June 13, 1944. A. VOORHIES, JR., ET AL 2,351,464

ALKYLATION OF ISOPARAFFINS

Filed July 12, 1941 2 Sheets-Sheet 1

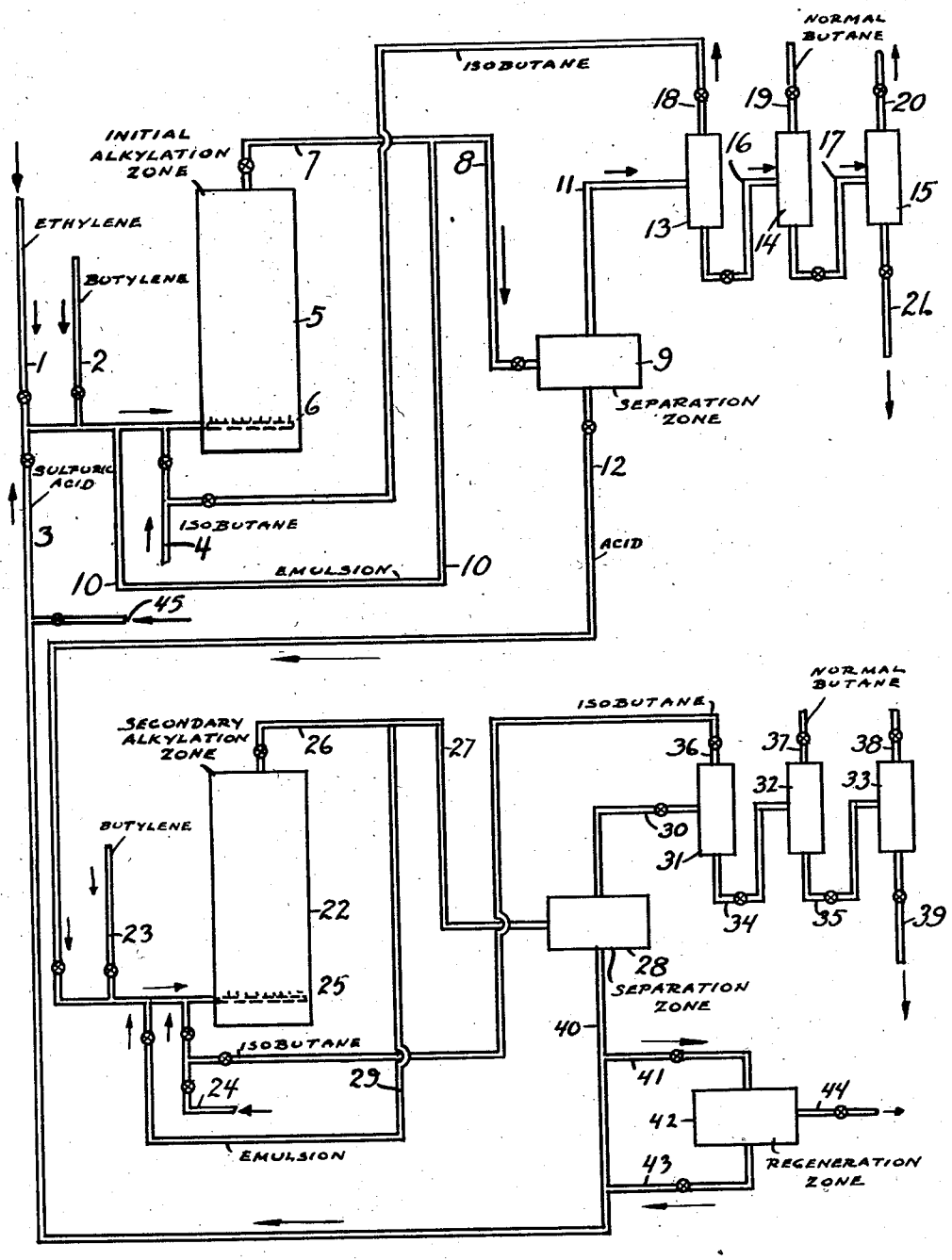


FIG.-1

Alexis Voorhies Jr.
Erwin M. Hatton Inventors

By P. K. Young Attorney

June 13, 1944. A. VOORHIES, JR., ET AL 2,351,464

ALKYLATION OF ISOPARAFFINS

Filed July 12, 1941 2 Sheets-Sheet 2

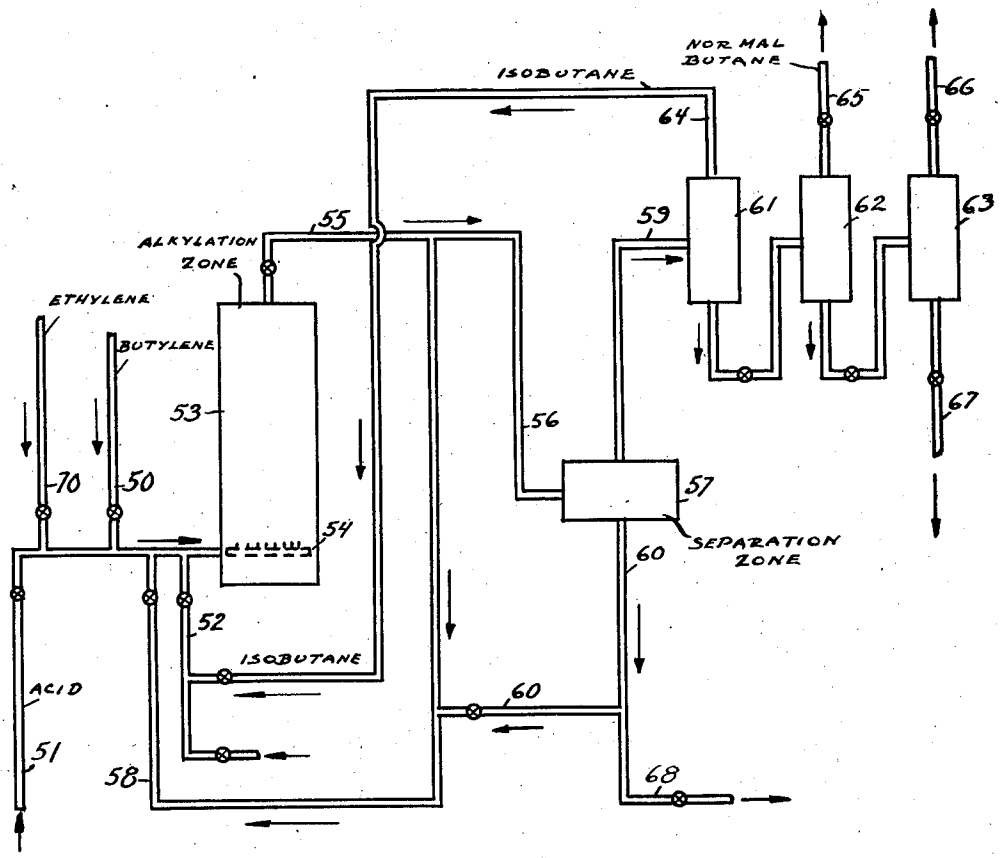


FIG. — 2

Alexis Voorhies Jr.
Ewen M. Hattox Inventors

By P. K. Young Attorney

Patented June 13, 1944 2,351,464

UNITED STATES PATENT OFFICE

2,351,464

ALKYLATION OF ISOPARAFFINS

Alexis Voorhies, Jr., and Erwin M. Hattox, Baton Rouge, La., assignors to Standard Oil Development Company, a corporation of Delaware

Application July 12, 1941, Serial No. 402,184

4 Claims. (Cl. 260—683.4)

The present invention is concerned with refining of mineral oils and is particularly concerned with the production of hydrocarbon constituents boiling in the motor fuel and the aviation fuel boiling ranges from relatively low boiling hydrocarbon constituents. In accordance with the present process, relatively low boiling olefins, particularly ethylene, are alkylated with isoparaffinic constituents employing a mineral acid catalyst. In accordance with the present invention the alkylation is carried out under conditions in which the alkylating catalyst intermittently contacts a feed stock comprising ethylene under alkylating conditions.

