March 23, 1965 J. W. MYERS 3,175,017

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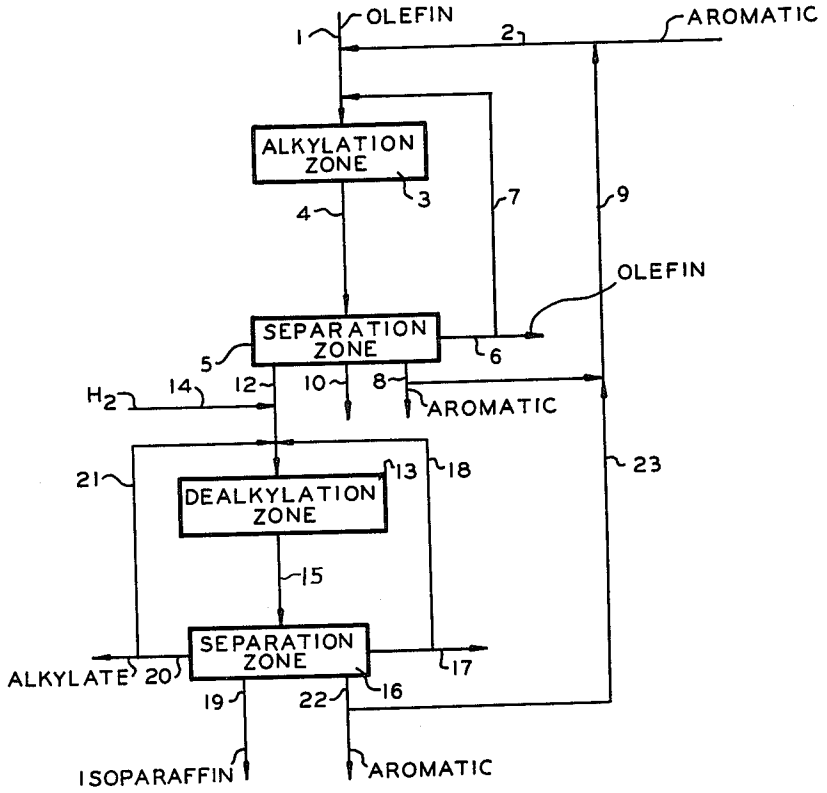
Filed Sept. 25, 1961



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United States Patent Office 3,175,017 Patented Mar. 23, 1965

3,175,017

CONVERSION OF NORMAL OLEFINS TO ISOPARAFFINS

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Filed Sept. 25, 1961, Ser. No. 140,523
9 Claims. (Cl. 260—672)

This invention relates to the alkylation and dealkylation of aromatic hydrocarbons. In one aspect this invention relates to the alkylation of an aromatic hydrocarbon with a C_5 or higher normal olefin to produce a secondary alkyl aromatic. In another aspect, this invention relates to the catalytic hydrodealkylation of secondary alkyl aromatic compounds to produce a paraffin from the alkyl group which is a branched chain hydrocarbon.

Paraffinic compounds which are branched chain or isoparaffinic in structure are very valuable as high octane gasoline blending components. In addition isopentane is useful for the manufacture of isoprene. I have now found that the desirable isoparaffin can be prepared by alkylation of aromatics with the normal olefins followed by subsequent catalytic hydrodealkylation.

Thus in accordance with this invention, there is provided a method for the utilization of C_5 or higher normal olefins, generally C_5 to C_{12} olefins, to produce the desired secondary alkyl aromatic compounds, and in addition, to achieve the conversion of the normal olefinic compounds to isoparaffinic compounds upon dealkylation of the alkylated aromatic compounds.

Thus, it is an object of this invention to provide a method for the conversion of normal olefin compounds to branched chain paraffins. Another object of this invention is to provide a two-step process for the formation of isoparaffins from C_5 and higher normal olefins.

Other aspects, objects and the several advantages of this invention are apparent from a study of the disclosure, the drawing and the appended claims.

The sole figure is a diagrammatic view of this invention.

Referring to the drawing, olefin is introduced to the process through the line 1 and is supplied, together with an aromatic compound introduced to the process through line 2, into alkylation zone 3. Zone 3 may be of any suitable design in which the alkylation catalyst is disposed and which the aromatic and olefinic compounds are satisfactorily contacted therewith. The alkylation of the aromatic with the olefinic compound may be effected by means of a well known catalyst such as phosphoric acid, sulfuric acid, zinc chloride, aluminum chloride, silica-alumina, hydrogen fluoride, etc., under suitable conditions of temperature, pressure and reaction time.

The alkylation products, which will include unconverted aromatic, mono-alkylated aromatic and di-alkylated aromatic compounds and in some cases unconverted olefin are directed through line 4 into separation zone 5. Zone 5 may comprise one or a plurality of suitable fractionating, distilling, absorbing and/or stripping means whereby the products introduced thereto may be separated into the desired fractions. Unconverted olefin may be withdrawn from zone 5 through line 6 and may be removed from the process, but preferably at least a portion thereof is recycled by way of lines 7 and 1 to zone 3 for further conversion therein. Similarly, unconverted aromatic compound may be withdrawn from zone 5 through line 8 and may be removed from the process, but preferably at least a portion thereof is recycled by way of lines 9, 2 and 1 to zone 3 for further conversion therein. If desired, a portion of the alkylated aromatic compound may be removed through conduit 10 for subsequent use thereof.

The alkylated aromatic compound is withdrawn from zone 5 through line 12 and is supplied to the dealkylation zone 13. Hydrogen from an extraneous source may be introduced to the process through line 14 and supplied by way of line 12 into zone 13. Zone 13 may be of any suitable design in which the catalyst is disposed and in which the reactants are satisfactorily contacted therewith.

The reaction products from zone 13 are directed through line 15 into separation zone 16 which may be the same or different than separation zone 5, but will be suitable to separate a hydrogen containing fraction, an aromatic containing fraction, and any remaining unconverted alkylated compound. The hydrogen containing fraction may be withdrawn from zone 16 through line 17 and may be removed from the process, but preferably at least a portion thereof is recycled by way of lines 18 and 12 to zone 13. When desired, the hydrogen fraction may be subjected to purification or other treatment in order to concentrate the hydrogen prior to recycling. An isoparaffin containing fraction is withdrawn from zone 16 through line 19 and is recovered as one of the desired products of the process. This fraction may, when desired, be subjected to any further fractionation or other treatment in order to separate the isoparaffin constituents thereof from the other constituents, if any. Unconverted alkylate may be withdrawn from zone 16 through line 20 and may be removed from the process, but preferably at least a portion thereof is recycled by way of lines 21 and 12 to zone 13 for further conversion therein. Likewise, this fraction may, when desired, be subjected to fractionation or other treatment in order to separate the unconverted alkylate from other constituents, if any, prior to recycling.

Under conditions of operation, recycle dealkylated aromatic compound is present in the dealkylation products and this aromatic compound can be separated in zone 16 and withdrawn therefrom through line 22 and removed from the process, but preferably at least a portion thereof is recycled by way of lines 23, 9, 2 and 1 to zone 3 for conversion therein.

The normal olefin stream or concentrates to be utilized in this invention can be produced in numerous ways. For example, a C_5 fraction recovered from a cracking operation and containing both olefins and paraffins can be extracted using about 65 weight percent sulfuric acid with the tertiary olefin subsequently recovered from the acid extract. The raffinate phase is thus relatively enriched in normal C_5 olefins, and can be used as a source of such olefins in the process of the present invention. However, the source of the normal olefins is not critical and the above is given for purposes of example only.

The normal C_5 and/or higher olefin is then used to alkylate an aromatic compound such as benzene to form a secondary alkyl aromatic. Numerous catalysts are known which will effect this process, e.g., aluminum chloride-hydrocarbon complex, hydrofluoric acid, boron trifluoride complexes, silica-alumina, etc. The reaction conditions for the various catalysts are different but are known to one skilled in the art. The secondary alkyl aromatic is then recovered for use in the hydrodealkylation step.

The hydrodealkylation step is carried out at a temperature in the range of about 450° F.–1,000° F, preferably about 500° F.–900° F., depending somewhat on the activity of the catalyst. Numerous catalysts are known for hydrodealkylation, including supported platinum, supported cobalt molybdate, etc. Suitable supports for the catalyst are alumina, boria-alumina, silica-alumina, silica-titania, halogenated alumina, and others, the acidic supports being generally preferred. Reaction pressure is ordinarily at least 100 p.s.i.g preferably in the range of about 200 to 2,000 p.s.i.g. Hydrogen is added in the ratio of

about 2:1 to 20:1, preferably in the range of about 3:1 to 10:1 moles per mole of alkyl aromatic. The hydrocarbon charge rate is ordinarily from about 0.1 to 10 LSHV, preferably 0.2 to 5 LSHV.

The secondary amyl- and higher secondary alkyl aromatics hydrodealkylate with the production of a high yield of branched chain paraffins of the same number of carbon atoms as the secondary alkyl substitutent group. Such a result is unpredictable since the secondary butyl groups produce the expected normal-butane.

The following example is provided for the purposes of further illustrating the present invention.

Example I

Mixed secondary-amylbenzenes (2- and 3-phenylpentane were hydrodealkylated over cobalt molybdate-on-boria-alumina at 600° F.–650° F., 800 p.s.i.g., 1 LHSV and 5 to 6 moles of hydrogen for each mole of hydrocarbon. The product compositions for two tests are given below:

Run Number	1	2
Temperature, ° F	596	645
Products, Weight percent:		
Propane	0.7	0.4
Isobutane	1.8	0.9
n-Butane	0.8	0.6
Isopentane	21.4	19.6
n-Pentane	1 2	2.9
Cyclopentane	0.	0.3
2-Methylpentane	0.0	0.3
Benzene	73.4	25.2
Residue		8.4
Coke	0.2	1.4
Total	100.0	100.0

It is evident from the above data that the isopentene was produced in a considerably larger proportion than the thermodynamic equilibrium proportion.

Example II

In a similar test with secondary butyl benzene, the butane in the effluent was substantially normal butane. The composition of the gaseous product from the test is given below:

Products, mol percent:	
Methane	2.8
Isobutane	4.1
n-Butane	93.1
	100.0

Example III

A mixture of 2-pentene and benzene in the mole ratio or 1:5 is contacted continuously with a hydrofluoric acid catalyst in a stirred reactor at 100° F. for a contact time of 20 minutes. The reactor emulsion is about 40 volume percent HF and 60 volume percent hydrocarbon. The reactor effluent is separated by gravity settling, the catalyst phase being returned to the reactor. The separated hydrocarbon phase is washed with water and aqueous caustic, dried and charged to a fractionating column. A mixture of 2- and 3-phenylpentane is recovered, and represents 80 per cent of the theoretical yield based on the 2-pentene charged. This mixture is then hydrodealkylated over cobalt molybdate-on-boria-alumna at 600–650° F., 800 p.s.i.g., 1| LHSV and 5 to 6 moles of hydrogen for each mole of hydrocarbon. The resulting product contains about 21.4 percent isopentane on the mixture.

The above examples show that compounds having less than 5 carbons in the alkyl portion of the alkylate are not suitable for purposes of this invention. Thus while secondary-amyl benzene is 19.6 to 21.4% converted to the iso-form, the corresponding amount of secondary butyl benzene produces only 4.1% isobutane when operating under otherwise the same conditions.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, drawing and the appended claims to the invention, the essence of which is that there has been provided a method for the conversion of C_5 and higher normal olefins to branched chain paraffins by a two-step process in which an aromatic hydrocarbon is alkylated with a normal olefin to produce a secondary alkyl aromatic and the secondary alkyl aromatic is catalytically hydrodealkylated with the production of a paraffin from the alkyl group having a branched chain structure.

I claim:

1. A process for the conversion of C_5 and higher normal olefins to branched chain paraffins which comprises alkylating an aromatic compound with a normal olefin so as to produce a secondary alkyl aromatic, and subsequently catalytically hydrodealkylating the resulting secondary alkyl aromatic compound and thereby producing a branched chain hydrocarbon from the dealkylated portion of the secondary alkyl aromatic compound.

2. The process of claim 1 wherein the hydrodealkylating step comprises contacting said hydrocarbon with a hydrodealkylating catalyst at a temperature of from about 450° F.–1,000° F., a pressure of from 100 to 2,000 p.s.i.g. and a liquid hourly space velocity of about 0.1 to about 5.

3. The process as defined in claim 2 wherein the hydrocarbon is contacted with the catalyst in the presence of hydrogen in the amount of from 2:1 to 20:1 moles per mole of alkyl aromatic compound.

4. A process for producing isoparaffins from a normal hydrocarbon having an alkyl group of at least 5 carbon atoms thereon which comprises alkylating an aromatic compound with an olefinic hydrocarbon containing at least 5 carbons in the presence of an alkylating catalyst, contacting the resulting alkylated aromatic compound with a hydrodealkylating catalyst and subsequently recovering the desired isoparaffinic compound.

5. The process of claim 4 wherein the hydrodealkylation step is carried out at a temperature in the range of from about 500° F.–900° F.

6. The process of claim 4 wherein hydrogen is added in the ratio of about 3:1 to about 10:1 moles per mole of alkyl aromatic compound.

7. The process of claim 1| wherein the dealkylation step comprises contacting a secondary amyl benzene with cobalt-molybdate-on-boria-alumnia at a temperature of about 600° F. to 650° F. and a pressure of about 800 p.s.i.g.

8. A process for the dealkylation of secondary alkyl aromatic hydrocarbons and simultaneous conversion of the alkyl portion thereof to an isoparaffin which comprises contacting a secondary alkyl aromatic hydrocarbon wherein the alkyl group contains at least 5 carbon atoms with a cobalt-molybdate-on-boria-alumnia catalyst in the presence of 5 to 6 moles of hydrogen for each mole of hydrocarbon at a temperature of about 600–650° F. and a pressure of about 800 p.s.i.g. and subsequently recovering the resulting isoparaffin therefrom.

9. The process of claim 8 wherein the secondary alkyl aromatic hydrocarbon is mixed secondary-amyl benzenes.

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