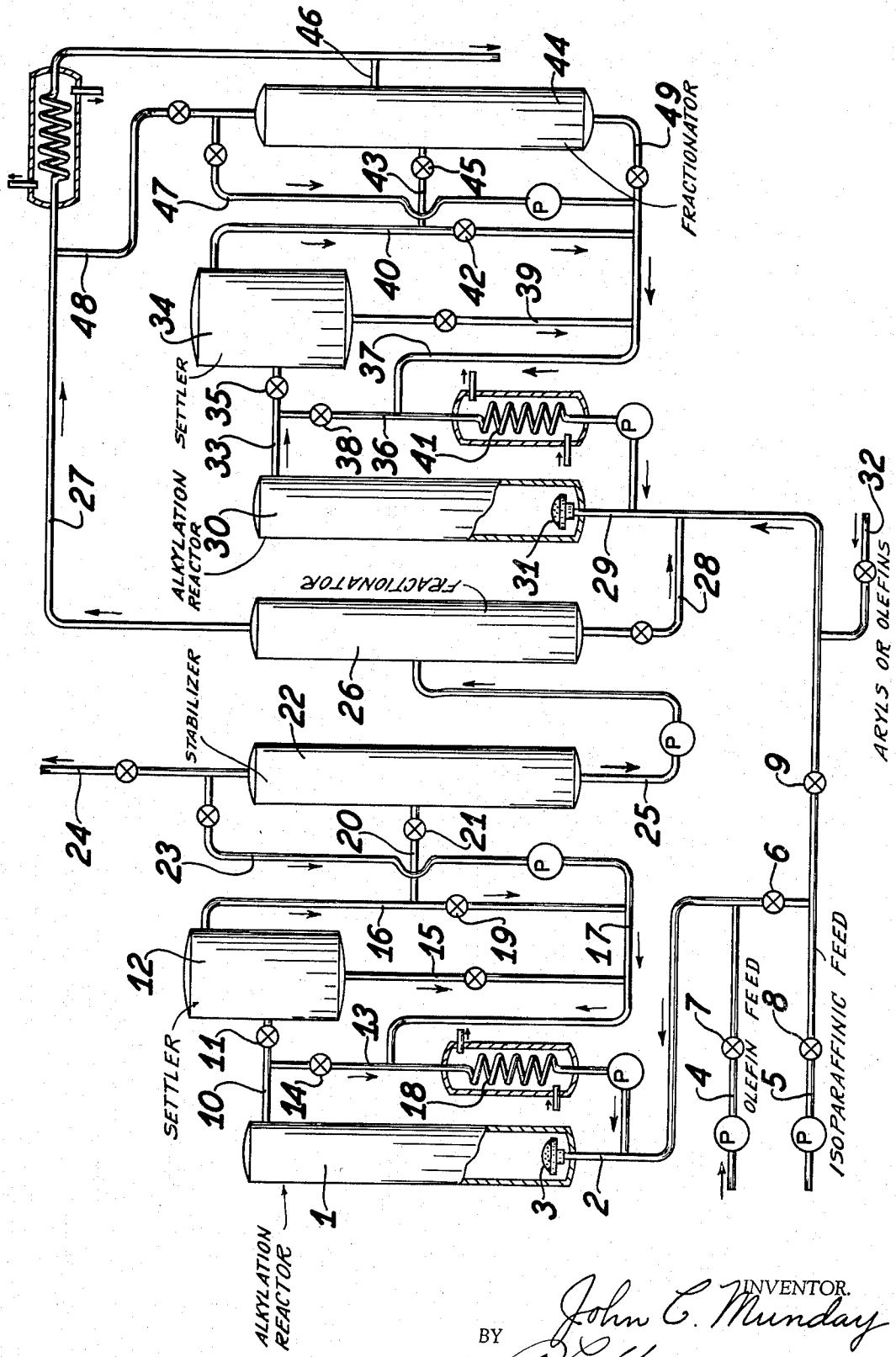
Dec. 15, 1942. J. C. MUNDAY 2,305,026

MOTOR FUEL AND PROCESS FOR MAKING SAME

Filed Dec. 7, 1938



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Patented Dec. 15, 1942

2,305,026

UNITED STATES PATENT OFFICE

2,305,026

MOTOR FUEL AND PROCESS FOR MAKING SAME

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Application December 7, 1938, Serial No. 244,345

17 Claims. (Cl. 196—10)

The present invention is directed to a method for producing a gasoline having a full boiling range and a high octane number from low boiling olefins and isoparaffins together with aromatics, if desired, and to a particular gasoline so produced.

