CATALYST TAILORING FOR COAL DERIVED LIQUIDS

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The United States energy requirements have refocused attention on coal processing for fuels in forms other than for direct combustion. Hydrogenation of coal and coal liquids is included in this renewed interest. Many reports (1, 2, 3) are available on studies directed toward upgrading coal and coal liquids by hydrogenation. A good portion of these efforts is directed toward testing and developing various active metals for catalysts. The nature and character of the carrier or support material have received somewhat less attention. With coal liquids, removal of nitrogen is particularly important, yet almost no work has been reported in this area.

The work reported in this paper is part of an overall program to specifically tailor catalysts for upgrading coal derived liquids. Attention here is given to the removal of sulfur and nitrogen atoms from a coal liquid.

The Pittsburg & Midway Coal Mining Company has developed a process to produce an ashless, low sulfur fuel from coal (4, 5, 6). Light oils and gas oils are also co-products from this solvent refined coal process. However, the nitrogen and sulfur in these oils must be removed if these oils are to be of value for further fuel processing. Our catalyst development work was at first directed toward upgrading these oils by the removal of their heteroatoms, particularly sulfur and nitrogen.

Since only limited quantities of the oil products from the solvent refined coal process were available from actual laboratory and pilot production, our initial work was performed on a coal liquid which has somewhat similar properties. For a comparative basis, results are reported on two catalysts which were obtained from Nalco Chemical Company. The first objective is to compare operating characteristics of these two catalysts, which have essentially identical composition but contain a rather different pore volume and pore size distribution. The catalyst properties are discussed below. The apparatus used in the study was a downflow, packed-bed reactor; details are also given below under experimental.

Feedstock. The feedstock used in this experiment was a raw anthracene oil which was obtained from the Reilly Tar & Chemical Corporation. The feed properties are given in Table 1, showing that the sulfur level was 0.45 wt% and nitrogen was 0.8 wt%.

Catalysts. The two Nalco Catalysts which were tested were Nalcomo 474 and Sphericat 474. These were both compounded with 3.5 wt% of cobalt oxide and 12.5 wt% molybdeum oxide on alumnia support. Pore volume was 0.463 cc per gram for the Nalcomo 474 and 0.981 cc per gram for the Sphericat 474. As shown in Figure 1, the Sphericat has a bimodal pore distribution with modes at about 30 angstroms for micropores and at 850 angstroms for macropores. The Nalcomo catalyst had a singular and rather narrow distribution at about 33 angstroms. These pore size distributions were determined from mercury penetration data to 60,000 psi. Figure 1 is a plot of dV/d (lnr), where

V = accumulative pore volume
r = pore radius

The total surface area per gram was about the same for both catalysts, and an 8/10 mesh size was used. Properties are shown in Table 2.

Apparatus. The experimental apparatus is diagramed in Figure 2. Anthracene oil was fed from a Ruska pump through preheated lines into the reactor. The feed oil was contacted with hydrogen just before the reactor inlet. The ½ inch diameter reactor was packed with from 13.7 to 15.8 grams of catalyst and had pre- and postheat zones of inert material. The reaction temperature was monitored with a traversing thermocouple in a thermowell located within the center of the reaction tube. Excellent temperature control was obtained by three massive aluminum blocks which were grooved and wound with resistance heating wires. The larger center block was maintained at the desired temperature by a controller, while the smaller top and bottom blocks were controlled manually to obtain flat temperature profiles. A typical profile is shown in Figure 3. Hydrogen flow was monitored by observing rates on a wet test meter placed in the exit line. The desired operating pressure was controlled by a back pressure regulator and was read on a Heise gage located at the reactor inlet.

Analysis. Sulfur analyses were made on a Leco Model 634-700 automatic sulfur analyzer which had been modified for relative low sulfur determinations. These modifications include slight adjustment in the techniques which are outlined in ASTM D 1552-64, and the addition of sodium azide to eliminate nitrogen interference. Nitrogen analyses were made by a commercial laboratory and by our own laboratory, both using a modified micro Kjeldhl technique. Distillations were performed according to ASTM D 1160 technique. Catalysts properties were obtained from information supplied by Nalco Chemical Company and by commercial laboratory analyses.

Experimental. Experiments were made over a temperature range of 600 to 800°F, a total pressure range of 500 to 2000 psig, and space times (based on reciprocal liquid hourly space velocities) of ¼ to 2 hours. Most of the experiments were made on Nalcomo 474 over these variable ranges, and the comparison of the two catalysts was made from data taken at a fixed set of conditions. These conditions were 700°F, 2000 psi pressure, and about one-hour space time. These two comparative runs each covered a total of over 40 hours oil-catalyst contact. There were several planned shutdowns during these experimental runs. The catalysts were presulfided before use. For ease of comparison, the experiments on these two 40-hour runs were performed at identical weight hourly space velocities. This means that the volume hourly space velocities were different because of a difference in the catalyst pellet density.

In trickle flow reactors there is always a question of adequate contacting

of oil and solid particles. In addition to other variables, particle size, superficial oil velocity, and superficial gas velocity may influence the nature of oil-solid contacting. Tests were made by varying superficial gas velocity by a factor of 10, and no noticeable influence on desulfurization or denitrogenation was observed over this range. There seemed to be adequate contacting of oil and solids for the particle sizes and velocities used within the study.

Results. The pressure, time and temperature effects for desulfurization of the Nalcomo 474 catalyst are shown in Figures 4, 5, and 6. The rate of desulfurization is rapid within the first 0.5 to 1.0 hours space time, and becomes quite slow thereafter. The maximum desulfurization appears to be fixed at around 90-95 percent removal. However, at 90 percent removal of sulfur from the feed oil, the product sulfur level is in the range of 400 parts per million. This is within the region where reporducibility of sulfur analyses is becoming limited by the techniques used. The effect of pressure between 500 and 2000 psi on desulfurization is the greatest at 600°F operation; whereas, there was little pressure response noted at 700 and 800°F. The multiple points shown in Figure 6 for 700°F and one hour space time were duplicates except for a difference of over 60 additional hours of oil-catalyst contact. There was negligible loss of catalyst desulfurization activity during the 70 plus hours total oil-catalyst contact of this sequence of experiments.

The extent of hydrocracking with the Nalcomo catalyst is shown in Table 3 for operation at 800°F and two hours space time. These represent maximum temperature and times used in the experiments. The extent of hydrocracking is quite dependent upon the pressure of the experiment. Two reference points are listed in the table. One shows the amount of 650°F+ material in the feed which was converted to lower boilers, and the other reference point is the amount of 500°F+ material converted. Note that the data indicate significant quantities of material boiling above 650°F were converted to lower boilers, but very little of this was converted to material boiling below 500°F. However, at 2000 psi and 800°F, significant hydrocracking to -500°F material occurs. The extent of hydrocracking at lower temperatures and pressures was, of course, lower than those shown in Table 3. Very little hydrocracking takes place at 600°F.

Shown in Figure 7 is a comparison of the desulfurization levels for both the Nalcomo 474 and the Sphericat 474 catalysts. The desulfurization activity of the Nalcomo catalyst achieved a level of about 92 percent removal after 10 hours on oil, and remained relatively steady between 88 to 90 percent for over 50 hours. The Sphericat 474 showed almost identical desulfurization characteristics from ten through 42 hours on oil. The Sphericat data tends to be slightly higher than those of the Nalcomo; however, within the limits of this study this is not shown unequivocally. For both catalysts, there is no noticable loss in desulfurization over 40-50 hours.

Figure 8 presents a comparison of the two catalysts for denitrogenation for over 40-50 hours oil-catalyst contact. Although the Nalcomo 474 catalyst maintained a stable denitrogenation activity, the Sphericat denitrogenation activity dropped rather quickly. Further, the ability of the Sphericat to remove nitrogen was always lower than that of the Nalcomo catalyst. In both cases the ability to remove nitrogen was limited. For Nalcomo this was no more than 60 percent at best; and for the Sphericat, no more than about 50 percent.

Discussion. The hydroprocessing of heavy liquid feedstocks for sulfur and nitrogen removal is representative of one of the most complex reaction

systems to be encountered. With solid, liquid and vapor phases present, there are many resistance zones which can limit mass transfer. Several critical dimensions of the reaction system must be considered. Among these are:

reactor bed length and diameter
catalyst particle size
liquid film thickness surrounding the solids
catalyst pore size and pore size distribution
size of the sulfur and nitrogen compounds

In processing heavy feedstocks the catalyst pores will be filled with liquids. The sulfur and nitrogen compounds must then transfer from the liquid film surrounding the pellets into the relatively quiescent liquid within the pores. These molecules then must diffuse through the liquid to the active solid surface. Hydrogen must transfer from the bulk gas phase into the external liquid film, and finally through the liquid filled pores to the reaction surface. There are three primary zones which may control the overall removal of heteroatoms:

1. Interparticle Resistance - the exterior catalyst surface must be supplied with reactants; gaseous or liquid.

2. Intraparticle Resistance - the reactants must diffuse through the porous catalyst structure.

3. Surface Phenomena - molecules must adsorb, desorb and react on the surface.

In this coal liquid study with the catalyst pores filled with liquid, and assuming that many of the sulfur and nitrogen containing molecules are relatively bulky species, the most likely controlling resistance of the overall process is the transport of these bulky molecules through the pores.

Interphase and interparticle mass transfer in the form of adequate liquid distribution over the solids, hydrogen transfer from the bulk phase, and liquid supply to the external pellet surface were probably not controlling. This is shown, in part, when no effect was observed when hydrogen flow rate was varied by a factor of ten. Liquid distribution over solids is partly controlled by the ratio of reactor diameter to that of the catalyst (7). Numbers from 5 to 25 have been suggested for this ratio for adequate liquid distribution. The value in this study was 6.2. The effect of backmixing in trickle-flow laboratory reactors has recently been discussed by Mears (8). For freedom from backmixing a value of 350 has been suggested as a conservative estimate for the ratio of reactor length to particle size. The value in this study was about 144.

Although specific experiments were not performed on various particle sizes in order to determine a catalyst effectiveness factor, a first estimate suggests that the effectiveness factors for both desulfurization and denitrogenation of this coal liquid fall between 0.3 and 0.6. These numbers are based on only very approximate estimates of effective diffusivities. Typical desulfurization data taken under similar conditions, but on petroleum stocks fall into this range. There are, of course, significant differences between these general feed types.

For catalysts operating with effectiveness factors in this range, significant reactant concentration gradients can exist within the solids. The smaller and more mobile hydrogen molecules can penetrate far deeper into the catalyst pellets than can the much larger liquid reactants. Some of the larger nitrogen and sulfur containing molecules believed to be in high temperature

coal tar liquids are shown in Table 4 (9). There is, of course, a spectrum of molecular sizes, and these shown in Table 4 may only be representative of the larger sulfur and nitrogen species, but not necessarily in anthracene oil. For illustrative purposes, consider a reactant molecule with a characteristic or critical diameter in the range of 10-15 A°. For comparison, critical diameters for smaller compounds are shown in Table 5. When the size of the diffusing molecules begin to approach the pore size, then diffusion becomes strongly retarded. This sort of retardation was probably operative with both the Nalcomo and Sphericat 474 catalysts. As shown in Figure 1, the micropores of both catalysts have modes at about 30 A° radius. Thus it seems likely that a significant diffusion limitation exists for the larger reactant species.

The end result to be expected is relatively low active surface utilization which is revealed in a low effectiveness factor. Values of 0.3 or lower can be expected. In a trickle-flow reactor operating on a gas oil, effectiveness factors as low as 0.3 were reported (10). The major limitation was said to be sulfur compound transport within the pores. Molecular sizing effect was shown by Maxted and Elkins (11) in comparing catalytic hydrogenation of cyclohexene and ethyl crotonate with supported platinum. Supports of varying pore structure were equally active in hydrogenating the smaller cyclohexene molecule; however, those of fine pore structures revealed a lower activity for hydrogenating the larger ethyl crotonate molecule.

In comparing the performance of the Sphericat and Nalcomo catalysts, the increased pore volume and bidispersed character of the Sphericat provided no advantage in the limited tests performed. Considerable evidence suggests that first expectations would be that the macropore structure and increased pore volume of the Sphericat would provide greater access to the active surface; thus, increased desulfurization and denitrogenation. At least gaseous diffusion is enhanced by increased macropore volumes (12, 13). In desulfurization studies on straight-run Kuwait gas oil, an increase in catalyst macropores resulted in increased sulfur removal (14). Significantly, these experiments were conducted under liquid filled pore conditions. In work by Beuther et al. (15), the hydrodesulfurization of a light catalytic gas oil increased with an increase in catalyst porosity up to a maximum and then fell off. However, this comparison was made at a constant liquid hourly space velocity such that a simple loss in total catalyst mass would eventually offset any gain in porosity enhancement. In a recent study on desulfurization of diesel oil, those catalysts with larger pore volumes were reported to be more active in removal (16).

Contrary to this evidence, the advantages of increased pore volume were not shown on the Sphericat catalyst when processing this coal liquid. Anisotropic structure of the spherical catalyst is a possible explanation. Satterfield et al. (7) reported that spherical, palladium-on-alumina pellets showed a layering effect with respect to pore regions. These pellets contained an outer, fine pore region followed by a coarser section, and then a second fine pore region. If the Sphericat catalyst used in this study contained such a micropore outer region, then at low effectiveness factors there would be no advantage shown by those coarser regions which contribute to the higher pore volume. Satterfield has also mentioned this anisotropic pore layering effect in another study utilizing spherical catalysts (17). Such characteristics could possibly be unique to spherical catalyst support preparation techniques.

Figure 1 indicates that both catalysts have a micropore structure in the order of 30-35 A° radius, which will account for most of the 270 m^2 of surface per gram of catalyst. Note in Figure 10 that the cumulative pore

volume curves are quite similar through about 0.37 cc/g (at about 45 A°). Up through this point, most of the surface will have been accounted for. The cumulative volumes beyond contribute relatively little to total surface area (volume in a hypothetical pore vylinder will be increasing with radius squared, but area with radius to only the first power). Apparently the desulfurization limitations lie in the micropore region and not in the macropore region.

The cause of the difference in denitrogenation behavior of the two catalysts is difficult to resolve. Thus far, the effective reaction zones within these catalysts have been assumed to be the same. The initially lower nitrogen removal of the Sphericat suggests that the pretreatment might have been sufficiently different to affect nitrogen but not sulfur removal. In any case, there is a loss in activity which indicates a greater carbon formation by the Sphericat. The immediate cause of this increased cracking to form carbon is not evident. A relative measure of the amount of carbon formed on each catalyst was not available since experiments were still underway on the Sphericat.

In general, satisfactory nitrogen removal is more difficult to obtain than that for sulfur. From studies made on pure compounds, the removal of nitrogen from large heterocyclic rings is a step-wise hydrogenation process (18, 19). Carbazole is a nitrogen containing compound found in coal liquids. Flinn, et al. (18) discussed a five-step, dual path sequence leading to the denitrogenation of this compound. This is shown in Figure 9 along with a sequance for pyridine. These complex sequences for denitrogenation are apparently more sensitive to subtle catalyst property differences that, in turn, have little effect in desulfurization.

Relatively little work has been done to tailor catalysts and support properties explicitly to removal of heteroatoms from coal liquids. Although a vast amount of work has been given to processing petroleum stocks, and some of this information can be applied to coal liquids, there are significant differences between coal and petroleum derived materials which require specific catalyst tailoring for these coal liquids. The removal of nitrogen from coal liquids will demand particular attention.

TABLE I

FEED OIL PROPERTIES

Carbon wt%	90.65
Hydrogen	5.76
Sulfur	0.45
Nitrogen	0.8
Ash	Nil
API Gravity @ 60°F	-7
*Distillation	
Initial	380°F
10 Vol%	450
30	570
50	650
70	700
90	815

*Normal boiling data determined from ASTM D 1160 data.

TABLE 2

CATALYST PROPERTIES

	Nalcomo 474	Sphericat 474
*CoO, wt%	3.5	3.5
*MoO_3, wt%	12.5	12.5
Support	Alumina	Alumina
Pore Volume, cc/g	0.463	0.981
*Surface Area, m^2/g	270	270
Pellet Density, g/cc	1.31	0.77
*Packed Bed Density, g/cc	0.73	0.48
Pellet Size	8/10 Mesh	8/10 Mesh

*Nalco Data

TABLE 3

Hydrocracking On

NALCOMO 474 at 800°F,

2 Hr. (liquid hourly space time)

Pressure, psi	500	1000	2000
*Percent Loss in 650°F+ Boilers	20	36	57
Percent Loss in 500°F+ Boilers	5	8	20

$$*\text{Percent Loss} = \frac{(\text{fraction } 650^{\circ}\text{F+ boilers in feed}) - (\text{fraction } 650^{\circ}\text{F+ boilers in product})}{(\text{fraction } 650^{\circ}\text{F+ boiler in feed})}$$

TABLE 4

Large Coal Liquid Compounds Containing Heteroatoms

$C_{42}H_{27}N$	
$C_{43}H_{27}N$	
$C_{72}H_{42}NO$	Average Formulas Suggested For Coal Tar Components (9)
$C_{96}H_{64}N_2O_4S$	
$C_{144}H_{88}N_3O_7$	

Phenanthridine

2, 4 - Dimethylbenzoquinoline

TABLE 5

CRITICAL DIAMETERS OF
SOME REPRESENTATIVE MOLECULES

Molecule	Critical Diameter (A)
Hydrogen	2.4
Hydrogen Sulfide	3.6
Methyl Mercaptan	4.5
Ethyl Mercaptan	5.1
Thiophene	5.3
Triethylamine	8.4

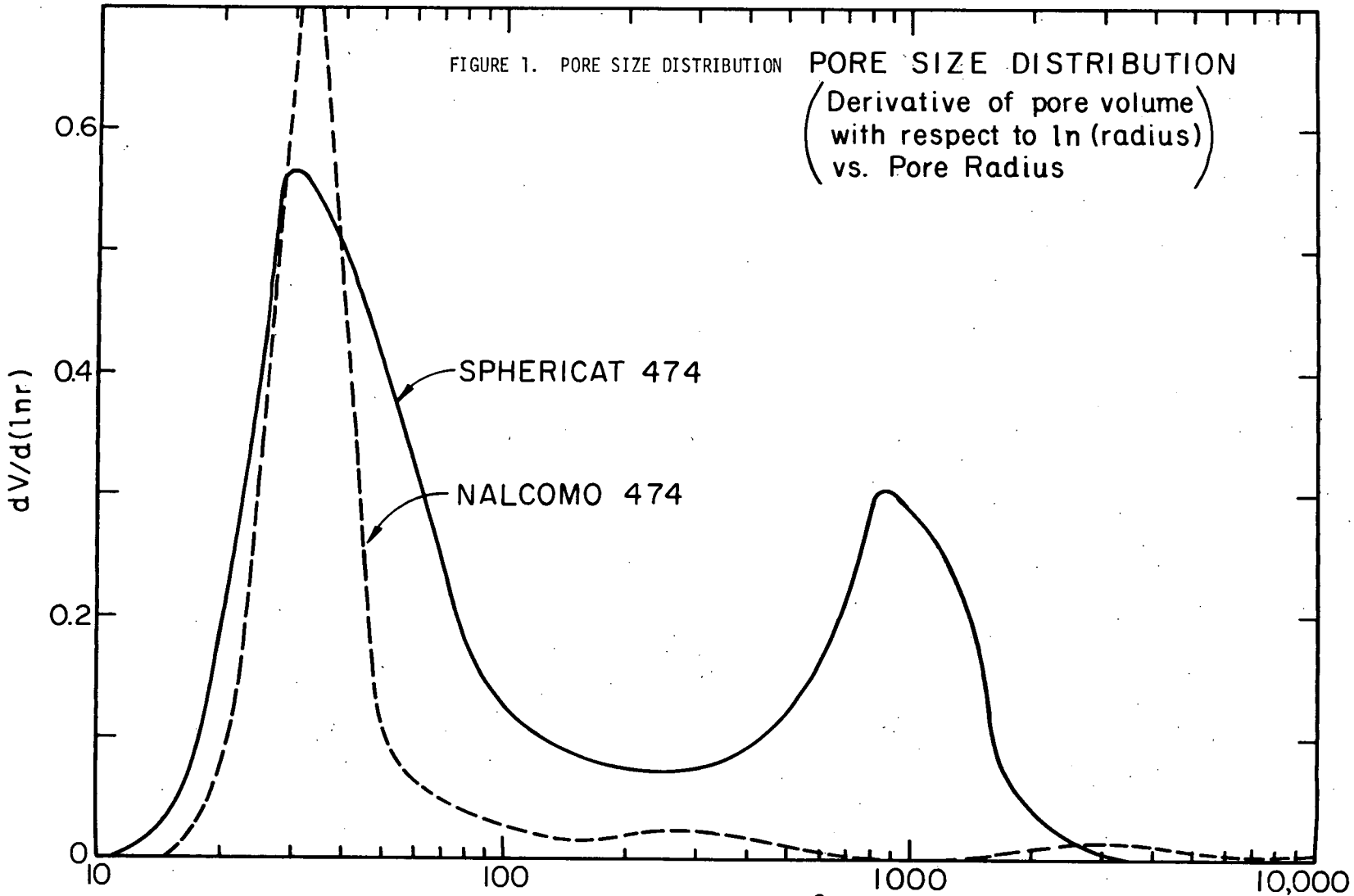
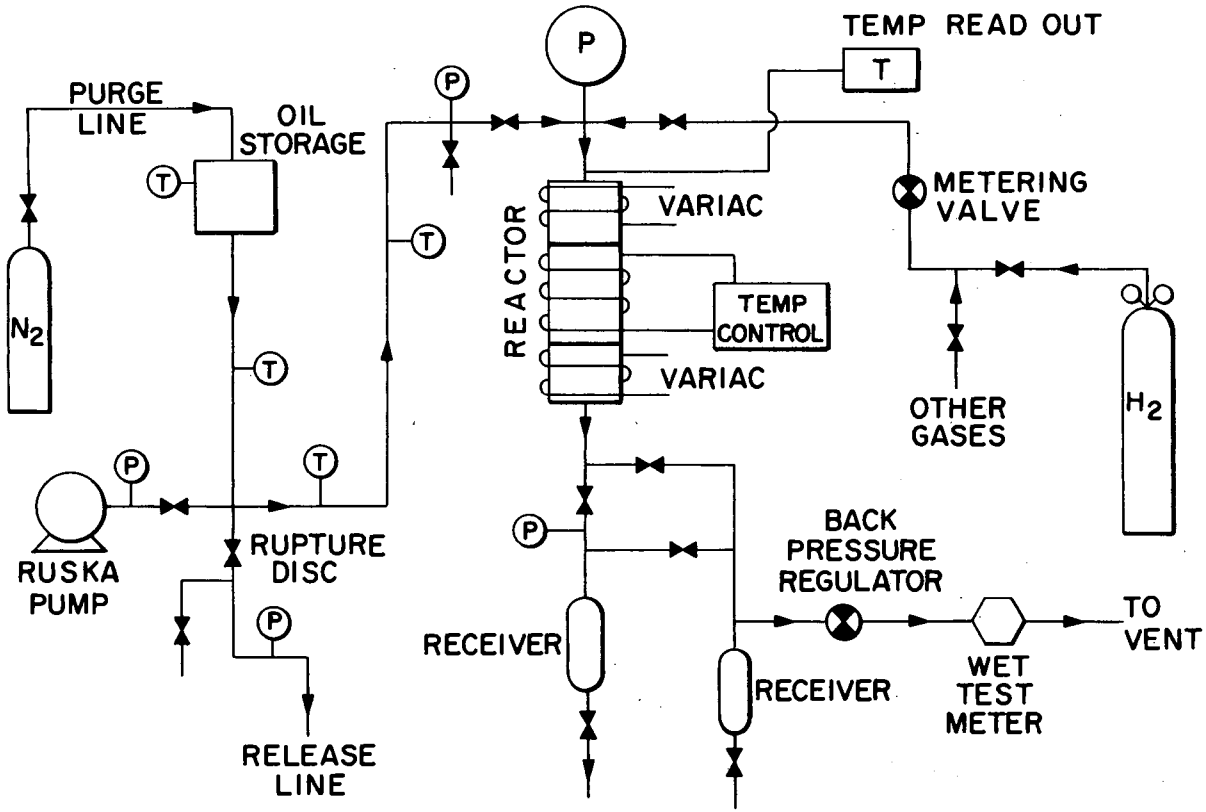


