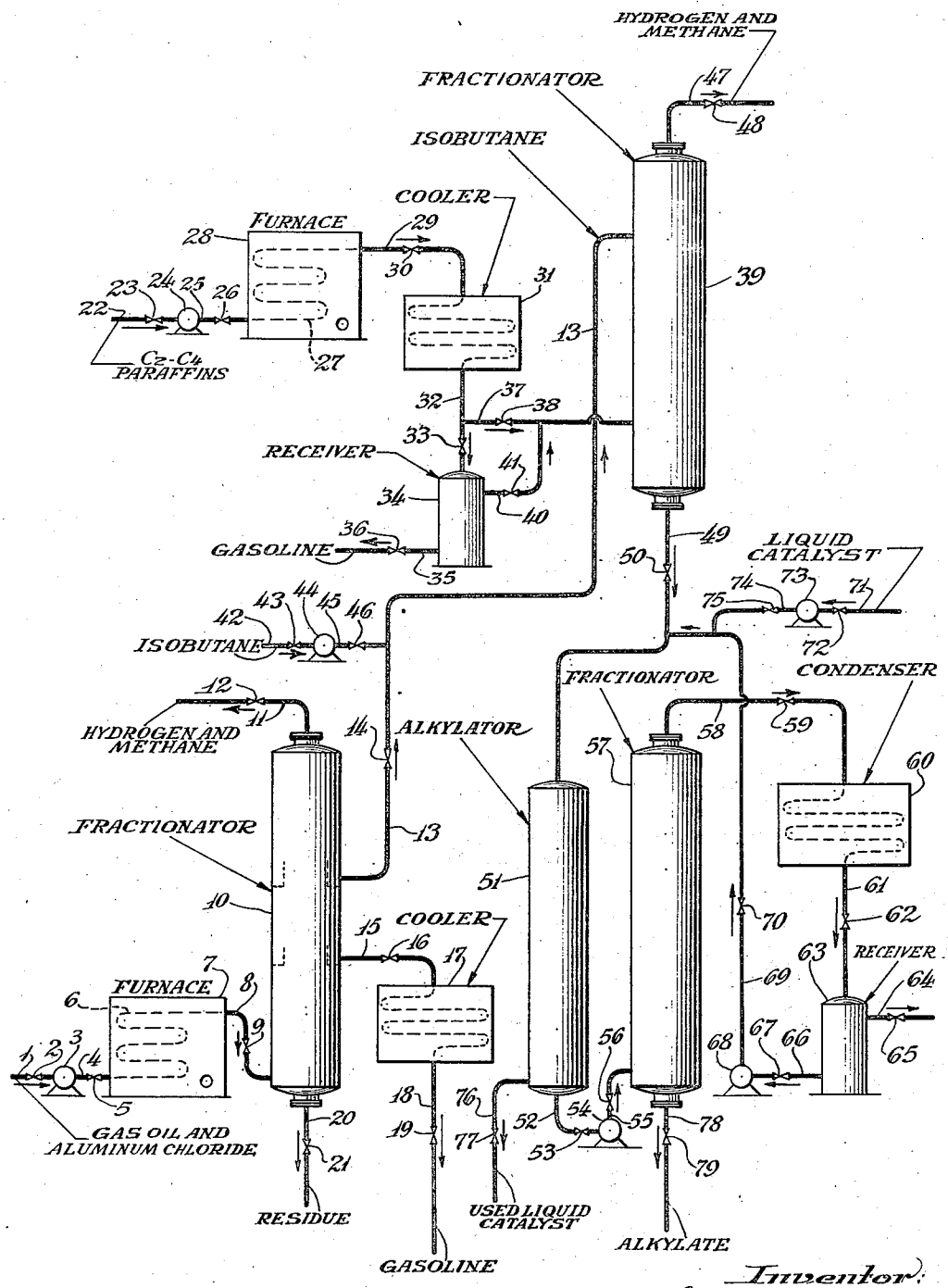
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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5 Claims. (Cl. 196—10)

This invention relates to the simultaneous treatment of paraffin gases and a hydrocarbon oil to produce therefrom substantial yields of motor fuel of high antiknock value.

