# United States Patent [19]

**Louder**

[11] **3,726,942**

[45] **Apr. 10, 1973**

[54] **PRODUCTION OF GASOLINE COMPONENTS INCLUDING 2-METHYL-2-METHOXYPROPANE**

[75] Inventor: **Kenneth E. Louder**, Wilmington, Del.

[73] Assignee: **Sun Oil Company of Pennsylvania**, Philadelphia, Pa.

[22] Filed: **Nov. 22, 1971**

[21] Appl. No.: **200,725**

[52] **U.S. Cl.**..............................................**260/683.61**
[51] **Int. Cl.**..................................................**C07c 3/54**
[58] **Field of Search**......................260/683.61, 683.3, 260/683.59, 683.58, 683.49, 614

[56] **References Cited**

UNITED STATES PATENTS

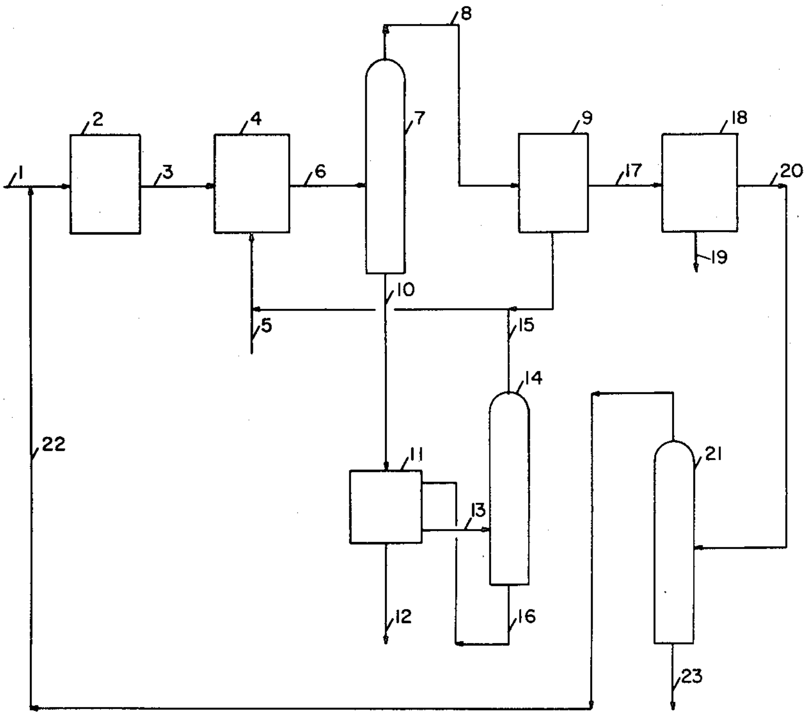
| | | | |
|---|---|---|---|
| 2,312,539 | 3/1943 | Frey | 260/683.61 |
| 2,366,716 | 1/1945 | Frey | 260/683.61 |
| 2,389,984 | 11/1945 | Jones | 260/683.61 |
| 3,660,520 | 5/1972 | Hemminger | 260/683.61 |

