120°C at atmospheric pressure, where the most volatile component, gamma picoline, starts boiling off. SRC will dissolve in a 7:2 solvent-to-coal weight ratio in the synthetic coal oil solvent at 110°C. This solution was picked as the feedstock. The reservoir, pump, valves and lines of the continuous apparatus were modified with electrical heating tapes to handle the hot solution.

Analytical Definitions - Liquid conversion data was obtained by comparing catalytically-treated product with the original 7:2 solution. Distillation of the 7:2 coal solution showed that 79% of it boils below 475°F; the remaining 21% of non-distillates decomposes above 475°F.

Distillation of the synthetic coal oil solvent alone showed 98% distills below 470°F; 2% decomposes above 470°F. Since essentially all the solvent boils below 700°F, but very little solid SRC distills below 700°F, liquid conversions for the project were defined as follows:

$$\text{liquid conversion} = \frac{\%\text{ total distillate in product} - \%\text{ total distillate in feed}}{\%\text{ non-distillate in feed}}$$

Liquid conversion is the percentage amount of non-distillate that becomes distillate. If no increase of distillate is noted in the product, the conversion is zero. If the total distillate becomes 100%, the liquid conversion is 100%.

Percent desulfurization is defined as follows:

$$\%\text{ de-S} = \frac{\%\text{ sulfur in product} - \%\text{ sulfur in feed}}{\%\text{ sulfur in feed}}$$

Denitrogenation is defined in the same manner. The 7:2 coal solution was 0.43% sulfur and 0.965 % nitrogen.

Preliminary Continuous Run - The first continuous run series was made at 450°C, 1000 psig, 100 ml. of Ni-4401 nickel tungsten catalyst, and hydrogen flow of 10,000 SCF/bbl oil. The distillation of the product is compared to the distillation of the 7:2 solution feed in Figure 7. Product 1, displayed on the distillation graph, was obtained at a liquid hourly space velocity (LHSV) of 2.

The distillation curves of product 1 and the 7:2 solution feed are graphed with temperature versus volume percent distillate collected. Eighty-one and a half percent of the product distilled below 700°F. The liquid conversion

$$= \frac{81.5\% \text{ (product distillates)} - 79\% \text{ (solution feed distillate)}}{21\% \text{ (solution feed non-distillates)}}$$

$= 12\%$.

For Product 2, LHSV was changed to $\frac{3}{4}$ and all other conditions remained the same as for Product 1. The reactor never reached steady state operation. The gas rate surged the entire period and did not settle to a steady value. The run was halted and cleaning attempted by pumping straight solvent. The reactor plugged abruptly and pressure rose rapidly. The entire system was shut down and allowed to cool. Later examination found a hard carbon block had set up in the reactor pipe.

Several important conclusions could be made about the run:

1) Modification of the reactor system had to be made. Outlet liquids and gases both passed through the back pressure regulator valve. Possibly liquids gummed up the valve and backed up into the reactor. The other possibility was that the reaction temperature of 450°C was too high and the solution feed cracked too far, to carbon.

2) Turn around time for cleaning and preparing the continuous reactor for the next run was too long. Batch bombs are faster and simpler to prepare, operate, and clean. Batch bombs were used thereafter to screen poor catalysts from promising ones.

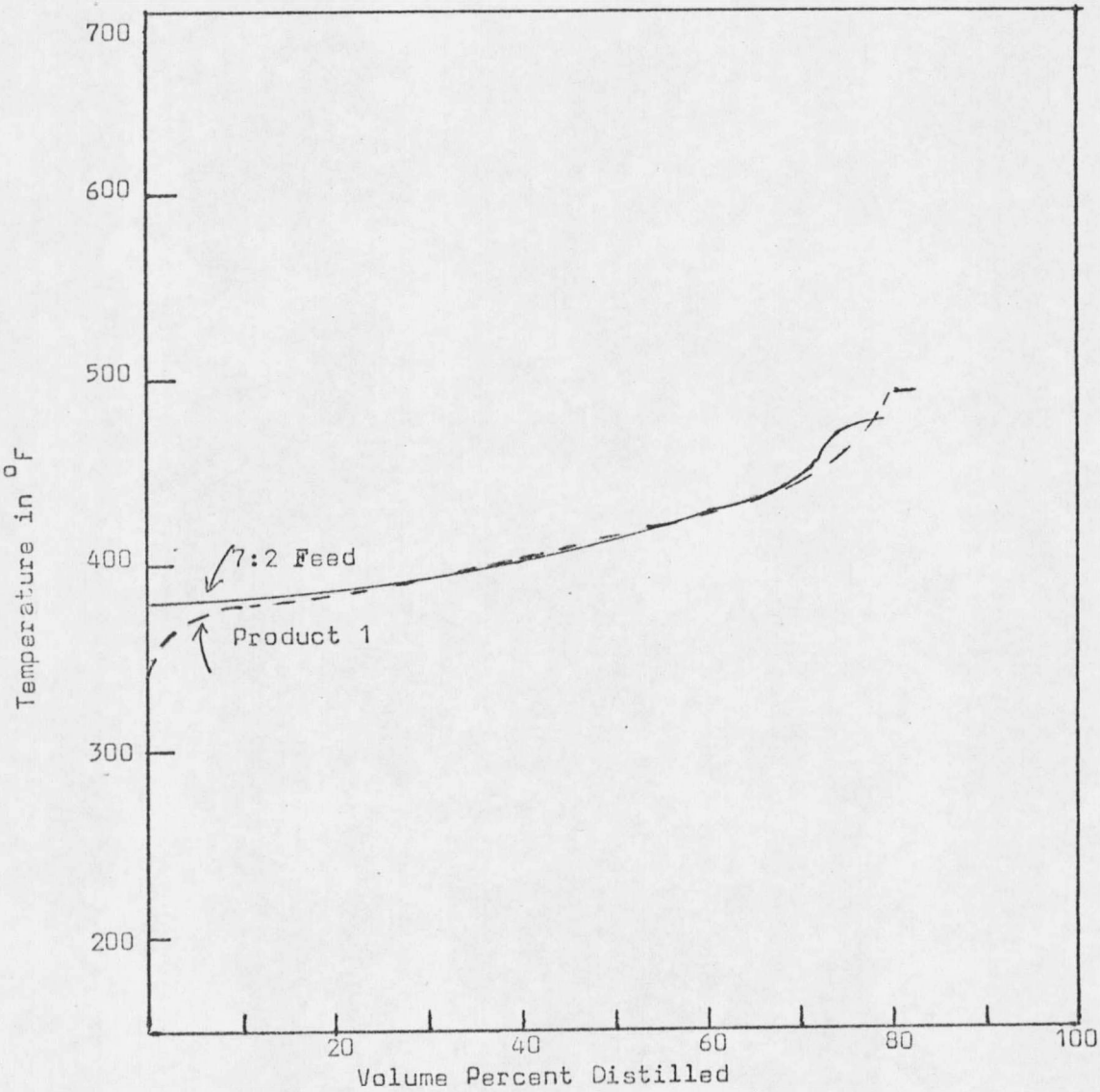


Figure 7. Product 1
Compared to 7:2 Solution Feed

Bomb Runs Studying Variables Other Than Catalyst Type - Eight bomb runs were made which tested variables other than catalyst. The runs are listed in chronological order on the first page of Appendix B, Batch Run Data.

The effect of initial charge pressure of H_2 was investigated. Two bombs were charged with 125 gr. of hot 7:2 coal solution and 20 grams of Ni-4401 catalyst, but one was pressurized to 2100 psig and the other to 500 psig. Run time was one-half hour at 415-420°C. Three observations were made:

1) During a run, bomb pressures increased with temperature to a peak, then decreased regardless of the temperature. 400°C was the lowest temperature at which the decrease was noted. This suggests that hydrogen is consumed by reaction and that 400°C is about the minimum reaction temperature.

2) The products were homogeneous, black, easy-pouring liquids at room temperature and pressure. The character of the 7:2 atmospheric solution feed is quite different. SRC precipitates from the 7:2 solution at less than 100-110°C.

3) The high pressure favored liquid conversion and mildly increased heteroatom removal. High versus low pressure product data are 29% to 12% liquid conversion, 53% to 44% desulfurization, and 35% to 20% denitrogenation.

A run with no solvent, just SRC and catalyst, was done. 38.9gr SRC and 20 gr. powdered catalyst were run at 725 psig and 420°C. A few drops of liquid formed; apparently solvent is needed for good catalyst contact.

The question arose whether the homogeneous products from the first two bomb runs were room temperature solutions because of temperature and pressure effects or catalyst effects.

The uncatalyzed fourth run listed in Appendix B confirmed that one half hour at 415-420°C and 750 psig initial pressure will dissolve SRC into a solution that stays homogenous when reduced to room temperature and pressure.

Solution-to-SRC ratio versus solution characteristics were tested in three more bomb runs without catalyst at 750 psig initial and one-half hour at 415-420°C. The results are listed in Table 8.

Table 8. Solvent Ratio Test Runs

Solvent-to-SRC Ratio	Solution Characteristics	Highest Pressure During Run
7:2	Homogeneous easy-pouring liquid	About 1600
2:1	Darker and more viscous than 7:2, but still pours easily	About 1600
1:1	Very sticky and viscous tar-like material	About 1600
3:2	Much more liquid than the 1:1	About 1600

Since high viscosity increases mass diffusion resistance, the 3:2 solvent-to-SRC solution was chosen as optimum for all future catalyst tests. The 3:2 solution will be much more concentrated than the 7:2 solution. That should help reactions and reduce error in conversion calculations.

Less severe temperatures and residence time will give a homogenous 3:2 solution, too. A 3:2 bomb run at 365°C for five minutes and 775 psig initial pressure yielded a product similar to the longer, more severe run at 420°C for one-half hour.

Catalyst Screening Bomb Runs - The reaction variables (temperature, pressure, run time, solvent type and amount, and solvent-to-SRC ratio) were all fixed in the catalyst screening bomb runs. The conditions of the runs are listed below:

Liquid charge - 175 gr total, in 3:2 solvent-to-SRC ratio

Initial H_2 pressure - 1900-2000 psig

Heat-up period - about 1 hour

Run temperature - 435-445°C

The one exception is CoMo - 0401, the first one of the series. It was run at lower temperature and pressure than the rest. Twenty milliliters of pellet-type catalysts or ten milliliters of homogeneous powder catalysts were used in each run. Less powder catalyst than pellets was used to partially compensate for the greater concentration of active catalytic material in homogeneous powders.

The entire catalyst must be considered in comparing the activity of one catalyst to the activity of another. Many factors influence the activity of a given catalyst. Factors influencing heterogeneous catalysts include:

- type and loading of catalytic metals
- support composition and crystalline structure
- support pore diameter and pore volume distribution
- active surface area

The size of a given pellet or powder can also affect pore diffusion limitation of reaction rate. All these properties vary among the

catalysts tested, as listed in the Description of Catalysts Used, Appendix A.

Because the catalysts vary in many respects, comparison of activities must be made between specific catalysts. Comparisons between catalysts with some similarities can be made, but extension of generalizations to broad classes of catalysts may not be possible.

All catalyst test bomb runs are listed chronologically beginning on the second page of Appendix B, Batch Run Data. A grouping by metal type of tested catalysts is listed in Table 9.

