

## Coal Hydrogasification Catalyzed by Aluminum Chloride

Walter Kawa, Sam Friedman, L. V. Frank, and R. W. HiteshueU.S. Bureau of Mines, 4800 Forbes Avenue  
Pittsburgh, Pennsylvania 15213

## INTRODUCTION

The Bureau of Mines has been investigating the use of high concentrations of catalysts in the hydrogenation of coal to oil. A large number of materials including aluminum chloride have been screened as possible catalysts. Equal weights of catalyst and coal were used in these experiments, whereas catalyst concentrations of one weight-percent or less have been used in most previous studies. Aluminum chloride is well known as a catalyst for many organic reactions including hydrocracking. However, it is not known to be an effective coal hydrogenation catalyst. In the screening experiment with aluminum chloride at 450° C, very little oil was produced, but an exceptionally high yield of hydrocarbon gases was obtained.

Hydrogenation of coal to hydrocarbon gases (hydrogasification) is one method whereby high-Btu gas will probably be produced in the future. Coal hydrogasification processes now under development are noncatalytic and are operated at temperatures of about 700° C and higher.<sup>1</sup> High temperatures are used mainly to obtain high gas production rates. At lower temperatures, a much longer reaction time is needed to eliminate tarry products and caking problems are more severe. The results obtained with aluminum chloride demonstrated that catalytic hydrogasification at a practical rate was feasible at temperatures considerably lower than 700° C.

The present study was made to further explore the use of aluminum chloride in a batch reactor. It is a brief investigation of the effects of temperature, catalyst concentration, and type of feed material on hydrogasification yields.

## EXPERIMENTAL

Equipment and Materials

The reactor was a 1.2-liter 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.<sup>2</sup> Charges were contained in a glass liner that fitted closely to the autoclave wall. The free volume of a charged and assembled autoclave was about 1.0 liter. Pressure was measured with a bourdon-tube type gage that was connected to and rotated with the autoclave. Temperature was measured with a chromel-alumel thermocouple in a thermowell positioned axially within the autoclave.

Experiments were made with high-volatile A bituminous coal from the Pittsburgh seam, high-volatile C bituminous coal from Rock Springs, Wyoming, a Pennsylvania anthracite, a Texas lignite, untopped high-temperature tar produced in a commercial slot-type oven, tar from low-temperature fluidized carbonization of a Texas lignite, and distillation residue from a Venezuelan crude oil. Analyses of feed materials are shown in table 1. Coal samples were pulverized to minus 60 mesh (U.S. Sieve) and dried in air at 70° C for about 20 hours.

Powdered anhydrous aluminum chloride of 99 percent purity was used. Charges of coal and aluminum chloride were premixed in the glass liner by rotating the liner and charge end-over-end for 2 hours. Hydrogen was obtained from commercial cylinders.

TABLE 1.- Analyses of feeds

Material	An-thra-cite	Hvab coal	Hvcb coal	Texas lignite	High-temp. tar	Low-temp. tar	Petro-leum residue
<u>Analyses, percent by weight</u>							
Moisture .....	0.3	0.1	0.9	1.9	trace	trace	0.0
Ash .....	36.7	7.5	1.7	18.7	trace	0.1	0.1
Ultimate, maf							
C .....	91.1	83.8	76.4	68.3	92.2	83.3	85.7
H .....	2.5	5.4	5.3	5.3	5.3	9.6	10.5
N .....	1.1	1.6	1.6	1.3	1.2	0.7	0.6
S .....	1.0	1.2	0.9	2.3	1.0	1.0	3.1
O <sub>2</sub> .....	4.3	8.0	15.8	22.8	0.3	5.4	0.1

1/ By difference.

### Operating and Analytical Procedures

All experiments were made with 50-gram charges of coal or other feed material. After purging air out of a charged and assembled autoclave, hydrogen was added to a specified initial pressure selected so that a pressure of 4,000 psi would be attained at reaction temperature. Rotation was started and the autoclave was heated to reaction temperature at a rate of about 7° C per minute. After a specified time at reaction temperature, the autoclave was cooled to room temperature at a somewhat slower rate.

Gases were depressurized through scrubbers that removed water vapor and acid gases (CO<sub>2</sub>, H<sub>2</sub>S, and HCl formed by reactions of AlCl<sub>3</sub>). The remaining gases were metered, collected in a holder, sampled, and analyzed by mass spectrometry. In some experiments, aluminum chloride condensed in the autoclave outlet and obstructed the flow of gases during the depressurizing step. Some gas loss was incurred, and, as a result, reported gas yields are low for those experiments. Light oil and water were removed by vacuum distillation to about 110° C and 2 to 3 mm of Hg. Solid and heavy liquid products remaining in the autoclave were washed with water to remove aluminum chloride. Material insoluble in water was separated into benzene-insoluble and benzene-soluble fractions, and the ash content of the benzene insolubles was determined. When about 2 grams or more of benzene-soluble product was formed, it was separated into n-pentane-insoluble (asphaltene) and n-pentane-soluble (heavy oil) fractions.

