METHOD FOR THE PREPARATION OF SOLID PETROLEUM PITCH

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3 Claims. (Cl. 196—50)

This invention relates to a process for the preparation of solid pitches from petroleum crude oils and more particularly to a process of excellent operability for the preparation of solid petroleum pitches having very high softening points and especially suitable for use as solid fuels.

The demand for distillate products from the petroleum, notably for gasoline and domestic fuel oils, has increased tremendously during recent years and has made it necessary to refine increased quantities of crude oils. There has not, however, been a corresponding increase in the demand for heavy residual fuel oils. As a result of this unbalanced demand, the disposal of residual fuel oils at a profit has become increasingly difficult. At the present time, residual fuel oils, commonly designated as No. 6 fuel oil, are generally sold at a lower price than the crude oil from which they are derived.

Several methods have been employed to increase the percentage of distillate oils obtained from the crude oils. Deeper and deeper cuts have been made into the crude by vacuum distillation to increase the amount of distillate oil available for use as a catalytic cracking charge stock. The increase in distillate oils obtained by this method is limited. If still deeper cuts in the crude oil are attempted, in many instances the distillate is contaminated with metals and has a high carbon residue which makes it unsuitable for use as a catalytic cracking charge stock. In addition, the residual oil obtained from many deeper vacuum reductions is of such a high viscosity that it must be cut with a lighter oil, commonly designated as a cutter oil to produce a salable No. 6 fuel oil. The cutter oil, which is usually a catalytic furnace oil, in most instances could be used in a domestic furnace oil and its blending with the highly viscous residual oils seriously reduces its value.

Another process that has been employed to eliminate the unbalanced demand for distillate and residual oils is the delayed coking process in which no residual oil is produced. This process requires multiple coking drums, expensive controls and piping, and coke removal equipment. Since it is necessary to place one of the coking drums offstream periodically to remove coke, the process is expensive to operate. Moreover, the distillate oils obtained in the delayed coking process are cracked oils which are not as good charge stocks for catalytic cracking operations as virgin distillate oils or distillate oils which have only been lightly cracked.

Another possible method of increasing the ratio of distillate oils to residual oils produced in a refinery is to produce solid petroleum pitches from some of the residual oils. These pitches, unlike petroleum coke, are liquid at the operating temperatures employed and are therefore removed from the unit as a liquid. This eliminates the need of multiple reactors, as in delayed coking, which must be periodically shut down to remove coke. While the pitches are solid materials, they will flow and fuse or cake when subjected to continued pressure, even at temperatures well below their melting point.

Since extremely large amounts of pitches would be produced if a substantial part of the residual oils were converted to the production of pitches, it is probable that the most important use of the pitches would be as a solid fuel. It is essential, therefore, that the pitches be capable of withstanding the pressures and temperatures likely to be encountered when stored in large piles without caking.

It has been found that pitches having softening points, as determined by the ring and ball test method (ASTM D36), above about 350° F. may be stored without danger of caking in piles of heights ordinarily used for storing solid fuels at temperatures normally encountered. On the other hand, pitches having softening points below about 325° F. will cake or fuse when stored in high piles at temperatures of approximately 100° to 130° F., which are likely to be encountered.

The preparation of petroleum pitches of low softening point, for example softening points below about 300° F., has offered no serious difficulties. In general, such low softening point pitches may be prepared from any crude oil by processes having satisfactory operability characteristics. However, petroleum pitches having softening points below about 300° F. are not satisfactory for use as solid fuels in many instances because of their poor storage characteristics. The preparation of pitches having softening points above about 350° F. is far more difficult. Processes employing extremely deep vacuum reductions are costly because of the very large steam requirements. Processes employing severe visbreaking and deep atmospheric flashing both steam generally have poor operability characteristics.