FIGURE 1. PORE SIZE DISTRIBUTION



EXPERIMENTAL APPARATUS

FIGURE 2. EXPERIMENTAL APPARATUS

FIGURE 3 TYPICAL REACTOR TEMPERATURE PROFILE

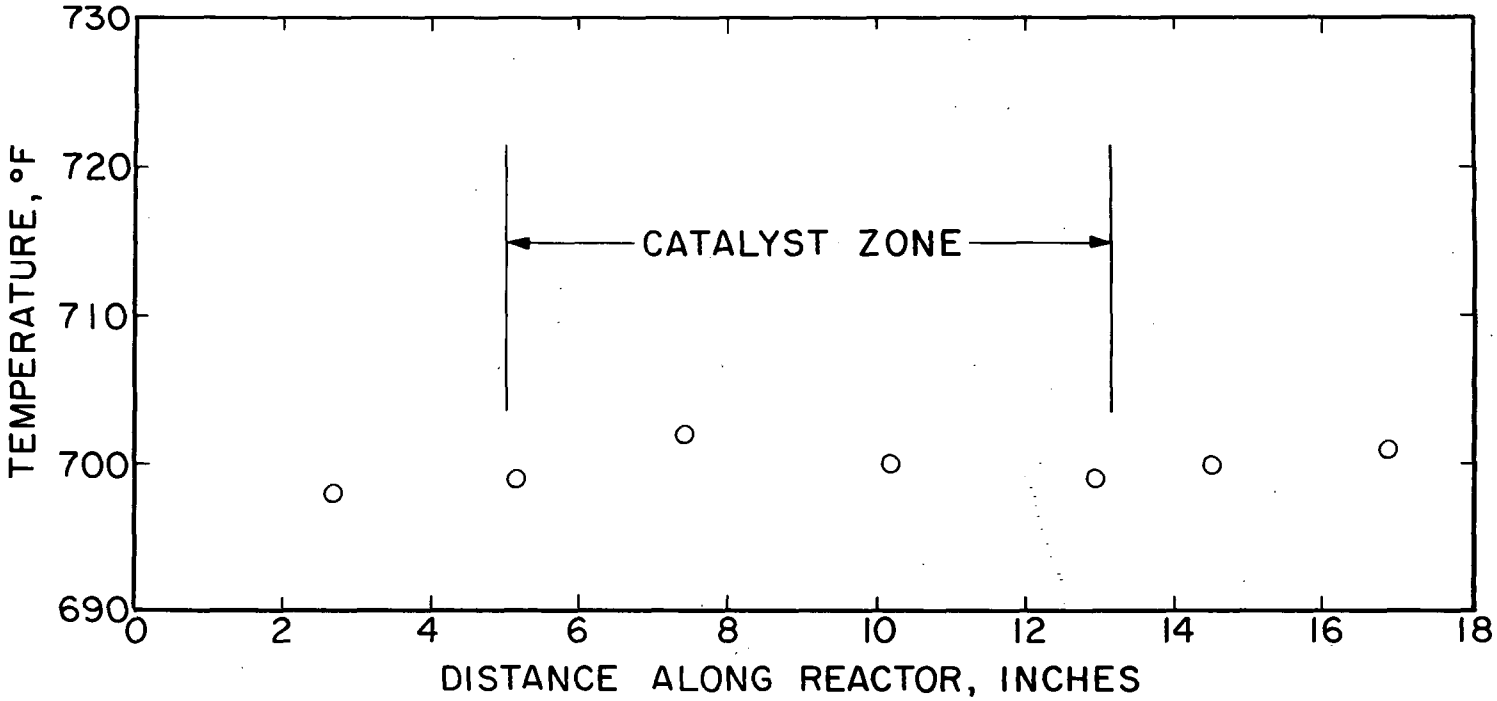


FIGURE 4

PERCENT SULFUR REMOVAL

AT VARIOUS SPACE TIMES-500 PSIG

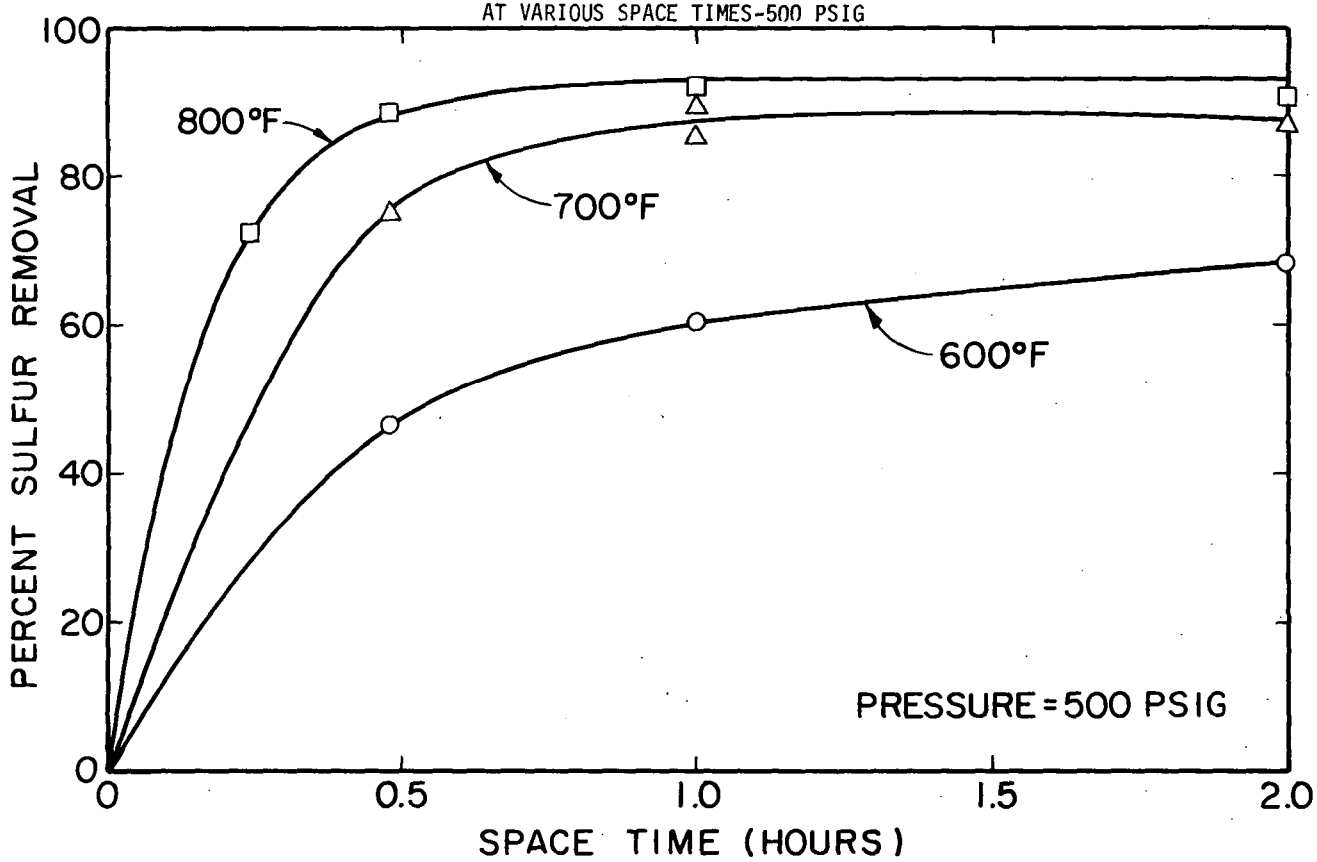


FIGURE 5

PERCENT SULFUR REMOVAL

AT VARIOUS SPACE TIMES-1000 PSIG

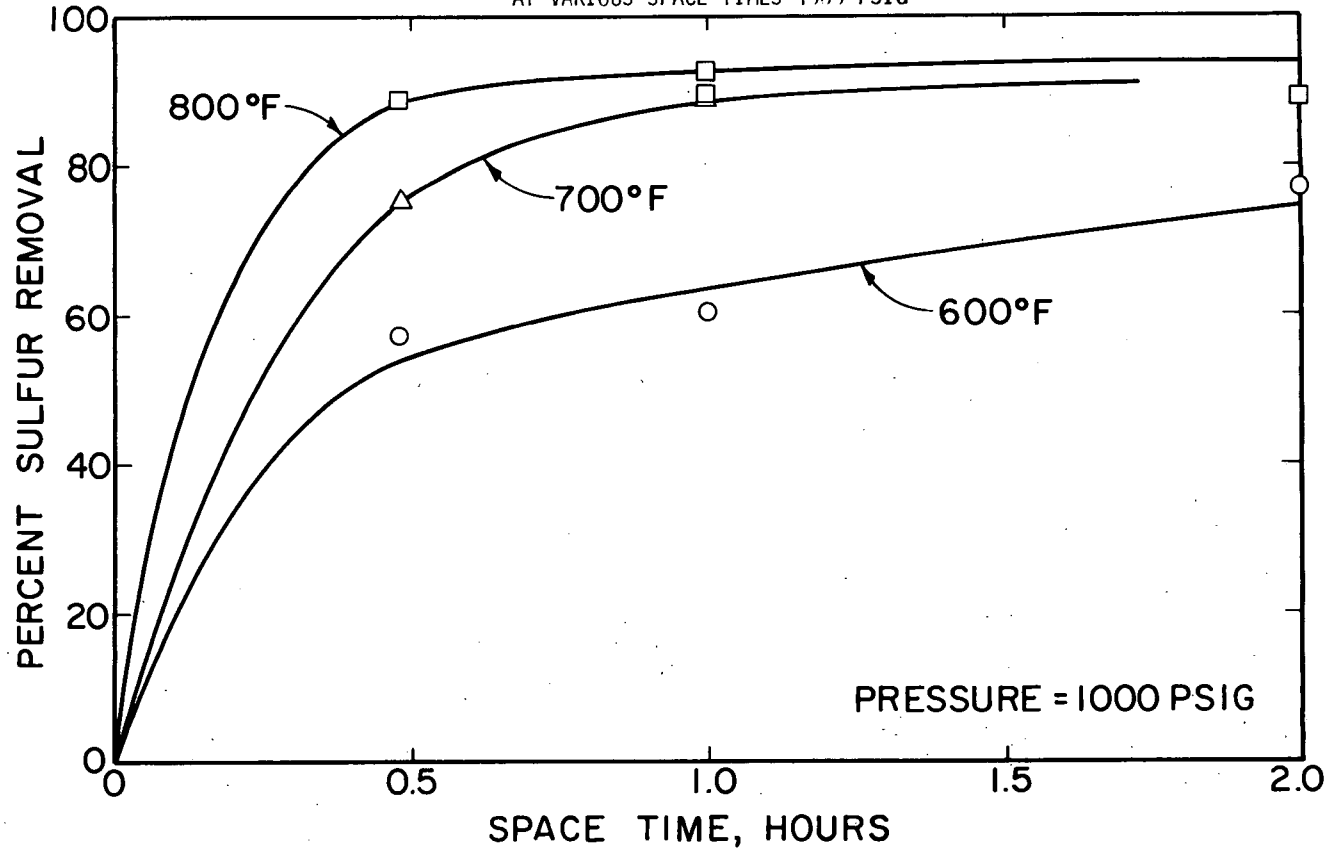


FIGURE 6

PERCENT SULFUR REMOVAL
AT VARIOUS SPACE TIMES-2000 PSIG

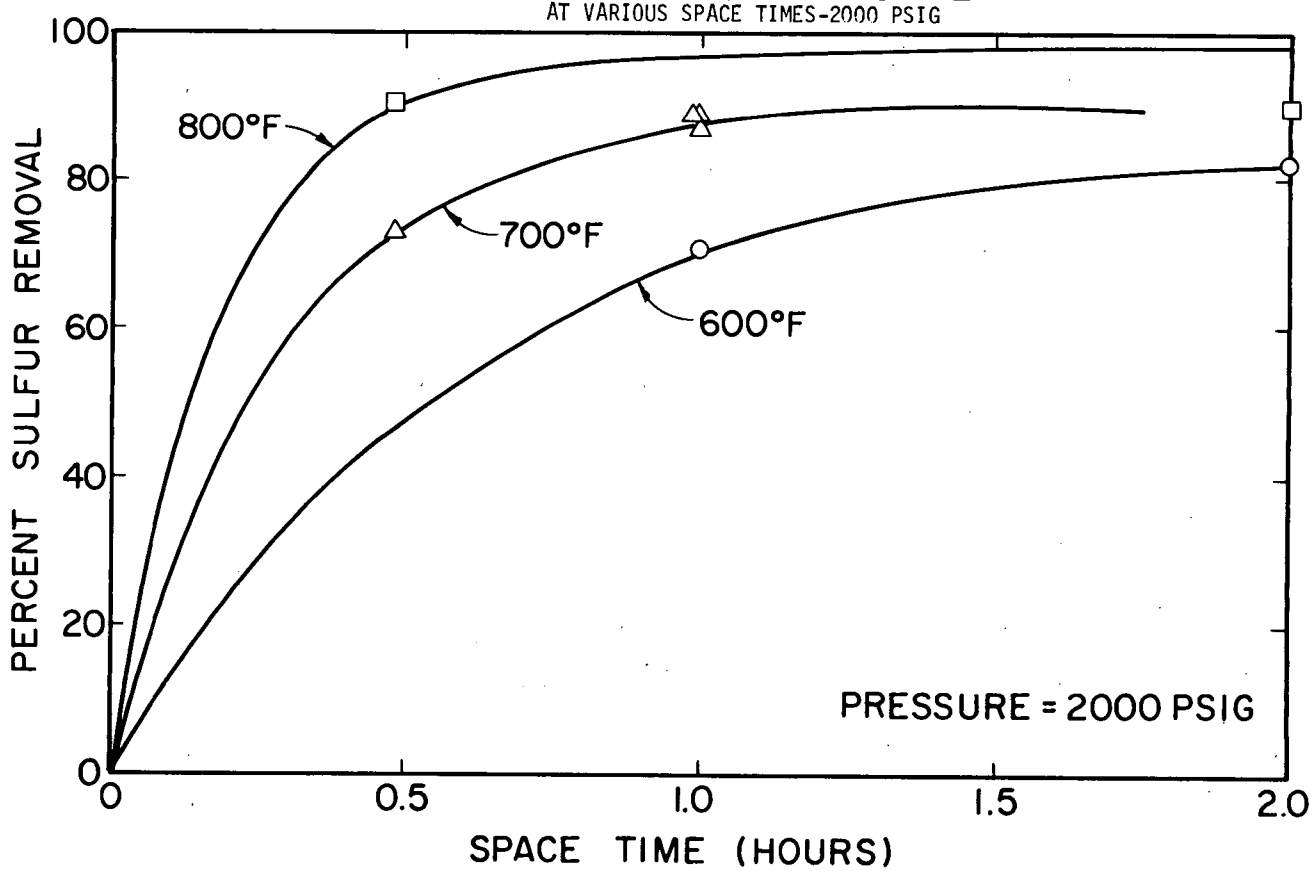


FIGURE 7

SULFUR REMOVAL AS FUNCTION OF CATALYST AGE

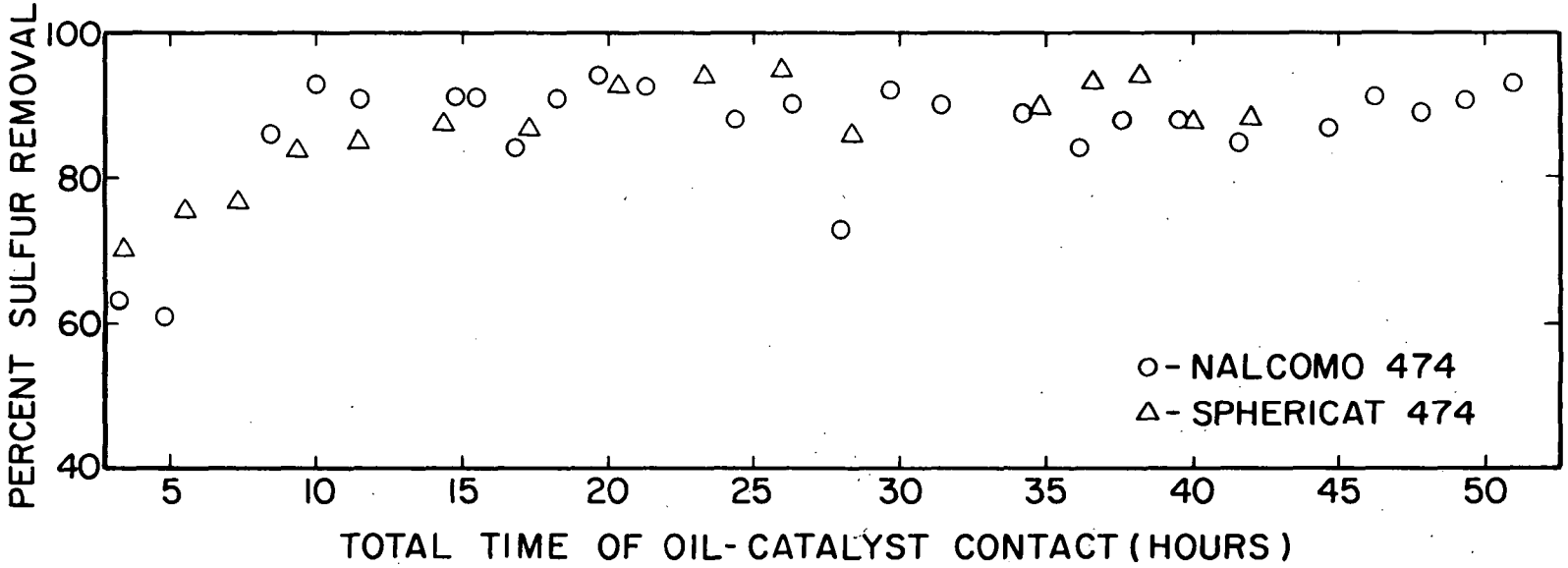
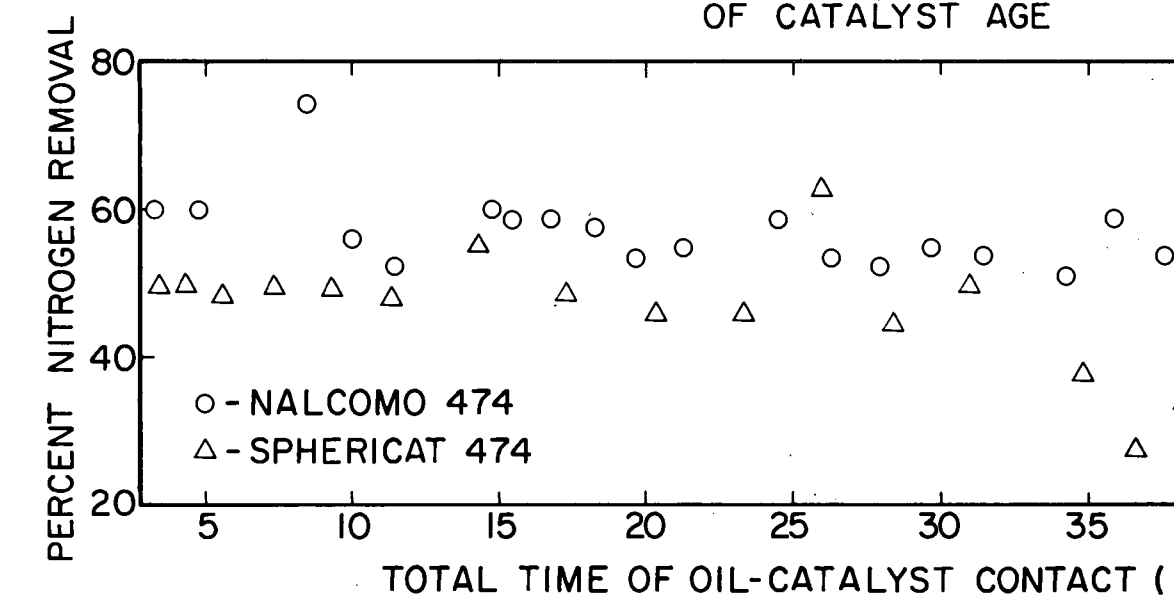


FIGURE 8

NITROGEN REMOVAL AS FUNCTION OF CATALYST AGE



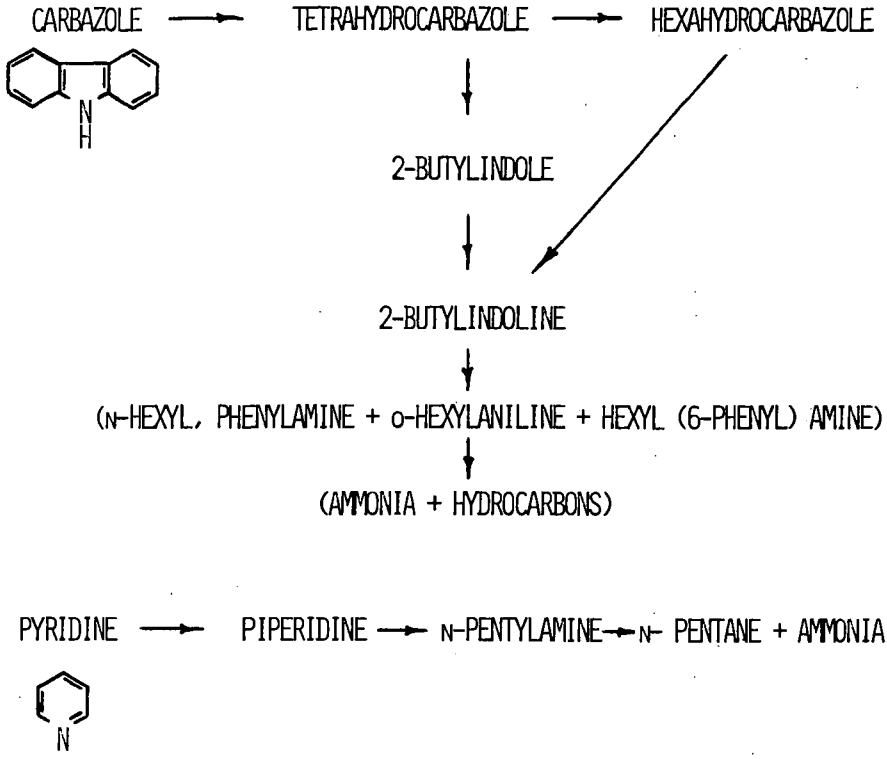
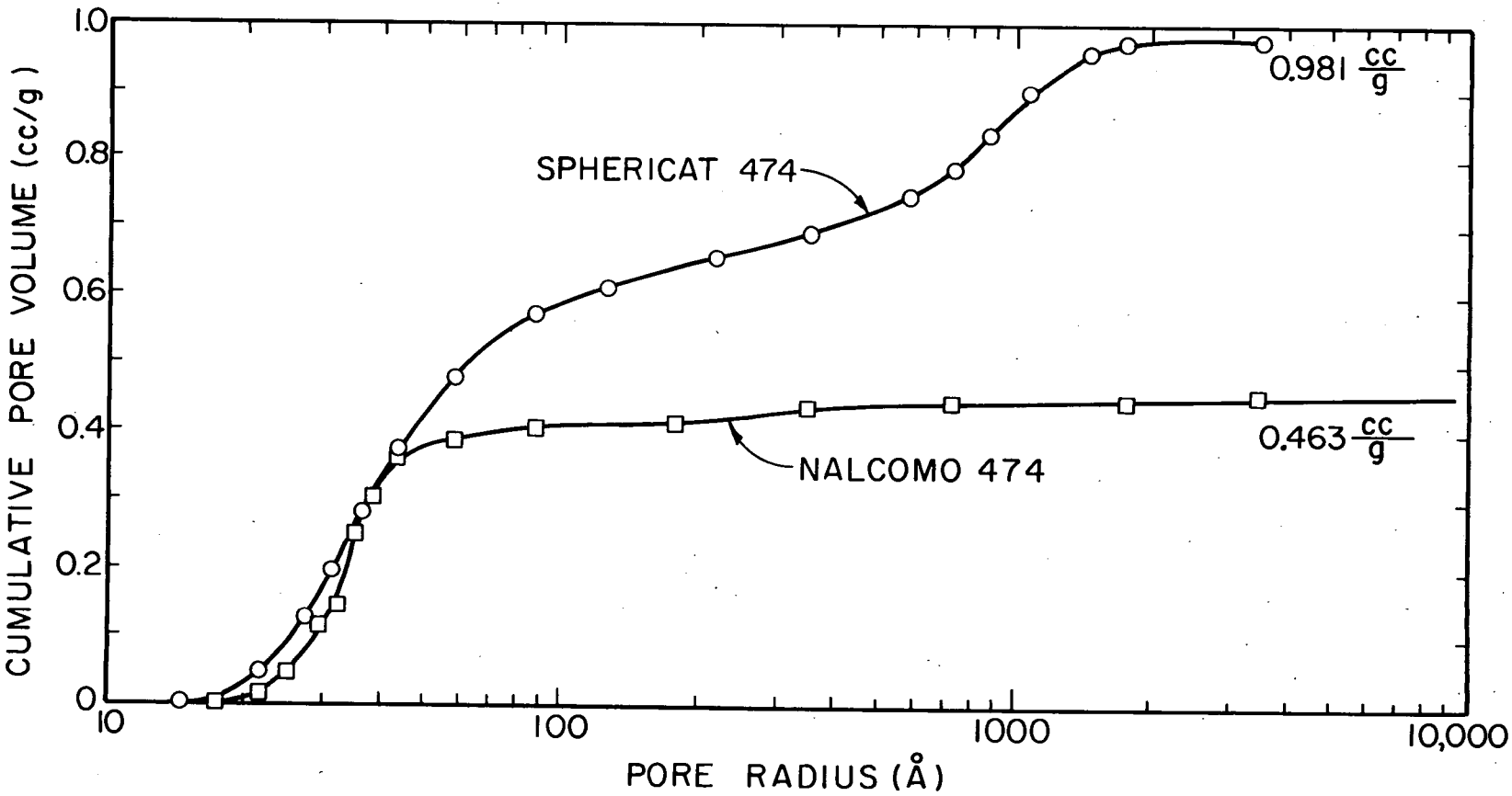


FIGURE 9

REACTION SEQUENCES FOR DENITROGENATION

FIGURE 10

CUMULATIVE PORE VOLUME
AS A FUNCTION OF PORE RADIUS



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DEPLETED URANIUM AS A CATALYST FOR HYDROCRACKING SHALE OIL

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INTRODUCTION

Crude shale oil, as produced by many retorting processes, contains considerable nitrogen and sulfur, has a lower hydrogen/carbon ratio than most high-quality petroleum oils, and has little material boiling in the gasoline range. Reduction of the boiling range and elimination of most of the nitrogen and sulfur are necessary in producing liquid products suitable for further processing to motor fuels by modern refinery methods. Hydrogenation under cracking conditions (here termed "hydrocracking") is one way of accomplishing these objectives. Development of hydrocracking catalysts for this purpose is important to future commercial use of the oil.

Uranium compounds have, at various times, been tested as hydrogenation catalysts. Prior to World War II, uranium was generally believed to occupy a position in the periodic table as a member of the chromium subgroup of elements together with chromium, molybdenum, and tungsten. In forming a characteristic solid trioxide and in displaying oxidation valences from 3 to 6 (11,13), uranium resembles molybdenum and tungsten, whose compounds have found considerable application as catalysts for hydrogenation-dehydrogenation reactions. These facts prompted the testing of uranium compounds for similar uses, and several patents were issued for these uses (1). Modern versions of the periodic table place uranium in the actinide series of elements in a position analogous to that of neodymium in the lanthanide series, which also has been reported to be a catalyst for hydrogenation-dehydrogenation reactions (14).

As a result of the atomic energy program, the Federal government has accumulated a large stockpile of "depleted uranium" -- the material remaining after the U-235 isotope has been removed. The extraordinary purification procedures used in its preparation encourage applications, such as catalyst use, where relatively high freedom from contaminants might be advantageous.

This paper reports the preparation and testing of two depleted uranium oxide catalysts for use in hydrocracking crude shale oil. The objectives of the hydrocracking experiments were to convert high-boiling shale oil into gasoline-boiling-range products and to eliminate sulfur and nitrogen from the gasolines produced.

CATALYST PREPARATION

One of the simplest methods of preparing a catalyst for heterogeneous catalytic reactions involves impregnating a porous solid material that serves as a catalyst support with a solution of the active ingredients, drying the impregnated support in an oven, and activating the dried catalyst by "calcining" or heating it in a furnace at a temperature that is usually at least as high as that to be used in the catalyzed reaction. When metal oxides are to be deposited on the supports, solutions of the nitrates often are used as the impregnating media because the nitrates usually have excellent solubility in water and are easily decomposed to the oxides by heating

(2,4,6,9,15,18). During the calcining step, the most stable oxides, which are characteristic of the metals, are formed.

When the catalysts are to be used for reactions that are conducted in hydrogen atmospheres, they often are pretreated with hydrogen gas to reduce the characteristic oxides that were formed during the calcining step to lower oxides, or to oxygen-free metals (2-4).

The uranium oxide catalysts tested in this work were prepared by the above methods. Uranyl nitrate, which has a high solubility in water and a low decomposition temperature (about 662°F (11)), was used for impregnating porous solid supports for the tests.

Catalyst Supports

Two different materials were used as catalyst supports. These were F-10 activated alumina, on which the uranium oxide was the sole added ingredient, and cobalt molybdate hydrodesulfurization catalyst with an alumina base.

The F-10 alumina was a standard, low-soda alumina, in the form of 8- to 14-mesh granules having approximately 100 square meters of surface area per gram. It was described by the manufacturer as a catalytic-grade alumina, and has been used extensively as a catalyst support.

The cobalt molybdate catalyst was in the form of 6- to 10-mesh granules having a surface area of about 350 square meters per gram. It contained 2.3 percent cobalt and 15.5 percent molybdenum in the form of the oxides on alumina. The uranium oxide catalyst using cobalt molybdate catalyst as a support was prepared following the experimental work with uranium oxide on alumina, which showed that the addition of uranium oxide to alumina increased the hydrocracking of high-boiling shale oil to lower boiling material. It was hoped that the presence of uranium oxide on cobalt molybdate would combine the benefits of excellent sulfur and nitrogen elimination provided by the cobalt molybdate with the increased conversion to lower boiling fractions provided by the uranium oxide.

Use of one catalytic agent deposited on another catalyst is far from new. Hendricks (8), in a Union Oil Co. patent for preparing cobalt molybdate catalyst, described a procedure for successive impregnation of a carrier by salts of molybdenum and cobalt with drying and calcining steps interspersed. Also, the numerous "polyfunctional" naphtha-reforming catalysts prepared by adding metallic agents to silica-alumina cracking catalysts are examples of such preparations.

Impregnation Procedure

In preparing the catalysts, a weighed amount of depleted uranium trioxide was dissolved in a stoichiometric quantity of 1.0 N nitric acid to form uranyl nitrate solution which was then diluted with sufficient water to cover the selected quantity of catalyst support. The support was immersed in the solution, and allowed to remain overnight, and any unabsorbed solution was decanted. The impregnated support was dried for 24 hours at 250°F and cooled, and the previously unabsorbed solution was slowly poured onto it while the support was being stirred. When this second contacting of the solution and support was completed, all of the solution was absorbed. The impregnated support was redried and then calcined overnight at 1,050°F in a stream of 2 volumes of dry air per volume of catalyst per minute to convert the uranyl nitrate to oxides.

As a matter of convenience, the oxides on the catalyst supports are referred to as UO_3, and the percentages reported as being present on the alumina and cobalt molybdate are the amounts of original uranium trioxide expressed as percentages of

the original dry carrier weights. Uranium trioxide loses oxygen at temperatures above 660°F to form lower oxides of complicated composition (11-13). Because of this loss, the uranium oxides on the calcined catalysts did not have the exact composition represented by the formula, UO_3. Also, before the catalysts were used they were pretreated overnight in the hydrogenation reactor, a treatment which would tend to remove some oxygen.

Catalysts containing UO_3 equal to 10 percent of the weight of the F-10 alumina and of the cobalt molybdate support were prepared. This percentage was used after earlier attempts to prepare a catalyst containing a monomolecular layer of UO_3, following the work of Russell and Stokes (16) as a guideline, were unsuccessful. It was calculated by the method of Innes (10) that a quantity of UO_3 equal to 29 percent of the weight of the carrier would be needed to form a monomolecular layer on F-10 alumina. In attempts to prepare a catalyst containing this amount of UO_3, it was found that the oxide formed a loose, bulky deposit that did not adhere well to the alumina. Other preparations containing 15 to 20 percent UO_3 also were unsuccessful for the same reasons. A catalyst containing UO_3 equal to 10 percent of the alumina weight appeared to have a stable deposit of uranium oxide that did not shed from the alumina. Uranium oxide amounting to 10 percent of the carrier weight was therefore used in preparing catalysts from F-10 alumina and from cobalt molybdate for use in hydrocracking experiments.

HYDROCRACKING EXPERIMENTS

Equipment and Procedure

A flow diagram of the equipment used for the hydrocracking tests is shown in figure 1.

The type 347 stainless steel reaction vessel, 40 inches long and $1\frac{1}{2}$ inches in internal diameter, contained a thermowell 9/16 inch in diameter. A section 12 inches long beginning 8 inches from the bottom of the reactor contained 300 cc of the catalyst supported in the heated zone of an electric furnace, and an upper 19-inch section serving as the preheater contained 4-mesh Alundum grain. Catalyst temperatures were measured by thermocouples placed $\frac{1}{2}$ inch below the top of the catalyst, $\frac{1}{2}$ inch above the bottom of the catalyst, and at $2\frac{1}{4}$-inch intervals in the catalyst bed. Additional thermocouples, placed along the outer wall of the reactor, were used with an automatic controller to regulate current to the elements of the electric furnace surrounding the reactor.

Hydrogen was measured by displacement with corrosion-inhibited water from a "flow-hydrogen" cylinder maintained at reaction pressure. Hydrogen and oil were mixed at the inlet to the reactor, and the mixture flowed downward through the preheating and catalyst-containing sections of the reactor.

Products from the reactor passed into a high-pressure separator maintained at reaction pressure and 350°F where the high-boiling oils were condensed. Vapors from the top of this separator passed into another, kept at 40°F, for separation of lower boiling oils from the gas stream. Backpressure on the system was maintained constant by bleeding gas from the cold separator through a meter and into a holder for sampling. Liquid products were kept in the separators until the end of each run, at which time the liquid products from the cold separator were drained into a receiver maintained at atmospheric pressure and temperature. Light ends (chiefly butanes and pentanes) liberated during this draining were condensed in a Dry Ice trap. Light ends from distillation of the combined liquid products were added to these light ends before mass spectrometer analysis.

Gasolines consisting of all liquids distilling up to a distillation-column head temperature of 400°F were separated by distillation of the combined liquid products

in an adiabatic glass laboratory column packed with stainless steel helices. All material heavier than gasoline was reported as "recycle oil."

Gases and light ends were analyzed with a mass spectrometer. Carbon deposits on the catalysts were determined by measuring the carbon dioxide obtained when air was passed through the reactor (which had been purged with helium at the end of each run) to regenerate the catalyst. Hydrogen consumption was calculated from analysis of the feed and products.

All of the hydrocracking experiments were conducted at 3,000 psig pressure with a hydrogen feed rate of 6,000 scf per barrel and a space velocity of 1.0 volume of oil per volume of catalyst per hour (V_o/V_c/hr), but different reaction temperatures were used for the individual experiments. Each experiment had an operating period of 6 hours.

Hydrocracking experiments with shale oil were made over uranium oxide on the alumina carrier at temperatures ranging from 890° to 1,002°F. Comparison experiments were made with the alumina carrier at temperatures of 890° to 1,004°F. Hydrocracking experiments with uranium oxide on cobalt molybdate were made at temperatures of 807° to 987°F; experiments with cobalt molybdate were run at a slightly higher range of temperatures, 842° to 1,010°F, producing approximately the same degree of hydrocracking as obtained with the uranium oxide on the cobalt molybdate.

Feedstock

The shale oil used for the catalytic hydrocracking experiments was crude oil produced in the gas-combustion retort, from which the small quantity of naphtha had been removed in a topping distillation. An exception to this was the untopped feed used for the experiments with the cobalt molybdate catalyst. Corrections for the 7.4 weight-percent naphtha in this feed were made in the conversion and yield calculations for this catalyst. Nitrogen and sulfur percentages in the topped and untopped feeds were essentially the same. The analysis shown in table 1 is similar to those of crude shale oils produced by many aboveground retorts.

CATALYST EVALUATION

Uranium Oxide on F-10 Alumina

To evaluate uranium oxide on F-10 alumina as a catalyst, information on the use of the alumina without the uranium oxide was necessary. Several experiments in hydrocracking shale oil over alumina were made at temperatures of 890° to 1,004°F to obtain this information. Comparable experiments were made with 10 percent uranium oxide on F-10 alumina as the catalyst at temperatures of 890° to 1,002°F. Yields and properties of the liquid products from the experiments are shown in tables 2, 3, and 4.

Figure 2A shows the weight-percent conversion obtained at different temperatures in the experiments with the alumina. (Conversion is the weight-percent of feed boiling above 400°F that is converted to all other products.) A linear regression curve fitted to the data by the method of least squares (7) had a coefficient of determination (r^2) of 0.97, showing that 97 percent of the variation in conversion at the different temperatures was accounted for by the regression line.

Figure 2B shows the weight-percent conversion obtained when the same shale oil was hydrogenated at a corresponding temperature range over alumina to which 10 weight-percent UO_3 had been added. Weight-percent conversion values for a straight line with a coefficient of determination of 0.96 drawn through the data were several percent higher than those obtained with the alumina support at corresponding temperatures.

Figure 3 shows the linear regression lines of figures 2A and 2B with the 95-percent confidence limits for each line. To prevent confusion, the data points were eliminated from this figure. The central line in each group of three lines is the regression line, and the two lines above and below it are the 95-percent confidence limits for that line. These curves may be interpreted as meaning that the chances are 95 out of 100 that the true straight-line regression for the uranium catalyst, after allowing for experimental error in gathering the data, falls between its 95-percent confidence limits, and similarly, that the chances are 95 out of 100 that the true straight-line regression for the alumina catalyst support falls between its 95-percent confidence limits. An appreciable gap is observed to exist between the lower 95-percent confidence limit for the uranium curve and the upper 95-percent confidence limit for the alumina curve. From this, it is concluded that a significant difference exists between the conversions obtained with the depleted uranium catalyst and those obtained with the alumina support at the same operating temperatures.

The regression equation for conversion versus temperature with the UO_3-containing catalyst is

$$C = -335.9 + 0.4158t, \qquad 1)$$

and that with the alumina is

$$C = -302.6 + 0.3730t, \qquad 2)$$

where C = weight percent conversion,
and t = reaction temperature in °F.

The higher conversions obtained with the UO_3-containing catalyst permit the use of appreciably lower operating temperatures to obtain a given degree of conversion than are necessary when using the alumina as a catalyst. For example, to obtain a 60-percent conversion of crude shale oil with the alumina, the required operating temperature is 972°F as calculated by equation (2). The same conversion may be obtained when using the UO_3-containing catalyst at 952°F as calculated by equation (1).

A portion of the difference in conversions obtained at corresponding temperatures with the two catalysts is accounted for by a difference in the amounts of gasoline produced. Figure 4A shows the gasoline yields obtained at various reaction temperatures with both catalysts. Although scatter of the data was great enough that more experiments would be needed to obtain unqualified statistical verification of the results, it appears that gasoline yields obtained when using the uranium catalyst were greater at corresponding temperatures up to about 990°F.

At the higher part of the temperature range studied, gasoline yields with both catalysts decreased because of an increase in the formation of low-molecular-weight gas. The decrease in gasoline yield appeared to be more rapid for the uranium catalist than for the alumina support at temperatures above about 980°F. This effect suggests the possible application of uranium oxide for catalytic use in hydrogasification of oils to produce synthetic pipeline gas.

Yields and properties of products from hydrogenation experiments may be conveniently expressed as functions of conversion. Figure 5 shows the relationships between weight-percent conversion and the gasoline yields, sulfur and nitrogen contents, hydrocarbon types, and octane numbers of the gasolines when using the uranium catalyst. Figure 6 shows similar relationships obtained when using the F-10 alumina.

A comparison of the two figures shows that the gasoline yields obtained with the two catalysts appeared to be about the same at corresponding conversion levels;

however, as previously discussed, corresponding conversions were obtained at lower temperatures with the uranium catalyst. The uranium catalyst appeared to show some activity for elimination of sulfur from the gasoline, but had a negative effect on the elimination of nitrogen. Hydrocarbon-type compositions of the gasolines produced with the two catalysts were about the same at corresponding conversion levels, and the trends established at the lower conversion levels continued at the higher conversion levels obtained with the uranium catalyst. Unleaded octane numbers of the gasoline fractions produced with the two different catalysts were nearly the same at corresponding conversion levels, but the leaded-octane numbers of the gasolines from the uranium-catalyzed experiments were higher (probably because of their lower sulfur percentages) than those of the gasolines produced with the alumina.

The gasoline obtained at the highest temperature (1,002°F) and conversion (about 78 weight-percent) with the uranium catalyst had research-method octane numbers of 87.6 unleaded and 98.8 with 3 ml of tetraethyllead, but the gasoline had poor color and color stability (probably because of its high nitrogen content of over 1 percent) and high gum content. It would, therefore, require further refining before it could be used in motor fuel.

Uranium Oxide on Cobalt Molybdate Catalyst

The effect of uranium oxide in promoting the conversion of high-boiling shale oil to lower boiling material, as shown by the results obtained with uranium oxide on alumina, suggests that it might beneficially be combined with a good hydrogenation catalyst to obtain the benefits of both materials, i.e., greater conversions than obtained with the hydrogenation catalyst and better quality gasoline fractions than obtained with the uranium oxide catalyst. To test this hypothesis, a catalyst was prepared consisting of 10 percent uranium oxide deposited on cobalt molybdate catalyst.

Yields and properties of liquid products from hydrocracking shale oil over the uranium on cobalt molybdate are given in table 5. Yields and properties of products from hydrocracking shale oil over the cobalt molybdate without the added uranium are given in table 6.

Figure 2C shows the weight-percent conversion when shale oil was hydrogenated over the uranium oxide on cobalt molybdate. Figure 2D shows the conversion when shale oil was hydrogenated over a sample of the cobalt molybdate catalyst without the uranium. Least-squares regression lines shown in the figures had coefficients of determination of 0.96 for the uranium oxide on cobalt molybdate and 0.97 for the cobalt molybdate data.

Figure 7 shows the regression lines from figures 2C and 2D with their 95-percent confidence limits. From the separation between the two sets of curves, it is concluded that the addition of uranium oxide to the cobalt molybdate catalyst resulted in a higher percent conversion of high-boiling feed to other products than obtained with the original cobalt molybdate at corresponding temperatures.

