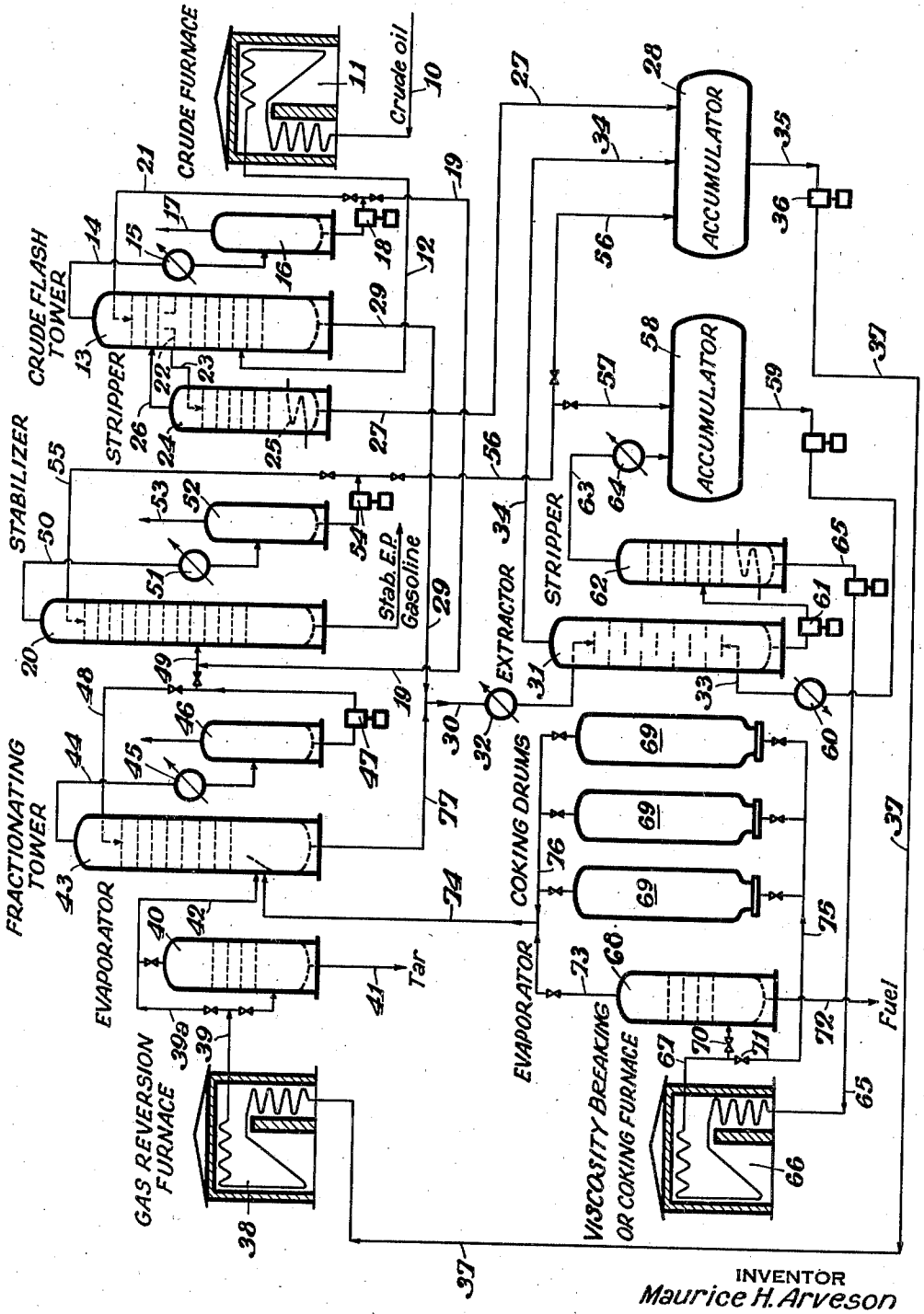
Nov. 19, 1940. M. H. ARVESON 2,222,060

CONVERSION OF HYDROCARBON OILS AND GASES

Filed Sept. 7, 1937



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Patented Nov. 19, 1940 2,222,060

