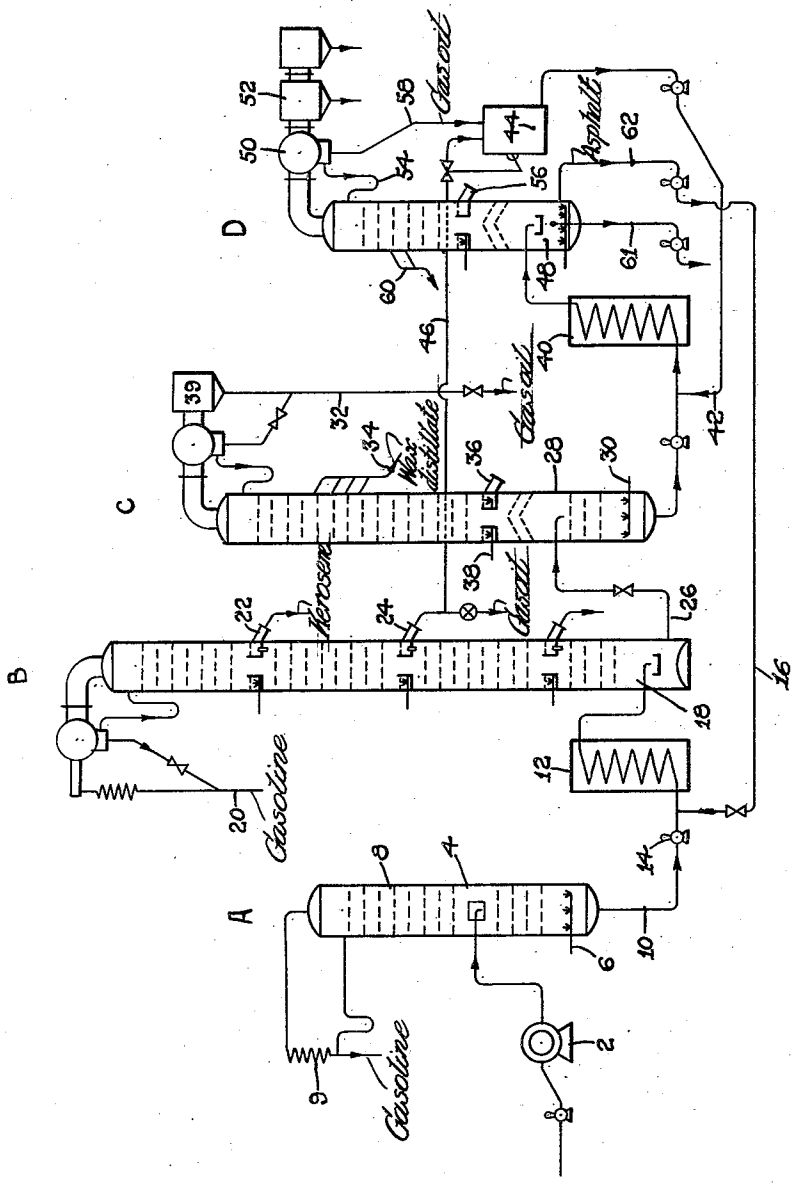
Feb. 11, 1936. G. B. COUBROUGH 2,030,281

METHOD FOR FRACTIONATING PETROLEUM MIXTURES

Filed Dec. 22, 1933



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Patented Feb. 11, 1936 2,030,281

UNITED STATES PATENT OFFICE

2,030,281

METHOD FOR FRACTIONATING PETROLEUM MIXTURES

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Application December 22, 1933, Serial No. 703,592

12 Claims. (Cl. 196—94)

The present invention relates to methods for fractionating petroleum mixtures.

The principal object of the present invention is to provide a method whereby the distillation may be closely controlled, whereby the temperature of distillation in any stage may be limited to such a value that undesirable decomposition does not occur, and whereby the maximum economy of installation and operation may be obtained.

With this and other objects in view, as will hereinafter appear, the present invention consists in the method hereinafter described and particularly defined in the claims.

The accompanying drawing is a diagrammatic view of the preferred form of plant for practicing the present invention.

The illustrated embodiment of the invention comprises a series of four columns A, B, C, and D in which the crude oil is successively distilled to obtain bottoms of progressively higher boiling points.

Crude oil heated in tubular heat exchangers is fed to column A where a light gasoline fraction is removed as an overhead product. For this heating step, the heat available from any suitable hot stream is utilized, it being desirable to avoid the use of a fired still in the first distillation step. The oil heated by the exchanger **2** is discharged into the vaporizing zone **4** of the column and is stripped with steam introduced at **6** in the bottom of the column. The vapors are rectified and/or washed with water in the decks **8** and the overhead light gasoline vapors are condensed at **9**.

