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 1½ 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 ½ inch below the top of the catalyst, ½ inch above the bottom of the catalyst, and at 2¼-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	Not analyzed	0.19	0.24	0.19	0.17
Nitrogen, wt. %	0.39	0.42	0.49		Lost	0.36	0.44	0.85
Hydrocarbons, vol. %:								
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.

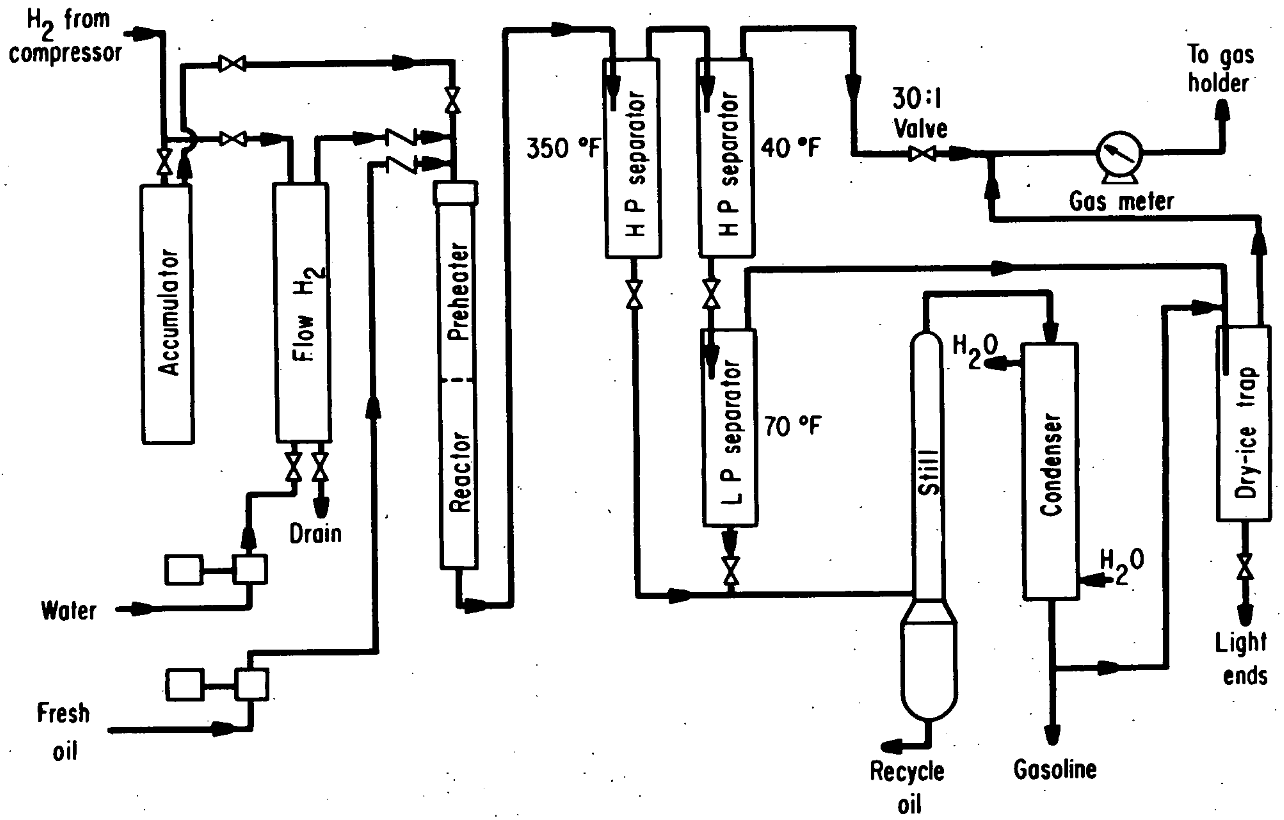

FIGURE I.-Hydrogenation Unit.

