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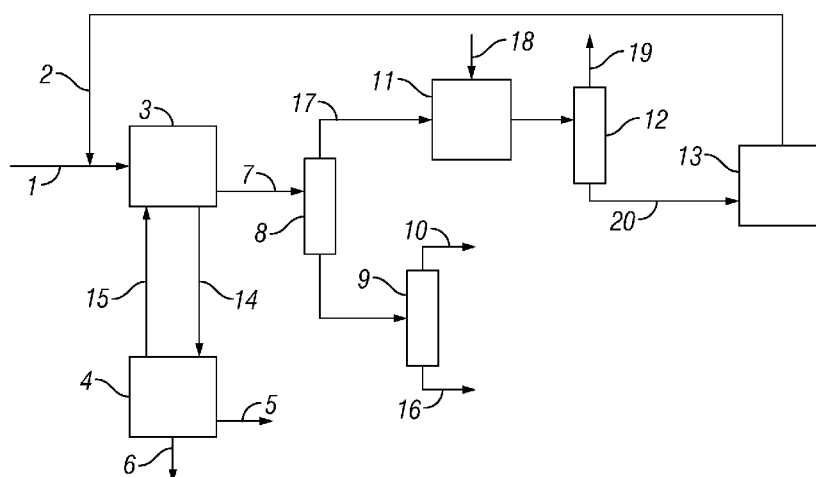
(54) **Title:** THE PRODUCTION OF 1-HEXENE FROM BUTADIENE RAFFINATE-1

FIG. 1

(57) **Abstract:** A process for producing 1-hexene and isobutylene high purity from raffinate-1 which comprises: (a) introducing raffinate-1 and a C₅₋₆ olefin recycle stream into an MTBE reactor and reacting the isobutylene in the raffinate-1 with methanol to produce MTBE, raffinate-2 and recycled C₅₋₆ olefins, (b) converting the MTBE to produce high purity isobutylene, (c) separating the recycled C₆ olefins from the recycled C₅ olefins and raffinate-2, (d) producing 1-hexene by separating it from other C₆ olefins, (e) introducing raffinate-2 and the recycled C₅ olefins to a hydroformylation reactor and reacting them with CO and H₂ to produce C₅₋₆ alcohols, and (f) dehydrating the C₅₋₆ alcohols to produce C₅₋₆ olefins which are recycled to the MTBE reactor.



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THE PRODUCTION OF 1-HEXENE FROM BUTADIENE RAFFINATE-1

Background of the Invention

1-hexene is a valuable comonomer for the production of the
5 production of linear low density polyethylene and is also used in
the synthesis of flavors, perfumes, dyes and resins. Another
significant use of 1-hexene is the production of linear aldehyde
via hydroformylation for later production of the short chain
fatty acid heptanoic acid. It is used in the manufacture of
10 polyol esters and plasticizer alcohols. Prior to the 1970's, 1-
hexene was manufactured by the thermal cracking of waxes. Today
it is commonly manufactured by two main routes: via full range
processes using the oligomerization of ethylene and, on a much
smaller scale, by the dehydration of alcohols. Shell Chemicals
15 uses the Shell Higher Olefins Process to produce a broad range of
linear alpha olefins using olefin metathesis and ethylene
oligomerization.

During steam cracking of liquid feeds such as naphthas, gas
oils, condensates, etc., substantial quantities of crude C₄
20 fractions are produced. These C₄ fractions contain large
quantities of butadiene (for instance, 40 to 50 wt%), linear and
branched butenes (for instance, 40 to 50 wt%), and alkanes (for
instance, about 10 wt%). It is common to produce butadiene from
the crude C₄ stream. During the butadiene extraction process, a
25 raffinate stream is produced consisting of the linear and
branched butylenes and alkanes. This stream is referred to as
raffinate-1 after it is selectively hydrogenated to reduce the
levels of trace butadiene.

