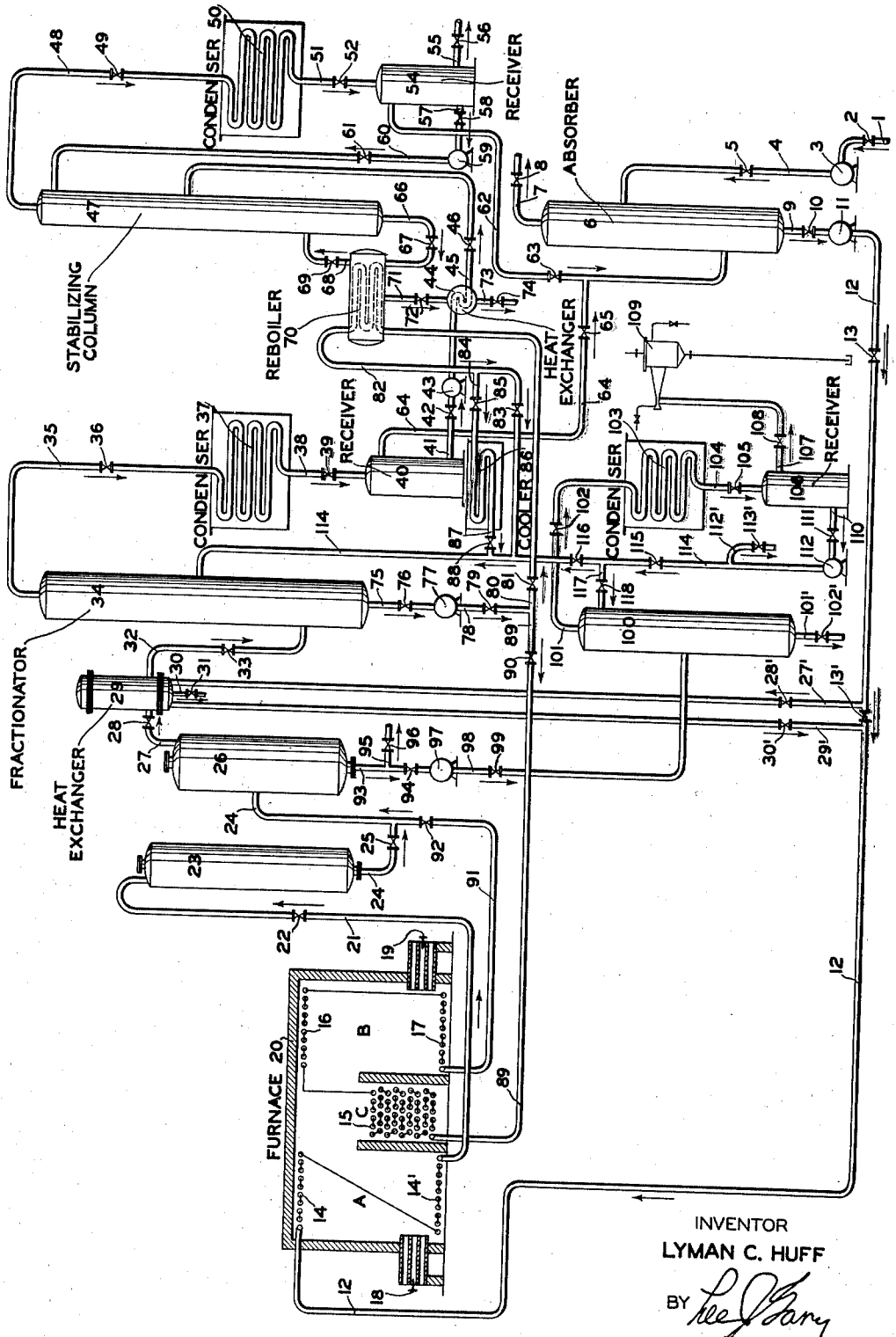
June 24, 1941. L. C. HUFF 2,246,592

CONVERSION OF HYDROCARBON OILS

Original Filed July 5, 1935



INVENTOR
LYMAN C. HUFF
BY Lee Gary
ATTORNEY

Patented June 24, 1941 2,246,592

UNITED STATES PATENT OFFICE

2,246,592

CONVERSION OF HYDROCARBON OILS

Lyman C. Huff, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

Application July 5, 1935, Serial No. 29,795
Renewed April 18, 1939

2 Claims. (Cl. 196—9)

The present invention refers to an improved process for the pyrolytic conversion of relatively heavy petroleum oils, such as topped crudes and the like, at elevated temperature and superatmospheric pressure for the production of high yields of good quality motor fuel and either marketable fuel oil or good quality asphalt, or both.

As applied to the treatment of relatively heavy oils the present invention eliminates the difficulty ordinarily encountered in cracking heavy oils due to the excessive formation and deposition of coke in the heating coil. This is accomplished by avoiding the excessive conversion of the heavy oils which also results in the production of a better quality liquid residue, particularly with respect to suspended carbonaceous material. By eliminating excessive conversion of the heavy oils and the presence of excessive amounts of carbonaceous material in the cracked residue the present process becomes particularly adaptable to the treatment of topped crudes or residual oils of an asphaltic nature for the production of both good quality motor fuel and good quality asphalt although the invention is not limited to the treatment of asphaltic charging stocks nor to the production of asphalt as the final residual product of the process.

In one embodiment, the invention comprises subjecting residual petroleum fractions of an asphaltic nature to conversion conditions of cracking temperature and substantial superatmospheric pressure in commingled state with low-boiling normally gaseous hydrocarbons absorbed by contacting the charging stock with the process gases, introducing the resulting heated and partially converted materials into an enlarged reaction chamber also maintained at superatmospheric pressure wherein the desired conversion reactions are completed, withdrawing both vaporous and liquid conversion products from the reaction chamber and introducing the same into a reduced pressure vaporizing chamber wherein separation of vaporous and residual liquid conversion products is accomplished, withdrawing the latter from the vaporizing chamber and subjecting the same to further distillation at