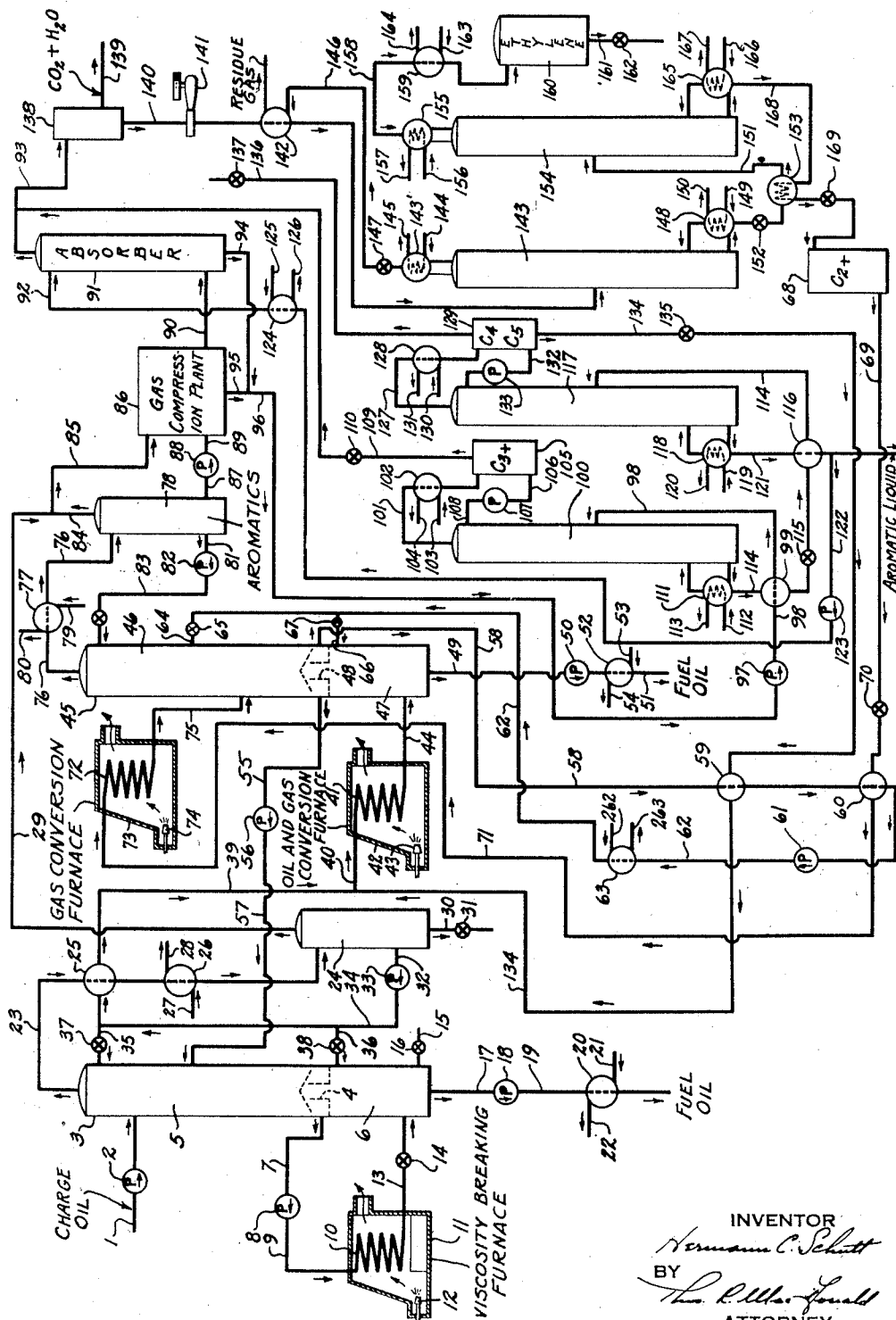


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METHOD OF REFINING HYDROCARBONS

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This invention relates to the art of refining hydrocarbon oil and, more particularly, to the art of refining such oil by thermal conversion to effect changes in the molecular structure.

Hydrocarbon oil, such as, for example, crude petroleum and its fractions has become increasingly important as a source of low molecular weight hydrocarbons of value as raw material for the synthesis of chemical compounds having general and specific industrial utility. There may be produced from reduced crude petroleum, for example, by thermal conversion operations, both liquid and gaseous conversion products. The quantities and the composition of the respective conversion products will be governed generally by the temperature and pressure conditions at which the conversion operations are carried out. Certain of the liquid conversion products produced are hydrocarbons of the aromatic series and are useful as motor fuel and as raw material for the chemical industry. Likewise, certain of the normally gaseous unsaturated hydrocarbons produced, such as, for example, ethylene, propylene, and butylene are of major utility as a base material for the production of innumerable chemical compounds.