The residue is withdrawn from column A by the pipe **10** and introduced into a pipe still **12** by means of a pump **14**. Prior to introduction into the pipe still, the oil is mixed with a relatively unvaporizable heat storage medium introduced by the pipe **16**. This heat storage medium preferably comprises asphalt obtained from the final distillation step of the process. The amount of asphalt thus introduced depends upon the amount present in the original crude and also upon the temperatures to which the oil is to be heated in the subsequent stages. With heating temperatures of approximately 700° F., the amount of asphalt introduced is preferably such as to bring the total asphalt content up to about 20% of the total volume of material entering the column B. The mixture, after being heated to approximately 700° F. in the pipe still, is discharged primarily into a flash vaporizing zone **18** at the bottom of the atmospheric column B. The vapors ascend through the column in contact with descending reflux, the overhead vapors being condensed at **20**, stripped side products being withdrawn at **22** and **24**. The side products are stripped as disclosed in the Snell Reissue Patent No. 18,722. The overhead product withdrawn at **20** is gasoline and the side products at **22** and **24** are kerosene and a part of the gas oil respectively. Owing to the presence of the heat storage agent in the mixture, the distillation of gasoline, kerosene and considerable gas oil can be effected at a reasonable temperature without the use of steam stripping. A considerable amount of heat can be added to the mixture in the pipe still so that the reduction of pressure taking place from the pipe still to the distillation tower will cause the vaporization of the lighter fractions to take place without any considerable reduction of temperature. The importance of this small reduction lies in the fact that the heat for the subsequent distillation under vacuum must be contained in the residue from the atmospheric vaporization step.

The residue is withdrawn from the bottom of the column B at a temperature of approximately 675° F. and is passed by a pipe **26** without further heating into the vaporizing zone **28** of the vacuum column C into which steam is introduced at the bottom, as indicated at **30**. The vapors ascend through the column in contact with descending reflux, an overhead gas oil product being collected at **32** and wax distillate being withdrawn from selected decks, as indicated at **34**. A slop cut may be withdrawn from a side stripping zone **36**, this slop cut being stripped of its wax distillate components by steam introduced at **38**. The column is maintained under a moderate vacuum (preferably corresponding to an absolute pressure of 50 to 100 mm. of mercury) by the vacuum jet **39**.

The residue from the column C is pumped from the bottom of the column into a pipe still **40**, the liquid being mixed prior to its introduction into the still with a diluent oil introduced at **42**. The operation from this point is identical with that described in my Patent No. 1,905,156. Preferably the diluent is gas oil taken from a tank **44** which is continuously replenished by a line **46** connecting with the gas oil draw-off **24**. The mixture is heated in the pipe still **40** to as high a temperature as possible without causing undesirable cracking, ordinarily between 700 and 725° F. The mixture is discharged immediately into a flash vaporizing zone **48** in which the vapors of the heavy lubricating stock (cylinder stock) and gas oil are vaporized by the heat contained in the entire mixture. This vaporization may be

carried out with or without the use of steam. The mixed vapors of cylinder stock and gas oil ascend through the column, the gas oil being condensed in an overhead condenser **50** which is connected with the vacuum jet system **52** for placing the column under an absolute pressure of 50 to 100 mm. of mercury. A part of the gas oil condensate is returned from the condenser **50** by a pipe **54** to the column to suppress the vapors of cylinder stock which are withdrawn at **56**, the remainder of the gas oil being taken off at **58** to pass into the tank at **44**. The purity of the cylinder stock and diluent may be enhanced by continuously bleeding a small amount of liquid from the upper decks of the column, as indicated at **60** and as described in my Patent No. 1,991,791.

A portion of the asphaltic residue is withdrawn as a product from the bottom of the column by a pipe **61** and the remainder is pumped through a pipe **62** into the pipe **16** for mixing with the feed entering the column B.

The action of the added asphalt in controlling the distillation in columns B and C depends on different effects due to the different pressure conditions existing in the two columns. In general, the addition of unvaporizable material, such as asphalt, acts to suppress the vaporization of the lighter materials owing to the mutual solution effect of all combinations of the mixture. Accordingly, the distillation of the desired fractions in column B necessitates a higher temperature than that which would be required if no asphalt were added. The greater the amount of added asphalt, the greater the temperature required. Sufficient asphalt may be added to increase the required temperature to substantially any desired value, but preferably short of the temperature at which decomposition or decolorization would occur. In practice, a temperature of about 650 to 700° F. is satisfactory.

The residue from column B therefore contains a considerably increased quantity of heat not only because of the increased temperature applied to the pipe still **12** but also because the presence of the asphalt has limited the temperature drop due to the vaporization of the lighter fractions. The residue in fact contains sufficient heat so that no further heating for the distillation in column C is necessary.

In column C, which is under vacuum, the action of the increased body of asphalt is actually to enhance vaporization. This follows from the fact that there is a considerable pressure drop from the feed line **26** to the column. Whereas the pressure drop from the outlet of the still to column B may be from only about 30 pounds absolute to 15 pounds, a ratio of 2 to 1, the pressure drop from the feed line **26** to the vaporizing chamber of column C is from about 15 pounds to 2 pounds (100 mm.), a ratio of 7½ to 1. If steam is used, the partial pressure of the oil is further reduced and the actual pressure ratio for column C is considerably higher. On a large reduction of pressure in the vaporizing chamber, the heat stored in the asphalt is immediately made available to vaporize the oils and the normal tendency of the asphalt to retard vaporization is completely overbalanced. This action of the asphalt in giving up its heat in column C is similar to that described in my Patent No. 1,911,993.

