Patented Dec. 30, 1952

2,623,843

UNITED STATES PATENT OFFICE

2,623,843

REFINING OF LIQUID OR SEMILIQUID CARBONACEOUS MATERIALS

Gerald E. Phillips, Cranford, N. J., assignor to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application August 31, 1949, Serial No. 113,470

4 Claims. (Cl. 196—56)

1

This invention relates to an improved method of treating or refining liquid or semi-liquid carbonaceous materials such as shale oil or petroleum residuum and particularly to processes which give improved yields of distillate oil.

Shale oil and heavy petroleum residuum have been subjected to pyrolytic treatments in order to increase the amount of distillate oil obtained therefrom. These processes, commonly termed coking, involve heating the petroleum residuum, shale oil or the like to temperatures of 700 to about 1100° F. and maintaining them at these temperatures until they are converted to gaseous material, liquid distillate fractions and solid coke. Since the gaseous material and coke are of limited usefulness or of less value than the distillate oils, it is obviously of advantage to so conduct the pyrolytic treatment of the shale oil or petroleum residuum as to obtain a maximum amount of distillate oil.

It is the object of this invention to provide the art with a novel method of treating shale oil or heavy petroleum residuum to increase the amount of distillate oil obtained therefrom.

It is also the object of this invention to provide the art with a method of pyrolytically treating or coking shale oil or heavy petroleum residuum which increases the yield of distillate oil primarily at the expense of coke formation.

These and other objects will appear more clearly from the detailed specification and claims which follow.

It has now been found that an improvement in liquid yields or distillate oils can be obtained by coking shale oil or petroleum residuum in the presence of spent shale fines.

The exact mechanism by which the shale fines effect this improvement in yield is not known but would appear to be catalytic in nature since an increase in liquid yield is not obtained when sand, an inert solid is substituted for the shale fines in the coking process. The catalytic effect of the shale fines in this coking operation is quite surprising since such fines do not appear to exert any appreciable effect in the cracking of ordinary gas oil. Moreover, other materials which have a catalytic effect in the cracking of gas oil have a detrimental effect upon the yield of distillate oil when used in the coking of shale oil or petroleum residuum.

The liquid to semi-liquid carbonaceous materials which can be advantageously coked in accordance with the present invention includes the total shale oil obtained upon retorting the shale or preferably the higher boiling portions thereof,

2

i. e., those portions boiling above 700° F. and petroleum residues obtained after subjecting petroleum crude oil to atmospheric or vacuum distillation to remove therefrom a major portion of the constituents which boil below about 800 to 900° F. at atmospheric pressure. The petroleum residues ordinarily comprise at most about 20 to 30 vol. % of the original oil and will have a boiling range above about 800 to 900° F.

The shale fines which may be utilized as catalysts in the coking operation in accordance with with the present invention may conveniently be the fines resulting from attrition of spent shale in the retorting or distillation of oil shale by the fluidized solids technique. The fines ordinarily represent from 30 to 70% of the spent shale and a representative size distribution of the spent shale fines is as follows:

Particle size:	Percent
Less than 10 microns	30–40
10–20 microns	30–40
20–40 microns	10–15
40+ microns	5–10

While particles of this size are desirable and conveniently obtained it will be understood that larger sized particles can also be used and that shale fines of any desired size can be obtained by grinding the spent shale. Such spent shale may contain up to around 10 to 12% of burnable carbonaceous material. The fines used in the coking operation in accordance with the present invention are recoverable for reuse in the coking operation by burning the coke or carbonaceous material that is deposited thereon during the coking operation. The amount of spent shale fines used may vary between about 2 to about 20, preferably from 5 to 15 pounds of fines per gallon of oil charged. Coking temperatures are ordinarily between about 700 to 1100° F., preferably from 950 to 1050° F. and are maintained until the distillate oil is driven off and the residue is converted to coke.

The following examples are illustrative of the present invention.

EXAMPLE 1

A sample of 18.5° API gravity shale oil obtained from fluid retorting of Colorado shale, was coked with and without the addition of 10 pounds of spent Colorado shale fines per gallon of shale oil. The following table presents yield and inspection data from these operations.

Table I

	Colorado shale oil from fluid retorting	Batch fire and steam coking of Colorado shale oil under atmospheric conditions—Maximum still temperature, 1,050 F.		
		Without fines	+10#/gallon spent shale fines	+10#/gallon spent burned fines [1]
Yield, weight percent on oil charged:				
Dry gas (C_3-)	----------	5.5	5.0	4.5
Distillate (C_4+)	----------	80.9	84.6	84.8
Coke	----------	13.6	10.4	10.7
Inspection of distillate:				
Gravity, °API	18.5	28.4	26.1	25.4
Aniline point, ° F	78	92	90	86
Say. vis. at 100° F., sec	378	39.7	44.8	46.7
Pour, °F	80	50	60	65
Conradson carbon, weight percent	8.61	0.24	0.52	0.82
Sulfur, weight percent	0.94	0.68	0.63	0.71
Nitrogen, weight percent	2.09	1.46	1.48	1.44
Inspection of coke:				
Carbon, weight percent	----------	85.3	----------	----------
Hydrogen, weight percent	----------	3.1	----------	----------

[1] Spent shale fines burned at 1,100° F. to remove burnable carbonaceous material (spent fines prior to burning contained 9.46% carbon and 0.53% hydrogen).

Coking in the presence of fines resulted in an improvment of around 4 weight percent of recoverable oil primarily at the expense of coke formation. The employment of burned spent shale fines offers only a slight yield improvement over raw spent fines. Coking in the presence of spent shale fines does not result in any degradation in product quality of the distillate over conventional coking.