An object of this invention is to provide a method for manufacturing from petroleum both unsaturated aliphatic and aromatic hydrocarbons.

Another object of this invention is to provide a method for manufacturing from petroleum an unsaturated normally gaseous hydrocarbon as a product.

Another object of this invention is to provide a method for manufacturing from petroleum an aromatic hydrocarbon product adapted to be used as motor fuel.

Another object of this invention is to provide a method for manufacturing aromatics from petroleum by thermal conversion at temperatures lower than the heretofore required temperatures.

Other and further objects of this invention will be apparent from the accompanying description, accompanying drawing, and the appended claims.

The accompanying drawing which forms part of the instant specification is a view in elevation schematically showing a combination of apparatus with which the method may be carried out.

In general, charge oil such as, for example, reduced crude is fractionated to separate the heavy portion which together with recycle oil is subjected to a viscosity-breaking heating operation.

There is obtained from the charge oil and the products of this operation, by fractionation and condensation, fuel oil, recycle oil, clean low boiling oil and uncondensable gas. This clean oil is admixed with a carefully selected hydrocarbon fraction comprising mainly C_4 and C_5 hydrocarbons, i. e., hydrocarbons having four and five carbon atoms per molecule. This selected fraction is preferably rich in unsaturated hydrocarbons, particularly di-olefins and branched chain mono-olefins. Unsaturated hydrocarbons illustrative of these groups are, for example, butadiene (1,3) and pentadiene (1,3) being di-olefins of the C_4 and C_5 hydrocarbons, respectively, and iso-butylene and 2 methyl butene (1) being branched chain mono-olefins of the C_4 and C_5 hydrocarbons. This hydrocarbon fraction characterized by such constituents functions in admixture with the clean oil to promote the formation of aromatics by thermal conversion at temperatures reduced from the high values heretofore required.

The clean oil admixed with the selected hydrocarbon fraction is subjected to a high temperature-low pressure thermal conversion operation productive of appreciable quantities of desired aromatic and unsaturated hydrocarbons, and the conversion products fractionated. There are obtained as products of this fractionating operation, a heavy fraction forming a synthetic fuel oil, an intermediate fraction containing oil suitable for recycling and a light gas-vapor fraction containing the unsaturates and aromatics desired as final products.

The fuel oil is withdrawn from the system and the intermediate fraction is re-fractionated with the charge oil and products of the viscosity-breaking operation. This intermediate fraction through re-fractionation yields clean recycle oil and also assists in more nearly accomplishing the desired substantially complete condensation of the products of this fractionating operation. In addition, the charge oil functions as an absorption medium to remove free carbon formed by the high temperature treatment from this intermediate fraction, thus producing a cleaner oil. The free carbon thus absorbed passes with the charge oil through the viscosity-breaking heating coil and is separated in the fuel oil from the viscosity-breaking operation.

The light gas-vapor fraction is cooled and normally incondensable gases are separated from condensate formed of which a portion is used as reflux oil in the fractionating operation. These uncondensed gases together with normally

uncondensable gases resulting from the viscosity-breaking operation are highly compressed in a gas compression plant, preferably in at least two stages coupled with intermediate and final compressed gas cooling and condensate separating stages.

The compressed gases are subjected to a selective absorption operation which separates from the gases substantially all of the five carbon atom hydrocarbons and an appreciable percentage of those four carbon atom unsaturated hydrocarbons desired in the so-called selected hydrocarbon fraction. The desired selective absorption is attained through the employment of an aromatic liquid as an absorption oil which, being intended to absorb C_4 and C_5 hydrocarbons primarily, is substantially free of five carbon atom hydrocarbons. The aromatic liquid has a greater affinity for di-olefins and branched chain mono-olefins of the C_4 and C_5 unsaturated hydrocarbons, or for saturated hydrocarbons. Thus, although substantially all of the saturated and unsaturated C_5 hydrocarbons will be absorbed by the aromatic absorption medium, desired unsaturated hydrocarbons of the C_4 hydrocarbons will be concentrated in the aromatic liquid, from which the selected hydrocarbon fraction to be mixed with the clean oil for subsequent thermal conversion is to be separated. The five carbon atom hydrocarbons of the selected fraction, being of higher molecular weight and reaction velocity, will react sufficiently during the conversion time period and a selective concentration of the more unstable compounds of this five carbon atom group is therefore not as essential.

