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HYDROGASIFICATION OF CARBONACEOUS MATERIAL

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ABSTRACT OF THE DISCLOSURE

Hydrogasifiication of carbonaceous material at temperatures of about 450° C. or below is accomplished by the use of relatively large amounts of aluminum chloride to catalyze the reaction.

Hydrogasification, i.e., reaction with hydrogen at elevated temperatures and moderate pressures, has previously been used for making gas of high calorific value directly from carbonaceous materials such as coal. Such processes have been uncatalyzed and have required temperatures of about 700° C. and above. The high temperatures employed in these prior art processes have, however, required the use of expensive reactors.

It has now been found, according to the process of the invention, that carbonaceous materials such as coals, tars, petroleum residues, oils, chars, etc., may be effectively converted to hydrocarbon gases in the C_1 to C_3 molecular weight range at temperatures of about 350 to 450° C. by employing relatively large amounts of aluminum chloride as catalyst. These temperatures permit the use of reactors employing much less expensive materials of construction. In addition, the process of the invention produces almost exclusively low molecular weight hydrocarbons, with essentially no liquid products.

In the process of the invention the carbonaceous material is mixed with dry $AlCl_3$ and the mixture is then subjected to a hydrogen pressure of about 1,000 to 8,000 p.s.i.g., preferably about 4,000 p.s.i.g., and a temperature of about 350 to 450° C. The optimum weight ratio of $AlCl_3$ to carbonaceous material will vary depending on the type of carbonaceous material and the temperature and pressure employed; however, a weight ratio of about 0.5 to 2.0 is usually satisfactory, with approximately equal weights of $AlCl_3$ and carbonaceous material generally being preferred.

The reaction may be carried out in any conventional apparatus, such as a high pressure autoclave, capable of providing the required temperature and hydrogen pressure. The carbonaceous material is preferably employed in a finely ground condition and in an essentially dry state. This is readily achieved by grinding to a particle size of about minus 60 mesh and drying at a temperature of about 50° to 100° C. to achieve a water content of about 0.1 to 0.5 percent.

The following examples will serve to more particularly illustrate the invention.

EXAMPLES 1–22

The apparatus employed in these examples was a cylindrical, batch-type high-pressure autoclave (suitable for service at 9,000 p.s.i.g. at 480° C.) fabricated from type 347 stainless steel. Its internal volume was 1.2 liters. Fabricated so as to fit closely within the autoclave chamber, while still being readily removable, was a cylindrical Pyrex liner, into which ground carbonaceous material and $AlCl_3$ catalyst were charged. To conduct an experiment, 50-gram samples of the carbonaceous material and the catalyst were first put into the Pyrex liner, which was then inserted into the autoclave and the sealing head made fast. The air was then purged from the autoclave chamber, and a cold hydrogen charge of about 2,000 p.s.i.g. (sufficient to provide 4,000 p.s.i. at reaction temperature) was introduced. Next, the loaded autoclave, mounted on a carriage, was set into rotation about its long axis at about 25 r.p.m. Heat was then applied so that the autoclave warmed up at the rate of 6° to 7° C. per minute until the desired reaction temperature (350° to 450° C.) was attained. This top temperature was maintained for approximately one hour, then the autoclave assembly was cooled in air to room temperature.

Experiments were made with high-volatile A bituminous coal from the Pittsburgh seam, high-volatile C bituminous coal from Rock Springs, Wyo., 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 as catalyst. 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.

Gases were depressurized through scrubbers that removed water vapor and acid gases (CO_2, H_2S, and HCl formed by reactions of $AlCl_3$). The remaining gases were metered, collected in a holder, sampled, and analyzed by mass spectrometry. 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.

TABLE 1.—ANALYSES OF FEEDS

	Material						
	Anthracite	HVAB coal	HVCB coal	Texas lignite	High-temp. tar	Low-temp. tar	Petroleum residue
Analyses, percent by weight:							
Moisture	0.3	0.1	0.9	1.9	Trace	Trace	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 [1]	4.3	8.0	15.8	22.8	0.3	5.4	0.1

[1] By difference.

Results are shown in Tables 2, 3 and 4.

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. 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 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.

TABLE 2.—EFFECT OF TEMPERATURE ON THE DISTRIBUTION OF PRODUCTS FROM HVAB COAL AT 4,000 P.S.I.

[50 grams of coal, 50 grams of $AlCl_3$]

	Time at temp., hrs.	Conversion, weight percent	Yields, weight-percent of MAF coal				
			Organic benzene insols.	Benzene-soluble oil	Hydrocarbon gases	Net water	Acid gases
Temp., ° C.							
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

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.

TABLE 3.—EFFECT OF $AlCl_3$ CONCENTRATION ON THE DISTRIBUTION OF PRODUCTS FROM HVAB COAL AT 300 C.

[50 grams of coal, 4,000 p.s.i., 1 hour at temperature]

$AlCl_3$ charged, grams	Conversion, weight percent	Yields, weight-percent of MAF coal				
		Organic benzene insols.	Benzene-soluble oil	Hydrocarbon 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	------

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 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.

TABLE 4.—DISTRIBUTION OF HYDROGENATION PRODUCTS FROM VARIOUS FEED MATERIALS

[50 grams of feed, 50 grams of $AlCl^3$, 4,000 p.s.i., 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
Do	450	26	<1	68	16
HVCB coal	300	74	5	10	26
Do	450	55	3	21	34
Lignite	300	78	<1	8	35
Do	450	33	15	13	44
High-temp. tar	315	25	47	21	1
Do	450	26	4	81	1
Low-temp. tar	300	3	8	74	9
Do	450	4	<1	71	10
Petroleum residue	450	3	1	91	------

What is claimed is:

1. A process for preparation of gases of high calorific value from carbonaceous material comprising reacting the carbonaceous material with hydrogen at a temperature of about 350 to 450° C. and a pressure of about 1,000 to 8,000 p.s.i.g. in the presence of an amount of aluminum chloride sufficient to catalyze the reaction.

2. The process of claim **1** in which the carbonaceous material is coal.

3. The process of claim **1** in which the carbonaceous material is tar.

4. The process of claim **1** in which the carbonaceous material is a petroleum residue.

5. The process of claim **1** in which the temperature is about 450° C.

6. The process of claim **1** in which the weight ratio of aluminum chloride to the carbonaceous material is from about 0.5 to 2.0.

7. The process of claim **6** in which approximately equal weights of aluminum chloride and carbonaceous material are employed.

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