subatmospheric pressure for the production of asphalt, separately withdrawing vaporous conversion products from the vaporizing chamber, subjecting the same to fractionation for the formation of reflux condensate comprising their insufficiently converted components and the recovery of fractionated vapors within the boiling range of motor fuel, which latter are condensed and collected, returning the reflux condensate to independently controlled conversion conditions of higher cracking temperature and superatmospheric pressure in a separate heating coil, introducing the heated products from said separate heating coil into the vaporizing chamber, subjecting said motor fuel product resulting from condensation of the fractionated vapors to stabilization for the removal therefrom of undesirable low-boiling components, whereby to control its vapor pressure, and contacting the uncondensed gaseous products of the process with said charging stock prior to its introduction into the first mentioned heating coil.

While the elements of plants for accomplishing the above objects may vary somewhat in their absolute and relative proportions depending upon the character of oil to be processed and the desired results, the essential features of operation comprised in the scope of the present invention are generally similar in all plants and the attached drawing has been provided to assist in describing a characteristic operation. The drawing shows diagrammatically, by the use of conventional figures in side elevation, an arrangement of interconnected elements in which the steps of the process may be conducted. As will be shown by a later example, the particular system illustrated is particularly applicable to residual stocks of high specific gravity.

Referring to the drawing, charging oil is introduced to the plant from any suitable source of supply, not shown, through a line 1 containing control valve 2 and is fed by pump 3 through line 4 and valve 5 into a point near the top of an absorption column 6, from which the unabsorbed fixed gases are discharged through line 7 containing control valve 8. The absorber may be of any conventional type containing a series of superimposed bubble trays or other suitable contacting means to insure substantially complete absorption from the gases supplied thereto of all hydrocarbons of 4 carbon atoms (the butanes and butylenes) and a portion of the propane, while leaving unabsorbed such gases as hydrogen, methane, ethane, ethylene, etc. The gas mixtures are admitted to the absorber from line 62 as will be described at a later point.