The process is particularly applicable to the treatment of paraffin gases containing 2–4 carbon atoms per molecule together with gas oil distillates and naphthas produced as intermediates in the distillation of crude petroleum oils, but it may be applied also to the simultaneous treatment of paraffin gases and distillates produced in the distillation of coal and of other hydrocarbonaceous oils produced by any means.

More particularly the process of this invention is concerned with the conversion of the aforementioned gaseous and liquid hydrocarbons under closely regulated conditions of operation conducive to the formation of high yields of motor fuel of good antiknock value.

In one specific embodiment the present invention relates to a process for producing high quality motor fuels which comprises cracking a hydrocarbon oil in the presence of aluminum chloride to form a substantial yield of isobutane, producing normally gaseous olefins from corresponding paraffins by thermal decomposition and/or catalytic dehydrogenation reactions, and alkylating said isobutane by said normally gaseous olefins to produce a substantially saturated alkylate of high antiknock value.

Substantial yields of isobutane may be obtained by heating hydrocarbon oils and hydrocarbon distillates in the presence of substantially anhydrous aluminum chloride, preferably in the presence of minor amounts of hydrogen chloride, using a relatively high reflux ratio, correspondingly low rates of distillation, and vapor temperatures at the outlet of the still of the order of 100–200° F. and preferably within the lower range. In some instances it may be preferable to add another metal halide to the aluminum chloride catalyst. The added metal halide may, for example, comprise a chloride of zirconium, zinc, iron, etc., which is relatively less active than aluminum chloride.

Normally gaseous paraffins as ethane, propane, and the butanes, either in admixture or individually, may be converted into substantial yields of gaseous olefins by thermal and/or catalytic methods. Pyrolysis or thermal conversion of the paraffinic gases into olefinic hydrocarbons may be effected at a temperature in the neighborhood of 1200–1400° F. and under a pressure of from substantially atmospheric to approximately 100 pounds per square inch. Olefinic hydrocarbons may be formed from the gaseous paraffins by dehydrogenation in the presence of a suitable catalyst at a somewhat lower temperature generally in the approximate range of 800–1200° F. Suitable dehydrogenating catalysts may comprise composites of refractory carriers and oxides of elements selected from the members of the left-hand columns of groups IV, V, and VI of the periodic table. The products from pyrolysis or dehydrogenation of the aforementioned gaseous paraffins may be cooled to separate a gaseous fraction containing both paraffins and olefins from relatively minor amounts of liquid hydrocarbons which may arise during the thermal treatment.

Isobutane formed by aluminum chloride cracking and the paraffin-olefin mixture formed from the paraffin gases may be commingled and fractionated to remove a light fraction comprising essentially hydrogen and methane. The remaining mixture of 2–4 carbon atom hydrocarbons containing both olefins and isobutane may then be subjected to alkylation in the presence of a catalyst such as sulfuric acid, hydrogen fluoride, boron fluoride with hydrogen fluoride or with fluorine, or aluminum chloride with hydrogen chloride, generally at a temperature in the approximate range of —15 to 200° F. and under sufficient pressure to keep in liquid phase a substantial proportion of the reacting hydrocarbons. Alkylation may be effected also in the presence of a calcined composite of an acid of phosphorus and a generally siliceous adsorbent at a temperature in the approximate range of 600–900° F. under a pressure of the order of 1000–3000 pounds per square inch.

These alkylating catalysts which may be used alternatively are not necessarily equivalent in their action and the exact operating conditions to be used in their presence are dependent upon their activities, the composition of the hydrocarbon mixture, and other factors.

The accompanying diagrammatic drawing illustrates one specific form of apparatus in which the process of the invention may be conducted:

Referring to the drawing, a mixture of a hydrocarbon oil and aluminum chloride (which is ordinarily less than 20% by weight of the charge) may be introduced through line 1 and valve 2 to pump 3 which discharges through line 4 and valve 5 to coil 6 disposed to receive heat from furnace 7. The heated mixture of oil and aluminum chloride may be discharged from coil 6 through line 8 and valve 9 to fractionator 10 of adequate design for separating a hydrogen-

methane fraction, isobutane, gasoline, and a higher boiling residue. Hydrogen and methane may be released from fractionator 10 through line 11 containing valve 12. Isobutane separated from other products as hereinabove set forth may be withdrawn from fracti nator 10 through line 13 containing alve 14 and therein conducted to further treatment as hereinafter described. Gasoline separated in fractionator 10 may be withdrawn therefrom through line 15 containing valve 16 to cooler 17 and thence through run-down line 18 and valve 19 to storage, while a residue of higher boiling materials may be discharged from fractionator 10 through line 20 and valve 21, the former, if desired, provided with a cooler, not shown.

