

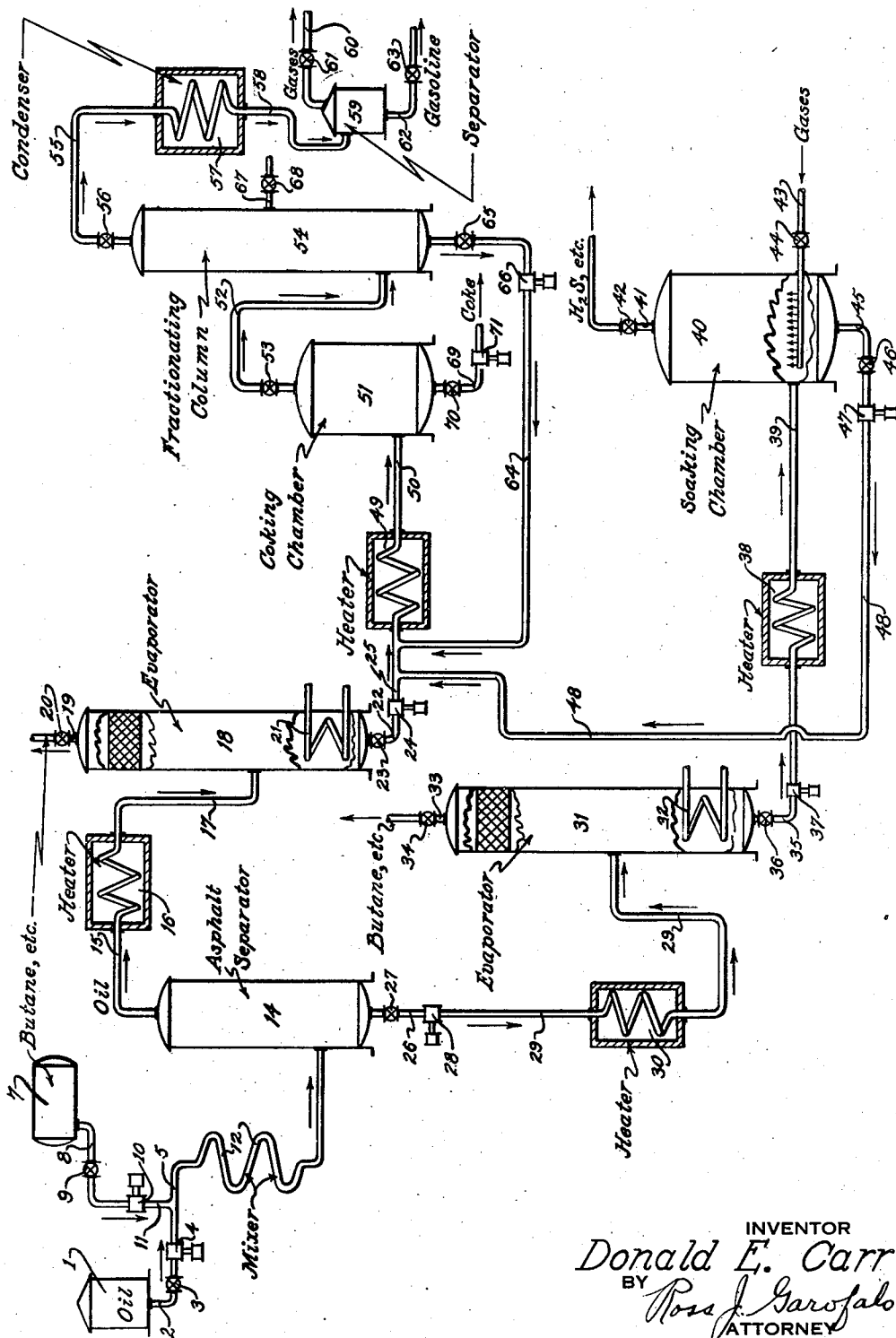
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PROCESS FOR TREATING OILS

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PROCESS FOR TREATING OILS

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This invention relates to a process for separating sulfur from oils. The invention relates particularly to a process for desulfurizing high sulfur residua obtained from sulfur bearing crude oils preparatory to subjecting the residua to coking operations to obtain coking distillates.

