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TREATMENT OF HYDROCARBONS

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This invention particularly refers to an improved process for the pyrolytic conversion of hydrocarbon oils to produce high yields of motor fuel of good antiknock value together with a co-operative interdependent process for polymerization of the olefinic components of the gaseous products resulting from said conversion to produce additional yields of liquid products within the boiling range of motor fuel and of exceptionally high antiknock value.

Polymerization of olefinic gases produced by the pyrolytic conversion of hydrocarbon oils, for the purpose of obtaining increased yields of high antiknock motor fuel, is becoming essential to the most economic operation of modern oil refineries. The present practice in such operations is to stabilize the motor fuel conversion product to the required vapor pressure (normally 8 to 12 pounds per square inch by the Reid method, depending upon climatic and seasonal conditions) and to subject the gaseous products liberated from the distillate by said stabilization, which include a large portion of the three and four carbon atom components of the cracked gases, to polymerization for the production and recovery of liquid polymers, comprising essentially materials boiling within substantially the range of motor fuel and of exceptionally high antiknock value, which may be stabilized to the desired vapor pressure and utilized as blending fluid in cracked or straight-run motor fuel or blends of the two, to increase their antiknock value.

This invention departs from the conventional process above outlined in several novel and advantageous respects and in one embodiment comprises the steps of subjecting a hydrocarbon oil to pyrolytic conversion, subjecting the gaseous products resulting from said conversion to primary and secondary absorption, recovering, by condensation of the vaporous conversion products of the desired end-boiling point and absorption of the high-boiling gases therein, a light distillate product of substantially motor fuel boiling range containing dissolved gases comprising substantially all of the polymerizable olefins resulting from said conversion, stabilizing said distillate to a relatively low vapor-pressure in order to obtain a distillate within the boiling range of motor fuel substantially free of gases of less than 5 carbon atoms and a gaseous product containing substantially all of the readily polymerizable olefinic components of the cracked gases (particularly propylene and butylenes), returning regulated quantities of the stabilized distillate to the first absorption step, from which the unsta-

bilized distillate containing substantially all of the readily polymerizable olefinic components of the cracked gases is obtained, subjecting the olefin-containing gases from said stabilization step to polymerization to produce liquid polymers of high antiknock value within the boiling range of motor fuel, stabilizing said liquid polymers to a relatively high vapor-pressure, and blending the high vapor-pressure polymers with the low vapor-pressure distillate from the first mentioned stabilization step to give a final motor fuel product of the desired vapor-pressure and of high antiknock value.

By utilizing the stabilized distillate product of the cracking operation as absorber oil in the first absorption stage of the system, substantially all of the 3 and 4 carbon atom gases are concentrated in the distillate recovered from said first absorption step and by subjecting this distillate to stabilization at relatively high pressure, for recovery therefrom of the gases to be subjected to polymerization, the present process avoids the use of a pump or compressor for supplying said gases to the polymerization stage of the process, which is operated at a substantial superatmospheric pressure. In the conventional combination cracking and polymerization system when high pressures are utilized in the condensing and gas separating steps and in the succeeding stabilizer so that the gases from the stabilizer may be supplied to the polymerization stage without subjecting the same to condensation and without the use of a pump or compressor, the gases will contain excessive quantities of low-boiling materials (below the 3 and 4 carbon atom series) which remain dissolved in the unstabilized distillate but are liberated in the stabilizer and which would not be polymerized to produce the desired products thereby necessitating polymerization equipment of increased size without beneficial results. This is avoided by the process of the present invention, due to the fact that substantially all of said undesirable light gases escape absorption in the first absorption stage of the system, due to the selective affinity of the stabilized distillate for the higher boiling gases, and particularly the unsaturated high-boiling gases, so that regardless of the high pressure employed in the subsequent stabilization step the gaseous products therefrom will not contain an objectionable quantity of the undesirable low-boiling gases.

