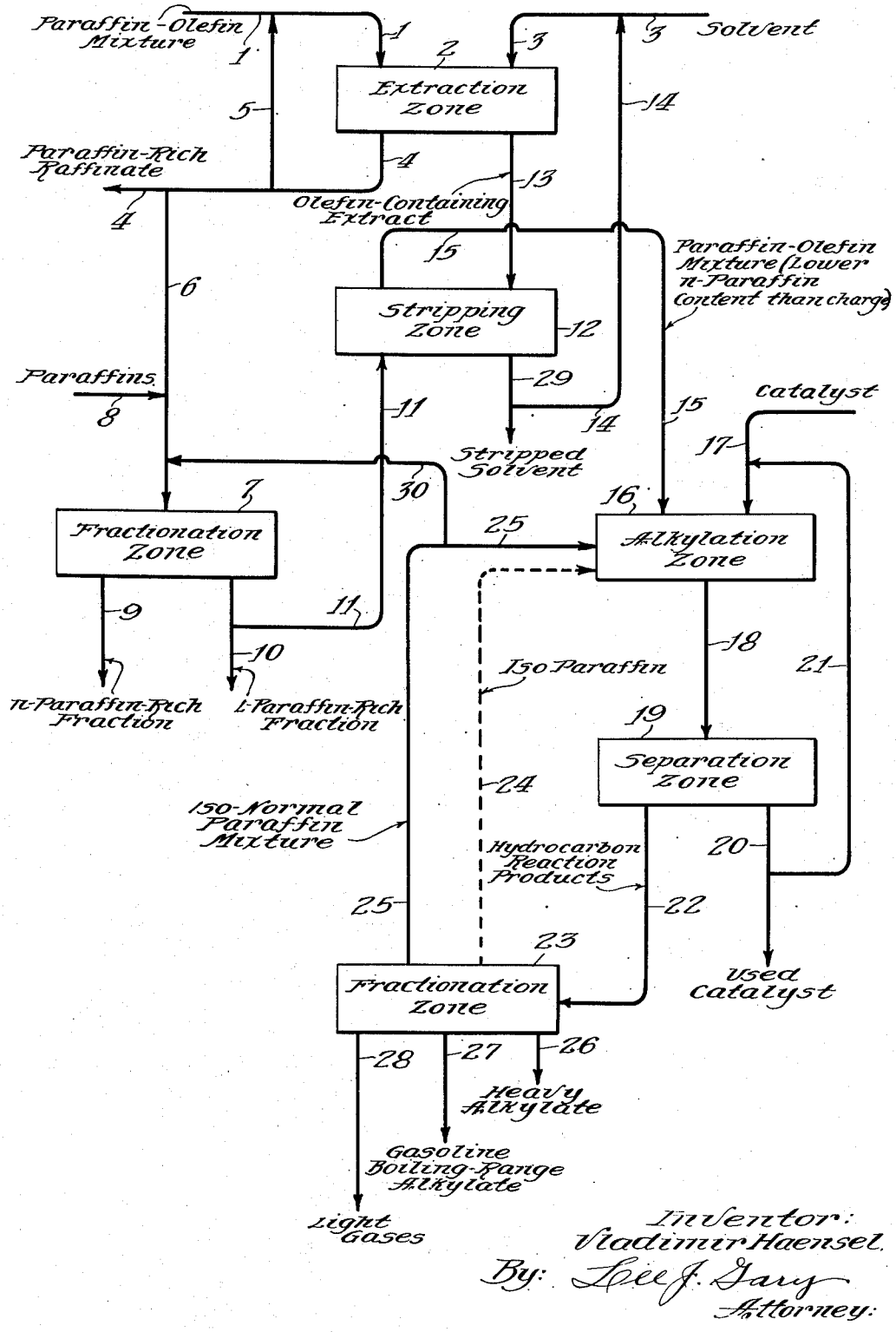
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ALKYLATION OF HYDROCARBONS

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ALKYLATION OF HYDROCARBONS

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This invention relates to the alkylation of isoparaffins with olefins for the production of higher molecular weight isoparaffinic hydrocarbons of gasoline boiling range which have high antiknock ratings and are, therefore, suitable for use as motor fuels.

