

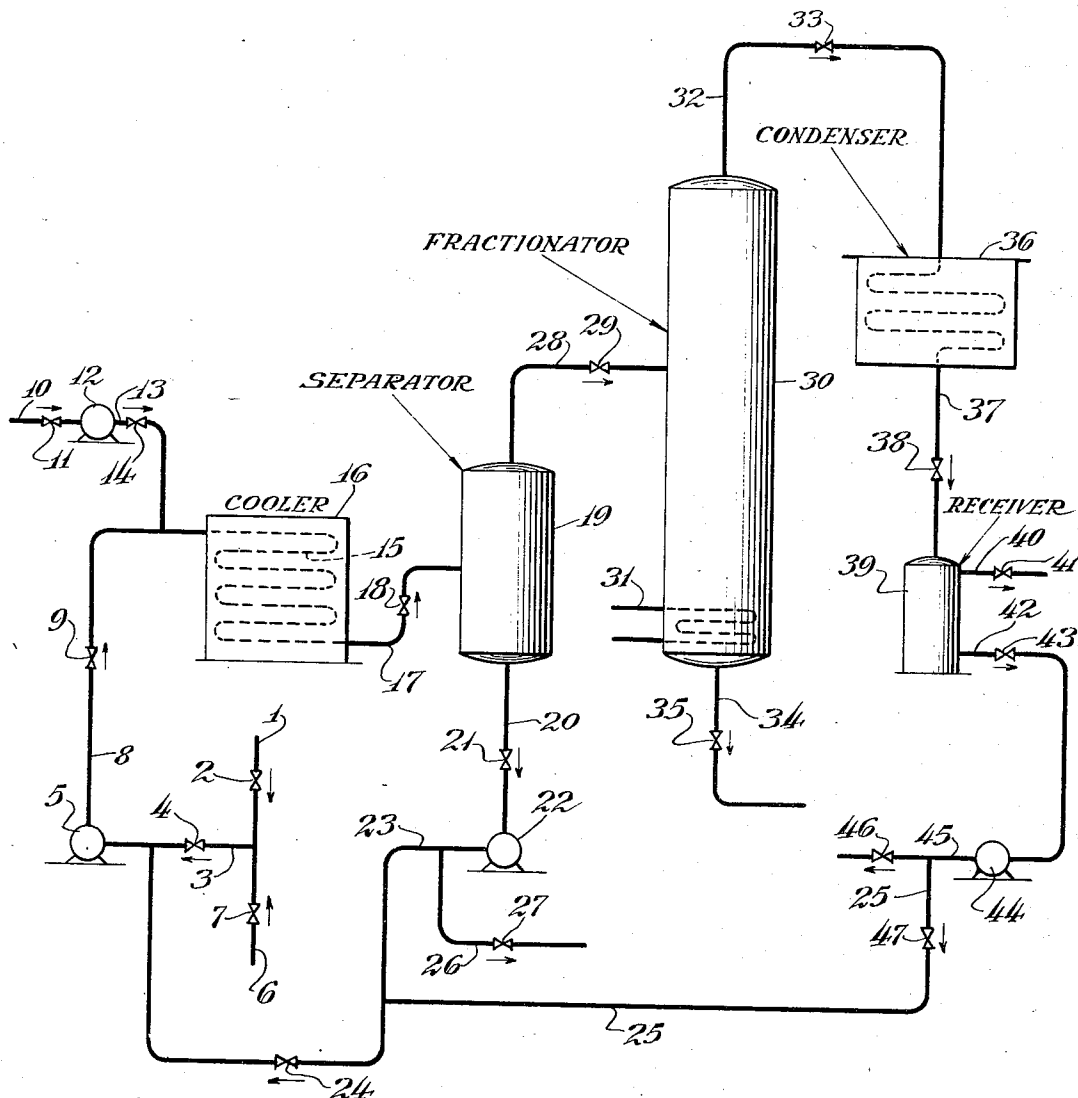
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ALKYLATION OF PARAFFIN HYDROCARBONS

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ALKYLATION OF PARAFFIN
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This invention is concerned with the interaction of branched chain paraffinic hydrocarbons with alkyl fluorides in the presence of a catalyst. It is more specifically concerned with a simple and easily regulated process involving the use of a liquid catalyst which is altered only slightly in the course of the reaction but which catalyzes the desired reactions with a maximum of efficiency.

Processes for the formation of higher molecular weight branched chain paraffins from lower boiling less highly branched chain paraffins are of importance from the standpoint of the motor fuel industry which demands increasing quantities of substantially saturated hydrocarbons boiling within the range of gasoline and particularly saturated motor fuels of high antiknock value.