UNITED STATES PATENT OFFICE

2,222,060

CONVERSION OF HYDROCARBON OILS AND GASES

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Application September 7, 1937, Serial No. 162,605

7 Claims. (Cl. 196—50)

This invention relates to a process of converting hydrocarbon oils and particularly heavy petroleum oils into gasoline. One of the objects of the invention is to separate a crude oil charging stock into intermediate and heavy constituents and subject them to separate conversion operations. Another object of the invention is to recover normally gaseous hydrocarbons undesirable in gasoline and convert them into gasoline by pyrolysis in the presence of the intermediate fractions first referred to. Still another feature of the invention is the extraction of clean cracking constituents from the residual fraction of the crude petroleum by the action of liquefied hydrocarbon gases under certain temperature conditions and conversion of the extracted hydrocarbons and gases. Other objects of the invention will become apparent from the following description.

The invention is illustrated by a drawing forming a part of this specification showing in diagrammatic form the flow of the oils and gases in the process. Referring to the drawing, crude oil is introduced by line 10 through pipe heater 11 wherein it is heated to a temperature of about 600–700° F. and partially vaporized. From the heater the oil is conducted by line 12 to fractionating tower 13 where the lighter constituents are permitted to vaporize and are fractionated. Gasoline and gases are withdrawn by line 14 through condenser 15 and thence to reflux drum 16. Uncondensed gases, including principally methane and hydrogen, are discharged by vent 17 and the gasoline condensate is withdrawn by pump 18 and line 19 to stabilizer 20. A portion of the gasoline distillate is returned by line 21 to serve as reflux in the fractionating tower 13.

Clean gas oil, which may include some heavy naphtha boiling within the gasoline boiling range, is withdrawn from the trap-out tray 22 by line 23, leading to stripper 24, where light gasoline constituents are removed by stripping with steam introduced at the bottom or by heating coil 25, the light vapors being conducted back to tower 13 by line 26. Gas oil from the base of stripper 24 is conducted by line 27 to accumulator drum 28.

Heavy unevaporated residue from the crude is withdrawn from the bottom of tower 13 by line 29 and line 30, leading to extractor 31. The temperature of the oil may be controlled by heat exchanger or cooler 32. Within extractor 31 the oil is intimately contacted with a stream of liquefied normally gaseous hydrocarbons introduced by line 33 flowing upward countercurrent to the heavy oil stream.

When heavy hydrocarbon materials, whether virgin or cracked, are treated with normally gaseous hydrocarbons in the liquid state, there is a region, reflected from the critical point, in which the separation occurs. As the temperature is raised toward the critical point, more and more material is precipitated from solution. It may be readily seen that if a mixture of normally gaseous hydrocarbons in the liquid state is charged to a gas conversion zone along with the heavy liquid hydrocarbons, liquid phase separation will occur, the heavier, more viscous layer tending to cling to the walls of the tube and aid in the formation of coke. In the extraction step it is desirable that the maximum amount of material be removed as a precipitate in extractor 31. This may be effected by operating the extractor in the near critical region. In the case of pure hydrocarbons this would be within a few degrees of the critical temperature of the solvent. With mixtures of hydrocarbons such as will be encountered in the operation of this process, the critical region will be dependent upon the exact composition of the mixture. It may be determined from data available in the literature or by direct determination on the materials to be used. Since quite effective separations can be obtained at temperatures somewhat below the critical temperature, I contemplate the use of temperatures as low as 75° below the critical temperature of the normally gaseous hydrocarbons used as a solvent. By way of illustration, operating temperatures for pure hydrocarbons are as follows:

	Degrees Fahrenheit
Ethane	40– 90
Propane	150–205
Butane	250–300

These temperatures represent the preferred range, and operations slightly below and slightly above these temperatures may be used. In the case of mixed solvents containing ethane, propane and butane, the temperature corresponding to the critical temperature used with pure hydrocarbons is the so-called pseudo critical temperature and in general will be slightly higher than the temperature calculated from the average of the molal concentration and critical temperature of each constituent. It is preferred to operate at or near the region of maximum precipitation or the region where the extract freed from solvent would have a minimum viscosity.