Condensate formed by the gas compression operation from the light gas-vapor fraction is combined with the rich absorption liquid and the combined liquids fractionated to recover aromatic hydrocarbons as a finished product, and the four and five carbon atom hydrocarbons as a selected fraction for admixture with the clean oil. A portion of the aromatic product thus recovered is employed as the lean absorption oil previously referred to, the remaining portion being removed from the system. The four and five carbon atom hydrocarbons forming the selected fraction are admixed with the clean oil and subjected therewith to the high temperature thermal conversion operation as has previously been described.

The uncondensed products of the fractionating operation together with gases, unabsorbed by the aromatic absorption liquid and substantially freed of di-olefins and other unstable hydrocarbons readily polymerizable to gums at a high pressure are preferably first freed of any water and carbon dioxide present and then fractionated under high pressure and at low temperature without danger of gum formation and deposition to recover unsaturated gaseous hydrocarbon desired as a finished product, from gaseous constituents of both higher and lower molecular weight, the lower molecular weight constituents being removed from the system.

The higher molecular weight gaseous constituents are subjected to a separate high temperature thermal conversion operation productive of additional quantities of desired unsaturated and aromatic hydrocarbons and are then fractionated with the products of the clean oil thermal conversion operation serving in this fractionating operation, by reason of their high heat content and stripping capacity, to promote a better

separation of aromatic hydrocarbons from the combined products of the respective thermal conversion operations.

As an example of carrying out this invention, reference may be had to the following description wherein the application of the method of this invention to the manufacture of liquid ethylene and an aromatic liquid as desired products from a reduced crude petroleum is described.

Referring now more particularly to the drawing, a reduced crude of 20°-30° A. P. I. gravity and at a temperature of from about 70° F. to about 400° F., preferably 400° F., is charged through a pipe 1 by means of a pump 2 into a heavy oil fractionator 3. The fractionator 3 is divided by means of a member 4 forming a combined collecting pan and vapor riser into intercommunicating fractionating sections 5 and 6, each of which is provided with suitable fractionating elements (not shown).

The fractionating section 5 is preferably suitably refluxed to provide a temperature gradient ranging from a temperature at the bottom of the section of from about 600° F. to about 650° F., preferably 625° F., to a temperature at the top of the section of from about 450° F. to about 550° F., preferably about 500° F.

The fractionating section 6 is preferably suitably refluxed to provide a temperature gradient therein ranging from a temperature at the bottom of the section of from about 750° F. to about 850° F., preferably about 800° F., to a temperature at the top of the section of from about 750° F. to 800° F., preferably about 775° F.

Liquid bottoms accumulating on the member 4 are withdrawn from the fractionating section 5 through a pipe 7 by means of a pump 8 and charged serially through a pipe 9, through a viscosity breaking heating coil 10 positioned in a suitable furnace 11 provided with one or more burners 12, and through a pipe 13 having a pressure reducing valve 14, into the fractionating section 6 of the fractionator 3.

The liquid bottoms in passing through the coil 10 are heated to a temperature at the coil outlet of from about 875° F. to about 925° F., preferably about 900° F., under a coil outlet pressure of from about 100 lbs. per square inch gage to about 300 lbs. per square inch gage, preferably about 200 lbs. per square inch gage. These pressure and temperature conditions are such as to effect a preliminary viscosity breaking cracking operation on the liquid bottoms productive of relatively low boiling hydrocarbons from which may be extracted a light clean oil more suitable as a charging stock for the subsequent high temperature cracking operation. The pressure on the heated bottoms issuing from the viscosity breaking coil 10 is reduced by means of the valve 14 to a pressure of from about 5 lbs. per square inch gage to about 40 lbs. per square inch gage, preferably about 20 lbs. per square inch gage, which is the pressure maintained in the fractionator 3.

The conversion products of the viscosity breaking operation are steam stripped in the fractionating section 6 with steam entering the fractionating section through a pipe 15 controlled by a valve 16 and the unvaporized fuel oil residue is withdrawn through a pipe 17 by means of a pump 18 which discharges the residue liquid serially through a pipe 19 and cooler 20 to storage. The cooler 20 is provided with cooling liquid inlet and outlet pipes 21 and 22 respectively.

The overhead products of the fractionating

section 6 rise upwardly through the vapor riser of the member 4 into the fractionating section 5 wherein they are further fractionated and a separation of heavy constituents to be recycled from the lighter constituents is made.

