

Hydrogenation of Asphaltene From Coal Using Halide Catalysts

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INTRODUCTION

The Bureau of Mines has been investigating the use of high catalyst concentrations in the hydrogenation of coal to oil as a possible means of lowering hydrogenation costs. The objective has been to find or develop catalysts that would permit the use of milder conditions than were used in the conventional (Bergius-I.G. Farben) process, or catalysts that would cause an increase in oil yield, a decrease in hydrogen consumption, or other benefit.

Conditions used in commercial-scale operations of conventional plants depended on the reactivity of the coal being hydrogenated and on the catalyst used. Temperatures ranged from 450° to 490° C and pressures were 3,500 to 10,000 psi. Catalysts were used in suspended form in concentrations of from less than one-tenth percent to about three percent. These high temperatures and pressures were not needed for the initial coal liquefaction reactions but were needed to hydrocrack asphaltenes at reasonable rates. Asphaltene is a high-molecular weight nondistillable substance that is formed as a principal intermediate in the coal-to-oil reaction sequence. In a kinetics study made with bituminous coal at about 6,000 psi with a conventional catalyst (SnS plus NH₄Cl), Weller obtained specific reaction rate constants for coal hydrogenation to asphaltene and other liquid and gaseous products that were 25 times greater at 400° C and 10 times greater at 440° C than the specific reaction rate constants for asphaltene hydrogenation.^{1/} The reactions were first order with respect to coal or asphaltene concentration. It thus became evident that the hydrogenation of coal to oil at practical rates at mild conditions, e.g., 400° C and 1,500 psi, would require the use of catalysts that are highly effective for hydrogenating asphaltene.

The Bureau recently made a coal hydrogenation catalyst study in which a wide variety of materials were screened as potential catalysts. Equal weights of these materials and coal were used at one set of conditions. This paper presents results of screening experiments made with ten halide catalysts that were effective for producing high yields of oil with low asphaltene contents. Results are also presented for experiments in which the same catalysts were used in the hydrogenation of asphaltene produced by mild hydrogenation of the coal.

EXPERIMENTAL

Equipment and Materials

The reactor used was a 1.2-liter batch autoclave that was placed in a horizontal position and rotated during an experiment. A complete description of the vessel and accessory equipment has been published.^{2/} Charges were contained in a glass liner that fitted closely to the autoclave wall. Pressure was measured with a bourdon-tube type gage that was connected to and rotated with the autoclave. Temperature was measured with a thermocouple positioned axially in the autoclave in a thermowell.

Pittsburgh-seam high-volatile A bituminous coal from the Bureau's experimental mine at Bruceton, Pennsylvania and asphaltene produced by uncatalyzed hydrogenation of the same coal were used as feeds. The coal was pulverized to minus 60 mesh (U. S. Sieve) and dried in air at 70° C for about 20 hours. Asphaltene was produced by hydrogenating 200-gram charges of coal in the batch autoclave at 4,000 psi and 425° C for 2 hours. Asphaltene produced in 35 runs was combined and used as a feed material.

It is the fraction of product that is soluble in benzene and insoluble in n-pentane. The yield was about 35 percent by weight of moisture- and ash-free (maf) coal used. By laboratory analysis, it was found to contain 8.5 percent benzene insolubles, 83.6 percent asphaltene, and 7.9 percent n-pentane-soluble oil. Ultimate analyses of the feeds are shown in table 1.

Table 1.- Analyses of coal and asphaltene feeds

Material	Analysis, wt pct						
	Mois- ture	Ash	Elemental composition, maf basis				
			C	H	N	S	O (diff.)
Coal, hvab ^{1/} ...	0.4	7.5	83.7	5.4	1.6	1.2	8.1
Asphaltene ...	0.9	0.0	88.7	6.4	1.9	0.4	2.6

^{1/} High-volatile A bituminous coal, Pittsburgh seam.

Halide catalysts were either technical or reagent grade chemicals and were used in powdered form. Catalysts and coal or asphaltene were premixed in the glass liners before charging into an autoclave. Hydrogen was obtained from commercial cylinders.

Operating and Analytical Procedures

All experiments were made with 50-gram charges of coal or asphaltene. After purging air out of a charged and assembled autoclave, hydrogen was added to an initial pressure selected so that the desired pressure would be reached on heating to reaction temperature. Rotation was started, the autoclave was heated at about 7° C per minute to reaction temperature, temperature was maintained for a specified time, then the autoclave was cooled to room temperature. Rotation was continued until the temperature was 250° C or less. The cooling rate to 250° C was about 4° C per minute.