It has been established that a gasoline containing hydrocarbons over the range of C_5 to C_{14} plus can be obtained by the reaction between low boiling or normally gaseous olefins and isoparaffins in the presence of an activating agent such as concentrated sulfuric or phosphoric acid, acid treated clays, sodium aluminum chloride complexes, metal halides, alone or in conjunction with alkyl halides, and the like. These gasolines usually have a fairly high octane number in the neighborhood of 90, and are of a predominantly saturated character.

It has now been found that the unsaturated constituents of these gasolines are composed of C_9 and higher hydrocarbons and that this fraction of the gasoline product has a much lower octane number than the other fractions and tends to hold down the overall octane number of the product. It has been proposed to recycle these heavy ends continuously to the reaction chamber in which they are produced so as to suppress their formation. This expedient gives the desired result, but when it is practiced the process does not yield a gasoline of full boiling range.

According to the present invention, a gasoline of full boiling range and of high octane number is produced by separating the C_{9+} hydrocarbons from the product of the above described process and reacting these heavier hydrocarbons which contain large quantities of olefins with low boiling aromatics or isoparaffins, or both, to produce hydrocarbons which are either branched chain paraffins or alkylated aromatics, or both, having a boiling range which complements that of the C_5–C_8 fraction previously recovered to yield a gasoline having a satisfactory distillation curve and a high octane number.

The process of the present invention is preferably carried out by the use of concentrated sulfuric acid having a strength in excess of 90%, preferably between 95 and 100%, as the activating medium. Two separate reaction zones are provided. To the one is fed a mixture of isoparaffins and olefins, preferably isobutane and butylene. The product from this zone is fractionated to produce a C_4 recycle stock, a C_5–C_8 saturated fraction boiling between about 80 and 270° F. and having an octane number in excess of 90, and a C_{9+} fraction. This latter fraction is fed to the second reaction zone together with an isoparaffin, such as isobutane, or an aromatic, such as benzol or toluol, or a mixture of both isoparaffins and aromatics. When aromatics are employed it is advantageous to feed in with the aromatics low boiling olefins such as ethylene, propylene and butylenes, since these serve to increase the content of alkylated aromatics of suitable boiling point in the final product. A C_{9+} fraction is recovered from the product from this zone and is combined with the C_5–C_8 fraction recovered from the first zone while the remainder of the product is recycled to the second zone.

For a more complete understanding of the present invention reference is made to the accompanying drawing in which the single figure is a diagrammatic illustration of a form of apparatus suitable for carrying out the present invention.

Referring to the drawing in detail, numeral 1 designates a reactor which is filled with sulfuric acid of a strength in excess of 90% and which is kept in circulation from bottom to top by suitably arranged pumps. Vessel 1 is provided at its lower end with an inlet line 2 which terminates in the reactor in a spray head 3 which may be replaced by a porous thimble or individual jets of minute diameter. A feed line 4 for olefinic material and a feed line 5 for isoparaffinic material are connected with inlet line 2. Line 2 is provided with a valve 6, line 4 with a valve 7, and line 5 with valves 8 and 9 for the purpose hereinafter specified. A draw-off line 10 is provided near the upper end of reactor 1 for the purpose of discharging reaction mixture through valve 11 into settler 12. Line 10 is provided, ahead of valve 11, with a return line 13 controlled by a valve 14 for the recycle of any desired amount of reaction mixture to the reactor 1. An acid draw-off line 15 connected to the bottom of settler 12 and a hydrocarbon draw-off line 16, connected to the top of settler 12, are connected, along with return line 13, to a return header 17 in which is a cooling coil 18 for controlling the temperature in reactor 1.

Line 16 is provided with a valve 19 by adjustment of which any desired amount of hydrocarbon product can be returned to the reactor 1. Ahead of valve 19, line 16 is provided with a branch line 20 which discharges the hydrocarbon product through valve 21 into a stabilizer 22, from the top of which C_4 hydrocarbons are withdrawn through line 23 and returned to header 17. Line 23 is provided with a branch line 24

through which C_4 or lighter hydrocarbons may be removed from the system, if desired. The remainder of the hydrocarbon product leaves stabilizer 22 through bottom draw-off line 25 by which it is discharged into fractionator 26 which is so operated that C_5–C_8 hydrocarbons are expelled in the vapor state through upper draw-off line 27, while C_{9+} hydrocarbons leave at the bottom through line 28 which is connected to feed inlet 29 of a second reactor 30.

The feed inlet 29 terminates in reactor 30 in a sprayhead 31. Feed line 5 is connected to inlet 29 and is provided with a branch line 32 for the introduction into the system of aromatics and olefins, such as ethylene, propylene, etc., if desired. By suitable manipulation of valves 6 and 9 in lines 2 and 5, respectively, the isoparaffin feed can be divided between the first and second zones.

