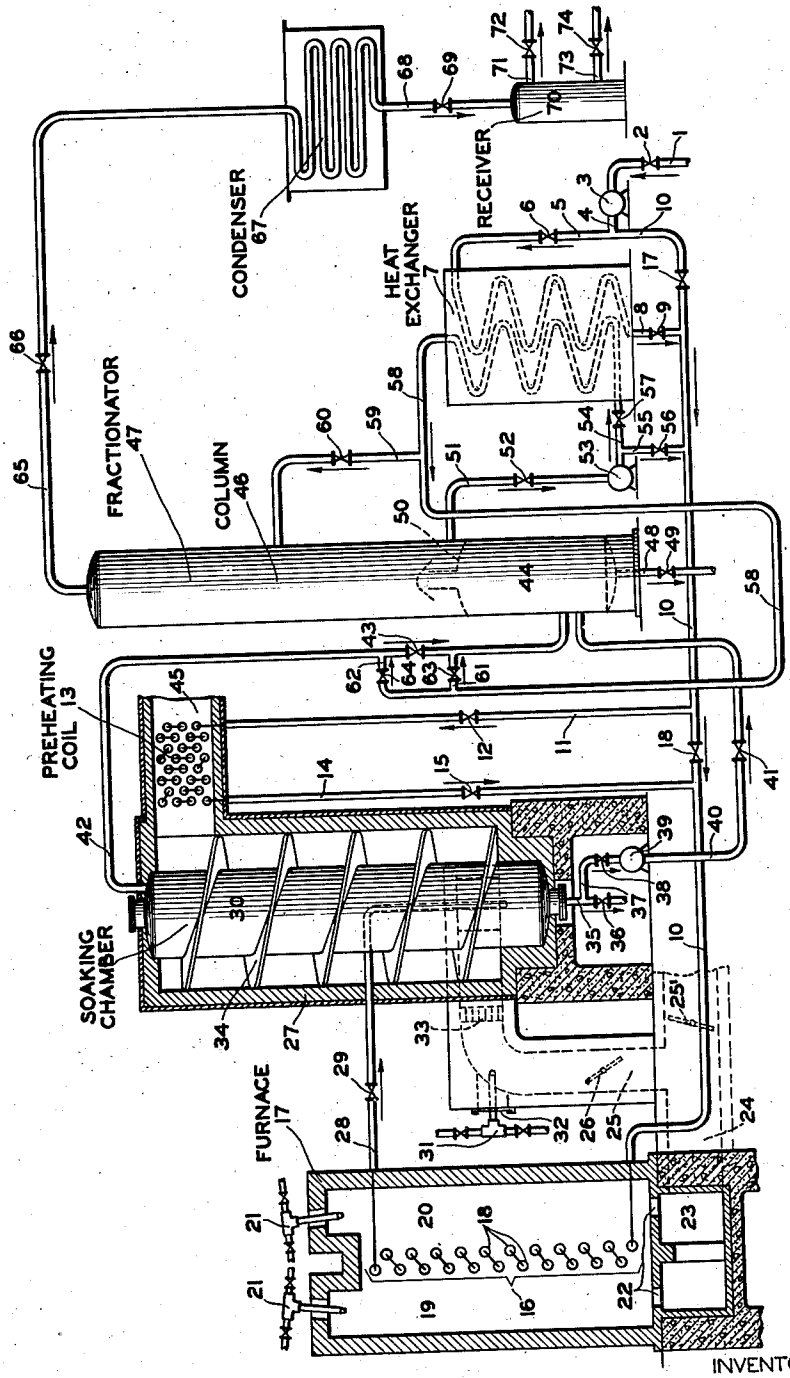
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CONVERSION OF HYDROCARBON OILS

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INVENTOR
LEV A. MEKLER
BY Lee Gary
ATTORNEY

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CONVERSION OF HYDROCARBON OILS

Lev A. Mekler, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

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This invention refers to an improved process and apparatus for the conversion of relatively low-boiling hydrocarbon oils such as, for example, gasoline, naphtha and other distillates containing a substantial quantity of materials within the boiling range of motor fuel.