The fractionator 3 discharges its well fractionated overhead products serially through a transfer pipe 23, a heat exchanger 25, and a water cooler 26 into a gas separator 24. The cooler 26 is provided with cooling liquid inlet and outlet pipes 27 and 28, respectively. The uncondensed constituents in the separator 24 are vented therefrom through a pipe 29 for further processing as will be more fully pointed out hereinafter and any water as may accumulate in the separator 24 is drained therefrom through a pipe 30 controlled by a valve 31.

The condensate in the separator 24 may be characterized as a clean oil and consist primarily of hydrocarbons having boiling points generally within the boiling range of gasoline and gas oil. This oil is withdrawn from the separator 24 through a pipe 32 by a pump 33 and discharged thereby through a pipe 34 from which pipes 35 and 36 having suitable control valves 37 and 38 respectively conduct the oil in suitable quantities to the fractionating sections 5 and 6 respectively wherein the cooled oil is employed to reflux vapors being fractionated and control the temperature in these sections.

The clean oil is also conducted from the pipe 34 by a pipe 39 through the heat exchanger 25 wherein it is heated, into a pipe 40 feeding a high temperature thermal conversion coil 41 positioned in a furnace 42 having a suitable burner 43. It is to be understood that the arrangement of the coil 41 in the furnace 42 as shown is by way of example only as the coil 41 may comprise any suitable number of convectively and/or radiantly heated sections for heating and/or thermally converting the oil. This will be obvious to those skilled in the art.

The oil, before entering the coil 41, is preferably admixed with a selected hydrocarbon fraction comprising mainly hydrocarbons having four and five carbon atoms. This fraction is recovered from the conversion products by subsequent steps of the method, as will hereinafter be pointed out, and is added to the oil in the feed pipe 40 through a pipe 134.

It is preferred that the high temperature thermal conversion coil 41 be operated with an outlet temperature of from about 1250° F. to about 1350° F., preferably about 1300° F., and at an outlet pressure of from about 10 lbs. per square inch gage to about 50 lbs. per square inch gage, preferably about 30 lbs. per square inch gage, although the exact temperatures and pressures employed will obviously be chosen so as to effect the optimum production of the products desired.

The conversion products are conveyed by the transfer pipe 44 into a main fractionator 45 having an upper fractionating section 46 and a lower fractionating section 47 separated from each other by means of a member 48 forming a combined vapor riser and collecting pan. Each of the fractionating sections is equipped with fractionating elements (not shown) in sufficient numbers to insure adequate fractionation of the vapors in each.

The fractionating section 46 is preferably suitably refluxed to provide a temperature gradient ranging from a temperature at the bottom of the section of from about 350° F. to about 450° F., preferably about 400° F., and a temperature at

the top of the section of from about 175° F. to about 225° F., preferably about 200° F.

The fractionating section 47 is preferably suitably refluxed to provide a temperature at the bottom of the section of from about 500° F. to about 600° F., preferably about 550° F., and a temperature at the top of the section ranging from about 400° F. to about 500° F., preferably about 450° F.

Synthetic fuel oil is separated from the conversion products in the fractionating section 47 and is withdrawn therefrom through a pipe 49 by means of a pump 50 and discharged thereby serially through a pipe 51 and cooler 52 to storage. Cooling liquid is caused to be circulated through the cooler 52 through the cooling liquid inlet and outlet pipes 53 and 54, respectively.

Fractionated vapors from the fractionating section 47 pass through the vapor riser of the member 48 into the upper fractionating section 46 from which liquid oil which collects on the collecting pan of the member 48 is withdrawn through a pipe 55 by means of a pump 56 and charged thereby through a pipe 57 to a suitably located tray in the fractionating section 5 for re-fractionation and recovery as recycle stock which, when discharged with the fractionator overhead products, aids in the approachment to the desired substantially complete condensation of the overhead products.

Liquid oil for refluxing the fractionating sections 46 and 47 is also withdrawn from the collecting pan of the member 48 serially through a pipe 58 and heat exchangers 59 and 60, by means of a pump 61, the oil being cooled in transit in heat exchangers 59 and 60 by indirect heat exchange with cooler liquid, as will be more fully pointed out hereinafter. The pump 61 discharges the partially cooled oil serially through a pipe 62 and cooler 63, in which latter the oil is further cooled by means of cooling liquid caused to be circulated through the cooler through liquid inlet and outlet pipes 262 and 263, respectively. The cooled oil flows from the pipe 62 through the pipe 64 in regulated quantities controlled by a valve 65 into the upper fractionating section 46 of the fractionator 45 and refluxes this section to maintain the temperature range desired therein. Similarly, cooled oil flows from the pipe 62 through the pipe 66 in regulated quantities controlled by a valve 67 into the lower fractionating section 47 of the fractionator 45 and refluxes this section to maintain the temperature range desired therein.

