TREATING HYDROCARBON FLUIDS

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This invention relates to treatment of hydrocarbon fluids. According to this invention relatively heavy hydrocarbon oils, such as reduced crudes or the like, containing asphaltic constituents are intimately mixed with liquefied normally gaseous hydrocarbons to effect precipitation and separation of the asphaltic constituents. The liquefied normally gaseous hydrocarbons comprise C5, C6 and C7 hydrocarbons and may be obtained from an extraneous source but are preferably recovered from gases separated from the products of conversion. The mixture of relatively heavy hydrocarbon oil and liquefied normally gaseous hydrocarbons is passed to a settling chamber wherein separation of the asphaltic constituents from the relatively heavy oil is effected. The liquid residue containing undesired heavy asphaltic or tarry constituents is withdrawn from the bottom of the settling chamber.

The deasphalted oil and liquefied normally gaseous hydrocarbons are withdrawn from the settling chamber and all or a portion of the liquid is passed through a conversion zone wherein it is raised to an elevated temperature and maintained under superatmospheric pressure to effect the desired conversion. The deasphalted oil contains substantially all the liquefied normally gaseous hydrocarbons which were used to deasphalt the relatively heavy oil and it is this solution of deasphalted oil and normally gaseous hydrocarbons which is passed through the conversion zone to produce lower boiling hydrocarbons from higher boiling normally liquid hydrocarbons, and higher boiling hydrocarbons from the normally gaseous hydrocarbons.

The products of conversion from the conversion zone are cooled and introduced into a separating chamber. The products of conversion are cooled to such a degree that all the normally liquid hydrocarbons are condensed and substantially all of the normally gaseous hydrocarbons are liquefied. The liquefied normally gaseous hydrocarbons and light liquid hydrocarbons function to precipitate undesired asphaltic constituents formed during the conversion. These asphaltic constituents are withdrawn from the bottom of the separating chamber.

The deasphalted products of conversion may be admixed with a portion of the deasphalted oil leaving the first mentioned settling chamber and the mixture heated by being passed in indirect heat exchange with the products of conversion leaving the conversion zone. The heated deasphalted oil alone or the deasphalted oil and deasphalted products of conversion are introduced into a fractionating zone to separate reflux condensate and a light hydrocarbon fraction within the gasoline boiling range from gaseous constituents containing normally gaseous hydrocarbons. The reflux condensate comprises a deasphalted cycle stock which is recycled to the conversion zone.

All or a part of the reflux condensate is heated by being passed in indirect heat exchange with the products of conversion leaving the conversion zone and the heated reflux condensate is then recycled to the conversion zone for further conversion treatment. If desired, liquefied normally gaseous hydrocarbons separated from conversion products or obtained from an extraneous source may be admixed with the deasphalted oil and the reflux condensate introduced into the conversion zone.

The gaseous constituents separated during the fractionation in the fractionating zone are cooled in order to liquefy normally gaseous hydrocarbons and then fractionated to separate liquefied normally gaseous hydrocarbons consisting mainly of propane from hydrogen, methane and ethane. Any gaseous constituents which leave the settling chamber and the separating chamber may be mixed with the gaseous constituents separated during the fractionation of the deasphalted products of conversion. The liquefied normally gaseous hydrocarbons are the ones used for admixture with the relatively heavy hydrocarbon oil in the first step of the process above described.

Instead of passing all of the liquefied normally gaseous hydrocarbons to the mixing chamber for admixture with the relatively heavy hydrocarbon oil, a part of the liquefied normally gaseous hydrocarbons may be mixed with the reflux condensate and the mixture recycled to the conversion zone. In addition to the liquefied normally gaseous hydrocarbons recovered in the process, liquefied normally gaseous hydrocarbons from an extraneous source may be introduced into the system. For example, liquefied normally gaseous hydrocarbons from an extraneous source may be introduced into the products of conversion passing to the separating chamber so as to increase the amount of normally gaseous hydrocarbons in the mixture.

In the drawing I have diagrammatically shown one form of apparatus suitable for carrying out the steps of my method, but other apparatus may be used.