The invention relates more specifically to a combination of interrelated steps whereby a hydrocarbon mixture comprising essentially paraffins and olefins is treated to alter the relative proportions of isoparaffins, normal paraffins, and olefins thereby producing a hydrocarbon feed of more suitable composition for the subsequent alkylation step.

In one specific embodiment my invention comprises the steps of subjecting an olefin-paraffin mixture to solvent extraction with a solvent having a relatively high selectivity for olefins, separating an olefin-containing extract from a paraffin-rich raffinate, subjecting said paraffin-rich raffinate to fractionation for the separation of normal paraffins from isoparaffins, introducing said olefin-containing extract and an isoparaffin-rich fraction from said fractionation step into a solvent stripping zone wherein the dissolved hydrocarbons are separated from said solvent by the stripping action of said isoparaffin-rich fraction, returning the stripped solvent to the extraction zone, subjecting the effluent hydrocarbon mixture from said stripping zone comprising isoparaffins and olefins, to the action of an alkylating catalyst under alkylating conditions, separating hydrocarbon phase from the alkylation step, subjecting it to fractionation to separate gasoline boiling range hydrocarbons and a fraction comprising essentially iso- and normal butanes, supplying a portion of the last named fraction into the first named fractionation step, and recycling another portion thereof to the alkylation zone.

A hydrocarbon mixture suitable for use in the alkylation of isoparaffins with olefins must normally meet the following requirements:

(1) The ratio of isoparaffins to olefins must be relatively high, e. g., from about 3:1 to as high as 20:1 or, in certain cases, even higher. It is known that the tendency toward undesirable polymerization of the olefins may be lowered and the selectivity of the alkylation reaction may be increased by maintaining this ratio at a high level. Various procedures well known to those skilled in the art have been adopted to aid in maintaining large molar excesses of isoparaffins within the reaction zone, but it is of fundamental importance that the combined hydrocarbon charging stock itself contain a substantial excess of isoparaffins over olefins.

(2) The normal paraffin content should be as low as possible. Normal paraffins introduced into the alkylation zone with the fresh feed tend to pass through the system substantially unchanged under conditions at which isoparaffins alkylate readily. The n-paraffins act as diluents and as such make it necessary to employ considerably larger reaction zones than would be required if they were not present. Furthermore, the presence of large amounts of normal paraffins such as n-butane, in the reaction products creates a difficult fractionation problem since the unconverted isoparaffins to be alkylated are commonly separated from the reaction products and blended with the desired amount of fresh feed to form the combined hydrocarbon charge to the alkylation zone.

(3) The olefin content of the charge should not be below certain known economically feasible levels. Although a high isoparaffin to olefin ratio in the charge is used in order that the alkylation reaction may predominate over polymerization and other competing side reactions, nevertheless it is not usually feasible from a commercial point of view to utilize a combined feed having an abnormally low olefin content. If the olefin content is very low, e. g., of the order of 1 to 3%, the yield per pass of alkylate will also be low and the cost of recycling large amounts of hydrocarbons will be high. Therefore, it is desirable from an economic standpoint to keep the olefin content of the combined feed above some rather arbitrarily defined minimum, e. g., 5 to 10%, or in certain instances even higher. The exact olefin content used in any particular instance will, of course, depend on many factors such as the nature of the charging stock, catalyst, operating conditions, etc.

Ordinary refinery gases such as butane-butylene mixtures or other C_4 fractions are commonly used as sources of fresh hydrocarbon feed to alkylation processes. Such fractions usually have relatively low isoparaffin to olefin ratios, e. g., of the order of 0.5:1 to 2:1, and are commingled with a substantial quantity of isobutane or an isobutane-rich hydrocarbon fraction to produce a combined feed of the desired isoparaffin to olefin ratio. Because of the molal excess of isoparaffin, a major portion thereof remains unalkylated in a single pass through the reaction zone, and is subsequently recovered and commingled with additional quantities of the olefin-containing feed, and then recycled to the alkylation zone.

Thus, it will be seen that a substantial quantity of isoparaffin is recycled within the system for the purpose of maintaining a high isoparaffin to olefin ratio in the combined feed, and is ultimately alkylated.