Yields are expressed as percentages by weight of moisture- and ash-free (maf) charge. Organic benzene insolubles are defined as total benzene insolubles minus ash. Benzene-soluble oil is the sum of the asphaltene, heavy oil, and light oil. Coal conversion is given on a percentage basis and is defined as 100 minus the percent of organic benzene insolubles.

### RESULTS AND DISCUSSION

The effect of temperature on the distribution of products from hvab coal is shown in table 2. Experiments were made with equal weights of coal and aluminum chloride at temperatures of 250° to 450° C for one hour. At temperatures of 300° C and lower, little or no hydrogenation of coal would occur in one hour at 4,000 psi when using low concentrations of conventional catalysts. In the presence of aluminum chloride, appreciable amounts of benzene-soluble oil and hydrocarbon gases were produced at 250° C. Oil yields decreased and hydrocarbon gas yields increased as temperature was increased. Conversion of coal increased between 250° and 300° C, but

TABLE 2.- Effect of temperature on the distribution of products from hvab coal at 4,000 psi  
(50 grams of coal, 50 grams of  $AlCl_3$ )

Temp., ° C	Time at temp., hr.	Conver- sion, weight- percent	Yields, weight-percent of maf coal				
			Organic benzene insols.	Benzene- soluble oil	Hydro- carbon gases	Net water	Acid gases
250	1	60	40	19	27	1	8
300	1	76	24	15	42	0	16
300	2	70	30	19	41	<1	20
350	1	81	19	3	59	0	-
450	1	74	26	<1	68	0	16

there was no significant trend in conversion between 300° and 450° C. At 300° C, increasing the reaction time to 2 hours resulted in no significant change in product distribution.

Very little light oil was produced at any temperature. Benzene-soluble oils produced at 250° and 300° C consisted of about two-thirds asphaltene and one-third heavy oil. Hydrocarbon gases produced at 250° C contained 35 percent methane, 17 percent ethane, 33 percent propane, 11 percent propylene, 3 percent butane, and 1 percent butylene on a volumetric basis. As temperature was increased, the proportions of lower hydrocarbons increased. Methane and ethane constituted 96 percent of the gas produced at 450° C.

Results obtained at 250° and 300° C may have practical significance as these temperatures are below the softening point of caking coals. In continuous hydrogasification systems, coal agglomeration and stoppage of flows is a problem with both caking and noncaking coals. Agglomeration is avoided in noncatalytic systems by pre-treatment of a coal to destroy its caking properties or by rapid heating and rapid devolatilization to a dry residue. It may also be possible to avoid agglomeration in a continuous system by using aluminum chloride as a catalyst at about 300° C. The hydrocarbon gas yield of about 40 percent obtained at 300° C would be sufficiently high in such a process as the unconverted coal could be used for hydrogen production and power generation. Production of small amounts of heavy liquids would probably cause no difficulties in a continuous system, but large amounts would be undesirable; heavy liquids would tend to bind solid particles and render such systems inoperable.

The effect of aluminum chloride concentration on the distribution of products from hvab coal was determined at 300° C. Time at temperature was one hour. The amount of aluminum chloride charged was varied between 12.5 and 100 grams. As can be seen in table 3, very little reaction occurred with 12.5 grams of aluminum chloride in the charge. Hydrocarbon gas yields increased sharply as the amount of aluminum chloride was increased to 50 grams but remained essentially unchanged with a further increase to 100 grams.

Aluminum chloride sublimates at 180.2° C. It boils at 182.7° C under a pressure of 755 mm of Hg. The form of the vapor is the dimer,  $Al_2Cl_6$ , up to 440° C. Calculations based on available vapor pressure data indicate that 100 grams of aluminum chloride would be completely vaporized at 240° C in a 1-liter system. As complete vaporization could occur at the conditions used in all experiments listed in table 3, it would appear that results in table 3 show a dependence of hydrocarbon gas yield on the amount of aluminum chloride in the gas phase. However, it is also possible that a coal-aluminum chloride complex forms before catalysis occurs, and that the amount

TABLE 3.- Effect of AlCl<sub>3</sub> concentration on the distribution of products from hvab coal at 300° C  
(50 grams of coal, 4,000 psi, 1 hour at temperature)

AlCl <sub>3</sub> charged, grams	Conver- sion, weight- percent	Yields, weight-percent of maf coal				
		Organic benzene insols.	Benzene- soluble oil	Hydro- carbon gases	Net water	Acid gases
12.5	4	96	4	1	<1	5
25.0	11	89	6	5	<1	9
37.5	25	75	11	11	1	11
50.0	76	24	15	42	0	16
100.0	73	27	16	40	0	-

of complex formed depends upon the amount of aluminum chloride charged (up to 50 grams). The literature indicates that the formation of an organo-aluminum chloride complex is a prerequisite for catalysis of many organic reactions by aluminum chloride. The complex is apparently formed by reaction of aluminum chloride with unsaturated organic structures. No effort was made in this investigation to determine whether or not complexes of coal and aluminum chloride were formed.

