

- [54] **LIQUEFACTION OF COAL**
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- [52] **U.S. Cl.** **208/10**
- [51] **Int. Cl.²** **C10G 1/06**
- [58] **Field of Search**..... 208/9, 10

1,994,075 3/1935 Krauch et al. 208/10
 3,502,564 3/1970 Hodgson 208/10

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- [56] **References Cited**
- UNITED STATES PATENTS**
- 1,835,425 12/1931 Pier 208/10
- 1,844,998 2/1932 Wietzel et al. 208/10
- 1,923,576 8/1933 Krauch et al. 208/10
- 1,946,341 2/1934 Szeszich 208/10
- 1,983,234 12/1934 Krauch et al. 208/10

[57] **ABSTRACT**
 This specification discloses the liquefaction of coal. The liquefaction procedure involves reacting the coal with hydrogen or with a mixture of carbon monoxide and water in the presence of, as a catalyst, a material derived from the naturally occurring underwater deposit known as a manganese nodule. The manganese nodule may be employed without pretreatment or may be pretreated by sulfiding. The catalyst, after it has become deactivated by use, may be processed to remove and recover one or more valuable metallic constituents.

21 Claims, No Drawings

LIQUEFACTION OF COAL

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to the liquefaction of coal and relates more particularly to the hydrogenative liquefaction of coal employing a catalyst.

2. Description of the Prior Art

U.S. Pat. No. 3,214,236 discloses hydrogenation as a conversion process in which manganese nodules are catalytically useful. This patent also discloses that the manganese nodule catalyst can be a source of manganese and other valuable metals after being spent in effecting the conversion process.

U.S. Pat. No. 3,509,041 discloses the use of manganese nodules, after pretreatment by base exchange to bond hydrogen ion thereto, in hydrocarbon conversion reactions, specifically cracking, hydrocracking, oxidation, olefin hydrogenation, and olefin isomerization.

SUMMARY OF THE INVENTION

In accordance with the invention, coal is liquefied by reacting the coal with hydrogen, or with carbon monoxide and water, in the presence of, as a catalyst, a material derived from the naturally occurring underwater deposit known as manganese nodules. In accordance with a specific embodiment of the invention, the manganese nodule is employed without treatment. In accordance with another specific embodiment of the invention, the manganese nodule may be pretreated by sulfiding. In accordance with still another specific embodiment of the invention, the catalyst, after it has become deactivated by use, is processed to remove and recover therefrom one or more valuable metallic constituents.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Coal can be processed in the absence of added catalyst to provide a liquid hydrocarbonaceous product. This liquefaction can be effected by reacting the coal at high temperatures with hydrogen or with a mixture of carbon monoxide and water. The yield of the liquid product obtained by this processing is comparatively low and an improvement in the yield of the liquid product can be obtained by carrying out the reaction in the presence of added catalyst. Catalysts which have been employed for this purpose include, for example, stannous chloride and a complex of nickel and molybdenum. However, while the yield of the liquid product employing these catalysts is increased, the cost of the added catalyst is a significant portion of the overall cost of the liquefaction procedure. Accordingly, it is desirable to provide a liquefaction procedure in which the cost of the added catalyst is a relatively insignificant portion of the overall cost of the operation.

By the process of the invention, an economical and effective liquefaction of coal is obtained. Manganese nodules are readily available in large quantities and are relatively inexpensive. Further, the material derived from the nodules is capable of providing satisfactorily high yields of liquid products from the coal. Thus, high yields of liquid hydrocarbonaceous product are obtainable from coal by a process in which the cost of the catalyst is practically negligible.