By the process of my invention a fresh feed is treated in a combination of steps with the net result that the normal paraffin content of the feed is substantially reduced. An important advantage thereby accrues since it will be readily seen that for two fresh feed stocks comprising essentially only C_4 hydrocarbons and having the same olefin content, the stock having the lower normal butane content will also have the higher ratio of isoparaffin to olefin. Thus, in feed stock B, shown below, which contains only 9% normal butane, the isoparaffin to olefin ratio is 2.0 as compared with feed stock A which contains 36% normal butane and has only a 1.1 isoparaffin to olefin ratio.

	Feed stock	
	A	B
Butylenes, mol percent	30	30
n-Butane	36	9
i-Butane	33	60
C_3 hydrocarbons	1	1
	100	100
Isoparaffin/olefin ratio	1.1	2.0

As a result of the higher initial isoparaffin to olefin ratio in the fresh feed, the amount of isoparaffin which must be recycled in order to produce a combined feed of the desired isoparaffin to olefin ratio is markedly decreased. The required equipment size for a given plant capacity is, therefore, decreased both from the viewpoint of reaction zones, pumping capacity, etc., and also from the fractionation standpoint.

A similar reduction in equipment size also results directly from the removal of normal paraffins from the system. As explained above, the normal paraffins apparently act largely as diluents at usual conditions for alkylating isoparaffins and their removal from the fresh feed effectively lowers the reactor size and fractionation requirements.

The reduction in fractionation requirements is of particular importance since separation of isobutane from normal butane is one of the most difficult and costly steps associated with alkylation processes. Moreover, it is impractical to attempt a removal of normal butane from a fresh butane-butylene feed stock by fractionation because the closeness of boiling points of the constituents results in a substantial loss of olefins. The solvent extraction method of the present invention solves this problem and permits the economical rejection of normal paraffins from the system.

The invention becomes of considerable importance in cases where it is necessary to produce aviation fuels from available stocks of diverse character, many of which do not inherently meet the requirements of a satisfactory alkylation feed. The process, for example, has particular merit in cases where it is desirable to alkylate directly the C_4 reaction products from a butane dehydrogenation unit. A hydrocarbon mixture of this type may contain for example, 25% butylenes, 6% isobutane, and 69% normal butane. Another application of my process is in cases where the initial olefin content of the fresh feed is too low for direct use in a commercial alkylation process.

The alkylation of isoparaffins with olefins may be conducted in the presence of a variety of catalysts including phosphoric acid, various active metal halides and hydrogen halides such as aluminum chloride and hydrogen chloride, aluminum bromide and hydrogen bromide, and the like. Of particular commercial importance are the liquid catalysts including certain mineral acids, e. g., concentrated sulfuric acid or hydrogen fluoride. Although the process may be used for the alkylation of normally liquid or normally gaseous hydrocarbons or mixtures thereof, it is particularly adapted for the alkylation of low boiling inoparaffins such as isobutane with normally gaseous olefins such as propylene and the butylenes. The latter hydrocarbons are readily available in substantial quantities from the cracking of petroleum oils and from the natural gasoline industry.

The invention will be more fully understood from the following description read in connection with the accompanying drawing which shows a schematic flow diagram of one manner in which the process may be carried out.

The hydrocarbon fresh feed is introduced through line 1 into extraction zone 2, and a solvent having substantial selectivity for olefins is introduced by means of line 3. The extraction zone may consist of a packed tower wherein the hydrocarbon charging stock is introduced at the bottom and passed upwardly in countercurrent flow to the solvent which is introduced at the top of the tower. Any suitable apparatus may be used for the extraction step, and several stages of extraction may also be used. The solvent may be used as an absorbing or scrubbing liquid for removing olefins from the gaseous hydrocarbon charge, but the extraction may also be carried out under sufficient pressure to maintain substantially liquid phase conditions for both the hydrocarbons and solvent.

Various solvents having marked selectivities for olefinic hydrocarbons may be used, but the preferred solvent is of the type which has a low solubility at ordinary temperatures and pressures but exhibits a considerable solubility at higher pressures, for example, from about 50 to about 200 atmospheres, and at elevated temperatures between about 125 and about 350° C. Among such solvents are water and dilute aqueous solutions of various oxygen- or nitrogen-containing organic compounds which I have found to possess high selectivity for the olefinic constituents of a paraffin-olefin mixture at the preferred conditions. In certain instances I have found it desirable to operate the extraction step above the critical temperature of the hydrocarbon solute since it has been observed that a use of these temperatures leads to considerable solubility without a substantial decrease in selectivity.