The absorption of oil vapors at this point having the general characteristics of the low-boiling fractions of gasoline has a two-fold advantage in that this material is recovered to augment the yield of the final light distillate product of the process and that the presence of appreciable quantities of such fractions in the heavy charging oil has a tendency to lessen coke deposition

in the primary heating coil, probably due to combination of the low-boiling materials with the heavy, coke-forming conversion products. The conditions employed for cracking the raw oil are hardly severe enough to effect substantial conversion of the light fractions, which, however, by virtue of their partial pressure in the heating tubes, serve to make possible the use of relatively higher temperatures and lower time factors in this zone.

Raw oil containing absorbed light hydrocarbons passes from the bottom of absorber 6 through line 9 and valve 10 to pump 11 from which it is fed through line 12 and valves 13 and 13' to a heating coil comprising tube banks 14 and 14' within furnace setting 20. Controlled quantities of the charging stock may be passed through a heat exchanger 29 by way of inlet line 27' and valve 28' and outlet line 29' containing valve 30', with valve 13' totally or partially closed. This diversion of flow serves to effect partial preheating of the enriched charging oil from absorber 6 and lower the temperature of the vapors from chamber 26, with which it passes in indirect heat exchange. Obviously, the amount of condensation caused by the cooling effect of the raw oil will to some extent control the quality and end-boiling point of the intermediate fractions recovered as reflux condensate in fractionator 34.

The element for heating and instigating cracking reactions in the charging stock consists, in the case illustrated, of two interconnected banks of horizontal tubes 14 and 14', respectively, which receive principally radiant heat from combustion gases generated by the combustion of fuel supplied to combustion and heating zone A of the furnace by means of suitable burners indicated at 18. The combustion gases from heating zone A pass downwardly over a separate bank of tubes 15, within the centrally located fluid heating zone C of the furnace, along with the gases from the other combustion and heating zone B, to be presently described.

Temperature and pressure conditions employed in the charging stock heating coil may be varied considerably depending on the quality of the charge but are generally within the limits of 850 to 950° F. and 100 and 500 lbs. per square inch.

Heated products are discharged from the charging stock heating coil through line 21 containing control valve 22 and pass into a reaction chamber 23, wherein substantial completion of the desired conversion reactions occurs and wherein a substantially superatmospheric pressure is maintained which may be substantially the same or somewhat lower than that in the last tubes of the heating element.

In the case here illustrated both vaporous and liquid products are discharged from the bottom of chamber 23 through line 24 containing pressure control valve 25 and enter a vaporizing chamber 26 maintained at substantially reduced pressure of the order of 100 lbs. per square inch to substantially atmospheric pressure, with a reduction in temperature in this zone due to the pressure reduction. In the vaporizing chamber separation of vaporous and liquid conversion products is accomplished, the former comprising substantially all of the gasoline boiling range fractions and other constituents having characteristics rendering them suitable for further conversion within the same system. The residual liquid, which is preferably of a fuel oil character at this point, is withdrawn through line 93 and a portion or all of it may, when desired, be cooled and stored for subsequent use after withdrawal through line 95 containing control valve 96. When it is desired to further reduce this residuum to produce a good grade of marketable asphalt it is further subjected to vacuum distillation, which will be described after the completion of the description of the cracking process.

The vaporous products from chamber 26 follow vapor line 27 containing control valve 28 and pass through heat exchanger 29 in general counter-flow to regulated portions of the charging oil composite, as previously described. Line 30 containing control valve 31 indicates a drain line which may be employed for removing heavy material condensed in the heat exchanger. Due to the cooling of the vapors in heat exchanger 29 this zone serves to separate therefrom heavy carbonizable liquids which might cause tube troubles if returned to further conversion with the reflux condensate.