Manganese nodules, as is known, are naturally occurring deposits of manganese, along with other metals,

including iron, cobalt, nickel, and copper, found on the floor of bodies of water. They are found in abundance on the floors of oceans and lakes. For example, they are found in abundance on the floor of the Atlantic and Pacific Oceans and on the floor of Lake Michigan. The nodules are characterized by a large surface area, i.e., in excess of about 100 square meters per gram. The nodules have a wide variety of shapes but most often those from the oceans look like potatoes. Those from the floor of bodies of fresh water, such as the floor of Lake Michigan, tend to be smaller in size. Their color varies from earthy black to brown depending upon their relative manganese and iron content. The nodules are porous and light, having an average specific gravity of about 2.4. Generally, they range from $\frac{1}{8}$ inch to 9 inches in diameter but may extend up to considerably larger sizes approximating 4 feet in length and 3 feet in diameter and weighing as much as 1700 pounds. In addition to the metals mentioned above, the nodules contain silicon, aluminum, calcium and magnesium, and small amounts of molybdenum, zinc, lead, vanadium, and rare earth metals.

The manganese nodules can be employed as the catalyst for the liquefaction of the coal substantially as mined, or recovered, from the floor of the body of the water in which they occur. Thus, the nodules, as mined, possibly after washing to remove sea water or lake water therefrom and mud or other loose material from the surface of the nodules, may be employed for coal liquefaction. The nodules, of course, may be crushed and sized to obtain a desired particle size.

In carrying out the process of the invention, any coal heretofore subjected to coal liquefaction procedures may be employed. These coals are bituminous, sub-bituminous, or lignite coals. Satisfactory results are obtained by employing such coals as high volatile "A-type" bituminous coal, for example Pittsburgh Seam coal, or high volatile "C-type" bituminous coal, for example Wyoming Rock Springs coal, and others.

The coal liquefaction operation may be carried out in the dry state. In this type of operation, the coal is mixed with the catalyst and the mixture subjected to the action of hydrogen or to the action of a mixture of carbon monoxide and water at a suitably high temperature. Both the coal and the catalyst are desirably crushed in order to effect intimate contact of the coal and the material derived from the manganese nodules. For example, both the coal and the catalyst may be crushed to a size that will pass through a 200-mesh screen. During the reaction, agitation of the coal and the catalyst, in the presence of the hydrogen, is desirably effected in order to obtain better contact of the reactants. Suitably, the reaction can be carried out employing apparatus such as a horizontal rolling autoclave.

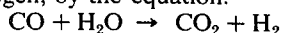
The coal liquefaction operation may also be carried out in a wet state. In this type of operation, the coal and the catalyst, desirably crushed, are mixed with a hydrogen rich solvent and the resulting wet mixture subjected to the action of the hydrogen at a suitably high temperature. Any type of hydrogen rich solvent previously used in the liquefaction of coal may be employed. Hydrogen rich solvents which may be employed include hydrocarbonaceous solvents such as gas oil. They also include those obtained by partial hydrogenation and distillation of coal tar.

The coal and the material derived from the manganese nodules may be employed in any ratio. Any finite amount of the material derived from the manganese

nodules appears to increase the yield of the liquid product. Preferably, however, the material derived from the manganese nodules is employed in the amount of at least 5% by weight of the coal and catalyst mixture. Greater amounts, on the other hand, improve the yield of the liquid product. Thus, it is preferred that the amount of material derived from the manganese nodules be at least 10% of the coal and catalyst mixture. Satisfactory results are obtained where the material derived from the manganese nodules is employed in an amount equal to that of the coal. Greater amounts, of course, may be employed, although with greater amounts the increases in yield may be compensated by decreased throughput in the liquefaction apparatus.

The liquefaction occurs when the coal and added catalyst mixture is reacted with hydrogen or with a mixture of carbon monoxide and water. The conversion occurs most efficiently with an excess of hydrogen or of carbon monoxide at elevated pressure. The pressure ordinarily should be at least 1000 pounds per square inch gage (psig). However, higher pressures of hydrogen are desirable. Thus, for example, the pressure may be at least 2000 psig. Satisfactory results are obtained with even higher pressures such as those of 2500 psig or 4600 psig.