Most of the commercial catalysts were sulfided; unsulfided catalysts are the two Girdler iron-chromates, Cr-0105 in one run, the iron-chromate on CAS-30KR silica alumina, the plain support CAS-30KR, and all the metal chlorides.

Table 9. Batch Catalysts Tested by Metal Type

Ni-Mo	- Harshaw HT-100	Supported Metal Chlorides	- $NiCl_2$ on Cellite 410
	- Harshaw HT-500		- $NiCl_2$ on CAS-30KR
	- MSU STK-1		- $CdCl_2$ on CAS-30KR
Ni-W	- Harshaw Ni-4401	Metal Chloride Powders	- $SnCl_2$
	- Harshaw Ni-4303		- $AlCl_2$
	- Ketjen HC-5		- $Cu\ Cl_2$
	- Ketjen 330-E3		- $ZnCl_2$
Co-Mo	- Harshaw Co-Mo 0401		
	- Harshaw Co-Mo 0603		
	- Harshaw HT-400		
Cr and Fe-Cr	- Harshaw Cr-0105	Others	- Harshaw W-0101
	- Harshaw Cr-0304		- Harshaw Mo-1201
	- Girdler G-3A tablets		- Harshaw Ni-3210
	- Fe-Cr on CAS-30KR		- Sn powder
			- CAS-30KR unloaded support

The catalysts are ranked according to distillate product quality in the following table. Table 10 lists the batch catalysts, distillate product distribution, and overall desulfurization and denitrogenation.

The Ni-4401 catalyst is listed twice: the very first batch run using 7:2 solution, and a later run using the standard 3:2 solution feed. Comparison with other catalysts must be made using the low solvent ratio results. As can be seen, sulfur and nitrogen removal were higher for the less concentrated solution. This indicates that heteroatom removal is easier from the light solvent fraction than from the heavy SRC fraction.

$NiCl_2$ is also listed twice: the 15% $NiCl_2$ is on $3M^2/gr.$ surface area support and the 24% $NiCl_2$ is on $43M^2/gr.$ surface area support. The supports are noted in detail in Appendix A. The high surface area support $NiCl_2$ had better hydrocracking and desulfurization.

The five best hydrocracking catalysts were:

- HT-400, 3% CoO, 15% MoO_3 on alumina
- HT-500, 3.2% NiO, 15.5% MoO_3 on alumina
- Ni-4303, 6% NiO, 19% WO_3 on alumina
- Ketjen 330-E3, 6.6% NiO, 19.8% WO_3 on alumina

and - $AlCl_3$ powder

Table 10. BATCH CATALYSTS - RANKED BY DISTILLATE CURVE QUALITY

Catalyst	Percent Naphtha IBP-425°F	Percent Fuel Oil 425-600°F	Percent Gas Oil 600-700°F	Percent Residue	Percent DeS	Percent DeN
$SnCl_2 \cdot 2H_2O$	-14	22	0	94	29	17
Girdler G-3 tablet (Fe_2O_3)	0	8	0	92	0	0
Cr-0304, unsul.	0	11	0	89	0	0
Cr-0105, unsul.	0	8	0	94	0	0
Sn powder	0	11	0	86	6	0
$CuCl_2 \cdot H_2O$	-5.5	8	8	89	46	22
38% $CdCl_2$ on silica alumina	-11	25	0	86	12	13
W-0101	-8	25	0	83	0	9
15% $NiCl_2$ on 86% silica	-5.5	19	0	86	18	15
CoMo 0603	-5.5	19	0	86	31	15
Fe_2O_3-Cr_2O_3 on silica alumina	-5.5	22	0	83	2	3
CoMo 0401	-5.5	19	0	86	28	8
Ni 3210	-3	17	0	86	0	7
Cr-0105. sulfid.	3	11	0	86	6	14
$ZnCl_2$, powdered	-8	19	11	80	65	35
STK-1	0	11	8	83	22	0
Ketjen HC-5	3	8	11	78	35	28
50-50 Ketjen 330-E3 and $CdCl_2$ on silica alumina	0	3	14	83	33	17
CAS-30KR silica alumina	5.5	-11	25	80	0	3
Mo-1201	5.5	11	0	83	18	17
Ni-4401 (low solvent ratio)	-5.5	25	0	80	37	14
Girdler G-3A Fe_2O_3 powder	0	22	0	78	14	19

(Table 10 - Batch Catalysts cont'd)

Catalyst	%Naptha	%Fuel Oil	%Gas Oil	%Residue	%DeS	%DeN
24% $NiCl_2$ on silica alumina	5.5	3	14	78	29	6
HT-100	3	17	0	80	42	21
$AlCl_3$ Powdered	0	25	0	75	31	48
Ketjen 330-E3	11	3	5.5	80	43	13
Ni-4303	8	14	0	78	31	20
HT-500	0	14	11	75	45	18
Ni-4401 (high solvent ratio)	24	4.5	0	71	53	35
HT-400	25	0	0	75	47	23

The four top heterogeneous catalysts have combinations of molybdenum or tungsten promoted with either cobalt or nickel. The product distributions of the five best catalysts varied, though conversion was generally highest in the middle or low boiling ranges. Three of the four pellet catalysts have surface areas of 200 M^2/gr; all four are mounted on alumina. Distillation graphs displaying the products of the two best catalysts are shown in Figures 8 and 9. Both have quite different curves when compared to the 3:2 solution feed curve but both gave overall liquid conversion of 25%.

The 3:2 solution feed has 64% distillates, and the HT-400 product has 73% distillates. Liquid conversion was $\frac{73 - 64}{36} = 25\%$. The distribution of the 3:2 solution feed in the three boiling ranges is 55% in Naphtha (IBP - 425°F), 9% in Gas Oil (600 - 700°F). An example of the boiling range distribution of conversion is given here for the Ketjen HC-5 product. It boiled as follows:

Naphtha range -	56%
Fuel Oil range -	12%
Gas Oil range -	4%
Total	72% distillates

Overall conversion to liquids $= \frac{72-64}{36} = 22\%$

Conversion to Naphtha $\frac{56-55}{36} = 3\%$ (rounded off)