In column D, the oils are distilled under the action of the diluent and in the presence of heat carried into the vaporizing zone by the augmented quantity of asphalt.

The addition of asphalt in one of the earlier columns of the process therefore permits a selective action to occur depending on the relative pressures in the different columns. For example, in column B, where the pressure reduction is relatively small, the asphalt retards vaporization and permits heating of the crude to such a temperature that sufficient heat can be stored for a subsequent distillation, whereas in the C column, the reduction of pressure permits the asphalt to give up its heat to increase the vaporization. It is to be noted that with respect to prevention of cracking, the actions are especially favorable. The maximum temperature of the oils is reached at some point in the pipe still **12**, but at this point, the heavy oils which are most sensitive to cracking are mixed with a large body of lighter fractions which inhibit the cracking reaction. As soon as vaporization takes place in column B, the temperature is no longer high enough to crack, and no further heat is applied in the passage from column B to column C.

As a particular example of operation on Mid-Continent crude containing about 10% of asphalt, the temperatures of feed to the various columns are approximately as heretofore given, namely, 350° F. for column A, 700° F. for column B, 675 to 690° F. for column C, and 725° F. for column D. Of each 100 parts of the original mixture, approximately 15 parts are taken off in column A, 10 parts of residuum are added prior to entrance to column B, 40 parts are taken off at **20**, **22**, and **24** in column B, and 20 parts of gas oil and wax distillate are taken off in column C, leaving the remainder of 20 parts cylinder stock and 20 parts asphalt to be handled in column D. 10 parts of asphalt are taken off as a product and the rest is returned to the feed of column B. If crude of lower asphalt content were treated, an increased quantity of asphalt should be recirculated. In any case, the amounts of asphalt and diluent recirculated are preferably such as to make the proportions of diluent, cylinder stock and asphalt in the feed to column D approximately equal, as described in my Patent No. 1,963,888.

Having thus described the invention, what is claimed is:

1. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column at substantially atmospheric pressure, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column in which the pressure on the oil is greatly reduced with respect to the pressure in the first column whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

2. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure to a temperature in excess of that which would be required for vaporization of the more volatile constituents if no asphalt were added, passing the heated mixture into a column at sub-

stantially atmospheric pressure, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column in which the pressure on the oil is greatly reduced with respect to the pressure in the first column whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

3. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column at substantially atmospheric pressure, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing gasoline, kerosene, and some gas oil and withdrawing a residue, passing the residue without further heating to a second column in which the pressure on the oil is greatly reduced with respect to the pressure in the first column whereby the presence of the asphalt residuum facilitates vaporization of gas oil and wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

4. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column under vacuum whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

5. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure to a temperature in excess of that which would be required for vaporization of the more volatile constituents if no asphalt were added, passing the heated mixture into a column, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column under vacuum whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

6. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column at substantially atmospheric pressure, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing gasoline, kerosene, and some gas oil and withdrawing a residue, passing the residue without further heating to a second column under vacuum whereby the presence of the asphalt residuum facilitates vaporization of gas oil and wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

7. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphalt heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column, introducing steam into said second column whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

8. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure to a temperature in excess of that which would be required for vaporization of the more volatile constituents if no asphalt were added, passing the heated mixture into a column, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column, introducing steam into said second column whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

9. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column at substantially atmospheric pressure, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing gasoline, kerosene, and some gas oil and withdrawing a residue, passing the residue without further heating to a second column, introducing steam into said second column whereby the presence of the asphalt residuum facilitates vaporization of gas oil and wax distillate, and withdrawing a mixture of heavy lubricating stock and asphalt as residue.

10. The method of fractionating a petroleum

mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column at substantially atmospheric pressure, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column in which the pressure on the oil is greatly reduced with respect to the pressure in the first column whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, withdrawing a mixture of heavy lubricating stock and asphalt as residue, heating said last mixture and separating the heavy lubricating stock from the asphalt, and returning a part of the asphalt to the original mixture introduced into said first-mentioned column.

11. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphaltic heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column under vacuum whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, withdrawing a mixture of heavy lubricating stock and asphalt as residue, heating said last mixture and separating the heavy lubricating stock from the asphalt, and returning a part of the asphalt to the original mixture introduced into said first-mentioned column.

12. The method of fractionating a petroleum mixture containing gasoline and heavier materials which consists in adding to the mixture a quantity of unvaporizable asphalt heat storage residuum, heating the entire mixture under pressure, passing the heated mixture into a column, the ratio of pressures on the mixture in the heater and in the column being small whereby the presence of the asphalt retards vaporization and prevents excessive reduction of temperature, vaporizing the more volatile constituents in said column and withdrawing a residue, passing the residue without further heating to a second column, introducing steam into said second column whereby the presence of the asphalt residuum facilitates vaporization of oils as volatile as wax distillate, withdrawing a mixture of heavy lubricating stock and asphalt as residue, heating said last mixture and separating the heavy lubricating stock from the asphalt, and returning a part of the asphalt to the original mixture introduced into said first-mentioned column.

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