The major portion of the vapors supplied to heat exchanger 29, which remain uncondensed therein, pass from the heat exchanger through line 32 and valve 33 to fractionator 34 of the conventional bubble tray variety or any other suitable form. This fractionator serves to separate the vapors of motor fuel boiling range and fixed gases as an overhead fraction from the higher boiling components of the vapors which are condensed as reflux condensate. Reflux condensate is withdrawn from the bottom of the tower through a line 75 and valve 76 and pumped by pump 77 through line 78, valve 79, line 89 and valve 90 to an independently heated tubular cracking element comprising tube banks 15, 16 and 17.

In the case here illustrated the heating coil to which the reflux condensate is supplied is also located within furnace 20 and the combustion gases from both combustion and heating zones A and B pass over the tubes of bank 15 imparting fluid heat thereto. The roof and floor tubes 16 and 17 are supplied with radiant heat from the materials undergoing combustion in heating zone B; fuel being supplied to this zone from a series of burners indicated at 19. The temperature and pressure conditions employed in the reflux heating coil are preferably somewhat more severe than those employed for the charging stock and may be of the order of from 900 to 1050° F. and 200 to 800 pounds, or more, per square inch. In the present operation the heated products from the reflux heating coil are directed to the vaporizing chamber 26 by way of line 91 containing control valve 92, which may join with line 24 previously mentioned.

The fractionated vapors and gases from fractionator 34 pass through line 35 and valve 36 to condenser 37, from which the resulting distillate and uncondensed gases flow through line 38 and control valve 39 to collection and separation in receiver 40. In order to effect stabilization of the distillate it is passed from receiver 40 through line 41 and valve 42 to a pump 43 from which it is directed through heat exchanger 44, line 45 and valve 46, recovering heat in the heat exchanger for effecting partial vaporization of the distillate before it passes into stabilizing column 47.

Column 47 is commonly operated at a pressure of from 75 to 150 pounds, or thereabouts, per square inch, a top temperature of 100 to 135° F. and a bottom temperature of 250 to 325° F. The function of the stabilizing column 47 is to

remove all of the normally gaseous constituents, including hydrogen, methane, ethane, ethylene, propane and propylene, and a certain portion of the butanes and butylenes, from the distillate supplied to this zone so that the vapor pressure of the resulting finished gasoline is of the order of from 8 to 12 pounds per square inch by the Reid test.

When the temperature of the entering materials after passing through heat exchanger 44 is not high enough to maintain the required temperature differential in the stabilizing column an auxiliary heating arrangement of any suitable form may be employed for reboiling the distillate from the bottom of column 47. In the case here illustrated heat for reboiling is obtained by the diversion of a portion of the reflux condensate from fractionator 34, which pass through line 80 and valve 81 to a closed coil in reboiler 70 and thence back to fractionator 34 either directly through line 82, valve 83 and line 114 or by way of line 84, valve 85, cooler 86, line 87, valve 88 and line 114. The function of cooler 86 is to control the temperature of the oil returned as refluxing liquid to fractionator 34 and thus assist in controlling the character of the fractionation in this zone. Reboiling of the material in the bottom of the stabilizing column is effected by withdrawing the non-vaporous distillate from column 47 through line 66 and valve 67 to reboiler 70 from which evolved vapors are returned to the column through line 68 and valve 69. Stabilized liquid representing the stabilized motor fuel product of the process is withdrawn from reboiler 70 at a point remote from inlet line 66 through line 71 and valve 72 and passes through heat exchanger 44, the function of which has been previously described, after which it may pass to further cooling and storage or to any desired further treatment by way of line 73 containing control valve 74.