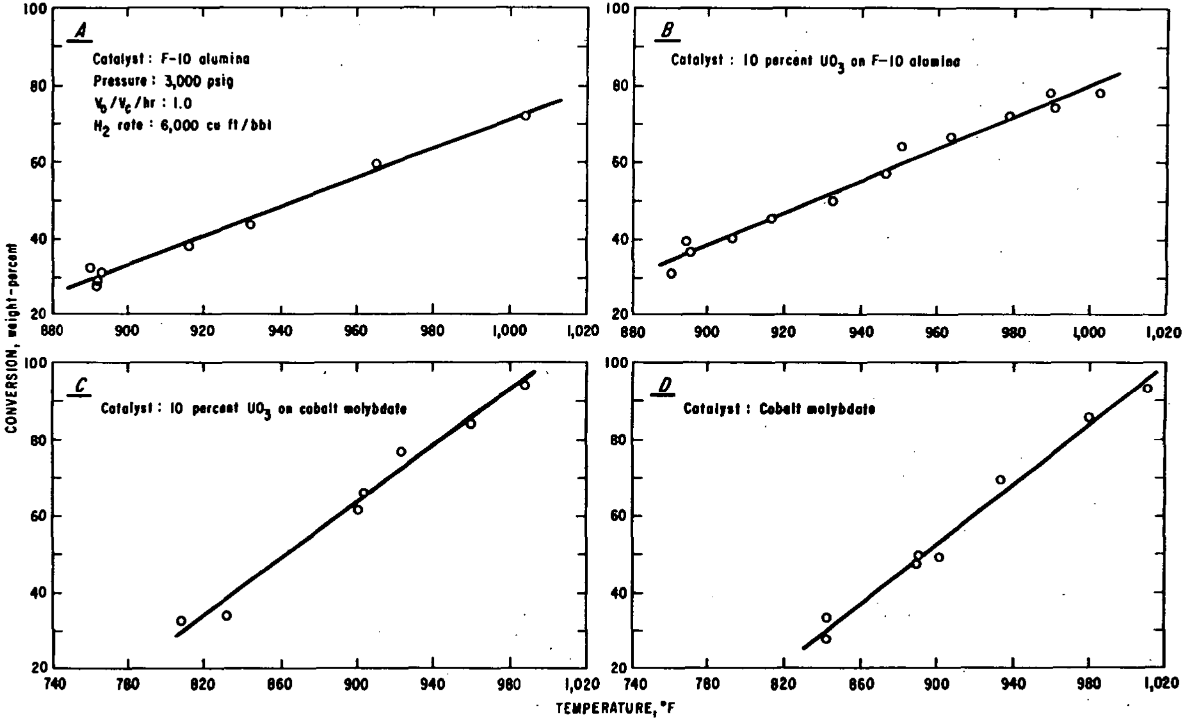

FIGURE 2.-Conversion of Shale Oil as Function of Temperature for Hydrogenating Shale Oil Over Various Catalysts.

