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LIQUEFACTION OF COAL

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The present invention relates to a process for the liquefaction of coal. More particularly, the present invention relates to the production of coal extract from coal by reacting the coal with phenolic-boron trifluoride complex.

Coal liquefaction has been practiced for many years. The most important reason for transforming the solid coal particles into liquid form is that the liquefied coal is, in general, more amenable to chemical reactions than the solid coal, e.g., hydrogenation of coal extract to make liquid fuels such as gasoline and jet fuel as compared with hydrogenation of coal. In addition, the coal extract may be used as fuel oil or coked to make electrode carbon.

One method for liquefying coal involves contacting the coal with a solvent at elevated temperatures and pressures whereby soluble coal constituents are transferred into the liquid solvent phase. Numerous solvents for this purpose have been proposed. (See chapter 19, Chemistry of Coal Utilization, H. H. Lowry (editor), John Wiley and Sons, 1945.) A common drawback with coal solvents used heretofore, however, is that high coal extract yields, i.e., amounting to more than about 50 weight percent of the feed coal, can normally only be obtained at a temperature above about 300° C., a pressure between about 50 and 200 p.s.i.g., and in the presence of hydrogen either from the solvent (hydrogen-transfer solvent such as tetralin) or from extraneous sources or both. Obviously the cost associated with maintaining high temperatures, high pressures, and supplying the expensive hydrogen is undesirable. Accordingly, the need exists for a coal liquefaction process which will give high conversions of coal to coal extract at low temperatures, low pressures, and without any hydrogen.

Low temperatures are particularly important when solvent extraction is being used as a means of separating the aromatic monomeric units of coal. High temperatures cause excessive thermal cracking which not only breaks the polymeric coal units into monomeric units, but also breaks the monomeric units, thus producing undesirable gas and coke.

It is an object of the present invention to provide a novel process for obtaining high yields of coal extract from coal without the prior art disadvantages mentioned above.

It is another object of the present invention to provide a novel solvent for the liquefaction of coal.

In accordance with our invention, it has been discovered that phenolic-BF₃ complex is a superior treating agent for the recovery of liquid constituents from coal. The phenolic-BF₃ complex does more than merely dissolve those coal constituents that are soluble therein, but the complex actually chemically reacts with coal to depolymerize it, thus forming additional components which are soluble in the complex.

It is to be understood that the term "phenolic-BF₃ complex," as hereinafter used, includes phenol-BF₃ complex; reactive alkyl phenol-BF₃ complexes, e.g., cresol-BF₃ complexes, and xylenol-BF₃ complexes; and reactive halogenated derivatives of the above complexes, e.g., 2-chlorophenol-BF₃ complex, 2,4-di-chlorophenol-BF₃ complex, 6-chloro-o-cresol-BF₃ complex and the like. As is well known in the art, only phenolic-BF₃ complexes which have at least one free ortho and/or para position are reactive.

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Coal, preferably in a comminuted form, is reacted with a phenolic-BF₃ complex such as phenol-BF₃ complex at a temperature in the range of 50 to 200° C., preferably 70 to 120° C. The reaction is conveniently conducted at autogenous pressures; however, if desired, higher pressures may be used. The solvent is generally used in a weight ratio of solvent to coal in the range of 0.25/1 to 10/1, preferably 0.50/1 to 5/1. Any conventional solvent extraction zone used by those skilled in the art may be employed, e.g., countercurrent, staged, continuous, or batch extraction.

EXAMPLE

High volatile bituminous coal obtained from the Pittsburgh Seam and having the following typical analysis was used in the following experiment.

Moisture	1.7
Volatile matter	38.5
Ash	12.6
Pyritic sulfur	2.5
Ultimate analysis:	Wt. percent DMMF *
H	5.77
C	80.36
O	10.58
N	1.40
S	1.89
	100.00

*DMMF means dry mineral matter free.

The coal was ground to -100 mesh (Tyler Standard screen) and stored under nitrogen until required. Samples were dried in a vacuum oven at 105° C. just prior to reaction.

An amount of 1600 grams of radioactive phenol (the number one carbon position comprises carbon 14, i.e., ¹⁴C) and 400 grams of coal were charged into a five-liter three-necked glass reaction flask equipped with stirrer, thermometer, condenser and gas inlet tube. The suspension was stirred and heated to 60-70° C. and the introduction of BF₃ was started. The mixture was heated to 100° C. and kept at this temperature until the end of the reaction period. The saturation with BF₃ took about two hours. After this time a very slow stream of BF₃ was bubbled through the system to keep the solution saturated with BF₃. The reaction time was 24 hours.

The first part of the reaction between coal and phenol-BF₃ complex is quite spectacular. Within a period of about 20 minutes the suspension becomes very viscous resembling a thixotropic gel due to the swelling and solvation of the coal particles. Shortly after this stage, the viscosity decreases rapidly indicating a further significant disintegration. After this time no individual coal particles can be separated from the mixture either by filtration or by centrifuging. On the other hand, when coal is extracted with phenol at 100° C. under similar conditions but without the addition of BF₃, the phenol solution can be easily separated from the coal particles by filtration, even after a 24-hour extraction period.

After the end of the reaction period, most of the BF₃ and excess phenol were removed by vacuum distillation. When the phenol content of the solution was reduced to about 50-60 percent, the distillation was interrupted and the fluid residue was poured into four liters of analytical reagent grade benzene. Most of the reaction product is insoluble in benzene and precipitates in a granular form which can be filtered easily. The precipitate was filtered, extracted a second time with two liters of hot benzene for three hours, and filtered again. The benzene solutions were combined, washed with 15 percent Na₂CO₃ solution, and distilled. Following the removal of benzene, the solution was vacuum fractionated in a 91-centimeter spin-

ning band column. After the recovery of the radioactive phenol and a smaller fraction consisting mostly of alkyl phenols, a pitch-like residue was left behind (benzene soluble fraction).

The solid precipitate was stirred with two liters of 15 percent aqueous Na_2CO_3 solution at 100°C . for eight hours to remove that part of the BF_3 which cannot be removed by vacuum distillation and remains in the residue (about 15 percent based on the weight of the residue). The benzene insoluble neutralized residue was filtered, dried, and then extracted with two liters of boiling methyl alcohol. After filtration, the extraction was repeated again with a second two liters of methyl alcohol. The methanol was evaporated from the solution and the solid residue was obtained (methanol soluble fraction).

A 50-gram sample of the methanol insoluble residue was extracted with 850 grams phenol at 100°C . for four hours. After the addition of 40 grams of Celite, the solution was filtered. The filtrate was concentrated by vacuum distillation and the extract was recovered by pouring the concentrate into a mixture of 80 percent n-heptane and 20 percent benzene. The precipitated solid was filtered and dried in a vacuum oven at 160°C . (phenol soluble fraction). The heptane-benzene solution was evaporated and a small amount (about 2 percent based on coal) of black pitch was recovered. This residue was added to the phenol soluble fraction. The phenol insoluble residue was extracted with 500 grams of pyridine at 100°C . for four hours. The solution was concentrated, poured into n-heptane, filtered and dried at 160°C . (pyridine-soluble fraction). The insoluble residue was dried in vacuum at 160°C . (pyridine insoluble fraction).

All fractions were analyzed for combined phenol content by analyzing for ^{14}C and comparison with the ^{14}C assay of the starting phenol. The phenolic hydroxyl content of the various fractions was determined by potentiometric titration in the presence of added 2,6-xylenol using sodium aminoethoxide in pyridine or ethylenediamine. The molecular weights of the benzene soluble, methanol soluble, and phenol soluble fractions were determined ebullioscopically in benzene, benzene-methanol and pyridine, respectively.

As a result of the above reaction of coal with phenol- BF_3 complex at 100°C . for 24 hours, about 80 weight percent of the coal dissolved in the complex.

As mentioned above, the reaction product was separated into fractions which were soluble in benzene, methanol, phenol and pyridine respectively. The yields of the various fractions are shown in Table I. The combined yield of soluble fractions and a solvent insoluble fraction is 122.7 percent (dry, mineral matter-free coal), indicating a total consumption of 22.7 percent phenol. On the basis of a blank experiment made with phenol and BF_3 , the amount of self-condensate formed from phenol was calculated to be 4.0 percent (based on DMMF coal). Consequently, the consumption of phenol in the reaction was 18.7 percent. The amount of coal components in each fraction adjusted for the combined phenol was calculated and the values are shown in Table I. The yields of benzene, methanol, and phenol solubles are 7.7, 1.8 and 52.0 percent, respectively. Normally, coal of this type would yield an extract of below one percent when treated with benzene. The combined phenol soluble extract amounts to 62 weight percent of the coal.

In a blank experiment in which another sample of the same coal was extracted with phenol at 100°C . for 24

hours, the coal extract yield was only 15.5 weight percent. The great increase in coal extract yield when using phenol- BF_3 complex is interpreted as a result of the simultaneous solvent extraction and depolymerization.

Table I
YIELD AND COMPOSITION OF COAL REACTION PRODUCTS

	Benzene Soluble	Methanol Soluble	Phenol Soluble	Pyridine Soluble	Insoluble
Total Yield, Wt. Percent					
DMMF Coal	15.2	4.0	61.2	12.3	30.0
Combined Phenol Content, Wt. Percent	49.4	55.7	15.0	10.5	10.5
Coal Fraction, Wt. Percent					
DMMF Coal	7.7	1.8	52.0	11.1	27.0
Ultimate Analysis of Coal Fraction, Wt. Percent:					
C	85.95	84.06	81.50	79.39	77.11
H	8.04	6.30	5.26	4.39	4.75
O	3.77	4.79	10.04	12.65	14.55
N	0.53	1.58	1.33	1.44	1.52
S	1.70	3.27	1.87	1.89	2.00

According to the provisions of the patent statutes, we have explained the principle, preferred construction, and mode of operation of our invention and have illustrated and described what we now consider to represent its best embodiment. However, we desire to have it understood that, within the scope of the appended claims, the invention may be practiced otherwise than as specifically illustrated and described.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for treating coal to recover liquid constituents therefrom which comprises reacting said coal with phenolic- BF_3 complex.
2. A process for recovering high yields of liquid constituents from coal at relatively mild conditions which comprises reacting said coal with phenolic- BF_3 complex at a temperature in the range of 50 to 200°C .
3. A process for recovering high yields of liquid constituents from coal at relatively mild conditions which comprises reacting said coal with phenol- BF_3 complex at a temperature in the range of 50 to 200°C .
4. A process for recovering high yields of liquid constituents from coal at relatively mild conditions, which comprises concurrently contacting said coal with a phenolic compound and BF_3 at a temperature in the range of 50 to 200°C .
5. A process for recovering high yields of liquid constituents from coal at relatively mild conditions, which comprises concurrently contacting said coal with phenol and BF_3 at a temperature in the range of 50 to 200°C .
6. The process of claim 5 wherein the temperature is between 70 and 120°C .
7. A process for recovering high yields of liquid constituents from coal at relatively mild conditions, which comprises passing BF_3 through a mixture of phenol and coal at a temperature in the range of 50 to 200°C .

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