It is contemplated to use pure hydrogen, recycled hydrogen, or hydrogen-forming mixtures of carbon monoxide and water in the liquefaction process. Inert or non-reactive gases such as nitrogen may be present, but in general such impurities should not exceed 50 mol percent of the gaseous mixture. It is known that mixtures of carbon monoxide and water react over catalyst to form hydrogen, by the equation.



and it is a feature of this invention that this conversion appears to be facilitated by the manganese nodule catalyst. Thus, the use of the manganese nodule catalyst allows use of carbon monoxide, which is less expensive than hydrogen to manufacture, without detriment to the conversion process.

The temperature during the liquefaction procedure should be at least 500°F. However, higher temperatures such as those of 800°F may be employed. Generally, any temperature heretofore employed for coal liquefaction will be satisfactory.

In accordance with specific embodiments of the invention, the liquefaction reaction may be carried out employing, as the catalyst, the manganese nodule with or without any pretreatment. Pretreatments to which the manganese nodules may be subjected include sulfiding.

Sulfiding pretreatment of the manganese nodules involves subjecting the manganese nodules to the action of hydrogen sulfide. The hydrogen sulfide employed may be pure or may be mixed with other gases. However, the hydrogen sulfide employed should be substantially free of hydrogen. The temperature of sulfiding may be from about 300°F to about 450°F and the time of sulfiding may be from about ½ hour to about 8 hours. The sulfiding may be effected by passing the hydrogen sulfide over the manganese nodules continuously during the sulfiding reaction. The space velocity of the hydrogen sulfide is not critical and any space velocity compatible with the equipment and such that some hydrogen sulfide is continuously detectable in the exit stream may be used.

In accordance with still another embodiment of the invention, the material derived from the manganese

nodules may, after being employed for liquefaction of coal, and having become deactivated to a predetermined extent, be treated for the recovery of valuable metals therefrom. Thus, the material derived from the manganese nodules, after becoming deactivated, may be treated to recover copper, or molybdenum, or any two, or all three, of these metals. Other metals may also be recovered from the catalyst. Manganese nodules, as previously mentioned, are relatively inexpensive. Thus, the extent to which they may become deactivated before no longer being employed for liquefaction of coal may be relatively small.

Removal of the copper and the nickel from the manganese nodules or from the spent catalyst may be effected by leaching with an aqueous solution of a strong acid. By strong acid is meant such acids as hydrochloric, sulfuric, and nitric acids. The molybdenum may be removed by leaching with aqueous base solutions such as aqueous solutions of sodium hydroxide or sodium carbonate. These solutions should have a pH of at least 8 and preferably should have a pH of at least 10. The leaching with the aqueous base solutions can be carried out at ambient temperatures or at the boiling point of the solution.

The following examples will be illustrative of the invention.

EXAMPLE 1

Manganese nodules obtained from the bottom of Green Bay in Lake Michigan were washed to remove lake water and mud therefrom and were then pulverized to pass through a 200-mesh screen. They were then washed with boiling water. The crushed and washed nodules had the following physical properties and chemical composition:

Physical Properties		
Surface Area	148	Square meters/gram
Particle Density	1.80	grams/cubic centimeter
Pore Diameter	67	Angstroms, average
Pore Volume	0.25	cubic centimeter/gram
Real Density	3.39	grams/cubic centimeter
Chemical Composition, wt. %		
Mn	5.44	
Fe	31.3	
CoO	.02	
Cu	.01	
MoO ₃	.04	
Ash	88.0	

A high volatile "C-type" bituminous coal from the D. O. Clark Mine No. 9, Superior, Wyo., often referred to as Rock Springs coal, was pulverized to pass through a 200-mesh screen. This coal had the following analysis, in weight percent, on a moisture- and ash-free basis: carbon — 77.79, hydrogen — 5.53, nitrogen — 1.70, sulfur — 0.85, and, by difference, oxygen — 14.59. Equal portions of the pulverized manganese nodules and coal were tumble-mixed and placed in an autoclave. The autoclave was flushed three times with nitrogen at 500 psig, flushed three times with hydrogen at 1000 psig, and pressured with hydrogen to 1200 psig as a starting pressure. The autoclave was rotated, and, while rotating at approximately 30 revolutions per minute, was heated over the course of about 2 hours to 427° c. (800° F.), held there for 1 hour, and then allowed to cool to room temperature.