Cracking operations of the type above mentioned which are ordinarily termed "reforming" operations generally employ a "soaking" section in the heating coil to which they are supplied for conversion, in which soaking section the oil, which has been previously heated to a high conversion temperature, is maintained for an appreciable predetermined time at a substantially constant temperature near that previously attained. Reforming operations, as now commonly practiced, differ from ordinary high-pressure cracking operations employing a tube and chamber type of system in three respects, namely, the higher temperatures and pressures to which the oil is subjected in the heating coil, the appreciably greater length of time during which the oil is subjected to conversion conditions in the heating coil and the fact that, in the best reforming operations, further conversion of the oil after it leaves the heating coil is arrested by one or more of several methods of cooling. While the conversion temperatures employed for reforming are, in many cases, within the range of those employed in vapor-phase cracking operations the reforming type of operation differs from the vapor-phase type principally with respect to the high superatmospheric pressure employed in the former and also with respect to the greater conversion time normally employed by the former.

The use of a "soaking" section such as above referred to necessitates a large furnace to accommodate the relatively long length of heating coil required for the soaking section and due to the fact that the temperature of the oil is not ordinarily increased more than 50°, or thereabouts, above the temperature attained in the preceding portion of the heating coil, the soaking section of the furnace and heating coil employs relatively low rates of heat input. Another disadvantage in this method of operation resides in the fact that any heavy residual liquid and polymerization products formed in the heating coil are required to remain therein for the same length of time as lower boiling products (which are substantially in vaporous state in the soaking section). This necessitates careful selection of the charging stock and accurate control of the heating conditions in order to avoid the excessive formation and deposition of coke in the heating coil.

The present invention obviates both of the disadvantages above mentioned, which are common to present reforming operations, by employing an enlarged externally heated chamber maintained at substantially the same pressure as that employed in the heating coil in place of the soaking section of the heating coil. The use of an enlarged chamber as the soaking section in this type of operation offers several distinct advantages over the use of a soaking section comprising an elongated tubular conduit of relatively small cross-section within a furnace. Separation of residual liquid and heavy polymerization products and removal of these materials from the cracking zone, without permitting their appreciable further conversion and coke formation, is readily accomplished in a chamber but not in a continuous coil. Considerably less pressure drop is encountered in the enlarged chamber than in a continuous soaking coil of the same cracking capacity so that an appreciably smaller pressure, as measured at the inlet to the heating coil, is required for maintaining the pressure in a soaking chamber the same as that in a soaking coil. By eliminating the elongated tubular soaking coil the size of the furnace required is, of course, greatly decreased and high rates of heating may be employed throughout the furnace and heating coil.

The desirability of employing high rates of heating in the heating coil and the fact that a relatively large volume of relatively high temperature combustion gases offer an ideal means for externally heating the soaking chamber make the process of the present invention particularly well suited to the use of a modern type of heater of relatively small size wherein high rates of heating and high tube efficiency is obtained by radiation from materials undergoing combustion and the hot refractory walls of the furnace to opposite sides of each tubular element of the fluid conduit. Relatively large volumes of relatively high temperature flue gases are obtained from this type of furnace when convection or economizer sections are not employed in conjunction with the radiant heating sections and, in the preferred embodiment of the present invention, flue gases from this type of furnace are utilized as a means of externally heating the soaking chamber and, as another feature of the invention, the oil supplied to the heating coil may be preheated, prior to its introduction thereto, by indirect heat exchange with the combustion gases after their contact with the external walls of the soaking chamber, thereby decreasing the load on the furnace, decreasing the temperature of the

final glue gases and increasing the overall heating efficiency obtained in the operation.

The accompanying diagrammatic drawing illustrates one specific form of apparatus embodying the features of the present invention. Referring to the drawing, hydrocarbon oil charging stock for the process is supplied through line 1 and valve 2 to pump 3 by means of which it is fed through line 4 and may be directed, all or in part, through line 5, valve 6, heat exchanger 7, line 8, valve 9, line 10, line 11, valve 12, preheating coil 13, line 14 and valve 15 back into line 10 and thence to heating coil 16. The charging stock is preheated in heat exchanger 7 by indirect heat exchange with hot reflux condensate from the fractionator of the system and in preheating coil 13 with combustion gases having passed over the external walls of the soaking chamber. These preheating operations will be later more fully described. All or a portion of the charging stock may by-pass heat exchanger 7 by means of valve 17 in line 10 and valve 18 in this line permits the charging stock to by-pass preheating coil 13, all or in part, when desired.