The term "operability" is used to designate the ability of a process to continue operation for long periods without shut-downs for cleaning fouled equipment. An indication of the operability of a process in which high boiling residual products are formed is the amount of insoluble carbonaceous sediment in the residual product. If the sediment is high, operating difficulties resulting from fouling of the process equipment may be expected. Usually, the operability of a process may be improved by reducing the severity of high temperature operations, such as cracking or flashing, in the process, and particularly the time the hydrocarbons are subjected to high temperatures.

This invention resides in the preparation of petroleum pitches having softening points of approximately 350° F. or higher by visbreaking a residue containing at least about thirty percent asphaltenes and having a softening point of 160° F. or higher. The visbroken residue is then flashed at a temperature which is sufficiently low to avoid cracking in the flash tower to produce a pitch of the desired softening point as a bottoms product.

Figure 1 is a diagrammatic flow sheet of the process for the preparation of petroleum pitches according to this invention.

Figure 2 is a plot showing the relationship of the fusion temperature of the petroleum pitches under simulated storage conditions to the ring and ball softening point of the pitches.

The data from which Figure 2 of the drawings was prepared were obtained by subjecting pitch of the indicated softening point to a pressure corresponding to the pressure exerted by a pile of the pitch forty feet high for a period of twenty-four hours. The fusion temperature is the temperature at which the pitch caked when stored under pressure for the period of time. The data presented in Figure 2 of the drawings were obtained for a petroleum pitch prepared from a Baxterville (Mississippi) crude. The fusion temperature for pitches prepared from
other crude may vary slightly from the fusion temperature of the Baxterville pitch of corresponding softening point. However, in most cases, it will be within about 10° F. of the fusion temperature of the pitches of corresponding softening point prepared from the Baxterville pitches.

Referring to Figure 2 of the drawings, it will be noted that a petroleum pitch having a softening point of approximately 350° F. fuses at a temperature slightly above 140° F. In addition to their good storing qualities, petroleum pitches having softening points in excess of about 350° F. are desirable as catalytic cracking materials and will be preferred to most pitches below that temperature because of their lower mastication point, ease of handling, and freedom from pitch inclusions. However, the petroleum pitches of this class are characterized by a high viscosity which has a decided effect upon the operation of the cracking unit, particularly in connection with the atomizing equipment. The effective flash temperature of the pitch should be considered as one of the most important factors in the selection of a cracking material.

The vacuum distillation of petroleum pitches is a conventional operation and will be described in general terms. The vacuum tower is provided with two or more trays or baffle plates, the lower portion of the tower being used for the removal of gases and the upper portion for the withdrawal of the pitch. The pitch is delivered to the vacuum tower from the atmospheric distillation tower by means of a pump, and is then passed through a preheater, or heated coils, before entering the vacuum tower. The pitch is then subjected to a vacuum of about 20 to 30 inches of mercury in the upper part of the tower, and the temperature is gradually raised to about 1300° F. The pitch is then passed through a series of coils which are maintained at a temperature of about 1030° F., corrected to 760 mm. of mercury pressure, for the purpose of reducing the viscosity of the pitch to a value suitable for atomization. The pitch is then passed through a series of atomizing nozzles, and the resulting spray is passed into the catalytic cracking unit, where it is subjected to a pressure of about 200 pounds per square inch, and a temperature of about 1500° F. The resulting gas is passed through coolers and condensers, where it is cooled to a temperature of about 100° F., and is then passed to the catalytic cracking unit.