The regression equation for conversion versus temperature with the UO_3-containing catalyst is

$$C = -264.6 + 0.3645t, \qquad 3)$$

and that with the cobalt molybdate is

$$C = -296.1 + 0.3876t, \qquad 4)$$

where, as before, C = weight percent conversion,
and t = reaction temperature in °F.

As an example of the difference in the temperatures required to obtain a given degree of conversion of heavy shale oil when operating with the experimental conditions of the data, it is calculated from equations (3) and (4) that a 60-percent conversion could be obtained at 890°F with the uranium-containing catalyst, but a temperature of 919°F would be required with the cobalt molybdate catalyst. The difference of 29°F in required operating temperatures would be a distinct advantage for the uranium-promoted catalyst.

Yields of C_5+ gasoline produced from the +400°F feed at different reaction temperatures when using the two catalysts are shown in figure 4B. It is observed that yields of gasoline produced at corresponding temperatures were greater when using the uranium-promoted catalyst at temperatures up to about 940°F. At higher operating temperatures, greater gasoline yields were obtained with the unpromoted cobalt molybdate catalyst. Gasoline yields with both catalysts decreased rapidly at the higher temperatures because of the formation of large amounts of gas, but the percentages of gas were much greater with the uranium-promoted catalyst than with the cobalt molybdate. This effect indicates that the addition of uranium to the catalyst could be beneficial in hydrogasification of heavy oil to produce pipeline gas.

Figures 8 and 9 show the yields of gasoline produced from the +400°F feed, and properties of the gasolines plotted as functions of conversion for the experiments with the two catalysts. Gasoline yields at corresponding conversion levels were about the same with both catalysts up to a conversion of about 65 percent. (As previously shown, lower temperatures were used to attain the conversion levels with the uranium-promoted catalyst.) At higher conversion levels, gasoline yields were greater with the cobalt molybdate, owing to the formation of gas when using the uranium-containing cobalt molybdate. Maximum experimental gasoline yields with the two catalysts were 45.1 weight-percent (58 volume-percent) produced with the uranium-containing catalyst at a conversion of 76.7 weight-percent (obtained at a temperature of 922°F) and 46.6 weight-percent (61.4 volume-percent) produced with the cobalt molybdate at a conversion level of 85.6 weight-percent (obtained at a temperature of 974°F).

The addition of uranium to the catalyst had an apparent negative effect on elimination of nitrogen at the lower conversion levels, but at the higher conversion levels the differences in nitrogen percentages of the gasolines were very small. Nitrogen percentages of the gasolines at conversion levels of 65 percent or more were from 0.01 percent to 0.02 percent for the experiments with uranium-containing cobalt molybdate, compared with about 0.005 percent for the experiments with cobalt molybdate. Sulfur contents of the gasolines were 0.02 percent or less throughout the experimental range with both catalysts. At the higher conversion levels, aromatic contents of the gasolines produced with the uranium-containing catalyst were greater than those of the gasolines produced with the cobalt molybdate, and octane numbers of the gasolines produced with the uranium-containing catalyst were slightly higher than those of the gasolines produced with cobalt molybdate.

SUMMARY AND CONCLUSIONS

The addition of 10 percent depleted uranium oxide to F-10 alumina and to cobalt molybdate increased the hydrocracking activity of these catalysts, permitting the use of lower operating temperatures to attain the same degree of conversion. At operating temperatures below about 940°F with uranium oxide on cobalt molybdate and about 990°F with uranium oxide on alumina, the increases in conversion caused increases in gasoline yields. At higher temperatures, the uranium-containing catalysts lost their advantage for gasoline production because of increased conversion of products to gas. These results suggest an investigation be made of depleted uranium for hydrogasification of heavy oils to produce pipeline gas.

Depleted uranium oxide displayed activity for hydrodesulfurization when on an alumina support, but did not enhance the already high desulfurization activity of the cobalt molybdate. The added uranium showed no advantage for nitrogen elimination from the liquid products.

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TABLE 1. - Properties of topped crude shale oil

ASTM distillation at 760 mm:		Specific gravity at 60/60°F	0.9408
I.B.P., °F	407	Sulfur, wt. %	0.68
5% rec., °F	502	Nitrogen, wt. %	2.18
10% rec., °F	538	Carbon, wt. %	83.96
20% rec., °F	601	Hydrogen, wt. %	11.40
30% rec., °F	648	Oxygen by diff., wt. %	1.78
40% rec., °F	Cracking	H/C atom ratio	1.62
E.P., °F	695	Vis., kinematic, cs.:	
Rec., vol. %	38	At 140°F	28.30
Res., vol. %	62	At 210°F	8.23
		Carbon res. (Rams.), wt. %	3.5

TABLE 2. - Hydrocracking of raw shale oil

Catalyst	F-10 activated alumina							
Catalyst temp., °F:								
Average	890	892	892	893	916	932	965	1004
Maximum	892	896	895	895	920	935	966	1009
H_2 consumed, scf/bbl	1180	800	740	720	900	1170	1570	2000
Product yield, wt. %:								
Gasoline	17.14	18.17	20.14	19.17	22.15	24.56	28.92	24.55
Light ends	2.27	1.49	1.85	3.17	2.09	2.70	3.14	4.94
Recycle oil	67.54	70.95	72.04	68.61	61.76	56.37	40.86	28.60
Gas	10.70	6.70	2.65	5.81	11.39	14.23	25.45	40.24
Catalyst deposit	1.20	1.20	1.45	1.75	1.07	0.80	0.80	1.26
C_5 + gasoline	18.37	20.73	20.99	20.81	22.54	26.70	37.44	27.11
Conversion	32.46	29.05	27.96	31.39	38.24	43.63	59.14	71.40
Product yield, vol. %:								
Gasoline	20.92	22.42	24.90	23.26	27.34	30.75	36.06	30.06
Recycle oil	69.28	73.10	74.13	70.60	63.28	57.29	40.35	26.92
C_5 + gasoline	22.72	26.23	26.12	25.70	27.92	33.90	48.72	33.86
Gasoline properties:								
Sp. gr. at 60/60°F	0.7747	0.7666	0.7651	0.7794	0.7660	0.7552	0.7583	0.7723
Sulfur, wt. %	0.37	0.37	0.36		0.19	0.24	0.19	0.17
Nitrogen, wt. %	0.39	0.42	0.49	Not	Lost	0.36	0.44	0.85
Hydrocarbons, vol. %:				analyzed				
Paraffins	48	47	53		56	48	50	40
Naphthenes	6	7	5		7	15	14	17
Olefins	32	34	30		25	25	21	16
Aromatics	14	12	12		12	12	15	27
Octane numbers:								
Res., clear	60.0	56.7	63.6		63.2	60.0	68.3	82.0
Res., + 3 ml TEL	72.5	73.0	76.8		78.3	76.6	84.0	93.4
ASTM distn. at 760 mm:								
I.B.P., °F	134	145	120		115	111	114	111
10% evap., °F	194	197	168		168	159	153	146
50% evap., °F	300	297	290		280	269	257	238
90% evap., °F	374	373	370		366	367	362	365
E.P., °F	400	390	392		390	387	387	385
Recycle-oil properties:								
Sp. gr. at 60/60°F	0.9218	0.9177	0.9190	0.9189	0.9229	0.9304	0.9575	1.0049
Sulfur, wt. %	0.40	0.37	0.41	0.27	0.30	0.33	0.31	0.35
Nitrogen, wt. %	1.72	1.98	1.54	1.92	2.00	1.95	2.46	2.61

TABLE 3. - Hydrocracking of raw shale oil

Catalyst	10% UO_3 on F-10 alumina					
Catalyst temp., °F:						
Average	890	894	895	906	916	932
Maximum	891	896	899	907	916	934
H_2 consumed, scf/bbl	610	1120	730	1450	1540	1590
Product yield, wt. %:						
Gasoline	20.68	18.83	20.47	22.03	24.93	25.83
Light ends	2.49	2.40	2.70	2.07	2.05	4.13
Recycle oil	68.88	61.05	63.60	60.12	55.10	50.63
Gas	4.15	13.66	8.70	13.72	15.51	17.30
Catalyst deposit	2.11	2.85	2.88	1.34	1.78	1.40
C_5 + gasoline	22.25	21.01	22.33	23.66	26.53	29.45
Conversion	31.12	38.95	36.40	39.88	44.90	49.37
Product yield, vol. %:						
Gasoline	25.60	23.38	25.48	27.37	31.02	32.30
Recycle oil	70.76	62.58	65.00	61.90	56.36	51.29
C_5 + gasoline	27.91	26.60	28.22	29.79	33.38	37.65
Gasoline properties:						
Sp. gr. at 60/60°F	0.7637	0.7618	0.7598	0.7610	0.7599	0.7563
Sulfur, wt. %	0.22	0.18	0.22	0.10	0.05	0.07
Nitrogen, wt. %	0.70	0.63	0.64	0.67	0.71	0.60
Hydrocarbons, vol. %:						
Paraffins	53	54	52	55	55	53
Naphthenes	8	6	7	7	5	11
Olefins	28	28	29	27	26	23
Aromatics	11	12	12	11	14	13
Octane numbers:						
Res., clear	62.9	58.1	61.5	61.3	66.1	64.0
Res., + 3 ml TEL	83.1	81.6	82.5	81.6	87.1	81.5
ASTM distn. at 760 mm:						
I.B.P., °F	114	95	104	112	114	111
10% evap., °F	179	175	173	171	170	166
50% evap., °F	292	289	285	289	284	276
90% evap., °F	372	372	364	371	368	357
E.P., °F	396	391	389	397	396	392
Recycle-oil properties:						
Sp. gr. at 60/60°F	0.9205	0.9224	0.9253	0.9185	0.9243	0.9334
Sulfur, wt. %	0.26	0.27	0.32	0.16	0.15	0.20
Nitrogen, wt. %	2.17	2.10	2.16	2.14	2.19	2.18

TABLE 4. - Hydrocracking of raw shale oil

Catalyst	10% UO_3 on F-10 alumina						
Catalyst temp., °F:							
Average	946	950	963	978	989	990	1002
Maximum	946	954	969	980	1006	991	1004
H_2 consumed, scf/bbl	1730	2110	2160	1920	2860	2740	2880
Product yield, wt. %:							
Gasoline	28.40	30.07	27.30	27.26	29.92	25.92	23.23
Light ends	3.87	3.37	6.63	7.24	3.42	4.34	6.58
Recycle oil	43.89	36.42	34.05	28.32	22.14	26.32	22.15
Gas	21.56	27.45	28.92	30.85	43.56	41.44	46.48
Catalyst deposit	1.74	2.55	2.96	5.77	1.66	2.55	2.41
C_5 + gasoline	31.79	33.64	32.65	31.85	32.79	30.59	28.42
Conversion	56.11	63.58	65.95	71.68	77.86	73.68	77.85
Product yield, vol. %:							
Gasoline	35.39	37.59	33.80	33.18	36.41	31.84	28.07
Recycle oil	43.87	36.09	33.50	27.05	20.76	25.15	20.51
C_5 + gasoline	40.40	42.87	41.72	39.86	40.67	38.78	35.71
Gasoline properties:							
Sp. gr. at 60/60°F	0.7587	0.7566	0.7636	0.7771	0.7770	0.7696	0.7824
Sulfur, wt. %	0.08	0.03	0.05	0.07	0.04	0.04	0.06
Nitrogen, wt. %	0.66	0.70	0.66	0.85	0.76	0.78	1.11
Hydrocarbons, vol. %:							
Paraffins	52	50	51	47	35	43	39
Naphthenes	11	13	15	13	27	16	17
Olefins	23	20	19	18	9	14	13
Aromatics	14	17	15	22	29	27	31
Octane numbers:							
Res., clear	68.6	70.3	71.5	76.0	80.5	81.6	87.6
Res., + 3 ml TEL	87.1	88.4	86.7	92.5	95.9	94.7	98.8
ASTM distn. at 760 mm:							
I.B.P., °F	112	93	94	115	111	90	114
10% evap., °F	162	154	161	165	154	143	161
50% evap., °F	271	267	261	264	232	248	247
90% evap., °F	371	371	363	373	346	365	370
E.P., °F	399	400	387	397	382	391	395
Recycle-oil properties:							
Sp. gr. at 60/60°F	0.9460	0.9543	0.9613	0.9898	1.0086	0.9897	1.0213
Sulfur, wt. %	0.16	0.17	0.22	0.16	0.25	0.14	0.18
Nitrogen, wt. %	2.39	2.40	2.36	2.67	2.47	2.46	2.87

TABLE 5. - Hydrocracking of raw shale oil

Catalyst	10% UO_3 on cobalt molybdate						
Catalyst temp., °F:							
Average	807	831	900	903	922	959	987
Maximum	843	857	923	922	951	985	1017
H_2 consumed, scf/bbl	1770	1740	2490	2550	3000	3340	3640
Product yield, wt. %:							
Gasoline	20.58	23.48	38.18	39.59	40.22	34.58	26.94
Light ends	2.41	2.27	2.80	3.56	6.12	7.95	6.80
Recycle oil	67.49	66.29	38.81	34.37	23.30	16.04	6.00
Gas	7.09	5.61	18.62	21.01	29.66	40.97	60.07
Catalyst deposit	0.44	0.15	0.81	0.30	0.24	0.54	0.70
C_5 + gasoline	22.30	24.49	40.54	42.39	45.13	37.65	31.04
Conversion	32.51	33.71	61.19	65.63	76.70	83.96	94.00
Product yield, vol. %:							
Gasoline	25.38	28.92	48.02	49.52	50.75	42.42	32.62
Recycle oil	72.58	71.74	42.77	37.91	25.30	16.36	5.54
C_5 + gasoline	27.92	30.41	51.53	53.66	57.99	46.95	38.65
Gasoline properties:							
Sp. gr. at 60/60°F	0.7629	0.7638	0.7518	0.7522	0.7457	0.7671	0.7768
Sulfur, wt. %	Trace	Trace	0.02	0.02	0.02	0.02	0.02
Nitrogen, wt. %	0.16	0.13	0.06	0.02	0.01	0.02	0.01
Hydrocarbons, vol. %:							
Paraffins	71	69	60	59	55	52	37
Naphthenes	15	16	21	22	23	14	14
Olefin							
Aromatics	14	15	19	19	22	34	49
Octane numbers:							
Res., clear	43.9	45.6	50.7	49.2	52.8	70.0	80.0
Res., + 3 ml TEL	67.6	70.4	80.7	74.2	75.3	87.7	94.5
ASTM distn. at 760 mm:							
I.B.P., °F	142	135	112	116	116	105	102
10% evap., °F	213	205	157	160	156	151	140
50% evap., °F	304	301	259	257	232	222	195
90% evap., °F	370	371	353	351	328	343	297
E.P., °F	401	400	378	378	356	390	353
Recycle-oil properties:							
Sp. gr. at 60/60°F	0.8748	0.8694	0.8581	0.8530	0.8663	0.9223	1.0190
Sulfur, wt. %	0.04	0.03	0.04	0.06	0.08	0.04	0.02
Nitrogen, wt. %	0.56	0.37	0.15	0.13	0.12	0.28	0.22

TABLE 6. - Hydrocracking of raw shale oil

Catalyst	Cobalt molybdate							
Catalyst temp., °F:								
Average	842	842	889	890	901	933	974	1010
Maximum	845	843	890	892	903	934	980	1012
H_2 consumed, scf/bbl	1370	1690	1480	1550	1480	1500	1370	1760
Product yield, wt. %:								
Gasoline	26.2	26.2	37.2	38.3	39.4	47.9	49.4	38.6
Recycle oil	66.8	61.7	48.6	46.6	47.2	28.4	13.3	6.4
Gas	4.0	9.4	11.7	12.2	10.7	20.9	34.1	52.3
Catalyst deposit	1.0	1.3	0.6	1.1	0.8	0.9	1.1	1.2
C_5 + gasoline	26.2	26.2	37.8	39.5	39.4	50.3	50.6	40.1
C_5 + gasoline formed 1/	20.3	20.3	32.8	34.7	34.6	46.3	46.6	35.3
Conversion 1/	27.9	33.4	47.5	49.7	49.0	69.3	85.6	93.1
Product yield, vol. %:								
Gasoline	32.5	32.6	46.9	48.4	49.8	61.0	63.1	48.7
Recycle oil	72.5	67.3	53.9	52.2	52.1	31.1	14.2	6.2
C_5 + gasoline	32.5	32.6	47.8	50.2	49.8	64.6	64.9	50.9
C_5 + gasoline formed 1/	25.8	25.9	42.6	45.3	44.8	61.1	61.4	46.0
Gasoline properties:								
Sp. gr. at 60/60°F	0.7560	0.7530	0.7458	0.7432	0.7563	0.7465	0.7354	0.7465
Sulfur, wt. %	0.01	0.02	0.02	0.02	0.02	0.01	0.01	0.02
Nitrogen, wt. %	0.03	0.03	0.01	0.01	0.01	0.005	0.005	0.005
Hydrocarbons, vol. %:								
Paraffins	60	62	61	60	59	58	58	55
Naphthenes	21	23	21	25	22	19	16	7
Olefins	1	1	1	1	1	1	1	1
Aromatics	18	14	17	14	18	22	25	37
Octane numbers:								
Res., clear	50	48	51	50	48	55	70	79
Res., + 3 ml TEL	74	71	74	74	73	78	84	92
ASTM distn. at 760 mm:								
I.B.P., °F	120	107	111	102	112	102	88	84
10% evap., °F	172	174	163	158	176	154	125	127
50% evap., °F	289	295	279	276	277	257	222	205
90° evap., °F	367	375	369	383	359	361	377	373
E.P., °F	399	397	384	394	387	393	391	387
Recycle-oil properties:								
Sp. gr. at 60/60°F	0.8643	0.8568	0.8477	0.8530	0.8472	0.8582	0.8922	0.9804
Sulfur, wt. %	0.01	0.02	0.02	0.03	0.02	0.02	0.07	0.07
Nitrogen, wt. %	0.16	0.27	0.06	0.03	0.07	0.06	0.15	0.13

1/ Expressed as % of + 400°F feed. Corrected for 7.4 wt. % (9.0 vol. %) naphtha in feed.

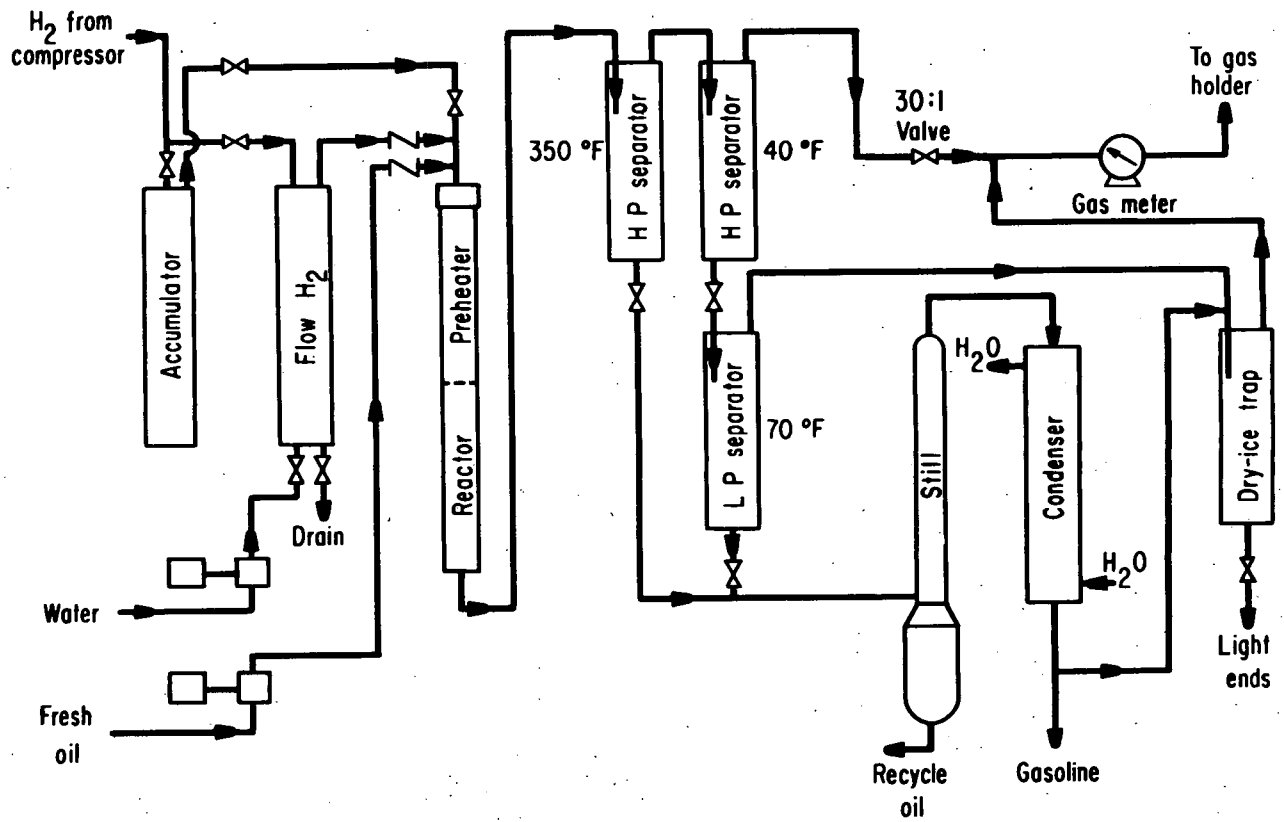

FIGURE 1.-Hydrogenation Unit.

RRS-808

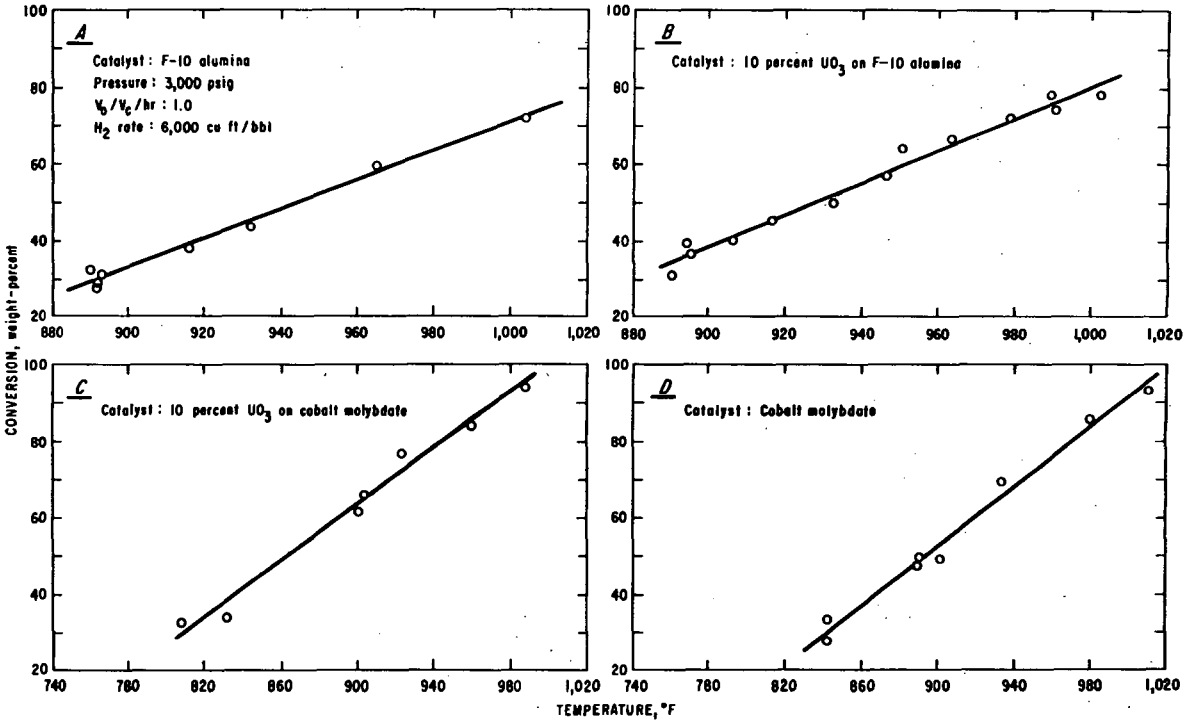

FIGURE 2.-Conversion of Shale Oil as Function of Temperature for Hydrogenating Shale Oil Over Various Catalysts.

OSCR-70-54

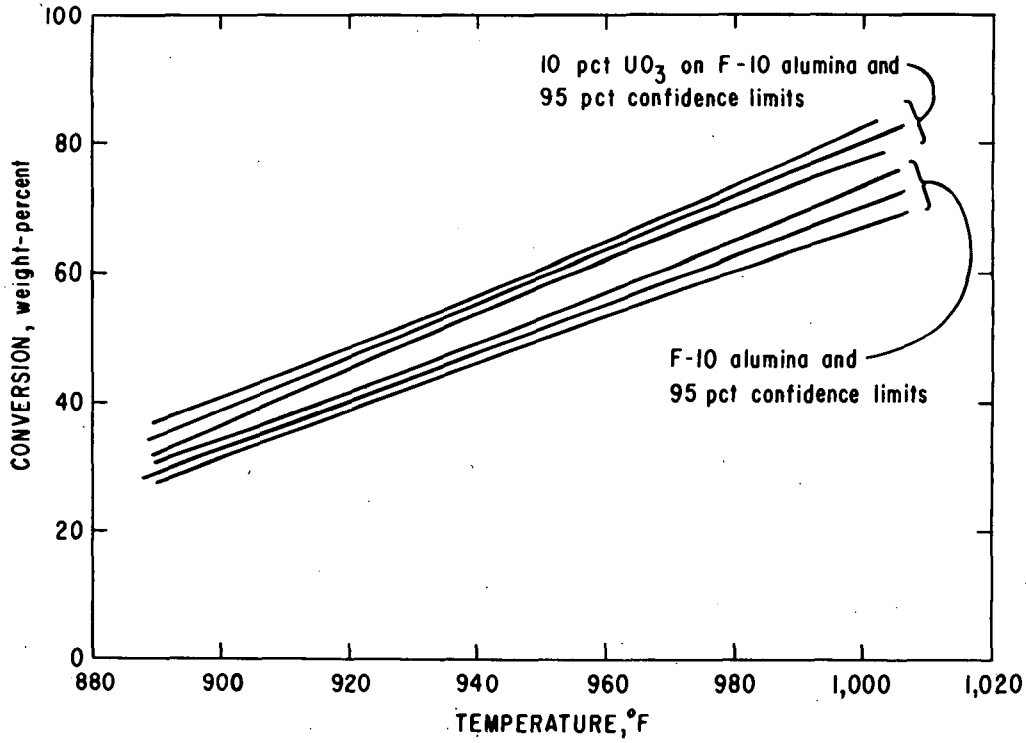

FIGURE 3.- Linear Regression Lines and 95 Percent Confidence Limits for Conversion as a Function of Temperature.

OSCR-70-55

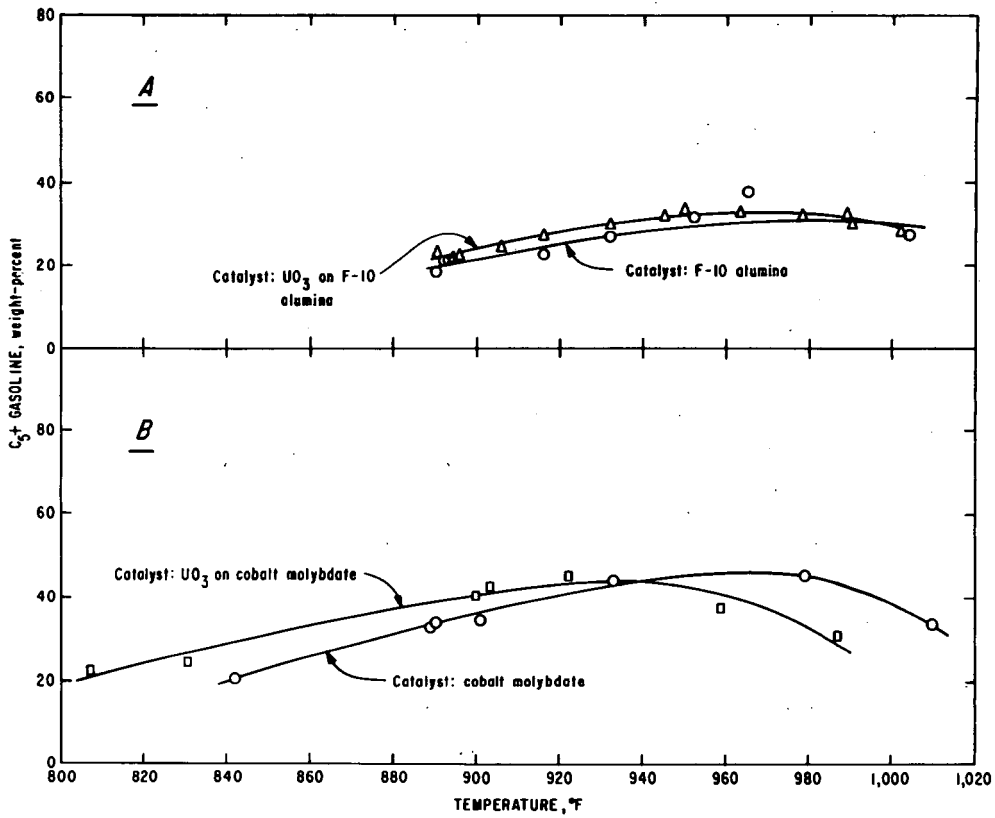

FIGURE 4.– Gasoline Yield as a Function of Reaction Temperature.

OSCR-70-58

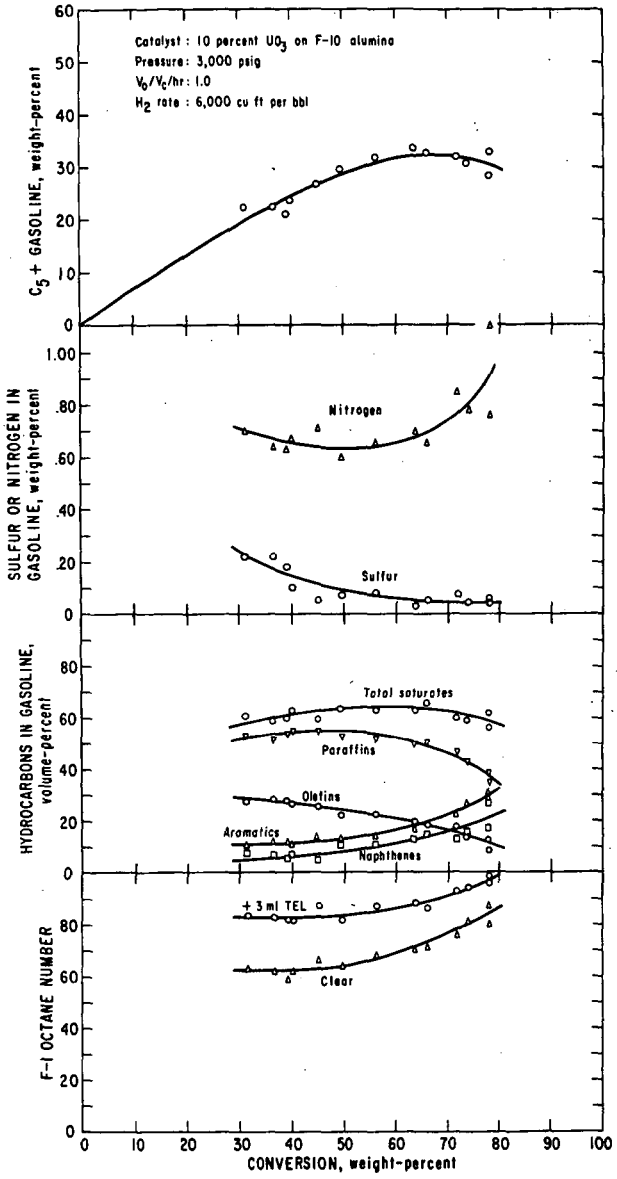

FIGURE 5.–Hydrogenation of Shale Oil Over Depleted UO_3 on F-10 Alumina.

OSCR-70-56

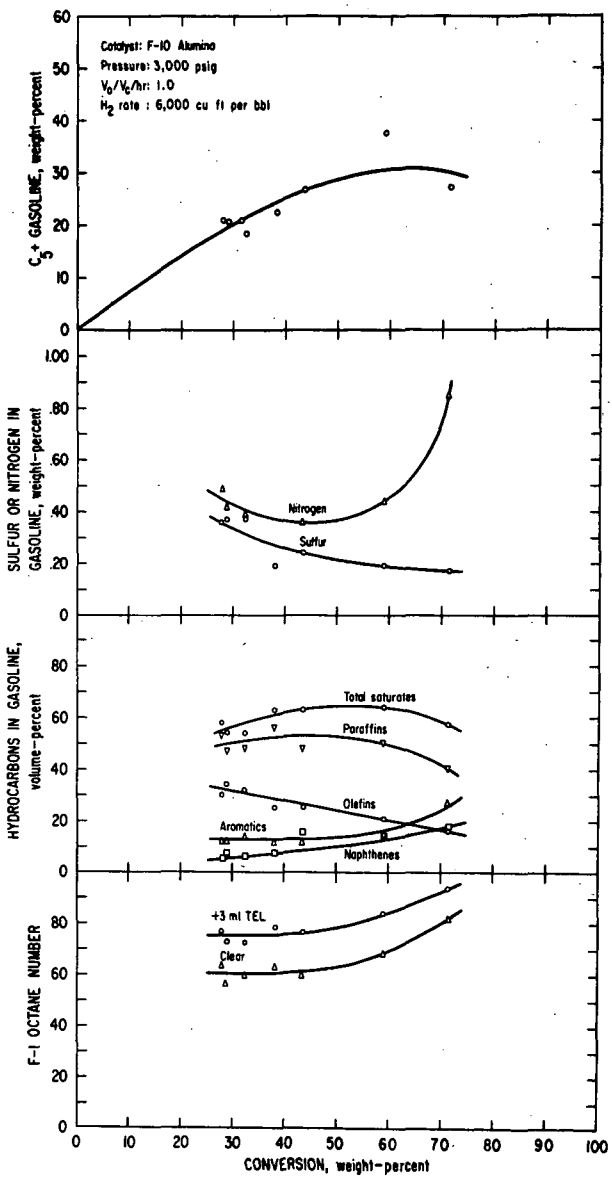

FIGURE 6.—Hydrogenation of Shale Oil Over F-10 Alumina.