One common use for the raffinate-1 stream is to send it to
30 a methyltertbutylether (MTBE) unit. The MTBE unit selectively
reacts the isobutylene portion (branched olefin portion) of the
raffinate-1 stream with methanol, for instance over an acidic
catalyst, to produce the gasoline additive. In the process of

producing MTBE and depleting the raffinate-1 stream of isobutylene, a new raffinate stream is produced that mainly contains linear butenes (for example, 2-butene and 1-butene) and saturates (for example, n-butane and isobutane). This new raffinate stream is referred to as raffinate-2 and is commonly sent on to an alkylation process to produce C₈ higher octane fuel.

With the recent ban on MTBE use in gasoline in the United States, many MTBE process units are no longer in use and there is a future expectation that MTBE use will also decline in the rest of the world. In addition, there is an over capacity of raffinate-1 because there is not enough alkylation capacity available to convert all of the raffinate-1 produced. It would be advantageous if these MTBE units could be used to produce alternate valuable products such as 1-hexene.

Summary of the Invention

One embodiment of the present invention is process for producing 1-hexene and high purity isobutylene from raffinate-1 which comprises:

(a) introducing raffinate-1 and recycled C₅₋₆ olefins into an MTBE reactor and reacting the isobutylene in the raffinate-1 with methanol to produce MTBE, raffinate-2 and recycled C₅₋₆ olefins,

(b) converting the MTBE to produce high purity isobutylene and methanol for recycle,

(c) separating the recycled C₆ olefins from the recycled C₅ olefins and raffinate-2,

(d) producing 1-hexene by separating it from other C₆ olefins,

(e) introducing raffinate-2 and the recycled C₅ olefins to a hydroformylation reactor and reacting them with carbon monoxide and hydrogen to produce C₅₋₆ alcohols, and

(f) dehydrating the C₅₋₆ alcohols to produce C₅₋₆ olefins which are recycled to the MTBE reactor.

Another embodiment of the present invention is a process for producing 1-hexene and isobutylene from raffinate-1 which comprises:

- (a) introducing raffinate-1 into an MTBE reactor and reacting the isobutylene in the raffinate-1 with methanol to produce MTBE and raffinate-2,
- (b) converting the MTBE to produce high purity isobutylene and methanol for recycle,
- (c) introducing raffinate-2 and recycled C₅ olefins to a hydroformylation reactor and reacting them with carbon monoxide and hydrogen to produce C₅₋₆ alcohols,
- (d) separating branched C₅ alcohols from the other alcohols produced in step (d),
- (e) separating 1-pentanol from the C₆ alcohols,
- (f) separating 1-hexanol from the branched C₆ alcohols,
- (g) dehydrating the 1-pentanol and 1-hexanol to produce 1-pentene and 1-hexene,
- (h) separating 1-hexene from 1-pentene to produce a 1-hexene stream, and
- (i) recycling the 1-pentene to the hydroformylation reactor.

In another embodiment of the present invention, a portion of raffinate-2 is directed to a separation unit and 1-butene is separated therefrom to produce a 1-butene stream. The remaining material is directed to the hydroformylation reactor.

Brief Description of the Drawing

Fig. 1 is a flow diagram illustrating the process of the present invention wherein the olefins are recycled to the MTBE reactor.

Fig. 2 is a flow diagram illustrating the process of the present invention wherein the olefins are recycled to the hydroformylation reactor.

Fig. 3 is a flow diagram illustrating an option of the embodiment of Fig. 2 wherein a portion of raffinate-2 is separated off and 1-butene is produced therefrom.

Detailed Description of the Invention

5 Mixed C₄ streams (also called C₄ fractions) are obtained in a number of petrochemical processes. These streams are usually from olefin steam crackers but may also come from refinery cat-crackers in which case they contain the same components but in different proportions. Steam cracking of
10 hydrocarbons is widely used to produce olefins such as ethylene, propylene, butenes (1-butene cis- and trans-2-butenes, isobutene), butadiene, and aromatics such as benzene, toluene and xylene. In an olefin plant, a hydrocarbon feedstock such as naphtha, gas oil or other fractions of whole
15 crude oil is mixed with steam. This mixture, after preheating, is subjected to severe thermal cracking at elevated temperatures (for example 800 to 850°C) in a pyrolysis furnace. The cracked effluent from the pyrolysis furnace contains gaseous hydrocarbons of great variety (from 1 to 35 carbon
20 atoms per molecule). This effluent contains hydrocarbons that are aliphatic, aromatic, saturated and unsaturated, and may contain significant amounts of molecular hydrogen. The cracked product of a pyrolysis furnace is then further processed in the olefin plant to produce, as products of the plant, various
25 individual product streams such as hydrogen, ethylene, propylene, mixed hydrocarbons having 4 or 5 carbon atoms per molecule (crude C₄ and C₅), and pyrolysis gasoline.

