

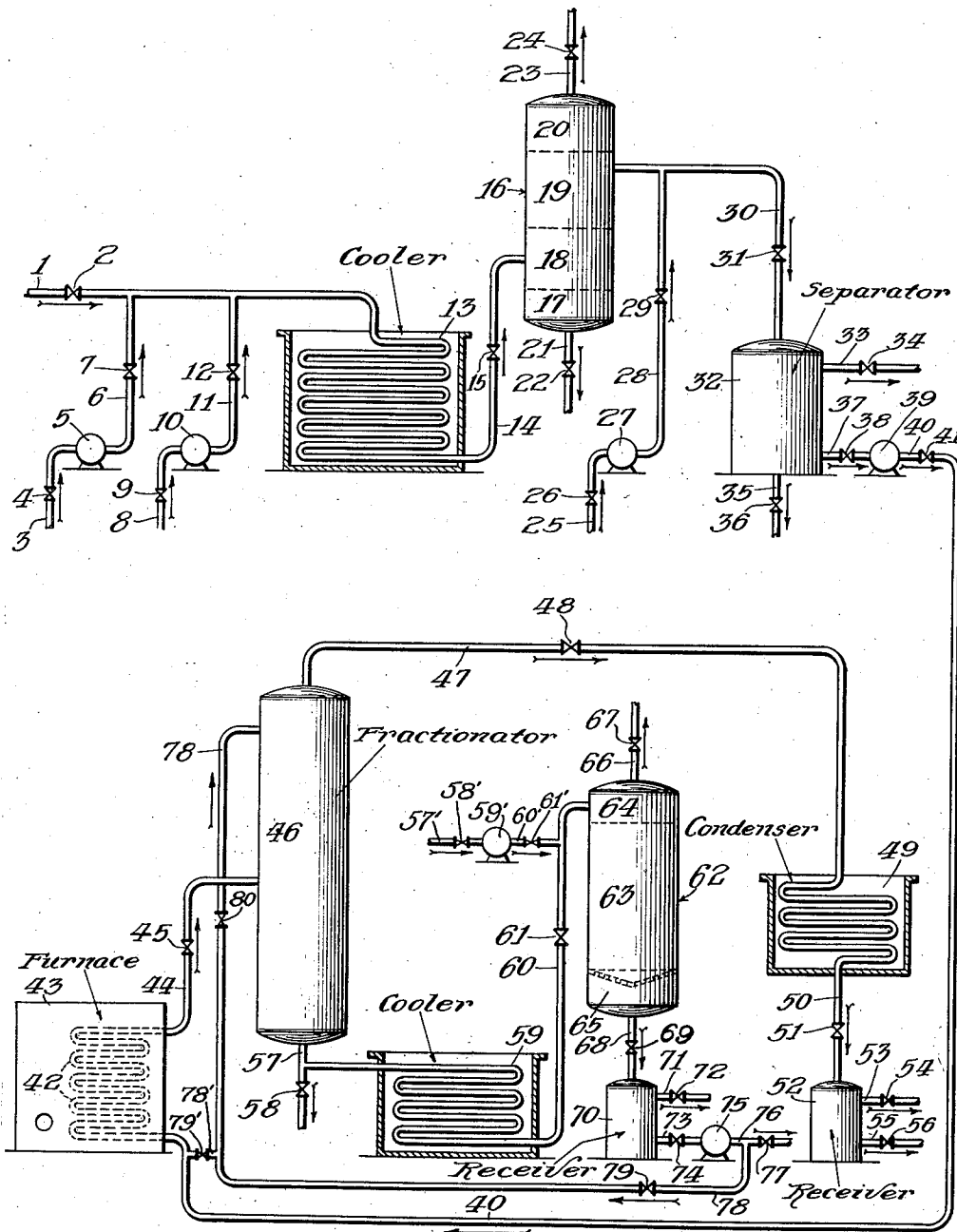
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MANUFACTURE OF HYDROCARBONS

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MANUFACTURE OF HYDROCARBONS

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7 Claims. (Cl. 196—10)

This invention refers more particularly to the manufacture, by synthetic reactions, of hydrocarbons utilizable as constituents of motor fuel.