There is performed concurrently with the performance of the high temperature thermal conversion operation on the clean oil and selected hydrocarbon fraction a separate high temperature thermal conversion operation on a gaseous charging stock recovered from conversion products of the respective thermal conversion operations, as will be more particularly pointed out hereinafter. This gaseous charging stock which on recovery is preferably accumulated as a liquid in a feed tank 68 under a pressure of from about 350 lbs. per square inch gage to about 550 lbs. per square inch gage, maintained therein, is caused to flow under the existing pressure serially through a pipe 69, a pressure reducing valve 70 positioned therein, heat exchanger 60 and pipe 71 to the inlet of a high temperature thermal gas conversion coil 72 positioned in a suitable furnace 73 having one or more suitable burners 74. The liquefied gas is caused to expand in flowing through the valve 70 and in doing so abstracts

heat from the oil flowing through the heat exchanger 60.

The gaseous charging stock is heated in transit through the coil 72 to a coil outlet temperature of from about 1300° F. to about 1500° F., preferably from 1400° F., under a coil outlet pressure of from about 10 lbs. per square inch gage to about 50 lbs. per square inch gage, preferably about 30 lbs. per square inch gage.

The temperature and pressure conditions maintained in the thermal gas conversion coil 72 will effect the formation of additional quantities of ethylene (and aromatic hydrocarbons) from the gaseous charging stock and the resultant conversion products are conveyed by a transfer pipe 75 into the lower part of the upper fractionating section 46 of the fractionator 45 wherein their heat content and stripping capacity aid the fractionation being performed therein, thus promoting a better recovery of aromatic hydrocarbons in the overhead products of the fractionator.

The overhead products of the fractionator 45 are conveyed therefrom serially through a transfer pipe 76 and cooler 77 into a gas-liquid separator 78. Cooling liquid is caused to be circulated through the cooler 77 by means of cooling liquid inlet and outlet pipes 79 and 80, respectively. The overhead products passing through the cooler 77 are cooled to the lowest possible temperature with the available cooling water to effect the condensation of the greatest possible amount of the overhead products and a portion of the liquid accumulating in the separator 78 is withdrawn therefrom through a pipe 81 by means of a pump 82 and discharged thereby through a pipe 83 to the top of the fractionator 45 for refluxing the vapors and assisting in the maintenance of the desired temperature range therein.

The separator 78 is maintained at substantially the pressure existing within the fractionator 45, namely, a pressure of from about 5 lbs. per square inch gage to about 45 lbs. per square inch gage, preferably about 25 lbs. per square inch gage, and constituents of the overhead products remaining uncondensed in the separator 78 under these temperature and pressure conditions are discharged therefrom through a pipe 84.

These uncondensed constituents, together with those vented from the separator 24 through the pipe 29, are conveyed by means of pipe 85 to a gas compression plant diagrammatically shown as 86. The net liquid product in the separator 78 is withdrawn therefrom through a pipe 87 by means of a pump 88 and charged thereby through a pipe 89 into the gas compression plant 86 where it is combined with condensate formed therein and discharged from the plant through a pipe 95.

In the gas compression plant 86, the uncondensed constituents are compressed, preferably in two or more successively higher pressure stages coupled with intermediate cooling and gas-liquid separating operations all in a manner well understood by those well skilled in the art. The constituents uncondensed in the gas compression plant under a final pressure of from about 100 lbs. per square inch gage to about 400 lbs. per square inch gage employed therein are conveyed at this pressure by the pipe 90 to an absorber 91, preferably equipped with fractionating trays (not shown).

The absorber 91 is preferably operated under a pressure of from about 100 lbs. per square inch gage to about 400 lbs. per square inch gage, preferably about 200 lbs. per square inch gage, using an aromatic liquid product of the method as an

absorption medium. The rate of circulation of the absorption medium is preferably maintained at such levels in conjunction with the pressure in the absorber as to extract from the gas fed to the absorber approximately 60% of the hydrocarbons having four carbon atoms and substantially 100% of the hydrocarbons having five carbon atoms.

The hydrocarbons having four carbon atoms produced by the high temperature thermal conversion operation on the clean oil and selected hydrocarbon fraction include about 5% butadiene and about 45% iso-butylene, each having a greater affinity for the aromatic liquid than normal butylene or normal butane has. Thus, under the conditions existing in the absorber 91, substantially all of the butadiene and iso-butylene will be absorbed in the aromatic distillate in effecting a separation from the gas feed to the absorber of approximately 60% of the hydrocarbons having four carbon atoms.