By stabilization of the motor fuel product of the conversion stage of the process to a relatively low vapor pressure (for example 2 to 4

pounds, or thereabouts, per square inch) the process of the present invention recovers, in the stabilizer gases supplied to the polymerization step, substantially all of the readily polymerizable olefinic gases produced by the cracking operation. In accordance with the conventional method of operation (whereby the motor fuel conversion product is stabilized to a vapor pressure of approximately 8 to 12 pounds per square inch, in order to give a motor fuel which will ignite readily in internal combustion engines) a large portion of the butylene as well as substantially all of the 5 and 6 carbon atom gases must be left in the distillate, thus robbing the polymerization process of olefinic gases which would give additional yields of the desired liquid polymers.

The present invention provides two methods for compensating for the reduced vapor pressure of the stabilized motor fuel conversion product of the process, which may be utilized in combination or either of which may be employed without the other. In accordance with one of these methods the liquid polymer product may be stabilized to a sufficiently high vapor pressure to give a final product of the desired vapor pressure when blended with the low vapor-pressure conversion product of the process. This ordinarily necessitates leaving at least a portion of the propane dissolved in the liquid polymer product. In accordance with the other method of operation the polymer product may be stabilized to a lower vapor-pressure, to substantially free the same of propane and lower boiling gases, in which case it will ordinarily be necessary to blend some paraffinic gases from an external source with the final motor fuel product of the process to give a product of 8 to 12 pounds vapor-pressure. Butane is preferably employed as a blending material for this purpose since the motor fuel will absorb a greater amount of the same for a given increase in vapor-pressure and give a correspondingly increased quantity of motor fuel.

It will be apparent from the foregoing that the various cooperative steps of the process of the invention provide a method whereby substantially all of the readily polymerizable olefinic gases resulting from pyrolytic conversion of hydrocarbon oils are concentrated in the gases supplied to the polymerization step of the system, to the substantial exclusion of lower boiling gases undesirable for charging to the polymerization step, and whereby paraffinic gases are substituted in the final motor fuel product of the process for the polymerizable olefins normally contained therein, the net result being the production of materially increased yields of motor fuel of high antiknock value.

Two types of processes are employed at present for the polymerization of gaseous olefins to produce high antiknock motor fuel. One type is essentially pyrolytic and involves the use of relatively high temperature and high superatmospheric pressures while the other employs a polymerization catalyst which permits the use of lower temperature and pressure conditions. Although the catalytic type of polymerization process is ordinarily preferred as the most satisfactory and economical of the two, either type may be employed within the scope of the present invention, since the novel features of the present invention will be found advantageous as applied to either type of polymerization process.

The accompanying diagrammatic drawing illustrates one specific form of apparatus embodying the features of the invention above outlined as

well as other features and advantages not previously described, the operation of which are more fully explained in conjunction with the following description of the drawing. Referring to the drawing, charging stock for the process, comprising a hydrocarbon oil of any desired type, 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 therefrom, all or in part, through line 6, valve 7 and line 12 to conversion in heating coil 14 or the charging stock may be introduced, all or in part, into fractionator 8 by passing the same through valve 5 in line 4. Any charging stock supplied to fractionator 8 commingles in this zone with the vaporous conversion products undergoing fractionation, thereby serving to assist cooling and fractionation of the vapors and at the same time effecting preheating of the charging stock. The resulting liquids, including heavy components condensed from the vapors in fractionator 8 and the total charging stock supplied to this zone or components thereof remaining unvaporized in the fractionator, depending upon the nature of the charging stock, are directed from the lower portion of the fractionator through line 9 and valve 10 to pump 11 by means of which they are supplied through line 12 and valve 13 to conversion in heating coil 14.

A furnace 15 of suitable form supplies the required heat to the oil passing through heating coil 14 to subject the same to the desired conversion temperature preferably at a substantial superatmospheric pressure. The resulting heated products are directed from the heating coil through line 16 and valve 17 into reaction chamber 18.