EXAMPLE 2

A sample of 16% residuum from West Texas crude (10.3° API gravity) was coked without additives and then under the same conditions but in the presence of (*a*) spent Colorado shale fines, (*b*) fine sand, (*c*) silica gel, (*d*) bauxite and (*e*) reburned spent shale fines. The following table presents data from the above coking operations along with results from coking the residuum with no additives present.

The mechanism of the improved yield of liquid products due to the employment of spent shale fines appears to be catalytic in nature in that an increase in liquid yield is not obtained when sand, an inert solid, as well as other materials such as silica gel and bauxite which are noncatalytic for cracking of hydrocarbons is substituted for the shale fines in the coking process.

EXAMPLE 3

Since the effect of spent shale fines upon the coking of liquid to semi-liquid carbonaceous materials appeared to be catalytic in nature two additional coking runs were carried out employing an atmospheric residuum from West Texas crude (16% on crude) into which two synthetic silica-alumina gels, commonly used as catalysts for cracking gas oil fractions were added. The results obtained with these additives is summarized in the following table in which the results obtained without additives and with spent shale fines is also included to facilitate comparison:

Table III

	16% resid. (RD-50)	Batch fire+steam coking under atmospheric conditions — Maximum still temperature, 1,050 ° F.			
		Without additives	+10#/gal. spent shale fines	+10#/gal. fresh 12% Al_2O_3 silica alumina cat.	+10#/gal. fresh 20% Al_2O_3 silica alumina cat.
Yield, weight percent on oil charged:					
Dry gas (C_3-)	---------	5.3	9.1	6.9	8.6
Distillate (C_4+)	---------	74.1	75.7	67.0	67.3
Coke	---------	20.6	15.2	26.1	24.1
Inspection of distillate (not corr. for R. L. E.):					
Gravity, ° API	10.3	30.2	30.1	27.6	25.9
Pour, ° F	90	65	60	80	65
Sulfur, weight percent	3.51	1.57	1.50	1.71	2.11
Conradson carbon, weight percent	15.0	0.21	0.40	0.32	0.45
SSU vis. at 100 ° F	---------	43.8	40.6	54	42.0

Comparison of the results obtained with shale fines with the results obtained with the synthetic silica-alumina catalytic solids, indicates a liquid yield advantage of approximately 9 per cent for

Table II

	16% Residue from W. T. crude	Batch fire and steam coking of the 16% residuum under atmospheric conditions—Maximum still temperature, 1,050° F.							
		Without additives	+10#/gal. spent shale fines [a]	+10#/gal. spent shale fines [b]	+5#/gal. spent shale fines [b]	+10#/gal. sand fines [c]	+10#/gal. silica gel (thru 200 mesh)	+10#/gal. bauxite (20/60 mesh)	+10#/gal. reburned spent shale fines [d]
Yield, weight percent on oil charged:									
Dry gas (C_3-)	---------	5.3	9.1	8.7	4.6	6.0	12.6	7.0	5.9
Distillate (C_4-)	100.0	74.1	75.7	75.9	76.3	73.9	71.5	68.8	76.0
Coke	---------	20.6	15.2	15.3	19.1	20.1	15.9	24.2	18.1
Inspection of distillate:									
Gravity, ° API	10.3	30.2	30.1	---------	---------	29.9	---------	---------	---------
Aniline point, ° F	---------	137	133	---------	---------	133	---------	---------	---------
Sulfur, weight percent	3.51	1.57	1.50	---------	---------	1.52	---------	---------	---------
Pour, ° F	90	65	60	---------	---------	55	---------	---------	---------
Say. vis. at 100° F	---------	43.8	40.6	---------	---------	41.4	---------	---------	---------
Conradson carbon, weight percent	15.0	0.21	0.40	---------	---------	0.54	---------	---------	---------
Inspection of coke:									
Carbon, weight percent	---------	88.17	---------	---------	---------	---------	---------	---------	---------
Hydrogen, weight percent	---------	3.07	---------	---------	---------	---------	---------	---------	---------

[a] Spent shale fines from fluid retorting of Colorado oil shale in a single vessel pilot unit.
[b] Spent shale fines from fluid retorting of Colorado oil shale in a two vessel pilot unit.
[c] Sand employed in coking was 80 mesh and finer.
[d] Reburned product from previous operations employing spent shale fines.

the shale fines. This shows the specific character of the catalytic effect of spent shale fines in the coking of liquid to semi-liquid carbonaceous materials or residual stocks.

The foregoing description contains a limited number of embodiments of the present invention. It will be understood that numerous variations are possible without departing from the scope of the following claims.

What is claimed and desired to be secured by Letters Patent is:

1. The method which comprises mixing shale oil containing a substantial portion boiling above 700° F. with spent unburnt Colorado oil shale fines containing up to 12% of burnable carbonaceous material and having a particle size distribution range substantially below 40 microns, in a ratio of 2 to 20 pounds of the spent shale fines per gallon of the oil, and coking the resulting mixture at coking temperatures between about 700 and 1100° F. to drive off distillate oil and convert the residue to coke.

2. A method according to claim 2 wherein the ratio of shale fines to oil is from 5 to 15 pounds per gallon of the oil.

3. A method according to claim 1 wherein the coking temperature is between 950 and 1050° F.

4. A method according to claim 3 wherein the oil consists essentially of a shale oil fraction boiling above 700° F.

GERALD E. PHILLIPS.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,467,758	Day	Sept. 11, 1923
1,773,839	Zieley et al.	Aug. 26, 1930
1,945,530	Carrick	Feb. 6, 1934
2,284,581	Kuhl	May 26, 1942
2,423,674	Agren	July 8, 1947
2,487,788	Buchan	Nov. 15, 1949
2,489,702	Coast	Nov. 29, 1949