Unabsorbed gas is vented from the absorber as an overhead product through a pipe 93 and enriched aromatic liquid is removed from the absorber 91 through a pipe 94. The enriched aromatic liquid, together with the liquid product of the gas compression plant 86 removed therefrom through the pipe 95, is conducted by means of a pipe 96 to the suction side of a pump 97 which discharges the liquid serially through a pipe 98 and heat exchanger 99 into a fractionator 100 equipped with suitable fractionating elements (not shown).

The fractionator 100 is operated at a pressure from about 200 lbs. per square inch to about 400 lbs. per square inch, preferably about 300 lbs. per square inch, and at a corresponding equilibrium temperature effective to secure a separation from the liquid feed of mainly those hydrocarbons having less than four carbon atoms. These hydrocarbons which form the overhead product of the fractionator are conducted by means of a pipe 101 through a cooler 102 provided with cooling liquid inlet and outlet pipes 103 and 104, respectively, into a combined reflux accumulator and gas separator 105. The condensate formed in the cooler 102 and collected in the accumulator 105 will consist mainly of three carbon atom hydrocarbons and is withdrawn from the accumulator through a pipe 106 by means of a pump 107 and returned in whole or in part to the fractionator 100 as reflux liquid through a pipe 108 to maintain the desired temperature gradient.

The uncondensed products in the accumulator 105 will consist mainly of hydrocarbons having less than three carbon atoms, together with some hydrogen, and are vented from the accumulator for further processing through a pipe 109 at a suitable pressure controlled by a valve 110 positioned therein.

Heat is supplied to the fractionator 100 in conjunction with a reboiling operation performed in a conventional reboiler 111 through which a reboiling medium is caused to be circulated through fluid inlet and outlet pipes 112 and 113, respectively. The reboiled bottoms are conducted by means of a pipe 114 serially through heat exchanger 99, pressure reducing valve 115 and heat exchanger 116 into a fractionating tower 117.

The fractionator 117 is equipped with suitable fractionating elements (not shown) and is operated at a pressure reduced somewhat from that maintained in the fractionator 100. Expansion occurring during the passage of the reboiled bottoms from reboiler 111 through the reducing valve 115 causes heat to be abstracted from the liquid

flowing through the heat exchanger 116 in indirect heat exchange with the reboiled bottoms forming the feed to the fractionator 117.

The fractionator 117 is operated under pressure and temperature conditions such as to effect a separation from the feed thereto of the four and five carbon atom hydrocarbons as an overhead product from heavier hydrocarbons forming the desired aromatic product. The fractionator 117 is preferably operated at a pressure of from about 100 lbs. per square inch gage to about 200 lbs. per square inch gage, preferably about 150 lbs. per square inch gage, and at a corresponding equilibrium temperature effective to secure the desired separation.

Heat is supplied to the fractionator 117 in conjunction with a reboiling operation performed in a conventional reboiler 118 through which a reboiling medium is caused to be circulated through fluid inlet and outlet pipes 119 and 120 respectively.

The aromatic product substantially free of four and five carbon atom hydrocarbons is conducted as a finished product from the reboiler 118 to storage through a pipe 121 being cooled in transit by indirect heat exchange with the feed to fractionator 117 passing through the exchanges 116. A portion of the cooled aromatic product is conducted from the pipe 121 by a pipe 122 serially through a cooler 124 into the pipe 92 by which it is conducted into the top of the absorber 91. The flow of the aromatic product through the pipes 122 and 92 is effected by means of a pump 123 and the liquid is cooled in transit by means of a cooler 124 through which cooling fluid is caused to be circulated by means of cooling fluid inlet and outlet pipes 125 and 126, respectively.

The overhead products of the fractionator 117, consisting mainly of hydrocarbons having four and five carbon atoms, are conducted, together with whatever lower boiling hydrocarbons may be present, by a pipe 127 through a cooler 128 into an accumulator-separator 129. Cooling liquid is caused to be circulated through the cooler 128 by means of cooling liquid inlet and outlet pipes 130 and 131, respectively. Substantially all the hydrocarbons of four and five carbon atoms are condensed in the cooler 128 and a portion of the condensate is returned through a pipe 132 by means of a pump 133 to the fractionator 117 as reflux liquid for maintaining the desired temperature range therein.