Reactor 30, like reactor 1, is filled with acid and is provided at its upper end with a draw-off line 33 which discharges into a settler 34 through a valve 35 ahead of which is a return line 36 connected to a return header 37 and controlled by a valve 38. Acid drain line 39 connects the bottom of settler 34 with return header 37, and hydrocarbon draw-off line 40 connects the top of settler 34 with return header 37 which is provided with a cooling coil 41 for the control of temperature in reactor 30.

The amount of hydrocarbons returned to reactor 30 through line 40 is controlled by valve 42 ahead of which is branch line 43 which discharges into fractionator 44 through valve 45. A side stream boiling between about 270° and 410° F. is drawn off from fractionator 44 through line 46 which joins product draw-off line 27. Low boiling hydrocarbons leave fractionator 44 through vapor line 47 by which they are conducted to return header 37. Line 47 is also connected to product draw-off line 27 by a branch line 48 whereby the vaporous products, if they are of suitable boiling range, may be added directly to the C_5–C_8 fraction. Heavy ends leave fractionator 44 through line 49 by which they are conveyed to return header 37.

It will be understood that in the above described operation the system is under such a pressure that the reactants are maintained in the liquid state. When other catalysts are employed, such as solid catalysts, the reaction may be conducted in the vapor phase.

The product resulting from the above procedure has in general a higher octane number than the gasoline of full boiling range obtained by alkylation in a single step. This is particularly true when in the second step only aromatics with or without additional low boiling olefins are reacted with the C_{9+} alkylation product. In this case the heavier ends of the gasoline contain considerable amounts of alkylated aromatics which have an initial octane number higher than that of the initial alkylated product.

It will be understood that in the production of a blended gasoline containing alkylated aromatics according to the present invention, it is not necessary that the alkylated aromatics be produced by reaction between the initial C_{9+} alkylated products and aromatics. If desired, the C_{9+} fraction produced by the reaction between isoparaffin and olefin may be used as a recycle medium to the first alkylation zone, and only the C_5–C_8 fraction withdrawn from the alkylation unit is blended with alkylated aromatics from any source which have a boiling range complementing that of the aforesaid C_5–C_8 fraction to produce a gasoline having the desired distillation curve.

As examples of such alkylated aromatics may be mentioned ethyl benzene, propyl benzene, isopropyl benzene, methyl-ethyl benzene o, m, p, trimethyl benzene 1, 2, 3, trimethyl benzene 1, 2, 4, trimethyl benzene 1, 3, 5, secondary butyl benzene, isobutyl benzene, tertiary butyl benzene, methyl-isopropyl benzene p, etc. Since the C_5–C_8 fraction has an end boiling point of about 275° F., a gasoline of full boiling range is obtained by blending this fraction with selected alkylated aromatics of the type enumerated. Such motor fuels are disclosed and claimed in copending application Serial No. 458,507, filed September 16, 1942, which is a continuation in part of the present application.

The nature and objects of the present invention having been thus described and illustrated, what is claimed as new and useful and is desired to be secured by Letters Patent is:

1. In the production of gasoline from low boiling olefins and isoparaffins, the steps which comprise subjecting an isoparaffin and an olefin to the action of an alkylation catalyst under conditions suitable to effect reaction between the two to produce a hydrocarbon product having a wide boiling range, dividing said product into a heavy fraction and a light fraction, the latter including substantially only C_8 and lower hydrocarbons, separately subjecting said heavy fraction to a further reaction with at least one hydrocarbon of the group consisting of isoparaffins and aromatic hydrocarbons under alkylation reaction conditions and in the presence of an alkylation catalyst, recovering from this latter reacted mixture a hydrocarbon fraction containing alkylated hydrocarbons boiling within the gasoline boiling range and combining at least a portion of said latter recovered fraction with the previously identified light fraction.

2. In the production of gasoline from low boiling olefins and isoparaffins, the steps which comprise subjecting an isoparaffin and an olefin to the action of an alkylation catalyst under conditions suitable to effect reaction between the two to produce a hydrocarbon product having a wide boiling range, dividing said product into a heavy fraction and a light fraction, the latter including only those hydrocarbons boiling within the gasoline boiling range, separately subjecting said heavy fraction to a further reaction with at least one hydrocarbon of the group consisting of isoparaffins and aromatic hydrocarbons under alkylation reaction conditions and in the presence of an alkylation catalyst, recovering from this latter reacted mixture a hydrocarbon fraction containing alkylated hydrocarbons boiling within the gasoline boiling range and combining at least a portion of said latter recovered fraction with the previously identified light fraction.