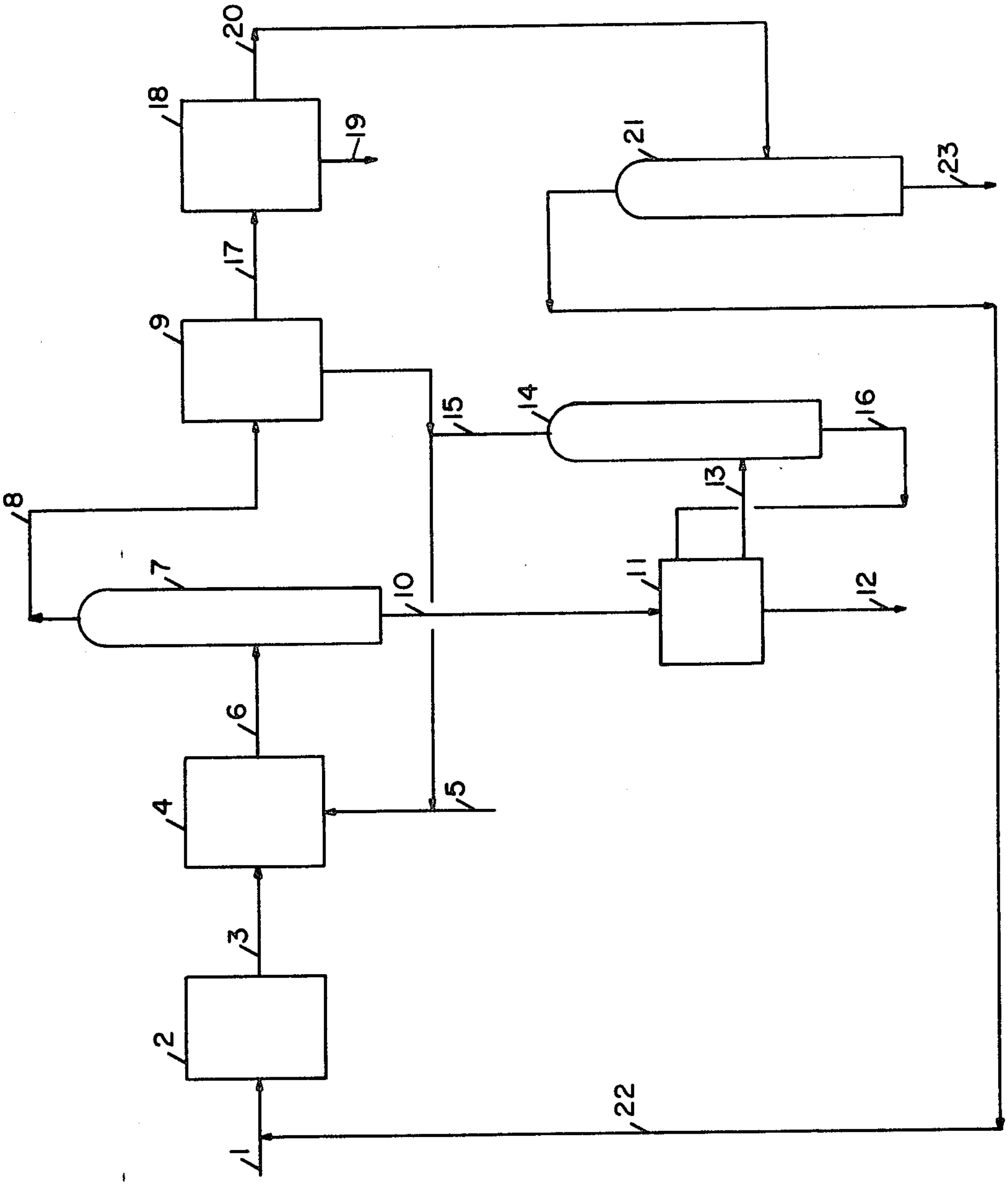
*Primary Examiner*—Delbert E. Gantz
*Assistant Examiner*—G. J. Crasanakis
*Attorney*—George L. Church et al.

[57] **ABSTRACT**

Process of producing 2-methyl-2-methoxypropane and alkylate from a stream of mixed $C_4$'s wherein said stream is fed to a dehydrogenation unit, the dehydrogenation unit effluent is fed to an etherification unit along with methanol which selectively reacts with the isobutene present to form 2-methyl-2-methoxypropane. The unreacted $C_4$'s are sent to an alkylation unit where the olefins present react with isobutane to form alkylate. The unreacted products of the process possess a higher overall octane rating than the alkylate which is normally produced.