In one specific embodiment the present invention comprises a process for alkylating branched chain paraffinic hydrocarbons by alkyl fluorides in the presence of liquid hydrogen fluoride to form higher boiling branched chain paraffinic hydrocarbons of motor fuel boiling range and high antiknock value.

Considerable quantities of branched chain butane, pentanes, and higher boiling paraffins are available in the gaseous and lower boiling products resulting from the distillation and/or cracking of petroleum oils and of other hydrocarbonaceous oils. Proper segregation by fractionation and other methods makes available substantial amounts of isoparaffinic hydrocarbons which may be alkylated by alkyl fluorides in the presence of catalysts to give higher boiling and more highly branched paraffinic hydrocarbon of improved antiknock value. In accordance with the present invention interaction of isoparaffinic hydrocarbons with alkyl fluorides is brought about in the presence of substantially anhydrous hydrogen fluoride. This reaction forms substantially saturated hydrocarbons of higher boiling range and simultaneously produces hydrogen fluoride which may be utilized further as catalyst for alkylating a further quantity of the isoparaffinic hydrocarbon charged.

Alkyl fluorides used as alkylating agents in the process of this invention may be formed by the addition of hydrogen fluoride to mono-olefinic hydrocarbons at a temperature within the approximate range of -60 to $+100^{\circ}\text{C}$., and more preferably at a temperature of the order of -30 to 0°C ., and under a pressure sufficient to maintain in liquid phase a substantial proportion of the reaction mixture. At the higher temperatures polymerization tends to occur which interferes

with the direct conversion of the original olefin into alkyl fluorides. Such a formation of alkyl fluorides may be brought about by the use of substantially anhydrous hydrogen fluoride or by employing a portion of the hydrogen fluoride obtained as a by-product of the present isoparaffin alkylating process.

Substantially anhydrous hydrogen fluoride utilizable as catalyst in the process of this invention is a liquid boiling at about 20°C . and accordingly it can be used in apparatus which is cooled to maintain temperatures below this point or it can be used at higher temperatures if sufficient pressure is maintained upon the apparatus. By maintaining an excess of isoparaffin at all times, generally up to approximately 20 times the molecular proportion of alkyl fluoride present, formation of olefin polymers is avoided with the result that there is a relatively high conversion of alkyl fluorides into alkylated paraffinic hydrocarbons. Also formation of hydrogen fluoride occurs during the alkylation reaction. The resulting hydrogen fluoride may be employed as alkylating catalyst or it may be utilized in the production of a further quantity of alkyl fluoride to be returned to the process.

In operating the present process a preferred procedure is to agitate a mixture of liquid hydrogen fluoride and an isoparaffin and gradually introduce thereto a mixture of an alkyl fluoride and an isoparaffin suitably below the surface of the hydrogen fluoride-isoparaffin mixture. In the batch operation of this process, the agitation may be stopped and the upper hydrocarbon layer removed and fractionated to recover unchanged paraffins and the desired alkylated products. Obviously the process may be made continuous by providing a mixing zone, as a reactor containing baffles and/or orifices, in which sufficient time may be given generally in the approximate range of 1-10 minutes for the completion of the desired alkylation reaction followed by a settling zone from which a hydrocarbon layer may be withdrawn and fractionated to recover desired alkylated products and unconverted isoparaffins for recycling, while the lower hydrogen fluoride layer may be pumped back to the alkylation step for further separation. The aforementioned reaction of an isoparaffin with an alkyl fluoride may be carried out at a temperature in the approximate range of -10 to 75°C . but preferably at a temperature of approximately 20°C . Pressure has been found to have little effect on the reaction but it should preferably be sufficient to compensate for the vapor pressure of the re-

actants. Reaction may be attained to advantage by contacting the isoparaffinic hydrocarbon, alkyl fluoride, and hydrogen fluoride in the liquid phase.

For the purpose of illustrating a characteristic apparatus in which the process may be conducted, the attached drawing shows diagrammatically in general side elevation and by the use of conventional figures an arrangement of interconnected units suitable for continuous operations. It is understood that minor features of apparatus construction may be modified without departing essentially from the generally broad scope of the invention.