The extract obtained in extractor 31 is conducted by line 34 to accumulator 28 where it is combined with the gas oil introduced therein as previously described. The mixture of gas oil, liquefied hydrocarbon gases and heavy oil extract is withdrawn from accumulator 28 by line 35 and pump 36 and conducted by line 37 to gas reversion furnace 38 wherein it is heated to a temperature preferably between 1,000 and 1,100° F. The product is discharged by transfer line 39 to evaporator 40 from which the unevaporated heavy fraction is discharged by line 41. The vapors are conducted by line 42 to fractionator 43 in which the gasoline and lower boiling constituents are separated and discharged by line 44 to condenser 45 and receiving drum 46. Alternatively, the vapors may be discharged directly from the cracking furnace 38 to the fractionating tower 43 by valved by-pass line 39a. Condensate from drum 46 is withdrawn by pump 47 which delivers a portion back to the tower 43 as reflux by line 48 and the remainder to stabilizer tower 20 by line 49. Propane and butane, together with some ethane and heavier hydrocarbons, are conducted by line 50 and condensed by condenser 51, after which they are collected in receiving drum 52. Uncondensable hydrogen and methane are discarded by vent 53, while the liquid condensate is withdrawn by pump 54 which returns a portion thereof to tower 20 by line 55 for the purpose of reflux. Alternatively, gases from 52 and line 53 which may contain C_2 and C_3 hydrocarbons may be sent to an absorber not shown, recovered and returned to accumulator 28 or accumulator 58. This permits one to avoid costly refrigeration in cooler 51 to condense the C_2 and C_3 hydrocarbons. Another portion is conducted by line 56 to accumulator 28 previously referred to and the remainder is conducted by line 57 to liquefied gas accumulator 58 which is employed as a supply of hydrocarbon solvent to be used in extractor 31. It is withdrawn from tank 58 by line 59 to heat exchanger 60 where the temperature is regulated to the desired point before introducing into extractor 31 by line 33.

Insoluble oil in the bottom of extractor 31 is conducted by pump 61 to stripper 62 where hydrocarbon solvent is vaporized and conducted by line 63 to condenser 64 and thence to drum 58. Unevaporated oil is conducted from stripper 62 by line 65 to viscosity breaking furnace 66 where it is heated to an intermediate temperature suitable for pyrolytic decomposition of the heaviest hydrocarbons into gasoline and intermediate boiling hydrocarbons suitable as charging stock for the cracking furnace 38. For this operation a temperature of about 850 to 925° F. is satisfactory.

The oil is withdrawn from furnace 66 by transfer line 67 and may be routed alternatively to evaporator 68 or to coking drums 69 by regulating valves 70 and 71. If it is desired to produce a heavy fuel oil as one product of the process, valve 70 is left open and valve 71 is closed, conducting the hot oil from furnace 66 into evaporator 68 whence the unevaporated residue is withdrawn by line 72, and the vapors are conducted by line 73 and line 74 to fractionating tower 43 previously mentioned.

If coke is the desired by-product of the process valve 71 is left open and valve 70 is closed directing the oil from line 75 to one of the heat insulated coking drums 69, where the unevaporated residue is allowed to coke by its contained heat and the volatile constituents are withdrawn as a vapor through vapor line 76 and line 74 to fractionator 43. When one of the drums 69 has been substantially filled with coke, the oil stream is diverted to another drum, preferably preheated and the first drum is cleaned. When cracking to coke instead of fuel oil, somewhat higher overall yields of gasoline are obtained in the process.

It is preferred to operate fractionating tower 43 to produce "end point gasoline" as a distillate and by this I mean gasoline having the desired distillation characteristics with respect to the higher boiling fractions thereof. Thus I may operate to produce gasoline of 400° F. end point although I may with equal facility produce gasoline having an end point somewhat higher or lower than this, e. g., 380° F. to 420° F. The unevaporated constituents in fractionator 43 are refluxed to the bottom thereof by suitable reflux cooling coils in the top or by introduction of reflux liquid through line 48 as previously described. The reflux is conducted from the bottom of the tower by line 77 and line 30 to cooler 32 whence it is introduced into extractor 31 along with the crude oil residue previously described. Any asphaltic constituents present in the reflux liquid remain undissolved in extractor 31 and are conducted therefrom via pump 61, stripper 62 and charge line 65 to the viscosity breaking furnace as previously described.