It is well known in the art to react relatively low boiling olefins such as olefins containing from 2 to 5 carbon atoms in the molecule with saturated hydrocarbons containing a tertiary carbon atom hereinafter referred to as tertiary hydrocarbons. These reactions are generally conducted by employing a feed stock containing olefins and saturated hydrocarbons containing tertiary carbon atoms and contacting the same under suitable conditions with a so-called alkylating catalyst. In general, the operation is conducted under conditions in which the mol ratio of the tertiary hydrocarbons to the olefins is relatively high. Temperature and pressure conditions vary considerably. For example, the alkylating temperature may range from about —20° F. or lower, to temperatures as high as 400° F. or higher. However, in general the alkylating temperatures are in the range from about 20° F. to about 70° F. Although a number of substances may be employed as alkylating catalysts such as aluminum chloride and the like, the preferred materials comprise mineral acids, particularly sulfuric acids, having a concentration in the range from about 88% to 100%.

Although these reactions have been entirely satisfactory in operations involving the reaction of olefins containing 3 and more carbon atoms in the molecule, they have not been satisfactory for the alkylation of ethylene due to excessive acid consumption. Heretofore it has been found that in a reaction involving the alkylation of ethylene the titratable acidity of the acid was materially lowered indicating an appreciable acid consumption. We have, however, now discovered that, provided an intermittent treatment be employed with respect to the ethylene and acid, unexpected desirable results are secured. For example, we have discovered that if the acid be employed for alkylation of olefins comprising ethylene in an initial stage and the acid segregated from the initial stage, it may be then readily employed for the alkylation of olefins free of ethylene in a secondary stage without incurring any substantial acid consumption as measured by titratable acidity. As a matter of fact, when operating in this manner the acid is apparently regenerated and the adverse effects of the ethylene removed in the secondary stage. The process of our invention may be readily understood by reference to the attached drawings illustrating embodiments of the same.

Figure 1 illustrates the modification of our invention wherein the olefin feed to the initial zone comprises ethylene and the olefin feed to the secondary zone is free of ethylene. The alkylating catalyst comprising sulfuric acid is passed serially through the respective zones. Figure 2 illustrates an adaptation of our process wherein ethylene is injected intermittently into the olefin feed mixture passing to the alkylation zone. Referring specifically to Figure 1 it is assumed that the alkylation catalyst comprises concentrated sulfuric acid and that it is desired to alkylate ethylene for the production of hydrocarbon constituents boiling within the motor fuel boiling range. The ethylene is introduced into the system by means of feed line 1, the butylene by means of line 2, and sulfuric acid by means of line 3. The tertiary hydrocarbon comprising isobutane is introduced into the acid solution of olefins by means of line 4. The entire mixture is then passed into initial alkylation zone 5 by means of jets 6 or equivalent means. Temperature and pressure conditions as well as time of contact in the initial alkylation zone 5 are adapted to secure the maximum yield of the desired product. The reaction mixture of acid emulsion

is removed from alkylation zone 5 by means of line 7. A portion of the acid emulsion is segregated from the main emulsion stream by means of line 8 and passed into separation zone 9. The main emulsion stream is recycled to alkylation zone 5 by means of line 10 through jets 6.

The portion of the emulsion stream passed to separation zone 9 separates into a hydrocarbon layer which is removed by means of line 11 and into an acid layer which is removed by means of line 12. The hydrocarbon layer is passed successively into distillation zones 13, 14, and 15 by means of lines 16 and 17. Temperature and pressure conditions are adjusted in zone 13 to remove overhead by means of line 18 isobutane which is preferably recycled to initial alkylation zone. Temperature and pressure conditions in zone 14 are adjusted to remove overhead by means of line 19 any normal butane constituents present in the feed, which may be disposed of as desired. The total alkylate product passed to distillation zone 15 is fractionated to segregate a desired aviation product which is removed overhead by means of line 20 and a heavy alkylate product which is removed by means of line 21 and handled as desired.