A butylene-containing extract is removed through line 13 and passes to stripping zone 12. The residual butane-rich raffinate is withdrawn through line 4, and a portion thereof may be continuously recycled by means of line 5 to the extraction zone. If desired, the unrecycled raffinate may be withdrawn from the system through line 4, but it is preferably introduced by means of line 6 to fractionation zone 7. If desired, a mixture of iso- and normal butanes may be added from an external source through line 8. Separation of the iso- and normal butane is effected in

fractionation zone 7 and the normal butane is rejected from the system through line 9. The isobutane is removed through line 10 and introduced by means of line 11 into stripping zone 12.

Zone 12 may comprise any suitable form of apparatus such as a packed tower, etc., wherein the solution of butylenes in the solvent is subjected to the stripping action of the isobutane stream. It will be apparent that the conditions of temperature and pressure in the stripping zone and of the entering streams of extract and isobutane may be adjusted to obtain an effluent mixture which will have the desired olefin content. The stripped solvent is withdrawn by means of line 29 and is preferably recycled through line 14 to extraction zone 2. The mixture of isobutane and stripped butylenes passes through line 15 and is introduced into alkylation zone 16 for contact with a liquid catalyst.

Alkylation zone 16 may comprise any of the well-known forms of alkylation equipment suitable for obtaining intimate contact between hydrocarbon reactants and a mineral acid catalyst under controlled conditions of temperature, pressure, and time of contact. The catalyst which may comprise, for example, sulfuric acid or hydrogen fluoride of about 90 to about 100% concentration, is introduced into the alkylation zone through line 17. The reaction mixture or emulsion passes through line 18 to separation zone 19 which may conveniently comprise a settling zone. The catalyst layer is removed through line 20 and a substantial portion thereof is recycled through line 21 to the alkylation zone 16. A portion of the used catalyst is continuously withdrawn from the system through line 20. In the case of hydrogen fluoride catalyst, the used hydrogen fluoride withdrawn from the system may be regenerated readily and returned to the system through line 17.

An upper hydrocarbon layer is removed from separation zone 19 through line 22 and introduced into fractionation zone 23. In certain instances, an unconverted isobutane stream may be recovered through line 24 and recycled to the alkylation zone. To obtain the major benefits of my invention, however, the isobutane-normal butane stream containing largely isobutane is removed in fractionation zone 23 and recycled by means of line 25 to the alkylation zone 16, at the same time diverting a portion of this total butane stream through line 30 in the first fractionation zone 7, in order to prevent the buildup of normal butane in the alkylation system. This procedure avoids the difficult and expensive fractionation of n- and iso-butanes in zone 23, thereby cutting down on plant and operating costs.

Light gases may be recovered through line 28, a gasoline boiling range alkylate is removed through line 27, and the higher boiling products of the process may be recovered through line 26.

The following examples will illustrate the nature of the results which can be obtained by the process of my invention, although it is not intended that the invention be unduly limited thereby. Data are presented from five runs using aqueous solutions of various organic compounds as solvents in the extraction of butane-butylene mixtures. Runs 1, 2, and 3 were made with a charging stock having the following molal composition: 17.0% i-C_4H_{10}; 51.8% n-C_4H_{10}; 11.8% n-C_4H_8-1; 9.4% i-C_4H_8; 0.6% C_5 and heavier hydrocarbons. The total olefin content of the charging stock was 30.6%. Runs 4 and 5 were made with a similar hydrocarbon charging stock in which the total olefin content amounted to only 23.7%.

	Run No.				
	1	2	3	4	5
Solvent	90.3% water, 9.7% methyl-ethyl ketone (by vol.).	90% water, 10% ethylene glycol (by vol.).	70% water, 50% acetone (by vol.).	50% water, 50% diethylene triamine (by vol.).	50% water, 50% ethanolamine (by vol.).
Temp., °C	186	183	185	190	204.
Press., atm.	83	73	77	59	68.
Per cent olefins in hydrocarbons dissolved in extract phase	64.7	58.3	51.8	39.9	36.5.
Selectivity ratio [1]	4.15	3.17	2.44	2.20	1.90.

[1] This ratio is defined as the volume ratio of olefins to paraffins in the extract phase divided by the same ratio in the hydrocarbon charge.