Chamber 18 is preferably operated at a substantial superatmospheric pressure which may be substantially the same or somewhat lower than that employed at the outlet from heating coil 14. The reaction chamber is also preferably insulated, although insulation is not shown in the drawing, to conserve heat so that the heated products supplied to this zone, and more particularly their vaporous components, are subjected therein to appreciable continued conversion. In the particular case here illustrated both vaporous and liquid conversion products are withdrawn in commingled state from the lower portion of chamber 18 and directed through line 19 and valve 20 into chamber 21.

Chamber 21 may be operated as a vaporizing and separating zone maintained at a substantially reduced pressure relative to that employed in the reaction chamber by means of which further vaporization of the liquid conversion products supplied to this zone is accomplished and wherein final separation of vaporous and residual liquid conversion products is effected. In such cases the non-vaporous liquid residue may be removed from the lower portion of chamber 21 through line 22 and valve 23 to cooling and storage or to any desired further treatment. Such further treatment may comprise, when desired, subsequent reduction of the residual liquid to coke in a separate system or in a separate zone of the same system, by any well known means, not illustrated. On the other hand, chamber 21 may, when desired, be operated as a coking zone wherein the liquid conversion products supplied to this zone from the reaction chamber are reduced to substantially dry coke. In such cases chamber 21 is preferably operated at a pressure ranging, for example, from 150 pounds, or thereabouts, per square inch, superatmospheric pressure, down to

substantially atmospheric pressure or a super-atmospheric pressure substantially the same as that employed in chamber 18 may be utilized in the coking zone, when desired. In case coke is produced in chamber 21 it may be allowed to accumulate within this zone to be removed therefrom in any well known manner, not illustrated, after the operation of the chamber is completed and, when desired, a plurality of coking zones may be employed, although not illustrated, which, in order to render the coking stage of the process continuous, preferably are alternately operated, cleaned and prepared for further operation although two or more coking chambers may be operated simultaneously, when desired.

Vaporous products are withdrawn from the upper portion of chamber 21 and directed through line 24 and valve 25 to fractionation in fractionator 8 wherein their components boiling above the range of the desired final motor fuel product of this stage of the system are condensed as reflux condensate which is returned, as previously described, to conversion in heating coil 14.

Fractionated vapors of the desired end-boiling point, comprising material within the boiling range of motor fuel and the gaseous products of the cracking operation, are withdrawn from the upper portion of fractionator 8 and directed through line 26 and valve 27 to condensation and cooling in condenser 28. The resulting distillate and gas passes through line 29 and valve 30 into column 31 which, in the particular case here illustrated, serves both as a receiver for collection of the motor fuel conversion product and an absorber for recovery of the high-boiling components of the gaseous conversion products, including substantially all of the propylene and butylene. When desired, regulated quantities of the distillate collected in the lower portion of column 31 may be recirculated by means of line 32, valve 33, pump 34, line 35 and valve 36 to the upper portion of fractionator 8 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 absorber oil employed in column 31, comprises, in the preferred embodiment of the invention, stabilized motor fuel recovered from within the system and supplied to column 31, as will be later more fully described. I have found that this particular material not only has a selective affinity for the high-boiling components of the gaseous conversion products, including the 3 and 4 carbon atom gases, but that it also has a tendency to absorb a higher portion of the unsaturated than the saturated gases. The gases leaving the upper portion of absorber 31 therefore comprise, principally, propane and lower boiling gases while at least a major portion of the propylene, butylene and higher boiling gases are concentrated in the distillate collected in the lower portion of absorber 31. This distillate is directed by means of line 32, valve 33, pump 34, line 35, line 37, valve 38, heat exchanger 39, line 40, valve 41, heat exchanger 42, line 43 and valve 44 to stabilization in stabilizing column 45, as will be later more fully described. The relatively low-boiling gaseous products pass from the upper portion of absorber 31 through line 46 and valve 47 to further absorption in column 48 wherein propane, principally, and any remaining higher boiling components of the gases are absorbed.