The balance of the condensate is conducted by means of a pipe 134 serially through a pressure reducing valve 135 and heat exchanger 59 into the feed pipe 40 of the clean oil thermal conversion coil 41 wherein, due to its presence, the light distillate produced by this conversion operation will contain a much higher percentage of pure aromatics than it would were the clean oil not admixed therewith.

The condensate in passing through the valve 135 expands and is thus sufficiently cooled to reduce the temperature of reflux oil in the heat exchanger 59. Where the coil 41 is operated at a high outlet pressure, it may be desirable to substitute a pump for the valve 135.

Any uncondensed constituents in the separator 129 may be vented therefrom through a pipe 136 and a pressure reducing valve 137, and recycled through the recovery system into which they may be fed at a suitable point of lower pressure.

The overhead gaseous products of the absorber 91 and the uncondensed gaseous constituents from the separator 105 which together form a rela-

tively small portion of the total gaseous conversion products are conducted by the pipe 93 into suitable treating apparatus, diagrammatically shown at 138, for removing carbon dioxide and water therefrom. Suitable agents and operations well known in the art, such as for example, calcium chloride, silica gel, water washing and the like, may be employed to accomplish the desired separation.

Carbon dioxide and water is discharged from the treating apparatus 138 through a pipe 139 and the gaseous constituents are conducted by a pipe 140 serially through a compressor 141 and a cooler 142 into a low temperature fractionator 143 equipped with suitable fractionating elements (not shown). The uncondensed constituents are compressed in the compressor 141 to a pressure of from about 500 lbs. per square inch gage to about 900 lbs. per square inch gage, preferably about 700 lbs. per square inch gage, and are then cooled in the cooler 142 to remove the heat of compression.

The fractionator 143 is operated at a pressure of from about 500 lbs. per square inch gage to about 900 lbs. per square inch gage, preferably about 700 lbs. per square inch gage, and at a corresponding equilibrium temperature at the top of the tower, for example from about -100° F. to about -150° F., preferably about -125° F. Refluxing of the fractionator 143 is accomplished by cooling and condensing a portion of the overhead products such as methane in a reflux condenser 143' through which a refrigerant at a suitably low temperature is caused to be expanded through fluid inlet and outlet pipes 144 and 145, respectively. The refrigeration may be obtained, for example, by expanding a liquefied refrigerant gas such as, for example, ethane or ethylene through the reflux condenser 143'.

The overhead products issuing from the reflux condenser 143' are conducted by means of a pipe 146 through a pressure reducing valve 147 and the cooler 142 either to the atmosphere, to a fuel gas main, or to storage, as may be desired. The overhead products, in passing through the pressure reducing valve 147, are preferably expanded and thereby further cooled. The cooled gases, in passing through the heat exchanger 142, remove the heat of compression from compressed gases passing to the fractionator 143.

Heat is supplied to the fractionator 143 in conjunction with a reboiling operation performed in a conventional reboiler 148 through which a reboiling fluid such as, for example, water at a normal temperature, is caused to be circulated through fluid inlet and outlet pipes 149 and 150, respectively. The bottoms product is conducted from the reboiler 148 by a pipe 151 serially through a pressure reducing valve 152 and heat exchanger 153 wherein it is heated to a second low temperature fractionator 154 equipped with suitable fractionating elements (not shown).

The fractionator 154 is operated to separate ethylene as an overhead product from the ethylene and higher molecular weight hydrocarbons forming the liquid feed to the fractionator. In effecting this desired separation, the tower is operated at a pressure of from about 400 lbs. per square inch gage to about 600 lbs. per square inch gage, preferably about 500 lbs. per square inch gage, at a corresponding top tower equilibrium temperature of from about -25° F. to about $+25^{\circ}$ F., preferably about 0° F. Refluxing of the tower to provide the desired low top tower temperature is accomplished by cooling and condensation of

a portion of the overhead products in a reflux condenser 155 through which a suitable refrigerant is caused to be expanded by means of fluid inlet and vapor outlet pipes 156 and 157, respectively.

The ethylene issuing from the reflux condenser 155 as an overhead product is conducted by a pipe 158 through a cooler 159 to an accumulator 160 from which liquid ethylene is removed as a finished product through a pipe 161 controlled by a valve 162.

The gaseous ethylene, in passing through the cooler 159, is refrigerated and condensed by indirect heat exchange with a refrigerant caused to be expanded through the cooler through fluid inlet and outlet pipes 163 and 164, respectively. The refrigerant employed in the reflux condenser 155 and the cooler 159 may advantageously be propane, carbon dioxide, ammonia and the like, although any other suitable refrigerant by which the desired low temperature may be attained may be employed.