OSCR-70-57

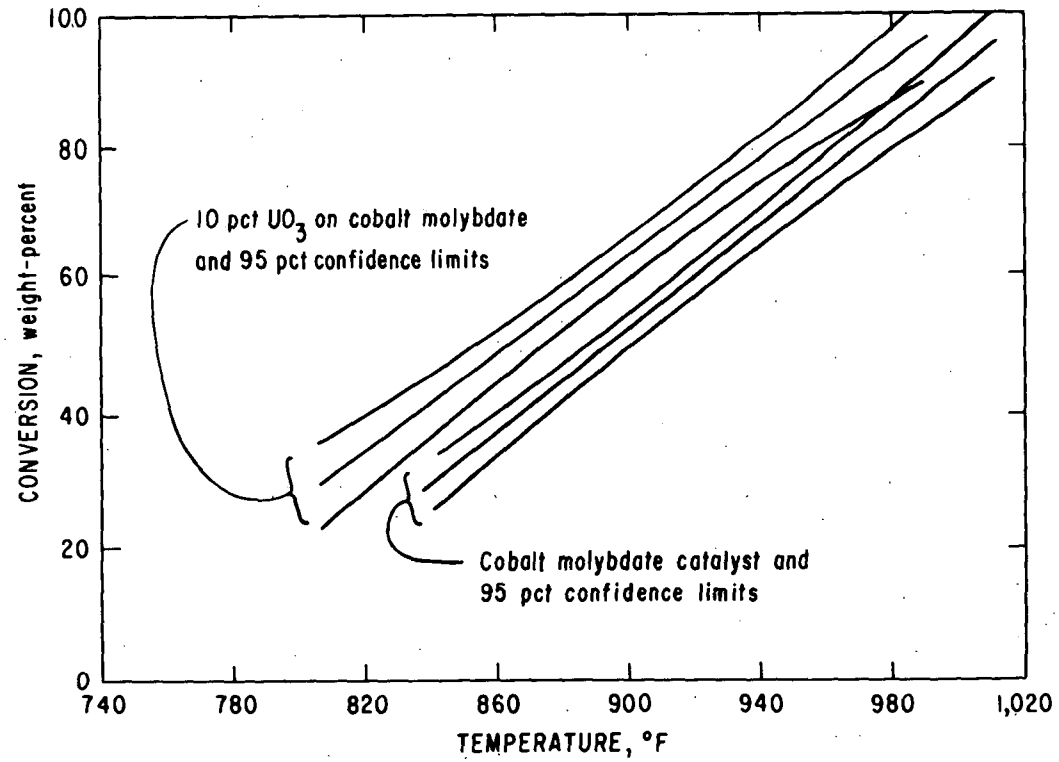

FIGURE 7.- Linear Regression Lines and 95 Percent Confidence Limits for Conversion as a Function of Temperature.

OSCR-70-60

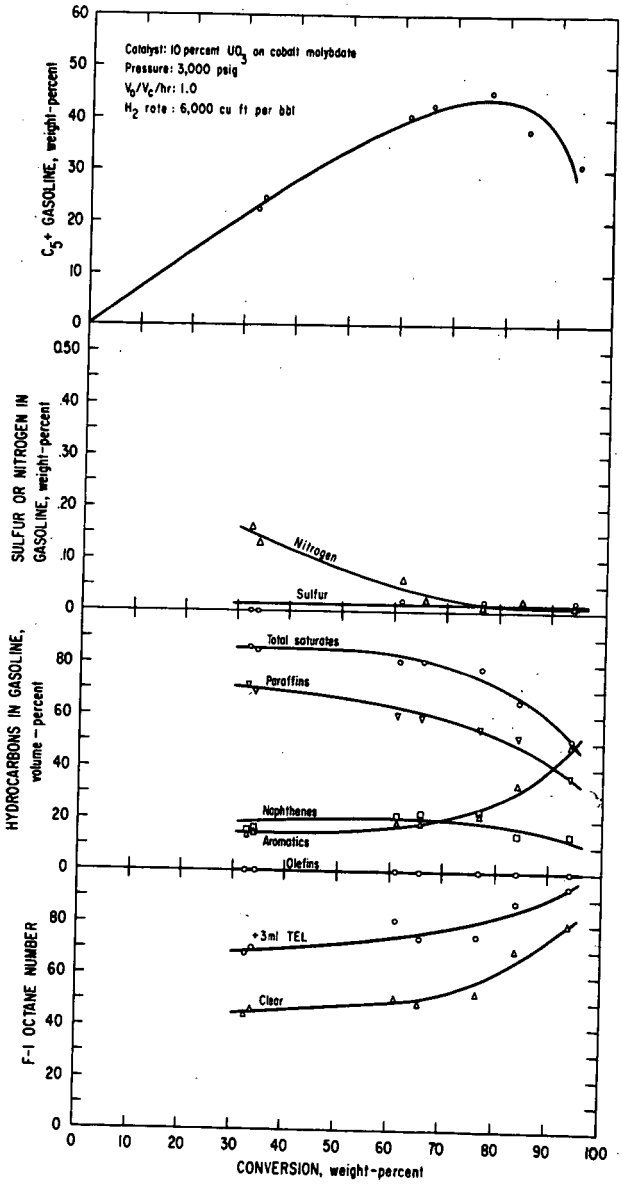

FIGURE 8.—Hydrogenation of Shale Oil Over Depleted UO_3 on Cobalt Molybdate Catalyst.

OSCR-70-61

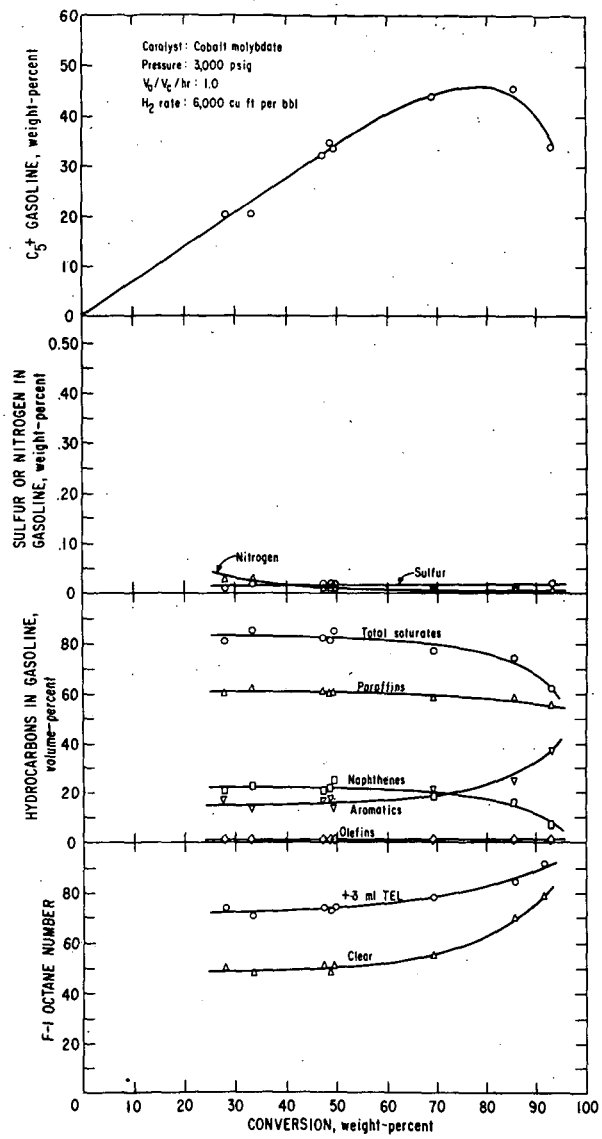

FIGURE 9.—Hydrogenation of Shale Oil Over Cobalt Molybdate Catalyst.

OSCR-70-62

EXPERIENCE WITH METHANATION CATALYSTS

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Introduction

Nearly all process schemes for making synthetic natural gas from coal include a catalytic methanation step for upgrading the raw synthesis gas to a high Btu pipeline gas. The Bureau of Mines, Pittsburgh Energy Research Center, has conducted bench-scale and pilot-plant studies of the methanation reaction with a variety of catalysts and reactors. This report discusses some of the work, comments on the preparation of the various types of catalysts and their performance, and outlines results of a recent tube-wall reactor pilot-plant test.

Laboratory-Scale Fixed-Bed Studies

Greyson and coworkers (3)[1/] examined the performance of many catalysts both in fixed-bed and fluidized-bed reactors. The fixed-bed reactors were single, steel-tube reactors, 0.622 inch ID by 12 inches long, cooled by boiling Dowtherm. Figure 1 shows a schematic diagram of the fixed-bed catalyst reactor. Various catalysts were tested in this unit.

Preparation of impregnated catalysts involved impregnating a catalyst support material with metal and promoters. To do this, a solution of the nitrate salts of the desired metals was added to a quantity of support to form a slurry. (Catalyst supports were cracking catalyst base and activated charcoal.) The slurry was then evaporated to dryness over a steam bath and then dried further in an oven at 600° C to convert the nitrate salts to oxides. The oxidized material was crushed to 6 to 8 mesh (U.S.). Activation of the catalyst for synthesis was achieved by reduction with hydrogen for 8 hours at 350 to 400° C and atmospheric pressure.

If a precipitated material was desired, the slurry of nitrate salts and support was treated with a solution of potassium carbonate. The treated slurry was then heated to the boiling point with constant stirring and filtered. The filter cake was washed with hot water and dried in an oven for about 16 hours. Supports for the precipitated catalysts included kaolin, kieselguhr, alumina, silica gel, and zirconia cement. The precipitated catalysts were crushed to 6 to 8 mesh sizes and then reduced with hydrogen prior to synthesis in the same manner as were the impregnated catalysts.

Preparation of iron nitride catalyst involved first a hydrogen reduction of 90 percent of the iron oxide and then treatment of the reduced iron with anhydrous ammonia at 350° C and atmospheric pressure until X-ray analysis showed that Fe_2N was obtained.

A magnetite and ball clay catalyst was prepared by firing a dried mixture of magnetite and ball clay at about 600° C. The sinter was then crushed, sized, and nitrided.

Raney nickel and Raney cobalt catalysts were partially oxidized with steam and then reduced with hydrogen. Plain nickel pellets were also subjected to the same activation treatment before the methanation reaction.

1/ Numbers in parentheses refer to list of references at the end of this paper.

Raney catalysts were also activated by extraction of the aluminum. A solution of sodium or potassium hydroxide was used to remove part of the aluminum from the alloy. The reactions proceeding during leaching are:

$$2\ Al + 2\ NaOH + H_2O = 2\ NaAlO_2 + 3\ H_2$$
$$2\ Al + NaOH + 4\ H_2O = NaAlO_2 + Al(OH)_3 + 3H_2$$
$$2\ AL + 3\ H_2O = Al_2O_3 + 3\ H_2$$

The remaining catalyst material consisting of unreacted alloy, AL_2O_3, and elemental nickel or cobalt was washed with water and charged wet into the reactor.

The simplest catalyst prepared was iron ore reduced with hydrogen. Table 1 lists some typical catalysts treated, the space velocities, and ratio of H_2 to CO of the feed gas. Selected methanation conditions as well as causes for termination of tests are also shown. These tests showed that the precipitated nickel catalysts and the extracted Raney nickel catalyst were the most active, yielding methane concentrations of more than 90 percent. The nickel impregnated catalysts ranked second in activity, generally yielding 40 to 60 percent methane in the product gas. The iron catalysts were third, yielding product gas with less than 40 percent methane. The iron catalysts also produced a considerable amount of liquid hydrocarbon, which is an undesirable byproduct with respect to a high-Btu gas plant. Carbon deposition was excessive on all catalysts whenever H_2/CO ratio in feed gas was 1. When the H_2/CO ratio was 2.5, carbon deposition was still excessive on iron catalysts but nearly eliminated on the nickel catalysts.

Laboratory-Scale Fluidized-Bed Studies

Various iron and nickel catalysts were prepared and studied in laboratory-scale fluidized-bed reactors. Figure 2 is a sketch of a 0.96-inch diameter by 72-inch long fluidized-bed reactor used in the tests. This reactor introduced the feed gas at three locations to minimize the temperature gradient in the catalyst bed. Provisions were also made for recycling the cold product gas. The recycle gas was preheated before entering the catalyst bed.

Iron catalysts were reduced or nitrided for fluidized-bed operation in the same manner as for fixed-bed operation, except that the catalyst particle size <80 mesh was smaller for fluidized-bed operation. Initial forms of iron catalyst tested included synthetic ammonia, Alan Wood magnetite, steel shot, and magnetite in ball clay. Performance of both the reduced and the nitrided iron catalysts was the same as it was during fixed-bed operation. At typical operating conditions of 340° C, 300 psig, and space velocities[2/] of 880 to 3000 hr^{-1}, carbon deposition was excessive, even with H_2O ratios in the feed gas as high as 3; methane content of the product gas was generally less than 30 percent; heating value of the product gas was 400 to 600 Btu/scf, well below the desired minimum of 900 Btu/scf; and yields of higher molecular weight hydrocarbon, C_3^+, were still high, amounting to up to 3 wt pct of the fresh feed.

Addition of over 2.6 percent steam to the feed gas prevented carbon deposition, but it also decreased the catalyst activity. Addition of up to 5 percent carbon did not reduce carbon deposition.

The procedures for preparing the nickel catalysts was essentially the same as that followed in the series of fixed-bed tests, except that ingredients and proportions were varied, and particle size was kept below 80 mesh. Because the nickel

2/ Space velocity is volume per hour of fresh feed gas at standard conditions (0° C, 1 atm.) per settled volume of catalyst.

Table I. Fixed Bed Experiments

Catalyst composition and pretreatment	H_2/CO ratio	Selected methanation conditions: Space velocity range, hr^{-1} 1/	Temp., °C	Pressure, psig	CH_4 vol., percent 2/	Heating value Btu/scf 3/	Termination of run due to
Cuban iron ore - reduced	1	100-300	321	300	37.5	896	Excessive carbon
Fused Fe_3O_4, reduced and nitrided N/Fe = 0.44	2	100-300	395	300	30.5	738	Excessive carbon
Fe_3O_4 (50%) and ball clay, reduced and nitrided N/Fe = 0.48	2	100-300	312	300	27.5	691	Excessive carbon
Fe-Ni-MgO-SiO_2 (58.8:12.4:2.21:0.2) N/Fe = 0.314, reduced and nitrided	1	300	273	300	39.7	706	Sufficient data, some carbon
Ni, ThO_2-Cr_2O_3 ppt. on kieselguhr (30.9:7.6:1.6:59.9) - reduced	1	100-300	320	0	60.8	785	Excessive carbon
10% Ni impregnated on steam-treated cracking catalyst base reduced	1	300	No appreciable activity				
5% Ni impregnated on cracking catalyst base - reduced	1, 2	300	398	300	44.6	874	Excessive carbon
5% Ni impregnated on cracking catalyst base plus K_2O-reduced	2.5	300	400	300	39.1	635	Excessive carbon
1% Ni impregnated on activated charcoal - reduced	1	100-300	No appreciable activity				
10% Ni ppt. on silica - reduced	1	100-300	355	300	48.3	(720)	Excessive carbon
NiO-Al_2O_3 ppt. on kaolin (100:200:125) - reduced	2	300	300	300	98.9	1071	Decreased activity
NiO-MgO ppt. on kaolin (100:200:125) - reduced	2.5	300	264	300	97.3	(1060)	Sufficient data
28% Ni, 5.5% Mn, 2.4% Al ppt. on kaolin - sintered and reduced	2.5	300	No appreciable activity				
NiO, MnO, Al_2O_3 ppt. on cracking catalyst - reduced	2.5	300	404	300	17.3	(470)	Insuff. activity
Ni pellets steam-treated - reduced	2.5	100-300	No appreciable activity				
Raney cobalt (50% Co, 50% Al), Al partly extracted with NaOH	2.5	300-2,800	286	300	92.1	(1050)	Excessive carbon
Raney nickel (42% Ni, 58% Al), steam-treated - reduced	2.5	300	No appreciable activity				
Raney nickel (42% Ni, 58% Al), Al partly extracted with NaOH	2.5	300-1,500	300	300	96.9	(1060)	Sufficient data

1/ Space velocity = Std volumes feed gas per hour per vol catalyst 2/ CO_2, H_2O free 3/ ( ) estimated.

catalysts were extremely active in comparison with the iron catalysts, the feed gas was more evenly distributed in the fluidized-bed reactor by a multiple feed system as shown in figure 2 rather than by a single feed system. Provision was also made to recycle product gas. Variation of the distribution of fresh feed gas in the reactor and variation of the ratio of recycled product gas to fresh feed permitted minimizing the temperature gradients in the catalyst bed to within 10° to 15° C, as opposed to the temperature gradients in excess of 100° C obtained when the fresh gas was introduced through a single port.

Table 2 describes the nickel catalysts tested and summarizes their performance.

The thorium-promoted nickel-alumina catalyst (L-6053) proved to be very active and, chemically, one of the most stable catalysts of the precipitated and impregnated type nickel catalysts. Special tests with the thorium-promoted nickel alumina catalyst suggests that drying the catalyst at 180° C, as compared with drying at 120° C or 220° C, resulted in an optimum in catalyst life. Operating at 370° C, 300 psig, fresh gas space velocity of 7000 hr^{-1}, H_2/CO ratio of 3.0, and recycle ratio of 1:1, maximum life of the thorium-promoted nickel alumina catalyst (dried at 180° C) was 550 hours, giving a methane productivity of 6500 lb/lb Ni (145,000 scf CH_4/lb Ni). Methane content of the product gas was generally more than 80 percent.

In fluidized-bed operation, partially activated Raney nickel catalyst (80-230 mesh size) performed as well as the thorium-promoted nickel catalyst (5). The Raney nickel catalyst was activated by extracting about 3 to 5 percent of the aluminum with caustic solution, and then washing the extracted material with water until the wash water gave a neutral reaction with litmus or pH paper. The wet catalyst was then charged into the reactor and dried with a flow of hot hydrogen until the catalyst bed became fluidized. The reactor was put into operation by pressurizing it to 300 psig under hydrogen, starting the flow of synthesis gas, and finally heating the catalyst from room temperature up to operating temperature. Operating at 370-394° C, 300 psig, $H_2/CO = 2.94$, a settled-bed space velocity of 7700 to 10,000 hr^{-1}, and recycle-fresh feed ratio ranging from 0.4 to 1.0, production of high-Btu product gas proceeded for a total of over 1000 hours. To achieve this length of service, the catalyst required two additional partial activations with caustic solution, one after 492 hours and another after 964 hours of operation.

Particle attrition is a suspected cause of substantial losses of nickel catalysts operating in fluidized-bed reactors. Weight loss in catalysts ranged from 8 percent for 6 hours of operation for an impregnated catalyst (L-6092) to 37 percent for 220 hours of operation for a precipitated catalyst (L-6036). An attrition-resistant nickel catalyst needs to be developed for fluidized-bed reactor operation.

Hot-Gas Recycle Reactor Catalyst

Catalysts for use in hot-gas recycle reactors were developed especially to give a low-pressure drop across the reactor (4, 2). The hot-gas recycle reactor removes the exothermic reaction heat by utilizing the sensible heat capacity of large volumes of recycle gas passing through the catalyst bed. A fraction of the recycle stream is cooled to remove the reaction heat and to condense out product water. Figure 3 shows a simplified sketch of the hot-gas recycle (HGR) methanator system.

One type of iron catalyst used in the HGR system consisted of lathe turnings cut from either 1018 carbon steel or wrought iron. Void volumes were about 87 percent to give acceptably low-pressure drops. The turnings were activated by oxidizing 20 percent of the iron to Fe_3O_4 with 600° C steam flowing at a space velocity of 400 hr^{-1} and then reducing the turnings with hydrogen for 60 hours at 400° C at a space velocity of over 4000 hr^{-1}.

Table II. Fluidized-bed Catalyst Evaluation

Theoretical catalyst composition 1/	Catalyst No.	H_2/CO	Av. temp. °C	Fresh feed, SVH	Recycle ratio	Life, 2/ hrs	Process life, lbs CH_4/lb Ni
NiO-100 (21.1%), Al_2O_3 159, kaolin 97	L-6025	2.5	350	7,100	1:1	45	-
NiO-100 (35.6%), Al_2O_3 7.3, MnO 25.6, kaolin 97	L-6036	2.5	330	2,800-10,000	0.8:1-1.3:1	220	-
NiO-100 (36.8%), Al_2O_3 7.3, MnO 25.6, kaolin 97	L-6036.2	3.0	345	7,500	1.5:1	132	1,200
NiO-100 (36.1%), Al_2O_3 7.3, Mno 25.6, activated alumina 75	L-6039	2.5	360	7,500	1:1	171	900
NiO-100 (7.1%), Mn 48, activated alumina 143	L-6042	2.5	345	7,500	0.8:1	6	-
NiO-100 (27.1%), Al_2O_3 7.3, MnO 25.6, Filtrol S-185	L-6051	3.0	350	7,500	0.7:1	237	2,500
NiO-100 (17.3%), Al_2O_3 7.3, ThO_2 11.0 activated alumina 240	L-6053	3.0	368	7,000	1:1	550	6,500
NiO-100 (42.4%), ThO_2 13.6, kieselguhr 78.4	L-6057	3.0	370	7,000	1:1	380	4,000
Co-100, Al 99	L-6049	3.0	381	14,000	2:1	1	-

1/ Based upon wt of ingredients ( ) Percentages of NiO determined analytically. 2/ Above 69% CO_2-free dry gas contraction.

NOTE: All catalysts except L-6049 were reduced at 350-400° C. 100 psig (All runs at 300 psig).

All catalysts were prepared by precipitating nitrate salts on various supports with K_2CO_3 except following:

L-6042 - Supports impregnated with nitrate salts which were later precipitated with K_2CO_3.
L-6049 - Raney cobalt 1% Al extracted with KOH solution

Nickel catalysts tested in the HGR system were in the form of parallel plate assemblies. The assemblies were made of plates sawed from an ingot of Raney nickel or of carbon steel plates, stainless steel plates, or aluminum plates that had been thermal-sprayed with either Raney nickel or nickel oxide powder. Thickness of the solid Raney nickel plates was 1/8-inch; thickness of the sprayed coatings ranged from 0.020 to .040 inch. Distance between plates was 1/8-inch. The Raney nickel catalysts were activated by caustic leaching of 10 to 20 percent of the aluminum followed by water washing to remove all caustic as previously described. The wet activated catalyst was charged to the reactor for synthesis. The sprayed nickel oxide coatings were activated in the reactor by reduction with hydrogen in the same manner as that used to reduce the iron catalysts.

Test results on performance of the iron and nickel catalysts confirmed the general superiority of the nickel catalysts over the iron in several respects. Activities of the nickel catalysts were several-fold that of the iron catalysts. Depending upon reactor conditions, estimated rates of conversion of $CO + H_2$ per unit geometric surface area were about 20 to 50 scfh/ft^2 for the nickel catalysts and about 2 scfh/ft^2 for the steel lathe turnings catalysts.

Carbon deposition was negligible for the nickel catalysts, whereas carbon deposition continued to build up on the iron catalyst and, in some cases, plugged the reactor.

Nickel catalysts yielded the higher heating value product gas with no oil byproducts, while the iron catalysts tend to yield about 3 to 4 percent of the hydrocarbon product as oil. Table 3 shows typical product gas yields over steel turnings,catalyst, the solid Raney nickel plate, and the sprayed nickel oxide plates. Much of the heating value of the product gas from the steel catalyst is due to the presence of C_2-C_5 hydrocarbons rather than a high yield of methane.

Tube-Wall Reactor Catalysts

The tube-wall reactor (TWR) system was developed to provide highly effective cooling of the catalyst by means of heat transfer through catalyst-coated tubes to boiling Dowtherm and thereby extend catalyst life. This type of cooling is efficient and permits operation with a much lower gas recycle ratio than that required in the HGR system; the recycle ratio ranges from 0 to 5 for the TWR system as compared with a range of 12 to 20 for the HGR system.

Figure 4 shows a sketch of a multi-tube tube-wall reactor pilot plant. The methanation reaction occurs on the outer surface of the catalyst coated tubes, while boiling Dowtherm removes the heat of reaction from the inner surface of the tubes.

Preparation of the flame-sprayed catalyst tubes for the TWR involves first a sand-blasting of the tube-wall surface, followed by flame-spray application of a commercial nickel aluminide about 0.003-inch thick for bonding purposes. A final flame-spraying of the surface is done with Raney nickel to obtain a catalyst thickness of about .020 to .025 inch. The catalyst is activated by the previously described procedure of alkali leaching at up to 95° C followed by water washing. Water washing must be sufficient to remove all excess alkali, as it is postulated that the presence of excess alkali promotes formation of Ni_3C during synthesis.

Bench-scale experiments with TWR indicated that a rapid decline in catalyst activity occurred with the activated Raney nickel catalyst if the reaction temperature was below 390° C. (1). Nickel carbide formation was the suspected cause of such rapid decline in activity. X-ray analyses of the spent catalyst and of loose material spalled from the spent catalyst tubes showed large amounts of Ni_3C. Nickel carbide formation is also a suspected cause of the short life of nickel catalysts

Table III. Hot Gas Recycle Methanation Results

Experiment No.	18 K	18 P	31 D	31 B	32 A
Catalyst bed size	3" dia x 10'		3" dia x 3'		3" dia x 2'
Catalyst	1018 steel turnings, oxidized 20%, reduced with 400° C H_2		Solid Raney nickel plates, 20% activated, with caustic		Sprayed nickel oxide plates, reduced with 400° C H_2
Pressure, ... psig	400	400	400	400	400
Temperature, °C.....(top)	300	300	300	301	300
(bottom)	340	340	397	353	361
(Av.)	320	320	380	330	324
Feed gas space velocity std vol/vol cat/hr	800	800	1284	1767	1830
Fresh feed, H_2:CO	3:1	2.5:1	2.92:1	2.94:1	2.95:1
Hot recycle: fresh feed	19:1	17:1	10:1	6:1	0
Cold recycle: fresh feed	4:1	4:1	2:1	8:1	11:1
Results:					
Conversion,..... % feed	88.4	91.0	99.0	98.1	93.5
Heating value,...Btu/scf dry	810	868	933	923	808
Product Gas Composition, %					
CH_4	43.6	38.8	90.4	88.5	71.2
C_2-C_5	10.6	15.7	.1	.2	.1
H_2	38.8	31.2	4.0	5.2	24.4
CO	1.3	2.2	.6	2.0	1.9
CO_2	4.4	11.0	3.2	2.3	.8
N_2	1.3	1.1	1.7	1.8	1.6
Oil production, % of total HC	3.2	3.7	0	0	0
Water vapor in recycle gas, %	4.8	4.7	8.1	2.8	2.1

Table V. Catalyst Analysis - TWR-6

Sample Description	Chemical analysis, wt. percent						X-ray analysis	Surface area determination, M^2/gm
	Ni	Al	Fe	C	S	Na		
Upper 9" of tubes (Gas Out)	70.1	12.5	0.2	4.3	0.1	0.1	Ni_3C	31.4
Middle 9" of tubes	67.9	14.4	.2	4.7	.1	.1	Ni_3C	33.4
Lower 9" of tubes (Gas In)	70.3	14.1	.3	5.4	.2	.1	Ni_3C	33.9
Loose material from baffles	68.7	11.3	.5	7.2	.1	.1	Ni_3C	30.3
Raney nickel unactivated	41.4	55.6	.1	--	.19	-	-	-

Conclusions

Suitable methanation catalysts of various forms can be prepared from iron or nickel, but nickel is far more effective in yield, activity, and desired selectivity. The activity of nickel catalysts is highly sensitive to sulfur poisoning and carbide formation; other important factors yet undetermined may exist. Major catalyst improvements needed include greater attrition resistance for fluidized-bed operation, less sensitivity to catalyst poisons and to temperature gradients for the HGR operation, and less sensitivity to catalyst poisons for TWR operation.

In the Bureau of Mines program, flame-sprayed Raney nickel catalyst in the TWR system has given the best methanation system thus far.

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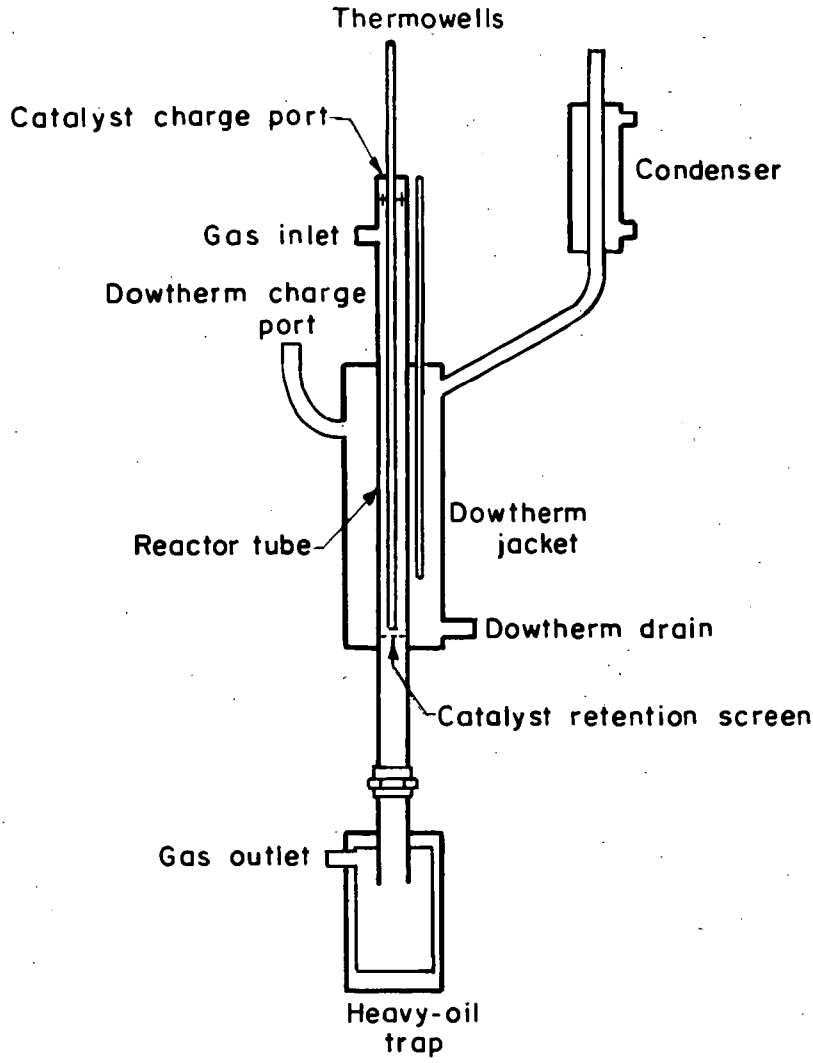

Figure 1 — Fixed-bed catalyst reactor.