The vacuum distillation of petroleum pitches is a conventional operation and will be described in general terms. The vacuum tower is provided with two or more trays or baffle plates, the lower portion of the tower being used for the removal of gases and the upper portion for the withdrawal of the pitch. The pitch is delivered to the vacuum tower from the atmospheric distillation tower by means of a pump, and is then passed through a preheater, or heated coils, before entering the vacuum tower. The pitch is then subjected to a vacuum of about 20 to 30 inches of mercury in the upper part of the tower, and the temperature is gradually raised to about 1300° F. The pitch is then passed through a series of coils which are maintained at a temperature of about 1030° F., corrected to 760 mm. of mercury pressure, for the purpose of reducing the viscosity of the pitch to a value suitable for atomization. The pitch is then passed through a series of atomizing nozzles, and the resulting spray is passed into the catalytic cracking unit, where it is subjected to a pressure of about 200 pounds per square inch, and a temperature of about 1500° F. The resulting gas is passed through coolers and condensers, where it is cooled to a temperature of about 100° F., and is then passed to the catalytic cracking unit.
in line 26 to a pressure suitable for visbreaking and pumps the residual oil through heating coils 36 in a visbreaking furnace 32. The temperature of the residual oil is increased to a temperature of 900° to 950° F. in the furnace 32. Visbreaking furnace 36 is operated to crack the residual oil in a short-time operation at relatively high temperature. The conversion to 400° F. end point gasoline does not exceed approximately fifteen percent of the residual oil.

The effluent from the visbreaking furnace is delivered through a line 34 and a pressure reducing valve 35 into an atmospheric flash tower 36 in which cracked heavy gas oil and lighter fractions are stripped overhead. Vaporization of the overhead products from the flash tower 36 may be aided by the introduction of steam through a line 38. The petroleum pitches of this invention are withdrawn from the bottom of the tower 36 and delivered to storage through a line 40.

The distillate from atmospheric flash tower 36 is delivered overhead through a line 42 to an atmospheric distillation tower 44. Distillation tower 44 is of conventional design and operation for the separation of the lower boiling fractions from a heavy bottoms oil, ordinarily used in No. 6 fuel oil, which is withdrawn from the tower 44 through the line 46. In the distillation tower 44 illustrated in the drawings, side streams of gasoline, naptha and gas oil are withdrawn through lines 48, 50, and 52, respectively, and gas is taken off overhead through a line 54.

In order to control the temperature of the material discharged from the visbreaking furnace 32 to prevent further cracking, a quench stream may be introduced into line 34 through line 56. The quench stream may be of steam, naptha, gasoline, or gas oil. In the flow sheet illustrated in Figure 1 of the drawings, a recycle line 58 is provided to return a quench stream from the distillation tower 44 to line 56 and then into line 34.

Petroleum pitches were prepared according to this invention from the residues of several crudes. The results of the runs for the production of petroleum pitches are set forth in the following table.

TABLE I

<table>
<thead>
<tr>
<th>Crude oil source</th>
<th>Western Venezuela</th>
<th>Eastern Venezuelan</th>
<th>Mars, hvy.</th>
<th>Baxterville</th>
<th>Kigwalla</th>
<th>Mersey</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run No.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Charge stock, percent of crude</td>
<td>9.7</td>
<td>11.6</td>
<td>11.6</td>
<td>11.6</td>
<td>12.6</td>
<td>46.2</td>
</tr>
<tr>
<td>Gravity, API</td>
<td>38°</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Softening point, ° F.</td>
<td>218</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>180</td>
<td>162</td>
</tr>
<tr>
<td>Asphalten content, weight percent</td>
<td>22.4</td>
<td>32.4</td>
<td>32.4</td>
<td>32.4</td>
<td>20.4</td>
<td>27.2</td>
</tr>
</tbody>
</table>

Operating conditions: Furnace temp., ° F | 925 | 925 | 925 | 925 | 925 | 925 | 925 | 925 | 925 |
Furnace pressure, p.s.i.g | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 | 200 |
Furnace oil vol. above 700 | 800 | 800 | 800 | 800 | 800 | 800 |
Flash temp., ° F | 700 | 700 | 700 | 700 | 700 | 700 | 700 | 700 | 700 |
Stripping steam, lb./bbll. of charge | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
Flame props: Specific gravity solid state, ° F | 1.29 | 1.54 | 1.43 | 1.37 | 1.05 | 1.21 | 1.10 | 1.17 | 1.05 | 1.21 | 1.1 |
Softening point, ° F | 347 | 344 | 309 | 280 | 245 | 341 | 337 | 364 | 342 | 356 | 300 |

* Propane asphalt.