In a more specific sense the invention has reference to a process which may be employed to supplement the cracking process and increase the yield of high anti-knock material obtainable. The particular steps by which this object is accomplished and the novel and useful effects produced will be shown in the following specification.

Gasoline boiling range hydrocarbons produced by decomposition reactions accompanying the pyrolysis of relatively heavy fractions of petroleum contain relatively higher percentages of unsaturated hydrocarbons of both an open chain and a closed chain character than similar boiling range straight run gasoline due to the dehydrogenating character of the decomposition reactions involved in cracking. The olefins and cyclic compounds thus produced are characterized by a greatly reduced tendency to detonate when used as fuel in internal combustion engines so that cracked motor fuels are uniformly superior to straight run for present day automobile engines which for the most part employ high compression ratios.

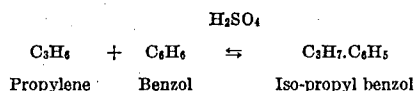
When attempts are made to increase the anti-knock value of cracked gasolines beyond a certain point, losses in gas and coke reach serious proportions, and a balance must be struck between yield and quality of product.

The present process may be employed to produce greatly increased yields of high anti-knock gasoline hydrocarbons while utilizing the olefinic constituents of the fixed gases, which for the most part are used only as fuel in present commercial practice.

In one specific embodiment the invention comprises treatment of aromatic or similarly reactive hydrocarbons with olefins in the presence of sulphuric acid to produce alkylated derivatives, separating said derivatives from sludge reaction products and fixed gases, fractionating said derivatives to produce a high anti-knock overhead gasoline which is cooled, condensed and collected and a reflux comprising hydrocarbons boiling higher than gasoline, partially dealkylating said higher-boiling reflux in the presence of suitable catalysts to produce further yields of gasoline boiling range derivatives and fractionating to recover the additional gasoline fraction thus obtained.

The reactions between olefins and aromatic hydrocarbons in the presence of sulphuric acid catalyst which lead to the production of alkylated derivatives of aromatics are quite general and are typified by the following equation showing the condensation of propylene and benzol to form iso-propyl benzol:

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The mechanism of this and similar reactions involving other aromatics and other olefins is apparently explained by assuming, first, the formation of alkyl sulfates and aromatic sulphonic acids and, second, the interaction of these primary acid derivatives to form the alkyl ring compound while the acid is regenerated. Some side reactions occur, of course, resulting on the one hand in loss of sulphuric acid due to oxidation reactions and the formation of undecomposable sulfo derivatives but in general the reactions may be forced from left to right in the equation by suitable choice of conditions, particularly in respect to limiting the strength of the acid employed and the maintenance of a temperature not far removed from ordinary atmospheric.

In all such alkylating reactions there is an attendant formation of more highly alkylated derivatives than the one shown on the right hand side of the equation, that is, di, tri, tetra and possibly even more highly alkylated derivatives. Many of the more highly alkylated aromatics have boiling points too high to permit their use as components of motor fuel and it is the purpose of the present invention to work over these higher boiling fractions which are incidentally produced and effectively reform them into hydrocarbons of desired boiling range, thereby increasing the yield of gasoline. Even when the amount of hydrocarbons boiling above the end point desired in gasoline is not excessive there may be too great a production of compounds boiling within the upper range of gasoline since many of the compounds formed in the reactions between propylene, butylenes and amylene boil within the range of approximately 200 to 240° C. Thus, not only may the compounds boiling above the gasoline end point be dealkylated but also those boiling within the upper boiling range which are produced in too great quantity for a balanced gasoline.

To indicate in a general way the sequence of operations involved in the present invention the attached diagrammatic drawing has been prepared which shows by the use of conventional figures in side elevation an arrangement of elements in which the process may be conducted

although the invention does not limit it to the particular details of the present drawing, since other modifications of plant equipment may be employed.