In the particular case here illustrated, the material utilized as absorber oil in column 48 com-

prises a selected relatively low-boiling fraction of the conversion products undergoing fractionation in fractionator 8. This material is particularly suitable for the purpose since it is substantially devoid of pentane and is of low molecular weight and low viscosity although other oil such as, for example, charging stock for the process may be employed as absorber oil in column 48, when desired. The absorber oil, in the case illustrated, is withdrawn from a suitable point in the upper portion of the fractionator through line 49 and valve 50 to column 51 wherein it is subjected to reboiling for the purpose of substantially freeing the same of entrained gases and low-boiling components within the range of the desired overhead product from the fractionator. The reboiling is accomplished by any well known means such as, for example, a closed coil 52 in the lower portion of the column through which any suitable heating medium is circulated. The vapors liberated in column 51 are returned therefrom through line 53 and valve 54 to fractionator 8. The reboiled condensate is withdrawn from the lower portion of column 51 through line 55 and valve 56 to pump 57 by means of which it is directed through line 58, valve 59, heat exchanger 39, line 60, valve 61, cooler 62, line 63 and valve 64 into absorber 48. The lean unabsorbed gases are released from the upper portion of column 48 through line 65 and valve 66. The enriched absorber oil passes from the lower portion of column 48 through line 67 and valve 68 to pump 69 by means of which it is returned through line 70 and valve 71 to fractionator 8.

The reheated distillate supplied, as previously described, to stabilizer 45 is preferably heated sufficiently in heat exchangers 39 and 42 to effect substantial vaporization thereof in column 45 and is preferably stabilized in this zone down to the vapor pressure of the order of, for example, 2 pounds, or thereabouts, per square inch. In this manner substantially all of the propylene, butylene and lower boiling gases as well as, when desired, some of the higher boiling gases are liberated from the distillate. Reboiling means such as a closed coil 72, through which any suitable heating medium may be circulated, is provided in the lower portion of the stabilizer and suitable cooling means such as coil 73, through which any suitable cooling medium may be circulated, is provided in the upper portion of the stabilizer. The stabilizer motor fuel is withdrawn from the lower portion of column 45 through line 74 and may pass, all or in part, therefrom through line 75 and valve 76 into line 120 wherein it is blended with the liquid motor fuel from the polymerization stage of the system and, when desired, with paraffinic gases from an external source, as will be later more fully described, to form the final motor fuel product of the process. Preferably regulated quantities of the stabilized distillate from column 45 are directed through valve 77 in line 74 to pump 78 by means of which this material is supplied through line 79, valve 80, heat exchanger 42, line 81, valve 82, cooler 83, line 84 and valve 85 to column 31, wherein it serves as an absorber oil in the manner previously described.

Heat exchangers 39 and 42 serve, as previously indicated, as a means of reheating the distillate supplied from absorber 31 to stabilizer 45 and also serve, respectively, as a means of cooling the absorber oils supplied from column 51 to absorber 48 and from stabilizer 45 to column 31. Additional cooling of the absorber oil supplied to col-

umn 31 may be accomplished, when desired, in cooler 83 and additional cooling of the absorber oil supplied to column 48 may be accomplished, when desired, in cooler 62. It will be understood, of course, that any or all of the heat exchangers and coolers may be by-passed when desired, although means for accomplishing this are not illustrated in the drawing, and that other means of cooling the absorber oils and heating the distillate supplied to the stabilizer may be utilized either alone or in conjunction with the means illustrated.

The olefin-containing gases are withdrawn from the upper portion of stabilizer 45 and may be directed through line 86 and valve 87 to pump 88 by means of which they are supplied through line 89, valve 90 to heating coil 91. Preferably, however, stabilizer 45 is operated at a slightly higher superatmospheric pressure than that desired in heating coil 91 and the succeeding polymerization equipment in order to avoid the use of a pump or compressor for the gases supplied to the polymerization system. Line 92 containing valve 93 is therefore provided as a means of by-passing pump 88.