In accordance with our invention the acid separated in zone 9 is passed to secondary alkylation zone 22 along with additional butene which is introduced by means of line 23 and isobutane which is introduced by means of line 24. Satisfactory mixing of the respective streams is secured by passing the mixture through jets or equivalent means 25. Temperatures, as well as the time of contact are adjusted to secure the maximum yield of the desired product. The acid emulsion is removed from alkylation zone 22 by means of line 26 and a small portion segregated by means of line 27 and passed to separation zone 28. The remainder of the emulsion is recycled to the secondary alkylation zone by means of line 29. In zone 28 a separation occurs between the hydrocarbon product and the acid. The hydrocarbon product is removed by means of line 30 and handled in a manner similar to that described with respect to the hydrocarbon product removed from zone 9. This hydrocarbon product is passed serially through distillation zones 31, 32, and 33 by means of lines 34 and 35. Temperature and pressure conditions in zone 31 are adjusted to remove isobutane overhead by means of line 36. This isobutane is preferably recycled to secondary alkylation zone 22. Temperature and pressure conditions in distillation zone 32 are adjusted to remove normal butane overhead by means of line 37. The total alkylate product is fractionated in zone 33 to remove overhead by means of line 38, the desired aviation fraction, and to remove by means of line 39 the heavy alkylate which may be disposed of in any manner desired.

In accordance with our invention, the acid layer removed from zone 28 by means of line 40 is recycled to initial alkylation zone 5. Under certain conditions a portion of this acid may be withdrawn from the system by means of line 41, regenerated in regeneration zone 42 and returned to the system by means of line 43. Totally spent acid may be withdrawn from the system by means of line 44, while fresh acid is introduced by means of line 45.

Referring specifically to Figure 2, an olefin stream comprising butylene and higher olefins is introduced into the system by means of line 50, while the acid is introduced by means of line 51, and the stream comprising isobutane by means of line 52. This mixture is introduced into alkylation zone 53 by means of jets 54 or equivalent means. Conditions in zone 53 are adjusted to secure the desired degree of alkylation. The acid emulsion is removed by means of line 55 and a small portion segregated by means of line 56 and passed to separation zone 57. The remainder of the acid emulsion is recycled to the initial alkylation zone by means of line 58. The emulsion passed to zone 57 separates into a hydrocarbon fraction which is removed by means of line 59 and into an acid layer which is removed by means of line 60. The hydrocarbon layer is passed serially through distillation zones 61, 62, 63 and handled in a manner similar to that described above. Isobutane is removed from zone 61 by means of line 64 and preferably recycled to zone 53. Normal butane is removed from zone 62 by means of line 65 and handled as desired. The desired alkylate is removed from zone 63 by means of line 66 while the heavy alkylate is removed by means of line 67. Spent acid may be withdrawn from the system by means of line 68 while fresh acid is introduced by means of line 51.

In accordance with our invention, ethylene is intermittently introduced into the system by means of line 70. For operating in this manner over a portion of the cycle the feed to the alkylation zone comprises ethylene while over the remainder of the cycle the feed to the alkylation zone is free of ethylene.

It is to be understood that the process of the present invention may be widely varied. The respective zones may comprise any suitable number and arrangement of units. The invention essentially comprises alternately contacting the alkylated catalyst with a feed stream comprising ethylene and then contacting the catalyst with a feed stream free of ethylene. For operating in this manner, excessive catalyst degradation is prevented and a substantial yield of alkylated ethylene secured. When operating on the portion of the cycle in which ethylene is present, it is to be understood that the respective streams may comprise streams segregated from refining operations and which contain various constituents containing approximately the same number of carbon atoms in the molecules. When operating on the portion of the cycle in which the feed stream is substantially completely free of ethylene it is preferred that the stream comprising essentially hydrocarbon constituents contain 4 or more carbon atoms in the molecule.

Any conventional alkylating conditions may be used in the present invention. The invention, however, is particularly adapted to operations in which the alkylating catalyst comprises a mineral acid catalyst such as sulfuric acid, fluorosulfonic acid or the like. It is particularly suitable in operations wherein the catalyst comprises a sulfuric acid having a concentration in the range from about 88 to about 100%.