Conversion to Fuel Oil $\frac{12-9}{36} = 8\%$

Conversion to Gas Oil $\frac{4-0}{36} = 11\%$

22%

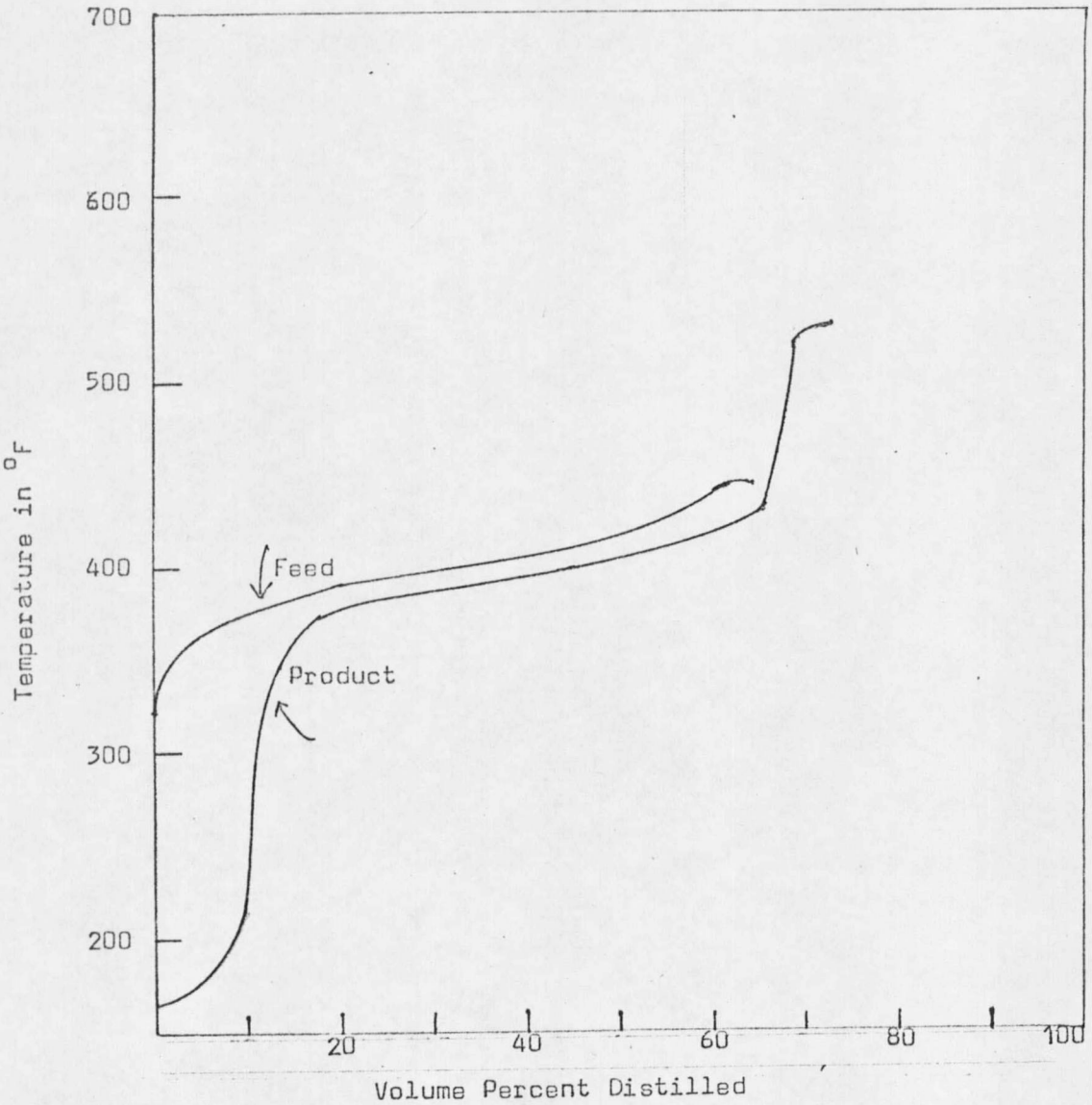


Figure 8. Distillation of HT-400 Product vs. 3:2 Solution Feed

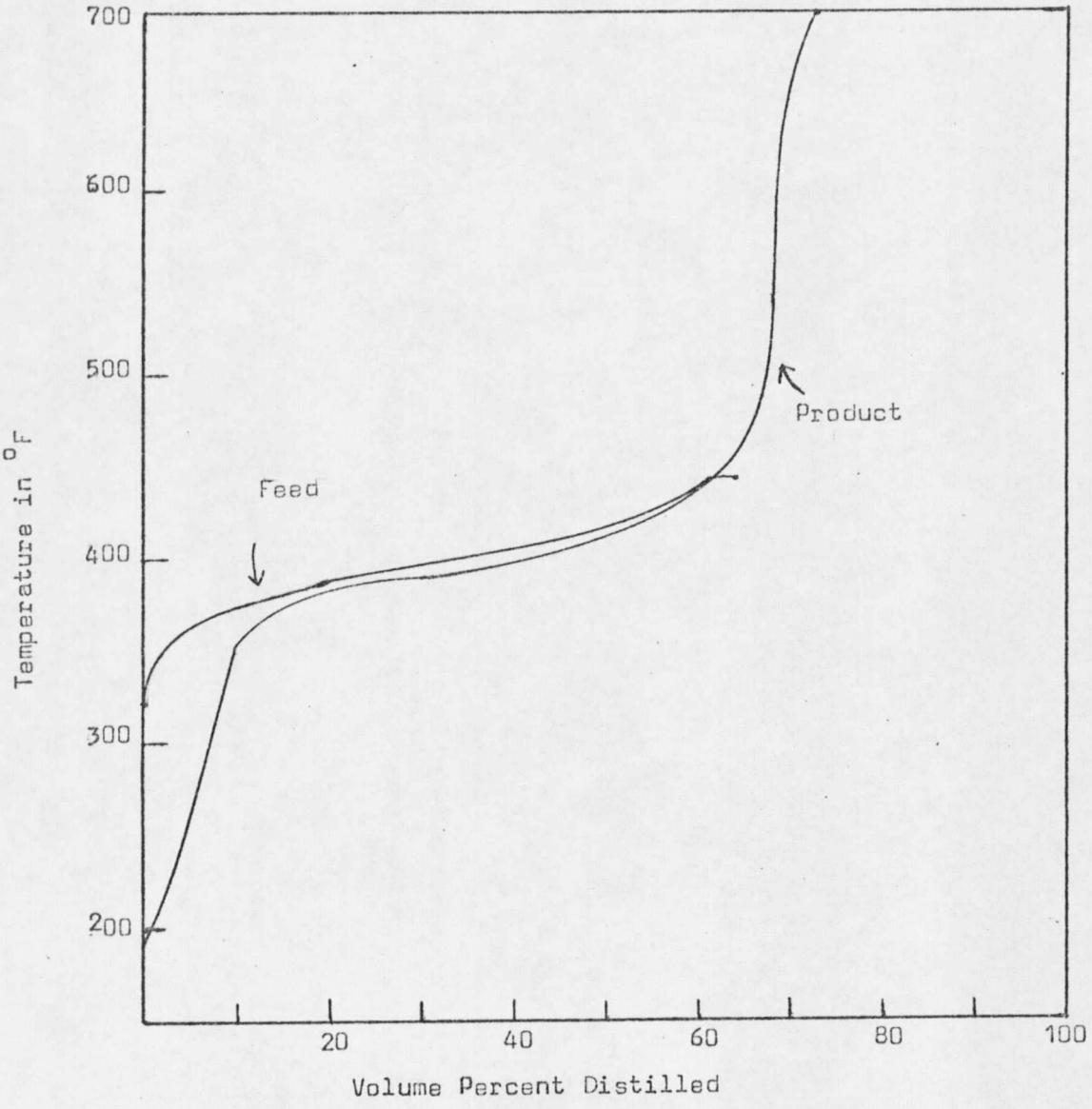


Figure 9. Distillation of HT-500 Product vs. 3:2 Solution Feed

Tables 11 and 12 show the five catalysts which accomplished the most sulfur and nitrogen removal. As a group, the metal chlorides did very well in heteroatom removal. Also, note that four of the five best hydrocracking catalysts are also in at least one of Tables 11 and 12. Table 10 shows that none of the "best" hydrocracking catalysts were poor heteroatom removers. Good hydrocracking seems to correlate with good heteroatom removal.

The heteroatom removal data point to one generalization that was also indicated in the literature search: nitrogen is consistently harder to remove than sulfur. Only one catalyst, $AlCl_3$, gave a greater percent reduction in nitrogen than sulfur (48% de-N vs. 31% de-S).

Comparisons of Some Ni-W, Ni-Mo, and Co-Mo Catalysts - Three Ni-W catalysts (Ketjen HC-5, Ketjen 330-E3, and Harshaw Ni-4303) have similar metal loadings, but difference supports and varying results. Unfortunately, each was on a different size pellet, so the possibility of pore diffusion effects makes generalizations uncertain.

The Harshaw catalysts HT-100 and HT-500 are both about 3% NiO, 16% MoO_3 on high area support, but HT-100 is 1/12" diameter and silicated; the HT-500 is 1/8" and just alumina. Surprisingly, nitrogen and sulfur removal for the two differ very little. Liquid conversion is less for the silicated, smaller particle.

HT-400 (3% CoO, 15% MoO_3 on alumina, 220 M^2/gr, and average

Table 11. BEST BATCH DESULFURIZATIONS

$ZnCl_2$ powdered	65%
HT-400 3% CoO, 15% MoO_3 on alumina	47%
$CuCl_2 \cdot H_2O$ fine crystals	46%
HT-500 3.2% NiO, 15.5% MoO_3 on alumina	45%
Ketjen 330-E3 6.6% NiO, 19.8% WO_3, 1.2% SiO on alumina	43%

Table 12. BEST BATCH DENITROGENATIONS

$AlCl_3$ powdered	48%
$ZnCl_2$ powdered	35%
Ketjen HC-5 6.5% NiO, 21% WO_3 on alumina	28%
HT-400 3% CoO, 15% MoO_3 on alumina	23%
$CuCl_2 \cdot H_2O$ fine crystals	22%

pore diameter 100 A^{o}) is similar to Co-Mo 0603 (3% CoO, 12% MoO_3 on alumina, 166 M^2/gr, 106 A^{o}). Both are 1/8" pellets, and the high surface area HT-400 did about 1/3 better in heteroatom removal.

Metal Chlorides - The unsupported chlorides (Sn, Cu, Zn, and Al) all melt below the reaction temperature; the supported chlorides (Ni and Cd) do not melt below reaction temperature. $AlCl_3$ was the best of all the chlorides for cracking and best of all catalysts for denitrogenation (48%). The supported chlorides were fairly average catalyst in both cracking and heteroatom removal; the unsupported chlorides ranged from poor to good hydrocrackers, but as a group their heteroatom removal was very good. Copper and zinc chloride were both among the best five nitrogen and sulfur removers.

Fe and Fe-Cr Catalysts - The first iron-chromate tested, Girdler G-3A powder, gave encouraging results: 22% overall conversion, 14% de-S, and 19% de-N. But the pellet form of G-3A proved ineffective, with low conversion and no heteroatom removal. Pore diffusion limitations and/or lower surface area probably caused the poor results. The intermediate area silica-alumina impregnated with Fe-Cr did not give good results either.

Other investigators at Montana State had better results with unsulfided chromates on support than with the same catalysts sulfided. Two unsulfided Cr catalysts did not give good results with the SRC 3:2 feedstock, though. The effect of sulfiding was tested by running

one of the Cr catalysts again, only sulfided. Hydrocracking and heteroatom removal all increased with sulfiding.

Other Effects - The unloaded support CAS-30KR silica alumina, 43 M^2/gr, was tested to help determine the effect of support. The plain support cracked fairly well (It is midway in the table), but had negligible heteroatom removal. One interesting sidelight--the plain support product was the only catalyst which had less distillate in the Fuel Oil range than the Solution Feedstock.

Conclusions of Bomb Tests - Batch screening of the catalysts showed several things:

- The best heterogeneous hydrocrackers were combinations of Mo or W promoted with Ni or Co on high area alumina.
- The best metal chloride catalysts were $AlCl_3$, $ZnCl_2$, and $NiCl_2$.

Since HT-400 (Co-Mo on alumina) was in each of the three catagories of "best" catalysts, it was chosen for continuous mode testing. Ketjen HC-5 (Ni-W or alumina) was chosen for continuous testing since it had the best denitrogenation of the heterogeneous catalysts. $AlCl_3$ was not chosen for testing because of catalyst recovery problems inherent with metal chlorides.

Continuous Runs

The effects of temperature, liquid hourly space velocity, and hydrogen flow-to-oil ratio were investigated, using the continuous

reactor described in the Materials, Equipment, and Procedure Section. See Appendix C, Continuous Runs: Conversion of SRC to Liquid, for all catalysts, run conditions, ond product results of the continuous runs. Fixed variables were:

- pressure - 1000 psig
- feed - 3:2 solution feed, prepared in bombs at 400°C
- Amount of catalyst - 70 ml.

Catalysts tested were HT-400 (CoMo on alumina), Ketjen HC-5 (Ni - W on alumina), MSU STK-7 (Co-Ni-Mo on alumina), and MSU STK 5-2-1 (Co-Ni-Mo on alumina). Complete catalyst descriptions are listed in the second part of Appendix A.

The products from the continuous runs were better than the products from the Bomb runs. Liquid conversions for HT-400 ranged from 25-66%. compared to 25% in the bomb; liquid conversion for Ketjen HC-5 were 44 to 61%, compared to 22% in the bomb.

Summary of Results from Continuous Runs - Of the four catalysts tested, the best desulfurization, 88%, was done by HC-5 (Ni-W). The best denitrogenation, 64%, was obtained by HT-400 (CoMo). The trend was observed that nitrogen is more difficult than sulfur to remove. All of the catalysts tested gave a 55-60% conversion to liquids during at least one set of conditions tested.

Overall liquid conversion tends to:

1) increase with increasing temperature

2) be best at LHSV from 1 to 2

3) maximize at 10,000 SCF/bbl for LHSV = 1 and 445°C.

Product distributions vary in no definable trend with temperature, LHSV, and H_2 ratio.

Heteroatom removal tends to:

1) increase as temperature increases

2) decrease as LHSV increases

3) maximize about 10,000 SCF/bbl for LHSV = 1 and 445°C.

Hydrocracking - The effects of temperature, liquid hourly space velocity, and H_2 ratio on hydrocracking are illustrated in the following three figures.

Figure 10 displays the effect of temperature on hydrocracking, using STK-7. The 420°C product has less liquid conversion and is more similar to the solution feed than is the 445°C product.

Figure 11 shows the HT-400 product distillations for three different space velocities. LHSV=2 product has the most naphtha range material, but the LHSV=1 product has the most overall conversion. The LHSV=3 product is not much different than the feedstock, but somewhat extended. From the Appendix, it can be seen that LHSV=2 gives the most naphtha for HC-5 also, but not for the other two catalysts.