**6 Claims, 1 Drawing Figure**




1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23

# PRODUCTION OF GASOLINE COMPONENTS INCLUDING 2-METHYL-2-METHOXYPROPANE

## BACKGROUND OF THE INVENTION

In the past refiners have used available streams of the four carbon atom hydrocarbons to produce trimethylpentanes as a high octane gasoline component by means of one of the known alkylation reactions. It has also been known that various branched chain ethers have high octane numbers but the expense involved in producing these ethers has prevented their widespread use.

## SUMMARY OF THE INVENTION

The present invention involves the preparation of 2-methyl-2-methoxypropane and isococtane from a stream of mixed n-butane, isobutane, n-butene and isobutene (mixed $C_4$'s). In accordance with the present invention isobutane typically in a stream of mixed butanes containing about 80 percent isobutane, about 15 percent n-butane and 5 percent butenes is fed along with a recycle stream of isobutane to a dehydrogenation unit operated at a low conversion per pass to improve selectivity in producing isobutene. The isobutene is then selectively reacted from the mixed stream of $C_4$'s to form ether by means of the etherification reaction. The reaction effluent is then subjected to a separation to provide a stream consisting essentially of n-butane, n-butene and isobutane. This stream of mixed $C_4$'s is then used as the feed for a sulfuric acid alkylation step. The removal of the isobutene is an advantage because it tends to produce relatively low octane alkylate apparently because some dimethylhexanes are produced instead of just the desired trimethylpentanes in the alkylation step. The isobutanes which do not react in the alkylation step are recycled through the dehydrogenation unit.

## DESCRIPTION OF THE DRAWING

The FIGURE is an overall flowsheet of the process of the present invention.

A stream **1** of mixed butanes which typically contains about 80 percent isobutane, 15 percent n-butane and 5 percent other hydrocarbons is fed to dehydrogenation unit **2**. The mixed stream of butanes and butenes are removed from the dehydrogenation unit **2** as stream **3** and fed to etherification unit **4**. Additionally, if available, any available stream of $C_4$'s containing the requisite amount of isobutene may also be fed to etherification unit **4**. Methanol is also fed to etherification unit **4** as stream **5**. The etherification unit selectively reacts the isobutene present with the methanol to produce 2-methyl-2-methoxypropane which is removed as stream **6** and fed to distillation column **7**. The $C_4$'s are removed from distillation column **7** as stream **8** and fed to methanol remover **9**. 2-Methyl-2-methoxypropane is removed from distillation column **7** as stream **10** and washed with water in washer **11** to remove methanol. The washed 2-methyl-2-methoxypropane is removed from water washer **11** as stream **12**. The water and methanol are fed as stream **13** from washer **11** to distillation column **14**. Methanol is removed from column **14** as stream **15** and recycled to etherification unit **4**. Water is removed from column **14** as stream **16** and recycled to washer **11**. The mixed $C_4$'s from methanol remover **9** are fed as stream **17** to alkylation unit **18**. Alkylate which is principally trimethylpentanes is removed from alkylation unit **18** as stream **19**. The unreacted $C_4$'s are removed from alkylation unit **18** as stream **20**. Stream **20** consists essentially of n-butane and isobutane and is fed to deisobutanizer **21**. The isobutane separated by deisobutanizer **21** is recycled to dehydrogenation unit **2** as stream **22**. The n-butane separated by deisobutanizer **21** is removed as stream **23**.