Heating coil 91 is located within a suitable furnace 94 by means of which the olefin-containing gases passing through the heating coil are heated to a temperature sufficient to effect their subsequent polymerization for the formation of liquid polymers within the boiling range of motor fuel under the pressure conditions and/or catalytic influence employed in this stage of the process. The heated gases are discharged from heating coil 91 through line 95 and may pass, in series, through the polymerizing chambers 98 and 98' by means of line 96, valve 97, line 99, valve 100, line 101, valve 102, line 96', valve 97', line 99' and valve 100'. Parallel flow of gases through the polymerizing chambers may be employed instead of series flow, when desired, by means which will be obvious from the drawing. It is, of course, also within the scope of the invention to employ a single polymerizing chamber or to employ any desired number of a plurality of such zones. When catalytic polymerization is employed the polymerizing catalyst is preferably disposed within the polymerizing chambers in such a manner that the olefin-containing gases passing there-through are intimately contacted with the catalyst.

Catalysts of the type generally known as "solid phosphoric acid" catalysts have been found particularly suitable for promoting the desired polymerization of the olefinic gases, such as propylene and butylene as well as, when desired, higher boiling olefins, and as a specific example of a catalyst suitable for this purpose I may employ a siliceous carrier or absorbent material such as kieselguhr impregnated with either ortho or pyrophosphoric acids or a mixture of the two, the mixture of acid and earth having been calcined to form a solid which may be ground to approximately 4 to 20 mesh or the pasty mixture may be extruded and the extruded shapes calcined, preferably at a temperature of the order of 500 to 600° F. to form the final catalyst. It is, however, also within the scope of the invention to use other catalysts such as, for example, sulphuric or hydrochloric acids in either liquid or so-called solid state as well as liquid phosphoric acid or, when desired, heavy metal salts such as aluminum, zinc and iron chlorides may be employed. The use of catalysts, generally, permits the use of lower temperatures and pressures than

when catalysts are not employed and also have other advantages. A detailed comparison of catalytic and non-catalytic methods is, however, not pertinent to the present invention since the invention is advantageous as applied to either type of process.

The polymerized gases withdrawn from the polymerizing chambers pass through line 103 to condensation and cooling in condenser 104 wherefrom the resulting liquid polymers and unpolymerized and uncondensed gases pass through line 105 and valve 106 to collection and separation in receiver 107, line 108 and valve 109 to pump 110 by means of which it is supplied through line 111 and valve 112 to stabilizer 113.

Stabilizer 113 is provided with suitable cooling means such as coil 114 in its upper portion and suitable reboiling means such as coil 115 in its lower portion and functions in the same manner, previously described, as stabilizer 45 except that the liquid polymer product removed from stabilizer 113 may, when desired, and does normally contain a proportionately greater amount of low-boiling gaseous products as compared with the motor fuel removed from stabilizer 45 so that the polymer product has a considerably higher vapor pressure. The gases liberated from stabilizer 113 consisting, principally, of propane and lower boiling gases are released from the upper portion of the stabilizer through line 116 and valve 117 and may, when desired, pass together with the uncondensed gases withdrawn from receiver 107 through line 118 and valve 119 to storage or elsewhere, as desired. The invention also contemplates when desired, the recirculation of all or a regulated or selected portion of these gases (particularly those resulting from stabilization of the liquid polymer product) to further polymerization within the system, by well known means not illustrated, particularly in case the liquid polymer product is stabilized to a relatively low vapor pressure whereby residual polymerizable gases are liberated therefrom.

The stabilized polymer product is withdrawn from the lower portion of stabilizer 113 through line 120 and valve 121 and preferably is commingled in this line with the lower vapor pressure distillate withdrawn, as previously described, from stabilizer 45 to form the final motor fuel product of the process, the vapor pressure of which may be regulated to suit requirements by controlling the vapor pressure of the polymer product or, when desired, paraffinic gases such as, preferably, butane from any suitable external source may be directed through line 122 and valve 123 into line 120 to commingle with the final motor fuel product of the process to increase its vapor pressure to the desired point.