In recent years, considerable attention has been directed by the petroleum refiners to the conversion of high asphalt content crude oil residue to obtain motor fuels of the gasoline type. One of the methods employed for obtaining motor fuels or distillates which may be converted by cracking into motor fuels is the so-called coking distillation method which consists essentially in subjecting the heavy petroleum residuum to sufficient heat as is necessary to remove substantially all of the vaporizable oil constituents from the residuum leaving a solid dry coke as an undistilled bottoms.

However, the residues primarily used for coking operations often contain fractions of high sulfur content which vaporize with the distillates during coking and are thus retained in the distillates. This, of course, results in a low grade motor fuel which must be treated to remove the sulfur to produce an acceptable motor fuel.

Experimentation has indicated that high sulfur residuum, such as that obtained from Santa Maria Valley crude oil, may be treated at relatively low non-coking temperatures to remove a considerable amount of sulfur in the form of hydrogen sulfide. Further study of this phenomenon under closely controlled conditions has shown that the loss of sulfur occurs almost entirely in the asphaltene fraction of the residuum. Under properly chosen temperature conditions, the amount of this fraction is not substantially changed and little coke is formed, but the sulfur content can be reduced considerably; whereas, the sulfur content of the oil fraction remains substantially constant. On the other hand, if conditions are selected which also result in the desulfurization of the oil fraction, the asphaltene fraction is found to coke badly.

I have discovered that the sulfur content of a very heavy high sulfur residuum may be considerably reduced by a selective thermal treatment of the residuum in analogy with the selective multiple coil cracking of crudes or reduced crudes wherein the crude or reduced crude is typically separated by distillation of such fractions as gasoline which may, if desired, be put through a high temperature reforming coil, as gas oil, which may be put through a medium temperature cracking coil and as fuel oil re-

siduum, which may be put through a low temperature viscosity reducing coil. As a matter of fact, the asphaltenes and oils present in heavy residuum are often more divergent in molecular weight and thermal stability than gasoline, gas oil and residuum fractions employed in the usual cracking process and therefore would require even more selective conditions to give optimum results.

In order to accomplish such a selective pyrolysis with heavy residues consisting of asphaltenes, resins and heavy lubricating oils, I subject the heavy residue to a preliminary separation of these constituents by means of solvent capable of dissolving the heavy lubricating oils and resins leaving the asphaltenes as an undissolved fraction. Preferably, the separation of the heavy residue by means of the solvent is carried out under such conditions as to produce an undissolved asphaltene fraction of about 350° F. melting point and a resinous oil which is liquid at room temperature. The asphaltene fraction is next subjected, either with or without prior removal of the solvent associated with this fraction, to cracking under controlled temperature conditions, preferably at about 675° F. for a rather extended soaking period. The main function of this pyrolysis is to eliminate a large portion of the sulfur in the asphaltenes as hydrogen sulfide which is separated along with other permanent gases from condensable distillates by appropriate methods. The partly desulfurized bottoms may then be subjected to coking, if desired, after adding the extracted oil fraction to these bottoms thus obtaining coking distillates of much lower sulfur content than would have been obtained without preliminary low temperature pyrolysis. Any of the coking methods now known or employed may be used. I prefer that the so-called delayed method consisting in passing the bottoms through a heating coil into a coking chamber, the heat input to the asphaltenes in the heating coil being sufficient to effect the coking when the heated asphaltenes are passed into the coking chamber.

Instead of adding the extracted oil fractions directly to the asphaltene fraction which is subjected to desulfurization, the extracted oil fraction may be separately treated by any of the well known desulfurization methods such as, for example, treatment with sulfuric acid, Edeleanu treatment with liquid sulfur dioxide, phenol treatment, etc. The thus partly desulfurized oil may then be blended with the partly desulfurized

asphaltene fraction and the blended materials then passed to the coking operation.