One of the important advantages of my process is the complete refining of all recycle oil and crude charging stock by means of selective hydrocarbon solvent, before cracking in the furnace 38 which is operated at conditions of high temperature, conducive to the production of gasoline of high knock rating. I have discovered that the presence of even small amounts of asphaltenes in the stock cracked under these conditions in the presence of liquefied hydrocarbon gases is detrimental to continuous, long-time operation of the cracking furnace, particularly when normally gaseous hydrocarbons are present in considerable proportions. As previously mentioned, I have discovered that in a gas reversion operation of this type wherein substantial amounts of normally gaseous hydrocarbons are present in the oil undergoing cracking, that separation of coke producing constituents of the oil is aggravated with the result that these constituents cling to the hot tube surfaces in the cracking furnace, impair heat transfer, and rapidly build up a layer of coke on the tubes which necessitates shutting down the furnace for cleaning after a relatively short period of operation. By completely refining the entire oil charged to heater 38 by means of liquefied hydrocarbon gases under conditions where the oil is extracted at a temperature in the vicinity of the critical temperature of the gas, I find that all asphaltic constituents are precipitated together with those naphthenic constituents of higher molecular weight, i. e., those higher boiling constituents of the oil having a relatively high carbon to hydrogen ratio, which my experience has shown decompose on cracking with the formation of undesirable coke in the pipe heater. By eliminating this material from the charging stock to the gas reversion heater I find it possible to operate the heater for consistently long periods of time without the necessity of shutting down for cleaning and I am also enabled to operate the heater at higher temperatures than has heretofore been considered advisable with the result

that a greater amount of the so-called fixed gases introduced into the heater with the heavy oil is caused to polymerize or react with the heavy oils undergoing cracking, giving larger yields of gasoline having a higher knock rating. With this improvement I may conveniently employ from 15 to 50% of liquefied normally gaseous hydrocarbons in the charge to reversion furnace 38.

I have referred in this specification to the use of normally gaseous hydrocarbons for the extraction of the heavy charging oil previous to cracking and gas reversion. By hydrocarbon gases I mean to include primarily those gases boiling below the pentane fractions and primarily I include propane, ethane, propylene, ethylene and the butanes and butylenes. It should be understood, however, that I may retain most of the butane in the gasoline produced in the process if desired by regulating the stabilizer 20. The hydrocarbon gases will also contain some methane but it is desirable to eliminate this gas, as previously described, since it performs no useful function in my process.

I prefer to employ the same composition of hydrocarbon gases in the extraction of the oil in tower 31 and in the charging stock to gas reversion furnace 38. However, if desired, I may alter the composition of the solution charged to the reversion furnace by adding heavier or lighter hydrocarbons to the accumulator tank 28 or by evaporating a portion of the lighter gas, e. g., ethane, therefrom by suitable means not shown.

Although I have described my process with respect to specific examples thereof, I intend that it be limited only by the following claims. It should be understood, of course, that the description of the process is entirely diagrammatic and that numerous valves, pumps, heat exchangers, etc. have been omitted from the drawing for convenience in describing the process.

Similarly, although I have described employing principally the hydrocarbon gases produced in the cracking operation itself from the decomposition of heavy oils, I may supplement these gases by importing liquid butane, propane, propylene, butylene, etc. from other sources, preferably introducing them into the system at the bottom of extractor 31 through line 33 or into accumulator 58. Imported hydrocarbon gases may also be introduced by dissolving them in the crude oil charged to the unit through line 10.