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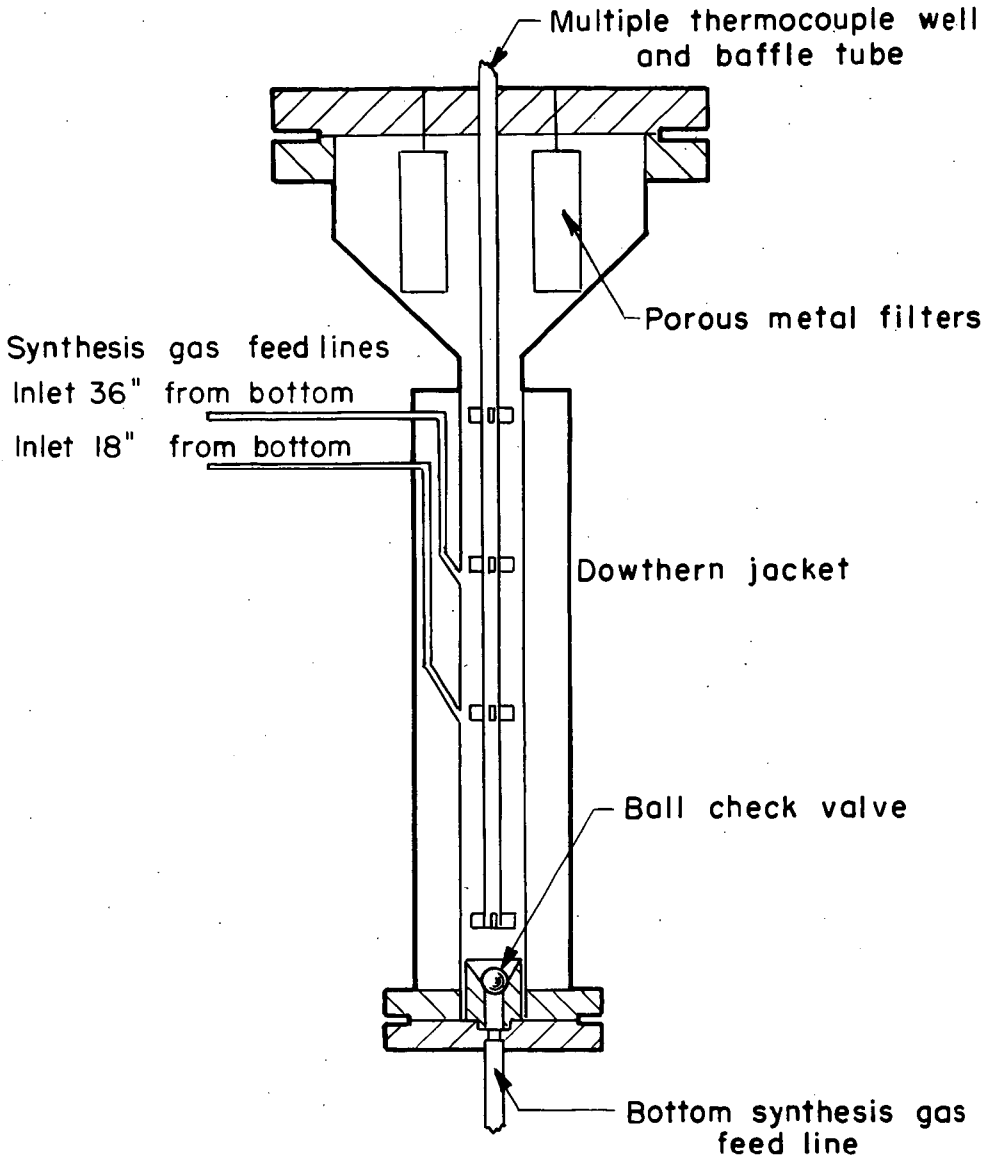

Figure 2 - Multiple-feed, fluidized-catalyst reactor.

L-12581

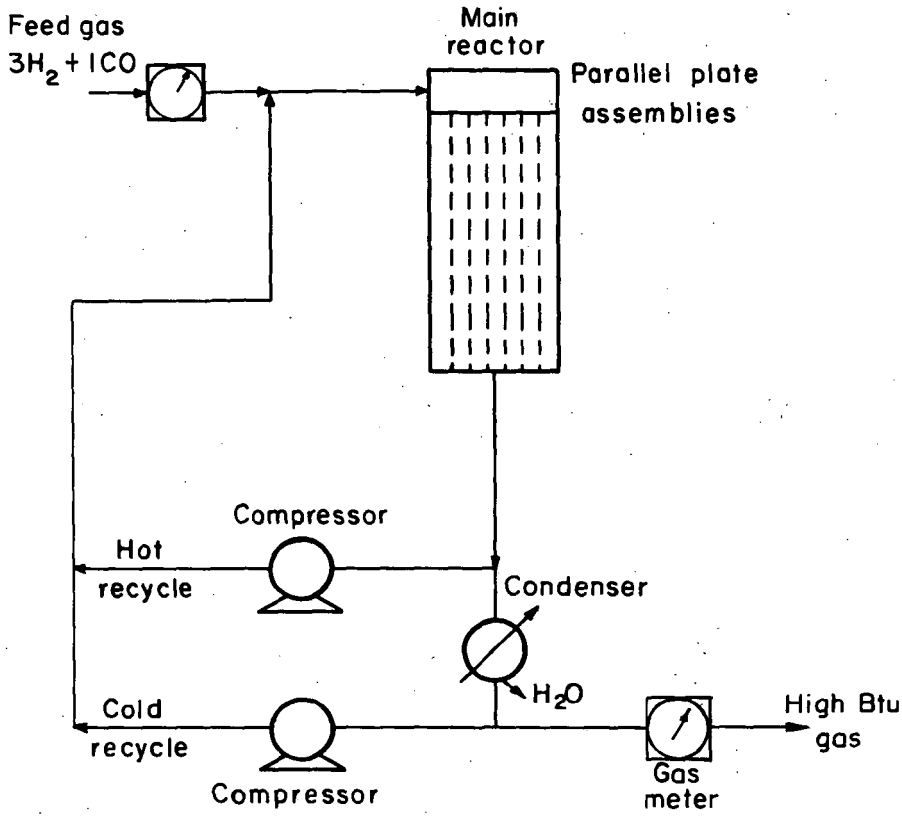

Figure 3 - Flowsheet of hot-gas recycle process.

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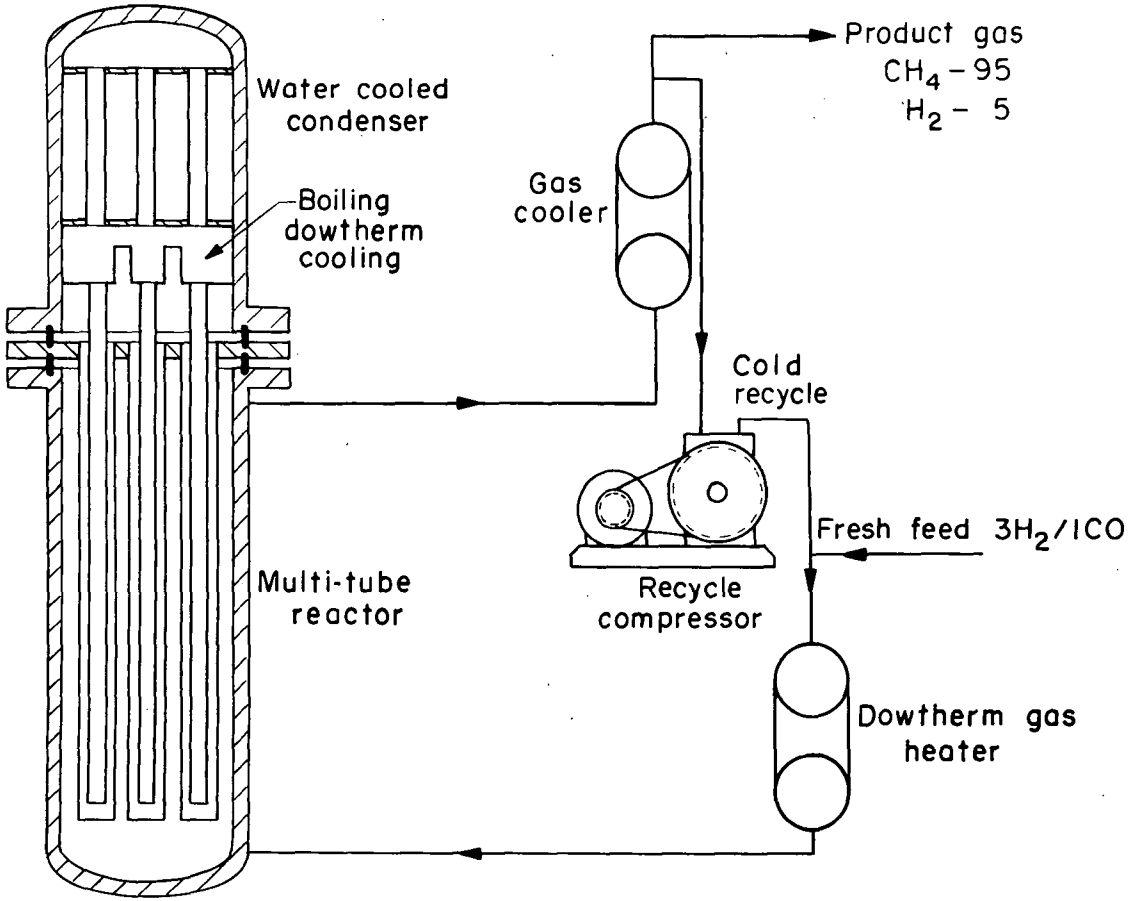

Figure 4-Simplified flowsheet of pilot plant for producing high-Btu gas

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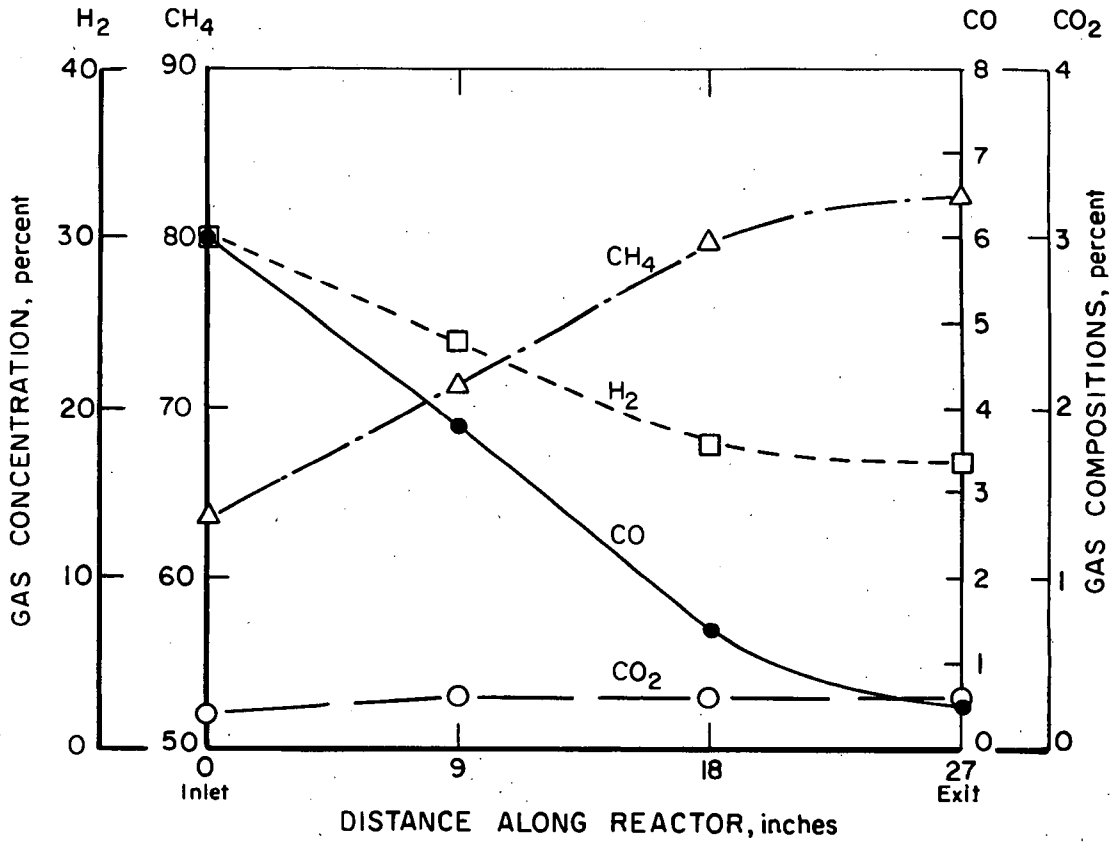

Figure 5 — Profile of gas composition (N_2, H_2O -free) along TWR reactor. Condition: 800 hours on stream, 390 °C average temperature, 300 psig, 500 scfh and 3:1 recycle.

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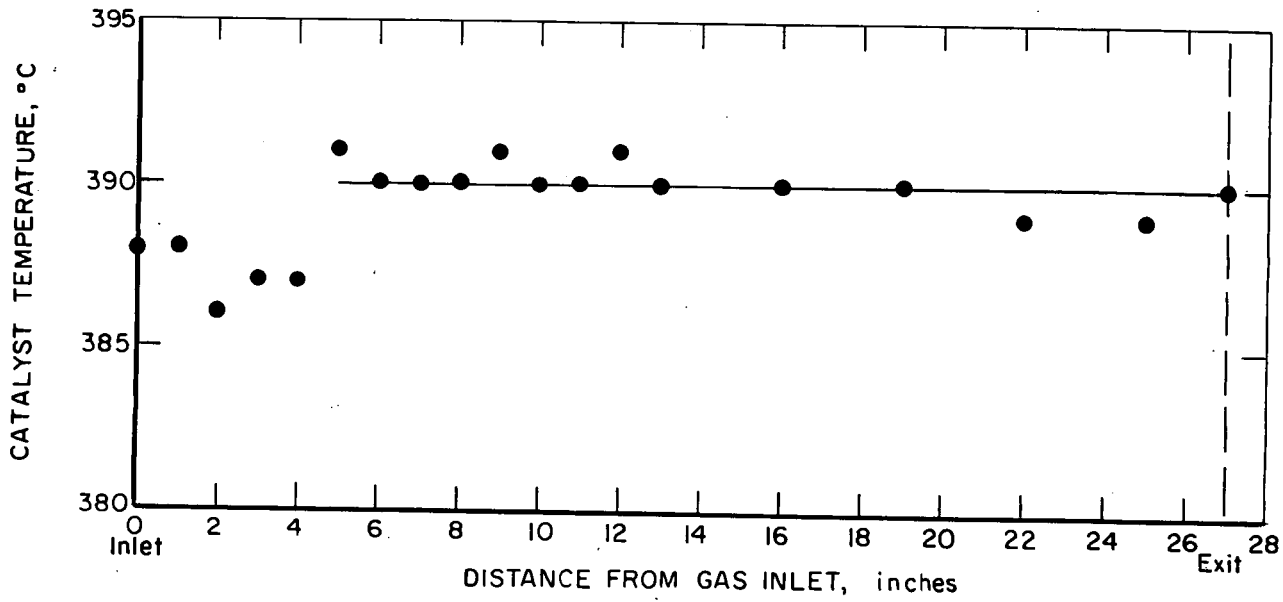

Figure 6 —Temperature profile —TWR-6, 526 hours on stream.

L-12583

BEHAVIOR OF NICKEL METHANATION CATALYSTS IN COAL-STEAM REACTIONS

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Introduction

The principal objective of the investigation is the direct conversion of coal-steam systems on to hydrocarbons in a single-stage reactor using multiple catalysts. The work has been described at a previous ACS symposium (1), and is sponsored by the Office of Coal Research of the United States Department of the Interior by contract with the University of Wyoming.

Depending upon catalysts and conditions, either gaseous or liquid hydrocarbon products predominate. In the case of gasification using nickel catalyst, methane is the principal hydrocarbon product. Excess steam rates will yield hydrogen, principally. In this reporting, however, gasification to produce methane will be the overriding consideration.

A potential advantage to the overall reaction is that the production of methane and carbon dioxide tends to be autothermal. The large heat requirement for gasification to only carbon monoxide and hydrogen could be avoided. The relatively small amount of heat needed to sustain the reaction would possibly be added to the reactants prior to injection into the catalyst bed proper.

In addition to the conversion of coal and lignite, other carboniferous materials have been gasified. These include waste paper, tire rubber, polyethylene plastic, and even manure and sewage sludge.

Description of Reactions

While the exact, step-wise sequence may not yet be known, observations on intermediate products obtained by operating the overall reaction in stages indicate two possibilities:

$$\begin{array}{rcl} C + H_2O & = & CO + H_2 \\ CO + H_2 & = & \tfrac{1}{2}CH_4 + \tfrac{1}{2}CO_2 \\ \hline C + H_2O & = & \tfrac{1}{2}CH_4 + \tfrac{1}{2}CO_2 \end{array}$$

or

$$\begin{array}{rcl} C + H_2O & = & CO + H_2 \\ CO + H_2O & = & CO_2 + H_2 \\ \tfrac{1}{2}CO_2 + 2H_2 & = & \tfrac{1}{2}CH_4 + H_2O \\ \hline C + H_2O & = & \tfrac{1}{2}CH_4 + \tfrac{1}{2}CO_2 \end{array}$$

The initiation reaction between coal and steam will occur at lower temperatures in the presence of alkali materials, chiefly potassium or sodium carbonate. The sequence is carried to completion by use of nickel catalysts. Various commercial nickel catalysts have been found to work. These catalysts in the active form are partially reduced oxides on various support materials, which are related to catalyst durability.

Experimental Systems

Studies on the integrated coal-steam-catalysts systems have been carried out in a one-inch diameter, semi-continuous flow reactor described previously (1). Superheated steam at reactor conditions is introduced continuously into a charge of coal and catalysts. Provision is also made for stratification or isolation of the nickel catalyst from the coal and alkali.

Studies on nickel catalyst behavior alone have been carried out in a half-inch diameter flow reactor. Provision is made for introducing various gases as reactants, chiefly CO, H_2, CO_2, and H_2S in varying combinations.

In all cases, reactor pressure is maintained by back-pressure regulators, and reaction temperature may be varied by tubular heaters. Pressures from atmospheric to 800 psi have been used, and temperatures up to 1500°F. The overall reaction is largely independent of pressure, but methane production quickly falls off above 1400°F.

Catalyst Behavior

Normally, nickel methanation catalysts are effective on streams of CO and H_2 at temperatures in the neighborhood of 700°F and are easily poisoned by sulfur. The H_2/CO ratio must be kept up to avoid carbonization and breakdown of the catalyst -- and may be resolved by the addition of steam.

In the integrated system, however, with all reactants mixed, operating temperatures of 1300°F can be maintained with no catalyst breakdown. Furthermore, at the higher temperature, equilibrium is away from the formation of sulfur compounds with the catalyst (2).

Hence, as a result, the effect of sulfur from the low-sulfur coals generally used has been nil. The sulfur content of the spent catalyst has been detected at 0.3%, of the same order as initially present.

As an additional benefit, the presence of sulfur may allay decarbonization of the catalyst (3,4). This has been found to be true in our own work.

The low-sulfur Wyoming coals have been found to retain much of their sulfur in the ash at these reaction conditions (possibly due in part to sulfur occuring as the sulfate).

The mechanical strength of the catalyst is of some concern at this point of the investigation. It is anticipated that a fluidized or ebullating bed will be utilized, and a high degree of strength is needed. Toward this end, techniques are being followed for depositing nickel on spheres of various materials. Perhaps ceramic supports will be required ultimately.

Experimental Results

The ultimate objective of most recent work on coal gasification is the production of a high-Btu gas. For a product of the order of 900 Btu/SCF, no modification of existing burners and jets would be required. The technology of CO_2-removal is already well-developed. Hence, on a CO_2-free basis, any product which is largely methane could be used as a full substitute for natural gas. With this in mind, a selected group of results are presented in Table I.

Table I

GASIFICATION OF COAL STEAM SYSTEMS

Run Number	274	361	312	356
Coal	Glenrock	Reynolds	Consol	Minnkota
Rank	Sub-bit	Sub-bit	Lignite	Lignite
Catalyst	Ni-0104	Ni-0104	G-65RS	Ni-0104
Pressure (psi)	250	250	250	250
Temperature (°F)	1200°	1400°	1350°	1400°
Gas Comp.				
CO_2	48.0	46.9	44.2	44.9
CO	--	--	--	--
H_2	1.8	3.1	8.7	5.1
C_1	50.4	50.0	47.1	50.0
SCF H_2/ton	562	855	2,733	1,689
SCF Hydroc/ton	15,725	13,783	14,795	16,556
Theo. C_1 yield	16,600	16,100	15,900	18,400
Btu/SCF (CO_2-free)	977	962	899	939

The coals, as used, were air dried from 25-30% moisture to about 5-20%. Yields are reported on an "as used" basis.

A different comparison is presented in Table II on average representative yields from various organic materials.

Table II

YIELD OF HIGH BTU GAS
(Standard Cu. Ft. per Ton)

	Actual	Theoretical
COAL	15,000	18,000
PAPER (RAW)	12,000	--
(CHAR)	20,000	--
TIRE RUBBER	24,000	25,600
POLYETH. PLASTIC	24,000	27,100
MANURE (CHAR)	14,000	--
SEWAGE SLUDGE		
(TREATED)	6,000	7,000
(CHAR)	7,000	9,000

In addition, various coal-derived chars and tars have been gasified, and also oil shale.

Conclusions

The investigations so far indicate without a doubt that it is chemically possible to convert coal and other carbonaceous materials with steam to directly yield hydrocarbons. It is a question now of demonstrating that this can be done feasibly in a fully-continuous system, with heat added only to the reactants. Toward this end, the detailed engineering design is underway for fabrication of a fully-continuous unit with a 6-inch diameter, fluidized reactor. Various ways of introducing the pulverized-coal feed will also be investigated with this unit.

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EXPERIMENTAL EVIDENCE FOR CATALYST ACTIVITY OF COAL MINERALS

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I. INTRODUCTION

In the P&M Solvent Refined Coal Process, coal is dissolved in a coal-derived solvent to produce a filterable liquid. This is accomplished by means of a mild liquid phase hydrogenation of the coal. Filterable solutions can be made by reacting about 1.0% to 1.5% by weight of hydrogen based on the moisture-ash-free (MAF) coal. The liquid is separated from the insoluble minerals and unreacted organic matter by filtration. The solvent is recovered for recycle by vacuum flashing and the residue product is recovered(1).

Sufficient solvent range liquid must be made from the coal to replace any mechanical losses and those losses due to formation of gas and low boiling liquids by further reaction of the solvent. When the hydrogenation is adequate, 85% to 95% of the MAF organic matter in the coal is reacted. In typical experiments, about 60% to 70% of the organic matter in coal can be recovered as a substantially ash-free residue from the vacuum flash operation. From 5% to 10% of the MAF coal will be distilled as liquid boiling in the solvent range. Some hydrocarbon gas, water, hydrogen sulfide, and liquids boiling below the solvent range account for the remainder of the reacted organic matter. The overall conversion of organic matter and the distribution of products which is formed can be altered by changing the operating conditions. When conditions favor increased hydrogenation, the yield of liquid products is increased with a simultaneous reduction in the amount of vacuum flash residue.

It is a matter of experience that these reactions can be run with many coals without the addition of catalytic agents. This paper reports some experiments which have been done to demonstrate the nature of the catalytic effects which can be attributed to mineral phases normally present in coals. These experiments treat hydrogenation by the use of hydrogen gas(5) and also by means of carbon monoxide and water as described by H. Appell and I. Wender(2). Part of the work was done by P&M and part by University of North Dakota staff in the Chemical Engineering Laboratories of the University of North Dakota. All of the work was supported by the U. S. Office of Coal Research as part of the development of the Solvent Refined Coal Process.

II. EXPERIMENTAL

A. SOLVENT

The solvent used in these experiments is the middle fraction obtained by redistilling anthracene oil under vacuum. The fraction in question boils between 100°C. and 230°C. at a pressure less than 3 mm of mercury. The distillation is done to standardize the material and facilitate studies of yield and conversion when coal is dissolved. Normally a filtrate will contain lower and higher boiling materials than the original solvent. These are presumed to be derived from the coal or to be due to further reaction of the solvent.

Anthracene oil is a complex mixture of aromatic hydrocarbons obtained by distilling coal tar. It may contain indenes, naphthalenes, acenaphthalenes, fluorenes, anthracenes, phenanthrenes, and pyrenes. Sulfur, nitrogen, and oxygen containing substances are also present. These elements may be substituted on the rings as -OH, -SH, or $-NH_2$, for example, or may be heteroatoms within the cyclic structures. Carbazole is a typical compound of this type. The molecular weights of the compounds in anthracene oil range from about 150 to about 400 with a mean value of about 200. A useful collection of spectra has been published by Karr and others which treats many compounds of this type[14].

Many of the aromatic structures present have the ability to react with hydrogen to form hydroaromatic derivatives. Under the influence of heat these hydroaromatic substances can transfer hydrogen to other molecules and the hydroaromatic material reverts to the aromatic form.

It is therefore practical to use the composition changes in this solvent to measure certain hydrogenation effects in coal solutions. The total hydrogen content of solvent samples can be measured by combustion analysis. These results have also been correlated with infrared studies of anthracene oil and solvent reclaimed from coal solutions. It is now practical to make quite precise estimates of hydrogen content by means of these infrared correlations. Changes of hydrogen content of 0.01% to 0.02% can be measured with confidence by this means. Since the infrared method has been used to evaluate many of the experimental results discussed in this paper, the calibration data and the combustion methods required to develop the working curves will be discussed in some detail.

B. COMBUSTION ANALYSIS OF SOLVENT

The apparatus used for carbon and hydrogen determination follows the recommendations of ASTM D 271 with a few modifications designed to favor increased precision and accuracy in routine analysis[3]. This is done by using 300 to 500 milligram samples instead of the 200 milligram samples specified in the ASTM method.

C. SOLVENT AND RECLAIM SOLVENT ANALYSIS BY INFRARED

It has been observed that the relative intensity of the absorbance at 3.28 microns compared to the absorbance at 3.41 microns changes as anthracene oil is hydrogenated. Raw anthracene oil, as received, tends to be lean in hydrogen while the solvent reclaimed from coal solutions made with raw anthracene oil tends to contain more hydrogen. When anthracene oil is catalytically hydrogenated, the ratio of the 3.28/3.41 micron absorbances decreases due to a considerable increase in the intensity of the 3.41 micron band and a small decrease in the 3.28 band.

As experience and samples run under various conditions accumulated, it became possible to observe this ratio over a considerable range of hydrogen content. Representative samples were run on the Perkin Elmer 237 grating spectrophotometer at slow speed. Using the general techniques of infrared quantitative analysis as presented in ASTM E-168, a baseline was drawn from the vicinity of 2.8 microns to the vicinity of 4.5 microns. The absorbance at 3.28 and at 3.41 microns was measured and the ratio of Absorbance @ 3.28/Absorbance @ 3.41 was calculated. This

ratio will be called the IR Ratio hereafter. Precise values for total hydrogen were obtained for these samples by combustion analysis. The results were plotted on a chart as percentage hydrogen versus the IR Ratio. A line was then drawn to establish a working curve. Data for the plot are shown in Table I and the working curve is shown as Figure 1. Sample spectra showing the appearance of the 3.28 and 3.41 micron region at different percentages of hydrogen in anthracene oil are presented in Figure 2.

TABLE I

ANALYTICAL DATA - ANTHRACENE OIL AND VARIOUS RECLAIM SOLVENTS

SUBSTANCE REPORTED	% CARBON	% HYDROGEN	IR RATIO
Middle fraction of hydrogenated reclaim solvent	91.42	6.901	0.431
Run PA 39 redistilled reclaim solvent	91.38	6.616	0.674
UND 373 reclaim solvent	90.64	6.412	0.792
UND 377 reclaim solvent	90.59	6.428	0.794
UND 376 reclaim solvent	90.85	6.407	0.818
Run PA 74 reclaim solvent	90.46	6.281	1.03
UND 277 reclaim solvent	90.33	6.132	1.06
Run PA 72 reclaim solvent	90.78	6.158	1.18
Continuous Run 2 reclaim solvent	90.65	6.092	1.28
Process Development Plant Run 66 reclaim solv.	90.41	5.987	1.29
Continuous Run 8 reclaim solvent	90.93	5.925	1.33
Run PA 73 reclaim solvent	90.90	6.151	1.36
Continuous Run 11 Sample 17 reclaim solvent	91.35	6.024	1.40
UND anthracene oil redistilled at atmos. press.	90.91	5.916	1.44
Continuous Run 7 reclaim solvent	91.05	5.895	1.54
Continuous Run 12 reclaim solvent	91.20	5.896	1.64
UND 357 reclaim solvent	91.09	5.828	1.75
Middle fraction of raw anthracene oil, sample 1	91.32	5.731	1.79
Middle fraction of raw anthracene oil, sample 2	91.01	5.741	1.78

Samples shown in Table I were taken from several different sources. PA runs are P&M batch autoclave materials. UND materials are from the University of North Dakota batch autoclave runs. Continuous run samples are from P&M laboratory continuous experiments. Some materials are retained from the Process D evelopment studies[5]. The original anthracene oils were from the Reilly Tar & Chemical Corp. plants at Cleveland, Ohio or Granite City, Illinois. The Granite City material is richer in carbazoles and this contributes some scatter to the data.

The IR Ratio changed from 0.43 to 1.8 while hydrogen changed from 5.73% to 6.90%. Thus, the precision of the IR Ratio corresponds to about 0.01% hydrogen. The precision of the combustion hydrogen value is about 0.03% to 0.05%. The calibration of a sensitive observation with a less sensitive one is difficult. However, the average slope established is the important information required and the number of data points available should establish this with acceptable accuracy.

It is also possible to run spectra in solution to obtain quantitative results. Anthracene oil and reclaim solvent are soluble in carbon tetrachloride and spectra can therefore be run using a solution in one cell and carbon tetrachloride in a matching cell in the reference beam. A more sophisticated differential measurement can be obtained by using the same concentration of raw solvent in the reference beam and reacted solvent in the measuring cell. In this system it is possible to relate the gain in hydrogen to a linear increase in the absorbance at 3.41 microns. Examples of this kind of data are presented in Table II.

TABLE II

DIFFERENTIAL ABSORBANCE AND HYDROGEN GAIN DATA

SUBSTANCE REPORTED	% HYDROGEN	GAIN IN % HYDROGEN	DIFFERENTIAL ABSORBANCE
Continuous Run 14 Sample 11	5.736	-00-	Reference
Continuous Run 15 reclaim solvent	5.938	0.202	0.135
Continuous Run 11 Sample 17	6.024	0.288	0.195
UND Run 360 reclaim solvent	6.112	0.376	0.314
Continuous Run 18 Sample 7	6.148	0.413	0.298
Run PA 74 reclaim solvent	6.281	0.545	0.362
Continuous Run 19 Sample 40 reclaim solv.	6.267	0.531	0.396
UND Run 376 reclaim solvent	6.407	0.671	0.467
Run PA 39 reclaim solvent	6.616	0.880	0.670
Middle fraction of hydrogenated reclaim solvent	6.901	1.165	1.13

When these results are plotted, most of the points fall on a straight line, as presented in Figure 3. It would be reasonable to assign most of the scatter observed to the errors inherent in the measurements made. This probably is not the case for the middle fraction of hydrogenated reclaim solvent, however. This observation deviates from the trend of the other data by an amount well outside the precisions of the elemental analysis and infrared measurement. The difficulty must be qualitative. Probably the result observed is an indication that more than one kind of structure can contribute to the absorbance at 3.41 microns and that new structures are being developed in the sample. The middle fraction of reclaim solvent, in question, was catalytically hydrogenated under severe conditions which resulted in removal of sulfur, oxygen, and nitrogen as well as hydrogenation of the oil. The formation of alkyl groups during this process could probably account for the difference observed. Problems of this kind are not serious enough to keep infrared measurements from being useful in the direct observation of hydrogen transfer reactions between anthracene oil and coal.

These correlations are based on anthracene oil or anthracene oil-derived solvents which have been used and reclaimed a limited number of times. Hydrogenation conditions were mild and some sulfur, oxygen, and nitrogen remains in the solvent being recycled. The application of this kind of method to other extensively hydrogenated material has not been done.

D. CATALYSIS OF REACTION WITH HYDROGEN

A diagram of the continuous reactor system used at the Kansas City Laboratory will be found at the end of this paper as Figure 4. The dissolver tube is a piece of high pressure tubing, 1 inch O.D. x 11/16 inch I.D. and 7 feet long. An experiment was designed to study the mixing behavior of materials in the dissolver tube using anthracene oil as the solvent and coal insolubles as the tracer. It was also expected that some information about the catalytic effects of the coal insolubles could be obtained by analysis of the solvent after processing through the dissolver.

The coal insolubles were recovered from the solution made in Process Development Plant Run 66 which has been reported previously(5). These insolubles had been carefully pyridine washed, followed by benzene and acetone rinses before being dried in a vacuum oven. The oven was cooled before removing the dried insolubles. Finall the insolubles were ground to pass a 100 mesh sieve before use. The ash content of this material was 46.14%. This lot of Kentucky No. 11 hvBb coal yields an ash which contains about 15% iron. Typical insolubles contain about 40% carbon and 2% hydrogen. The 5.5% total sulfur present was distributed: 0.1% pyritic sulfur, 0.5% sulfate sulfur, 1.9% organic sulfur, and 3.0% sulfide sulfur. Therefore, much of the iron is present as FeS although the presence of some oxide is not precluded. The organic material present is the most refractory carbonaceous part of the coal an has almost no tendency to react to further processing.

Experimental Procedure:

The reactor was lined out using the middle fraction of raw anthracene oil, MFRAO, as feed. This solvent was reported at the end of Table I with an average hydrogen of 5.736% and IR Ratio of 1.79. Operating conditions were: 1000 psig hydrogen, temperature 425°C., liquid space velocity 0.60/hr., gas space velocity 239/hr. The effluent liquid was sampled at half hour intervals and an infrared spectrum was run to measure the IR Ratio. At the end of 5 hours a sample was collected for a period of one hour and this sample showed an IR Ratio of 1.80 which was only a minor change when compared to the input solvent sample.

During this period, the weighed slurry feed vessel was filled with 3800 grams of MFRAO and 200 grams of washed coal insolubles. This slurry was switched into the feed loop at the end of the 6 hour line out period. Beginning immediately, samples were taken at 5 minute intervals (samples being collected for 4 minutes of each interval) for the first hour. During the second hour, samples were taken 15 minutes apart (for 5 minutes intervals). During the third hour, samples were taken 30 minutes apart (for 5 minutes intervals). Samples were taken hourly thereafter until the IR Ratio appeared to be nearly constant. Finally a sample was collected for a full hour to conclude the experiment. The slurry was pumped for a total of seven hours. All material not collected as samples was accumulated in a waste vessel. The infrared spectrum of selected samples was recorded. The samples were then analyzed for insoluble material by filtration followed by ashing the filter paper. In some cases the minerals were so fine that part of the material passed through the filter paper. In these cases the results were corrected by ashing the filtrate as well. The results were expressed as weight percent coal insolubles by using the previously determined ash content of the insoluble material.