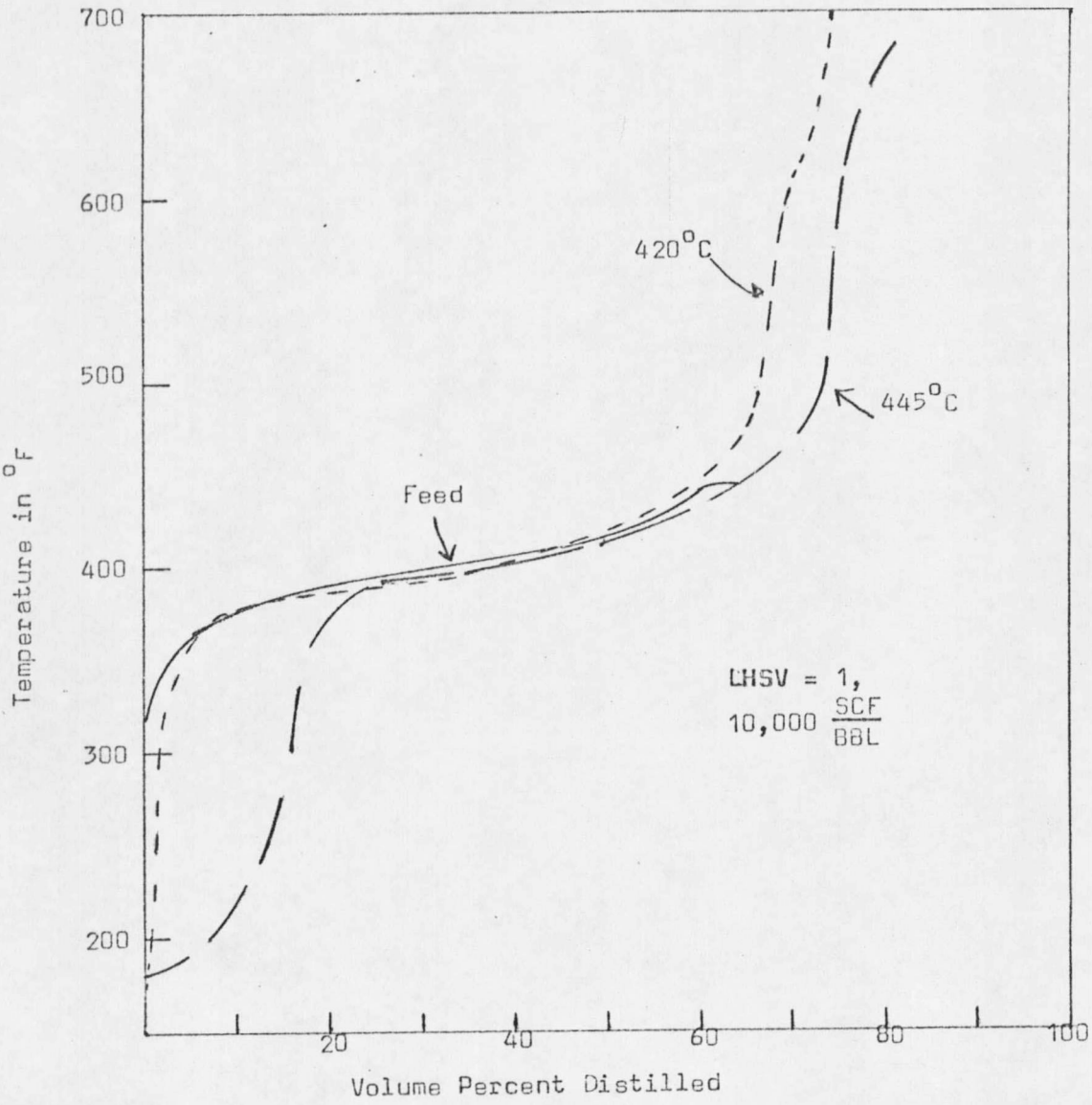


Figure 10. Effect of Temperature on Hydrocracking by STK-7

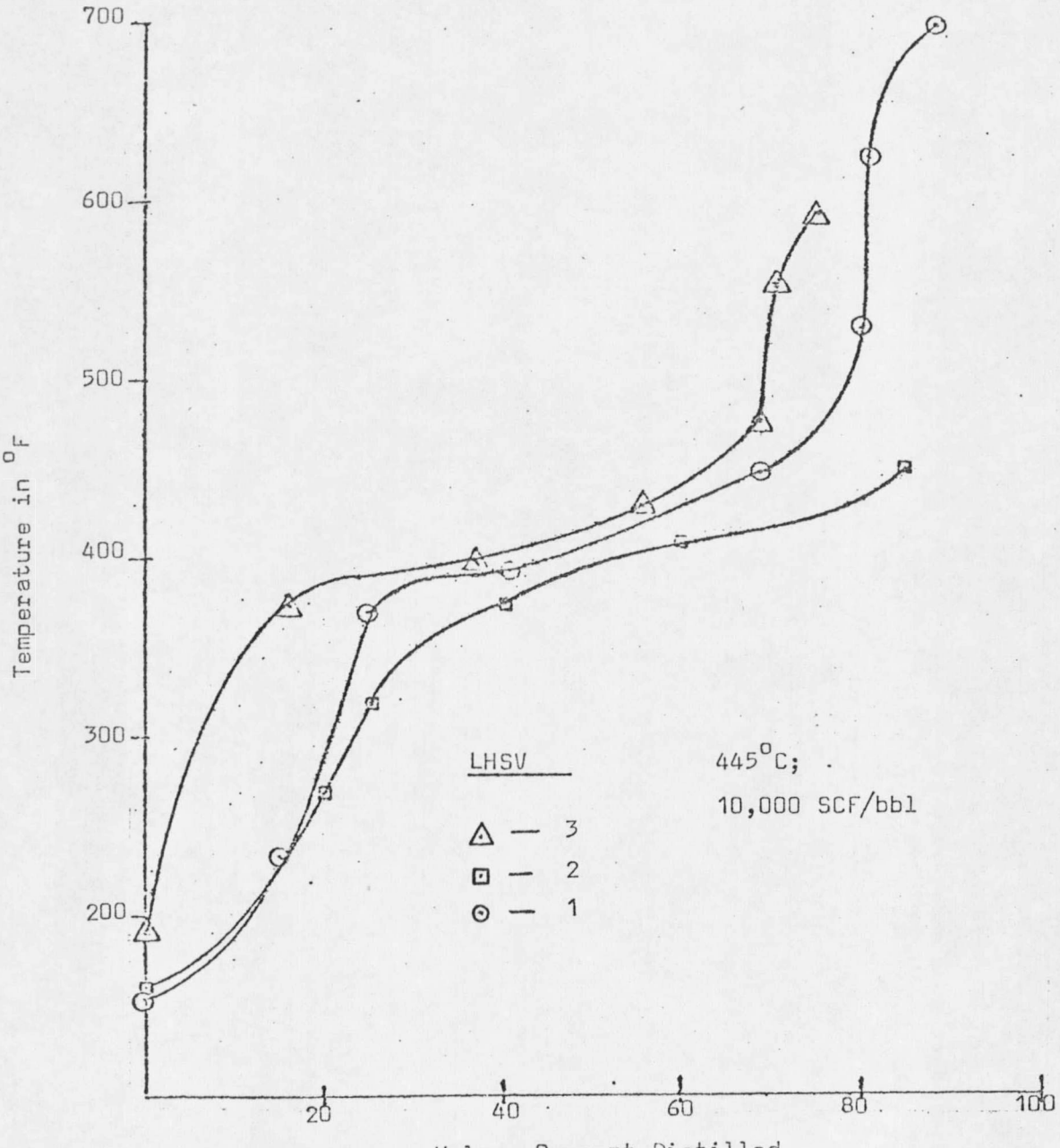


Figure 11. Effect of LHSV on Hydrocracking by HT-400

Figure 12 shows the effect of H_2-to-oil ratio on hydrocracking by STK 5-2-1. The 10,000 SCF/bbl product shows improvement over the 5,000 SCF/bbl product. Increasing the rate to 13,000 SCF/bbl in the HC-5 and STK-7 run did not improve the liquid conversion nor naphtha range conversion.

Limited data is available on the effect of H_2 ratio at a space velocity other than 1. Appendix A reveals the best overall conversion for STK 5-2-1 at LHSV=2 and 445^{o}C came at a H_2 ratio of 7500 SCF/bbl.

Heteroatom Removal - Eight figures display the effects of temperatures, LHSV, and H_2 ratio on sulfur and nitrogen removal.

Nitrogen and sulfur removal both increased with temperature. Figures 13 and 14 display data plots of sulfur and nitrogen removal versus temperature for two different catalysts.

Both desulfurization and denitrogenation increase as LHSV decreases. Figures 15 and 16 display the tendency. One data point in Figure 16 does not follow the trend.

Variation of effects of H_2-to-oil ratio is displayed in Figures 17 and 18 for heteroatom removal at LHSV=1 and 445^{o}C. Desulfurization for HC-5 and STK-7 peaked or leveled off at H_2 ratios of about 10-11 M SCF/bbl. Sulfur removal did not vary much for STK 5-2-1.

Denotrogenation results conflicted for HC-5 and STK-7, as seen in Figure 18. The STK 5-2-1 run was made to determine the effect of low H_2 ratios. A point at 10,000 SCF/bbl was obtained for both the first

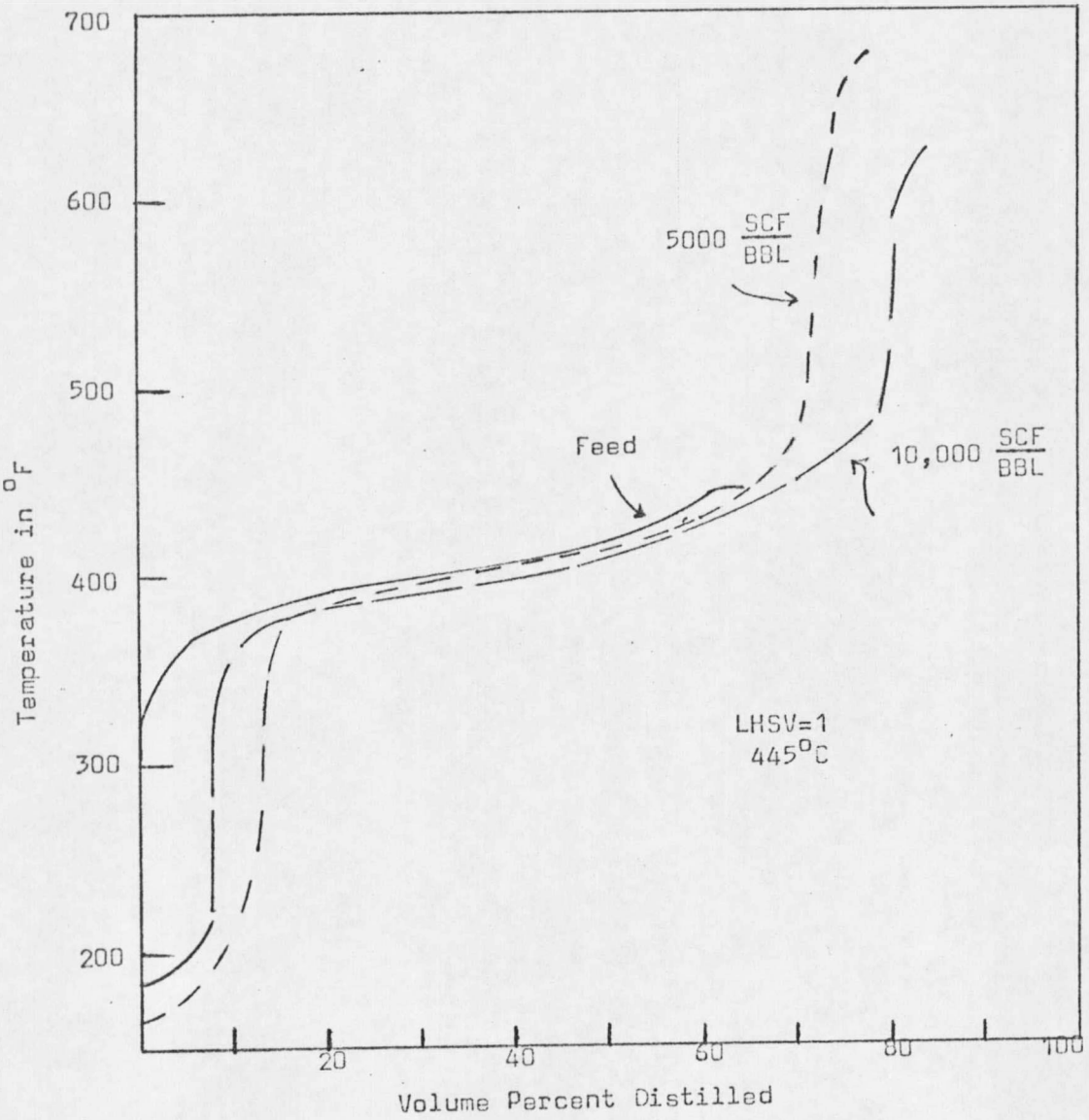


Figure 12. Effect of H_2 Ratio on Hydrocracking by STK 5-2-1.