Referring to the drawing a liquid isoparaffin hydrocarbon fraction may be introduced through line 1 containing valve 2 to line 3 containing valve 4 to pump 5 while hydrogen fluoride is introduced to line 3 by way of line 6 containing valve 7. Pump 5 discharges through line 8 and valve 9. The mixture of isoparaffin and hydrogen fluoride being conducted through line 8 is therein commingled with a regulated and continuous stream of an alkyl fluoride or of an alkyl fluoride-isoparaffin mixture introduced through line 10 and valve 11 to pump 12 which discharges through line 13 and valve 14 to line 8, already mentioned, from which the commingled mixture passes to coil 15 contained in cooler 16 of any suitable construction and capacity for maintaining the temperature of reaction below any desired level while simultaneously permitting sufficient time of contact for completion of the desired reactions. From coil 15 the reaction products follow line 17 containing valve 18 to separator 19 in which is effected a separation of hydrogen fluoride and hydrocarbons. The hydrogen fluoride layer is withdrawn from separator 19 through line 20 containing valve 21 to pump 22 which discharges through line 23 and valve 24 into line 3 leading to the suction side of pump 5 so that the hydrogen fluoride catalyst may be recycled. If desired, a portion of the hydrogen fluoride being discharged by pump 22 through line 23 may be conducted therefrom through line 26 and valve 27 to storage or to other use such as the preparation of additional alkyl fluorides by reaction of hydrogen fluoride with a mono-olefin.

The hydrocarbon layer in the upper portion of separator 19 may be passed through line 28 and valve 29 to fractionator 30 containing reboiler coil 31 and provided with vapor line 32 and valve 33 through which lower boiling hydrocarbons may be released as an overhead fraction while higher boiling alkylated products may be withdrawn from the bottom of fractionator 30 through line 34 containing valve 35 to further cooling, not shown, and to storage.

The unconverted lower boiling hydrocarbons passing through line 32 may be conducted through condenser 36 and run-down line 37 containing valve 38 to receiver 39 equipped with conventional gas release line 40 containing valve 41 and with a liquid draw-off line 42 containing valve 43 leading to pump 44 which discharges through line 45 containing valve 46 to storage if desired, but ordinarily through line 25 containing valve 47 and leading to the suction side of pump 5, already mentioned, to permit recycling of unconverted isoparaffins to further alkylation.

The exact temperature and pressure to be employed when alkylating various isoparaffins with various alkyl fluorides will depend upon the activity and physical characteristics of the reactants involved so that best results will be obtained when

conditions are first determined on small scale apparatus. As a rule excessively elevated temperatures are neither necessary nor desirable and only sufficient pressure should be used to prevent excessive evaporation of the catalyst or of the isoparaffin and alkyl fluoride.

The following specific examples are introduced as representative of results obtainable by the process described, although with no intention of unduly limiting the generally broad scope of the invention;

EXAMPLE I

A pressure autoclave equipped with a mechanical stirrer was charged with 100 parts by weight of anhydrous hydrogen fluoride and 200 parts by weight (3.5 molecular proportions) of isobutane. The autoclave was maintained at 20° C. while 124 parts by weight (2.0 molecular proportions) of isopropyl fluoride was introduced thereto over a period of 1 hour during which time the reaction was accompanied by an evolution of heat.

The reaction mixture recovered was separated into 135 parts by weight of hydrogen fluoride, 102 parts by weight of isobutane, and 170 parts by weight of a colorless and substantially saturated liquid hydrocarbon mixture which was found to contain substantially no fluorine. Fractional distillation of the liquid hydrocarbon mixture obtained showed it to have the composition given in Table I:

TABLE I

Distillation of liquid product formed from isobutane and isopropyl fluoride in the presence of hydrogen fluoride

Fraction:	Volume per cent
Pentanes.....	7
Hexanes	15
Heptanes	45
Octanes	10
Nonanes	5
Nonane to 200° C. boiling pt.....	10
Fraction boiling above 200° C.....	8

EXAMPLE II

A mixture of 112 parts by weight of isopentane, 105 parts by weight of hydrogen fluoride, and 79 parts by weight of isopropyl fluoride was agitated for 2.5 hours at 35° C. in a pressure autoclave similar to that indicated in Example I. The reaction mixture recovered contained 9 parts by weight of propane, 10 parts by weight of isobutane, 18 parts by weight of unconverted isopentane, and 113 parts by weight of a higher boiling substantially saturated hydrocarbon mixture. A distillation of the substantially saturated hydrocarbon mixture showed it to have the composition indicated in Table II.