Crude C₄ streams may contain varying amounts of n-butane, isobutane, 1-butene, 2-butene (cis- and/or trans-) isobutene
30 (isobutylene), acetylenes (ethyl acetylene and vinyl acetylene), and butadiene. Crude C₄ may typically be subjected to butadiene extraction or butadiene selective hydrogenation to remove most, if not essentially all, of the butadiene and

acetylenes present. Thereafter, the C₄ raffinate (called raffinate-1) is subjected to a chemical reaction (for example, etherification, hydration, dimerization) wherein isobutylene is converted to other compounds (for example, MTBE, tertiary butyl alcohol or diisobutylene). The remaining C₄ stream containing mostly n-butane, isobutane, 1-butene and 2-butene is called raffinate-2.

In solvent extraction, a raffinate is a liquid stream that remains after extraction with an immiscible liquid to remove solutes from the original liquor. Raffinate-1 and raffinate-2 can be regarded as stages in the processing of crude C₄ streams. The first stage of the process is to remove, by solvent extraction, the valuable butadiene which may be 40 to 50 wt% of the stream. What is left is raffinate-1. It generally consists of isobutylene, the two normal isomers, butene-1 and butene-2, and small quantities of butanes and other compounds. Removal of the isobutylene by reaction with methanol to produce MTBE leaves raffinate-2.

MTBE is manufactured by the chemical reaction of methanol and isobutylene.



It may be produced by reacting the isobutylene with methanol over a catalyst bed and may take place in either a liquid phase or mixed gas/liquid phase reactor. One type of catalyst commonly used is an acidic ion exchange resin. An alternative catalyst is sulfuric acid. The manufacture of MTBE from raffinate-1 is well known. One process for making MTBE is described in U.S. Patent No. 4,440,963 which is incorporated herein by reference in its entirety. The reaction of isobutylene in the raffinate-1 with methanol may take place at a methanol:isobutylene molar ratio of about 0.05 to 10, a

temperature in the range of about 15°C to about 150°C at a pressure sufficient to maintain the reactants substantially in the liquid state, typically about 0.2 to about 2 MPa. The reaction mixture may be distilled to produce high purity MTBE.

5 Processes for making MTBE are well known and are available commercially for license.

The olefin recycle stream may contain some branched byproduct which was originally produced in the hydroformylation reactor. One of the advantages of this embodiment of the present invention is that a separate distillation to remove the branched byproduct is not necessary. The branched byproduct may be removed during the MTBE reaction and may be separated from the isobutylene in the decomposition step.

Under suitable conditions, MTBE is decomposed into isobutylene and methanol. This decomposition is a reversible endothermic chemical reaction. When this reaction is situated downstream from MTBE synthesis from a C₄ fraction, it results in the separation of the different isomers in this cut by a less costly method than others commonly used such as concentrated sulfuric acid extraction. The isobutylene obtained by MTBE composition is very pure and meets the specifications required for subsequent polymerization into butyl rubber or methyl methacrylate.

MTBE feedstock may first be fractionated to remove light ends and heavies. The high purity MTBE may then be fed to the decomposition reactor where MTBE is converted to isobutylene and methanol. The decomposition reaction may take place in vapor phase and be performed with high selectivity. The heat of reaction may be supplied by medium pressure steam. The methanol may be extracted from the reactor effluent in a water wash. The aqueous stream may be fractionated to recover the wash water and MTBE for recycle, and to produce high quality methanol. The water-washed reactor effluent may be

fractionated to remove heavies (including MTBE for recycle) and light ends, leaving a high purity (>99.9%) isobutylene product.

