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HYDROGENATION LIQUEFACTION OF COAL EMPLOYING ZINC CATALYSTS

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The invention herein described and claimed may be manufactured and used by or for the Government of the United States of America for governmental purposes without the payment of any royalties thereon or therefor.

This invention relates to the liquefaction of coal and its conversion products to obtain liquid products, by means of hydrogenation in the presence of catalysts. It is known that when coal is heated to such high temperatures as 450° C. in the presence of active catalysts under high hydrogen pressures such as 1000 pounds or higher that in the process hydrogen is consumed; and gaseous, liquid, and solid products result. The liquid product of primary liquefaction is complex in structure, and consists of materials that are liquid at atmospheric conditions and distillable without decomposition within a reasonable range of temperature. The liquid product carries dissolved and suspended semi-solid and solid matter. These amounts vary with the extent of hydrogenolysis.

Untreated coal contains only about 10 percent of benzene-soluble material. The solubility of hydrogenated coal in this solvent increases with the extent of hydrogenation. Therefore, solubility in benzene has been used to determine the extent of coal liquefaction. Because of the ease of measuring the amount of benzene-insoluble material, the percentage of liquefaction is determined on this basis. The "percent liquefaction" is based on the organic matter in the benzene-insoluble material; it was obtained by the formula

$$\text{Percent liquefaction} = \frac{\text{Original coal} - \text{benzene-insoluble}}{\text{Original coal}}$$

the amount being expressed on the ash-free, dry basis of the coal.

The present invention relates more particularly to methods for effecting the liquefaction of coal by high temperature hydrogenation wherein finely divided alloys of zinc or certain mixtures of finely divided zinc with other metals are employed as catalysts. Alloys of zinc, comparing favorably in the high order of liquefaction with tin are: Zinc-tin, zinc-antimony, and zinc-arsenic. Likewise, powdered mixtures of zinc with tin, zinc with antimony, and zinc with arsenic give high percentages of liquefaction. The present invention is a continuation-in-part of our U. S. Patent application, Serial No. 60,393, filed on November 16, 1948, now abandoned.

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It has been previously proposed to destructively hydrogenate coal employing finely divided metals. There are several patents thereon. Patent literature shows too the importance of volatile halogens as catalysts in the primary liquefaction of coal.

Evidence obtained from the experimental work leading to this invention indicates that destructive hydrogenation of coal involves three reactions: First, the initial cracking of the complex, high molecular weight compounds of which coal is composed, results in the production of a semi-liquid asphaltic material; second, the hydrogenation of asphaltic material with the formation of oils; and third, hydrogenation of the oily products to produce light fractions.

All these reactions are catalytic, and use of tin compounds has been proven to be satisfactory. However, tin is both expensive and hard to get because of geographical locations in which it exists in a natural state. So the use of other catalysts which would promote liquefaction of coal yet would be more accessible and less expensive is desirable. Similarly, the replacement of tin by a catalyst which is less expensive due to the inclusion of less expensive substance with the tin is desirable.

In accordance with the present invention, finely divided zinc alloys or finely divided mixtures of zinc with other metals are employed as catalysts to effect in a positive manner the extent of coal liquefaction. We have found that by the addition of such catalysts to the charge, the order of percent of coal liquefaction substantially approximates that which is achieved by the employment of finely divided tin alone.

In order to further illustrate the invention, the examples below are given, which, however, should not be construed as limiting the invention. Example I has been included for comparative purposes, that the order of coal liquefaction, wherein the standard tin catalyst has been used, may function as a basis for comparison.

EXAMPLE I

[For comparison]

A typical Pittsburgh-bed (Bruceton) coal is finely ground and made into a paste with an equal part by weight of tetralin. One percent of tin is added to this paste and the mixture autoclaved with hydrogen under about 1000 p. s. i.

initial hydrogen pressure at the conditions shown in the following table:

Duration of reaction, hours	Temp., ° C.	Percent of coal liquefied	Percent of asphalt formed
½	400	80.0	67.2
1	400	81.6	44.7
3	400	89.2	39.0
½	415	83.4	49.3
1	415	85.9	23.0
3	415	86.9	19.0

In this and the two succeeding examples, the reaction pressure becomes about 2000, varying somewhat with the temperature. For that reason, it seems best to specify the initial pressure, which in each example was 1000 p. s. i. hydrogen pressure.

EXAMPLE II

When a similar mixture of coal and tetralin is hydrogenated under the same conditions but with one percent of a powdered zinc-antimony alloy added as the catalyst to this paste, the extent of coal liquefaction is slightly lower than in the above example, but yet good at the corresponding higher temperature after 1 to 3 hours' duration.