The effectiveness of aluminum chloride as a catalyst for the hydrogasification of coals of various ranks, tars, and a petroleum residue was investigated at 300° and 450° C with a reaction time of one hour. Experiments were made using equal weights of feed material and catalyst. Results are shown in table 4. In the experiments with coals, the highest yields of hydrocarbon gases were obtained from hvab coal at both temperatures. Conversion of anthracite was only about 3 percent at 300° C, but an appreciable yield of hydrocarbon gases (24 percent) was obtained from anthracite at 450° C. At 450° C, yields from hvcb coal and anthracite were nearly equal while a considerably lower yield was obtained from the lignite. High yields of hydrocarbon gases were obtained from both high- and low-temperature tars at 450° C and from low-temperature tar at 300° C. High-temperature tar was much less reactive at 315° C. Yields of organic benzene insolubles obtained in the experiments with high-temperature tar were 25 and 26 percent, whereas the tar initially contained 9 percent. The increase of insolubles indicates that appreciable polymerization or condensation of the tar occurred at both temperatures. The highest yield of hydrocarbon gases (91 percent) was obtained from petroleum residue at 450° C.

The results shown in table 4 indicate that the amenability of a carbonaceous material to hydrogasification catalyzed by aluminum chloride increases with increasing hydrogen content and with decreasing oxygen content of the material. The least suitable material for hydrocarbon gas production was the lignite which contained the most oxygen. Much of the oxygen in coals is normally removed as water during hydrogenation. Reaction of water with aluminum chloride would produce hydrochloric acid and decrease the aluminum chloride concentration. The yields of acid gases shown in table 4 provide evidence that reaction with water did occur. Acid gas yields increased nearly linearly with increasing oxygen content of the feed. Yields of hydrogen sulfide and carbon dioxide obtained from coals would amount to only a few percent. In the experiments in which yields of acid gases were high, most of the gas would therefore be hydrochloric acid.

Equilibrium data indicate that negligible amounts of aluminum chloride would react with either hydrogen or hydrogen sulfide at the conditions used in this study. However, a nearly quantitative reaction with water to form alumina and hydrochloric acid would occur at equilibrium. Aluminum oxychloride and aluminum hydroxychlorides

TABLE 4.- Distribution of hydrogenation products  
from various feed materials

(50 grams of feed, 50 grams of  $AlCl_3$ , 4,000 psi, 1 hour at temperature)

Feed material	Temp., ° C	Yields, weight-percent of maf charge			
		Organic benzene insols.	Benzene-soluble oil	Hydro-carbon gases	Acid gases
Anthracite .....	450	80	<1	24	6
Hvab coal .....	300	24	15	42	16
Hvab coal .....	450	26	<1	68	16
Hvcb coal .....	300	74	5	10	26
Hvcb coal .....	450	55	3	21	34
Lignite .....	300	78	<1	8	35
Lignite .....	450	33	15	13	44
High-temp. tar ....	315	25	47	21	1
High-temp. tar ....	450	26	4	81	1
Low-temp. tar ....	300	3	8	74	9
Low-temp. tar ....	450	4	<1	71	10
Petroleum residue .	450	3	1	91	-

are other possible products of the reaction with water. In this study, reaction with water probably approached equilibrium as very little water was recovered in any of the experiments:

Further evaluation of aluminum chloride as a coal hydrogasification catalyst will require additional information concerning the chemical and physical changes the aluminum chloride undergoes during hydrogasification. With this information, an estimate of catalyst consumption can be made, catalyst recovery procedures can be devised, and the feasibility of operating a continuous system can be assessed.

#### SUMMARY

This investigation has shown that aluminum chloride in high concentrations is an effective catalyst for hydrogasification of various carbonaceous materials. With equal weights of hvab coal and aluminum chloride at 4,000 psi and 450° C for one hour, a hydrocarbon gas yield of 68 percent and a benzene-soluble oil yield of less than 1 percent are obtained. The oil yield increases and the gas yield decreases as the temperature is decreased. However, the gas yield of 27 percent at 250° C is still appreciable. At 300° C, hydrocarbon gas yields obtained from hvab coal increase sharply with increasing concentrations of aluminum chloride up to a 1:1 ratio with coal. In general, the amenability of a carbonaceous material to hydrogasification catalyzed by aluminum chloride increases with increasing hydrogen content and with decreasing oxygen content of the material.

#### REFERENCES

1. Lewis, P. S., Sam Friedman, and R. W. Hiteshue. High B.t.u. Gas by the Direct Conversion of Coal. Advances in Chemistry Series, No. 69, Fuel Gasification, 1967, pp. 50-63.
2. Hawk, C. O. and R. W. Hiteshue. Hydrogenating Coal in the Batch Autoclave. BuMines Bull. 622, 1965, 42 pp.