If desired, this extracted oil may be separately cracked to produce gasoline fractions and heavy oil fractions and the latter may either be blended with the desulfurized asphaltene fraction passing to the coking operation or it may again be extracted to separate it into oily constituents and an asphaltic fraction. The latter may be cycled to the asphaltene fraction passing to the desulfurization operation or if desired, the entire heavy oil fraction produced from the cracking operation to produce the gasoline may be recycled to the oil undergoing extraction in which case the oil contained in the heavy oil fraction will be recycled together with the extracted oil from the fresh charge to the cracking operation and the asphaltene fraction contained in the heavy oil fraction will be recycled together with the asphaltene fraction from the fresh charge to the desulfurization and coking stages.

In order to effect the separation of the heavy residuum into asphaltenes and heavy resinous lubricating oil, the heavy residuum is mixed with an appropriate quantity of solvent such as, for example, one to six volumes of liquid butane at a temperature of about 150° F. under a pressure of 125 lbs. per square inch and the mixture is allowed to stratify into two layers, i. e. an upper layer of the resinous oil dissolved in the solvent and a lower layer of the asphaltenes containing some oil and solvent. The upper layer is decanted from the asphaltene layer and each layer may then be heated to a temperature sufficient to distill the solvent contained therewith.

As solvents adapted to separate the heavy residuum into the aforementioned asphaltene and resinous lubricating oil fractions, I prefer to use a liquefied normally gaseous hydrocarbon, such as ethane, ethylene, propane, propylene, butane, butylene and iso-butane or mixtures thereof. Butane is a preferred solvent for this purpose. However, I may employ such other solvents as pentane, hexane, gasoline, naphtha, alcohol, ether, mixtures of alcohol and ether, acetone and other solvents capable of dissolving the oil and resins but not the asphaltenes. It will be understood that the amount of solvent employed and the operating temperature and pressure conditions must be controlled to suit the particular solvent and the stock being treated in order that a proper solution of only the resinous oil constituents is obtained.

It is thus an object of my invention to remove sulfur from heavy asphaltic oils. It is a specific object of my invention to remove sulfur from the asphaltene fraction of the heavy asphaltic oil by pyrolysis.

Another object of my invention resides in separating the heavy asphaltic oil into an asphaltene fraction and a resinous oil fraction and separately desulfurizing the asphaltene fraction by pyrolysis. Another object is to subject the desulfurized asphaltene fraction to a coking operation preferably after adding thereto the separated resinous oil fraction. A specific object of the invention is to effect the separation of the oily fraction from the asphaltene fraction by means of a solvent.

Other objects, features and advantages of my invention will be apparent from the following description of my invention taken from the drawing which represents a schematic arrangement of

apparatus for carrying out a preferred embodiment of my invention.

Referring to the drawing, a heavy road oil of asphalt produced by distilling a sulfur-containing asphalt base crude oil to separate gasoline, kerosene, gas oil to leave a residue consisting of asphaltenes, resins and heavy lubricating oils is taken from storage tank 1 via line 2 controlled by valve 3 and is pumped by pump 4 into line 5. A light hydrocarbon solvent such as butane is taken from tank 7 via line 8 controlled by valve 9 and pumped by pump 10 through line 11 into line 5. The amount of butane introduced into line 5 will depend upon the characteristics of the oil and the degree to which it is topped. Generally, however, from one to six volumes of the butane is mixed with the oil. The mixture then passes through mixing or turbulence coil 12 into asphalt separator 14 where sufficient time is provided to permit a heavy or hard asphalt to settle or stratify from the solution of oil and butane. The supernatant solution of oil and butane is withdrawn from the top of the asphalt separator via line 15 and passed through heater 16 where the oil is heated to a sufficiently elevated temperature to vaporize the butane when passed into the evaporator 18 via line 17. In evaporator 18, the butane is vaporized from the oil and is withdrawn via line 19 controlled by valve 20. Additional heat may be provided in evaporator 18 by circulating steam through closed coil 21. The de-butanized oil at the bottom of the evaporator 18 is withdrawn via line 22 controlled by valve 23 and is pumped into line 25 by pump 24.