OSCR-70-54

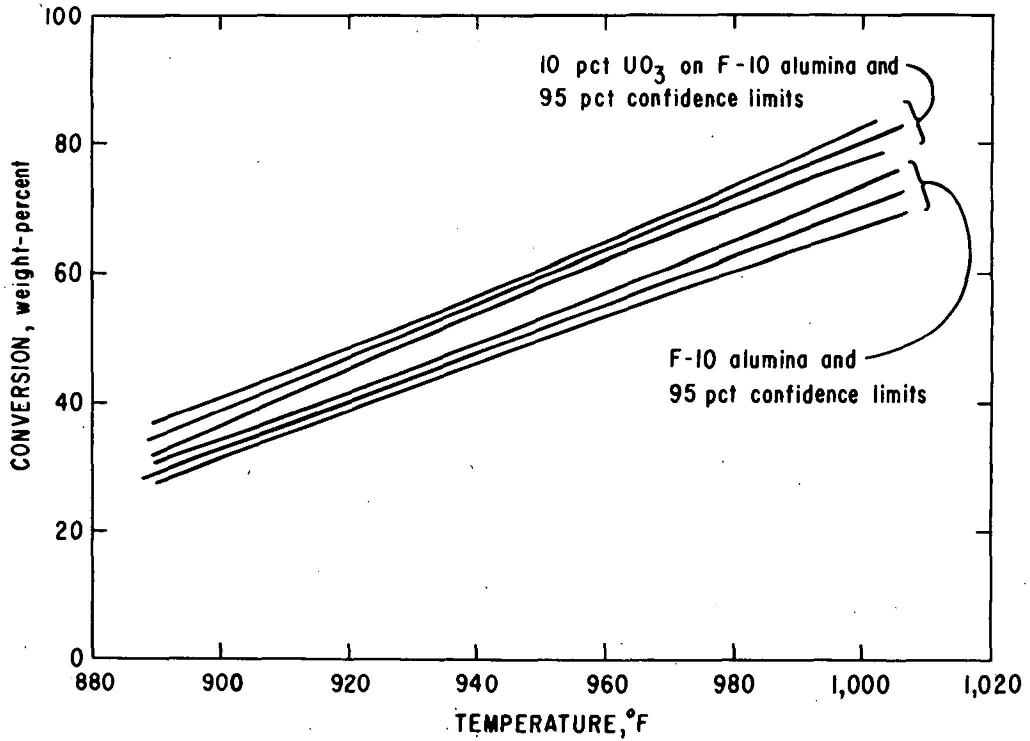

FIGURE 3.– Linear Regression Lines and 95 Percent Confidence Limits for Conversion as a Function of Temperature.

OSCR-70-55

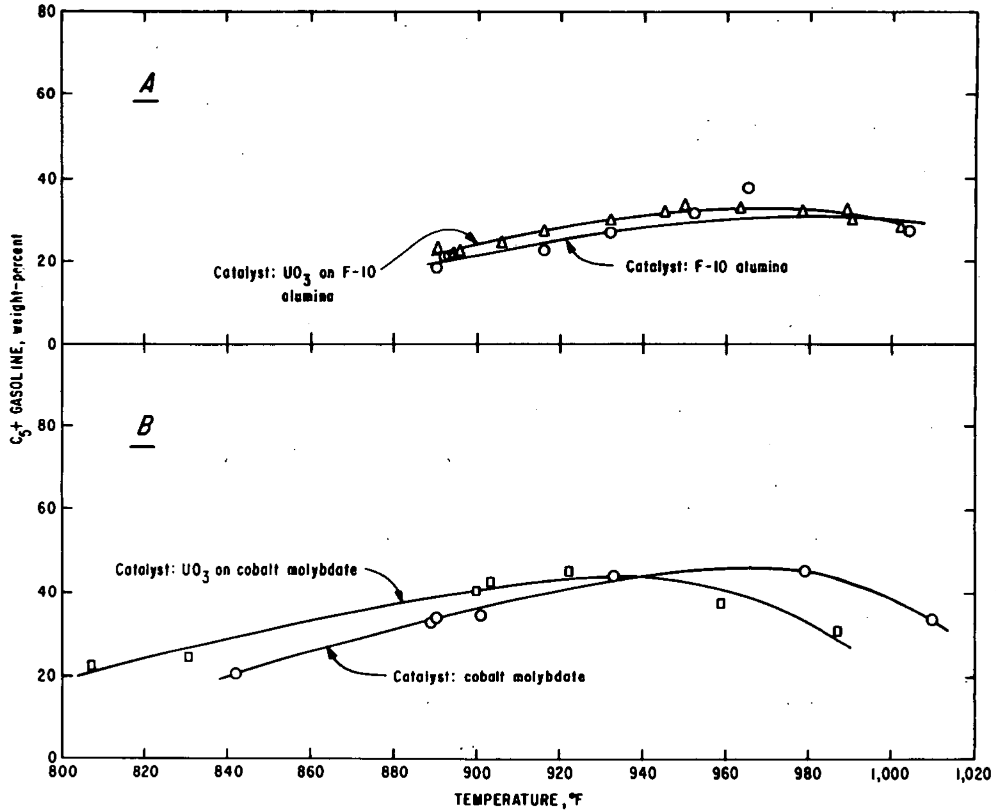

FIGURE 4.— Gasoline Yield as a Function of Reaction Temperature.