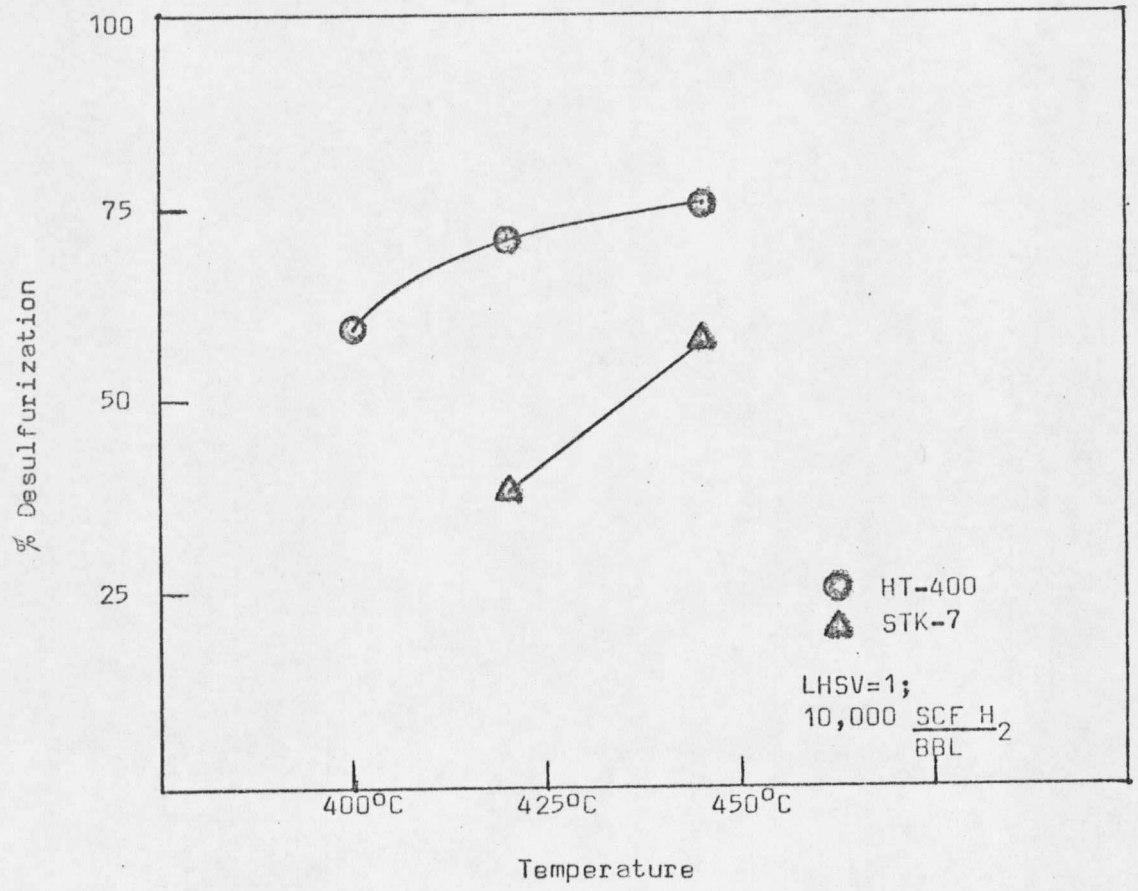


Figure 13. Percent Desulfurization vs. Temperature

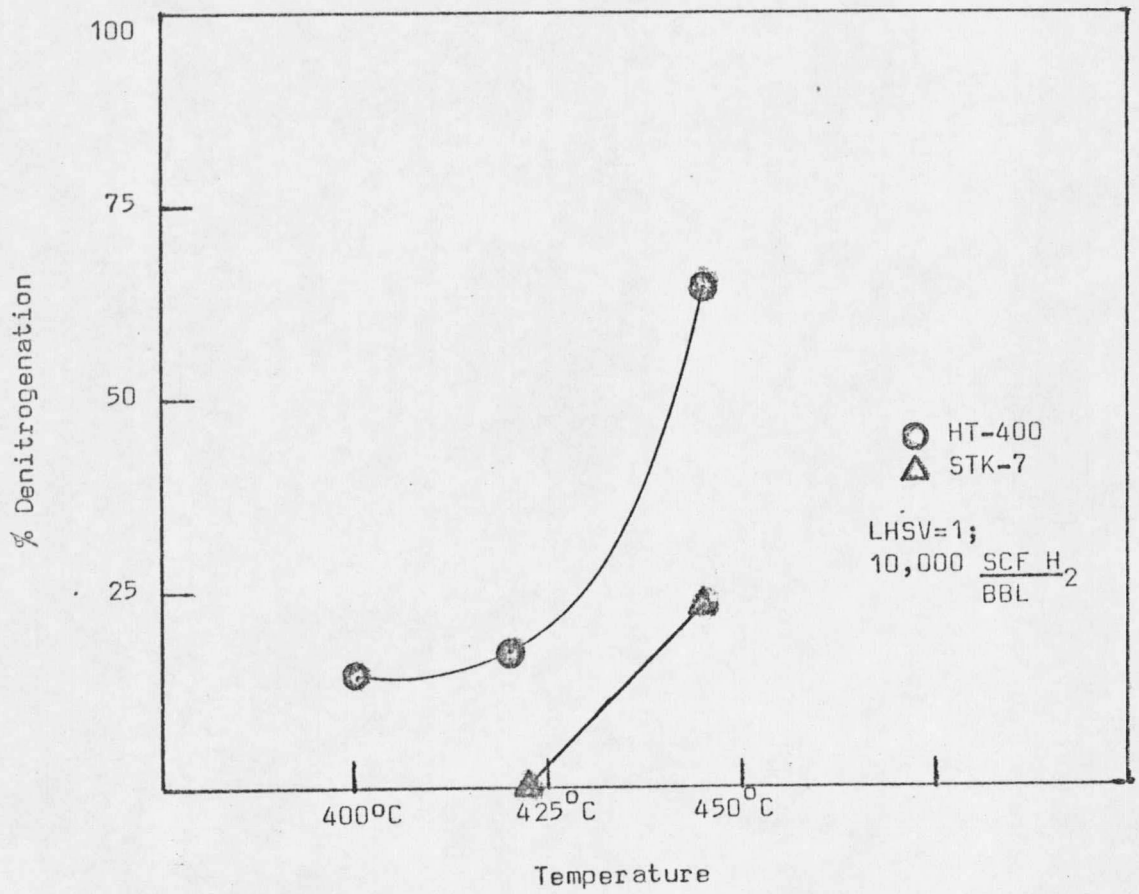


Figure 14. Percent Denitrogenation vs. Temperature

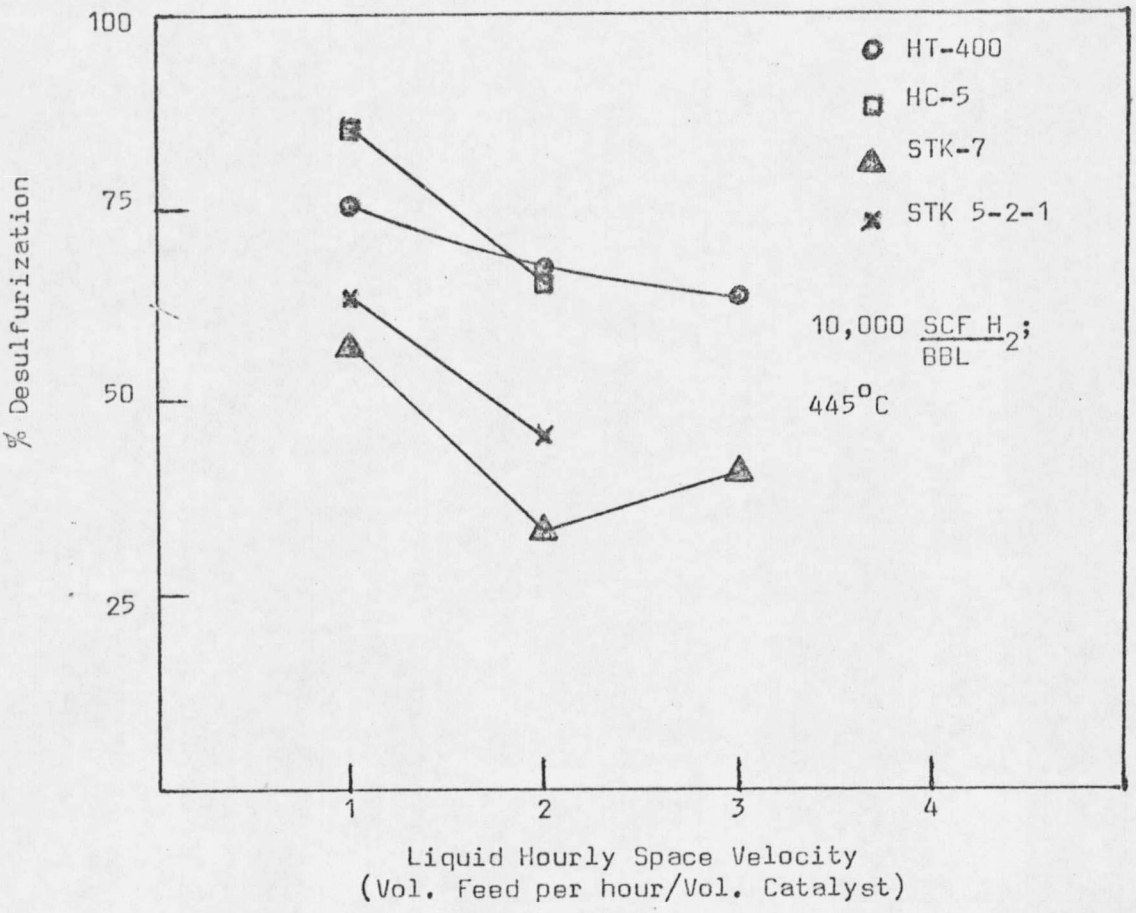


Figure 15. Percent Desulfurization vs. LHSV

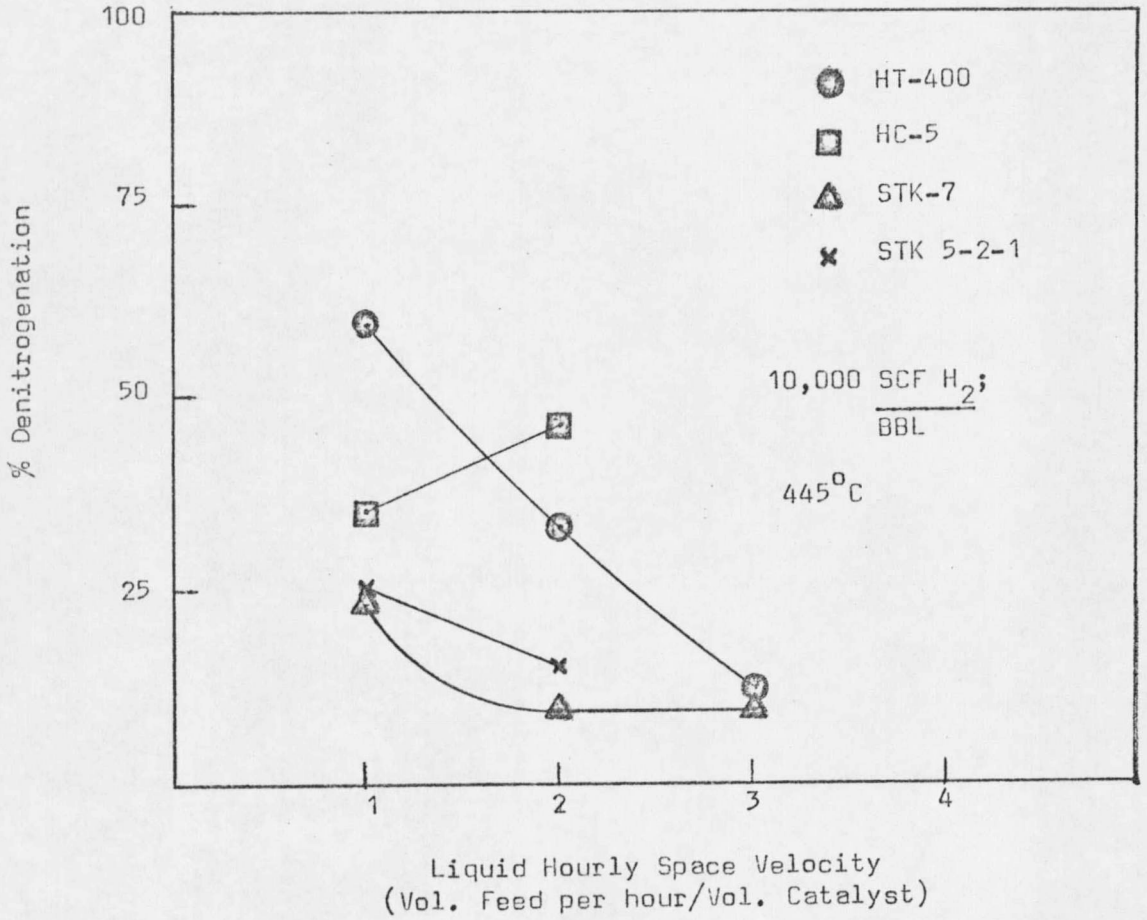


Figure 16. Percent Denitrogenation vs. LHSV