The MTBE decomposition reaction is accompanied by secondary reactions such as the oligomerization of isobutylene (mainly the formation of dimers), the dehydration of methanol into dimethylether, and the hydration of isobutylene into tertbutyl alcohol. The decomposition is catalyzed by solids with an acid nature. The main catalysts used are of the sulfonic resin type but solid acid catalysts including zeolites, silica-alumina, supported phosphoric acid, etc., have also been used. We believe that the forward reaction (MeOH + isobutylene) best takes place over a sulfonic acid resin and that the decomposition reaction (MTBE $\rightarrow$ isobutylene + MeOH) best takes place over a solid acid catalyst.

The formulation of the catalyst and the nature of the active acid sites have great influence on the reaction. By choosing suitable operating conditions, for instance, a low enough operating pressure and thus a low enough temperature, together with a small amount of catalyst employed in the reaction section, the side reaction of methanol dehydration may be completely suppressed so that only a very small amount of diisobutylene is formed. Suitable operating temperatures and pressures for this reaction may be approximately 150°C to 225°C and 1.1 Mpa to 0.608 Mpa.

The separation of the C₆ olefins from the C₅ olefins and the raffinate-2 may be accomplished by distillation. The separation of the 1-hexene from the other trace C₆ olefins may be accomplished by distillation if needed.

Raffinate-2 and the C₅ olefins are then introduced into a hydroformylation reactor and reacted with carbon monoxide and hydrogen (syngas). The hydroformylation is carried out in the presence of a hydroformylation catalyst.

In a hydroformylation process, olefins are converted to aldehydes, alcohols or a combination thereof by reaction of at least a portion of the olefins with carbon monoxide and hydrogen according to an Oxo process. As used herein, an "Oxo process" refers to the reaction of an olefin with carbon monoxide and hydrogen in the presence of a metal catalyst (e.g., a cobalt catalyst) to produce an alcohol containing one more carbon atom than the starting olefin. In other hydroformylation processes, a "modified Oxo process" is used. As used herein, a "modified Oxo process" refers to an Oxo process that uses a phosphine, phosphite, arsine or pyridine ligand modified cobalt or rhodium catalyst. Preparation and use of modified Oxo catalysts are described in U.S. Patent No. 3,231, 621, to Slaugh, entitled "Reaction Rates In Catalytic Hydroformylation"; U.S. Patent No. 3,239,566 to Slaugh et al., entitled "Hydroformylation Of Olefins;" U.S. Patent No. 3,239,569 to Slaugh et al., entitled "Hydroformylation Of Olefins;" U.S. Patent No. 3,239,570 to Slaugh et al., entitled "Hydroformylation Of Olefins;" U.S. Patent No. 3,239,571 to Slaugh et al., entitled "Hydroformylation Of Olefins;" U.S. Patent No. 3,400,163 to Mason et al., entitled "Bicyclic Heterocyclic Sec- And Tert-Phosphines;" U.S. Patent No. 3,420,898 to Van Winkle et al., entitled "Single Stage Hydroformylation Of Olefins To Alcohols Single Stage Hydroformylation Of Olefins To Alcohols;" U.S. Patent No. 3,440,291 to Van Winkle et al., entitled "Single Stage Hydroformylation Of Olefins To Alcohols;" U.S. Patent No. 3,448,157 to Slaugh et al., entitled "Hydroformylation Of Olefins;" U.S. Patent No. 3,488,158 to Slaugh et al., entitled "Hydroformylation Of Olefins;" U.S. Patent No. 3,496,203 to Morris et al., entitled "Tertiary Organophosphine-Cobalt-Carbonyl Complexes;" U.S. Patent No. 3,496,204 to Morris et al., entitled "Tertiary Organophosphine-Cobalt-Carbonyl

Complexes;" U.S. Patent No. 3,501,515 to Van Winkle et al.,
entitled "Bicyclic Heterocyclic Tertiary Phosphine-Cobalt-
Carbonyl Complexes"; U.S. Patent No. 3,527,818 to Mason et al.,
entitled "Oxo Alcohols Using Catalysts Comprising Ditertiary
5 Phosphines;" U.S. Patent No. 7,087,777, entitled "A Process For
Preparing A Branched Olefin, A Method Of Using The Branched
Olefin For Making A Surfactant, and a Surfactant " and in U. S.
Patent No. 6,861,450 entitled "Process for the Preparation Of A
Highly Linear Alcohol Composition," all of which are
10 incorporated herein by reference in their entirety. Methods of
alcohol production are also described by Othmer, in
"Encyclopedia of Chemical Technology" 2000, Fourth Edition; and
by Wickson, in "Monohydric Alcohols; Manufacture, Applications
and Chemistry" Ed. Am. Chem. Soc. 1981, both of which are
15 incorporated herein by reference.