It will be noted from the data presented in the above table that the softening point of the pitch will depend to a important extent upon the crude oil from which the charge stock to the visbreaking operation was derived. For example, pitches having softening points above 350° F. may be prepared from Baxterville and Mersey crudes with visbreaking temperatures of 925° F. without the addition of steam in the atmospheric flash distillation following the visbreaking, even though the residue constitutes a long cut of the crude.

The softening point of the residue charged to the visbreaker is of extreme importance in determining the softening point of the pitch obtained. A comparison of run No. 2 and run No. 5 shows that an increase in the softening point of the residue of an Eastern Venezuela crude from 165° to 180° F. results in an increase in the softening point of the resultant petroleum pitch even though the steam introduced into the atmospheric distillation tower was reduced from 79.9 to 43.7 pounds per barrel of charge. Both residues were visbroken at the same temperature prior to the flash distillation. The softening point of the residue charged to the visbreaker is additionally important to the operability of the process. If lower softening point residues are charged to the visbreaker, the amount of heavy oil introduced into the atmospheric flash tower is increased. A pitch of the desired softening point can then be obtained either by markedly increasing the temperature of the atmospheric flash distillation which results in the formation of coke in the flash tower or by increasing the steam rate which may be limited by the design of the equipment.

The softening point of the pitch also depends upon the severity of the visbreaking. For example, it will be noted from run No. 2 and run No. 3 that increasing the visbreaking temperature of an Eastern Venezuela residue having a softening point of 180° F. from 925° to 940° F. allows a reduction in the steam required in the flash tower from 44 pounds per barrel of charge to 0 without appreciably reducing the softening point of the pitch.

The softening point of the pitch is also determined by the temperature and steam rate employed in the atmospheric flash distillation of the visbroken residue. In the examples set forth in the table, the temperature in the flash tower was substantially constant in all runs with the exception of the run in which residues from Baxterville and Mersey crudes were the charge stocks. The steam introduced into the flash tower is then a measure of the effect of increased severity of flash conditions. As shown by runs Nos. 3 and 4, an increase in the steam introduced into the flash tower from 0 to 17.9 pounds per barrel of charge resulted in an increase of 20° F. in the softening point of the pitch, even though the residue charged to the visbreaker and the visbreaking conditions were the same in both instances.

This invention has been described for the preparation of pitches by visbreaking residues obtained by distillation of certain crudes. Residues obtained by other
procedures such as those using selective solvents to separate heavy asphaltic residues from the remainder of the crude may also be used. An example of a suitable process for the preparation of the charge stock to the visbreaker is propane deasphalting. Residues prepared by propane deasphalting, like those prepared by distillation methods, must have a softening point above 160° F. and an asphaltene content above about thirty percent, to allow the preparation of pitches of the desired softening point in a process of satisfactory operability. Data for an experimental run on a residue obtained by propane deasphalting a Kuwait crude are presented under run No. 10 of the table. In that run, the asphaltene content of the residue was slightly below thirty percent which made it necessary to employ very severe visbreaking conditions, as indicated by the high furnace temperature and the high specific gravity of the pitch, to obtain a pitch of the desired softening point. The conditions of run No. 10 are near the borderline of satisfactory conditions. It is probable that a process employing the visbreaking conditions of run No. 10 and using the residue of that run for charge stock to the visbreaking would not be satisfactory for continuous operation and it would be desirable to prepare a residue of higher asphaltene content for use as a charge stock to the visbreaker. The visbreaking of high softening point residues of selected crude oils and subsequent flash distillation of the visbroken residuum according to the method here described produces a petroleum pitch of a very high softening point. Because of the very high softening point of the pitch, it may be stored under the pressure and at the temperatures commonly encountered in the storage of solid fuels without fusing. Moreover, the process of this invention avoids conditions encouraging the formation of coke, and as a result has excellent operability characteristics.