I claim:

1. In the process of simultaneously converting heavy oils and fixed gases into gasoline by gas reversion wherein a solution of the heavy oil and fixed gases is heated in a gas reversion zone to an elevated conversion temperature between about 1000 and 1100° F. after which the products are separated into gasoline and cycle oils in a fractionating zone, the improvement comprising avoiding the deposition of coke in said gas reversion zone resulting from the action of the hydrocarbon gases on naphthenic and asphaltic constituents present in said heavy oil, by initially subjecting said heavy oil to the selective solvent action of said hydrocarbon gases in liquid form maintained at a temperature in the vicinity of somewhat below the critical temperature of said gases, separating an asphaltic-naphthenic fraction from said heavy oil solution, charging the resulting solution of heavy oil and liquefied gas to said gas reversion zone, substantially eliminating solvent gases from said asphaltic-naphthenic fraction, subjecting said asphaltic-naphthenic fraction to viscosity breaking at a lower conversion temperature, separating the products of conversion thereof into a vaporized fraction and a residue, introducing said vaporized fraction with said heavy oil into said fractionating zone and combining said cycle oils withdrawn from said fractionating zone with said heavy oil before subjecting said heavy oil to the selective solvent action of said hydrocarbon gases.

2. The process of converting heavy hydrocarbon oils into gasoline by pyrolysis which comprises initially separating said oil by selective extraction with a liquefied normally gaseous hydrocarbon solvent at a temperature subjacent to the critical temperature of said solvent, whereby the heavy oil is separated into an insoluble fraction and a solution, subjecting the insoluble fraction to a cracking operation under relatively low temperature liquid phase conversion conditions whereby it is converted into an unvaporizable asphaltic oil and a vaporized fraction consisting substantially of hydrocarbons heavier than gasoline, separating said unvaporizable asphaltic oil and conducting said vaporized fraction to a fractionating zone, subjecting said solution of heavy oil and liquefied normally gaseous hydrocarbons to a gas reversion operation wherein it is heated to a relatively high temperature and a substantial part of said heavy oil and gases is converted into gasoline, introducing said conversion products into said fractionating zone with the products of said first mentioned cracking operation and fractionating the hydrocarbons in said fractionating zone into a gasoline and lighter vaporized fraction and an unvaporized reflux liquid and recovering the gasoline from said vaporized gasoline containing fraction.

3. The process of claim 2 wherein the reflux liquid from said fractionating zone is recycled with the heavy oil introduced into said extraction zone.

4. The process of claim 2 wherein the hot conversion products from said gas reversion heating zone are discharged into an evaporating zone from which a heavy unvaporized tar fraction is separated before introducing said conversion products into said fractionating zone.

5. The process of claim 2 wherein the unvaporizable constituents from said relatively low temperature cracking operation are separated as a liquid residue from said vaporized fractions conducted to said fractionating zone.

6. The process of claim 2 wherein the said unvaporizable constituents from said relatively low temperature cracking operation are permitted to accumulate in a thermally insulated chamber where they are coked by their contained heat and the volatile products of said coking reaction are conducted, together with the vaporized oil fractions, to said fractionating zone.

7. In the process of converting heavy hydrocarbon oils into gasoline motor fuels, the improvement comprising fractionating a crude petroleum and separating a clean virgin gas oil therefrom, conducting the unvaporized residuum to an extraction operation wherein liquefied hydrocarbon gases of the character of propane and butane are employed at a temperature in the vicinity of the critical temperature of said gases to separate the said residuum into an asphalt-free soluble portion and an asphaltic insoluble portion, subjecting the insoluble portion to a viscosity breaking operation under relatively low temperature liquid phase conversion conditions whereby it is converted into an unvaporizable fraction and a vaporized fraction consisting sub-

stantially of hydrocarbons heavier than gasoline, separating said unvaporizable fraction and conducting said vaporized fraction to a fractionating zone, combining the solution of said asphalt-free soluble portion and liquefied hydrocarbon gases with said clean virgin gas oil to produce a gas reversion feed stock, subjecting said gas reversion feed stock to a temperature of about 1000 to 1100° F. whereby an extensive decomposition and recombination of the high boiling oils and gaseous hydrocarbons takes place with the formation of gasoline, fractionating the products of said gas reversion in said fractionating zone with the products of said viscosity breaking operation to recover said gasoline and recycling the remaining oils boiling above the gasoline range to said extraction operation in combination with said residuum.

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