From these data it is apparent that, by means of a solvent extraction step, highly olefinic concentrates may be obtained which may readily be blended with isobutane to obtain improved charging stocks for alkylation. In runs 1, 2 and 3 the initial olefin content of 30.6% is increased to 64.7%, 58.3% and 51.8% olefins respectively. In runs 4 and 5, the initial olefin concentration of 23.7% is increased to 39.9% and 36.5% respectively. The relative effectiveness of the several solvents employed is also reflected in the value of the selectivity ratio in each case.

The paraffin-rich raffinate in each case is fractionated to separate isobutane which is then used as a stripping medium to strip or desorb the hydrocarbons from the solvent. Operating conditions in the stripping zone may be varied over a substantial range, but in general the pressure is preferably lower than the pressure in the extraction zone. However, both extraction and stripping zones may be operated at approximately the same conditions of temperature and pressure if desired.

The effluent hydrocarbon mixture from the stripping zone in each case has a substantially lower normal butane content than the feed. This mixture is charged to a sulfuric acid or hydrogen fluoride alkylation process which may be operated at a temperature of 25 to 50° C. in the case of sulfuric acid and at about 10 to 100° C. in the case of hydrogen fluoride catalysts. In either case, the pressure is preferably maintained high enough to insure substantially liquid phase operation. An isoparaffin to olefin ratio of from about 4:1 to about 20:1 is maintained in the alkylation zone by recycling a substantial quantity of isobutane within the system. Under these conditions, a yield of 300° F. end-point alkylate of the order of about 180 to 250 weight per cent based on the olefins charged may be obtained. This product is highly isoparaffinic and has an A. S. T. M. octane number of 93 to 95. During fractionation of the reaction products, a total unconverted butane mixture is separated and is recycled in part to the alkylation step. A side

stream is continuously separated from this recycle stream and is subjected to fractionation in the raffinate fractionator, as shown is the drawing, in order to prevent a build-up of normal butane within the alkylation system.

I claim as my invention:

1. A method for preparing a mixture rich in isoparaffins and olefins from a hydrocarbon fraction containing the same and normal paraffins which comprises extracting olefins from the fraction with an aqueous solvent having a relatively high selectivity for olefins, fractionating the resultant paraffinic raffinate into a normal paraffin part and an isoparaffin part, stripping the olefin extract of its olefins by contacting the same with at least a portion of the isoparaffin part and recovering the resultant isoparaffin-olefin mixture.

2. A method for preparing a mixture rich in isoparaffins and olefins from a hydrocarbon fraction containing the same and normal paraffins which comprises subjecting the fraction to the action of an aqueous solvent having a relatively high selectivity for olefins at a temperature above the critical temperature of said olefins to form an olefin extract, fractionating the resultant paraffinic raffinate into a normal paraffin part and an isoparaffin part, stripping the olefin extract of its olefins by contacting the same with at least a portion of the isoparaffin part and recovering the resultant isoparaffin-olefin mixture.

3. The process of claim 1 further characterized in that the solvent comprises an aqueous solution of an organic solvent.

4. The process of claim 1 further characterized in that the solvent comprises an aqueous solution of methyl ethyl ketone.

5. A process which comprises subjecting a hydrocarbon fraction containing normal and isoparaffins and olefins to the action of an aqueous solvent having a relatively high selectivity for the olefins to form an olefin extract, fractionating the resultant paraffin raffinate into a normal paraffin part and an isoparaffin part, stripping the olefin extract of its olefins by contacting the same with at least a portion of said isoparaffin part, subjecting the resultant isoparaffin-olefin mixture to alkylation and reacting the isoparaffins with the olefins, separating unconverted paraffins from the resultant reaction products and supplying at least a portion of said unconverted paraffins to the fractionating step.

6. A process which comprises subjecting a C_4 fraction containing butanes and butenes to the action of an aqueous solvent having a relatively high selectivity for the butenes to form a butene extract, fractionating the resultant butane raffinate into a normal butane fraction and an isobutane fraction, stripping the butene extract of its butenes by contacting the same with at least a portion of the isobutane fraction, subjecting the resultant isobutane-butene mixture to akylation to react the isobutane and butenes, separating unconverted butanes from the resultant reaction products and supplying at least a portion of the unconverted butanes to the fractionating step.

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