3. In the production of gasoline from low boiling olefins and low boiling isoparaffins, the steps which comprise subjecting the reactants to the action of an alkylation catalyst under suitable alkylation reaction conditions, fractionating the reacted mixture into a fraction predominating in C_8 and lower hydrocarbons and a fraction predominating in C_9 and heavier hydrocarbons, separately subjecting the C_9 and heavier hydrocarbon fraction to a further reaction with at least one hydrocarbon of the group consisting of isoparaffins and aromatic hydrocarbons in the

presence of an alkylation catalyst under suitable alkylation reaction conditions, recovering from this latter reacted mixture a fraction comprising predominantly C_9 and heavier hydrocarbons and combining at least a portion of this fraction with the first-mentioned C_8 and lighter hydrocarbon fraction.

4. In the production of gasoline from low boiling olefins and low boiling isoparaffins, the steps which comprise subjecting an isoparaffin and an olefin to the action of an alkylation catalyst under suitable alkylation reaction conditions to produce a hydrocarbon product having a wide boiling range, dividing said product into a heavy fraction and a light fraction, the latter including substantially only C_8 and lower hydrocarbons, separately subjecting said heavy fraction to a further reaction with an isoparaffin under alkylation reaction conditions and in the presence of an alkylation catalyst, recovering from the product of this latter reaction a hydrocarbon fraction containing alkylated hydrocarbons boiling within the gasoline boiling range and combining at least a portion of said latter recovered fraction with the previously mentioned C_8 and lower hydrocarbon fraction.

5. In the production of gasoline from low boiling olefins and isoparaffins, the steps which comprise subjecting the reactants to the action of an alkylation catalyst under conditions suitable to effect reaction between the two to produce a hydrocarbon product having a wide boiling range, dividing said product into a heavy fraction and a light fraction, the latter including only those hydrocarbons boiling within the gasoline boiling range and containing C_8 and lower hydrocarbons, separately subjecting said heavy fraction to a further reaction with at least one aromatic hydrocarbon under alkylation reaction conditions and in the presence of an alkylation catalyst, recovering from this latter reacted mixture a hydrocarbon fraction containing alkylated aromatic hydrocarbons boiling within the gasoline boiling range and combining at least a portion of said latter recovered fraction with the previously mentioned light fraction.

6. In the production of a motor fuel having a boiling range between about 80 and about 410° F. by reacting C_4 olefins and isobutane, the steps which comprise maintaining two reaction zones under alkylating conditions and containing sulfuric acid having a concentration between about 90 and about 100%, introducing continuously into the first alkylation zone C_4 olefins and isobutane, continuously removing and recovering from the reacted mixture unreacted reactants, normally liquid substantially saturated C_5–C_8 hydrocarbons boiling between 80 and about 270° F., and a C_9 and heavier fraction, withdrawing the C_5–C_8 fraction, continuously feeding the C_9 and heavier fraction, additional C_4 olefins and at least one mono-nuclear aryl hydrocarbon to the second alkylation zone, recovering from said second alkylation zone a reaction product of C_9 and higher hydrocarbons having boiling range between about 270 and about 410° F. and combining said fraction with the C_5–C_8 fraction having a boiling range between about 80 and about 270° F. produced in the first alkylation zone, to produce a motor fuel having a boiling range between about 80 and about 410° F., having that portion boiling below 270° F. comprising acyclic paraffins and that portion boiling above 270° F. comprising nuclear alkylated mono-nuclear aromatic hydrocarbons.

7. A process as in claim 6 wherein the unreacted reactants from the first alkylation zone are returned to that zone and wherein the fractions from the second alkylation zone boiling below 270° F. and above 410° F. are returned to the second alkylation zone, as formed.

8. A process as in claim 6 wherein isobutane is added to the C_4 olefins and at least one mono-nuclear aryl hydrocarbon to constitute a portion of the fresh feed introduced into the second alkylation zone.

9. A method according to claim 5 in which a normally gaseous olefin is added to the second reaction mixture.

10. A method according to claim 2 in which the isoparaffin is isobutane.

11. A method according to claim 4 in which the isoparaffin is isobutane.

12. A method according to claim 2 in which the isoparaffin is isobutane and the olefin is a butylene.

13. A method according to claim 4 in which the isoparaffin is isobutane and the olefin is a butylene.

14. In the production of gasoline from low boiling olefins and isoparaffins, the steps which comprise maintaining a pair of reaction zones containing an alkylation catalyst and maintained under suitable alkylation conditions, continuously feeding low boiling olefins to the first of said reaction zones, continuously feeding a low boiling isoparaffin to both of said reaction zones, continuously recovering a mixture of hydrocarbons higher than C_8 from said first reaction zone, continuously feeding this mixture to the second reaction zone, and continuously recovering from said second reaction zone a reaction product of C_9 and higher hydrocarbons.

15. A method according to claim 2 in which the alkylation catalyst is sulfuric acid having a strength of at least about 90%.

16. A method according to claim 4 in which the alkylation catalyst is sulfuric acid having a strength of at least about 90%.

17. A method according to claim 14 in which the alkylation catalyst is sulfuric acid having a strength of at least about 90%.

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