While the preferred method of operation is ordinarily to substantially free the polymer product supplied to stabilizer 113 of propane, any residual propylene and lower boiling gases so that butanes may be blended with the final motor fuel product to increase its vapor pressure to the desired degree it is, of course, also within the scope of the invention to leave a sufficient quantity of low-boiling gases in the liquid polymer to give the desired vapor pressure in the final blended product. In many cases when the latter method of operation is employed stabilization of the polymer product may be dispensed with entirely.

It will, of course, be understood that the invention is also applicable to practically any type of cracking system including both the so-called

"vapor-phase" and the "liquid vapor-phase" type of process as well as various catalytic processes. There are, furthermore, numerous modifications of the type of cracking process illustrated including reforming, selective cracking, non-residuum or coking operations, residuum operations and various combinations thereof, all of which are entirely within the scope of the invention.

In an apparatus of the character illustrated and above described, the preferred range of operating conditions suitable for accomplishing the objects of the process may be approximately as follows: The heating coil of the cracking stage of the system may employ a conversion temperature measured at the outlet therefrom ranging, for example, from 850 to 1000° F., preferably with a superatmospheric pressure at this point in the system of from 100 to 800 pounds, or thereabouts, per square inch. Substantially the same or a somewhat lower superatmospheric pressure is preferred in the reaction chamber and the succeeding vaporizing or coking chamber is preferably operated at a substantially reduced superatmospheric pressure ranging, for example, from 150 pounds, or thereabouts, per square inch down to substantially atmospheric pressure. The pressure employed in the vaporizing or coking chamber may be substantially equalized or somewhat reduced in the succeeding fractionating and condensing portions of the system, although the pressure employed is preferably sufficient to permit the use of a superatmospheric pressure of from 50 to 150 pounds, or more, in the absorption stages of the system without the use of a pump or compressor for supplying the light conversion products thereto. Preferably, the stabilizing column to which the motor fuel conversion product of the process is supplied is operated at a sufficient superatmospheric pressure to permit passage of the gases therefrom through the polymerization stage of the system without the use of a pump or compressor, the preferred range in this zone being from 150 to 300 pounds, or thereabouts, per square inch. The temperature to which the olefin-containing gases are subjected in the heating coil of the polymerization stage of the system may range, for example, from 350 to 550° F., or thereabouts, and except for the drop in pressure, due to friction, loss of head, etc., through the polymerization stage, the pressure employed therein preferably is somewhat increased in the succeeding stabilizer, ranging for example, from 150 to 300 pounds, or thereabouts, per square inch superatmospheric. The pressure employed in the stabilizing column to which the liquid polymer is supplied, when such a zone is utilized may range, for example, from 100 to 300 pounds per square inch, superatmospheric, and preferably a superatmospheric pressure of approximately 200 pounds, or more, is preferred in this zone. Due to the slightly exothermic nature of the polymerization reaction the temperature in the catalyst chambers will vary somewhat, particularly in case two or more chambers are employed in series. Normally, however, a temperature of the order of 300 to 450° F. is obtained in the initial stages of the polymerization treatment with a subsequent maximum temperature of the order of 450 to 550° F. or more.

As a specific example of the operation of the process of the invention as it may be accomplished in an apparatus of the character illustrated and above described, employing a charging stock comprising a 25° A. P. I. gravity Mid-continent topped crude, the temperature em-

ployed at the outlet from the cracking coil is approximately 960° F. with a superatmospheric pressure at this point in the system and in the succeeding reaction chamber of approximately 200 pounds per square inch. The vaporizing chamber to which both vaporous and liquid products from the reaction chamber are supplied is operated at a superatmospheric pressure of approximately 75 pounds per square inch. This pressure is substantially equalized in the succeeding fractionating and condensing portions of the system as well as the two absorption columns. The stabilizing step to which the motor fuel conversion product is supplied is operated at a superatmospheric pressure of approximately 225 pounds per square inch and this pressure is substantially equalized throughout the polymerization stage of the system, a pressure of approximately 275 pounds per square inch being employed in the stabilizing step to which the liquid polymer product is supplied. The temperature at the outlet from the heating coil of the polymerization stage is approximately 400° F. The cracked motor fuel from the first absorption stage, which contains substantially all of the gases boiling above propane, is stabilized to a vapor-pressure of approximately 2 pounds per square inch and the resulting gases from the stabilizer, which are supplied to the polymerization step, contain substantially all of the propylene and butylene produced by the cracking operation, the heavier gases being left, in this particular case, in the stabilized motor fuel from the cracking operation. The polymer product is stabilized to a vapor pressure of approximately 25 pounds per square inch, substantially only propane and lighter gases being removed therefrom by said stabilization. The stabilized polymer gasoline is blended with the cracked gasoline and a small amount of butane from an external source is blended therewith to give a final motor fuel having a vapor pressure of approximately 10 pounds per square inch. The following is an approximate analysis of the gases taken at various points in the system:

	From absorber 48	From stabilizer 45	From stabilizer 113
	Percent	Percent	Percent
Lighter than propylene.....	92.7	14.1	27.7
Propylene.....	2.7	20.2	5.9
Propane.....	3.7	32.5	64.1
Butylene.....	0.5	17.5	0.3
Butane.....	0.4	15.7	2.0
Heavier than butane.....	0.0	0.0	0.0

This operation will yield, per barrel of charging stock, approximately 58.2 per cent of motor fuel having a Reid vapor-pressure of approximately 10 pounds per square inch and an octane number by the motor method of approximately 70. Of this 58.2 per cent approximately 52.5 per cent, based on the charging stock, is cracked gasoline, approximately 4.8 per cent is polymer gasoline and the remaining 0.9 per cent, or thereabouts, is added butane.

As a means of comparison in an operation similar to that above outlined except that the motor fuel conversion product of the process is subjected to stabilization in the conventional manner and the stabilizer reflux comprising a high proportion of the propylene and butylene components of the process gases subjected to polymerization, the yield of motor fuel, including the polymer product, when producing a 10 pound vapor-pressure gasoline, is approximately 54 per

cent based on the charging stock and the octane number is slightly less than that obtained in the above operation.

I claim as my invention:

1. In the production of gasoline by the cracking of hydrocarbon oils wherein the final gasoline-containing condensate is separated from incondensable gases and then stabilized, the method which comprises removing from the final condensate by said stabilization substantially all of its propylene and butylene content, thereby forming a condensate of lower vapor pressure than motor fuel, scrubbing said gases with at least a portion of the stabilized propylene and butylene-free condensate to absorb in the latter propylene and butylenes contained in the gases, supplying the resultant enriched condensate to the stabilizing step for the removal therefrom of the absorbed propylene and butylenes, subjecting the propylene and butylenes evolved by the stabilization, including those absorbed from the gases, to polymerization to produce gasoline boiling polymers therefrom, stabilizing the resultant polymer product to a higher vapor pressure than said condensate to retain a substantial proportion of 4 carbon atom hydrocarbons therein, and blending the thus stabilized polymer product of relatively high vapor pressure with said condensate of lower vapor pressure than motor fuel.

2. The process of producing a high yield of high antiknock motor fuel of desired volatility which comprises initially separating cracked gasoline condensate from the uncondensed gases formed during cracking, distilling from said cracked gasoline condensate substantially all constituents and dissolved gases lower boiling than the C_5 hydrocarbons to produce debutanized gasoline condensate, scrubbing the first-mentioned gases with at least a portion of said debutanized condensate to absorb in the latter hydrocarbons of less than 5 carbon atoms contained in the gases, supplying the resultant enriched condensate to the distilling step for the removal of the absorbed hydrocarbons therefrom, subjecting C_4 hydrocarbons contained in the distilled constituents and dissolved and absorbed gases from said distilling step to polymerization, separating unpolymerized hydrocarbons from the polymers thus formed, blending debutanized gasoline and polymers and adding sufficient C_4 hydrocarbons to produce a high antiknock motor fuel of desired volatility.