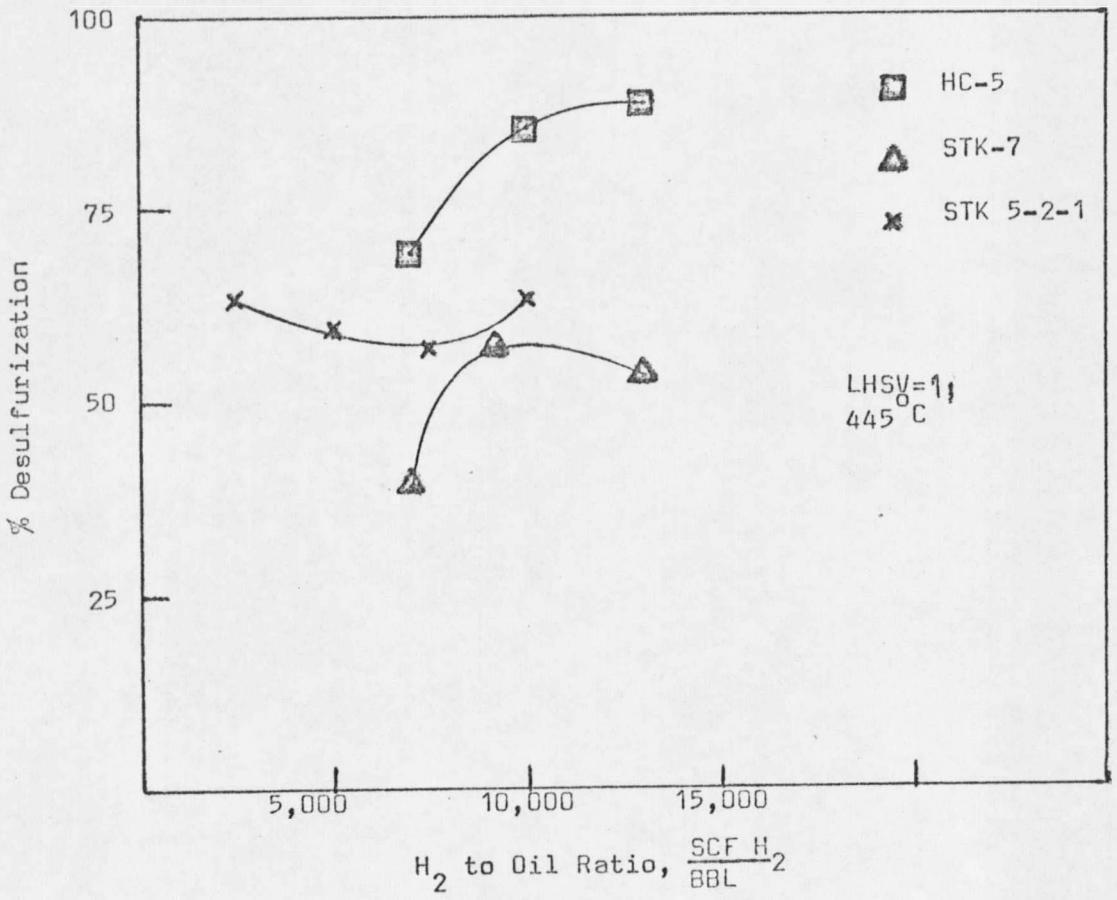


Figure 17. Percent Desulfurization vs. Hydrogen-to-Oil Ratio

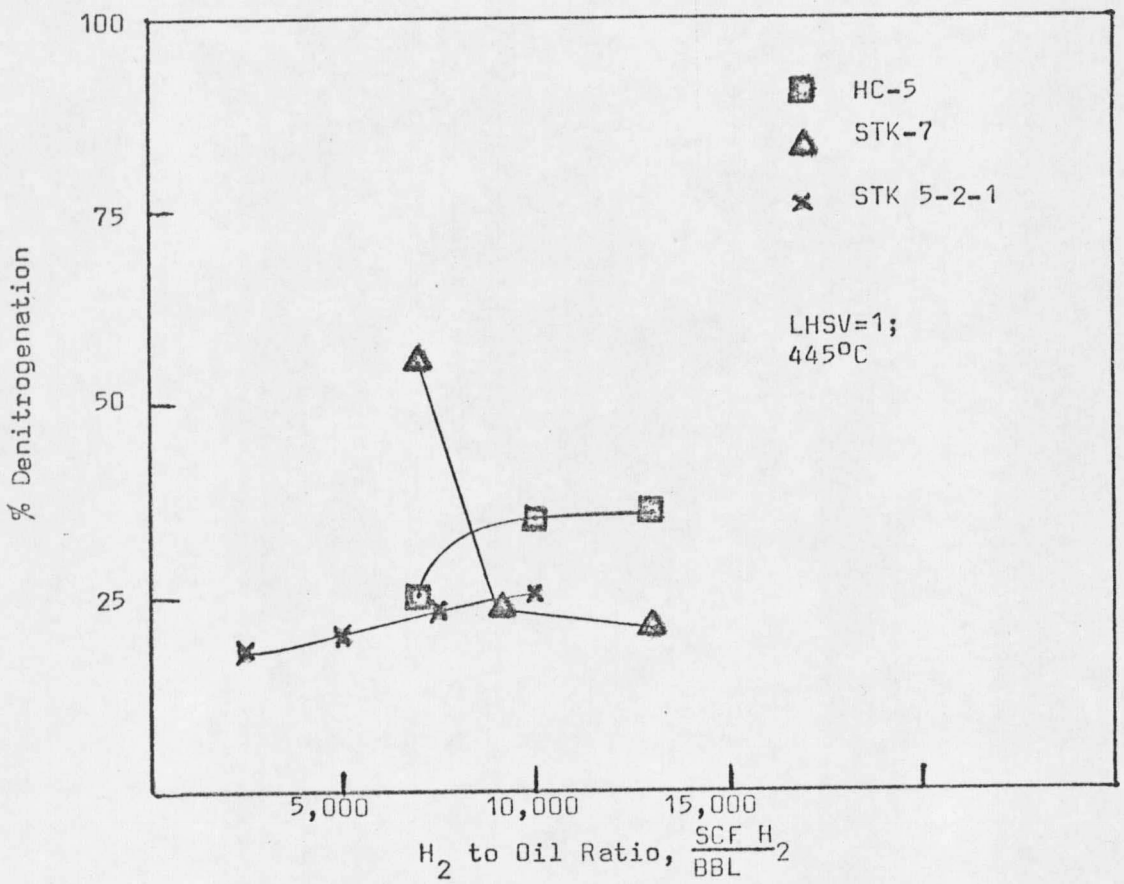


Figure 18. Percent Denitrogenation vs. Hydrogen-to-Oil Ratio

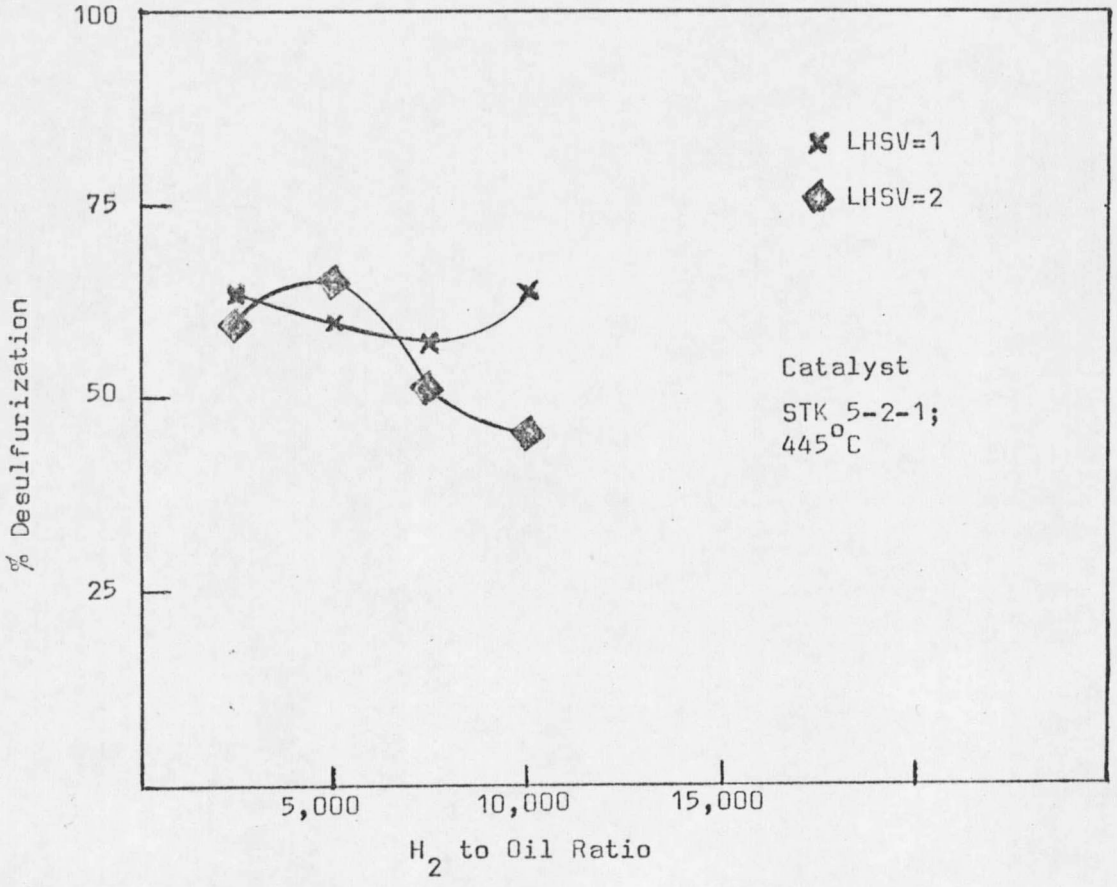


Figure 19. Percent Desulfurization vs. Hydrogen to Oil Ratio at different liquid hourly space velocities