Duration of reaction, hours	Temp., ° C.	Percent of coal liquefied	Percent of asphalt formed
½	400	47.9	34.0
1	400	49.2	24.2
3	400	56.3	22.2
½	415	58.0	20.8
1	415	67.4	22.6
3	415	74.6	26.6

EXAMPLE III

When a similar mixture of ground coal and tetralin, containing 0.5 percent tin and 0.5 percent of zinc-antimony alloy as the catalyst, is autoclaved with hydrogen under 1000 p. s. i. initial hydrogen pressure, the results shown in the following table are obtained.

Duration of reaction, hours	Temp., ° C.	Percent of coal liquefied	Percent of asphalt formed
½	400	70.1	36.5
1	400	84.2	26.3
3	400	87.9	13.0
½	415	84.5	27.4
1	415	86.5	17.1
3	415	88.4	9.0

From Example III, it will be seen that when 50 percent of the tin had been replaced by an equal quantity of a zinc-antimony alloy the percent of coal liquefaction was the equal of that in Example I, but for one run.

That the satisfactory yield in percent of liquefaction of coal and also the effectiveness of our process's catalysts, as compared with tin may stand out distinctly, a table is presented below, wherein the conditions of operation, that is, initial hydrogen pressure, reaction temperature, time of duration, are analogous: Initial hydrogen pressure, 1000 p. s. i. g.; reaction temperature, 450° C.; duration of reaction, 60 minutes. Runs were made both in the absence and in the presence of a hydrocarbon liquid pasting oil which proves that the latter is not necessary.

Table I

Run No.	Charge, in grams			Percent of liquefaction	Percent of asphalt formed
	Coal	Vehicle	Catalyst		
922	50		.5Sn+.275NH_4Cl	86.6	26.9
663	50		1.25Zn+1.88NH_4Cl	83.1	21.9
1000	50	50 tetralin	.5Sn+.27NH_4Cl	89.8	27.9
1011 [1]	50	50 tetralin	.25Sn+.25Zn-Sb+.25NH_4Cl	90.45	37.9
666	50		.5Zn+.05Sn+1.13 NH_4Cl	86.2	26.4
274 [1]	50		.5Zn-Sn+.275NH_4Cl	85.5	20.2

[1] In runs 1011 and 274 supra which embody the process in the use of zinc-antimony and zinc-tin alloy, respectively, the analysis of the alloy components was 50 percent Zn, 50 percent Sb, and 50 percent Zn, 50 percent Sn, respectively.

While we have thus described the process of our invention in a specific manner and under designated conditions, we wish it to be understood that our invention is not limited to the manner and conditions above described, but is adaptable to a wide range of temperatures, pressures, and times of treatment. Particular conditions will vary usually with the type of coal material being processed and the yield and products distribution desired, as is well known in the art.

Temperatures of from 400° to 600° C. and pressures of 30 to 200 atmospheres are the preferred conditions for carrying out our invention. Nevertheless, satisfactory results can be obtained within the temperature range 275° to 700° C. or above, and pressures may range from as low as about 5 atmospheres up to as high as 1000 atmospheres. The time of operation may vary from about one-half to three hours.

The proportion of catalyst in the charge introduced into the converter should be sufficient to complete the process in a practical time and usually will be within the range of from 0.1 to about 10 parts of catalyst per 100 parts of the coal-oil paste. While the catalyst may be recovered from the reaction products, any excess would not be economical; and we prefer to add the catalyst in amounts of 0.5 to 1 part by weight to each 100 parts by weight of coal-oil paste charged to the converter.

As used in this specification and the appended claims, the term "coal" is intended to include, and should be understood as including, all types, classes, and ranks of solid bituminous fuels such as anthracite coal, bituminous coal, semi-bituminous coal, subbituminous coal, "brown" coal, lignite, peat, and the like. The term "pasting liquid" will be understood to include various liquids, more particularly an oil from liquid products from coal hydrogenation, coal carbonization tars, oils from crude petroleum distillation, or such oxygenated carbon compounds as the phenols, for example, cresol.

Obviously, many modifications and variations in the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations

should be imposed as are indicated in the impending claims:

We claim as our invention:

1. A process for producing liquid products by the hydrogenation of coal, the improvement which comprises reacting coal at temperatures of about 275°–700° C. with hydrogen under superatmospheric pressure in the presence of a catalyst comprising a finely divided alloy of zinc with antimony, thereby producing a high order of percentage of coal liquefaction, said catalyst being essentially the sole catalytic material employed in said hydrogenation.

2. A process for producing liquid products by the hydrogenation of coal, the improvement which comprises reacting coal, admixed with an oil which has been derived in part at least from liquid products from a prior coal hydrogenation, at temperatures of about 275°–700° C. with hydrogen under superatmospheric pressure in the presence of a catalyst comprising a finely divided alloy of zinc with antimony, thereby producing

a high order of percentage of coal liquefaction, said catalyst being essentially the sole catalytic material employed in said hydrogenation.

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