The asphalt settling at the bottom of the asphalt separator 14 is withdrawn via line 26 controlled by valve 27 and is pumped by pump 28 through line 29 and heater 30 where it is heated to a sufficiently high temperature to melt the asphalt and vaporize residual butane when passed into evaporator 31. Vaporization of butane in evaporator 31 is aided by superheated steam circulated through closed coil 32. The overhead from evaporator 31 is withdrawn via line 33 controlled by valve 34. This overhead may be combined with the overhead from evaporator 18 which may then be compressed under pressure sufficient to liquefy the butane, cooled and returned to butane storage tank 7.

The de-butanized asphalt at the bottom of the evaporator 31 is withdrawn via line 35 controlled by valve 36 and is pumped by means of pump 37 through heater 38 where the asphalt is heated to a temperature of about 700° F. and is passed via line 39 into the soaking chamber 40 where the asphalt is subjected to cracking under controlled temperature conditions, the temperature preferably being held to 670° F. for a rather extended soaking period. In chamber 40, the pyrolytic action results in the removal of sulphur in the form of hydrogen sulphide from the asphaltenes as explained above. The hydrogen sulphide is removed via line 41 controlled by valve 42. Part of the necessary heat input during this soaking period may be conveniently provided by the introduction of hot gases via line 43 controlled by valve 44. If desired, hot volatile fractions from the pyrolysis of the oil fraction described hereafter or from similar volatile fractions of simultaneous gas-oil cracking or reforming processes may be introduced into the asphalt in the soaking chamber 40. The introduction of such gases under the surface of the asphalt serves also to agitate the material and facilitate the evaporation of any distillable fractions formed

during the pyrolysis of the asphalt. If desired, the gases issuing from the soaking chamber via line 41 may be subjected to absorption to remove the hydrogen sulphide and the remaining gases containing condensable hydrocarbons may be subjected to condensation to recover any oil fractions present in the gases.

The desulphurized asphalt may be withdrawn via line 45 controlled by valve 46 and pumped by pump 47 through line 48 into line 25 where it combines with the oil from evaporator 18. The blend of asphalt and oil is then heated in heater 49 to a coking temperature of approximately 900° F. and is passed via line 50 into the coking chamber 51 where the oil is subjected to coking by any of the well known coking methods. The coking distillates produced in the coking chamber are withdrawn via line 52 controlled by valve 53 and subjected to fractionation in fractioning column 54, gasoline vapors and light gases being removed from the column via line 55 controlled by valve 56, condensed in condenser 57 and passed via line 58 into separator 59 where uncondensed gases are withdrawn via line 60 controlled by valve 61. Gasoline is withdrawn via line 62 controlled by valve 63. Heavier oil fractions may be recycled to line 25 by pump 66 via line 64 controlled by valve 65. Also a light gas oil fraction suitable for cracking may be withdrawn from the side of the column via line 67 controlled by valve 68 and may be passed to suitable cracking apparatus not shown. If desired, this fraction may also be recycled to line 25 and passed through the heater 49 into the coking chamber 51 where it is subjected to further conversion into lighter fractions.

The coke formed in chamber 51 may be removed by any of the well known means and withdrawn from the chamber via line 69 controlled by valve 70 and pump 71.

In the foregoing description of the invention as taken from the drawing, the oil phase or the asphalt phase or both phases removed from the asphalt separator 14 may be passed directly through the heaters 38 and 49 and these fractions may thus be heated in the presence of the butane instead of first stripping the butane from these phases. The presence of these light gases during the soaking or coking operations inhibits the formation of like gases from the oil fractions being subjected to the elevated temperatures under pressure.