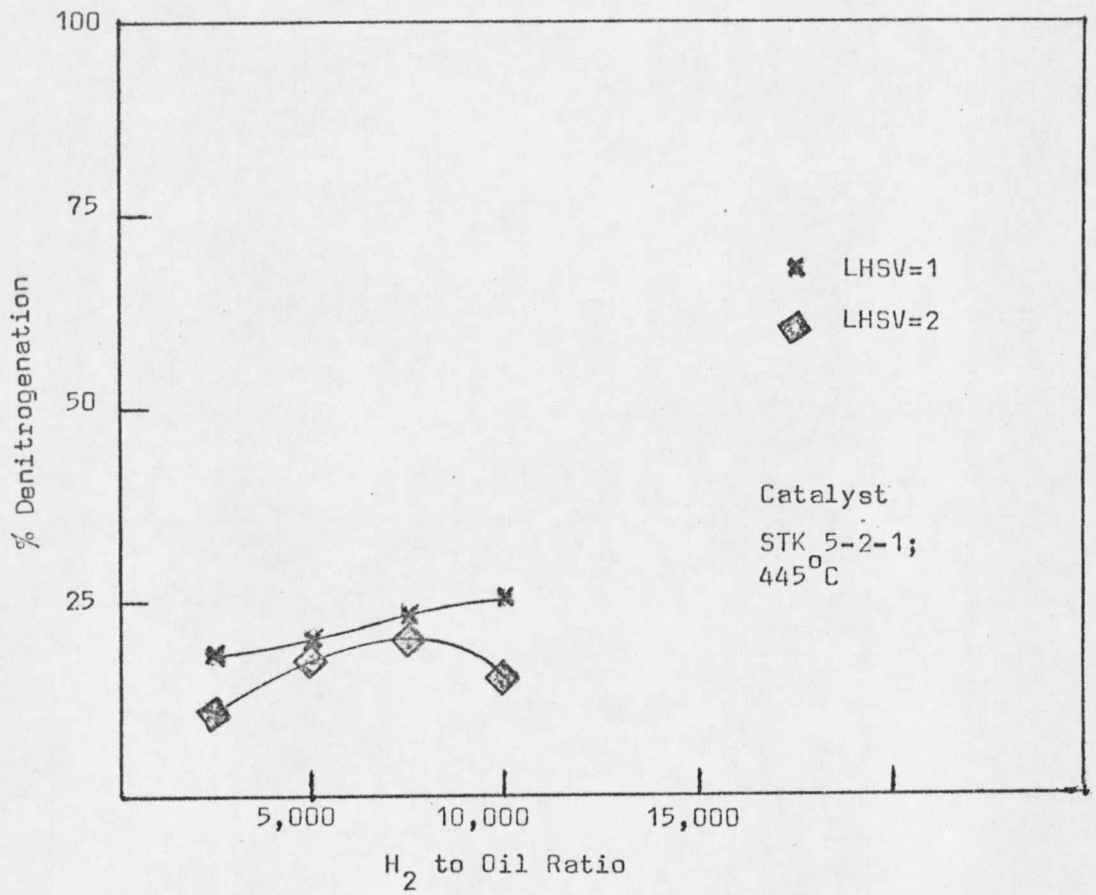


Figure 20. Percent Denitrogenation vs. Hydrogen to Oil Ratio at different liquid hourly space velocities

and last samples of the run. The first sample had an unusually high nitrogen removal, but the last sample correlated with all the others. Since the high point for STK-7 was also from the first sample of the run, it can be concluded that the two MSU catalysts have a high initial activity which steadied out later in the run. Therefore, nitrogen removal does indeed peak at 10,000 SCF/bbl for steady-state catalyst activity.

Figures 19 and 20 compare effects of H_2 ratio for two space velocities over the same catalyst. Desulfurization is nearly level at LHSV=1 over the range of H_2 ratios; but at LHSV=2, desulfurization peaks at 5000 SCF/bbl and decreases at higher ratios (See Figure 19). Figure 20 shows that denitrogenation over the range of H_2 ratios is similar for both LHSV=1 and LHSV=2. The nitrogen removal peaks at slightly lower H_2 ratio, 7500, for the higher space velocity.

Looking at Appendix C, the continuous run data, Ketjen HC-5 catalyst displayed the highest consistent heteroatom removal over a range of hydrogen-to-oil ratios. HT-400 has the highest consistent heteroatom removal over the range of space velocities LHSV=1 to 3.

CONCLUSIONS

1. Conversion from nondistillates to distillates can be obtained up to 55-60% with commercial and lab-prepared catalysts in a continuous reactor.

2. The best heterogeneous catalysts tested in bombs had combinations of molybdenum or tungsten promoted with cobalt or nickel.

3. Metal chloride homogeneous catalysts are good heteroatom removers; aluminum chloride was the best chloride catalyst overall.

4. The best Mo-W-Co-Ni catalysts tested had relatively high surface area.

5. Nitrogen is harder to remove from solvent-refined coal than sulfur is.

6. Increased temperature gives increased hydrocracking and heteroatom removal.

7. Liquid hourly space velocities from 1 to 2 give the best hydrocracking and heteroatom removal.

8. Ten thousand SCF/bbl hydrogen-to-oil ratio gives the best hydrocracking and heteroatom removal for 445^{o}C, LHSV = 1, 1000 psig, and 70 ml. of catalyst.

RECOMMENDATIONS

Short Term

1. Investigate the effects of film and pore diffusion in the continuous reactor. The proper catalyst size and mass flow rate can then be employed to minimize diffusion limitations.

2. Use an electric H_2 flow meter to accurately monitor input gas.

3. Do chromatrographic analysis of product gases. This will allow a material balance on the system and correlation of gas-make versus variables.

4. Consider using SRC II liquid products as reactor feed. That would eliminate the use of a solvent.

5. Measure the surface acidity of catalysts tested. Recent literature indicates acidity is an important variable. Perhaps a high acidity was the reason the chromate catalysts previously tested did not work well.

Long Term

1. Continue testing new commercial hydrotreating catalysts.

2. After film and pore diffusion effects are minimized, compare various catalyst support composition, pore size, and metal loadings.

3. Find optimum conversion pressure. Literature suggests pressures significantly higher than 1000 psig give increased liquid yields for a given temperature.

4. Consider use of a homogeneous catalyst in feed over a packed bed with high gas-liquid contact area. Recent work has improved recovery techniques for catalytic amounts of metal chlorides from coal liquids.

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APPENDICES

APPENDIX A

DESCRIPTION OF CATALYSTS USED

BATCH RUN CATALYSTS

Harshaw Ni-4401 E 1/10"
6% NiO, 19% WO_3, 25% Al_2O_3, 50% SiO_2.

Harshaw Co-Mo 0401 T1/8"
3% CoO, 9% MoO_3 on alumina, silica promoted 160 m^2/gr, 0.40 cc/gr

Harshaw W-0101 T 1/8"
10% WO_3 on alumina 75 m^2/gr, 0.37 cc/gr

Harshaw HT-100 E 1/12"
3.8% NiO, 16.8% MoO_3, 1.5% silica on alumina
175 m^2/gr, 0.54 cc/gr

Harshaw Mo-1201 T 1/8"
10% MoO_3 on alumina 160 m^2/gr, 0.36 cc/gr

Harshaw Cr-0304 unsul. T 1/8"
33% Cr_2O_3 on silicated alumina
120 m^2/gr, 0.26 cc/gr

Harshaw Co-Mo 0603 T 1/8"
3% CoO, 12% MoO_3 on alumina
166 m^2/gr, 0.44 cc/gr

Tin powder

Harshaw Ni-4303 E 1/12"

6% NiO, 19% WO_3 on alumina
152 m^2/gr, 0.54 cc/gr

Harshaw Ni-3210 T 3/16"
35% NiO on proprietary support
175 m^2/gr, 0.45 cc/gr

Girdler G-3A powder
82% Fe_2O_3, 10% Cr_2O_3

$SnCl_2 \cdot 2H_2O$

(Description of Catalysts Used - cont'd)

Harshaw Cr-0105 unsul. T 1/8"
9% Cr_2O_3, 1.5% K_2O on alumina
67 m^2/gr, 0.34 cc/gr

Harshaw Cr-0105, sulfided T 1/8"

Harshaw HT-400 E 1/8"
3% CoO, 15% MoO_3 on alumina
220 m^2/gr, 0.55 cc/gr

$AlCl_3$ powder

$CuCl_2 \cdot H_2O$ fine crystals

$ZnCl_2$ powder

15% $NiCl_2$ on Johns-Mansville Cellite 410 silica [1.] 1/4"

Harshaw HT-500 E 1/8"
15.5% MoO_3, 3.2% NiO on alumina
210 m^2/gr, 0.44 cc/gr

38% $CdCl_2$ on Johns-Mansville CAS-30KR silica alumina [2.] T 1/8"

Ketjen HC-5 1.5 mm (1/16")
21% WO_3, 6.5% NiO on alumina
200 m^2/gr, 0.62 cc/gr

Silica Alumina T 1/8"
CAS-30KR [2.]
43 m^2/gr, 0,61 cc/gr

13.5% Fe_2O_3, 10% Cr_2O_3 on CAS-30 KR [2.]
silica alumina

24% $NiCl_2$ on CAS-30KR [2.] silica alumina

Ketjen 330-E 3 mm (1/8")
19.8% WO_3, 6.6% NiO, 1.2% SiO_2 on alumina
193 m^2/gr, 0.43 cc/gr

[1.] Cellite 410 - 86% SiO_2, 9% Al_2O_3, 2% Fe_2O_3, 1% CaO
3 m^2/gr, mean pore diameter
0.82 microns; 0.56 cc/gr