Gases were depressurized through a cold trap where light oil and water vapors were condensed and then through scrubbers that removed acid gases (CO₂, H₂S, and any hydrogen halide formed by catalyst reactions). The remaining gases were metered, collected in a holder, sampled, and analyzed by mass spectrometry. Light oil and water were then removed by vacuum distillation to about 110° C and 2 to 3 mm of Hg. These conditions are equivalent to an atmospheric distillation to about 290° C. Material remaining in the autoclave was washed out with benzene and then continuously extracted with benzene in a Soxhlet apparatus. The insoluble and soluble fractions were both water washed to remove the halide catalysts. An ash determination was made on the product insoluble in benzene and water. After water washing, the benzene solubles were separated into n-pentane insoluble (asphaltene) and n-pentane soluble (heavy oil) fractions.

The autoclave was weighed on a bullion balance before charging with hydrogen, after depressurizing, and after vacuum distillation. The weight of hydrogen charged was estimated from previous autoclave calibrations of hydrogen weight versus pressure. Bullion balance weighings permitted accurate determinations to be made of the weights of groups of products as follows: (1) Gases and vapors depressurized, (2) vacuum distillate, and (3) heavy liquids and solids. Actual recoveries were adjusted to correspond to values determined by bullion balance weighings by assuming that losses (or gains) in each group of products were distributed among the components of that group in the same proportions as actual recoveries.

Yields are expressed as weight-percent of maf charge. Organic benzene insolubles are defined as benzene and water insolubles minus ash; coal conversion on a percentage

basis is 100 minus the percent of organic benzene insolubles. Light oil includes oil recovered by vacuum distillation, oil condensed from gases during depressurization, and small amounts of pentanes in the scrubbed gases. Hydrocarbon gases consist of C₁ to C₄ hydrocarbons.

RESULTS AND DISCUSSION

Coal Hydrogenation Yields

Table 2 shows yields obtained in catalyst screening experiments made with equal

Table 2.- Distribution of products from the hydrogenation of Pittsburgh-seam coal
(50 grams of coal, 4,000 psi, 425° C, 1 hour)

Exp. No.	Catalyst	Catalyst-to-coal weight ratio ^{1/}	Yields, weight-percent of maf coal						Net water
			Organic benzene insols.	Asphaltene	Heavy oil	Light oil	Hydrocarbon gases	Acid gases and CO	
1	None	-	37	28	13	6	6	3	7
2	NiI ₂ .6H ₂ O	1.0	18	2	21	38	10	4	12
3	NiBr ₂	1.0	20	4	29	33	10	6	5
4	ZnI ₂	1.0	10	1	5	55	17	7	10
5	I ₂	1.0	23	1	8	48	15	3	11
6	ZnBr ₂	1.0	10	2	8	56	14	3	13
7	ZnCl ₂	1.0	12	2	16	45	14	4	11
8	SnCl ₂ .2H ₂ O	1.0	18	7	40	29	6	4	1
9	CdI ₂	1.0	17	3	24	37	13	1	12
10	FeI ₂ .4H ₂ O	1.0	20	9	13	41	10	2	5
11	SnI ₂	1.0	8	14	42	20	6	5	5
12	ZnCl ₂	0.01	33	26	18	8	8	4	7
13	SnCl ₂ .2H ₂ O	0.01	12	38	34	7	4	5	7
14	SnCl ₂ .2H ₂ O ^{2/}	0.01	7	7	36	18	26	1	9

^{1/} Does not include water of hydration.

^{2/} Thirty minutes at 480° C.

weights of halide catalysts and coal at 4,000 psi and 425° C for 1 hour. High coal conversions of 88 to 92 percent were obtained with 4 of the catalysts. Conversions were 77 to 83 percent with the remaining catalysts as compared to 63 percent without a catalyst. However, assuming that asphaltene was a principal intermediate product, all of the halides were very effective for asphalt hydrogenation. Asphaltene contents of the benzene-soluble oils (sum of asphaltene, heavy oil, and light oil) ranged from 1.6 percent with ZnI₂ to 18 percent with SnI₂.

The last three experiments listed in table 2 were made with a conventional catalyst concentration of 1.0 percent. ZnCl₂ at 1.0 percent was a very poor catalyst. Coal conversion was only 4 percent higher than without a catalyst, and asphaltene was the principal liquefaction product. SnCl₂ is one of the best of the conventional catalysts. With 1.0 percent SnCl₂ at 425° C, a high conversion of 88 percent was obtained, but the product oil was high in asphaltenes. The last experiment, which was made with SnCl₂ at 480° C, demonstrates that a high coal conversion and low asphaltene yield are obtained at conventional conditions. It also illustrates the advantage of

lower temperature hydrogenation from the standpoint of hydrocarbon gas production and consequent hydrogen consumption. The hydrocarbon gas yield at 480° C was 26 percent as compared to 14 to 17 percent at 425° C with the most effective of the halide catalysts.