## DESCRIPTION OF THE INVENTION

The starting material may be either the $C_4$'s available from distillation of crude petroleum or this straight run distillate blended with $C_4$'s obtained from a cracking unit. Generally such a stream will contain from 10 to 30 percent n-butane, from 50 to 80 percent isobutane, from 0 to 20 percent n-butene and from 0 to 10 percent isobutene. The starting material is combined with the isobutane being recycled from the alkylation unit. Generally this stream of recycle isobutane will be from 200 to 300 percent of the original starting material. The combined streams are fed to the dehydrogenation unit which is operated at a low conversion of from 5 to 15 percent so as to provide a selectivity of greater than 93 percent. As used herein percent conversion is the percent of isobutane reacted and selectivity is the amount of isobutene produced over the amount of isobutane reacted. This dehydrogenation may readily be performed by a variety of techniques. For instance the dehydrogenation agent can be carbonyl sulfide in which case the reaction is carried out in the vapor phase in the substantial absence of molecular oxygen using a molar ratio of isobutane to carbonyl sulfide of from 1 to 10, a residence time of 0.1 to 5 minutes, preferably 0.4 to 3 minutes, a temperature of 537° to 570° C., and 5 to 50 p.s.i. absolute. The process may also be carried out using nickel sulfide on alumina. If desired an inert gas diluent such as nitrogen, hydrogen or methane may be used up to an amount equal to 25 moles of diluent per mole of isobutane in the feed.

After dehydrogenation the $C_4$'s are separated from other reactants if required, and fed to the etherification unit. The etherification catalysts used herein are relatively high molecular weight carbonaceous materials containing at least one $-SO_3H$ group as the functional group. These catalysts are exemplified by the sulfonated coals ("Zeo-Karb H," "Nalcite X" and "Nalcite AX") produced by the treatment of bituminous coals with sulfuric acid and commercially marketed as zeolitic water softeners or base exchangers. These materials are usually available in a neutralized form and in this case must be activated to the hydrogen form by treatment with a strong mineral acid such as hydrochloric acid and water washed to remove sodium and chloride ions prior to use. The sulfonated resin type catalysts are preferred for use in the present invention. These catalysts include the reaction products of phenol-formaldehyde resins and sulfuric acid ("Amberlite IR-1," "Amberlite IR-100" and "Nalcite MX"). Also useful are the sulfonated resinous polymers of coumarone-indene with cyclopentadiene, sulfonated polymers of coumarone-indene with furfural, sulfonated polymers of coumarone-indene with cyclopentadiene and furfural and sulfonated polymers of cyclopentadiene with furfural. The most preferred cationic exchange resins are strongly acidic exchange resins consisting essentially of sulfonated polystyrene resin, for instance, a divinylbenzene cross-linked polystyrene matrix having from 0.5 to 20 percent and preferably from 4 to 16 percent of copolymerized divinylbenzene therein to which are ionizable or functional nuclear sulfonic acid groups. These resins are manufactured and sold commercially under various trade names such as "Dowex **50**," "Nalcite HCR" and "Amberlyst **15**." As commercially obtained they have solvent contents of about 50 percent and can be used as is or the solvent can be removed first. The resin particle size is not particularly critical and therefore is chosen in accordanace with the manipulative advantages associated with any particular size. Generally a mesh size such as 10 to 50 mesh (United States Sieve Series) is preferred. The reaction may be carried out in either a stirred slurry reactor or in a fixed bed continuous flow reactor. The catalyst concentration in a bath process should be sufficient to provide the desired catalytic effect. Generally catalyst concentration should be 0.5 to 50 percent (dry basis) by weight of the reactor contents with from 1 to 25 percent being the preferred range.

In a continuous reactor, which is preferred, the catalyst concentration may be defined by volumetric hourly space velocity; that is, the volume of isobutene processed per volume of catalyst per hour. The volumetric hourly space rate can be about 0.1 to 100 based on isobutene, generally is from 0.5 to 25 and preferably is from 0.5 to 10.

The 2-methyl-2-methoxypropane is formed by reacting the isobutene in the mixture of $C_4$'s with methanol. A mole ratio of methanol to isobutene of from 1 to 10 is generally used with from 1 to 5 being preferred. Generally the etherification is carried out at from 60° to 300° F. and preferably at 120° to 200° F. Below these temperatures the reaction becomes slow while above these temperatures by-products begin to appear. Pressure is selected to ensure that the charges and products remain as liquids during the reaction, typical pressures are 30 to 300 p.s.i.g.

The etherification reaction selectively removes the isobutene from the stream of mixed $C_4$'s. This is a distinct advantage when the $C_4$'s are being used in sulfuric acid alkylation because the alkylation product of isobutene and isobutane provides an alkylate having a Research octane of only 92.7 whereas the alkylation product of isobutane and 1-butene and 2-butene have Research octanes of 96.8 and 96.2 respectively.(1) The inclusion of the isobutene apparently leads to the formation of an increased amount of dimethylhexanes rather than the preferred trimethylpentanes. Since the isobutene is being converted into 2-methyl-2-methoxypropane which has an octane number above 110 it is readily apparent that a substantial improvement in the octane number of the material produced from the original stream of $C_4$'s is obtained through the use of the present invention over the conventional alkylation of the entire stream of $C_4$'s.

The effluent from the etherification step is distilled to separate the unreacted $C_4$'s (n-butane, isobutane and n-butene) from the 2-methyl-2-methoxypropane and methanol. This separation may be done by distillation. Such distillation generally leaves 0.4 volume percent methanol in with the $C_4$'s which are to be alkylated. It is desirable to reduce the amount of methanol still further to below say 10 p.p.m. to reduce its dilution effect on the sulfuric acid used in the alkylation step. This is advantageously done by a water wash. An alternative is to use molecular sieves. The unreacted $C_4$'s now containing only about 8 to 50 percent and preferably 8 to 25 percent of the original isobutenes are sent to the alkylation unit.

The alkylation step is carried out by charging the stream of n-butane, isobutane, n-butene and unreacted isobutene to an alkylation unit with a total hydrocarbon contact time of from 20 to 30 minutes. The reactor contains sulfuric acid generally in a concentration of from 88 to 95 percent. The sulfuric acid is continuously withdrawn from the reactor and new sulfuric acid of 98 to 99.5 percent concentration is charged to the reactor to maintain the desired acid strength. The alkylation product is continuously removed from the reactor by separating the hydrocarbon and acid layers in a settling zone and sending the hydrocarbon layer to distillation zone where the unreacted $C_4$'s are removed overhead. The reactor is maintained at from 0° to 80° F. and preferably from 20° to 60° F. The contents of the reactor are agitated to maintain the reactants in contact with the sulfuric acid. The unreacted $C_4$'s from the alkylation unit are principally n-butane and isobutane. These are separated in a deisobutanizer which preferably is about a 70 tray tower operated at about 130 p.s.i.g. and about 170° F. The isobutane from the deisobutanizer is recycled with the original feed through the dehydrogenation unit. In a less preferred aspect of the invention the alkylation step can be performed by other means such as hydrofluoric acid alkylation.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

A refinery stream containing 15 mole percent n-butane, 80 mole percent isobutane, 2 mole percent isobutylene and 3 mole percent n-butenes is fed at a rate of 5,790 lbs./hour (stream **1** in the Figure) and is combined with a recycle stream (**22**) fed at a rate of 15,248 lbs./hour (263 mole percent of stream **1**) containing 15 mole percent n-butane, 245 mole percent isobutane, 1 mole percent isobutene and 2 mole percent n-butenes, and fed to a dehydrogenation unit. As used throughout this example the mole percentages of each stream are based on 100 mole percent in the original stream 1 and not 100 mole percent in the particular stream being described. The dehydrogenation unit (**2**) is maintained at 550° C. Carbonyl sulfide is charged to the dehydrogenation unit at a mole ratio of 5:1 isobutane:carbonyl sulfide. The dehydrogenation unit is operated at atmospheric pressure and the residence time of the isobutane therein is 2.5 minutes to provide a conversion of 11.8 percent. After removal of non-$C_4$'s the effluent (**3**) from the dehydrogenation unit contains 20,928 lbs./hour of 25 mole percent n-butane, 275 mole percent isobutane, 53 mole percent isobu-

---

1. Reported when using 99 percent feed acid, 10° C., 300 rpm, a residence time of 5 minutes and an isobutane to olefin ratio of 15:1, by K. W. Li, R. E. Echert and L. F. Albright, "Industrial and Engineering Chemistry," Process Des. Develop., Vol. 9, No. 3, 1970.

tene and 10 mole percent n-butenes which is fed to the etherification unit (**4**). Methanol (37 mole percent, 1,184 lbs./hour stream **5**) is fed to etherification unit (**4**) along with recycled methanol to maintain the mole ratio of methanol to isobutene in excess of one in the etherification unit. The etherification unit contains 3,000 pounds of "Amberlyst 15," **a** 16 to 40 mesh sulfonated cross-linked polystyrene resin with 4.9 meq./g. available hydrogen ion. The etherification unit is maintained at 60° C., the WHSV based on isobutene is one and the conversion of isobutene to 2-methyl-2-methoxypropane is 70 percent. The product 2-methyl-2 - methoxypropane is removed as a stream containing 37 mole percent (3,256 lbs./hour) of 2-methyl-2-methoxypropane and 2 mole percent (116 lbs./hour) of isobutane. The remaining $C_4$'s are separated from methanol by distillation to provide a stream of 18,740 lbs./hour containing 25 mole percent n-butane, 273 mole percent isobutane, 16 mole percent isobutene and 10 mole percent n-butenes, which is fed to the alkylation unit. The alkylation unit is maintained at 40° F., 14 p.s.i.g. and a 93 percent sulfuric acid concentration. Also fed to alkylation unit is an olefin rich stream of $C_4$'s from a catalytic cracking unit which stream consists of 870 lbs./hour (13 mole percent) n-butane, 3,016 lbs./hour (52 mole percent) isobutane, 1,120 lbs./hour (20 mole percent) isobutene, and 1,960 lbs./hour (35 mole percent) n-butenes. The effluent from the alkylation unit contains 2,320 lbs./hour (940 mole percent) n-butane, 14,442 lbs./hour isobutane, 712 lbs./hour isobutylene and 168 lbs./hour n-butenes and 8,664 lbs./hour alkylate which effluent is fed to a deisobutanizer which separates the alkylation as a bottoms, stream containing 1,450 lbs./hour n-butane, 232 lbs./hour isobutane, 56 lbs./hour isobutylene and 56 lbs./hour n-butenes.

The invention claimed is:

**1**. A process for producing gasoline components including 2-methyl-2 methoxypropane comprising combining a feed stream consisting essentially of four carbon atom hydrocarbons and containing from 10 to 30 percent n-butane, from 50 to 80 percent isobutane, from 0 to 10 percent isobutene and from 0 to 20 percent n-butenes with a recycle stream containing from 5 to 40 percent n-butane, from 50 to 90 percent isobutane, from 0 to 10 percent isobutene and from 0 to 10 percent n-butenes to form a combined stream, feeding said combined stream to a dehydrogenation unit to dehydrogenate from 5 to 15 percent of the isobutane in the combined stream to form isobutene, feeding the resulting stream from said dehydrgenation unit to an etherification unit to convert greater than 50 percent of the isobutene present to 2-methyl-2-methoxypropane, separating at least 90 percent of the unreacted four carbon atom hydrocarbons and feeding said hydrocarbons to an alkylation unit to form an alkylate containing trimethylpentanes and recycling the unreacted isobutane from said alkylation unit as said recycle stream.

**2**. The process of claim **1** wherein the etherification unit contains a sulfonated resin as an etherification catalyst.

**3**. The process of claim **2** wherein at least 75 percent of the isobutene present in the feed to the etherification unit is reacted with methanol to form 2-methyl-2-methoxypropane.

**4**. The process of claim **3** wherein the mole ratio of methanol:isobutene in contact with the etherification catalyst is from 1:1 to 10:1.

**5**. The process of claim **4** wherein the recycle stream is from 200 to 300 volume percent of the original feed stream.

**6**. The process of claim **5** wherein the alkylation unit is operated at from 0° to 80° F. and contains from 88 to 99 percent sulfuric acid.

* * * * *