Heating coil 16, wherein the oil to be subjected to conversion within the process is heated to the desired relatively high conversion temperature, is located within a furnace 17 of any suitable form and, in the particular case here illustrated, this zone is of the type wherein high rates of heating are imparted to the heating coil and to the oil passing therethrough by direct radiation from the flames, combustion gases and hot refractory walls of the furnace to opposite sides of each of the tubular elements 18 of the fluid conduit. In the particular case here illustrated a single tube bank, comprising two vertically parallel rows of horizontally disposed tubes 18, is centrally located between combustion zone 19 and combustion zone 20 of the furnace, the tubes in the two rows being arranged in staggered formation so that opposite sides of each tube are exposed to direct radiation. Combustion zones 19 and 20 are each supplied by means of suitable burners 21 with controlled amounts of combustible fuel and air and the burners are preferably directed at an angle toward the side walls of the furnace so that the walls are washed by the flames and thereby heated to a highly radiant condition. This also avoids excessive washing of the tubes by the hot combustion gases and prevents impingement of the flames against the tubes. The combustion gases are removed through suitable openings 22 in the floor of the furnace to flue 23 from which they may be directed through flue 24 controlled by a damper 25' to a stack, not shown, or preferably they are directed, all or in part, from flue 24 through duct 25 controlled by damper 26 to the furnace setting or jacket 27 which encloses soaking chamber 30, as will be later more fully described. The oil is heated to a relatively high conversion temperature as it passes through heating coil 16 and the hot conversion products are discharged from the heating coil through line 28 and valve 29 into soaking chamber 30.

Chamber 30 is an enlarged externally heated chamber replacing what is commonly termed the "soaking" section of heating coils of the type normally employed in reforming operations and is preferably operated at substantially the same pressure as that employed at the outlet from heating coil 16. A sufficiently high temperature is maintained around the soaking chamber to keep the vaporous conversion products at or near the maximum temperature attained in the heating coil. This is accomplished, in the case here illustrated, by supplying hot combustion gases to the annular space surrounding the soaking chamber enclosed by a furnace setting or jacket 27 of any suitable form.

Provision is made, as previously described, for supplying a regulated portion or all of the hot combustion gases from furnace 17 to the heating zone surrounding the soaking chamber and provision is also made for supplying fresh combustion products to this zone by means of the combustion of fuel of any suitable form supplied by a suitable burner 31 to duct 25. These fresh combustion products may serve to augment and increase the temperature of the flue gases from furnace 17 when required or the soaking chamber may, when desired, be heated entirely by the fresh combustion gases without employing flue gases from furnace 17, although this is not the preferred method of operation of the process.

In case it is desired to cool the combustion gases, prior to their introduction into the heating zone surrounding the soaking chamber, provision is made for supplying controlled amounts of air to duct 25 by means of suitable air inlet doors 32. One or a plurality of suitable checker walls 33 in duct 25 may be employed, when desired, to effect mixing of the combustion gases and air or of the flue gases and fresh combustion gases, prior to their introduction into the heating zone surrounding the soaking chamber. In the particular case here illustrated the heating gases are tangentially supplied through duct 25 to the heating zone surrounding the soaking chamber and a helical baffle 34 of suitable metal, metallic alloy or refractory material is provided in this zone in order to increase the path of travel and the velocity of the heating gases around the soaking chamber, thereby increasing the heat input through the chamber and also insuring better distribution of heat around the chamber.

Another method of partially cooling the combustion gases from furnace 17 to the desired temperature, prior to their contact with chamber 30, which is entirely within the scope of the present invention, although not illustrated, comprises disposing a suitable heating coil in the flue connecting furnace 17 with furnace 27, for preheating the oil supplied to heating coil 16 or for any other desired purpose, or, when desired, an air preheater, not illustrated, for preheating a portion or all of the air supplied to furnace 17 may be employed in flue 24.