Asphaltene Hydrogenation Yields

Experiments with coal and high concentrations of halide catalysts showed these catalysts to be effective for producing oils low in asphaltene when starting with coal. Experiments with a primary asphaltene and the same catalysts were made to determine whether the halide catalysts were equally effective when the starting material was asphaltene. Conditions used were 4,000 psi, 425° C, and 1 hour at temperature with a catalyst-to-asphaltene ratio of 1.0 by weight. Results are shown in table 3 along

Table 3.- Distribution of products from the hydrogenation of asphaltene^{1/}
(50 grams asphaltene, 50 grams catalyst, ^{2/}4,000 psi, 425° C, 1 hour)

Exp. No.	Catalyst	Yields, wt pct of moisture-free asphaltene charged.							Percent reduction of insol. plus asphaltene
		Organic benzene insols.	Asphaltene	Heavy oil	Light oil	Hydrocarbon gases	Acid gases and CO	Net water	
15	None	5	67	20	2	5	1	1	22
16	NiI ₂ .6H ₂ O	7	1	37	43	10	1	3	91
17	NiBr ₂	3	5	48	31	11	2	3	91
18	ZnI ₂	6	2	22	50	14	3	4	91
19	I ₂	4	5	25	58	13	2	2	90
20	ZnBr ₂	8	2	20	57	10	1	3	89
21	ZnCl ₂	4	7	31	37	14	1	4	88
22	SnCl ₂ .2H ₂ O	6	10	50	21	8	1	0	83
23	CdI ₂	4	14	63	18	7	<1	3	80
24	FeI ₂ .4H ₂ O	21	5	9	49	17	1	5	72
25	SnI ₂	5	23	48	19	6	1	3	70

^{1/} The asphaltene feed composition was 0.9 percent moisture, 7.6 percent organic benzene insolubles, 83.6 percent asphaltene, and 7.9 percent oil on a weight basis.

^{2/} Does not include water of hydration.

with results obtained without a catalyst. All of the catalysts were very effective for asphaltene reduction. However, a more significant measure of catalyst effectiveness is the extent of reduction of both the organic benzene insolubles and the asphaltene. As shown in table 3, reduction of these two components of the feed was 22 percent without a catalyst and 70 to 91 percent with catalysts. Lowest reductions were obtained with SnI₂ and FeI₂. In the experiment with FeI₂, the yield of asphaltene was low at 5 percent, but the yield of hydrocarbon gases was highest and an appreciable amount of insolubles was produced, presumably by condensation reactions. The formation of undesirable solids and gases is indicative of an imbalance in cracking and hydrogenation activities with FeI₂. Significant amounts of insolubles were not formed in any of the other experiments including the experiment without a catalyst.

The effects of reaction variables on asphaltene hydrogenation yields were investigated briefly. Using results obtained with equal weights of ZnCl₂ and asphaltene at

4,000 psi and 425° C for 1 hour as a basis for comparison, experiments were made at higher and lower pressures, temperatures, and catalyst concentrations and with longer and shorter times at temperature. Results are shown in table 4. In the first group

Table 4.- Asphaltene hydrogenation yields using ZnCl₂ catalyst.
Effects of pressure, temperature, time, and ZnCl₂ concentration.
(50 grams of asphaltene)

Exp. No.	ZnCl ₂ -to-asphal. weight ratio	Press., psi	Temp., ° C	Time, min.	Yields, wt pct of moisture-free asphaltene charged				Hydro-carbon gases	Percent reduct. of insol. plus asph.
					Organic benzene insols.	As-phal-tene	Heavy oil	Light oil		
26	1.0	2,000	425	60	5	9	29	39	13	83
21	1.0	4,000	425	60	4	7	31	37	14	88
27	1.0	8,000	425	60	2	3	45	34	15	95
28	1.0	4,000	400	60	4	9	43	36	12	86
29	1.0	4,000	450	60	6	1	23	45	19	92
30	1.0	4,000	425	15	5	8	37	30	10	86
31	1.0	4,000	425	30	4	6	39	34	11	89
32	1.0	4,000	425	120	3	4	42	38	16	92
15	0.0	4,000	425	60	5	67	20	2	5	22
33	0.01	4,000	425	60	2	41	44	7	6	53
34	0.5	4,000	425	60	4	7	52	26	11	88
35	2.0	4,000	425	60	7	2	14	48	28	90

of experiments which were made at 2,000, 4,000, and 8,000 psi, the pressure dependence of reactions involved in insolubles and asphaltene reduction was found to be small. Reductions were 83 percent at 2,000 psi and 95 percent at 8,000 psi. Light oil yields decreased with increasing pressure indicating an apparent pressure inhibition of the heavy oil-to-light oil conversion step. This group of experiments shows that with a high concentration of ZnCl₂ at 425° C asphaltene can be hydrogenated at a practical rate at 2,000 psi or possibly at lower pressures.