TABLE II

Distillation of liquid product formed from isopentane and isopropyl fluoride in the presence of hydrogen fluoride

Boiling range of fraction, °C.	Volume per cent
50-75	12
75-95	10
95-125	23
125-150	13
150-175	12
175-225	21
Above 225°	9

These results indicate that approximately equal molecular proportions of isopentane and isopro-

pyl fluoride reacted to produce the substantially saturated hydrocarbon mixture of a composition indicated in Table II.

The character of the process of the present invention and particularly its commercial value are evident from the preceding specification and examples given, although neither section is intended to be unduly limiting in its generally broad scope.

I claim as my invention:

1. A process for producing alkyl derivatives of a branched chain paraffin which comprises subjecting said branched chain paraffin to contact with an alkyl fluoride in the presence of hydrogen fluoride.
2. A process for producing alkyl derivatives of a branched chain paraffin which comprises subjecting a molal excess of said branched chain paraffin to contact with an alkyl fluoride in the presence of hydrogen fluoride.
3. A process for producing alkyl derivatives of a branched chain paraffin which comprises subjecting a molal excess of said branched chain paraffin to treatment with an alkyl fluoride in the presence of hydrogen fluoride at a temperature between about -10 and about $+75^{\circ}\text{C}$. under sufficient pressure to maintain substantially liquid phase conditions.
4. A process for producing isomeric octanes which comprises subjecting isobutane to treatment with a butyl fluoride in the presence of hydrogen fluoride.
5. A process for producing isomeric octanes which comprises subjecting a molal excess of isobutane to treatment with a butyl fluoride in the presence of hydrogen fluoride.
6. A process for producing isomeric octanes which comprises subjecting a molal excess of isobutane to treatment with a butyl fluoride in the presence of hydrogen fluoride at a temperature between about -10 and about $+75^{\circ}\text{C}$. and under sufficient pressure to maintain substantially liquid phase conditions.
7. A process for alkylating a liquid isoparaffin hydrocarbon which comprises intimately mixing said hydrocarbon with liquid hydrogen fluoride; introducing an alkyl fluoride to the mixture; cooling to maintain the reaction mixture at a temperature between about -10° and about $+75^{\circ}\text{C}$., separating products of the reaction into unconverted isoparaffin and alkyl fluoride, alkylated products, and hydrogen fluoride; and returning unconverted isoparaffin, alkyl fluoride, and hydrogen fluoride to further reaction.
8. A process for producing alkyl derivatives of an isoparaffin which comprises subjecting an isoparaffin in admixture with normal paraffins to treatment with an alkyl fluoride in the presence of hydrogen fluoride.
9. A process for producing alkyl derivatives of an isoparaffin which comprises subjecting a molal excess of an isoparaffin in admixture with normal paraffins to treatment with an alkyl fluoride in the presence of hydrogen fluoride.
10. A process for producing alkyl derivatives of branched chain paraffins which comprises subjecting a molal excess of branched chain paraffins in admixture with normal paraffins to treatment with an alkyl fluoride in the presence of hydrogen fluoride at a temperature between about -10 and about $+75^{\circ}\text{C}$. under sufficient pressure to maintain substantially liquid phase conditions.
11. A process for producing a substantially saturated alkylation product which comprises subjecting a mixture of isobutane and normal butane to treatment with an alkyl fluoride in the presence of hydrogen fluoride at a temperature between about -10 and about $+75^{\circ}\text{C}$. under sufficient pressure to maintain substantially liquid phase conditions.
12. A process for producing a substantially saturated alkylation product which comprises subjecting a mixture of isopentane and an alkyl fluoride to contact with hydrogen fluoride at a temperature between about -10 and about $+75^{\circ}\text{C}$. under sufficient pressure to maintain substantially liquid phase conditions.
13. A process for producing isomeric heptanes which comprises subjecting a molal excess of isobutane to treatment with a propyl fluoride in the presence of hydrogen fluoride at a temperature between about -10 and about 75°C . and under sufficient pressure to maintain substantially liquid phase conditions.
14. A process for producing isomeric octanes which comprises subjecting a molal excess of isopentane to treatment with a propyl fluoride in the presence of hydrogen fluoride at a temperature between about -10 and about $+75^{\circ}\text{C}$. and under sufficient pressure to maintain substantially liquid phase conditions.
15. A process for synthesizing hydrocarbons which comprises reacting a branched chain paraffin with an alkyl fluoride in the presence of substantially anhydrous hydrogen fluoride.
16. A process for synthesizing hydrocarbons which comprises reacting a branched chain paraffin with an alkyl fluoride in the presence of a liquid alkylating catalyst consisting essentially of hydrogen fluoride.

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