Referring now to the drawing, the reference character 10 designates a line through which
heavy hydrocarbon oil is passed by the pump 12. The relatively heavy hydrocarbon oil may be any heavy oil containing asphaltic or residual constituents such as, for example, a Mid-Continent reduced crude oil having an A. P. I. gravity of about 25. The relatively heavy hydrocarbon oil is intimately mixed with liquefied normally gaseous hydrocarbons which consist mainly of C5, C6, C7 hydrocarbons and which contain a predominating amount of propane. The liquefied hydrocarbons are passed through line 14.

The liquefied normally gaseous hydrocarbons used for deasphalting are recovered from gaseous constituents separated from the liquefied products during the later stages of the process, but, if necessary, liquefied normally gaseous hydrocarbons from an extraneous source may be added. The liquefied normally gaseous hydrocarbons are maintained at a temperature of about 75° F. and maintained under a pressure of about 125-175 pounds per square inch. About three to five volumes of the liquefied normally gaseous hydrocarbons are used to about one volume of the heavy hydrocarbon oil to be deasphalted. The liquefied normally gaseous hydrocarbons and the heavy hydrocarbon oil are mixed in the mixing chamber 5 6 under a pressure of about 125-175 pounds per square inch and at a relatively low temperature, for example 75° F. to maintain the normally gaseous hydrocarbons in liquefied form, and the mixture is then passed through line 18 to a settling chamber 20 wherein asphaltic and residual constituents are precipitated and collect in the bottom of the settling chamber from which they are withdrawn through line 22. The liquefied normally gaseous hydrocarbons used for deasphalting the relatively heavy oil in the deasphalted oil and all or a portion of the deasphalted oil without separation of the liquefied normally gaseous hydrocarbons is passed through a conversion zone presently to be described.

The deasphalted oil containing the liquefied normally gaseous hydrocarbons used for deasphalting the oil is withdrawn from the settling chamber 20 and passed through line 25 by pump 28 and all or a portion of the deasphalted oil and liquefied hydrocarbons is passed through line 30 and introduced into the conversion zone 32 in heater 34 wherein the deasphalted oil and liquefied normally gaseous hydrocarbons are maintained under superatmospheric pressure of about 200 to 1000 pounds per square inch and at an elevated temperature of about 900 to 1150° F. to convert higher boiling hydrocarbon liquids to lower boiling liquids and to convert normally gaseous hydrocarbons to higher boiling hydrocarbons. A mixture separated from the products of conversion has a high-anti-knock value.

Before being introduced into the conversion zone 32, the deasphalted oil is preferably mixed with an additional quantity of liquefied normally gaseous hydrocarbons passing through line 38 and reflux condensate passing through line 50 which are separated during fractionation of the products of conversion as will be hereinafter described. The deasphalted oil, reflux condensate and liquefied normally gaseous hydrocarbons in passing through the conversion zone 32 are maintained under conversion conditions to effect the desired extent of conversion. From the above it will be seen that the deasphalted oil and liquefied normally gaseous hydrocarbons used for deasphalting the heavy oil are passed through the conversion zone 32.

The products of conversion leave the conversion zone 32 through line 42 having a pressure reducing valve 44. The products of conversion under lower pressure are then passed through heat exchangers 45 and 46 in order to cool the products of conversion and to condense normally liquid hydrocarbons and to liquify normally gaseous hydrocarbons. If desired, or if necessary, additional cooling means may be provided. The cooled products of conversion are then passed into a separating chamber 52 wherein the products of conversion are maintained under pressure and at a temperature to maintain normally gaseous hydrocarbons such as propane in liquid state. The liquefied normally gaseous constituents and relatively light normally liquid hydrocarbons precipitate out the asphaltic constituents formed during the conversion and a separation thereof takes place in the separating chamber 52.

A part of the liquid containing relatively heavy oil and liquefied normally gaseous hydrocarbons and passing through line 5 6 may be passed through line 64 and in the mixing chamber 5 6 further cooled and the products of conversion before they are introduced into separating chamber 52.

The introduced relatively heavy oil is deasphalted in separating chamber 52 and the deasphalted oil is mixed with the deasphalted products of conversion. I may introduce liquefied normally gaseous constituents from an extraneous source into the line 66 through line 58 by pump 60 before the cooled products of conversion are introduced into the separating chamber 52. The asphaltic and residual constituents are withdrawn from the bottom of the separating chamber 52 through line 64.