In the investigation of the effect of temperature, results at 400° C were very similar to those at 425° C. Raising the temperature to 450° C caused appreciable decreases in asphaltene and heavy oil yields and increases in light oil and hydrocarbon gas yields. The data indicate that asphaltene hydrogenation would be practical at 400° C and that this low temperature would be preferred because of the lower gas-to-oil ratio than at the higher temperatures.

Experiments made to investigate the effect of reaction time at 425° C showed that all of the reactions involved in molecular weight reduction were initially quite rapid, but the rates decreased considerably as time progressed. In 15 minutes, the reduction of insolubles and asphaltene was 86 percent and light oil production was 30 percent. With increasing time, the reduction of insolubles and asphaltene proceeded much more slowly, reaching a value of 92 percent in 2 hours. This amounts to a reduction of less than 50 percent of the insolubles plus asphaltene that remained after 15 minutes. During the same period, the light oil yield increased to only 38 percent. These decreases in hydrocracking rates are an indication of some loss of catalyst

activity. To some extent, it is also likely that as hydrogenation progressed the concentration of structural types more resistant to hydrogenation progressively increased in the solids and heavy liquids remaining.

The last group of experiments in table 4 shows the effect of increasing the catalyst-to-asphaltene ratio from 0.01 to 2.0. With a ratio of 0.01, reduction of insoluble plus asphaltene was appreciable at 53 percent. The reduction reached a value of 88 percent with a ratio of 0.5 and remained essentially constant with further increases to 1.0 and 2.0. However, the extent of heavy oil conversion to light oil continued to increase with increasing catalyst concentration. The data from this group of experiments show that although the depth of hydrogenation increased over the entire range of catalyst concentrations used, very high concentrations may not be necessary to obtain high conversions of asphaltene to heavy oil in relatively short reaction times.

Composition of Hydrogenation Products

Ultimate analyses of asphaltenes and heavy oils in the products of several asphaltene hydrogenation experiments are shown in table 5. The principal differences

Table 5.- Ultimate analyses of asphaltene and heavy oil products of asphaltene hydrogenation
(50 grams of asphaltene, 50 grams of catalyst, 4,000 psi, 425° C, 1 hour)

Exp. No.	Catalyst	Elemental composition, weight-percent				
		C	H	N	S	O (diff.)
<u>Asphaltene</u>						
20	ZnBr ₂	89.0	5.8	1.0	-	-
21	ZnCl ₂	91.2	6.0	0.6	0.2	2.0
22	SnCl ₂ ·2H ₂ O	89.9	6.7	0.9	0.1	2.4
<u>Heavy Oil</u>						
16	NiI ₂ ·6H ₂ O	89.1	10.9	0.0	0.05	0.0
20	ZnBr ₂	89.7	9.7	0.3	0.05	0.25
21	ZnCl ₂	90.3	8.5	0.3	0.1	0.8
22	SnCl ₂ ·2H ₂ O	88.1	8.8	0.05	0.1	2.95

between the compositions of the residual asphaltenes and the asphaltene feed was the lower nitrogen and sulfur contents of the unconverted asphaltenes. Heavy oils contained appreciably more hydrogen than the feed and much less nitrogen and sulfur. Percentages of oxygen varied considerably. As oxygen determinations were by difference, their values are not highly meaningful.

Ultimate and fluorescent indicator adsorption (FIA) analyses of light oils produced in several experiments with both coal and asphaltene are presented in table 6. All of the oils contained less than 0.1 percent each of nitrogen and sulfur. Considering the high aromaticity of the coal from which the oils were produced, their aromatics contents of about 17 to 36 percent by volume were surprisingly low. The aromatics and saturates fractions of the light oils produced in coal experiments with ZnBr₂ and ZnCl₂ were analyzed completely by gas-liquid chromatography. More than

Table 6.- Analyses of light oils from coal and asphaltene hydrogenation
(50 grams coal or asphaltene, 50 grams catalyst, 4,000 psi, 425° C, 1 hour)

Exp. No.	Catalyst	Feed	Elemental composition, wt pct					FIA analysis, vol pct		
			C	H	N	S	O (diff.)	Aro- matics and oxy- genates	Satur- ates	Ole- fins
2	NiI ₂ .6H ₂ O	Coal	86.7	13.2	0.0	<0.1	0.0	20.9	78.6	0.5
16	NiI ₂ .6H ₂ O	Asph.	86.5	13.3	0.0	<0.1	0.2	17.4	82.5	0.1
6	ZnBr ₂	Coal	87.2	12.7	<0.1	<0.1	0.0	30.9	68.6	0.5
20	ZnBr ₂	Asph.	86.5	12.7	0.0	<0.1	0.8	30.7	69.0	0.3
7	ZnCl ₂	Coal	87.1	12.7	<0.1	<0.1	0.1	32.8	66.8	0.4
21	ZnCl ₂	Asph.	86.6	12.2	<0.1	<0.1	1.1	35.6	64.0	0.4

90 percent of the oils consisted of compounds having boiling points under 200° C. The saturates were mainly paraffins, but the ratio of iso-to-normal paraffins was about 9 to 1 in both oils. Total cyclics (aromatics and naphthenes) amounted to about 47 percent. These analyses clearly indicate that the halide catalysts are highly active for nuclear hydrogenation and ring opening reactions.

Light oils produced from coal and from asphaltene using the same catalyst differed in composition by only small amounts. The differences are probably within the limits of the reproducibility of experiments and the analytical accuracy. This similarity of compositions provides additional evidence in support of the premise that asphaltene is a principal intermediate in the hydrogenation of coal to oil.

Elemental balances were made for the experiment with ZnCl₂ and asphaltene. The amounts of nitrogen, sulfur, and oxygen eliminated were found to be 90, 80, and 68 percent, respectively. Hydrogen consumption was 4.5 percent by weight of asphaltene charged.

Practical Utilization of High Concentrations of Halide Catalysts

Process advantages that apparently would be achieved by using high concentrations of halide catalysts include operation at lower pressure and temperature and production of less hydrocarbon gas with a resultant decrease in hydrogen consumption. Serious technical and economic problems that would be expected in commercial-scale coal hydrogenation are corrosion problems and problems associated with economic recovery and regeneration of the catalyst.

Of the ten halides used in this study, only NiI₂, NiBr₂, FeI₂, and ZnI₂ have melting points above 425° C and could be used as components of solid-phase catalysts. Iodine would be a vapor, while the remaining catalysts would be liquids. In a process, the use of gaseous or liquid catalysts would necessitate continuous feeding and withdrawal of such catalysts. In the presence of the amounts of hydrogen, hydrogen sulfide, and water that would be expected at coal hydrogenation conditions, reduction of the metal halide catalysts to the corresponding metals and conversions to oxides and sulfides are potential catalyst consuming reactions. Available free energy data for these reactions indicate that the metal halide is the thermodynamically favored form in each instance in the absence of an organic liquid phase. The halides may also react with ammonia to form complexes such as those formed with ZnCl₂ during coal extract hydrogenation,^{2/} or they may interact with and be retained in the product oil.^{2/} Some

of the catalyst reactions might possibly be avoided through the use of scavengers or by other controls of the partial pressures of gaseous reactants and products. The addition of a metal or oxide that preferentially reacts with hydrogen sulfide might prevent catalyst loss through sulfiding reactions, while reaction of a halide catalyst with hydrogen might be suppressed by adding a small amount of the corresponding hydrogen halide to the feed gas. The practicability of such measures is presently not known.

SUMMARY

Iodine and halides of Ni, Zn, Sn, Cd, and Fe, when used as catalysts in high concentration at 4,000 psi and 425° C, were found to be very effective for hydrogenating bituminous coal to oils containing only small amounts of asphaltene. When the feed material was an asphaltene produced by mild hydrogenation of the same coal, these catalysts were equally effective for converting the asphaltene to oil. Low-boiling oils produced from both coal and asphaltene were very similar in composition. These data show that the halides used are highly selective for hydrogenating asphaltene to oil. This is the slow and rate-controlling step when hydrogenating coal in the presence of conventional catalysts. A pressure of 3,500 psi or higher and a temperature of at least 450°C are required in conventional coal hydrogenation to reach low levels of asphaltene production in relatively short reaction times. With high concentrations of ZnCl₂, asphaltene hydrogenation to oil was readily accomplished in this study at 2,000 psi and 425° C and also at 4,000 psi and 400° C. Although halide catalysts in high concentration offer some process advantages, their practical utilization will require efficient and low-cost recovery and regeneration of the catalysts.

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