3. In a process for the conversion of hydrocarbon material, the method which comprises, subjecting hydrocarbons to conversion conditions of temperature and pressure and separating a final gasoline condensate from incondensable gases, subjecting said condensate to stabilization, removing from said condensate substantially all of its hydrocarbons having less than 5 carbon atoms, thereby forming a condensate of lower vapor pressure than commercial gasoline, scrubbing said gases with at least a portion of said condensate of lower vapor pressure than commercial gasoline to absorb in the latter hydrocarbons of less than 5 carbon atoms contained in

the gases, supplying the resultant enriched condensate to the stabilizing step for the removal therefrom of the absorbed hydrocarbons of less than 5 carbon atoms, subjecting hydrocarbons of less than 5 carbon atoms evolved by the stabilization, including hydrocarbons absorbed from said gases, to polymerization to produce gasoline polymers therefrom, stabilizing the resulting polymer products to a higher vapor pressure than said condensate to retain a substantial proportion of 4 carbon atom hydrocarbons therein, and blending the thus stabilized polymer products of relatively high vapor pressure with said condensate of lower vapor pressure than commercial gasoline to form a product of about the volatility of commercial gasoline.

4. A process for producing a high yield of anti-knock motor fuel from the products of hydrocarbon oil conversion, which comprises separating from said products a final gasoline condensate and an olefinic gas, removing from said final condensate, by stabilization thereof, substantially all of its hydrocarbons of less than 5 carbon atoms to the molecule, thereby forming debutanized gasoline condensate, scrubbing said olefinic gas with at least a portion of the debutanized condensate to absorb in the latter olefinic hydrocarbons of less than 5 carbon atoms contained in the gases, supplying the resultant enriched condensate to the aforesaid stabilization for the removal of the absorbed hydrocarbons therefrom, polymerizing 4 carbon atom olefins evolved by said stabilization, including hydrocarbons absorbed from said gas, to form gasoline boiling polymers, blending such polymers with debutanized gasoline from the stabilizing step and adding sufficient 4 carbon atom hydrocarbons to form a blend having the desired volatility of motor fuel.

5. A process for producing a high yield of anti-knock motor fuel from the products of hydrocarbon oil conversion, which comprises separating from said products a final gasoline condensate to the aforesaid stabilization for the removal of the absorbed hydrocarbons therefrom, subjecting C_4 hydrocarbons contained in the distilled constituents and dissolved and absorbed gases from said distilling step to polymerization, separating unpolymerized hydrocarbons from the polymers thus formed, blending debutanized gasoline and polymers and adding sufficient C_4 hydrocarbons to produce a high antiknock motor fuel of desired volatility.

6. The process of producing a high yield of anti-knock motor fuel from the products of hydrocarbon oil conversion, which comprises separating from said products a final gasoline condensate and an olefinic gas, removing from said final condensate, by stabilization thereof, substantially all of its hydrocarbons of less than 5 carbon atoms to the molecule, thereby forming debutanized gasoline condensate, scrubbing said olefinic gas with at least a portion of the debutanized condensate to absorb in the latter olefinic hydrocarbons of less than 5 carbon atoms contained in the gases, supplying the resultant enriched condensate to the aforesaid stabilization for the removal of the absorbed hydrocarbons therefrom, polymerizing 4 carbon atom olefins evolved by said stabilization, including hydrocarbons absorbed from said gas, to form gasoline boiling polymers, stabilizing the resultant polymer products to a higher vapor pressure than said debutanized condensate to retain a substantial proportion of 4 carbon atom hydrocarbons therein, and blending such stabilized polymer products of relatively high vapor pressure with debutanized gasoline from the stabilizing step to form a product of about the volatility of commercial gasoline.

CLARENCE G. GERHOLD.

CERTIFICATE OF CORRECTION.

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July 11, 1939.

CLARENCE G. GERHOLD.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 6, second column, line 43, claim 5, strike out the words and syllable "to the aforesaid stabilization for the re-" and insert instead and an olefinic gas, removing from said; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 22nd day of August, A. D. 1939.

Leslie Frazer

(Seal)

Acting Commissioner of Patents.