OSCR-70-58

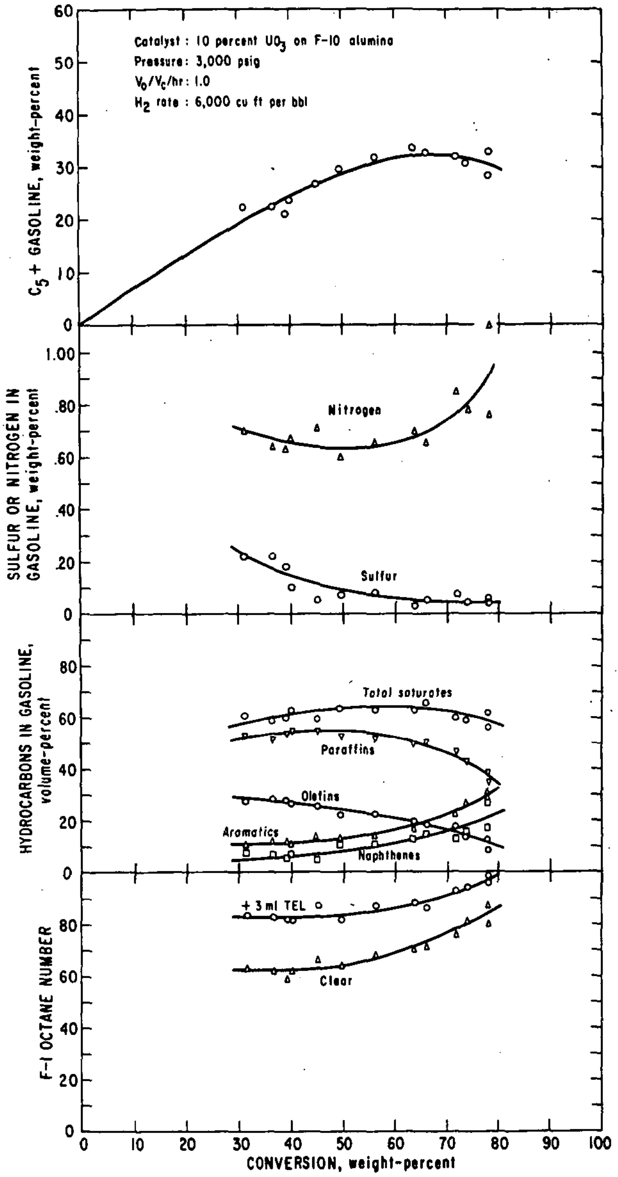

FIGURE 5.–Hydrogenation of Shale Oil Over Depleted UO_3 on F-10 Alumina.

OSCR-70-56

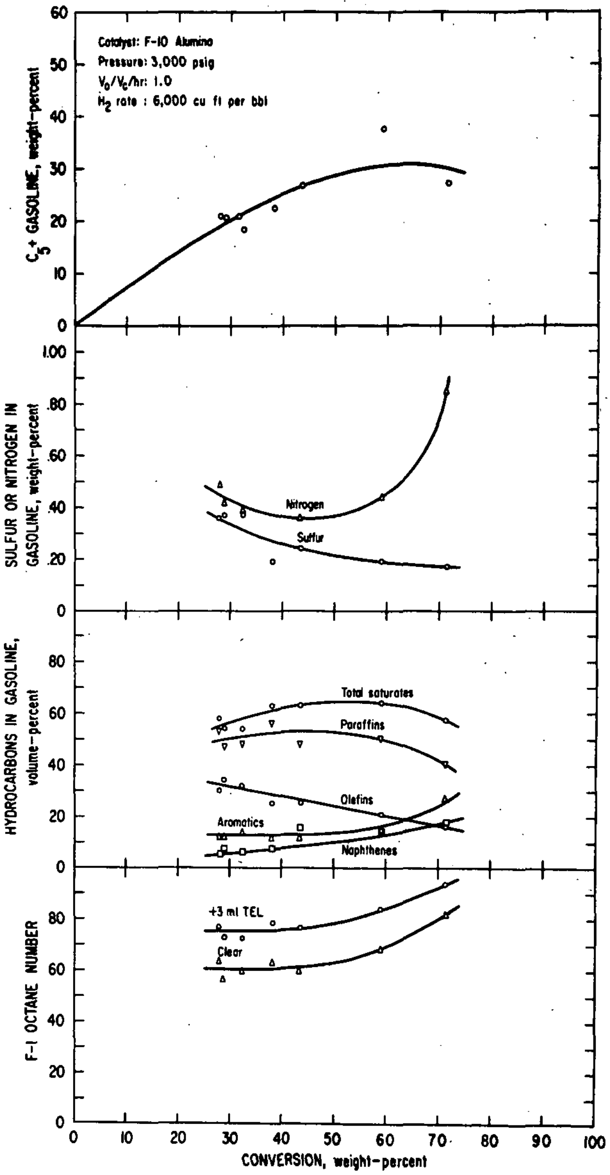

FIGURE 6.—Hydrogenation of Shale Oil Over F-10 Alumina.