A fraction comprising essentially paraffinic hydrocarbons with 2–4 carbon atoms per molecule may be admitted through line 22 and valve 23 to compressor 24 which discharges through line 25 and valve 26 to coil 27 disposed to receive heat from furnace 28. Heating coil 27 may be subjected to a temperature of the order of 1200–1400° F. in order to effect substantial conversion of paraffin gases to olefinic hydrocarbons. Heated products contained in coil 27 may be conducted therefrom through line 29 and valve 30 to cooler 31 and thence through run-down line 32 and valve 33 and receiver 34 in which may be collected hydrocarbons of gasoline boiling range formed during pyrolysis of the gaseous paraffin fraction. Receiver 34 is provided with a liquid draw-off line 35 containing valve 36. If desired, all or a part of the pyrolysis products passing through run-down line 32 may be conducted therefrom through line 37 and valve 38 to fractionator 39 to which isobutane may be admitted through line 13, already mentioned. Gaseous products which may accumulate in receiver 34 may be withdrawn therefrom through line 40 and valve 41 to line 37, already mentioned.

If desired, isobutane from an outside source may be introduced through line 42 and valve 43 to pump or compressor 44 which discharges through line 45 and valve 46 to line 13, already mentioned, through which an isobutane fraction may be conducted to near the top of fractionator 39 thereby assisting in controlling the temperatures therein and aiding in separating a hydrogen-methane fraction from higher boiling gaseous products containing isobutane and olefins. Fractionator 39 may comprise a distilling column of adequate dimensions for separating a fraction comprising essentially hydrogen and methane which may be discharged therefrom through line 47 and valve 48.

Alternatively the fraction comprising essentially paraffins with 2–4 carbon atoms per molecule may be converted into a substantial proportion of olefins by contact with a dehydrogenating catalyst at a temperature in the approximate range of 800–1200° F. This treatment may be carried out by disposing a granular dehydrogenating catalyst within heating coil 27 or in another suitable reactor provided with means for heating to the required temperature. Dehydrogenation may also be carried out by preheating the paraffin gas, as already described, in heating coil 27 and then admitting the heated gas to a reactor, not shown, containing granular dehydrogenating catalyst such as a composite of activated alumina with chromium sesquioxide. As a further alternative a finely divided dehydrogenating catalyst may be mixed with the paraffin gas fraction and conducted through a suitable heating coil. With the latter type of operation, means, not shown, will be provided for separating used powdered catalyst from the mixture of dehydrogenation products and unconverted paraffins which is thence conducted to fractionator 39, already mentioned.

From fractionator 39 a hydrocarbon mixture containing isobutane and gaseous olefins may be conducted through line 49 and valve 50 to alkylator 51 which may consist of a baffled reactor or other suitable vessel provided with adequate means for cooling or heating to maintain the temperature required for alkylation in the presence of a chosen catalyst. When alkylation is effected in the presence of a liquid catalyst, alkylator 51 may also be provided with a stirrer or other means of agitation.

In case a granular fixed catalyst is employed such as a calcined composite of an acid of phosphorus and a generally siliceous adsorbent, the alkylator may be a cylindrical reactor designed to operate under the necessary conditions of temperature and pressure.

The exact conditions of temperature and pressure used in any given alkylation will be determined by the catalyst employed, the composition of the reaction mixture, and by other factors.

During the reaction, alkylation products and unconverted isobutane are withdrawn from alkylator 51 through line 52 and valve 53 by pump 54 which discharges through line 55 and valve 56 to fractionator 57 in which unconverted isobutane may be separated from the alkylation products and may be withdrawn through line 58 and valve 59 to cooler 60 and thence through run-down line 61 and valve 62 to receiver 63 provided with gas release line 64 containing valve 65. From receiver 63 condensate comprising essentially unconverted isobutane may be withdrawn through line 66 and valve 67 by pump 68 discharging through line 69 and valve 70 into line 49, already mentioned, through which the fraction containing isobutane and olefins is conducted to alkylation.

