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(54) IMPROVEMENTS IN OR RELATING TO THE SEPARATION OF SOLIDS FROM COAL PYROLYSIS AND GASIFICATION OILS

(71) We, THE LUMMUS COMPANY, a Corporation organised and existing under the Laws of the State of Delaware, United States of America, of 1515 Broad Street, Bloomfield, New Jersey 07003, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to the production of a liquid product from coal and more particularly, to the separation of solids from a liquid produced by the pyrolysis or gasification of coal.

In the pyrolysis or gasification of a coal, there is produced a liquid product which contains finely divided solids. In general, such solids are separated from the liquid product by filtration. Attempts to effect separation of such solids by gravity difference separation techniques, e.g. centrifugation or gravity settling, have not been overly successful as a result of the limited difference in specific gravity between the solids and such liquid products.

According to this invention there is provided a process for separating char-containing solids from a coal pyrolysis or gasification oil, comprising separating said char-containing solids from said oil by gravity difference separation in the presence of a promoter liquid, said promoter liquid having a characterisation factor of at least 9.75, a 5 volume percent distillation temperature of at least 250°F and a 95 volume percent distillation temperature of at least 350°F and no greater than 750°F, and recovering oil substantially free of solid material.

It is an advantage of the present invention that it makes it possible to separate solids from liquids produced by the pyrolysis or gasification of coal by making use of the specific gravity differences between the solids and liquids.

The liquid which is employed to enhance and promote the separation of insoluble material is generally a hydrocarbon liquid having a characterisation factor (K) of at least 9.75 and preferably at least 11.0 wherein:

$$K = \sqrt[3]{\frac{T_B}{G}}$$

wherein T_B is the molal average boiling point of the liquid (°R); and G is the specific gravity of the liquid (60°F/60°F).

The characterisation factor is an index of the aromaticity/paraffinicity of hydrocarbons and petroleum fractions as disclosed by Watson and Nelson Ind. Eng. Chem. *25* 880 (1933), with more paraffinic materials having higher values for the characterisation factor (K). The promoter liquid which is employed in the present invention is one which has a characterisation factor (K) in excess of 9.75.

The following Table provides representative characterisation Factors (K) for various materials:

TABLE

Anthracene	8.3
Naphthalene	8.4
425-500°F Coal Tar Distillate	8.8
550-900°F Coal Tar Distillate	9.1
600-900°F Coal Tar Distillate	9.0
400-450°F Coal Tar Distillate	9.4
Benzene	9.8
Tetrahydronaphthalene	9.8
o-xylene	10.3
Decahydronaphthalene	10.6
Cyclohexane	11.0
425-500°F Boiling Range Kerosene	11.9
n-Dodecylbenzene	12.0
Propylene Oligomers (pentamer)	12.2
Cetene	12.8
Tridecane	12.8
n-Hexane	12.9
Hexadecane or cetane	13.0

The liquid which is used to enhance and promote the separation of insoluble material is further characterised by a 5 volume percent distillation temperature of at least 250°F and a 95 volume percent distillation temperature of at least 350°F and no greater than 750°F. The promoter liquid preferably has a 5 volume percent distillation temperature of at least 310°F and most preferably of at least 400°F. The 95 volume percent distillation temperature is preferably no greater than 600°F. The most preferred promoter liquid has a 5 volume percent distillation temperature of at least 425°F and a 95 volume percent distillation temperature of no greater than 500°F. It is to be understood that the promoter liquid may be a single hydrocarbon, e.g. tetrahydronaphthalene, in which case the 5 volume percent and 95 volume percent distillation temperatures are the same, i.e. the hydrocarbon has a single boiling point. In such a case, the boiling point of the hydrocarbon must be at least 350°F in order to meet the requirement of a 5 volume percent distillation temperature of at least 250°F and a 95 volume percent distillation temperature of at least 350°F. The promoter liquid is preferably a blend or mixture of hydrocarbons.

The 5 volume percent and 95 volume percent distillation temperature may be conveniently determined by ASTM No. D 86-67 or No. D 1160 with the former being preferred for those liquids having a 95 volume percent distillation temperature below 600°F and the latter for those above 600°F. The methods for determining such temperatures are well known in the art and further details in this respect are not required for a full understanding of the invention. It is also to be understood that the reported temperatures are corrected to atmospheric pressure.

As representative examples of suitable promoter liquids, there may be mentioned: kerosene or kerosene fraction from paraffinic or mixed base crude oils; middle distillates, light gas oils and gas oil fractions from paraffinic or mixed based crude oils; alkyl benzenes with side chains containing 10 or more carbon atoms: paraffinic hydrocarbons containing more than 12 carbon atoms; white oils or white oil fraction derived from crude oils; alphaolefins containing more than 12 carbon atoms; fully hydrogenated naphthalenes and

substituted naphthalenes; propylene oligomers (pentamer and higher); and tetrahydronaphthalene, heavy naphtha fractions, etc. The most preferred liquids are kerosene fractions; white oils; fully hydrogenated naphthalenes and substituted naphthalenes; and tetrahydronaphthalene.

The amount of liquid promoter used for enhancing and promoting the separation of insoluble matter will vary with the particular liquid employed, and the coal used as starting material. As should be apparent to those skilled in the art, the amount of liquid promoter used should be minimised in order to reduce the overall costs of the process. It has been found that by using the liquid of controlled aromaticity, in accordance with the teachings of the present invention, the desired separation of insoluble material may be effected with modest amounts of liquid promoter. In general, the weight ratio of liquid promoter to coal-derived liquid may range from 0.2:1 to 3.0:1, preferably from 0.3:1 to 2.0:1 and, most preferably from 0.3:1 to 1.5:1. In using the preferred promoter liquid of the present invention which is a kerosene fraction having 5 percent and 95 percent volume distillation temperatures of 425°F and 500°F respectively, promoter liquid to coal-derived liquid weight ratios in the order of 0.3:1 to 0.6:1 have been particularly successful. It is to be understood, however, that greater amounts of liquid promoter may be employed, but the use of such greater amounts is uneconomical.

The solid-containing liquid derived from the pyrolysis of coal (a pyrolysis oil) is produced by pyrolysis procedures known in the art. In general, the coal is pyrolysed at a temperature in the order of from 550°F to 1550°F at a pressure of from 0 to 100 psig to produce a coal pyrolysis gas. The pyrolysis is generally effected in the presence of steam, nitrogen, oxygen or mixtures thereof. In general, the coal pyrolysis is effected in a plurality of low pressure fluidised beds to produce a pyrolysis gas and char, with the pyrolysis oil being recovered from the pyrolysis gas. Low pressure rotary kilns, as well as moving bed or flash techniques, can also be employed.

The pyrolysis oil, produced by the pyrolysis of coal, which is treated in accordance with the present invention includes fine char particles, as measured by quinoline insolubles (ASTM D-2318-66), with the quinoline insoluble content being from 2.5% to 15%, by weight. The ash content of the pyrolysis oil is in the order of from about 0.5% to 3.0%, by weight. In general, the pyrolysis oil contains from 5% to 50%, by weight, of non-distillable liquid on a quinoline insoluble free basis.

The pyrolysis oil which is recovered from the solid separation is substantially free of solid material; i.e. the quinoline insolubles is less than 0.2 wt.%, and generally less than 0.1 wt.%, with the ash content being less than 0.2 wt.% and generally less than 0.1 wt.%.

The solid-containing liquid recovered from the gasification of coal (a gasification oil) is produced by gasification procedures, known in the art. In general, gasification is effected at a temperature of from 1000°F to 2000°F, at a pressure of from 50 to 1200 psig. The gasification is generally effected in the presence of oxygen and/or steam. A coal gasification oil, containing coal solids, is generally recovered as a by-product.

The by-product coal gasification oil treated in accordance with the invention includes fine char particles, with the quinoline insolubles content being from 2.0% to 15.0%, by weight. The ash content of such gasification oil is in the order of from about 1.0% to 8.0%, by weight. In addition, the coal gasification oil contains from 5% to 50%, by weight, of a non-distillable liquid, on a quinoline insoluble free basis.

The gasification oil which is recovered from the solid separation is substantially free of solid material; i.e. the quinoline insoluble content is less than 0.2 wt.% and generally less than 0.1 wt.% and the ash content is less than 0.2 wt.%, generally less than 0.1 wt.%.

The separation of the insoluble material is effected by a technique which utilises the difference in specific gravity between the liquid and solids; e.g. centrifugation or gravity settling.

The separation of the insoluble material is generally effected at a temperature from 300°F to 600°F, preferably from 450°F to 600°F, and a pressure from 0 psig to 500 psig, preferably at a pressure from 0 psig to 300 psig. It is to be understood that higher pressures could be employed, but as should be apparent to those skilled in the art, lower pressures are preferred. The insoluble material is preferably separated by gravity settling with the substantially solid free liquid being recovered as an overflow and the insoluble material as underflow. In such gravity settling, the amount of underflow should be minimised in order to minimise the loss of heavier products in the underflow. The underflow withdrawal rate to obtain desired results is deemed to be within the scope of those skilled in the art. In general, such a rate is from about 20 to about 40 wt.% of the total feed. The residence time for such settling is generally in the order of from about 0.2 to about 6 hours, and preferably from about 0.2 to 3.0 hours.

The quinoline insoluble containing fraction recovered from the gravity difference separation can be subjected to a stripping operation to recover further valuable components thereof.

The invention will be further described with respect to the following examples:

Example 1

950 grams of de-ashing feedstock, properties of which are defined in Table 1, was preheated to 250°F and then charged into a 2300 ml electrically heated, stainless steel shaker bomb. The said shaker bomb is outfitted with a multiplicity of valved side draw off nozzles and a valved bottom draw off nozzle. The contents of the shaker bomb were heated with shaking to 540 ± 10°F. 335 gms of promoter liquid (characterisation factor of 10.8, 5 volume percent distillation temperature of 325°F and a 95 volume percent distillation temperature of 400°F) were then quickly added, and the admixture was again heated to 540 ± 10°F with shaking. The contents of the bomb were allowed to settle for two hours at 540 ± 10°F. An overflow product was withdrawn from one of the lower side draw off nozzles and collected in a tared 1 gallon container which was vented through a water cooled external reflux condenser. An underflow product was withdrawn through the bottom draw off nozzle and collected in a 1 qt. container which was also vented through an external reflux condenser. The amount of overflow product collected was 864 grams and its residual ash content and quinoline insolubles content were found to be 0.02 wt.% and < .05 wt.%, respectively.

TABLE 1

Coal pyrolysis oil

Specific Gravity @ 215/60°F	1.092
Specific Gravity @ 175/60°F	1.108
Pour Point, °F	90
Ash Content, Wt.%	1.64
Benzene Insolubles, wt.%	10.12
Quinoline Insolubles, wt.%	8.45
ASTM Vacuum Distillation Data Volume % Distilled	Overhead Temperature in °F Corrected to 760 mm Hg Absolute Pressure
0.0	348
5.0	433
10.0	474
20.0	571
30.0	652
40.0	740
50.0	825
60.0	890
70.0	945
76.0	971
Wt. % + 971°F Distillation Residue...	32.2 wt. %

Example II

1035 gms of preheated (250°F) de-ashing feedstock, whose properties are defined in Table 1, was charged to the electrically heated shaker bomb used in Example 1. The bomb's contents were heated with shaking to 540 ± 10°F. 302 gms of the same promoter liquid used in Example 1 were then quickly added, and the contents of the shaker bomb were again heated to 540 ± 10°F with shaking. The bomb's contents were then allowed to settle for two hours at 540 ± 10°F. An overflow product weighing 872 gms was withdrawn through an appropriate valved side draw-off nozzle. An underflow product was then withdrawn through the valved bottom nozzle and collected in a 1 qt. container. A representative sample of overflow product was found to contain an ash content and quinoline insolubles content of .05 wt.% and about .07 wt.%, respectively.

U.S. Patent Specification No. 3,856,675 discloses a process for separating ash-containing solids from a coal liquefaction product by gravity settling with a promoter liquid of the type used in the present invention; however, the coal liquefaction product which is treated in accordance with U.S. Patent Specification No. 3,856,675 has characteristics different from those of the liquids treated in accordance with the present invention. In particular, the coal liquefaction product has a quinoline insoluble content of from 5 to 15% with the ash content of said quinoline insolubles portion comprising from about 43 to 69 wt.% of the total quinoline insolubles. In contrast, the ash content of the quinoline insolubles fraction of the feeds treated in accordance with the present invention is about 20 wt.%. In addition, the absolute density of the particulate matter present in the pyrolysis and coal gasification oils is substantially less than the absolute density of the particulate matter present in the coal liquefaction product. As a result of such differences, it would be expected that it would not be possible to separate particulate matter from a pyrolysis or coal gasification oil by gravity difference separation, even when using a promoter liquid of the type described in U.S. Patent Specification No. 3,856,675.

The present invention is particularly advantageous in that solids can be separated from coal pyrolysis oils and from gasification oils by separation techniques which employ specific gravity difference, notwithstanding the limited difference in specific gravity between the solids and liquid.

WHAT WE CLAIM IS:

1. A process for separating char-containing solids from a coal pyrolysis or gasification oil, comprising separating said char-containing solids from said oil by gravity difference separation in the presence of a promoter liquid, said promoter liquid having a characterisation factor of at least 9.75°F, a 5 volume percent distillation temperature of at least 250°F and a 95 volume percent distillation temperature of at least 350°F and no greater than 750°F, and recovering oil substantially free of solid material.

2. A process according to claim 1 wherein the oil is a coal pyrolysis oil.

3. A process according to claim 1 wherein the oil is a coal gasification oil.

4. A process according to claim 1 or claim 2 or claim 3 wherein the oil has a quinoline insoluble content of from 2.5% to 15%, by weight, and an ash content of from 0.5% to 3.0%, by weight.

5. A process according to any one of the preceding claims wherein the separation is effected by gravity settling.

6. A process according to claim 4 wherein the oil substantially free of solid material is recovered as a net overflow having a quinoline insoluble content of less than 0.2 wt.% and an ash content of less than 0.2 wt.%.

7. A process according to any one of the preceding claims wherein the promoter liquid has a characterisation factor of at least 11.0, a 5 volume percent distillation temperature of at least 310°F and a 95 volume percent distillation temperature of no greater than 600°F.

8. A process according to any one of the preceding claims wherein the promoter liquid is employed in an amount to provide a liquid promoter to pyrolysis oil weight ratio of from 0.2:1 to 3.0:1.

9. A process according to any one of the preceding claims wherein the promoter liquid has a 5 volume percent distillation temperature of at least 425°F and a 95 volume percent distillation temperature of no greater than 500°F.

10. A process substantially as herein described in Example 1.
11. A process substantially as herein described in Example II.
12. A product of a process according to any one of the preceding claims.

FORRESTER KETLEY & CO.,
Chartered Patent Agents,
Forrester House,
52 Bounds Green Road,
London N11 2EY.
- and also at -
Rutland House,
148 Edmund Street,
Birmingham B3 2LD.
Scottish Provident Building,
29 St. Vincent Place,
Glasgow G1 2DT.
Agents for the Applicants.

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