The following is a specific example of one embodiment of my invention: A California crude oil obtained from Santa Maria Valley having a sulphur content of approximately 4.5% was distilled to remove gasoline, kerosene, gas oil, to produce a heavy residue of road oil consistency and having a melting point of approximately 110° F. The asphalt residue had a sulphur content of approximately 5.5%. Approximately six volumes of liquid butane under pressure was mixed with a portion of the asphalt residue at a temperature of 150° F. and the mixture was allowed to stratify into two layers. The lower layer consisted of a hard asphalt of about 350° F. melting point. This fraction was then heated to remove the liquid butane contained in it and was then subjected to cracking under controlled conditions maintaining a temperature of 675° F. for approximately three hours to remove hydrogen sulphide. The upper phase from the asphalt separator consisting of butane and resinous lubricating oil was stripped of butane and was then blended with the desulphurized as-

phalt. A test on the blend now showed approximately 3.8% of sulphur. This blend was then heated to approximately 900° F. and passed into a coking chamber to obtain a coking distillate having approximately 2.9% of sulphur.

In another run, a portion of the heavy road oil containing the 5.5% of sulphur was subjected directly to the aforementioned coking operation to produce a coking distillate. This coking distillate contained approximately 3.9% of sulphur.

The foregoing description of my invention is not to be taken as limiting my invention but merely as illustrative of one mode of carrying it out as many variations may be made thereon as will be recognized by those skilled in the art which are within the scope of the following claims.

I claim:

1. A process for separating sulfur from sulfur-bearing asphaltic oils which comprises separating said asphaltic oil into an asphaltene fraction and an oil fraction and heating said asphaltene fraction in the absence of added hydrogen at a temperature of approximately 675° F. for a sufficient period of time to separate sulfur in the form of hydrogen sulfide.

2. A process for separating sulfur from sulfur-bearing asphaltic oils which comprises commingling said asphaltic oil with a solvent in which the asphaltene fraction contained in said asphaltic oil is insoluble in said solvent but in which the oil fraction contained in said asphaltic oil is soluble, separating a solution of oil and solvent from an undissolved asphaltene fraction and heating said asphaltene fraction in the absence of added hydrogen at a temperature of approximately 675° F. for a sufficient period of time to separate sulfur in the form of hydrogen sulfide.

3. A process as in claim 2 in which the solvent comprises a liquefied normally gaseous hydrocarbon.

4. A process as in claim 2 in which the solvent comprises liquid butane.

5. A process for the coking distillation of sulfur bearing asphaltic oils which comprises separating said asphaltic oil into an asphaltene fraction and an oil fraction, heating said asphaltene fraction at a temperature sufficiently elevated to separate sulfur in the form of hydrogen sulfide, blending said heated asphaltene fraction with said separated oil fraction and subjecting said blend of asphaltene and oil fractions to coking distillation.

6. A process for the coking distillation of sulfur bearing asphaltic oil which comprises commingling said asphaltic oil with a solvent in which the asphaltene fraction contained in said asphaltic oil is insoluble but in which the oil fraction contained in said asphaltic oil is soluble, separating a solution of oil and solvent from an undissolved asphaltic fraction, heating said asphaltene fraction at a temperature sufficiently elevated to separate sulfur in the form of hydrogen sulfide, blending said heated asphaltene fraction with said separated oil fraction and subjecting said blend of asphaltene and oil fractions to coking distillation.

7. A process for the coking distillation of sulfur bearing asphaltic oils which comprises separating said asphaltic oil into an asphaltene fraction and an oil fraction, separately separating sulfur from said asphaltene and oil fractions, blending said treated asphaltene and oil frac-

tions and subjecting said blend of asphaltene and oil fraction to coking distillation.

8. A process for the coking distillation of sulfur bearing asphaltic oils which comprises separating said asphaltic oil into an asphaltene fraction and an oil fraction, separately heating said asphaltene fraction at a temperature sufficiently elevated to separate sulfur in the form

5 of hydrogen sulfide, separately cracking said oil fraction to produce a gasoline fraction and a heavy oil fraction, blending said heavy oil fraction with said asphaltene fraction and subjecting said blend of heavy oil and asphaltene fractions to coking distillation.

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