To compare the effect of the manganese nodules on the liquefaction of the coal, a similar procedure was

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carried out with the exception that manganese nodules were not mixed with the coal.

The table gives the results of the liquefaction procedure.

TABLE I

	Weight Percent on a Moisture-Ash-Free Basis	
	With Catalyst	Without Catalyst
Coal converted	81.5	33.4
Light Oil (To C ₁₆)	7.7	4.4
Heavy Oil (C ₁₆₊)	27.8	6.9
Total Oil	35.5	11.3
Asphaltenes	22.2	1.4
Hydrocarbon Gases	9.5	6.9
H ₂ S + CO ₂	2.2	3.5
Water	12.1	10.4
Losses	—	—

It will be seen from the table that the presence of the catalyst resulted in a marked increase in the amount of the coal converted and in the amount of total oil obtained.

EXAMPLE 2

In this example a bituminous coal from Pennsylvania was employed. The coal was a high volatile "A-type" bituminous coal often referred to as Pittsburgh Seam coal. This coal had the following analysis, in weight percent, on a moisture- and ash-free basis: carbon — 83.2, hydrogen — 5.6, nitrogen — 1.6, sulfur — 1.2, and, by difference, oxygen — 8.4. The manganese nodules were obtained from the bottom of Sturgeon Bay (an inlet of Green Bay, in Lake Michigan). The granules were crushed to pass through a 200-mesh screen and were washed in boiling water. The crushed and washed nodules had the following physical properties and chemical composition:

Physical Properties		
Surface Area	137	Square meters/gram
Particle Density	1.04	grams/cubic centimeter
Pore Diameter	199	Angstroms, average
Pore Volume	0.68	cubic centimeter/gram
Real Density	3.58	grams/cubic centimeter
Chemical Composition, wt. %		
Mn	14.1	
Fe	30.2	
Ni	.15	
CoO	< 0.1	
MoO ₃	< 0.1	
Cu	< 0.02	
Ash	82.9	

The liquefaction procedure was carried out similarly as in Example 1.

To compare the effect of the catalyst on the liquefaction, a similar procedure was carried out employing the coal but without employing the catalyst.

The results are set forth in the table.

TABLE II

	Weight Percent on a Moisture-Ash-Free Basis	
	With Catalyst	Without Catalyst
Coal converted	74.7	47.1
Light Oil (To C ₁₆)	9.3	5.5
Heavy Oil (C ₁₆₊)	24.3	13.9
Total Oil	33.6	19.4
Asphaltenes	24.0	8.3
Hydrocarbon Gases	7.5	10.6
H ₂ S + CO ₂	.6	.9
Water	8.1	7.8
Losses	1.0	—

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It will be seen from this table also that the presence of the catalyst resulted in a marked increase in the amount of the coal converted and in the amount of total oil obtained.

EXAMPLE 3

In this example, three runs were carried out. In the first run, no catalyst was employed. In the second and third runs, catalyst was employed in the amount of 9.1% of the weight of the catalyst and coal mixture. The second run was carried out with a reaction time of 1 hour and the third run was carried out with a reaction time of 2 hours. The coal was Pittsburgh Seam coal and had been pulverized to pass through a 200-mesh screen. The catalyst was the same as that employed in Example 2. The coal or mixture of coal and manganese nodules was placed in a horizontal rolling autoclave and the autoclave was flushed with nitrogen and then with hydrogen, pressured to 1200 psig hydrogen starting pressure and heated while rotating over the course of the reaction to 427° C. (800° F.)

The results of the runs are given in the table.