Heat is supplied to the fractionator 154 in conjunction with a reboiling operation performed in a conventional reboiler 165 through which a suitable reboiling medium is caused to be circulated through the fluid inlet and outlet pipes 166 and 167, respectively. The bottoms product comprising liquid ethane and hydrocarbons of higher molecular weight particularly saturated and unsaturated three and four carbon atom hydrocarbons recovered therewith, is conducted from the reboiler 165 by a pipe 168 serially through the heat exchanger 153 and a flow control valve 169 for controlling the liquid level in the reboiler 165, into the feed tank 68 supplying the high temperature gas conversion coil 72.

It will be understood that although there has been described the application of the method to the manufacture and recovery of ethylene as a finished product, that such description is by way of example only as other normally gaseous hydrocarbon products, for example propylene or butylene, may be manufactured and recovered from the hydrocarbon oil through the application of the method as will be apparent to those skilled in the art.

It will be observed that the object of this invention has been accomplished and there has been provided a method for commercially manufacturing from hydrocarbon oils such as petroleum, gaseous hydrocarbon products of substantial purity such as ethylene, propylene, butylene or the like, and liquid hydrocarbon products containing a high percentage of pure aromatics.

It will be observed that certain features and sub-combinations are of utility and may be employed without reference to other features and sub-combinations. This is contemplated by and is within the scope of the appended claims. It is further obvious that various changes may be made in details within the scope of the appended claims without departing from the spirit of this invention. It is, therefore, to be understood that this invention is not to be limited to the specific details shown and described.

Having thus described this invention, what is claimed is:

1. The method comprising mixing a selected hydrocarbon fraction with a low boiling hydrocarbon oil; subjecting the mixture to a high temperature thermal conversion operation; separating a normally gaseous unsaturated hydrocarbon from the conversion products as a desired

product; separating an aromatic liquid from the conversion products as a desired product; separating mainly hydrocarbons having four and five carbon atoms from the conversion products by an absorption operation and employing them as the selected hydrocarbon fraction; and, employing a portion of the aromatic liquid as lean oil in the absorption operation.

2. The method comprising mixing a selected hydrocarbon fraction with a low boiling hydrocarbon oil; subjecting the mixture to a thermal conversion operation; separately subjecting a normally gaseous hydrocarbon charging stock to a higher temperature thermal conversion operation; separating a normally gaseous unsaturated hydrocarbon as a desired product from the conversion products of both said conversion operations; separating an aromatic liquid from these conversion products as a desired product; separating mainly hydrocarbons having four and five carbon atoms from these conversion products by an absorption operation and employing them as the selected hydrocarbon fraction; employing a portion of the aromatic liquid as lean oil in the absorption operation; and, recovering the normally gaseous hydrocarbon charging stock from conversion products not absorbed by the lean oil during the absorption operation.

3. The method comprising mixing a selected hydrocarbon fraction with a low boiling hydrocarbon oil; subjecting the mixture to a high temperature thermal conversion operation productive of normally gaseous unsaturated hydrocarbons and aromatics; separately subjecting a normally gaseous hydrocarbon charging stock to a high temperature thermal conversion operation productive of normally gaseous unsaturated hydrocarbons and aromatics; dephlegmating the conversion products of both conversion operations and recovering as products an aromatic liquid and uncondensed hydrocarbon gas; compressing the gas to obtain additional aromatic liquid; subjecting the compressed gas to an absorption operation with an aromatic absorption medium; subjecting the rich absorption medium together with aromatic liquid previously recovered to a series of fractionating operations and recovering an aromatic liquid as a finished product and mainly hydrocarbons having four and five carbon atoms as the selected hydrocarbon fraction; employing aromatic liquid recovered as a finished product as the absorption medium; compressing the unabsorbed gases; subjecting the unabsorbed compressed gases to a series of high pressure low temperature fractionating operations and recovering as products thereof a desired normally gaseous hydrocarbon product and the normally gaseous charging stock.

4. Method comprising subjecting a clean hydrocarbon oil admixed with a selected hydrocarbon fraction comprising mainly C₄ and C₅ hydrocarbons to a thermal conversion operation at a temperature of from about 1250° F. to about 1350° F.; subjecting mainly normally gaseous C₂ hydrocarbons to a separate thermal conversion operation at a temperature of from about 1300° F. to about 1500° F.; dephlegmating conversion products of both conversion operations in a common dephlegmating zone; and, recovering a normally gaseous unsaturated hydrocarbon and an aromatic liquid from dephlegmated gas-vapor products of the dephlegmating operation.

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