The deasphalted products of conversion are withdrawn from the separating chamber 52 and passed through line 66 by pump 67 and then through heat exchanger 69 to heat and vaporize the deasphalted products of conversion while at the same time cooling the products of conversion passing through line 65. The heated and vaporized deasphalted products of conversion are then passed through line 66 and introduced into a fractionating tower 70 wherein the denser is separated from lighter hydrocarbon constituents as will be described hereinafter in more detail. If a higher temperature is required for fractionation, the material flowing through line 67 may be passed through any suitable additional heating means (not shown). The deasphalted products of conversion passing through line 66 may be admixed with a portion of the deasphalted oil withdrawn from the settling chamber 20 and passing through line 74 and the mixture introduced into fractionating tower 70.

The gaseous constituents leaving the top of the separating chamber 52 through line 76 and leaving settling chamber 20 through line 78 may be combined and passed through line 83 to fractionating tower 85 together with gaseous constituents separated from the products of conversion as will be later described hereinafter. In this fractionating tower 85, provided with suitable reflux, the gaseous feed is fractionated to separate liquefied normally gaseous constituents from uncondensed vapors containing hydrogen, methane and ethane drawn through line 85. If desired, a compressor and cooler may be used to bring the feed stock to optimum conditions of temperature and pres-
sure before passing the feed stock to the fractionating tower 86.

The liquefied normally gaseous hydrocarbons are withdrawn from the bottom of the fractionating tower 86 and are passed through line 90 by pump 91. A portion of the liquefied normally gaseous hydrocarbons may be passed through line 94 and then through line 94 for admixture with the relatively heavy hydrocarbon oil which is introduced through line 10. If desired, additional amounts of liquefied normally gaseous hydrocarbons may be passed through line 95 by pump 96 and introduced into line 10. Another portion of the liquefied normally gaseous hydrocarbons withdrawn from the bottom of fractionating tower 86 may be passed through line 98 for admixture with the desasphalted oil passing through line 90 and reflux condensate passing through line 100 before the mixture is introduced into the conversion zone 32. Additional quantities of liquefied normally gaseous hydrocarbons from an extraneous source may be introduced into line 98 by being passed through line 100 by pump 102.

The separation of the desasphalted products of conversion into reflux condensate, a light hydrocarbon fraction containing gasoline constituents and gaseous constituents will now be described. The heated and vaporized products of conversion are fractionated in the fractionating zone 10 to separate reflux condensate containing hydrocarbon constituents which are too heavy for the light hydrocarbon fraction. The reflux condensate comprises desasphalted cycle stock which can be recycled to the conversion zone, if desired, for further conversion treatment. The reflux condensate is withdrawn from the bottom of the fractionating zone 10 through line 100 and a portion thereof or all of the reflux condensate may be withdrawn from the system through line 103 and passed to storage. A portion or all of the reflux condensate may be passed through line 100 by pump 102 and then through heat exchanger 43 for indirect heat exchange with the products of conversion leaving the conversion zone whereby the reflux condensate is preheated and the products of conversion are cooled a certain amount before being passed through the second heat exchanger 43. The heated reflux condensate is then passed through line 50 for mixture with the desasphalted oil passing through line 30 as above described.

The vapors leaving the top of fractionating zone or tower 70 are passed through line 110 to a second fractionating zone or tower 112 wherein further fractionation is effected to separate a relatively light hydrocarbon fraction within the gasoline boiling range from gaseous constituents. Instead of using the two fractionating towers 70 and 112, I may use one fractionating tower and remove a desired fraction or fractions as side cuts. The relatively light hydrocarbon fraction is withdrawn from the bottom of the fractionating zone or tower 118 through line 120. The gaseous constituents leave the top of the fractionating zone or tower 118 through line 122 and are preferably mixed with the gaseous constituents passing through line 98 and the mixture of the gaseous constituents is further treated to separate liquefied normally gaseous hydrocarbons therefrom in the fractionating zone or tower 96 as described above. Suitable reflux liquid is provided for the fractionating zones or towers 70, 98 and 118.