TABLE III

Run Number	Weight Percent on a Moisture-Ash-Free Basis		
	1	2	3
Coal Converted	45.6	64.6	70.0
Light Oil (To C ₁₆)	6.8	7.6	8.9
Heavy Oil (C ₁₆₊)	11.5	19.3	21.8
Total Oil	18.3	26.9	30.7
Asphaltenes	5.32	20.7	15.5
Hydrocarbon Gases	12.30	8.5	14.6
H ₂ S + CO ₂	1.1	.7	.5
Water	8.6	7.8	7.8
Losses	—	—	.9

EXAMPLE 4

In this example, a solvent was employed. The coal and the catalyst were the same as the coal and catalyst in Example 3. The amount of the catalyst was 9.1% of the weight of the catalyst and coal mixture. The solvent was obtained by partial hydrogenation and distillation of coal tar. The catalyst-coal mixture was dispersed in three times its weight of the solvent in a magnetically stirred stainless steel autoclave. A temperature of 430°C. and a pressure of hydrogen of 2500 psig were maintained in the autoclave for a period of 1 hour. The results are given in the table. For purposes of comparison, the table includes the results obtained in Run 2 of Example 3 wherein a solvent was not employed. In the table, the figures are in weight percent on a moisture- and ash-free basis.

TABLE IV

	Solvent	No Solvent
Coal Converted	79	65
Total Oil	16	27
Total Asphaltenes	43	21
Total Liquid Product	59	48
Hydrocarbon Gases	6	9

It will be observed from the table that an increase in the extent of coal conversion and an increase in the amount of liquid product are obtained when the reaction is run in the presence of the solvent.

EXAMPLE 5

In this example, the catalyst employed was pretreated by sulfiding. The catalyst was the same as the catalyst employed in Example 2 and sulfiding was carried out by treating with hydrogen sulfide at 400° F. for 1 hour. The coal was the same as the coal in Example 3. The amount of catalyst was 9.1% of the weight of the catalyst and coal mixture. Similarly to Example 4, the liquefaction was carried out in the presence of a solvent, the solvent being the same as the solvent as employed in Example 4. The mixture of solvent, catalyst, and coal was placed in an autoclave and maintained at a temperature of 430° C. and a hydrogen pressure of 2500 psig for 1 hour. The results are given in the table. In the table, the figures are in weight percent on a moisture- and ash-free basis. For purposes of comparison, the table includes the results obtained in Example 4 wherein the catalyst had not been pretreated by sulfiding.

TABLE V

	Catalyst Sulfided	Catalyst Not Sulfided
Coal Converted	84	79
Total Oil	38	16
Total Asphaltenes	41	43
Total Liquid Product	79	59
Hydrocarbon Gases	5	6

The data in the table show that sulfiding the nodules prior to admixture with the coal produces an increase in the amount of coal converted and an increase in the amount of liquid product.

EXAMPLE 6

The Pittsburgh Seam Coal, more fully described in Example 2, and Sturgeon Bay nodules, more fully described in that same example, were used in this example.

Equal portions of coal and manganese nodules, both pulverized to pass through a 200 mesh screen, were placed in a horizontal rolling autoclave. A weight of water, equimolar with the amount of carbon monoxide to be subsequently added, was also placed in the autoclave. The vessel was flushed thoroughly with carbon monoxide, then filled with carbon monoxide to the desired starting pressure, and heated while rotating over the course about 2 hours to 430°C (805°F). A similar experiment was done but without added catalyst for the purpose of comparison. The results are summarized in Table VI.

Table VI

	No Added Catalyst	50% (wt) Sturgeon Bay Nodules
CO Pressure at room temp.	1200 psi	1200 psi
Total pressure at reaction temp.	4300 psi	4600 psi
Reaction temp.	430 °C	430 °C
Reaction time	2 hours	2 hours
Conversion and Product Distribution — wt% calculated on the basis of moisture- and ash-free coal.		
Conversion	44	~80
Asphaltene	13.5	20.0
Oil	13.1	40.5
Hydrocarbon gases	10.3	10.8
Losses & Other Products	7.1	~8.7
Total Liquid Product (asphaltene & oil)	26.6	60.5
Oil/Asphaltene Ratio	1.0	2.0
Gas Composition at End of Run (mole %)		
H ₂	9.5	23.0
CO	64.6	30.0

Table VI-continued

	No Added Catalyst	50% (wt) Sturgeon Bay Nodules
CO ₂	21.1	42.8
Hydrocarbons	4.0	4.0
H ₂ /CO ratio	99.2	99.8
	.15	.77

This example illustrates the effectiveness of the nodule catalyst in increasing the degree of conversion, in effecting conversion of the carbon monoxide and water to hydrogen and carbon dioxide, and additionally in increasing the quality of the liquified product as evidenced by the unusually high ratio of oil to asphaltene in the liquid product.