In order to further illustrate our invention, the following examples are given which should not be construed as limiting the same in any manner whatsoever:

Example 1

A number of alkylation operations were conducted in which in the initial stage the feed com-

prised ethylene and in which in the secondary stage the feed was free of ethylene. The results of these operations were as follows:

	Operation 1		Operation 2	
	Stage 1	Stage 2	Stage 1	Stage 2
Catalyst	98% H_2SO_4	Acid from stage 1.	97% H_2SO_4	Acid from stage 1.
Feed	Ethylene, Butylene, Isobutane	Butylene, Isobutane	Ethylene, Butylene, Isobutane	Butylene. Isobutane.
Mol ratio: isobutane/olefin	5.8	5.6	5.5	6.4
Mol ratio: C_2H_4/C_4H_8	2.2	0	2.0	0
Total reaction time, minutes	120	120	120	120
Temperature, °F.	70	70	70	18
Product (C_5+):				
Wt. percent yield on C_4H_8	216	188	249	170
Vol. percent C_5 [1] (50–105 °F.)	1.6	5.1	4.5	4.7
Vol. percent C_6 (105–165 °F.)	21.9	6.2	23.2	5.9
Vol. percent C_7 (165–180 °F.)	1.2	1.3	1.2	1.2
Vol. percent C_8 (180–265 °F.)	68.3	80.7	65.7	80.0
Vol. percent C_9+(>265° F.)	7.0	6.7	5.4	8.2
Octane No. (A. S. T. M.) C_5–C_8	97.6	93.9	94.7	94.3
Used acid titratable acidity, percent	91.7	92.3	91.6	93.8

[1] Denotes hydrocarbon constituents containing approximately the number of carbon atoms in the molecule.

From the above it is apparent that an appreciable alkylation of the ethylene was secured in stage 1 of the respective operations. This is evident from the substantial increase in yield of C_8 constituents in stage 1 as compared to stage 2 of the respective operations. Furthermore, it is apparent that by operating as described in the present process unexpected desirable results were secured. For example, the acid passed serially through the respective stages was of a better quality as it was removed from stage 2 than stage 1.

Example 2

A number of operations were conducted wherein in one operation ethylene and butylene were added simultaneously while in the other operation carried out in accordance with the present invention, butylene was added subsequent to the addition of ethylene and butylene. The results of these operations are as follows:

	Butylene added subsequent to the addition of ethylene and butylene	Ethylene and butylene added simultaneously
Catalyst	98% H_2SO_4	98% H_2SO_4
Feed	Isobutane	Isobutane.
Mol ratio: Isobutane/olefin	6.0	6.8
Mol ratio: C_2H_4/C_4H_8	1.4	1.4
Total reaction time, minutes	180	120
Time of feed addition, do	150	90
Temperature, °F.	70	70
Product (C_5+):		
Wt. percent yield on C_4H_8	216	235
Vol. percent C_5 (50–105 °F.)	5.1	3.3
Vol. percent C_6 (105–165 °F.)	16.0	15.6
Vol. percent C_7 (165–180 °F.)	1.1	2.2
Vol. percent C_8 (180–265° F.)	71.3	74.4
Vol. percent C_9+(>265° F.)	6.5	4.5
A. S. T. M.-octane No. C_5–C_8	95.1	95.0
Used acid, titratable acidity	96.5	93.7

From the above it is apparent that unexpected improvements are to be secured with respect to acid conusmption by operating as described.

What we claim is new and wish to protect by Letters Patent is:

1. Improved alkylation process which comprises intermittently contacting under alkylating conditions an acid of the class consisting of sulfuric acid and fluorosulfonic acid with a feed stream comprising ethylene and isoparaffins, and a feed stream comprising olefins and isoparaffins free of ethylene.

2. Process as defined by claim 1 in which the acid comprises an 88 to 100% concentrated sulphuric acid.

3. Improved alkylation process which comprises contacting an acid of the class consisting of sulfuric acid and fluorosulfonic acid, isoparaffins, and olefins comprising ethylene in an initial alkylation zone under alkylating conditions, segregating a portion of the emulsion removed from said initial alkylation zone and separating the acid therefrom, contacting said separated acid with isoparaffins and olefins free of ethylene in a secondary alkylation zone under alkylating conditions, segregating a portion of the emulsion removed from said secondary alkylation zone and separating the acid therefrom, recycling said separated acid to said initial alkylation zone.

4. Process as defined by claim 3 in which the acid comprises an 88% to 100% sulphuric acid.

ALEXIS VOORHIES, JR.
ERWIN M. HATTOX.