The overhead products from stabilizing column 47 pass through line 48 containing control valve 49 and through a condenser 50, which may operate at subatmospheric temperature, if desired, and the resulting condensate, along with fixed gases, passes through line 51 containing control valve 52 to separation in an accumulator 54. The liquid condensate collected at this point will comprise principally four-carbon-atom hydrocarbons with traces of propane and some pertanes, and if desired a portion thereof may be withdrawn to separate storage through line 55 and valve 56. The amount necessary for refluxing at the top of the stabilizing column is withdrawn through line 57 and valve 58 and recirculated by pump 59 through line 60 and valve 61 to column 47. Fixed gases from receiver 40 may pass to absorber 6 by way of line 64 and valve 65, and similarly gases from receiver 54 may be supplied to the absorber through line 62 and valve 63.

In order to make asphalt from the non-vaporous residual liquid from chamber 26, pump 97 supplies all or any desired portion thereof through line 98 and valve 99 to a vacuum evaporator 100. Using a subatmospheric pressure at this point of the order of from 3 to 5 inches or more of mercury absolute pressure enables the efficient and rapid production of marketable asphalts in this zone. The asphalt may be withdrawn to storage through line 101' and a valve 102'. Vapors from the vacuum evaporator pass through line 101 and valve 102 to condenser 103 and thence the resulting condensate and gas passes through line 104 and valve 105 to a receiver 106. The requisite vacuum is maintained in column 100, in the case here illustrated, by withdrawing the fixed gases from receiver 106 through line 107 containing control valve 108 to a barometric condenser 109, which may be of any conventional form and therefore need not be described in detail.

The overhead distillate products from the asphalt evaporator pass through line 110 and valve 111 to a pump 112, which discharges through line 114. This product will ordinarily comprise an oil suitable for example as light domestic or industrial fuel and a regulated portion or all of this material may be discharged through branch line 112' and valve 113' to storage or elsewhere as desired and regulated quantities thereof may be used as a refluxing medium in column 100 to control the distillation in the vacuum evaporator by passing the same through valve 115 in line 114 and thence through line 117 containing control valve 118 into the upper portion of the evaporator. On the other hand all or any desired portion of the condensate collected in receiver 106 may be returned for further conversion to the light oil heating coil of the system. It may be supplied direct to this zone, by well known means not illustrated, or may first be utilized as a cooling and refluxing medium in fractionator 34 by supplying the same thereto through valve 116 in line 114.

As previously stated the process of the present invention is particularly adapted to producing commercially valuable products upon relatively heavy charging stocks and the following example is introduced to illustrate the character of the results commonly obtainable, though the scope of the invention is not to be correspondingly limited.

The oil from which the charging stock for the process was derived was an Albanian crude having the following properties:

ANALYSIS OF TOPPED CRUDE

Gravity, ° A. P. I.	11.6
Specific gravity	0.9888
Flash (Cleveland open cup), ° F.	225
Fire (Cleveland open cup), ° F.	270
Flash (Pensky-Martens), ° F.	205
Viscosity, furol @ 122° F., sec.	174
Sulfur—per cent	4.15
Cold test, ° F.	13
B. S. & W.—per cent	0.3

100 cc. distillation

I. B. P. ° F.	441
5%	505
10	534
20	603
30	646
40	676
50	693
60	705
70	716
80	723
Per cent over	87.5
Per cent coke by wt.	12.4
Per cent @ 572° F.	15.5

The topped crude which represented 78.3% of the original crude oil was cracked in a plant corresponding in essential details with the one shown in the drawing to produce a maximum yield of 375° F. end-point gasoline while processing the residuum from the flash chamber to produce asphalt of from 80 to 100° penetration. In the following table are summarized the over-

all results of a run which extended over a period of several days.