OSCR-70-57

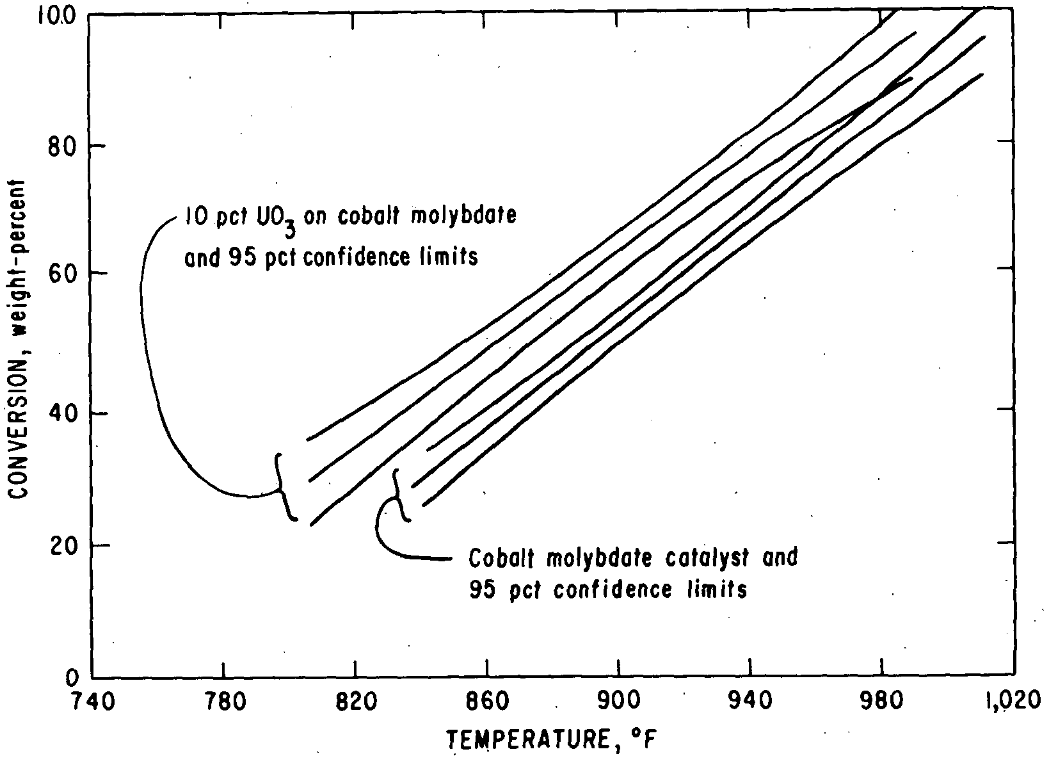

FIGURE 7.- Linear Regression Lines and 95 Percent Confidence Limits for Conversion as a Function of Temperature.