When the alkylation reaction is carried out in the presence of a normally liquid catalyst, fresh catalyst may be introduced as desired from an outside source through line 71 and valve 72 to pump 73 which discharges through line 74 and valve 75 into line 69, already mentioned. Used liquid catalyst may also be withdrawn from alkylator 51 by way of line 76 and valve 77. After removal of unconverted isobutane in fractionator 57 a substantially saturated alkylate of high octane number may be withdrawn through line 78 and valve 79 to storage or to distillation, not shown, to separate fractions of desired boiling range.

It is generally preferable to add a small proportion of a hydrogen halide to the mixture of hydrocarbon oil and aluminum chloride being conducted to cracking to produce isobutane. It may also be advantageous to introduce a hydrogen-containing gas with the hydrocarbons charged to cracking as well as to alkylation. This may be accomplished, by means not shown, but apparent to one skilled in the art, utilizing a portion of the hydrogen-methane fraction formed in the process, particularly that available from the products of paraffin pyrolysis or dehydrogenation.

The results obtainable by these various alternative types of operation are not necessarily equivalent since the results obtained are generally dependent upon the materials charged, the

particular catalyst employed, the conditions of operation, and other factors.

The following specific example is introduced to show results normally obtainable in the operation of the process, although with no intention of unduly limiting the broad scope of the invention.

A California gas oil admixed with approximately 15% by weight of granular anhydrous aluminum chloride and 1% by weight of anhydrous hydrogen chloride may be conducted through a tubular heater maintained at about 600° F. to a fractionator in which the top temperature may be kept at approximately 100° F. Products obtainable from this step comprise approximately 25% by volume of liquid isobutane and 43% by volume of saturated aviation gasoline with 81 octane number. The isobutane may be commingled with an olefin-containing fraction formed by pyrolyzing a propane-butane fraction at approximately 1300° F. under a pressure of 100 pounds per square inch. The commingled mixture containing approximately 4 molecular proportions of isobutane per molecular proportion of olefinic hydrocarbon may be contacted at 45° F. with sulfuric acid of 98% concentration to produce a substantially saturated alkylate of 92 octane number.

The character of the present invention and its novelty and utility in producing gasoline from paraffin gases and hydrocarbon oils containing substantially no gasoline can be seen from the preceding specification and example given, although neither section is intended to limit unduly its generally broad scope.

I claim as my invention:

1. A process for the production of high octane rating gasoline which comprises cracking a hydrocarbon oil to produce isobutane, fractionating the cracked products to separate a liquid isobutane fraction, simultaneously and concurrently subjecting normally gaseous paraffins to dehydrogenation to produce a substantial yield of normally gaseous olefins, scrubbing the conversion products from said dehydrogenation with said liquid isobutane fraction under conditions suitable for producing a liquid mixture comprising the liquid isobutane and said normally gaseous olefins and subjecting said mixture to alkylation to alkylate the isobutane with said normally gaseous olefins.

2. The process of claim 1 further characterized in that the dehydrogenation step comprises thermal dehydrogenation.

3. The process of claim 1 further characterized in that the dehydrogenation step comprises catalytic dehydrogenation.

4. A process for the production of high octane rating gasoline which comprises cracking a hydrocarbon oil in the presence of aluminum chloride to produce isobutane, fractionating the cracked products to separate a liquid isobutane fraction, simultaneously and concurrently subjecting normally gaseous paraffins to dehydrogenation to produce a substantial yield of normally gaseous olefins, scrubbing the conversion products from said dehydrogenation with said liquid isobutane fraction under conditions suitable for producing a liquid mixture comprising the liquid isobutane and said normally gaseous olefins and subjecting said mixture to alkylation to alkylate the isobutane with said normally gaseous olefins.

5. A process for producing antiknock motor fuel which comprises subjecting hydrocarbons to conversion to produce isobutane therefrom, fractionating the resultant products to separate a liquid isobutane fraction therefrom, simultaneously subjecting normally gaseous paraffins to dehydrogenation to convert a substantial portion thereof into normally gaseous olefins, fractionating the gaseous products of the dehydrogenation in countercurrent contact with said liquid isobutane fraction and under conditions to form a liquid mixture of isobutane and normally gaseous olefins, and subjecting said mixture to alkylation to react normally gaseous olefins with isobutane.

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