The invention also contemplates the countercurrent flow of heating gases and vaporous conversion products in the "soaking" zone, although provision for only concurrent flow is illustrated in the drawing. This may be accomplished by introducing the heating gases into the upper portion of furnace 27 and withdrawing the same from the lower portion thereof, by well known means not shown, the heated products from heating coil 18 being supplied to the lower portion of chamber 30, as illustrated. This method of operation is particularly advantageous in case it is desired to employ a substantially uniform vapor temperature in chamber 30 and it also tends to avoid any excessive heating in this zone of the heavy liquid conversion products which collect in the lower portion thereof. In case a higher initial temperature and/or a decreasing vapor temperature is desired in the chamber 30

concurrent flow of vapors and heating gases is preferably employed in the soaking zone.

The heating gases, after their passage around chamber 30, are directed through flue 45 to a suitable stack, not shown, and, in accordance with the embodiment of the invention here illustrated, these gases are directed over a suitable preheating coil 13 to which oil subsequently supplied for conversion to heating coil 16 is directed, as previously described, recovering heat therein from the flue gases.

It is also within the scope of the invention to supply any quantity of the combustion gases from furnace 17, which are not supplied to furnace 27 directly to flue 45 to commingle with the gases from furnace 27 prior to their contact with preheating coil 13, thereby supplying additional heat to this zone and utilizing the waste heat in that portion, if any, of the relatively hot combustion gases from furnace 17 not required for heating chamber 30. This may be accomplished by means of a continuation of flue 24 communicating with flue 45 ahead of heating coil 13, although, for the sake of simplicity, this provision is not shown in the drawing.

Chamber 30, in addition to its function as a soaking zone, serves as a zone of separation for the vaporous conversion products and any residual liquid and heavy polymerization products formed in heating coil 16 and/or chamber 30. The lower portion of chamber 30, in the case here illustrated, is insulated but unheated and the heavy liquid conversion products may be momentarily collected within this zone and may be withdrawn therefrom through line 35 and valve 36 to cooling and storage or elsewhere, as desired, or preferably, this material is directed through line 37 and valve 38 to pump 39 by means of which it is supplied through line 40 and valve 41 to reduced pressure vaporizing chamber 44, which will be later more fully described.

The vaporous conversion products, after being subjected during their passage upward through chamber 30 to the relatively high conversion temperature maintained in this zone are withdrawn from the upper portion thereof and directed through line 42 and valve 43 into chamber 44 preferably being cooled sufficiently, prior to their introduction into this zone, to prevent any substantial further conversion thereof. This cooling is preferably accomplished, at least in part, by substantial reduction in the pressure imposed upon the vaporous products as they pass through valve 43 in line 42 and in part, when desired, by other cooling means, which will be later more fully described.

Reduced pressure vaporizing chamber 44 is, in the case here illustrated, located within the lower portion of column 46, the upper portion of which comprises fractionator 47. Further separation of any undesirable high-boiling polymerization products or residual liquids from the vaporous conversion products is accomplished in chamber 44 and when heavy liquids from chamber 30 are supplied to this zone, in the manner previously described, further vaporization thereof may be accomplished under the reduced pressure conditions maintained in chamber 44. The high-boiling liquid conversion products remaining unvaporized in chamber 44 may be withdrawn therefrom through line 48 and valve 49 to cooling and storage or elsewhere, as desired.

The vaporous conversion products pass from the upper portion of chamber 44 through a suitable partition or deck 50, which separates the vaporizing chamber from the fractionator, into fractionator 47 wherein their components boiling above the range of the desired final motor fuel product of the process are condensed as reflux condensate. The reflux condensate may be allowed to collect within the lower portion of fractionator 47 above partition or deck 50 and is withdrawn therefrom through line 51 and valve 52 to pump 53 by means of which it is fed through line 54 and may be returned, all or in part, through line 55, valve 56 and line 10 to heating coil 16 for further conversion or the hot reflux condensate may be directed through valve 57 in line 54 to heat exchanger 7, wherein it serves to preheat the charging stock by indirect heat exchange therewith, as previously indicated. The partially cooled reflux condensate is discharged from heat exchanger 7 through line 58 and a regulated portion or all of these partially cooled products may, when desired, be directed through line 59 and valve 60 back into fractionator 47 at any suitable point or plurality of points in this zone to serve as a cooling and refluxing medium. Preferably at least a portion of the partially cooled reflux condensate from heat exchanger 7 is utilized to cool the hot vaporous products from soaking chamber 30, prior to their introduction into chamber 44. This may be accomplished by introducing the cooled reflux condensate into the stream of hot conversion products passing through line 42 or either or both sides of pressure reducing valve 43 by means of lines 61 and 62 controlled, respectively, by valves 63 and 64.