OSCR-70-60

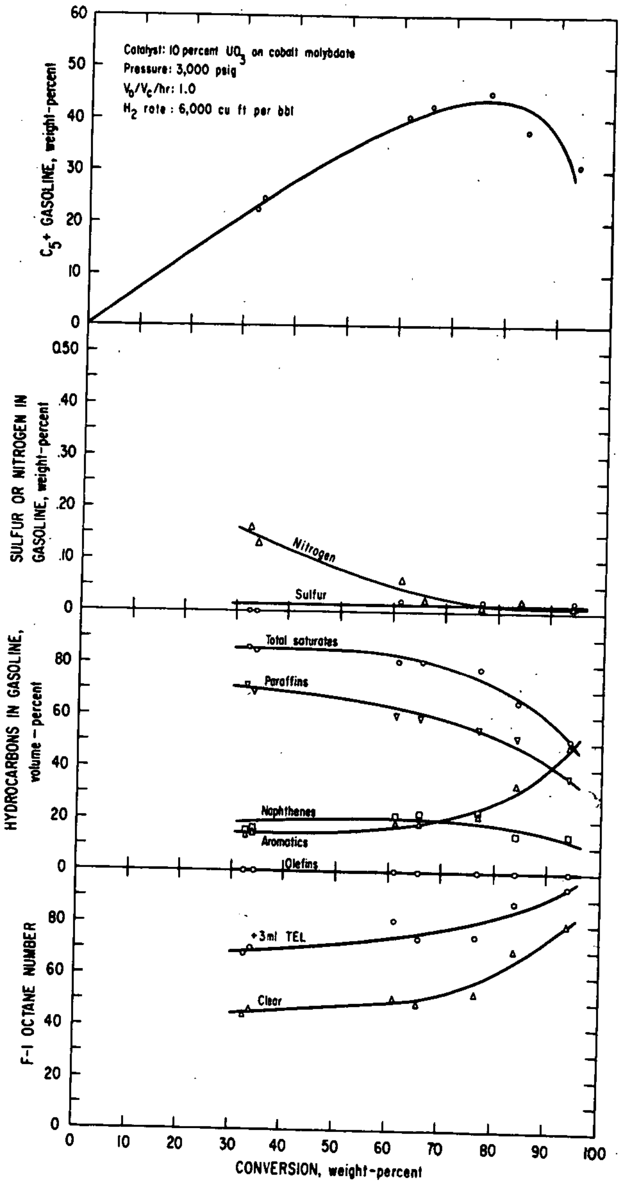

FIGURE 8.–Hydrogenation of Shale Oil Over Depleted UO_3 on Cobalt Molybdate Catalyst.

OSCR-70-61

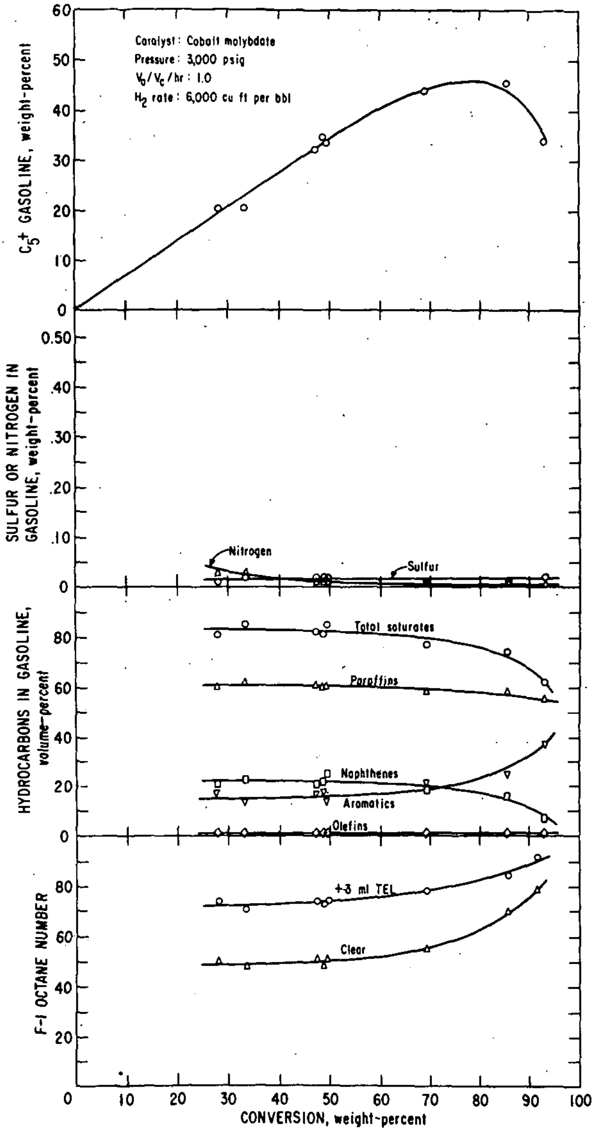

FIGURE 9.—Hydrogenation of Shale Oil Over Cobalt Molybdate Catalyst.

OSCR-70-62