Discussion:

The experiment generated a total of 33 samples. Eleven of these were used to line out the reactor and were only analyzed by infrared. An ash analysis was done on all of the samples made with coal-insolubles slurry feed. The infrared spectrum was run on selected samples as required to develop a smooth curve showing the change in solvent composition. The results are given in Table III.

TABLE III

DATA FOR HYDROGEN CONTENT OF EFFLUENT SOLVENT VS PERCENT INSOLUBLES

SAMPLE NUMBER	TIME FROM SLURRY START	IR RATIO OF SAMPLE	% HYDROGEN FROM WORKING CURVE	GAIN IN % HYDROGEN	% INSOLUBLES IN EFFLUENT
11	Last Lineout	1.80	5.725	Reference	None
12	5 min.				Nil
13	10 min.				Nil
14	15 min.				0.001
15	20 min.				0.035
16	25 min.				0.093
17	30 min.				0.133
18	35 min.	1.79	5.733	0.008	0.234
19	40 min.				0.305
20	45 min.				0.339
21	50 min.				0.475
22	55 min.				0.614
23	60 min.				0.641
24	65 min.	1.76	5.750	0.025	0.747
25	80 min.	1.73	5.770	0.045	0.949
26	95 min.	1.69	5.790	0.065	1.19
27	110 min.	1.68	5.800	0.075	1.37
28	125 min.	1.61	5.845	0.120	1.61
29	155 min.	1.58	5.863	0.138	1.89
30	185 min.	1.56	5.875	0.150	2.19
31	245 min.	1.47	5.935	0.210	2.90
32	305 min.	1.49	5.921	0.196	2.60
33	360 to 420	1.46	5.940	0.215	3.16

Figure 5 is a graphical presentation of the course of the IR Ratio and the percent insolubles as a function of time. It can be seen that the ratio decreases as the concentration of insolubles increases. It is noteworthy that fluctuations in the concentration of insolubles also correspond to fluctuations in the IR Ratio.

Figure 6 is a graphical presentation of the gain in percentage hydrogen in the solvent as a function of the percentage of insolubles in the reactor effluent. It can be seen that the amount of hydroaromatic hydrogen, as indicated by the infrared spectrum, increased in proportion to the concentration of insolubles. Without the insolubles present the solvent showed almost no tendency for this reaction to take place under the same operating conditions.

The catalytic properties of iron are well documented in the literature[10,11,12,13]. Probably FeS is the active compound since it is the most abundant form of iron present under these conditions. This is also the form isolated at the end of the reaction. Activity has been reported for iron oxide, but considerable opportunity exists for sulfide formation by reaction with hydrogen sulfide from coal.

The insolubles fed in this experiment contained 5.5% iron. The slope of the straight line shown in Figure 6 therefore is the response due to building up a concentration of only 0.15% of iron in the effluent product. This corresponds to a rate of hydrogen addition of about 1.4% per percentage of iron in the slurry under these operating conditions. Many high sulfur bituminous coals fed in a 2:1 solvent to coal slurry will line out with 0.5% to 1.0% of iron in the slurry. The reaction rates which are observed in uncatalyzed systems are in accord with the idea that iron is the principal active agent involved.

E. CATALYSIS OF HYDROGENATION BY REACTION WITH CARBON MONOXIDE AND WATER

It has been previously reported that coal can be hydrogenated by reaction with carbon monoxide and water[2]. This reaction may be done with coal alone, or with coal slurried in a solvent. Anthracene oil is suitable for the purpose and the solutions which result have substantially the same properties observed when hydrogen is used to produce similar conversions. Appell and Wender have reported alkali metal carbonates as catalysts and have mentioned the alkaline ash content of lignite[6]. Increased conversion with increased sodium content has been demonstrated by York who also comments on iron oxide as a catalyst[7]. None of the results given are very detailed and further studies were therefore done to define the requirements for catalysis of the carbon monoxide-water reagent system more clearly.

These studies involved a program of chemical analysis and autoclave studies which were conducted as a cooperative effort by P&M and University of North Dakota workers. An excellent series of lignite samples with varying sodium content was provided by the Grand Forks Station of the Bureau of Mines. These were sub-sampled to provide both groups with comparable materials.

Preliminary work established that substantially all of the sodium, reported by the Bureau of Mines ash analysis for these samples, could be extracted by exchange with 0.01 molar calcium chloride solution. To accomplish this exchange a 6.000 gram sample of the lignite was stirred with 125 ml. of the 0.01 molar calcium chloride solution, which was then filtered into a 200 ml. volumetric flask The material in the filter was then rinsed with additional calcium chloride solution until the flask was filled to the mark. The sodium content of the filtrate was determined by means of the Technicon AutoAnalyzer flame photo-

meter system using lithium as the internal standard. The manifold was essentially that recommended by Ussary and Gehrke for fertilizer analysis[8]. Further work showed that residual chloride in the exchanged lignite could be reduced to trace levels by careful washing with distilled water.

Seven lignite samples were available for these studies. These were coded UND samples 71-1 through 71-7. Some of these have been reported in Bureau of Mines literature while others have been reported only informally by means of analytical report sheets. The data and available cross reference numbers will be found in Table IV. In most cases, the sodium analysis by the extraction method checked total sodium as calculated from the ash and proximate analysis. A difference was noted in the case of the 71-1 sample which was traced to a lower ash content combined with a slightly higher water content in this subsample. Since this sample had already been used in a number of different experiments, it was necessary to use corrected values for the sodium and iron content of this sample.

The UND workers also prepared a calcium exchanged and a hydrochloric acid washed sample of the 71-1 lignite. Both were carefully washed with distilled water and dried to about the original moisture content. A detailed comparison of the 71-1 sample, the calcium exchanged sample, and the hydrochloric acid washed sample will be found in Table V.

TABLE V

COMPOSITION OF TREATED 71-1 LIGNITE SAMPLES

ANALYSIS	AS RECEIVED	CALCIUM EXCHANGED	HCl WASHED
% Moisture in lignite	32.94	29.73	30.98
% Ash in lignite	6.63	6.058	2.896
% Iron in ash	4.96	5.04	4.69
% Chloride in lignite	0.0058	0.091	0.024
% Total sodium in lignite	0.686	0.019	0.017
% Sodium in ash	10.35	0.3	0.6

The results of the calcium exchange experiments together with the HCl wash experiment suggest some rules which may be applicable to lignites in general. It appears likely that most of the sodium is in the material as a counter ion to polymeric acids which make up a considerable part of the functional groups in lignite. Calcium can be readily added by exposing the lignite to calcium ion and can be readily removed by acid washing the lignite. Part of the iron is removed by HCl washing. This observation suggests that iron and perhaps other elements may also serve as counter ions to acidic functions. Residual iron after the HCl wash is probably present as pyrite. The location of potassium and magnesium has not been studied. Ion exchange properties have been reported in recent lignite symposia[15,16].

Experimental Procedures:

A one gallon batch autoclave was used to conduct a number of experiments designed to study the catalytic effects involved in the solution of lignite using carbon monoxide and water as hydrogenation reagents. This apparatus has been previously described[9]. In these experiments charges of lignite, solvent, and water were adjusted so that weights of MAF lignite, solvent, and water were the same from

TABLE IV

BUREAU OF MINES DATA - PROXIMATE, ULTIMATE, AND ASH ANALYSIS OF LIGNITE SAMPLES

UND SAMPLE NO.	71-1	71-2	71-3	71-4	71-5	71-6	71-7
Mine	Baukol-Noonan	Beulah	Baukol-Noonan	Velva	Knife River	Savage	Savage
County				Ward	Mercer		
State	N.D.	N.D.	N.D.	N.D.	N.D.	Mont.	Mont.
B. of M. Designation	BN 4	B-STD	BN 2	V 5	BHL	S-1	S-2
B. of M. Sample No.	GF71-476		GF67-685	GF70-652	GF70-1289		
Proximate Analysis							
Moisture	28.46	30	27.95	28.33	28.33	34	30
Volatile Matter	28.83	29.09	29.28	31.74	30.76	27.05	29.53
Fixed Carbon	34.62	33.40	36.48	34.88	33.82	31.19	30.82
Ash	8.09*	7.51	6.29	5.15	7.09	7.77	9.65
Ultimate Analysis							
Carbon			48.44	46.58	46.89		
Hydrogen			6.18	6.40	6.24		
Nitrogen			0.83	0.78	0.68		
Sulfur	0.36	0.72	0.35	0.40	0.85	0.67	0.56
Oxygen			37.91	40.74	38.25		
Ash	8.09*	7.51	6.29	5.15	7.09	7.77	9.65
Ash Analysis							
SiO_2	27.2	20.2	16.4	18.8	16.1	21.3	35.7
Al_2O_3	15.9	11.3	7.7	8.6	10.5	13.0	20.3
Fe_2O_3	7.1	9.8	7.6	6.6	9.6	10.0	5.3
TiO_2	0.3	0.4	0.2	0.4	0.2	0.3	0.6
P_2O_5	0.1	0.5	0.2	0.2	0.3	0.8	0.6
CaO	16.7	21.8	18.4	32.5	23.2	22.7	16.4
MgO	4.3	8.0	4.1	8.1	7.4	9.3	7.0
Na_2O	13.5*	6.3	26.8	10.0	4.8	0.4	0.4
K_2O	0.5	0.3	0.3	0.5	0.3	0.3	0.9
SO_3	13.4	21.4	13.1	12.6	25.2	21.9	12.8
Other	0.6	--	2.1	1.2	1.9	--	--
Ignition Loss	0.4	--	3.1	0.5	0.5	--	--
Na calculated from ash	0.809*	0.351	1.25	0.382	0.252	0.023	0.028
Na by calcium exchange	0.681	0.433	1.26	0.380	0.252	0.028	0.028

*Na analysis for 71-1 subsample was revised. Ash on this sample was 6.63% and contained 10.35% total sodium. This is 0.686% sodium in the lignite compared to the calcium exchange value of 0.681%.

trial to trial. An initial pressure of 1200 psig of carbon monoxide was used and the heating was standardized in an effort to reproduce average and peak temperature profiles throughout the two hour reaction period. Peak pressures could not be reproduced because variable amounts of carbon monoxide and water were consumed and variable amounts of gaseous reaction products were made. The results are evaluated by elemental and infrared analysis of reclaim solvent and the vacuum bottoms samples produced. Conversion and yield data were obtained.

The experiments were done with several kinds of materials. These are described in the following paragraphs to relate run numbers, materials, and procedure details.

1. UND Run 357. This was a blank run in which the autoclave was charged with 150 grams of distilled water plus 500 grams of raw anthracene oil. The reactor was pressurized with 1200 psig of carbon monoxide. The reactor was heated to 795°F. and held at temperature for two hours. (This final temperature was used to obtain some correlating data for comparison to the continuous unit operating at 425°C.)

2. UND Run 360. The conditions and charges were the same as UND Run 357 except that 1.25 grams of sodium bicarbonate were added.

3. A series of experiments was done by using the lignite samples with a range of sodium contents supplied by Bureau of Mines. These were charged to the reactor in amounts calculated to contain a constant weight of MAF lignite, solvent, and water. The solvent for all runs was the middle fraction of raw anthracene oil supplied by the Kansas City group. See Table I for duplicate analysis of this oil. Bureau of Mines ash and proximate analysis data together with the checking sodium and iron analysis where appropriate have been used to calculate the mineral phase compositions. The reactor was brought to an average temperature of 716°F. with peak temperatures of 725°F. to 730°F. Reaction temperature was maintained for 2 hours to allow comparison with other UND runs. UND Runs 378, 379, 380, 382, 387, 388, and 389 comprise the experiments in this series.

4. UND sample 71-1 was used to study the effect of added sodium bicarbonate on the reaction. These experiments are UND Runs 373, 375, and 376. One trial used potassium carbonate. This was UND Run 377. The standard operating conditions described in paragraph 3 above were used for all runs.

5. The HCl washed sample of 71-1 lignite was used as the feed lignite in an experiment. The standard charges and operating conditions used were the same as those outlined in paragraph 3 above. This was UND Run 390.

6. The calcium exchanged 71-1 lignite was used as the feed lignite in the standard experiment. This was UND Run 391.

Discussion:

Table VI presents a summary of run numbers, operating conditions, and materials used. The number of millimoles of sodium, potassium, calcium, and iron in each reactor charge is also presented. The results of infrared or elemental analysis of reclaimed solvent and vacuum distillation residues for each run are also included.

Inspection of the data disclosed that a strong correlation existed between gain in hydrogen and increased sodium in the charge. In the solvent reclaimed from the

solvent blank run (UND 357) the change in hydrogen content was hardly measurable. Adding only 1.25 grams of sodium bicarbonate to this same charge caused the solvent alone to gain a readily measurable amount of hydrogen. In the various experiments using lignites with a range of sodium contents, or where sodium bicarbonate was added, an increase in reaction correlated with an increase in sodium content. Substitution of potassium carbonate for sodium bicarbonate did not appear to make a substantial difference (Run UND 377 versus UND 373).

The effect of removing substantially all of the sodium from a lignite was investigated by the calcium exchange and the hydrochloric acid washing experiments. In both cases the lignites remained reactive although a marked reduction in reactivity was observed. The gain in hydrogen by the reclaim solvent correlates with the amount of iron in the lignite while the considerable difference in the amount of calcium in the samples does not seem to have much effect on the solvent composition (Runs UND 390 and UND 391 versus UND 378).

It was found by trial that the gain in hydrogen by the reclaimed solvent could be fitted to a smooth curve if the gain in hydrogen were plotted versus the sum of the millimoles of sodium, potassium, and iron. This plot is given as Figure 7.

After some speculation it was decided that a plot of the H/C mole ratio in the vacuum distillation residues versus the total millimoles of sodium, potassium, and iron charged would be an appropriate data treatment for this material. The curve for the vacuum distillation residues is given as Figure 8. The H/C mole ratio is not affected by the presence of variable residual amounts of ash, sulfur, oxygen, or nitrogen which might be factors in comparing materials from different lignites. The presence of ash in some residues was not thought to be particularly significant because its presence is largely due to failure to completely de-water some of the solutions before filtration. As a result of this data treatment only two points are off the curve by significant amounts. These are the materials from UND Run 382, in which the 71-3 sample was used, and UND Run 391, in which the calcium exchanged lignite was used. The solvent from these runs seems to fit the correlation curve better than does the distillation residue data. This may be due to the greater effect of distillation technique on the residues since it is difficult to bring all materials to exactly the same end point.

An alternative would be to assume that the calcium remained in contact with the lignite phase and exerted a small selective effect on the material which tended to remain in the vacuum residue. It is possible to move the calcium exchanged material data point to the line by arbitrarily assigning a relative weight of about 0.3 times the number of millimoles of calcium in each sample and adding these values to the total millimoles of sodium, potassium, and iron charged. This moves all points outward and produces some change in the curve shape. The initial points are nearly linear on such a plot.

Another aspect of the reaction can be studied by observing the composition of the gas which is vented at the end of the reaction. The original gas charge was 10.545 moles of carbon monoxide. The reaction generates hydrogen. Part of this reacts with the lignite and the solvent and part remains unreacted in the gas phase. Carbon dioxide is formed in this reaction and may also be formed by decarboxylation reactions as a result of heating the lignite. Some unreacted carbon monoxide remains. Table VII gives the data for vent gas composition as a function of the sum of sodium, potassium, and iron. A graphical presentation of

TABLE IV

DATA FOR CATALYTIC EFFECTS STUDY - LIGNITE - CARBON MONOXIDE - WATER

UND RUN NUMBER	357	360	373	375	376	377	378	379	380	382	383	387	388	389	390	391
Materials & Conditions																
Lignite Sample			71-1	71-1	71-1	71-1	71-1	71-5	71-6	71-3	71-2	71-1	71-6	71-7	71-1	71-1
Grams Charged			165	165	165	165	165	159.5	170	153.6	164.4	163.1	168.9	175.8	159.2	165.4
Grams Solvent	500	500	350	350	350	350	350	350	350	350	350	350	350	350	350	350
Grams Water Added	150	150	155	155	155	155	155	161.5	150.3	164.9	155.7	154.6	151.7	154.8	152	151.7
Peak Pressure Psig	4200	4180	4490	4110	4190	4190	4315	4380	4455	4395	4570	4550	4360	4200	4520	4580
Catalyst Added Gm.	None	1.25	2.50	5.00	10.0	2.05									HCl	Ca
Kind		A	A	A	A	B									Wash	Exchange
Millimoles of Minerals In Reactor Charge																
Sodium	---	14.9	79.0	108.6	168.2	49.2	49.2	17.5	1.7	83.5	25.0	49.2	1.7	2.2	1.0	1.3
Potassium	---	---	1.2	1.2	1.2	30.9	1.2	0.7	0.8	0.8	0.8	1.2	0.8	3.2	---	---
Calcium	---	---	32.5	32.5	32.5	32.5	32.5	46.8	53.4	31.7	48.0	32.5	53.4	49.3	---	70.5
Iron	---	---	9.7	9.7	9.7	9.7	9.7	13.6	16.5	9.2	15.1	9.7	16.5	11.2	4.0	9.0
Total Na+K+Fe	None	14.9	89.9	119.6	179.1	89.8	60.1	31.8	19.0	93.5	40.9	60.1	19.0	16.6	5.0	10.3
Reclaim Solvent Data																
IR Ratio	1.746	1.134	0.792	0.773	0.818	0.794	0.776	0.831	0.976	0.814	0.846	0.814	0.990	1.155	1.347	1.164
H Value From IR	5.75	6.19	6.49	6.51	6.46	6.49	6.51	6.43	6.32	6.47	6.43	6.47	6.30	6.16	6.01	6.15
H by Combustion	5.82	6.11	6.412	6.562	6.407	6.427										
Gain in % H (IR)	0.02	0.46	0.76	0.78	0.73	0.76	0.78	0.70	0.59	0.74	0.70	0.74	0.57	0.43	0.28	0.42
Vacuum Residue Data																
H by Combustion	---	---	6.93	6.928	6.84	6.834	6.844	6.496	6.090	6.263	6.361	7.172	6.063	6.151	5.564	6.146
C by Combustion	---	---	83.54	81.97	80.59	83.97	85.05	85.03	84.96	82.62	82.24	85.94	84.83	85.60	85.69	84.97
H/C Mole Ratio	---	---	0.985	1.007	1.012	0.969	0.970	0.910	0.854	0.903	0.922	1.006	0.852	0.836	0.773	0.862

A = $NaHCO_3$ B = K_2CO_3

the data is given as Figure 9.

TABLE VII

VENT GAS DATA

RUN NO.	LIGNITE SAMPLE	TOTAL Na+K+Fe	MOLES VENTED	MOLES HYDROGEN	MOLES CARBON DIOXIDE	MOLES CARBON MONOXIDE
378	71-1	60.1	11.46	3.01	4.20	4.25
379	71-5	31.8	11.04	1.53	4.03	5.47
380	71-6	19.0	9.67	1.01	2.23	6.42
382	71-3	93.5	12.74	3.78	6.15	2.80
383	71-2	40.9	13.53	2.52	4.80	6.15
387	71-1	60.1	11.96	2.40	5.00	4.35
388	71-6	19.0	10.35	0.63	2.88	6.53
389	71-7	16.6	10.06	0.275	2.40	7.38
390	71-1 HCl	5.0	10.06	0.168	1.56	8.21
391	71-1 Ca	10.3	10.16	0.222	2.03	7.85

When coal is dissolved in a solvent system of this kind, a complex product distribution is formed. As the organic matter in the coal is reacted it tends to lose oxygen and sulfur with the formation of water, carbon dioxide, and hydrogen sulfide. As the organic phase becomes hydrogenated it dissolves in the solvent and both solvent and coal derived material break down into smaller and more hydrogen rich molecules if conditions are favorable. At the temperatures which prevail, many thermal bond ruptures are produced and repolymerization may produce higher molecular weight products if the free radicals formed are not efficiently terminated. The net effect of these competing reactions can be altered by changing process conditions. The product distribution, (hydrocarbon gas, light liquids, solvent range liquids, heavy oils, vacuum distillation residue, unreacted organic matter, and minerals), must be defined in detail to obtain a complete description of the chemical changes which occur. Meaningful discussions of conversion and yield must of necessity involve much detail and tend to elude simple exposition.

One kind of experimental product can be evaluated by fairly direct and simple methods. The reaction can be run on lignite without the use of solvent and the conversion can be measured directly by observing the solubility of the reaction product in appropriate solvents. Benzene is conventional for this purpose, but it is usual that the residue from such extractions will still be further attacked by other solvents such as acetone or pyridine. Such conversion data is arbitrary in nature and the justification for use of any particular solvent depends on a correlation with some proposed separation process or potential end use application. Pyridine solubility correlates well with product solubility in hot anthracene oil. Only three of these samples have been run in the non solvent system. The results are found in Table VIII.

Again it is observed that the conversion increases as the total sodium, potassium, and iron content of the reactor charge increases. (See Runs 384 and 386.) However, the result for Run 385, using 71-3, is again low compared to the trend of other data. (See also Run 382.) The cause is unknown, but perhaps the organic matter in this lignite is more difficult to convert. The solvent phase run in contact with this lignite in Run 382 seems to have gained a normal amount of hydrogen. This kind of a problem may be an indication of the risks involved in attempting

close comparisons using different coals as source materials. The ion exchange properties of lignite should allow facile addition of controlled amounts of metallic ions to produce materials in which the organic phase would be strictly comparable. Such materials could become the basis for quite sophisticated catalysis and reaction rate studies.

TABLE VIII

NON SOLVENT RUN YIELDS

RUN NO. UND	LIGNITE SAMPLE	TOTAL MILLIMOLES Na+K+Fe	PRODUCT YIELD - PERCENT OF MAF COAL		
			Volatile Matter	Benzene Extractable	Pyridine Extractable
384	71-6	19.0	24.8	42.0	50.0
385	71-3	93.5	38.2	57.7	64.1
386	71-1	60.1	42.9	66.4	67.8

III. SUMMARY AND CONCLUSIONS

The information presented in this paper is the result of a number of exploratory experiments designed to reconfirm or amplify detail for a number of effects reported in the literature. The secondary objective has been to add techniques which may be useful in evaluating the effect of catalysts, and process variables, on the reactions of coal and associated solvent or liquid phases. For this reason some of the analytical work has been stressed.

The catalytic properties of iron, and FeS in particular, for hydrogenation of coal are established beyond question in the literature. The experiment done with the continuous reactor outlines a rather different way to show this affect and also illustrates the utility of an instrumental method which is sensitive and quite rapid. It has been established that the hydrogen transfer capacity of the anthracene oil-derived solvent changes in response to process variables. (It may gain or lose hydrogen depending on conditions.) When this material is used as a solvent for coal, the hydrogen transfer effects are important but rehydrogenation of solvent appears to depend on catalysis by the coal minerals.

The reaction of carbon monoxide and water also depends on catalysis. This reagent system failed to react with anthracene oil until sodium bicarbonate was introduced. The alkali content of lignite appears to be the main source of activity in this coal. Most lignites do contain some iron which contributes to the overall effect. Lignites contain some potassium but generally the amount is too small to be useful. The other extractable ion generally present is calcium. Its probable location as a counter ion to polymeric acid functions suggests that it may also become catalytically active as the lignite is decomposed. These experiments have not been conclusive, but a lower order of activity for calcium seems probable.

The hydrogenation effects may be followed by observing solvent or vacuum bottoms compositions. Correlating conversion data based on composition of gaseous products is also obtainable. These changes can also be shown by observation of the detailed distribution and yield of liquid and vacuum distillation products although such detail has not been presented here.

It seems probable that the ion exchange properties of lignite could be utilized to prepare carefully controlled materials for reactivity studies. These materials could be used in the autoclave or in the continuous reactor to develop quantitative relationships for the elements of interest.

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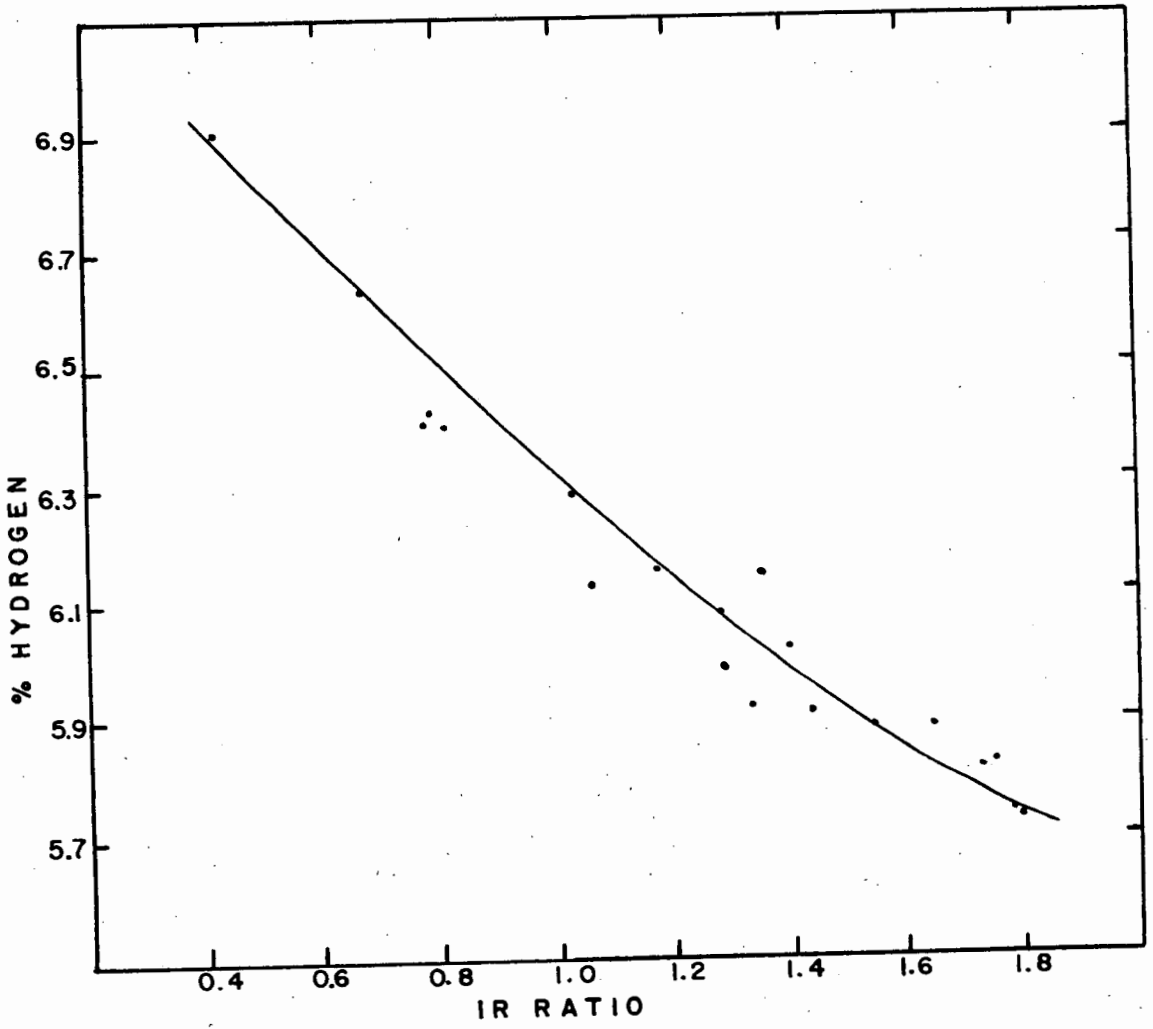
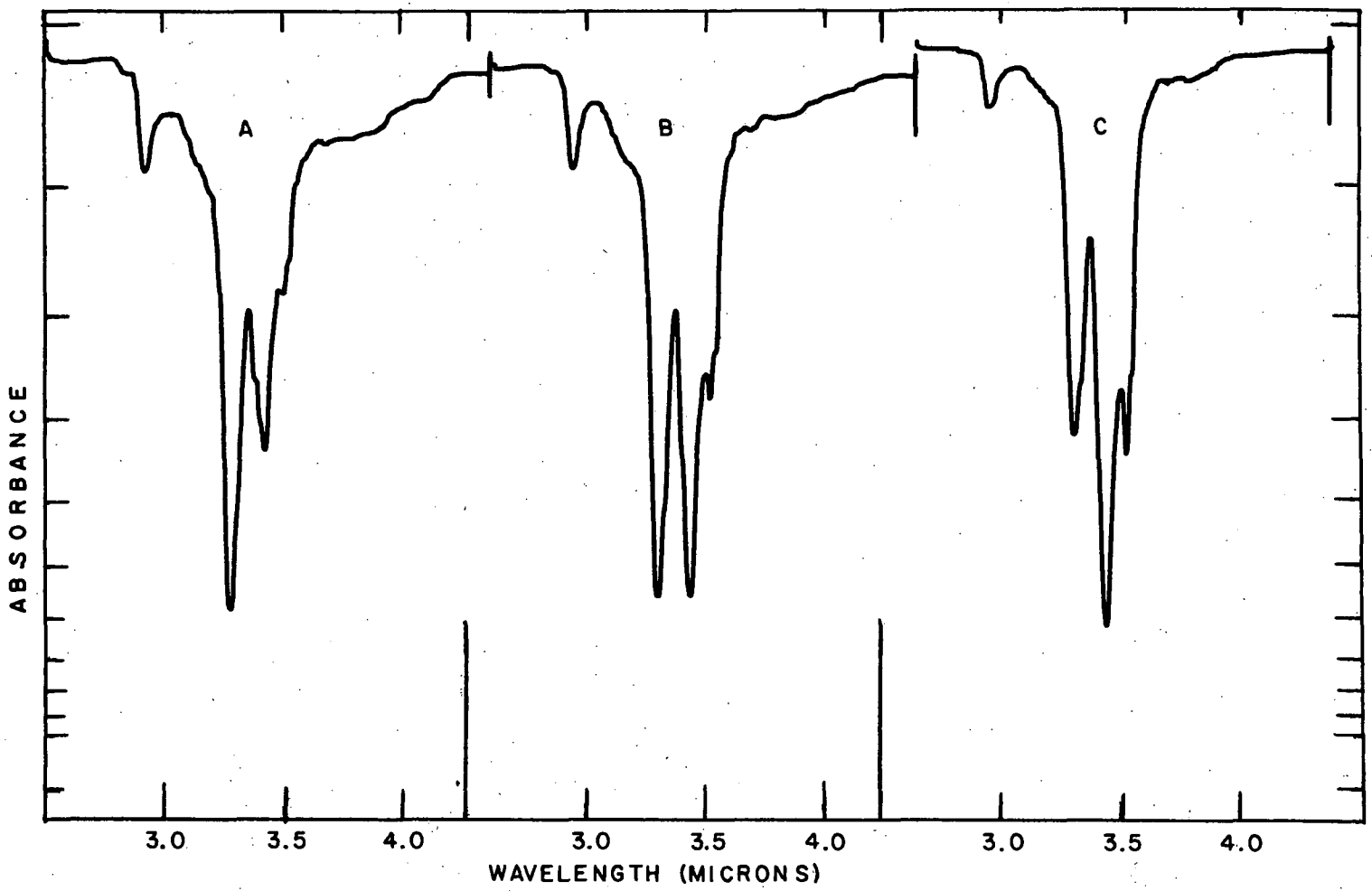


Figure I. WORKING CURVE % H IN SOLVENT



A. MIDDLE FRACTION OF RAW ANTHRACENE OIL. B. MIDDLE FRACTION PARTLY HYDROGENATED.
C. MIDDLE FRACTION OF HYDROGENATED RECLAIM SOLVENT.