[2.] (see next page)

(Description of Catalysts Used cont'd)

50-50 mix of Ketjen 330-E3 and 30% $CdCl_2$
on CAS-30KR

MSU STK - 1
15.8% MoO_3, 6.5% NiO on CAS-30KR[2] silica alumina

Girdler G - 3A T 3/16" x 3/8"
82% Fe_2O_3, 10% Cr_2O_3 70 m^2/gr, 0.04 cc/gr

CONTINUOUS RUN CATALYSTS

Harshaw Ni-4401 E 1/10"
6% NiO, 19% WO_3, 25% Al_2O_3, 50% SiO_2

Harshaw HT-400 E 1/16"
3% CoO, 15% MoO_3 on alumina 220 m^2/gr, 0.55 cc/gr

Ketjen HC-5-E 1.5 (1/16")
21% WO_3, 6.5% NiO on alumina 200 m^2/gr, 0.62 cc/gr

MSU STK - 7 E 1/8"
17.1% MoO_3, 1.5% NiO, 1.4% Co_3O_4
on Norton 6176[3] alumina

MSU STK 5 - 2-1 E 1/16"
23.9% MoO, .48% NiO_x, .75% CoO_2
on Norton 6176[3] alumina

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[2] CAS-30KR - 51% SiO_2, 46% Al_2O_3, 0.7% Fe_2O_3, 0.3% CaO
43 m^2/gr; mean pore diameter 0.52 microns; 0.61 cc/gr

[3] Norton 6176 - 99.85% Al_2O_3, 0.014% NaO_2, 0.120% SiO_2,
0.065% Fe_2O_3
250 m^2/gr, 0.8-1.1 cc/gr

APPENDIX B. BATCH RUN DATA

CATALYST	Solvent-to-SRC Wt. Ratio	Initial Cold H_2 psig	Final Cold H_2 psig	Run Temp °C	Conversion to Liquids (Vol.%)	% deS	%deN
Harshaw Ni-4401	7:2	2100	1000	425	29%	53%	35%
Harshaw Ni-4401	7:2	500	275	415	12%	44%	20%
Harshaw Ni-4401 powdered	solid SRC only	725	600	420	solid	---	---
No catalyst	7:2	750	675	417	---	9%	7%
No catalyst	2:1	725	675	420	---	1%	0%
No catalyst	1:1	750	625	418	---	0%	9%
No catalyst	3:2	750	700	417	---	4%	14%
No catalyst	3:2+	750	---	365	---	4%	15%

*Note: Solid SRC is 2.28% nitrogen and 0.68% sulfur.
Synthetic coal oil solvent is .59% nitrogen and .36% sulfur.

S & N analyses listed in table are for both solvent and SRC still mixed as the product.

+ Special short-time run: heated to 365°C, held for 5 minutes, quenched. All other runs held at run temperature for 1/2 hr.

BATCH RUN DATA

CATALYST	Solvent-to-SRC Wt. Ratio	Initial Cold H_2 psig	Final Cold H_2 psig	Run Temp ^oC	Conversion to liquids (vol. %)	% deS	% deN
Harshaw Co-Mo0401	3:2	800	400	425	13.9%	28%	8%
Harshaw W-0101	3:2	2000	1600	438	16.7%	0%	9%
Harshaw HT-100	3:2	1900	1000	440	19.4%	42%	21%
Harshaw Mo-1201	3:2	1900	1500	430	16.7%	18%	17%
Harshaw Cr-0304 unsulfided	3:2	1900	1700	435	11.1%	0%	0%
Harshaw CoMo-0603	3:2	1925	1000	435	13.9%	31%	15%

BATCH RUN DATA

CATALYST	Solvent-to-SRC Wt. Ratio	Initial Cold H_2 psig	Final Cold H_2 psig	Run Temp ^oC	Conversion to Liquids	% deS	% deN
Sn powder	3:2	2000	1675	435	13.9%	.6%	0%
Harshaw Ni-4303	3:2	2000	1100	435	22.2%	31%	20%
Harshaw Ni-3210	3:2	2025	1625	437	13.9%	0%	.7%
*none (feedstock run)	3:2	1950	1750	430	0%	0%	1%
Girdler G-3A Fe_2O_3 powder	3:2	2025	1650	437	22.2%	14%	19%
$SnCl_2.2H_2O$ crystals	3:2	2000	950	425	5.5%	29%	17%
Harshaw Cr-0105 unsulfided	3:2	2075	1900	435	5.5%	0%	0%

* Run #24 was the basis for calculation of conversion yield for all 3:2 solvent ratio runs.

BATCH RUN DATA

CATALYST	Solvent-to SRC ratio	Initial Cold H_2 psig	Final Cold H_2 psig	Run Temp ^oC	Conversion	% deS	% deN
Harshaw Cr-0105 sulfided	3:2	2000	1600	435	13.8%	6%	14%
Harshaw HT-400	3:2	2000	1200	445	25 %	47%	23%
$AlCl_3$, powdered	3:2	2075	1275	450	25 %	31%	48%
$CuCl_2 \cdot H_2O$ fine crystals	3:2	1975	1000	440	11.1%	46%	22%
$ZnCl_2$, powdered	3:2	1900	900	441	19.4%	65%	35%
15% $NiCl_2$ on silica (A)	3:2	2025	1500	440	13.8%	18%	15%
Harshaw HT-500	3:2	1950	850	442	25 %	45%	18%
38% $CdCl_2$ on silica alumina (B)	3:2	1900	1000	443	13.8%	12%	13%
Ketjen HC-5	3:2	2025	1400	441	22.2%	35%	28%

(A) $3 m^2/gr$; mean pore diameter = 0.82u; 86% SiO_2, 9% Al_2O_3, 2% Fe_2O_3, 1% CaO

(B) 43 m^2/gr; mean pore diameter = 0.52u; 51% SiO_2, 46% Al_2O_3, 0.7% Fe_2O_3, 0.3% CaO

BATCH RUN DATA

CATALYST	Solvent-to Wt SRC Ratio	Initial H_2 Pressure	Final H_2 Pressure	Run Temp °C	Conversion	%deS	%deN
Silica-Alumina (B)	3:2	2000	1950	435	19.5%	0%	3%
13.5% Fe_2O_3 10% Cr_2O_3 on silica alumina (B)	3:2	1950	1650	435	16.6%	2%	3%
24% $NiCl_2$ on silica alumina (B)	3:2	1875	1225	442	22.2%	29%	6%
Ketjen 330-3E	3:2	2000	1050	442	19.4%	43%	13%
50-50 mix of Ketjen 330-3E and 38% $CdCl_2$ on silica alumina	3:2	1925	1100	447	16.6%	33%	17%
MSU STK-1	3:2	1900	1450	437	16.6%	22%	0%
Girdler G-3 Fe_2O_3 tablet	3:2	1800	1400	452	8.3%	0%	0%
Harshaw Ni 4401	3:2	1825	1175	442	19.4%	37%	14%

B. 43 m^2/gr; mean pore diameter = 0.52u; 51% SiO_2, 45% Al_2O_3, 0.7 Fe_2O_3, 0.3% CaO

APPENDIX C

CONTINUOUS RUNS: CONVERSION OF SRC TO LIQUID

CATALYST		LHSV	SCF/BBL H_2	TEMP (°C)	% deS	% deN	% NAPTHA IBP-425°F	% FUEL OIL 425-600°F	% GAS OIL 600-700°F	RESIDUE
Harshaw Ni - 4401 E 1/10" *		2	10,000	450	7	20	14	-2	0	88
Harshaw	A.)	1	10,000	445	75	64	11	35	21	33
	B.)	2	10,000	445	67	33	58	0	0	42
	C.)	3	10,000	445	63	12	0	31	0	69
	D.)	1	10,000	420	71	17	-5	22	14	69
	E.)	1	10,000	400	59	14	0	11	14	75
Ketjen HC-5 E 1/16"	A.)	2	10,000	445	65	46	28	33	0	39
	B.)	1	10,000	445	85	35	11	21	24	44
	C.)	1	7,000	445	69	25	0	28	17	55
	D.)	1	13,000	445	88	36	0	26	18	56
MSU STK-7 E 1/8"	A.)	1	7,000	445	39	55	42	11	19	28
	B.)	1	9,200	445	57	23	5	28	14	53
	C.)	1	13,000	445	53	21	3	31	19	47
	D.)	3	10,000	445	41	9	0	28	14	58
	E.)	2	10,000	445	33	9	-3	25	19	58
	F.)	1	10,000	420	38	0	-5	22	11	72

Note: * 7:2 solvent -to- SRC atmospheric solution used. All others used a 3:2 ratio feed; pretreated at high pressure and temperature.

CONTINUOUS RUNS: CONVERSIONS OF SRC TO LIQUID

CATALYST		LHSV	SCF/BBL H_2	TEMP (^{o}C)	% deS	% deN	% NAPTHA IBP-425^{o}F	% FUEL OIL 425-600^{o}F	% GAS OIL 600-700^{o}F	% RESIDUE
MSU	A.)	1	10,000	445	63	59	36	22	11	31
STK-5-2-1	B.)	2	5,000	445	65	17	6	19	11	64
E 1/16"	C.)	1	7,500	445	57	23	11	21	10	58
	D.)	1	5,000	445	59	20	8	17	14	61
	E.)	2	2,500	445	59	11	-10	22	13	75
	F.)	1	2,500	445	63	18	-7	32	14	61
	G.)	2	7,500	445	51	20	5	24	13	58
	H.)	2	10,000	445	45	15	-1	29	0	72
	I.)	1	10,000	445	37	25	13	33	10	44

Note: Ni - 4401 run used 100 ml catalyst, but all others used 70 ml.
Catalyst was diluted 50-50 with inert 1/8" support.
Pressure of runs approximately 1000 psig.

APPENDIX D

AVERAGE PORE DIAMETER CALCULATIONS

For a catalyst pellet with pore length L and average pore diameter D -

$$\text{Pore Volume} = \frac{\pi}{4} \cdot D^2 \cdot L$$

$$\text{Surface Area} = \pi \cdot D \cdot L$$

$$\frac{\text{Pore Volume}}{\text{Surface Area}} = \frac{\pi/4 \cdot D^2 \cdot L}{\pi \cdot D \cdot L}$$

$$= \frac{D}{4}$$

$$\therefore \quad 4 \cdot \frac{\text{Pore Volume}}{\text{Surface Area}} = D$$

APPENDIX E

LIST OF TERMS

Asphaltols - coal conversion products soluble in pyridine but not in benzene.

Asphaltene - soluble in benzene but not in pentane

Oil - soluble in pentane

Scissile - capable of being cut or split easily

Beneficiation - physical cleaning to separate rock and ash from coal

NMR - nuclear magnetic resonance specostropy

Heterogeneous catalysts - catalysts in a different phase than the reactants. Usually denotes solid catalyst used in fluid reactants.

Homogeneous catalysts - catalysts in the same phase as the reactants

LHSV - liquid hourly space velocity. Defined as:

$$\frac{\text{Volume liquid per hour}}{\text{Volume of active catalyst}};$$

It is a measure of residence time.

Psig - pounds per square inch, gauge.

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Henton, Lee Morgan
Catalytic hydrogenation of PAMCO solvent-refined coal

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