SUMMARY OF CRACKING CONDITIONS

Temperature at outlet from charging stock heater, ° F.	920
Pressure at outlet from charging stock heater, lbs. per sq. in.	225
Temperature at outlet from reflux heater, ° F.	950
Pressure at outlet from reflux heater lbs. per sq. in.	350
Average temperature in reaction chamber ° F.	870
Pressure in reaction chamber lbs. per sq. in.	225
Pressure in vaporizing chamber lbs. per sq. in.	50
Absolute pressure in asphalt reducing still lbs. per sq. in.	1.5

YIELDS, PER CENT BY WEIGHT OF CHARGING STOCK

	Per cent
Motor fuel of approx. 375° F. end-boiling point	50
Asphalt (80 penetration)	42
Fixed gases	8

PROPERTIES OF LIGHT DISTILLATE PRODUCT (UNTREATED GASOLINE)

Specific gravity	0.748
Octane number	80
Mg. of gum/100 cc. by copper dish	100
Initial boiling point, ° F.	95
5% over at, ° F.	122
10% over at, ° F.	144
20% over at, ° F.	176
50% over at, ° F.	266
90% over at, ° F.	365
End point, ° F.	376

PROPERTIES OF ASPHALT

Penetration at 77° F.	81
Ductility, cm.	100+
Solubility in carbon bisulfide, per cent	99.3
Solubility in carbon tetrachloride, do.	99.0
Solubility in 86 A. P. I. paraffin naphtha per cent	75

The practical features of the process will be evident to those conversant with oil refinery operations from the preceding data on conditions of operation, yields, and the qualities of the principal products. However, neither the descriptive material nor the numerical data are to be construed as imposing undue limitations upon the generally broad scope of the invention.

I claim as my invention:

1. In a process for the conversion of hydrocarbon oils wherein intermediate liquid conversion products of the process are subjected to conversion conditions of cracking temperature and superatmospheric pressure in a heating coil and then introduced into a reduced pressure vaporizing chamber wherein vaporous and residual liquid conversion products are separated, the vaporous conversion products subjected to fractionation for the formation of reflux condensate comprising said intermediate liquid conversion products which are supplied to the heating coil for said conversion, fractionated vapors of the desired end-boiling point subjected to condensation, the resulting distillate and uncondensed gases collected and separated and the distillate subjected to stabilization whereby to liberate therefrom dissolved gases and undesirable low-boiling components for the purpose of reducing its vapor pressure, the improvement which comprises subjecting said uncondensed gases together with the gaseous products liberated from the distillate by said stabilization to absorption by contact with charging stock for the process comprising an oil of higher boiling characteristics than said reflux condensate, subjecting charging stock from the absorption stage, containing absorbed high-boiling components of the gases, to independently controlled conversion conditions of elevated temperature and superatmospheric pressure in a separate heating coil and communicating reaction chamber maintained under higher pressure than the vaporizing chamber, introducing the resulting conversion products from the reaction chamber into said reduced pressure vaporizing chamber, withdrawing residual liquid from said vaporizing chamber, subjecting the same to further distillation at subatmospheric pressure for the formation of asphaltic residue, recovering the latter, subjecting the vapors evolved by said further distillation of the residual liquid to condensation and returning resulting condensate to the fractionating stage of the cracking system.

2. A conversion process which comprises subjecting a residual petroleum oil to cracking conditions in a cracking zone, simultaneously cracking a recycle stock, formed as hereinafter set forth, at higher temperatures than said residual oil in a second cracking zone, discharging the cracked products from both said zones into a reduced pressure vaporizer and therein separating the same into vapors and a liquid residue, fractionating the vapors to condense heavier fractions thereof, removing liquid residue from said vaporizer and reducing the same to an asphaltic material by further distillation thereof under subatmospheric pressure, introducing condensate resulting from said further distillation into contact with said vapors undergoing fractionation as a refluxing medium for the vapors, thereby combining said condensate with reflux condensate separated from the vapors by the fractionation, supplying the resultant condensate mixture to the second cracking zone as said recycle stock, finally condensing the fractionated vapors and separating the resultant distillate from normally incondensible gases produced in the process, scrubbing such separated gases with said residual petroleum oil prior to the introduction of the latter to the first-mentioned cracking zone, whereby to absorb heavier components of the gases in the residual oil, and supplying the absorbed gaseous components to the first-mentioned cracking zone together with said residual oil.

LYMAN C. HUFF.