If desired, additional quantities of an oil charge to be converted may be introduced into the line 30 for admixture with the desasphalted oil. This additional quantity of oil charge may be passed through line 124 by pump 125.

The desasphalted oil of the products of conversion may be facilitated in separating chamber 70 by dissolving in the mixture, under relatively high pressure, a quantity of relatively light gaseous hydrocarbons such as a mixture of methane and ethane, for example. Such gases being good anti-solvents for asphaltic material effect the desired separation of asphaltic constituents at a higher temperature than would be required otherwise. When such gases are used, they are introduced into the separating chamber 70 and are later separated by fractionation and removed from the system rather than being returned to the conversion zone 32. These relatively light gaseous hydrocarbons may replace part of the normally gaseous hydrocarbons containing propane used for desasphalting. Or such relatively light gaseous hydrocarbons may be introduced into settling chamber 29.

While I have given a specific example of my invention, this is merely for the purpose of illustration and different operating conditions may be used and various changes and modifications may be made without departing from the spirit of my invention.

I claim:

1. A method of treating hydrocarbons which comprises mixing relatively heavy hydrocarbon oil with liquefied normally gaseous hydrocarbons containing a relatively large proportion of propane, passing the mixture to a settling chamber wherein asphaltic constituents are separated and a desasphalted oil containing normally gaseous hydrocarbons in solution is obtained, passing at least a part of the desasphalted oil containing normally gaseous hydrocarbons through a conversion zone wherein they are raised to an elevated temperature and maintained under super-atmospheric pressure to effect the desired conversion, cooling the products of conversion to condense normally liquid hydrocarbons and liquefy a substantial part of normally gaseous hydrocarbons, passing the cooled liquid products to a separating chamber to separate asphaltic constituents from desired products of conversion, admixing at least a part of the desasphalted oil with the desasphalted products of conversion, heating the admixed desasphalted oil and desasphalted products of conversion by indirect heat exchange with the products of conversion leaving said conversion zone, fractionating the vapors from the heated desasphalted oil and desasphalted products of conversion by indirect heat exchange with the products of conversion leaving said conversion zone, recycling heated reflux condensate to said conversion zone, cooling the last mentioned normally gaseous constituents to liquefy normally gaseous hydrocarbons and passing liquefied normally gaseous hydrocarbons containing propane from gaseous constituents, using at least a part of the last mentioned liquefied normally gaseous hydrocarbons for mixture with and desasphalting of the relatively heavy hydrocarbon oil to be converted, admixing another portion of the last mentioned liquefied normally gaseous hydrocarbons with the recycled reflux condensate and desasphalted oil charged to said conversion zone.
2. A method of treating hydrocarbons which comprises mixing relatively heavy hydrocarbon oil with liquefied normally gaseous hydrocarbons containing a relatively large proportion of propane to effect separation of asphaltic constituents from the relatively heavy hydrocarbon oil, passing the deasphalted oil and normally gaseous hydrocarbons through a conversion zone wherein they are raised to an elevated temperature and maintained under superatmospheric pressure to effect the desired conversion, cooling the products of conversion to condense normally liquid hydrocarbons and to liquefy a substantial part of normally gaseous hydrocarbons, separating asphaltic constituents from the cooled products of conversion, admixing at least a part of the deasphalted oil with the deasphalted products of conversion, heating the admixed deasphalted oil and deasphalted products of conversion by indirect heat exchange with the products of conversion leaving said conversion zone, fractionating the vapors from the heated deasphalted oil and deasphalted products of conversion to separate reflux condensate and a lighter hydrocarbon fraction containing gasoline constituents from normally gaseous constituents, heating reflux condensate by indirect heat exchange with the products of conversion leaving said conversion zone, recycling heated reflux condensate to said conversion zone, cooling the last mentioned gaseous constituents to liquefy normally gaseous hydrocarbons and separating liquefied normally gaseous hydrocarbons containing propane from gaseous constituents, using at least a part of the last mentioned liquefied normally gaseous hydrocarbons for mixture with and deasphalting of the relatively heavy hydrocarbon oil to be converted.

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