Figure 2. COMPARATIVE SPECTRA

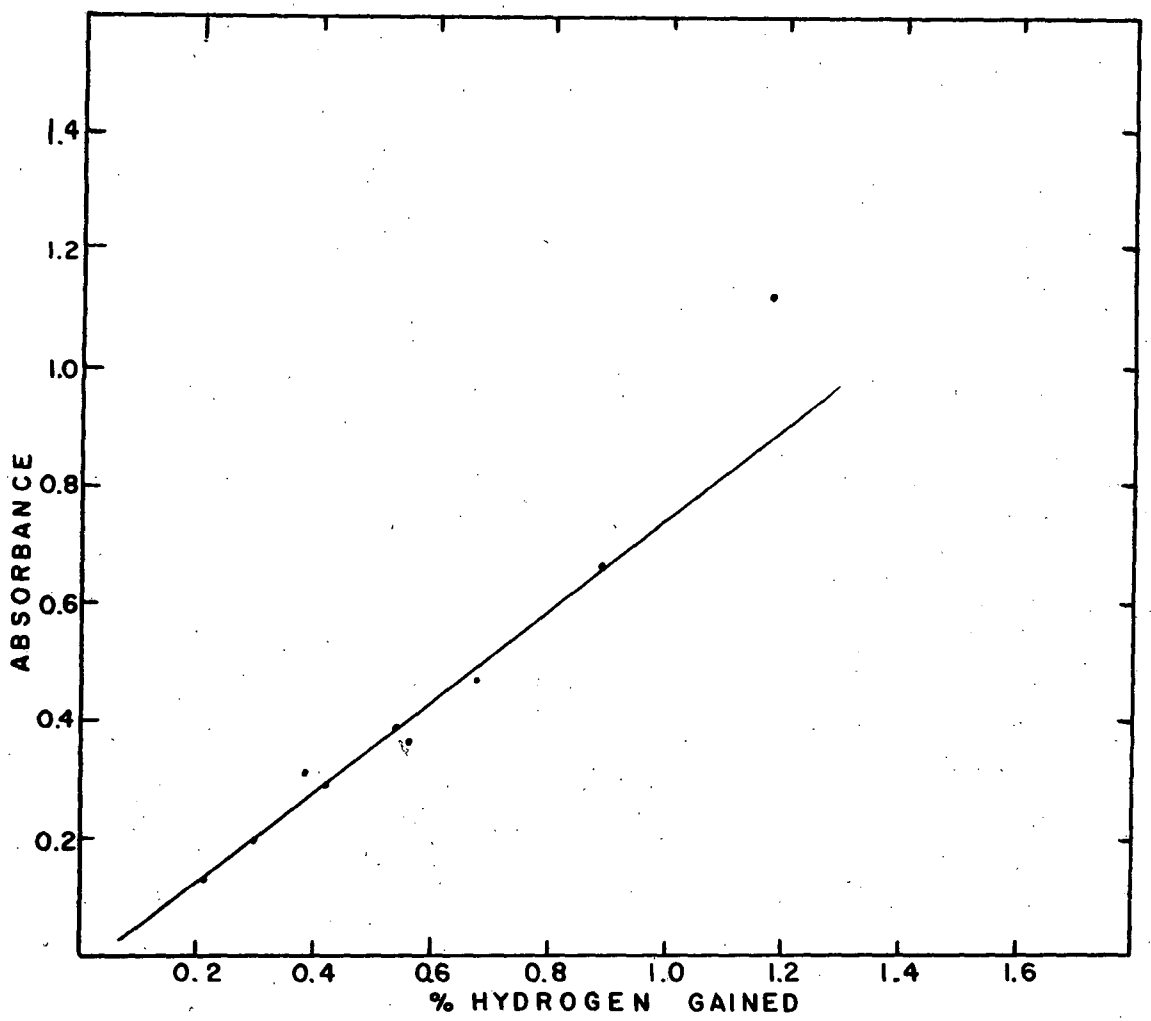


Figure 3. DIFFERENTIAL IR WORKING CURVE

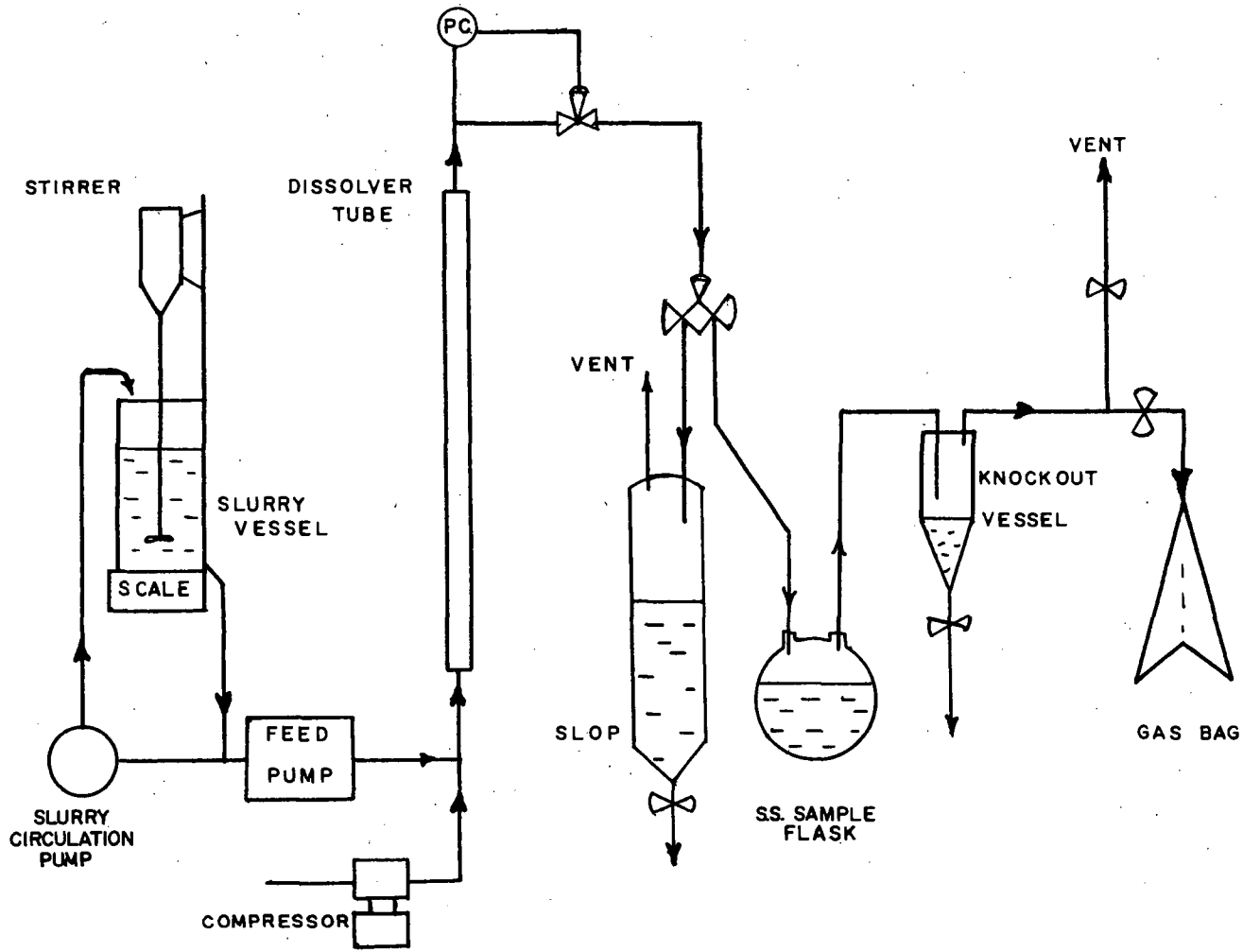


Figure 4. SIMPLIFIED FLOW DIAGRAM - CONTINUOUS DISSOLVER

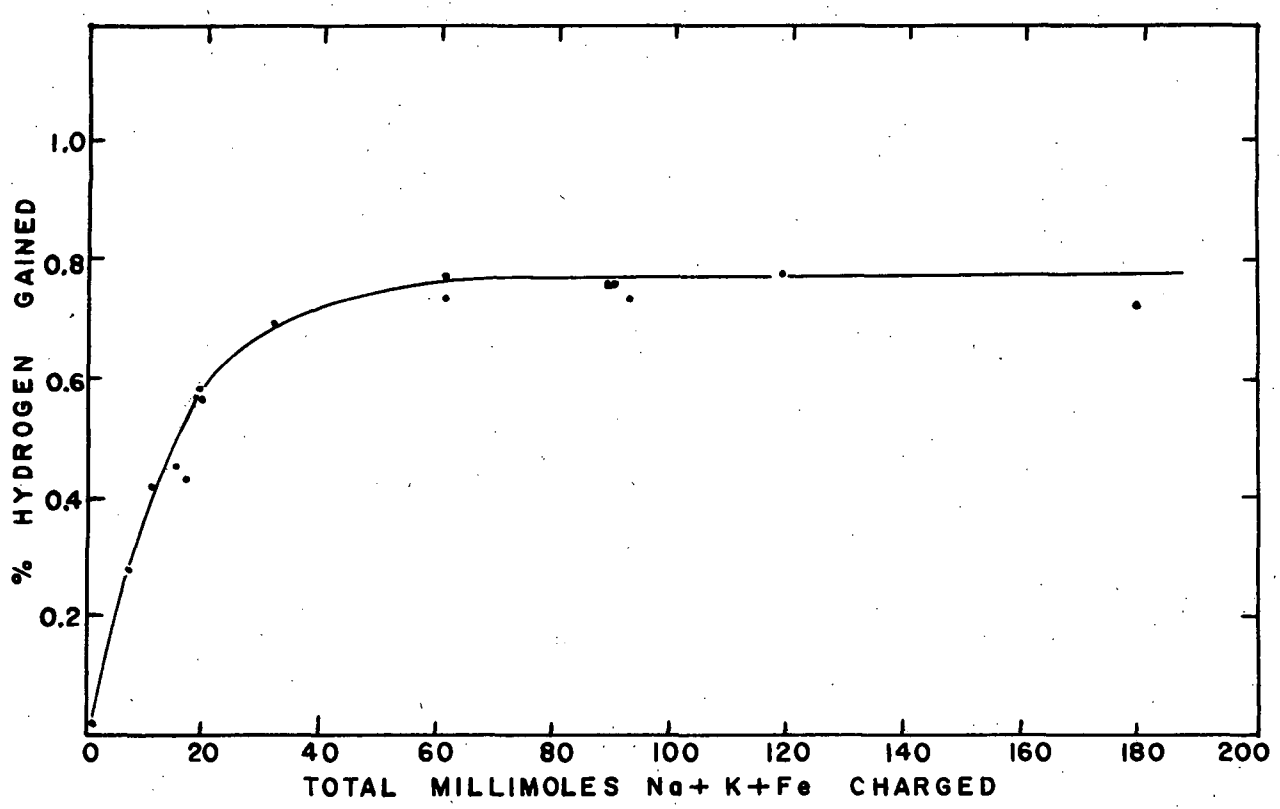


Figure 7. HYDROGEN GAINED BY RECLAIM SOLVENT

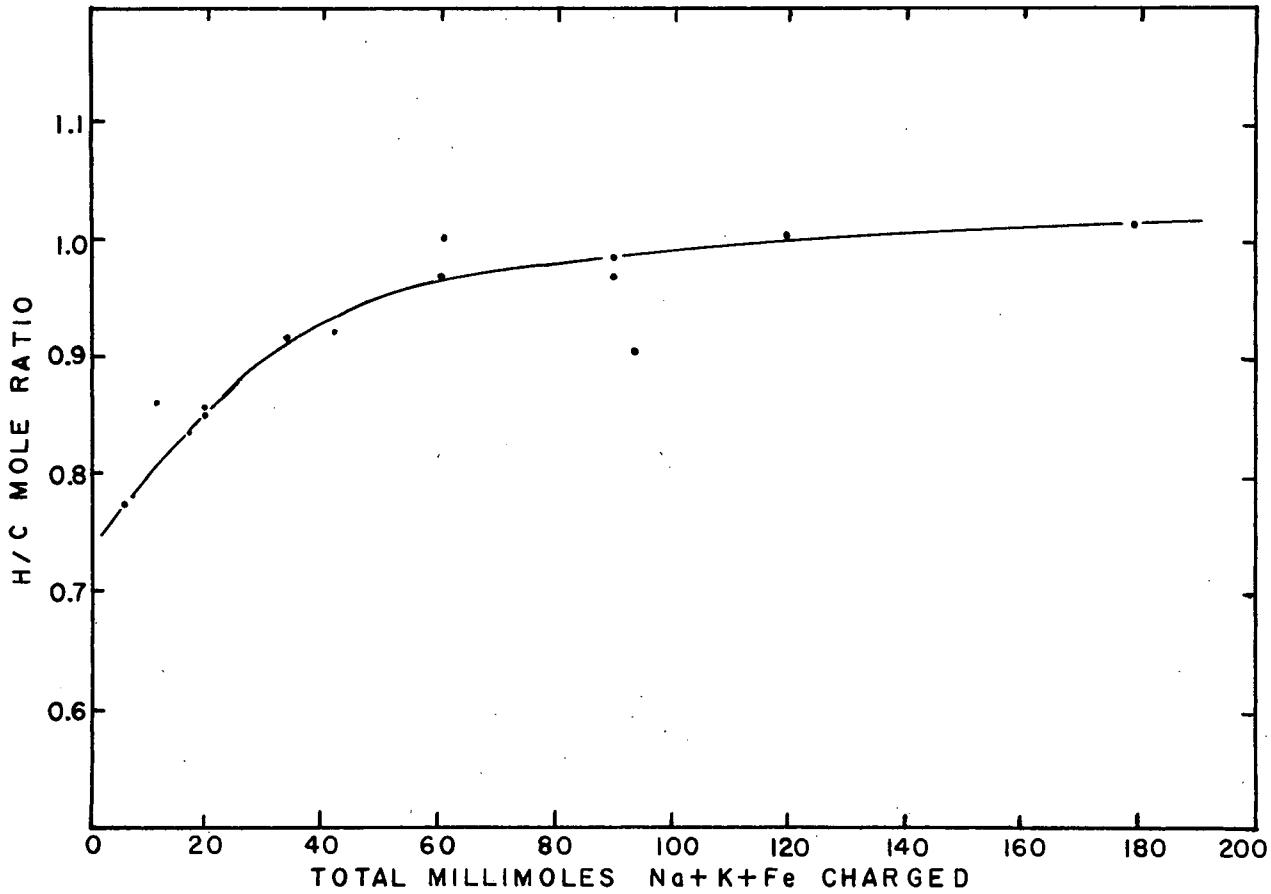


Figure 8. COMPOSITION OF VACUUM DISTILLATION RESIDUES

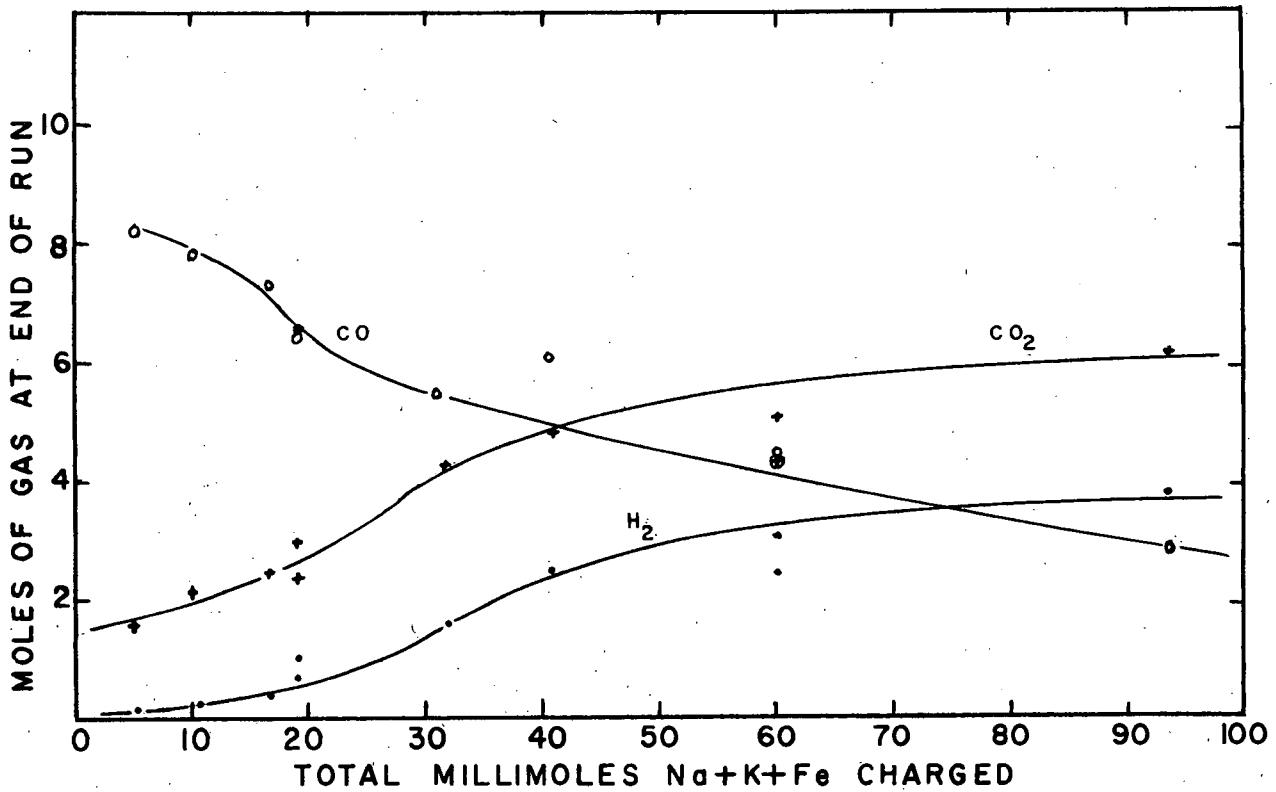


Figure 9. VENT GAS COMPOSITION AT END OF EXPERIMENT

DEVELOPMENT OF CATALYSTS FOR THE HYDROCRACKING OF POLYNUCLEAR AROMATIC HYDROCARBONS

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INTRODUCTION

Hydrocracking reactions of polynuclear aromatic hydrocarbons and heterocyclic compounds proceed essentially through a multi-step mechanism of hydrogenation, isomerization, cracking and rehydrogenation in that order. Multi-functional catalysts containing hydrogenation, isomerization and cracking activities will thus be the most suitable catalysts for reactions of this type. Cracking catalysts like the silica-aluminas and molecular sieves and hydrogenation catalysts like metallic platinum, palladium,nickel and oxides and sulfides of cobalt, molybdenum, nickel and tungsten were used in suitable combinations in the preparation of multi-functional catalysts used in the industrial processing of petroleum feed stocks (1-3). The industrial catalysts may not be quite suitable for use in the processing of highly aromatic feed stocks like the coal oils and their activities and selectivities may have to be modified to make them suitable for use. Not much work was published in the open literature on the activities and selectivities of different catalysts in the hydrocracking of polynuclear aromatic hydrocarbons. Flin et al (4) and Sullivan et al (5) studied the hydrocracking of different aromatic hydrocarbons over catalysts containing nickel sulfide on silica-alumina in flow systems. The principal reactions occured during hydrocracking were found to be hydrogenation, cracking, isomerization, alkylation and paring. Qader and Hill (6) later reported product distributions obtained in the hydrocracking of naphthalene and anthracene over dual functional catalysts containing oxides of cobalt, molybdenum, nickel and silica-alumina. In the present communication, the data on the kinetics and mechanisms of hydrocracking of naphthalene, anthracene and pyrene are reported. The activities and selectivities of oxides and sulfides of cobalt, molybdenum, nickel and tungsten and different cracking catalysts are also discussed.

EXPERIMENTAL

Pure grade hydrocarbons and catalysts were used. The catalysts contained 20 and 80 per cent by weight of hydrogenation and cracking catalysts respectively. The hydrocracking work was done in a stirred tank reactor of 300 c.c. capacity. Experiments were done with 10 gm of the hydrocarbon and 2.5 gm. of the catalysts in the temperature range of 450° - 500°C and pressure of 500 - 1250 psi.

RESULTS AND DISCUSSION

Coal oils contain large quantities of polynuclear aromatic hydrocarbons and heterocyclic compounds. An understanding of the conversion

of polynuclear structures to smaller molecules will help in developing efficient processes for the conversion of coal oils. Hydrocracking is a versatile method for the conversion of higher aromatics to lower ones and catalysts containing hydrogenation and cracking activities will be the most suitable for this reaction. In this work, Naphthelene was hydrocracked over catalysts containing prereduced oxides and sulfides of Mo, Ni, Co and W and silica-alumina. The product distributions obtained with the oxide catalysts are given in Tables I and II. The principal products of naphthalene hydrocracking are Tetralin, indanes, ethylbenzene, toluene and benzene (Table I). At higher conversion levels (Table II), butyl benzenes and compounds boiling higher than naphthalene were also formed. The higher compounds were found to be mainly alkyl naphthalenes and Tetralins. Similar product distributions were obtained when naphthalene was hydrocracked over sulfide catalysts as shown in Tables III and IV. The data show that the oxide and sulfide catalysts affect the hydrocracking reaction in a similar way. The product distribution data obtained with different cracking catalysts and molybdenum oxide are given in Table V. The data show that the catalysts have different activities but yield similar products. It is, therefore, evident that the hydrocracking pattern of naphthalene remains same irrespective of the catalyst used. The catalysts, however, vary in their activities and selectivities. The product distribution data of naphthalene hydrocracking suggest a three step reaction mechanism as shown in Figure 1. In the first step, naphthalene gets hydrogenated to Tetralin which then gets isomerized in a second step to methylindan. Methylindan will then crack in a third step to indan and alkylbenzenes. The indan further cracks to alkylbenzenes. The analysis of the gaseous products given in Table VI also supports the mechanism given in Figure 1. A similar mechanism was earlier proposed by Qader et al (7) in the hydrocracking of naphthalene over a H-mordenite catalyst. The kinetics of each individual step of the naphthalene hydrocracking reaction were evaluated in the temperature range of 450° - 500°C at a constant hydrogen pressure of 1000 psi. All the steps were found to be first order reactions with respect to the concentration of naphthalene and the activation energies were calculated from plots of Arrhenius equation. The rate constants of the hydrogenation, isomerization and cracking reactions were found to be consistent with equations 1 - 3.

$$k_{\text{Hydrogenation:}} \quad 1 \times 10\, e^{-8,600/RT}\ \text{min.}^{-1} \qquad (1)$$

$$k_{\text{Isomerization:}} \quad 1 \times 10^{1.6} e^{-18,400/RT}\ \text{min}^{-1} \qquad (2)$$

$$k_{\text{Cracking:}} \quad 1 \times 10^{3.8} e^{-28,100/RT}\ \text{min}^{-1} \qquad (3)$$

The activation energies indicate that hydrogenation is controlled by both physical and chemical processes, isomerization and cracking mainly by chemical reaction. The effect of hydrogen pressure on the first order rate constants is shown in Figure 2. The rate constants

increased almost linearly with pressure. The hydrogenation rate constant increased relatively more when compared to the isomerization rate constant which increased more than the cracking constant. The data indicate that the overall order of the reaction is more than one, being greater than zero with respect to hydrogen concentration and the rates are influenced to different degrees by physical and chemical processes.

The product distributions of anthracene hydrocracking are given in Tables VII-IX. The main products obtained were hydrogenated anthracenes, hydroanthracene isomers containing 5 member saturated rings of the acenaphthene type, naphthalenes, Tetralins and alkylbenzenes. Some compounds higher than anthracene were also formed. The hydrocracking pattern was found to be the same irrespective of the catalyst type used. The hydrocracking rate, however, varied with the catalyst type.

The product distribution data suggest a multi-step reaction mechanism occuring in the hydrocracking of anthracene as shown in Figure 1.

The principal reactions occuring during anthracene hydrocracking are hydrogenation, skeletal isomerization and cracking. The hydrogenation of anthracene was earlier reported (8) to take place in a stepwise manner forming di-, tetra- and octahydroanthracenes in that order. But at high temperatures, the dihydroanthracene did not form to any significant extent. Under the conditions (450° - 500°C) used in this work, dihydroanthracene did not appear in the product to any significant extent. No isomerization of the hydroanthracenes to acenaphthene type structures was reported in the above work (8). However, Sullivan et al (5) reported the formation of isomeric hydrophenanthrenes containing 5-member saturated rings in the hydrocracking of phenanthrene. In this work, the isomeric hydroanthracenes containing 5-member saturated rings were formed as shown in Figure 1. Though compounds containing one 5-member ring are shown in the mechanism, it is possible that compounds containing two 5-member rings might form from octahydroanthracene. The naphthalenes and Tetralines will undergo hydrocracking according to the mechanism shown in Figure 1. The kinetics of the overall hydrogenation and cracking steps of the anthracene hydrocracking reaction were evaluated in the temperature range of 450° - 500°C at a constant pressure of 1000 psi. Both the steps were found to be first order reactions with respect to the concentration of anthracene and the activation energies were calculated from plots of Arrhenius equation. The rate constants were found to be represented by equations 4 and 5 in the temperature range 450° - 500°C.

$$k_{\text{Hydrogenation:}} \quad 1 \times 10^{1.2}\, e^{-11,100/RT}\ \text{min}^{-1} \qquad (4)$$

$$k_{\text{Cracking:}} \quad 1 \times 10^{0.2}\, e^{-16,200/RT}\ \text{min}^{-1} \qquad (5)$$

The activation energies indicate that hydrogenation and cracking are mainly controlled by chemical processes. The effect of hydrogen pressure on the first order rate constants is shown in Figure 3. The rate constants increased linearly with pressure. The relative increase in the rate

constants was large in case of hydrogenation when compared to cracking. The data indicate that the reactions are controlled by chemical processes to different degrees The mechanism of anthracene hydrocracking remained same irrespective of the catalyst used. However, the rates of hydrocracking varied with the catalyst type. The data given in Table X show that cobalt sulfide is the most active hydrogenation catalyst followed by tungsten sulfide, nickel sulfide and molybdenum sulfide in that order. The hydrocracking activities also decreased in the same order though the same cracking catalyst is used. This indicates that cracking increases with hydrogenation probably due to the increased formation of hydroanthracenes. It, therefore, appears that a more active hydrogenation catalyst also enhances cracking reactions indirectly. The hydrogenation and cracking rate constants of anthracene also varied with the type of cracking catalyst used as shown in Table XI. The low alumina catalyst exhibited higher cracking activity. The hydrogenation rate constant was also high in case of the low alumina catalyst though the same hydrogenation catalyst is used in both the cases. This indicates that cracking increases hydrogenation indirectly.

The product distribution data of pyrene hydrocracking (Table XII and XIII) indicate that the oxide and sulfide catalysts yield similar product distributions. The hydrocracking reaction proceeds through a multi-step mechanism of hydrogenation, isomerization and cracking. The pyrene gets converted to phenanthrenes through a two step mechanism of hydrogenation and cracking. Then the phenanthrenes formed get converted to naphthalenes which in turn get converted to alkylbenzenes. The principal steps involved in the conversion of pyrene to benzenes are shown in Figure 1. The pyrene hydrocracking data were evaluated by first order kinetics and the first order rate constants were found to be represented by equations 6 and 7:

$$k_{Hydrogenation}: \quad 1 \times 10^{2.1}\, e^{-7,100/RT}\ min^{-1} \qquad (6)$$

$$k_{Cracking}: \quad 1 \times 10^{0.6}\, e^{-10,200/RT}\ min^{-1} \qquad (7)$$

The activation energies indicate that hydrogenation is controlled by both physical and chemical processes and cracking by chemical reaction.

The reactivities of the different polynuclear aromatic hydrocarbons vary due to differences in their chemical,physical and electronic properties. The first order rate constants of the hydrocarbons given in Table XIV indicate that anthracene is the most reactive hydrocarbon and naphthalene the least reactive.

ACKNOWLEDGMENT

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TABLE I. NAPHTHALENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	MoO_3	NiO	CoO	WO_3
Liquid Product Analysis, Mole %				
Benzene	0.75	0.69	0.97	Trace
Toluene	0.75	1.39	1.30	Trace
Ethyl benzene	0.5	Trace	0.65	0.27
Xylenes	-	-	-	-
Propyl benzenes	-	-	-	-
Decalins	-	-	-	-
Butyl benzenes	Traces	-	-	Traces
Indan	1.6	0.5	1.2	1.09
Methyl Indan	3.42	2.28	3.68	3.0
Tetralin	5.02	2.78	4.88	2.73
Naphthalene	87.93	90.59	84.69	92.89
Higher Compounds	Traces	1.74	2.6	-

TABLE II. NAPHTHALENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	MoO_3	NiO	CoO	WO_3
Liquid Product Analysis, Mole %				
Benzene	0.63	1.7	0.37	0.47
Toluene	1.19	3.1	0.79	1.25
Ethyl benzene	2.54	5.5	3.47	0.78
Xylenes	-	-	-	-
Propyl benzenes	0.63	0.56	Trace	Trace
Decalins	Trace	0.9	Trace	Trace
Butyl benzenes	5.09	4.9	4.17	1.41
Indan	3.45	4.0	2.46	1.72
Methyl Indan	6.1	5.11	4.0	3.0
Tetralin	35.66	27.9	37.26	22.04
Naphthalene	38.85	41.37	41.25	60.62
Higher Compounds	5.09	4.9	5.98	8.66

TABLE III. NAPHTHALENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	MoS_2	NiS	Cos	WS_2
Liquid Product Analysis, Mole %				
Benzene	3.8	1.49	Trace	1.34
Toluene	3.04	1.49	Trace	1.67
Ethyl Benzene	1.90	1.49	Trace	0.67
Xylenes	-	-	-	-
Propyl benzenes	-	-	-	- -
Decalins	-	-	-	-
Butyl benzenes	Trace	Trace	-	Trace
Indan	2.74	1.30	1.5	1.70
Methyl Indan	6.0	3.17	2.94	5.01
Tetralin	8.36	4.47	3.11	6.71
Naphthalene	74.14	85.56	92.44	81.85
Higher Compounds	Traces	Traces	Traces	4.02

TABLE IV. NAPHTHALENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst	MoS_2	NiS	Cos	WS_2
Liquid Product Analysis, Mole %				
Benzene	0.16	0.44	Trace	Trace
Toluene	0.48	1.17	0.52	0.47
Ethylbenzene	0.8	0.88	0.87	0.94
Xylenes	-	-	-	-
Propylbenzenes	-	-	-	-
Decalins	-	-	-	-
Butylbenzenes	1.61	2.2	1.05	2.36
Indan	0.8	2.1	1.02	1.30
Methyl Indan	1.61	6.0	1.6	2.17
Tetralin	28.98	25.32	21.89	29.69
Naphthalene	61.85	55.22	66.9	58.45
Higher Compounds	3.7	6.62	6.12	4.58

TABLE V. NAPHTHALENE HYDROCRACKING

	Hydrogenation Catalyst: Reduced MoO_3			
Cracking Catalyst:	SiO_2-(High) Al_2O_3	SiO_2-(Low) Al_2O_3	XZ-36	H-Zeolon
Liquid Product Analysis, Mole %				
Benzene	0.66	6.15	8.86	11.94
Toluene	3.34	6.15	6.66	5.11
Ethylbenzene	3.78	5.64	3.33	2.73
Xylenes	-	-	-	-
Propylbenzenes	-	Traces	-	-
Decalins	-	Traces	-	-
Butylbenzene	4.45	4.61	2.22	1.7
Indan	1.58	6.23	7.32	3.41
Methyl Indan	5.10	12.23	9.34	13.65
Tetralin	34.52	17.94	20.00	23.89
Naphthalene	44.54	35.68	33.33	32.42
Higher Compounds	2.0	5.33	8.88	5.11

TABLE VI. NAPHTHALENE HYDROCRACKING

PRODUCT NUMBER:	1	2	3	4
Analysis, Vol. %				
Methane	Nil	Trace	6.2	13.6
Ethane	Trace	4.25	15.6	16.6
Propane	100	95.75	78.1	62.5
Butane	Trace	Trace	Trace	8.3

TABLE VII. ANTHRACENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	MoO_3	NiO	CoO
Composition of Liquid Product, Mole %			
Anthracene	4.46	5.57	5.9
Tetrahydroanthracene	20.6	25.80	19.5
Octahydroanthracene	13.9	8.62	8.2
Hydroanthracene isomers	3.2	2.80	3.27
Naphthalenes	41.95	43.14	44.1
Benzenes	13.50	13.20	18.5

TABLE VIII. ANTHRACENE HYDROCRACKING

Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst:	MoS_2	NiS	CoS	WS_2
Composition of Liquid Product, Mole %				
Higher Boiling Compounds (Unidentified)	3.69	5.15	6.66	2.51
Anthracene	32.28	23.71	20.0	22.61
Tetrahydroanthracene	6.45	4.63	2.85	5.40
Octahydroanthracene	13.83	15.86	14.27	14.56
Hydroanthracene Isomers	1.10	2.87	3.80	5.01
Naphthalenes	37.24	40.17	43.21	41.04
Benzenes	4.54	7.52	9.13	8.77

TABLE IX. ANTHRACENE HYDROCRACKING

Hydrogenation Catalyst: MoS_2

Cracking Catalyst:	Silica-(High) Alumina	Silica-(Low) Alumina	H-Zeolon
Composition of Liquid Product, Mole %			
High Boiling Components (unidentified)	3.69	6.11	0.85
Anthracene	32.28	22.77	19.17
Tetrahydroanthracene	6.45	3.88	21.92
Octahydroanthracene	13.83	16.66	27.50
Hydroanthracene isomers	1.10	6.32	9.1
Naphthalenes	37.24	35.42	16.30
Benzenes	5.34	8.76	5.05

TABLE X. RATE CONSTANTS OF ANTHRACENE

Temp: 450°C Press: 1000 psi
Cracking Catalyst: Silica-(High) Alumina

Hydrogenation Catalyst	$k_{Hydrogenation} \times 10^4$	$k_{Hydrocracking} \times 10^4$
CoS	650	268
MoS_2	510	136
NiS	590	206
WS_2	600	263

TABLE XI. RATE CONSTANTS OF ANTHRACENE

Temp: 475°C, Press: 1000 psi

Hydrogenation Catalyst: MoS_2

	$k_{Hydrogenation} \times 10^4$	$k_{Hydrocracking} \times 10^4$
Silica-(High) Alumina	510	136
Silica-(Low) Alumina	610	208

TABLE XII. PYRENE HYDROCRACKING

Hydrogenation Catalyst:	MoO_3	NiO	CoO	WO_3
Liquid Product Composition, Mole %				
Pyrene	67.18	73.72	83.27	71.64
Hydropyrenes	21.09	16.94	13.50	15.5
Phenanthrenes	3.12	1.69	1.35	3.86
Hydro Phenanthrenes	Nil	Nil	Nil	5.97
Hydrophenanthrene Isomers	7.03	4.14	1.5	Nil
Naphthalenes	1.56	3.29	0.37	2.97
Benzenes	Nil	0.16	Nil	Nil

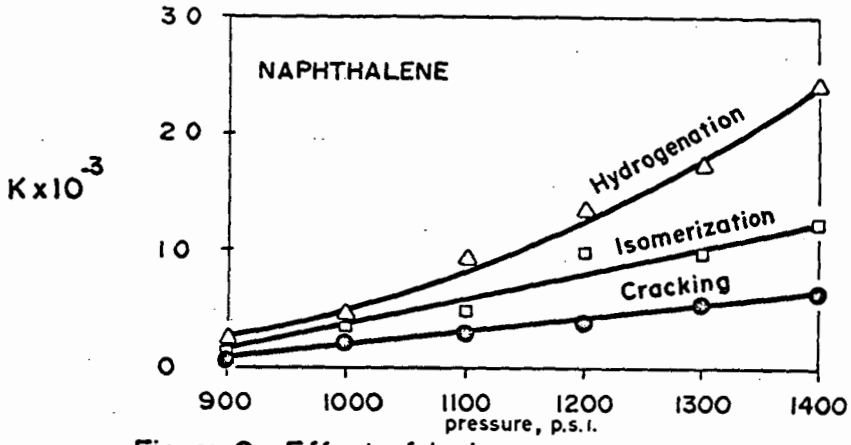

Figure 2. Effect of hydrogen pressure on rate constant

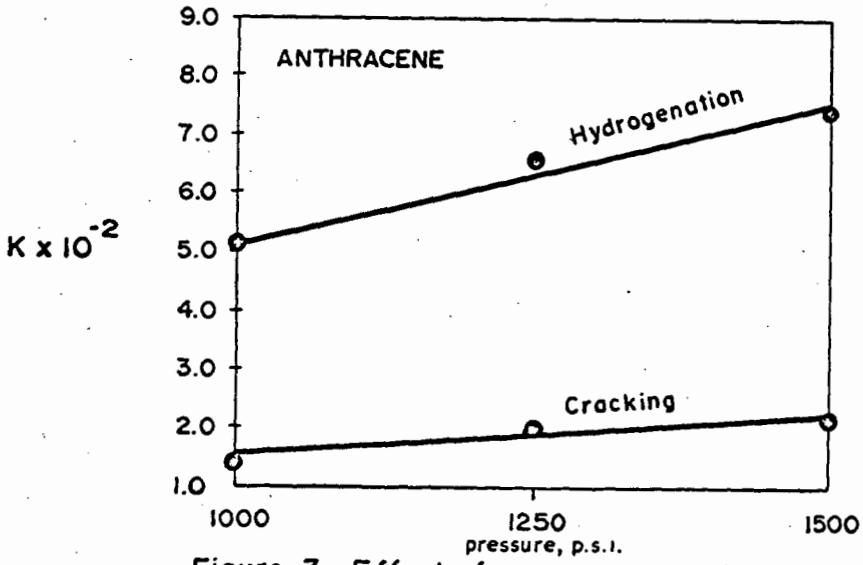

Figure 3. Effect of pressure on rate constant

FUTURE CATALYTIC REQUIREMENTS FOR SYNTHETIC ENERGY FUELS

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ENERGY FUEL NEEDS

Until recently, any discussion of energy fuel requirements would have featured such topics as higher octane for gasoline, lower cost fuels for generation of electricity, and incentives for increasing fuel consumption. Now, dominant issues are protection of the environment, provision of fuels secure within our national borders, and more efficient use of fuels. These new issues have been dictated by the realization that the growth of energy utilization in the United States is so great as to exceed our capability to produce the projected needs of oil and gas, the belief that increasing importation is reaching a level unacceptable from the viewpoints of both national security and balance of trade, and the growing determination to prevent pollution even at relatively high cost.