5 Referring to the drawing, line 1 is an inlet gas line through which gas mixtures containing olefins may be admitted through valve 2, it being assumed that the gases are under sufficient pressure to take care of the pressure needs of the treatment both in respect to static conditions and necessary flow differentials. Thus olefinic gas mixtures resulting from the cracking of petroleum or other hydrocarbon oils either for gasoline or gas production may be admitted, the olefinic content of such gases varying with the charging stock used and the conditions of cracking. Sulphuric acid is most effective in causing the union of olefins higher than ethylene with aromatics and the most effective mixtures therefore are those containing high percentages of propylene, the butylenes and the amylene which may run from 30 to 40% of many gas mixtures encountered as by-products in oil cracking operations.

20 Benzol or other aromatic homologs or mixtures thereof may be introduced to the system through line 3 containing control valve 4 and be delivered by pump 5 through a line 6 containing control valve 7 to mix with the gases in line 1.

The necessary amount of sulphuric acid may be introduced through line 8 containing control valve 9 and be delivered by pump 10 through a line 11 containing a control valve 12. The acid may be added also by utilizing the customary blow case although this is not shown in the present drawing. Olefinic gases, aromatic hydrocarbons and sulphuric acid are thus brought together in line 1 and may be passed through perforated plates or other obstructions or mixing devices to insure thorough contact, the mixture passing through a cooling coil 13 for maintaining some optimum low temperature which will depend upon the character of the hydrocarbons undergoing reaction and the products desired. In general, since the object of the invention is to handle the alkylation reactions so that substantially only compounds suitable for use in gasoline are produced, the temperature is maintained at some fairly low point and may be carried as low as 30 to 40° F., if desired.

50 The reaction products consisting of sludge acid, alkylated hydrocarbons, unchanged aromatics and residual gases then pass through a line 14 containing control valve 15 and enter a separator 16. In this separator layer 17 has been marked off to indicate a layer of settled sludge acid which may be removed through a line 21 containing control valve 22 and either reused if not entirely spent or subjected to suitable regenerating steps. Layer 18 indicates a zone in which emulsion conditions obtain. Zone 19 indicates a layer of alkylated and unchanged hydrocarbons and zone 20 may consist principally of gas which is vented through line 23 containing control valve 24 and which may be recycled if its olefinic content indicates, or used as fuel if the olefins have been economically removed.

70 Since a certain amount of alkyl sulphates may be dissolved in the liquid hydrocarbon reaction products it is usually advantageous to destroy these by reaction with caustic soda both because they add sulphur to the products and because they have a tendency to decompose in the subsequent fractionating step and cause difficulties due to foaming. Thus caustic soda solution may be picked up by pump 27 through line 25 con-

taining control valve 26 from a source of supply not shown and pumped through line 28 containing control valve 29 into line 30 containing the hydrocarbon effluent from the separator, the mixture of neutralized oil and sludge caustic then passing through valve 31 to separator 32. This separator may be provided with a gas release line 33 containing control valve 34 for releasing any gas which may be carried over, this gas being generally similar to those released through line 23 and disposed of in a similar manner. Line 35 containing control valve 36 indicates a draw line for the removal of the spent neutralizing caustic.

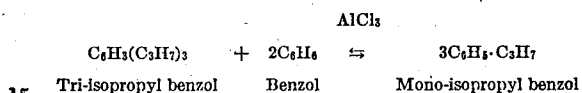
15 The alkylated hydrocarbons are then preferably subjected to fractionation and the heavier portions thereof partially dealkylated in the second stage of the process. To this end line 37 containing control valve 38 leads to a pump 39 which discharges through line 40 containing control valve 41 into and through a tubular heating element 42 disposed to receive heat from furnace 43. During passage through the heating element the mixture is heated sufficiently to enable the substantially complete separation and removal of gasoline fractions, the heated and partly vaporized hydrocarbons then passing through line 44 containing control valve 45 into a fractionator 46, which also receives dealkylated or reformed hydrocarbon mixtures from line 78 as will be later described. The gasoline vapors evolved from the fractionator are subjected to the usual process of cooling, condensation and collection, passing successively through vapor line 47 containing control valve 48, condenser 49, run-down line 50 and control valve 51 to enter a final receiver 52 which is provided with the usual gas release line 53 containing control valve 54 and a draw line 55 containing control valve 56 for the removal of the finished product to storage.

40 The hydrocarbon refluxes from fractionator 46 which may be considered as "over-alkylated" product are according to the present invention subjected to the action of suitable catalysts in the presence of further quantities of benzol or other aromatics to effect a shift of the alkyl groups from the more highly alkylated to the less highly alkylated hydrocarbons so that in a sense fresh aromatic is alkylated by groups already attached to aromatic rings and an equilibrium is established with the production of a further quantity of low boiling gasoline fractions.

55 Thus the high boiling alkylated products may be withdrawn through line 57 and pass through the cooler 59 for reducing their temperature to a point suitable for further reaction, a valve 58 permitting the rejection of a portion of the refluxes from the system if desired. After passing through cooler 59 the hydrocarbon liquids continue through line 60 containing control valve 61 and are mixed with fresh quantities of some aromatic such as benzol which is introduced into line 60 by way of line 57', control valve 58', pump 59', line 60' and valve 61', the mixture then entering a treater 62.

65 In this treater a catalyst mass comprising such materials as the chlorides of heavy metals, particularly aluminum or zinc chlorides, may be supported upon some relatively inert spacing or carrying material as a bed 63 which divides the treater into upper and lower liquid spaces 64 and 65 respectively. Since some gas may be evolved at this stage of the process a vent line 66 containing control valve 67 is provided for their release.

The reactions occurring in the de-alkylating or re-forming treater 62 are typified by those shown in the following equation though the reaction shown is of a relatively simple character in comparison to the sum total of those which may occur when reaction is brought about between fresh hydrocarbons and alkylated products of a highly mixed character such as may have been produced when alkylating aromatics with mixed olefins in the first stage.



According to the above equation the tri-isopropyl benzol may be considered to represent highly alkylated material unsuitable for use as a component of gasoline while the benzol represents freshly introduced aromatic and the product represents a less highly alkylated aromatic boiling within the range of gasoline. The actual course of the reaction as pointed out is much more complicated and may perhaps result in the splitting off of a certain amount of low boiling hydrocarbons such as methane, ethane, propane, etc., though the extent of such reactions, which represent loss of reactive material, may be minimized to a large extent by proper control of operating conditions.

Since the equilibrium mixture resulting from the treatment in treater 62 will still contain a certain percentage of high boiling compounds, it is subjected to fractionation to remove gasoline and heavy fractions recycled as before. Thus the hydrocarbon mixture from the bottom of treater 62 is passed through line 68 containing control valve 69 to an intermediate receiver 70 provided with the usual gas release line 71 containing control valve 72 and a liquid draw line 73 containing control valve 74. A recycling pump 75 then preferably returns the material produced at this point back to the fractionator by way of line 76, line 78 and control valve 79. Valve 77 in line 76 permits the withdrawal of a portion of the re-formed liquid mixture which is not returned to the fractionator. In the hook-up shown the material returned to fractionator 46 from line 78 acts as reflux liquid to assist fractionation, thus throwing the burden of the heating of the tower upon the original alkylated product from the first stage which passes through heating element 42 as previously described. If desired, a portion of the recycled liquid may be passed through the heating element by diversion through line 78' and valve 79', with suitable manipulation of valve 80.

For present purposes it has been assumed that no sludge layer accumulates in receiver 70, that is, that the catalyst in treater 62 remains more or less intact, however, any sludge layer which may accumulate in receiver 70 due to the washing action of the liquids passing over the catalyst mass may be withdrawn from the bottom of the receiver through suitable bottom lines though these are not shown in the drawing.

Among a large number of possible examples of the value of the process disclosed the following may be taken as indicative of the beneficial results obtained.

Beginning with the cracking step which produces a highly olefinic gas mixture, a 24 A. P. I. gravity Mid-Continent residuum may be cracked in a commercial type of cracking plant at a temperature of 930° F., and pressure of 250 pounds

per square inch to produce the following approximate yields.

Cracking yields

Product	Yield	Percent by weight of charge
Gas, 1.20 sp. gr.	700 cu. ft./bbl. of oil	20
Gasoline, 56° A. P. I. gravity	65% by volume	56
Intermediate recycle stock, 28° A. P. I. gravity	5% by volume	5
Coke	60 lbs./bbl. of oil	19

The gas produced may contain approximately 20 to 25% of olefins such as propylene and the butylenes with the percentage of propylene predominating.

The total fixed gases thus produced may be passed together with approximately 5 gallons of commercial benzol per barrel of stock cracked and about 5% by weight of 66° Baumé sulphuric acid (based on the benzol) through mixing and cooling devices generally similar to those described in connection with the drawing. After de-alkylating in the presence of an aluminum chloride contact mass according to the second stage of the process the yield of synthetic products per barrel of oil originally cracked may be approximately 7.5 gallons, this product having an anti-knock value twice that of the original benzol which was added to combine with the olefins. By blending this synthetic liquid with the cracked gasoline as produced the volume yield of gasoline is therefore raised from 65 to 82%, the anti-knock value being at the same time raised from 65 to 80.

On the basis of the foregoing figures there is no question of the value of the process when operated in conjunction with cracking since both the yield and quality of the gasoline is increased and a large percentage of the gaseous products are conserved. However, the specific numerical data given are not to limit the scope of the invention thereto nor is the description of operations given in connection with the drawing to exercise a limiting action since many other types of plants may be utilized to effect similar economies.

I claim as my invention:

1. In the alkylation of aromatic hydrocarbons of the benzene series wherein there is produced a mixture of alkylated derivatives boiling within and above the motor fuel range, the method which comprises separating from said mixture a fraction boiling within the motor fuel range and a fraction containing the alkylated derivatives heavier than motor fuel, and dealkylating the last-named fraction sufficiently to convert a substantial portion thereof into hydrocarbons boiling within the motor fuel range.

2. In the alkylation of aromatic hydrocarbons of the benzene series wherein there is produced a mixture of alkylated derivatives boiling within and above the motor fuel range, the method which comprises separating from said mixture a fraction boiling within the motor fuel range and a fraction containing the alkylated derivatives heavier than motor fuel, and dealkylating the last-named fraction sufficiently to convert a substantial portion thereof into hydrocarbons boiling within the motor fuel range, combining the motor fuel hydrocarbons thus formed with the first-mentioned fraction and collecting the resultant blend as a product of the process.

3. The method as defined in claim 1 further characterized in that the heavier alkylated derivatives of said last named fraction are dealkylated by reaction with an additional quantity of a hydrocarbon of the benzene series.

4. The method as defined in claim 2 further characterized in that the heavier alkylated derivatives of said last-named fraction are dealkylated by reaction with an additional quantity of a hydrocarbon of the benzene series.

5. A process which comprises reacting hydrocarbon material of the benzene series with an olefinic gas thereby forming a mixture of alkylated derivatives boiling within and above the gasoline range, separating the mixture into a fraction containing the alkylated derivatives heavier than gasoline and a fraction containing alkylated derivatives within the gasoline boiling range, dealkylating the first-named fraction sufficiently to convert a substantial portion of the heavier alkylated derivatives into hydrocarbons boiling within the gasoline range, and blending the gasoline-boiling hydrocarbons thus formed with the second mentioned fraction.

6. A process which comprises reacting hydrocarbon material of the benzene series with an olefinic gas thereby forming a mixture of alkyl-

ated derivatives boiling within and above the gasoline range, separating the mixture into a fraction containing the alkylated derivatives heavier than gasoline and a fraction containing alkylated derivatives within the gasoline boiling range, dealkylating the first-named fraction sufficiently to convert a substantial portion of the heavier alkylated derivatives into hydrocarbons boiling within the gasoline range by reacting the heavier derivatives with additional hydrocarbon material of the benzene series, and blending the gasoline-boiling hydrocarbons thus formed with the second mentioned fraction.

7. In the alkylation of aromatic hydrocarbons of the benzene series by reaction thereof with normally gaseous olefin hydrocarbons and wherein there is formed a mixture of alkylated derivatives boiling within and above the gasoline range, the improvement which comprises separating said mixture into a fraction boiling within the gasoline range and a heavier fraction, dealkylating said heavier fraction sufficiently to form gasoline boiling hydrocarbons, and combining the latter with the lighter derivatives formed in the alkylation step.

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