Fractionated vapors of the desired end-boiling point are withdrawn from the upper portion of fractionator 47 and are directed through line 65 and valve 66 to condensation and cooling in condenser 67. The resulting distillate and gas passes through line 68 and valve 69 to collection and separation in receiver 70. Uncondensable gas may be released from the receiver through line 71 and valve 72. Distillate may be withdrawn from receiver 70 through line 73 and valve 74 to storage or to any desired further treatment. When desired, a regulated portion of the distillate collected in receiver 70 may be recirculated, by well known means, not shown in the drawing, to the upper portion of fractionator 47 to serve as a cooling and refluxing medium in this zone for assisting fractionation of the vapors and to maintain the desired vapor outlet temperature from the fractionator.

The preferred range of operating conditions which may be employed to accomplish the objects of the present invention in an apparatus such as illustrated and above described may be approximately as follows: The heating coil may employ an outlet conversion temperature ranging, for example, from 950 to 1050° F., preferably at a superatmospheric pressure of the order of 300 to 800 pounds, or more, per square inch. The soaking chamber is preferably maintained at substantially the same pressure as that employed at the outlet from the heating coil and a conversion temperature within substantially the same range above mentioned is also preferably maintained in this zone although the average temperature maintained in the soaking chamber may be somewhat higher or somewhat lower than that employed at the outlet from the heating coil. A substantially reduced pressure relative to that employed in the soaking chamber is preferred in the succeeding vaporizing and separating chamber ranging, for example, from 150 pounds, or

thereabouts, per square inch, down to substantially atmospheric pressure and this pressure may be substantially equalized or reduced in the succeeding fractionating, condensing and collecting portions of the system. The temperature of the conversion products supplied from the soaking chamber to the reduced pressure vaporizing chamber is preferably reduced to a temperature ranging, for example, from 600 to 800° F., or thereabouts, although this provision is not so essential to the successful operation of the process as in other reforming operations wherein no previous separation of vaporous and heavy liquid conversion products is accomplished.

As a specific example of the operation of the process of the present invention as it may be accomplished in an apparatus such as illustrated and above described, the charging stock, which comprises a Pennsylvania distillate of about 50° A. P. I. gravity, is preheated by indirect heat exchange with reflux condensate from the fractionator of the system and by additional heating, in a preheating coil utilizing residual heat in the combustion gases from the heating zone surrounding the soaking chamber, to a temperature of approximately 600° F. and is quickly heated in a heating coil and furnace of the type illustrated to an outlet conversion temperature of approximately 970° F. at a superatmospheric pressure of about 500 pounds per square inch. Combustion gases are withdrawn from the heating coil furnace at a temperature of approximately 1200° F. and are circulated around the soaking chamber, serving to maintain the vaporous products in this zone at an average temperature of approximately 980° F. Heavy liquid conversion products are withdrawn from the unheated lower portion of the soaking chamber and supplied to the reduced pressure vaporizing chamber to which the vaporous products from the soaking chamber are separately supplied after being cooled by pressure reduction and by commingling with relatively cool reflux condensate from the fractionator to a temperature of approximately 760° F., a superatmospheric pressure of approximately 100 pounds is maintained in the vaporizing and separating chamber and is substantially equalized in the succeeding fractionating, condensing and collecting portions of the system. This operation will produce, per barrel of charging stock, approximately 83 per cent of motor fuel having an octane number of approximately 70 and a small amount of heavy residual liquid, the remainder being chargeable, principally, to uncondensable gas.

I claim as my invention:

1. A reforming process which comprises passing a relatively low-boiling hydrocarbon oil distillate containing low anti-knock gasoline fractions in a continuous stream through a fluid conduit within a furnace, quickly heating the oil during its passage through the fluid conduit to a reforming temperature at substantial superatmospheric pressure by heat supplied to the fluid conduit predominantly by radiation from materials undergoing combustion within the furnace and the hot refractory furnace walls, introducing the highly heated oil from the heating coil into the unheated lower portion of an enlarged vertical chamber, the upper portion of which is externally heated, separating the vaporous and liquid conversion products in the lower portion of said chamber, withdrawing the latter therefrom, withdrawing hot combustion gases from said furnace after at least a major portion of their radiant heat component has been transmitted to said fluid conduit, passing the same in regulated quantities around the outer periphery of the upper portion of said chamber whereby to heat the chamber and maintain the vaporous products therein at a temperature near the maximum attained by the oil in the heating coil, withdrawing vaporous conversion products from the upper portion of the chamber, cooling the same sufficiently to retard any substantial further conversion thereof, introducing the resulting partially cooled products into a reduced pressure vaporizing and separating chamber wherein separation of their vaporous and non-vaporous components is accomplished, subjecting the vapors to fractionation whereby their components boiling above the range of the desired final light distillate product of the process are condensed as reflux condensate, subjecting fractionated vapors of the desired end-boiling point to condensation and recovering the resulting distillate.

2. A process as claimed in claim 1 wherein charging stock for the process is preheated, prior to its introduction into said fluid conduit, by indirect heat exchange with said combustion gases after contact of the latter with said chamber.

3. A process as claimed in claim 1 wherein reflux condensate recovered by said fractionation of the vaporous conversion products is returned to the fluid conduit for further conversion.

4. A process as claimed in claim 1 wherein regulated quantities of the reflux condensate formed by said fractionation of the vaporous conversion products are partially cooled by indirect heat exchange with hydrocarbon oil charging stock for the process and regulated quantities of the partially cooled reflux condensate are commingled with the stream of vaporous products passing from said heated chamber to the succeeding vaporizing and separating zone.

5. A process as claimed in claim 1 wherein regulated quantities of the reflux condensate formed by said fractionation of the vaporous conversion products is partially cooled by indirect heat exchange with hydrocarbon oil charging stock for the process and regulated quantities of the partially cooled reflux condensate are returned to the fractionating stage of the system to assist cooling and fractionation therein.

6. In the reforming of light hydrocarbon distillates containing low anti-knock gasoline fractions to enhance the anti-knock value thereof, the method which comprises passing the low anti-knock distillate in a restricted stream through a heating coil and heating the same therein to reforming temperature under substantial superatmospheric pressure, then introducing the distillate, promptly upon its elevation to reforming temperature, into the lower portion of an enlarged vertical soaking chamber maintained under substantially the same pressure as prevails at the outlet of the coil, said lower portion of the chamber being unheated and there being effected in this unheated portion of the chamber a separation of vapors from residual liquid and heavy polymerization products, externally heating the remaining portion of the chamber sufficiently to maintain the vapors therein at or near the maximum temperature attained by the distillate in the coil, removing said liquid and heavy products from the lower portion of the chamber, passing the vapors upwardly through the heated portion of the chamber and retaining them in the chamber for a sufficient time to effect substantial reforming thereof into high anti-knock gasoline,

removing the reformed vapors from the upper portion of the chamber and fractionating and condensing the same.

7. In the reforming of light hydrocarbon distillates containing low anti-knock gasoline fractions to enhance the anti-knock value thereof, the method which comprises passing the low anti-knock distillate in a restricted stream through a heating coil and heating the same therein to reforming temperature under substantial superatmospheric pressure, then introducing the distillate promptly upon its elevation to reforming temperature, into the lower portion of an enlarged vertical soaking chamber maintained under substantially the same pressure as prevails at the outlet of the coil, said lower portion of the chamber being unheated and there being effected in this unheated portion of the chamber a separation of vapors from residual liquid and heavy polymerization products, externally heating the remaining portion of the chamber sufficiently to maintain the vapors therein at or near the maximum temperature attained by the distillate in the coil, removing said liquid and heavy products from the lower portion of the chamber, passing the vapors upwardly through the heated portion of the chamber and retaining them in the chamber for a sufficient time to effect substantial reforming thereof into high anti-knock gasoline, removing the reformed vapors from the upper portion of the chamber and introducing the same into a vaporizing chamber maintained under substantially lower pressure than the soaking chamber, discharging the liquid products withdrawn from the lower portion of the soaking chamber into said vaporizing chamber, separately removing vapors and residue from the vaporizing chamber and fractionating and condensing the former.

8. The process as defined in claim 1 further characterized in that the liquid products withdrawn from the lower portion of the first-named chamber are discharged into said reduced pressure chamber.

LEV A. MEKLER.