Oil and gas now supply 75 percent of energy needs in the United States, whereas coal supplies only 20 percent. Our energy resources are about the reverse, coal representing about 75 percent of the currently used fossil fuel resources. Additionally, large supplies of oil shale exist.

The solution to these problems, at least for many decades, is the large-scale manufacture of synthetic fuels that are clean burning, together with more efficient fuels utilization in generating electricity using systems such as advanced power cycles or magnetohydrodynamics.

Recent projections by the Bureau of Mines anticipate a 3.5 percent annual increase in demand for energy. Hence, our energy needs will double in the next 15 years, and are expected to triple by the end of the century. (Figure I and Table I). In 1970, 69 quadrillion Btu's were used in the U.S. In practical terms this is equivalent to consumption for every person, every day, of 50 pounds of fossil fuels, namely, 22 of oil, 14 of coal, and 14 of gas. By the end of the century, coal, oil, and gas needs are each projected to double. Nuclear power generation, while growing rapidly, will then still supply only one-fourth of energy needs.

The future supply of fuels must also take into account various consumer groups or use sectors of energy (2). The four sectors home and commercial, industrial, transportation, and generation of electricity (Table II) now are fairly evenly divided. Each is expected to grow, although fuels for generating electricity, including nuclear, will assume a much larger relative importance, being twice any of the other sectors by the year 2000. Each of the energy uses has special requirements which are reflected in different fuels characteristics. Fortunately, synthetic fuels can provide for each of the energy use sectors as summarized below:

I. Home, commercial, some industrial:
   High-Btu gas
   (essentially methane, 1000 Btu/Ft^3)

II. Generation of electricity, some industrial:
   (a) Low-sulfur, low-ash oil
   (b) Low-Btu gas
   (CH_4, H_2, CO mixture, with or without N_2, 150-400 Btu/Ft^3)

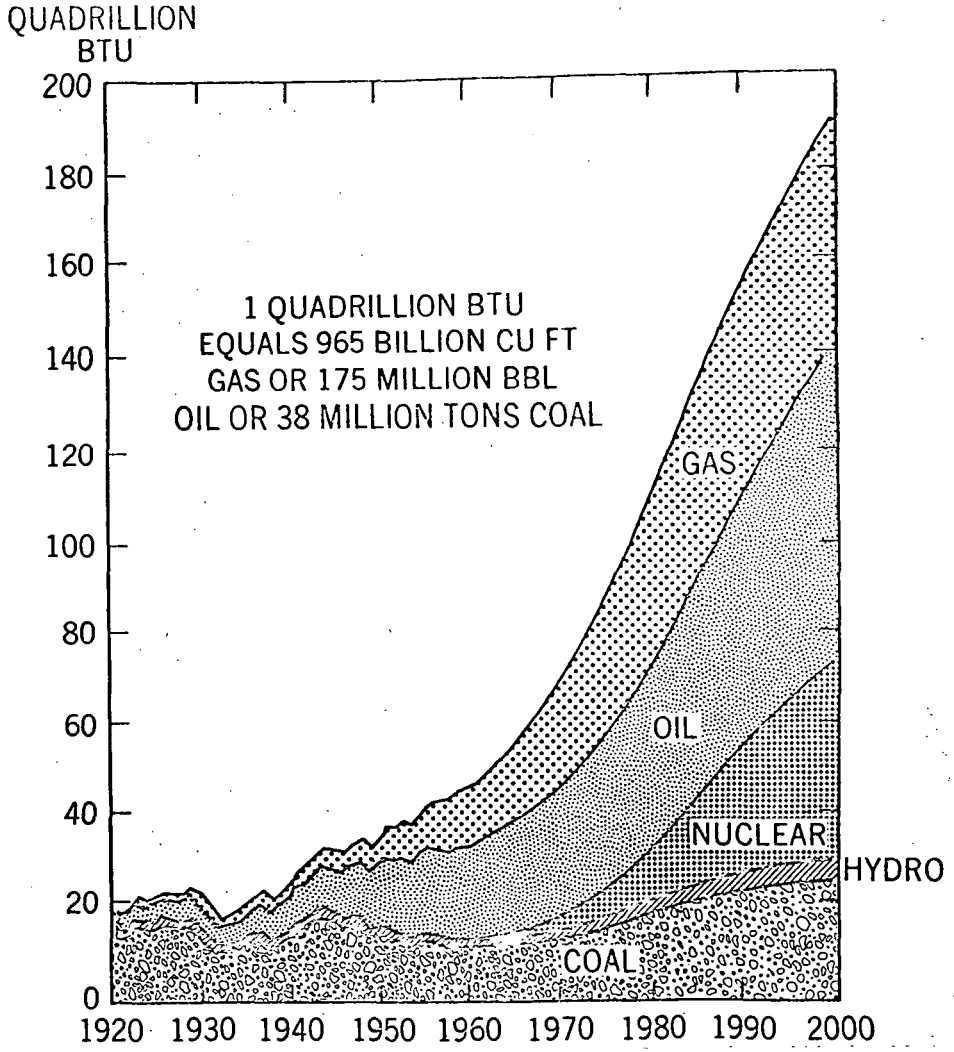


Figure 1 - Energy Usage and Fuels Projections,
U.S. Bureau of Mines. (1)

U.S. DEMANDS - QUADRILLION Btu

	1970	1975	1985	2000
Petroleum	30	36	47	66
Natural Gas	23	29	39	51
Coal	14	16	22	26
Hydropower	2.6	2.8	3.5	5
Nuclear	0.2	4.8	21	43
TOTAL	68.8	89	133	192

Table I - Reference, U.S. Bureau of Mines.

	QUADRILLION BTU	
	1970	2000
Home & Commercial	14.0	21 - 41
Industrial	20.3	32 - 59
Transportation	16.5	36 - 52
Electricity Generation	16.5	75 - 85
	67.3	165 - 239

Table II. Energy Consumption by Major Consumer Groups.

III. Transportation:
(a) Gasoline
(b) Gaseous fuel such as methane and/or hydrogen

GASIFICATION OF COAL

Pipeline gas now supplies one-third of our national energy needs and in use is by far the fastest growing of all our fossil fuels. The demand/supply situation, shown in Figure 2, reveals that a shortage has already begun and there will be a large deficit by 1985. Recently, plans have been announced by a number of companies to manufacture synthetic gas from naphtha and coal (4). Insofar as coal is concerned, the older process of gasification used in Europe is the only technology proven commercially. There is a great opportunity to improve technology in modern conversion processes now under development, and specifically through the use of catalysts. In order to provide a basis for the role which improved catalysts could play, the steps of the Bureau of Mines SYNTHANE coal gasification process (5,6,7) are shown in Figure 3. The process steps are pretreatment of the coal with oxygen (to prevent caking and sticking), gasification (reaction with steam and oxygen), purification (removal of CO_2, H_2S), shift ($CO + H_2O \rightarrow H_2 + CO_2$) to bring H_2/CO ratio to 3/1, and finally methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$).

Gasification Catalysis

The most desirable situation would be to have the reaction between coal and steam proceed as follows: $C + 2H_2O \rightarrow CH_4 + CO_2$). But this does not happen rapidly enough at lower temperatures, while at higher temperature thermodynamic equilibria are unfavorable for high methane yields. Individual reactions important in gasification are:

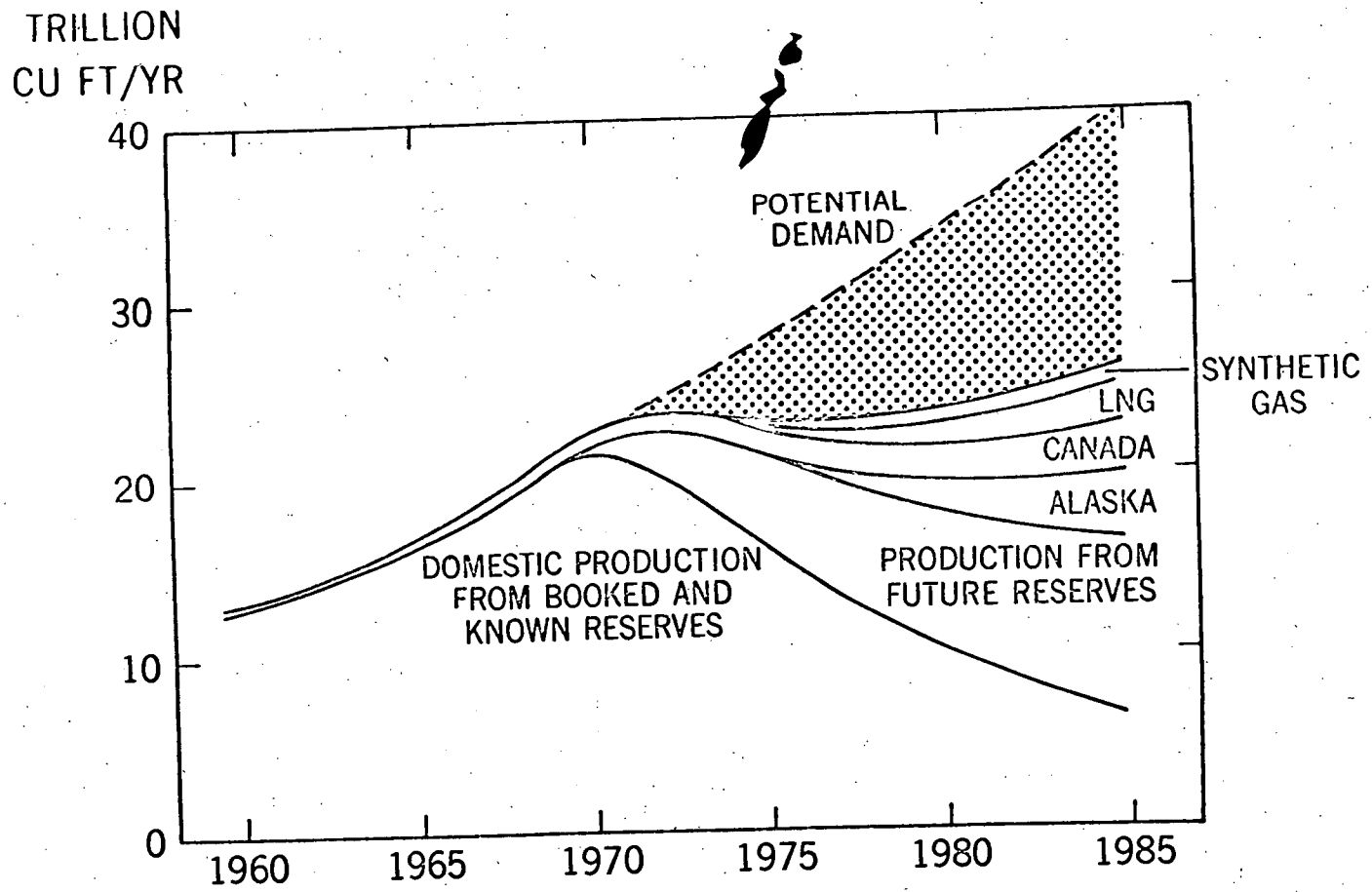
(1) $C + O_2 \rightarrow CO_2$
(2) $C + H_2O \rightarrow CO + H_2$
(3) $C + 2H_2 \rightarrow CH_4$

It is endothermic reaction (2) which is too slow. A partial solution to this problem is provided in the SYNTHANE process by having the single fluid bed gasifier operate with two zones. The lower zone is at about 1800°F (982°C), at which temperature reaction (2) occurs relatively rapidly. The upper zone, from which the gas exits, is at about 1400°F (760°C), so that the methane formed by coal devolatilization and reaction (3) is maximized.

There is a need to catalyze reaction (2) to decrease equipment needs and, more importantly, to permit operation at a lower temperature, because of thermodynamic equilibrium considerations, a higher methane content of the gases leaving the gasifier is achieved at lower temperatures.

Catalysis of the steam carbon reaction has been reported recently by the Bureau of Mines (8), and is also discussed later in the section concerned with the related process of naphtha gasification. Earlier investigators have shown that the percentage of methane in water gas made from coke can be increased significantly by adding lime or certain other salts to coke. In experiments carried out at 850°C (1562°F) and 300 psig, Haynes, Nelson, and Field (8) passed steam over a pretreated bituminous coal to which was admixed 5 wt% added material whose catalytic properties were to be determined. The results are given in part in Table III.

Additional experiments were carried out using nickel, either as an added salt or in a novel approach in which an inert probe coated with Raney nickel was inserted into the gasifier.



UNITED STATES GAS SUPPLY
TRILLION CUBIC FEET/YEAR

Figure 2. Reference. Humble Oil and Refining Company. (3)

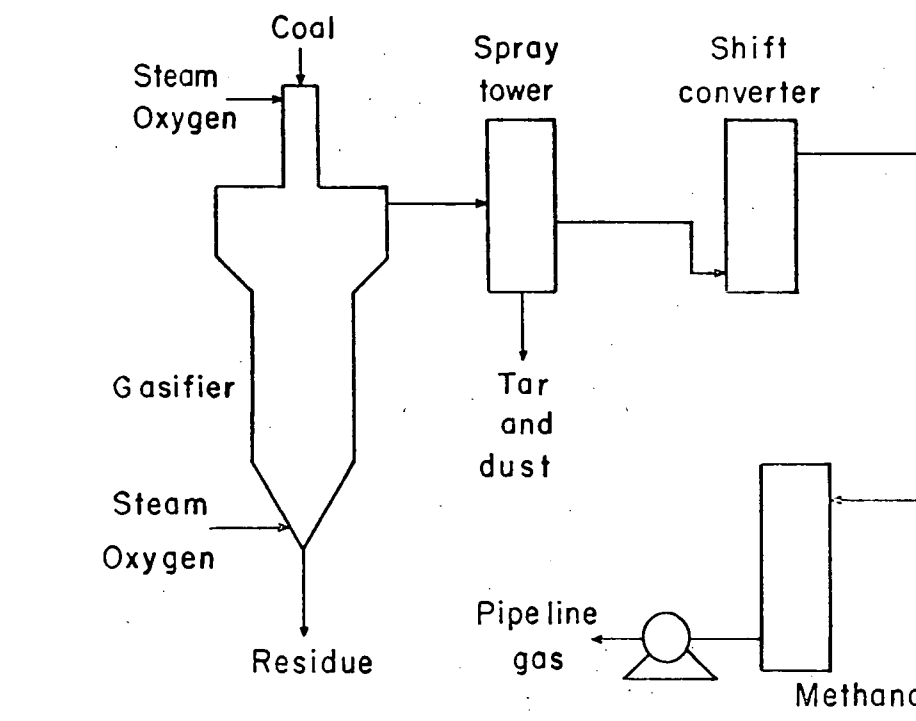


Figure 3 - SYNTHANE Coal Gasification Process

CH_4	H_2	CO	C gasified
Li_2CO_3 - 21	K_2CO_3 - 83	K_2CO_3 - 91	K_2CO_3 - 62
Pb_3O_4 - 20	Li_2CO_3 - 55	Li_2CO_3 - 72	Li_2CO_3 - 40
Fe_3O_4 - 18	Pb_3O_4 - 39	Fe_3O_4 - 60	Pb_3O_4 - 30
MgO - 17	CuO - 37	Cr_2O_3 - 55	Cr_2O_3 - 26
Cr_2O_3 - 16	MgO - 35	Pb_3O_4 - 52	MgO - 26
CuO - 15	Fe_3O_4 - 33	CuO - 49	Fe_3O_4 - 23
Al_2O_3 - 14	Al_2O_3 - 33	Al_2O_3 - 45	CuO - 22
K_2CO_3 - 6	Cr_2O_3 - 25	MgO - 28	Al_2O_3 - 22

Table III. Coal Gasification - Percentage Increase of CH_4, H_2, CO and Carbon Gasified Upon Addition of 5% of Salts Shown.

The overall results of this investigation show that the use of suitable additives improves the steam-coal gasification reaction considerably. In connection with possible benefits to the "SYNTHANE" process, it appears that appropriate additives could significantly increase production of methane and hydrogen in the gasification step, thereby reducing both the size of gasifier required and the processing work required downstream of the gasifier, such as the shift reaction, CO_2 removal, and catalytic methanation.

The study of gasification catalysts thus far has shown the following:

1. Alkali metal compounds and many other materials such as oxides of iron, calcium, magnesium, and zinc significantly increase the rate of carbon gasification and the production of desirable gases such as methane, hydrogen, and generally carbon monoxide during steam-coal gasification at 850°C (1562°F) and 300 psig.

2. The greatest yield of methane occurred with the use of a probe insert flame-sprayed with Raney nickel catalyst which has a limited life of activity. Significant methane increase resulted from the addition of 5 percent by weight of Li_2CO_3, Pb_3O_4, FE_3O_4, MgO, and many other materials.

3. The increased gasification resulted whether the extent of coal gasification was small or great.

4. Catalytic effectiveness decreased above 750°C (1382°F).

5. Residue from total gasification of coal mixed with potassium compounds still contained a significant concentration of potassium (over 10 percent) and was effective as an additive in increasing production of hydrogen and methane.

Shift Catalysis

The shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, is moderately exothermic, and the equilibrium is affected by temperature to a considerable extent as follows:

	ΔH calories per mole	$K = \frac{(CO_2)\ (H_2)}{(CO)\ (H_2O)}$
227°C (440°F)	- 9,520	126
327°C (620°F)	- 9,294	27
427°C (790°F)	- 9,051	7

Although high operating temperatures are desirable from the standpoint of rate of catalytic reaction, they are undesirable from the viewpoint of equilibrium which becomes unfavorable with increasing temperature.

Prior to 1963 the "standard" shift catalyst was a relatively sulfur-resistant catalyst of 70-85% iron oxide promoted by 5-15% Chromia. It was operated at about 650°F (343°C). Because of equilibrium limitations at this relatively high temperature, it was the practice to use two catalyst beds with interbed cooling and CO_2 removal.

In naphtha gasification, a guard case has been advocated to prevent fouling of the shift catalyst by unsaturated hydrocarbons, especially acetylenes, or by a combination of oxygen and diolefins. Examples of the guard catalyst are Ni-Mo-Al_2O_3 or Ni suboxide on sepiolite (9).

The shift conversion processing steps were greatly simplified when catalyst manufacturers made low-temperature shift catalyst available to the industry in 1963. This is a copper-zinc based catalyst, sometimes containing chromia, which is active at temperatures as low as 375°F (10). It is used in the 375-450°F (200-232°C) range where the equilibrium of the shift reaction is so favorable to carbon dioxide and hydrogen formation that the carbon monoxide content can be reduced to the 0.3-0.5 mole percent range without intermediate removal of CO_2. The catalyst is more sensitive to poisons, particularly sulfur and chloride, than the high-temperature shift catalyst.

Recently, shift catalysts have been described which are very active so that they can operate at low temperatures, are active in their sulfided form, and are resistant to loss of activity and loss hardness, even if contacted inadvertently with liquid water. Auer, Lorenz, and Grundler (11) described a new type of catalyst - a cobalt/molybdenum catalyst supported on spinel - which can be operated successfully below 600°F (316°C). The catalyst is active as a sulfide, so that H_2S partial pressure and the H_2S/H_2O ratio are important. It was reported that start-up procedure is of critical importance, since the catalyst in its oxidized form is active to the exothermic methanation reaction. Unless care is taken in sulfidation, temperatures increase to about 1700°F (927°C), which deactivates the catalyst. Using a start-up procedure that avoided overheating, an active catalyst was put on stream and long plant life was attained.

Shift catalyst work has been directed particularly to the manufacture of hydrogen. However, the improvements made also demonstrate the opportunity for developing improved catalysts for manufacture of synthetic fuels - namely, those active at lower temperatures, able to withstand sulfur, and capable of avoiding coke formation.

Methanation

The methanation reaction, $CO + 3H_2 \rightarrow CH_4 + H_2O$, is highly exothermic. The heat of reaction is minus 50, 353 calories at 127°C (260°F). Catalytic methanation has been known for 70 years and has been utilized extensively in removing small amounts of CO from hydrogen-containing gases. For every 1% CO the temperature rise is over 100°F (380°C). The equilibrium is unfavorable at high temperatures, so a temperature over 825°F (440°C) is avoided, and a maximum of 2% ($CO + CO_2$) in the feed is usual. The composition of a typical catalyst is 77% Ni oxide and 22% Al_2O_3. It is easily poisoned by sulfur and also rendered inactive by carbon deposition and by sintering. Greyson (12) has reviewed methanation thoroughly from thermodynamic and catalytic viewpoints. The group VIII transition elements mainly iron, nickel, and cobalt, appear to be the most suitable for use as methanation catalysts. A very wide range of catalysts has been reported, especially by memebers of the British Gas Research Board and the U.S. Bureau of Mines. Likewise a variety of reaction systems has been used to overcome the severe problems of the high heat release.

The U.S. Bureau of Mines made a fairly complete study of a reduced and nitrided steel-shot catalyst. The effects of temperature on the activity and specificity of this catalyst in a fluidized-catalyst-bed reactor are shown in Figure 4. The formation of hydrocarbons higher than methane is indicated, and is a reminder of the other type of reaction - namely, the Fischer-Tropsch reaction - in which the synthesis of hydrocarbons in the gasoline range is the objective. Greyson also discussed catalyst life in terms of sulfur poisoning, thermal stability, and carbon deposition.

Recently, Forney and associates (13, 14) have described a very interesting catalyst termed the tube-wall reactor. This catalyst is prepared by flame-spraying a nickel-aluminum alloy on tubes of 2-inch diameter so as to form a bonded layer. The coating is then partially leached with caustic to form a Raney-type catalyst adherent to the tube wall. By having a heat transfer material such as Dowtherm on one side of the tube, which makes for a more practical engineering system, and the SYNTHANE pilot plant is being designed with this form of a tube-wall reactor.

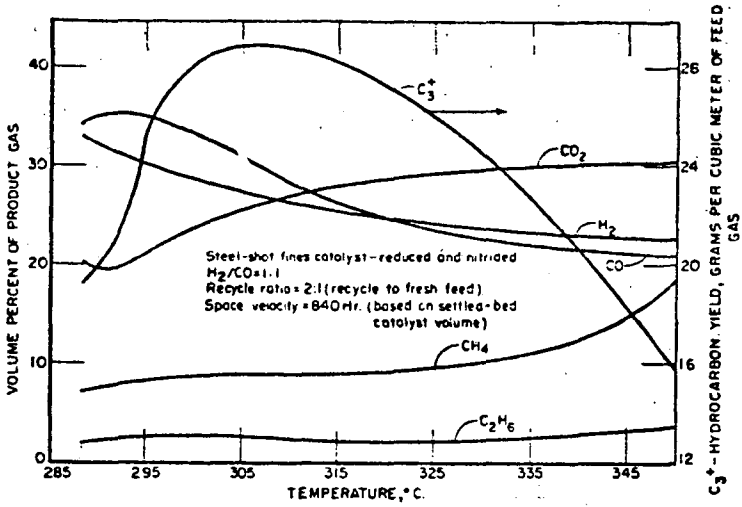


Figure 4. Effect of temperature on products; 100 psig.

Further improvements in methanation catalysts are one of the most fertile fields for research. Catalysts are needed that are much less sensitive to sulfur (present requirement is about 0.1 ppm H_2S) and that are able to withstand higher temperature increases without sintering and loss of activity. Also needed are catalytic reactor systems capable of removing heat without costly equipment or high recycle gas rates.

Catalysis for Synthetic Fuels Manufactured by Naphtha Reforming

Reforming naphtha consists of its reaction with steam to produce a gaseous mixture containing CO_2, CO, H_2, and CH_4. These gases may be employed for hydrogen manufacture or for their fuel gas utility. The development of nickel-containing catalysts permitted the introduction of a continuous process in England with great success (15).

For manufacture of hydrogen, a low area catalyst operating at high temperature is most suitable. For maximum production of methane however, a high area catalyst active at lower temperature is preferable. Elevated pressure and temperature are employed. Recently (1971), with the critical shortage of gas in the U.S., six plants have been announced for naphtha gasification in the U.S. using the British CRG Process.

The relationship between catalytic formulation and catalytic performance is crucial (16). The main causes of catalyst failure are sintering, with resultant loss of active area, and fouling by the deposition of coke. First of all, it is necessary to keep the $(CO)/(CO_2)$ ratio low enough to prevent the reaction $2\ CO \rightarrow C + CO_2$ from occurring. More important it is necessary to catalyze the oxidation of carbon with steam ($C + H_2O \rightarrow CO + H_2$). It has been found possible to operate at a lower steam ratio (defined as moles of steam per carbon atom in the feed) with a supported nickel catalyst, using a basic support.

The influence of supports on carbon-forming tendencies has been tested (17), and the results are expressed as minimum steam ratio to prevent coking. For china clay support it is about 10, for alumina about 4.3, and for magnesia 3.7, under one set of conditions. From these results it was deduced that the greater the acidity of the support, the greater the ease of carbon formation. This consistent with the fact that silica-alumina is a good cracking catalyst.

Urania and alumina have been used as supports for nickel-containing steam-reforming catalysts (17). It has been reported that urania is more active in promoting steam cracking than gamma-alumina, because it is an oxygen0deficient compound.

In order to operate at an even lower steam ratio, a further catalytic species must be incorporated which catalyzes the steam oxidation of carbon. (16, 18). This becomes more important as the moleculer size of the hydrocarbon charge increases, since larger molecules crack and form polymers more rapidly. The steam-carbon reaction rate must exceed the rate of hydrocarbon cracking and carbon deposition. The group I alkalies fulfill this function without excessively poisoning the reforming activity of the nickel.

Probably the success of alkalized nickel-reforming catalysts is due primarily to their ability to increase the rate of removal of carbon residues from the nickel surface by steam gasification ($C + H_2O \rightarrow CO + H_2$).

The available evidence suggests that the mobility of alkalies on the catalyst surface accounts for their effectiveness in catalyzing the steam-carbon reaction. The mobility of the alkalies has several other effects, including some loss in activity of the nickel, neutralization of acid catalyst sites, and physical loss of alkali. Incorporation of a non-volatile alkali-containing constituent has been reported which, during the operation of the reformer, very slowly decomposes, liberating alkali (15).

Although the excellent catalytic work on steam-reforming catalysis is of great interest for reforming naphtha, the ideas and findings should also be applicable in future development of catalysts for solid and residual fuels gasification. Here, also, the incorporation of alkali substances can become of greatest importance.

Coal Liquefaction Catalysis

Coal liquefaction has assumed a new importance in its potential for manufacture of a clean-burning fuel for powerplants. There is a great need for a low-sulfur, low-ash synthetic fuel to satisfy environmental requirements. The rapidly escalating prices of such a fuel now make coal liquefaction attractive for this purpose.

As is well known, coal liquefaction has already been demonstrated in the remarkable German achievement of providing synthetic fuels from coal during World War II. Iron or tin catalysts were used successfully to hydrogenate coal to liquid form. Since that time, great improvements have been made by the petroleum industry in providing catalysts such as platinum alumina and cobalt-molybdena-alumina capable of upgrading crude oils. These catalysts will contribute greatly in converting low-quality tar from coal into high-quality petroleum products including gasoline.

A number of new catalytic systems have been reviewed recently (19). These include transition metal complexes, alkali metals, volatile catalysts, hydrogen-donor liquids, reductive alkylation, hydrogen generated by reaction of CO and water, and basic catalysts.

Particular mention should be made of the invention of the ebullated catalyst bed reactor utilized by the H-Coal process. (20) The catalyst brings about coal liquefaction and hydrodesulfurization. A unique feature of this reactor system is the ability to operate a catalyst system continuously with a feed consisting of solids, liquid, and gas. The upward flow of the feed maintains the catalyst in a state of random motion that results in a system of minimum pressure drop, isothermal conditions, and continuous passage of unconverted coal and ash from the reactor. Catalyst can be added to and removed from the reactor during operation.

Another process of considerable promise is known as the PAMCO or solvent refined coal process (21). A mixture of coal and oil is contacted with hydrogen at 1000 psi or more, bringing about coal liquefaction. A tar is produced which can be filtered when hot so as to make a low-ash fuel product. Some desulfurization occurs also, so that by starting with a fairly low sulfur coal such as lignite, a low-sulfur synthetic fuel is obtained. While no catalyst is added, it seems likely that certain elements in the ash are effective in hastening the action of hydrogen.

Recent work at the Bureau of Mines has shown that under similar conditions CO containing gases plus water bring about coal liquefaction even more readily than hydrogen alone (22).

In another approach by the Bureau of Mines (23), it was reported that under conditions of highly turbulent flow of hydrogen, a high-sulfur bituminous coal suspended in coal tar can be hydrodesulfurized by continuous processing through a fixed bed of pelletized cobalt-molybdena-alumina catalyst. High yields of low-sulfur oil were obtained. For example (table IV), using the feed containing 30% coal of 3.4% sulfur suspended in a tar of 0.6% sulfur and process conditions of 200° psig and 450°C (842°F), the whole liquefied product was 93% of the feed and had 0.4% sulfur. The benzene-soluble fraction of this product gave an 87% yield of fuel oil having only 0.14% sulfur.

	OPERATING PRESSURE psi	
	4000	2000
Sulfur in Feed - wt. pct.	1.41	1.41
Sulfur in Whole Product - wt. pct.	0.30	0.42
Yield of Whole Product - wt. pct. feed	94.0	92.9
Oil (Hexane + Benzene Sol) - wt. pct. product	91.2	87.1
Sulfur in Oil - wt. pct.	0.09	0.14
Residue (Ash + Organic) - wt. pct. product	8.8	12.9
Sulfur in Residue - wt. pct.	2.91	1.88
Product, wt. pct.		
Hexane Sol	82.1	69.2
Benzene Sol, Hexane insol.	9.1	17.9
Benzene Insol. Residue	8.8	12.9

Table IV. Hydrodesulfurization of Indiana No. 5 Steam Coal Suspended in Tar (30:70 Coal: Tar) at 450°C Over Co-Mo-Al_2O_3 Catalyst.

Special catalyst and process techniques are needed because of the unusual chemical nature of coal, which contains fairly large molecules containing clusters of aromatic nuclei, and relatively high quantities of heteroatoms, and because of the presence of ash.

Such catalysts should have a pore size distribution so that large coal molecules enter freely, but ash, consisting of fine clay particles, is excluded. Catalysts are needed that are capable of breaking up the nuclear clusters, and that have a high ratio of hydrogenation/cracking functions so as to minimize hydrogen consumption. Maintenance of activity is most important. Possibly entirely novel chemistry is needed; for example, alkylation, which is now known to cause solubilization, presumably by bringing irregularities to the coal structure.

In summary, catalytic coal liquefaction, although having an outstanding history, presents a tremendous field for future catalytic developments using modern technology (24).

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Reference to trade names is made to facilitate understanding and does not imply endorsement by the Bureau of Mines.