We claim:

1. A process for the preparation of a petroleum pitch having a ring and ball softening point above about 350° F., a specific gravity below about 1.20 and substantially complete solubility in trichloroethylene and carbon disulfide comprising reducing an asphaltic base petroleum crude oil to form a residue having an asphaltene content above about thirty percent and a softening point above 160° F., severely visbreaking the residue in a once-through short-time coil operation at a temperature of 900° to 950° F., quenching the visbroken material as it is discharged from the visbreaking coil, and flashing the visbroken residue at substantially atmospheric pressure at a temperature not exceeding 810° F. to produce a petroleum pitch as a bottoms product.

2. A process for the preparation of petroleum pitches having ring and ball softening points above about 350° F., consisting essentially of distilling an asphaltic base petroleum crude oil in an atmospheric distillation to produce a bottoms fraction, deeply vacuum distilling the bottoms fraction to produce a residue having a ring and ball softening point above 160° F. and an asphaltene content of at least about 30 percent, thermally cracking the residue in an onestream, coil-only operation at a temperature of about 900° to 950° F. to convert about 15 percent of the residue to 400° F. end point gasoline and lighter fractions, and flashing the visbroken residue at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

3. A process for the preparation of solid petroleum pitches having ring and ball softening points above about 350° F. consisting essentially of separating a residue having a ring and ball softening point above 160° F. and an asphaltene content in excess of about 30 percent from an asphaltic base petroleum crude oil, severely visbreaking the residue in a once-through, coil-only thermal cracking operation at a temperature of about 900° to 950° F., and flashing the visbroken residue at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

4. A process as set forth in claim 3 in which steam is added during flashing of the visbroken residue.

5. A process as set forth in claim 3 in which the visbroken residue is quenched prior to flashing at substantially atmospheric pressure.

6. A process for the preparation of petroleum pitches having ring and ball softening points above about 350° F., comprising distilling an asphaltic base petroleum crude oil in an atmospheric distillation to produce a bottoms fraction, vacuum distilling the bottoms fraction to produce a residue having a ring and ball softening point above about 160° F. and an asphaltene content of at least about 30 percent, severely visbreaking the residue in a coil-only thermal cracking operation at a temperature of about 900° to 950° F. in which the coil volume above 750° F. is approximately 0.012 to 0.015 of the flow of throughput per day to yield about 15% 400° F. end point gasoline and lighter fractions based on the residue, and flashing the visbroken residue at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

7. A process for the preparation of petroleum pitches having ring and ball softening points above about 350° F., comprising distilling an asphaltic base petroleum crude oil in an atmospheric distillation to produce a bottoms fraction, extracting the bottoms fraction with a selective solvent to produce a residue having a ring and ball softening point above about 160° F. and an asphaltene content of at least about 30 percent, severely visbreaking the residue in a coil-only, once-through thermal cracking operation at a temperature of about 900° to 950° F. in which cracking to 400° F. end point gasolines is limited to about 15 percent, and flashing the visbroken residue at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

8. A process for the preparation of a petroleum pitch substantially completely soluble in trichloroethylene and having a ring and ball softening point above about 350° F. and a specific gravity below about 1.20, comprising distilling an asphaltic base petroleum crude oil in an atmospheric distillation to produce a bottoms fraction, vacuum distilling the bottoms fraction at conditions of temperature and pressure adapted to produce a residue having a ring and ball softening point above about 160° F. and an asphaltene content above about 30 percent, severely visbreaking the residue in a coil thermal cracking operation at a temperature of about 900° F. to 950° F. to form about 15%, based on the residue, 400° F. end point gasoline and lighter fractions, and flashing the thermally cracked product in the presence of added steam and at substantially atmospheric pressure and a temperature below 810° F. to produce the pitch as a bottoms product.

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