In general, on completion of the liquefaction reaction, the product mixture will contain ash, catalyst, and some unconverted carbonaceous residue in addition to hydrocarbonaceous liquid. The hydrocarbonaceous liquid may be recovered by filtration, centrifugation, distillation, extraction or suitable combinations thereof, and is suitable for use as a liquid fuel without further treatment. Alternatively, it may be further refined by solvent extraction or other techniques to recover aromatic hydrocarbons, petrochemical feedstocks or lubricants.

We claim:

1. A process for the liquefaction of coal comprising: reacting said coal with hydrogen or with a mixture of carbon monoxide and water, said reacting step being conducted at a temperature of at least 500°F and at a pressure of at least 1000 psig, in the presence of, as a catalyst, the naturally occurring underwater deposit known as manganese nodules; and recovering hydrocarbonaceous liquid.

2. The process of claim 1 wherein said reaction is carried out in the dry state.

3. The process of claim 1 wherein said reaction is carried out in the wet state in the presence of a solvent.

4. The process of claim 1 wherein said manganese nodules are in the amount of at least 5% by weight of said coal and said catalyst.

5. The process of claim 1 wherein said manganese nodules are in the amount of at least 10% by weight of the mixture of said coal and said catalyst.

6. The process of claim 1 wherein said reacting is conducted at a pressure of at least 2000 pounds per square inch gage.

7. The process of claim 1 wherein, when said material has become deactivated catalytically to a predetermined extent, valuable metal is recovered therefrom.

8. The process of claim 7 wherein said valuable metal is recovered from said material by leaching said material with an aqueous solution of a strong acid.

9. The process of claim 7 wherein said valuable metal is recovered from said material by leaching said material with an aqueous solution having a pH of at least 8.

10. The process of claim 1 wherein said naturally occurring manganese nodules are subjected to the action of hydrogen sulfide prior to said reacting step.

11. The process of claim 10 wherein said manganese nodules are subjected to the action of said hydrogen sulfide at a temperature from about 300°F to about 450°F.

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12. The process of claim 10 wherein said manganese nodules are subjected to the action of said hydrogen sulfide for a time from about 1/2 hour to about 8 hours.

13. The process of claim 10 wherein said manganese nodules are subjected to the action of said hydrogen sulfide at a temperature from about 300°F to about 450°F and for a time from about 1/2 hour to about 8 hours.

14. The process of claim 10 wherein said reaction is carried out in the dry state.

15. The process of claim 10 wherein said reaction is carried out in the wet state in the presence of a solvent.

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16. The process of claim 10 wherein said manganese nodules are in the amount of at least 5% by weight of the mixture of said coal and said nodules.

17. The process of claim 10 wherein said manganese nodules are in the amount of at least 10% by weight of the mixture of said coal and said nodules.

18. The process of claim 17 wherein said manganese nodules are Lake Michigan nodules.

19. The process of claim 10 wherein said reacting is conducted at a pressure of at least 2000 pounds per square inch gage.

20. The process of claim 1 wherein said manganese nodules are Lake Michigan nodules.

21. The process of claim 10 wherein said manganese nodules are Lake Michigan nodules.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,923,634

DATED : December 2, 1975

INVENTOR(S) : Anthony J. Silvestri and Paul A. Naro

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 4, line 6 reads "copper copper" should be
--copper, nickel--

Col. 5, line 10 reads "33.4" in the middle of line
should be under --Without Catalyst--
33.4

Signed and Sealed this
twenty-third Day of March 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks