

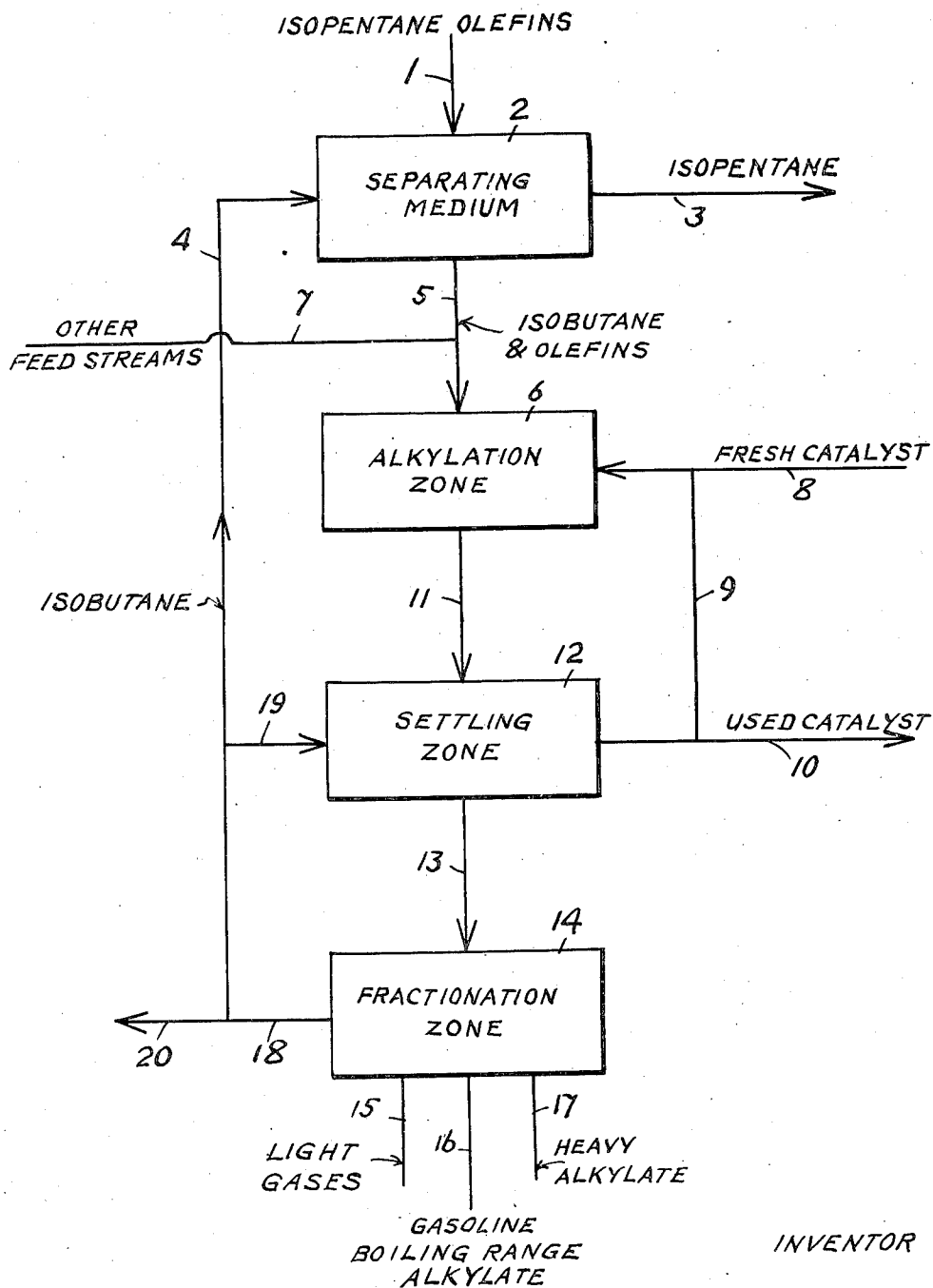
Aug. 30, 1949.

J. I. HARPER

2,480,240

ALKYLATION OF ISOPARAFFINS

Filed Nov. 20, 1945.



WITNESS:

Robt. H. Mitchell

INVENTOR

James I. Harper

BY
Bussor and Harding
ATTORNEYS.

UNITED STATES PATENT OFFICE

2,480,240

ALKYLATION OF ISOPARAFFINS

James I. Harper, Media, Pa., assignor to Sun Oil Company, Philadelphia, Pa., a corporation of New Jersey

Application November 20, 1945, Serial No. 629,800

5 Claims. (Cl. 260—683.4)

1

This invention relates to alkylation of isoparaaffins with olefins for the production of motor fuels having a high octane rating. More particularly the invention relates to the preparation of motor fuels or gasoline of high anti-knock rating from certain feed stocks involving inter-related treating steps adapted to modify such feed stocks to render these more suitable for the alkylation operation.

In the prior art alkylation processes the reaction has been for the most part between isobutane and butylenes. In some instances, in order to make available additional olefins, the C₃ fraction has been employed with the C₄ fractions. Whenever the hydrocarbon fraction selected for alkylation has contained C₅ hydrocarbons these have been passed into the alkylation operation without any pretreatment of the nature described herein-after. Isopentane which is a rather good motor fuel constituent and which frequently is present in a feed stock comprising C₅ hydrocarbons would thus be passed along with the remainder of the charge to the alkylation operation.

It has now been found that the selective removal of isopentane from the hydrocarbon feed, prior to alkylation, materially increases the octane value of the motor fuel or gasoline produced. Apparently, in the prior art practice, the isopentane, under alkylating conditions, reacted with the olefins present to form relatively poor anti-knock hydrocarbon compounds.

Accordingly, the invention comprises an alkylation operation wherein isopentane contained in the alkylation feed is substantially removed selectively under non-alkylating conditions prior to the alkylation step.

In a modification the invention comprises an alkylation operation wherein isobutane is alkylated with an olefin, a C₅ hydrocarbon fraction containing isopentane and amylenes is treated to provide a fraction rich in isopentane and a fraction rich in amylenes and the portion rich in amylenes free from the portion rich in isopentane is passed to the alkylation step.

In another modification the invention comprises an alkylation operation wherein isobutane is alkylated with amylenes, a C₅ hydrocarbon fraction containing isopentane and amylenes is passed into a medium to separate therefrom under non-alkylating conditions a portion rich in amylenes and a portion rich in isopentane and to retain the portion rich in amylenes in said medium while the portion rich in isopentane is not retained, passing isobutane in excess of that which can be alkylated with the retained amyl-

2

enes through said medium to recover the amylenes therefrom substantially free of isopentane, passing the isobutane containing the recovered amylenes to an alkylation zone, alkylating the isobutane with the amylenes in said zone, discharging alkylated products from said zone, separating isobutane from said products and returning said separated isobutane to said medium.

In a further modification the invention comprises an alkylation operation wherein isobutane is alkylated with an olefin, a C₅ hydrocarbon fraction containing isopentane and amylenes is passed into a medium to separate under non-alkylating conditions a portion rich in amylenes and a portion rich in isopentane and to retain the portion rich in amylenes in said medium while the portion rich in isopentane is not retained, passing isobutane in excess with an olefin to an alkylation zone, alkylating a portion of the isobutane with the olefin in said zone, discharging alkylated products from said zone, separating isobutane from said products, passing said separated isobutane through said medium to recover amylenes therefrom substantially free of isopentane and returning the isobutane containing the recovered amylenes to said alkylation zone.

Other modifications and advantages are apparent from this specification and the appended claims.

The treatment of the feed stock to effect separation of the isopentane therefrom may be accomplished in various ways. In one method of effecting the separation the medium can consist of silica gel. For example, a C₅ hydrocarbon fraction containing isopentane and amylenes is passed into contact with a bed of silica gel, properly activated, to adsorb a portion rich in amylenes while a portion rich in isopentane is not retained. Isobutane can then be passed through the silica gel to recover or desorb the adsorbed amylenes, thereby forming a composite feed stock which can be fed to an alkylation zone.

In order to preserve the amylenes unaltered until these are subjected to alkylating conditions in presence of the isobutane it is essential according to the invention to recover the amylenes under non-alkylating conditions, that is, the separation of isopentane from amylenes is effected under non-reacting conditions. The separation is so effected that the amylenes are recovered through use of a separating medium and under conditions such that no substantial chemical reaction will take place which can cause any combination between molecules of the amylenes or between molecules of the amylenes and mole-

3

cules of the stream with which the amylenees are recovered. Thus, the separation of the isopentane from the amylenees can also be accomplished through solvent extraction, employing, for example, liquid sulfur dioxide, by azeotropic distillation, employing, for example, methyl alcohol, or by any other suitable means including extractive distillation, selective absorption, etc.

The conditions employed in the separation steps of the process will depend upon the separating media employed. These are readily determinable within the skill of the art as will appear hereinafter.

The conditions in the alkylation step are preferably those now known to the art.

To more clearly set forth the invention reference is made to the drawing schematically showing a flow diagram of an embodiment thereof wherein a catalytic alkylation zone is employed.

In the figure, a feed stock, comprising isopentane and amylenees, is introduced through line 1 into separating medium or zone 2 wherein the isopentane is selectively separated from the amylenees. Zone 2 is preferably a tower or vessel containing activated silica gel. The hydrocarbon stream, in liquid phase, is percolated through zone 2 until the effluent therefrom through line 3 shows no substantial difference in composition when compared with that of the feed stock fed thereto. This is an indication that the silica gel has adsorbed its capacity of amylenees and that the feed stock is now passing through substantially unchanged. At this stage the flow of the feed stock stream is discontinued. Isobutane from the alkylation reaction, to be described hereinafter, is now fed in through zone 2, by means of line 4. The isobutane stream, in liquid phase, is likewise percolated through the bed or body of silica gel. This results in substantial desorption of the adsorbed amylenees. Thus, the effluent isobutane from zone 2 will contain a substantial proportion of desorbed amylenees. This operation will be continued until the effluent contains only a negligible portion of amylenees, indicating that the silica gel has been substantially freed or stripped of its amylene content. The operation is preferably effected at ordinary temperatures encountered in plant practice, although other temperatures may be employed in certain instances. The exact times of flow of the hydrocarbon stream and of the isobutane, or desorbing stream, into the silica gel bed are determined by the concentrations of isopentane and amylenees in the respectively resulting effluents. Obviously it is impractical to continue the adsorption of amylenees until the effluent will have exactly the same isopentane concentration as the feed stream. It is also obvious that the desorption step will not be advantageously continued until all of the amylenees have been desorbed. It is sufficient to state that one skilled in the art will readily determine when the flow of the hydrocarbon stream and the flow of the isobutane stream, respectively, shall be discontinued. In order to provide for continuous operation, there are provided at least two silica gel beds or zones. While one zone is used to supply an isobutane-amylene feed to the alkylation zone, the other is employed to adsorb amylenees and vice versa, thereby providing a continuous flow of feed stock, from which isopentane has been selectively removed, to the alkylation zone.

Specifically and by way of illustration of a typical amylene separation, through 10,000 lbs. of silica gel located in a suitable filter bed, there

4

is percolated 445 gallons of a pentane-amylene stream having the composition:

	Gallons
Amylenes -----	143
Isopentane -----	225
n-Pentane -----	77
	445

The pentane-amylene stream is followed by 1285 gallons of isobutane. The first 563 gallons of percolate is segregated and distilled to remove 236 gallons of isobutane, which is recycled leaving a substantially saturated pentane stream having the compositions:

	Gallons
Isopentane -----	211
n-Pentane -----	73
Amylenes -----	43

The remaining percolate, 1166 gallons, is fed to the alkylation zone and has the composition:

	Gallons
Isobutane -----	1,049
Amylenes -----	100
Isopentane -----	13
n-Pentane -----	4

As stated, several zones may be employed for the separation step or the cycle may be repeated employing the same zone or silica gel bed.

The isobutane-amylene stream is passed through line 5, with other feed streams entering the operation through line 7, into alkylation zone 6. Fresh catalyst is fed through line 8 into the alkylation zone. The conditions maintained in this zone are known in the art and can be those indicated in the table. The catalyst can be hydrofluoric acid, sulfuric acid, or any other catalyst suited to the alkylation step. The reaction in zone 6 is effected with the reactants in liquid phase following which the reacted mass is passed through line 11 to a settling zone 12, wherein the acid and hydrocarbon products settle into two layers. The acid is returned through line 9 for re-use. A portion preferably removed, through line 10, is treated and then returned to the process for re-use or is discarded as desired. It is obvious that in place of a liquid catalyst, a solid alkylation catalyst can be employed.

The hydrocarbon layer from settling zone 12 is passed into a fractionating zone wherein it is separated into desired products and unreacted isobutane which is recycled. As shown in the drawing, the hydrocarbons are passed through line 13 into fractionation zone 14. From this zone isobutane is recovered and recycled to separating zone 2 and thus continually re-used in the process. Any overall excess isobutane can be removed through line 20. Light gases, gasoline boiling range alkylate and heavier alkylate products are removed through lines 15, 16 and 17, respectively.

It will be obvious to those skilled in the art that the benefits which are derived through practice of the invention upon a feed stream containing isopentane and amylenees can be derived to an extent by treating only a portion of such feed stock. Thus, the invention is practiced where isopentane is present in the alkylation zone and isopentane has been selectively removed from a portion of all of the feed stock to the operation, said feed stock comprising isopentane and amylenees. Obviously it is preferred to substantially completely remove all of the isopentane as far as this is practically possible.

5

In the table, run 1 shows results obtained with a conventional butylene alkylation feed stock in which propylene, isopentane and amylenes were present in incidental amounts only. In run 2, an isopentane and amylenes containing stream was added with the result that the octane number of the product was severely reduced. In run 3 only isopentane, and no amylenes, was added with a loss of octane number even greater than that obtained in run 2 where both isopentane and amylenes were added. A study of these data clearly show that isopentane is responsible for the loss in octane number when a C₅ fraction, containing both isopentane and amylenes, is added to an alkylation feed stock.

Feed composition (basis—100 gallons of butylenes)

	Run 1	Run 2	Run 3
Non-reactants (Propane, N-Butane, N-Pentane).....	85.5	99.0	89.4
Propylene.....	3.0	3.1	3.9
Isobutane.....	106.0	105.0	112.0
Butylenes.....	100.0	100.0	100.0
Isopentane.....	2.7	81.0	52.5
Amylenes.....	0.9	51.5	2.9
<i>Product Quality</i>			
F-2 Octane Number.....	91.9	91.1	90.5
F-3 Octane Number with 4 cc. T. E. L./U. S. Gal.....	107.8	105.6	105.1

Operating conditions.—Substantially constant at the following values:

Ratio isobutane to olefins.....	5.5:1
Reaction temperature.....°F.....	100
Pressure.....P. s. i. g.....	250
Space time.....minutes.....	21.5
Titrate acidity.....per cent.....	86.2
Acid: Hydrocarbon ratio.....	50:50

The foregoing description sets forth the invention in sufficient detail to allow one skilled in the art to practice it. It should be understood, however, that the description has been made for disclosure purposes only, reasonably wide variations in its procedure and application are possible.

I claim:

1. In an alkylation operation wherein isobutane is alkylated with an olefin, the steps of treating under non-alkylation conditions a C₅ hydrocarbon fraction containing isopentane and amylenes to provide a portion rich in amylenes and a portion rich in isopentane and passing the portion rich in amylenes free from the portion rich in isopentane to the alkylation operation.

2. In an alkylation operation wherein isobutane is alkylated with amylenes the steps of passing a C₅ hydrocarbon fraction containing isopentane and amylenes into a medium to selectively separate under non-alkylating conditions a portion rich in amylenes and a portion rich in isopentane and to retain the portion rich in amylenes in said medium while the portion rich in isopentane is not retained; passing isobutane in excess of that which can be alkylated with the retained amylenes through said medium to recover the amylenes therefrom substantially free of isopentane; passing the isobutane containing the recovered amylenes to an alkylation zone, alkylating the isobutane with the amylenes in said zone; discharging alkylated products from said zone; separating isobutane from said products;

6

and returning said separated isobutane to said medium.

3. In an alkylation operation wherein isobutane is alkylated with an olefin the steps of passing a C₅ hydrocarbon fraction containing isopentane and amylenes into a medium to selectively separate under non-alkylating conditions a portion rich in amylenes and a portion rich in isopentane and to retain the portion rich in amylenes in said medium while the portion rich in isopentane is not retained; passing isobutane in excess with an olefin to an alkylation zone; alkylating a portion of the isobutane with the olefin in said zone; discharging alkylated products from said zone; separating isobutane from said products; passing said separated isobutane through said medium to recover amylenes therefrom substantially free of isopentane; and returning the isobutane containing the recovered amylenes to said alkylation zone.

4. In an alkylation operation wherein isobutane is alkylated with an olefin the steps of passing a C₅ hydrocarbon fraction containing isopentane and amylenes into contact with an adsorbent to selectively adsorb a portion rich in amylenes from said fraction and to form a portion rich in isopentane which is not retained; passing isobutane in excess with an olefin to an alkylation zone; alkylating a portion of the isobutane with the olefin in said zone; discharging alkylated products from said zone; separating isobutane from said products; passing said separated isobutane into contact with said silica gel to desorb the amylenes therefrom; and returning the isobutane containing the desorbed amylenes to said alkylation zone.

5. In an alkylation operation wherein isobutane is alkylated with an olefin the steps of passing a C₅ hydrocarbon fraction containing isopentane and amylenes into contact with silica gel to selectively adsorb a portion rich in amylenes from said fraction and to form a portion rich in isopentane which is not retained; passing isobutane in excess with an olefin to an alkylation zone; alkylating a portion of the isobutane with the olefin in said zone; discharging alkylated products from said zone; separating isobutane from said products; passing said separated isobutane into contact with said silica gel to desorb the amylenes therefrom; and returning the isobutane containing the desorbed amylenes to said alkylation zone.

JAMES I. HARPER.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
2,306,253	McMillan	Dec. 22, 1942
2,374,819	Kanhofer et al.	May 1, 1945
2,374,996	Herthel	May 1, 1945
2,375,867	Newman	May 15, 1945
2,384,311	Kearby	Sept. 4, 1945
2,385,133	Gwin	Sept. 18, 1945
2,391,160	Hillman et al.	Dec. 18, 1945
2,398,101	Lipkin	Apr. 9, 1946
2,399,240	McAllister et al.	Apr. 30, 1946