A hydroformylation catalyst used in the hydroformylation
reactor may include a metal from Group VIII of the Periodic
Table. Examples of Groups VIII metals include cobalt, rhodium,
nickel, palladium or platinum. The Group VIII metal may be
20 used as a complex compound. A complex compound may be a Group
VIII metal combined with a ligand. Examples of ligands
include, but are not limited to, a phosphine, phosphite,
arsine, stibine or pyridine ligand. Examples of
hydroformylation catalysts include, but are not limited to,
25 cobalt hydrocarbonyl catalyst, cobalt-phosphine ligand
catalyst, rhodium-phosphine ligand catalyst or combinations
thereof.

A source of the Group VIII metal may be a salt. Salts of
acids with a pKa value from about 2 to about 6 when measured in
30 water at 20 °C, may be used. Examples of suitable acids
include nitric acid, sulfuric acid, organic acids and sulfonic
acids. Examples of organic acids include octanoic acid,
dichloroacetic acid, trifluoroacetic acid perfluoropropionic

acid and combinations thereof. Examples of sulfonic acids include p-toluenesulfonic acid, benzenesulfonic acid, methanesulfonic acid and combinations thereof.

Ligands of a hydroformylation catalyst may be made of
5 monophosphines. A monophosphine may include three hydrocarbon groups, three oxy groups, or combinations of hydrocarbon groups and oxy groups. Examples of monophosphine ligands include, but are not limited to, triamylphosphine, trihexylphosphine, dimethylethylphosphine, tricyclopentylphosphine,
10 tricyclohexylphosphine, diphenylbutylphosphine, diphenylbenzylphosphine, phenyl[bis(2-pyridyl)]phosphine, triethoxyphosphine, triphenylphosphine, or combinations thereof.

In other embodiments, bidentate phosphine ligands may be
15 used. Examples of bidentate phosphine ligands include, but are not limited to, 1,2-bis(dimethylphosphino)ethane, 1,2- and 1,3-bis(dimethylphosphino)propane, 1,2-bis(diperfluorophenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane
20 or combinations thereof.

In some embodiments, phosphine ligands may include phosphabicyclo-hydrocarbons. Examples of phosphabicyclo-hydrocarbons include, but are not limited, 9-hydrocarbyl-9-phospha-bicyclononane and P, P-bis(9-phosphabicyclononyl)-
25 hydrocarbons in which the smallest P-containing ring contains at least 5 carbon atoms.

A phosphine ligand may be used in amounts in a molar ratio of phosphine to metal (e.g., cobalt) range from about 0.5 to about 2. In certain embodiments, a molar ratio of alkyl
30 phosphine to metal may be in a range of about 0.6 to about 1.8. In addition to the metal and the phosphine ligand, the hydroformylation catalyst may also include additional components for enhancing the stability of the metal/phosphine

system. In some embodiments, a hydroformylation catalyst may include additional components for improving the alcohol selectivity. Examples of additional components are potassium hydroxide and sodium hydroxide. The additional component may
5 be used in a molar ratio of additional component to metal from about 0 to about 1.

A source of carbon and hydrogen for a hydroformylation process in the hydroformylation reactor may be a gas. Examples of gases include, but are not limited to, carbon monoxide,
10 hydrogen or synthesis gas. A ratio of carbon monoxide to hydrogen applied may be in a range from about 1.0 to about 10.0. In certain embodiments, a hydrogen to carbon monoxide molar ratio may be in a range from about 1.5 to about 2.5. It should be understood that the gas feed may be a mixture of
15 carbon monoxide and hydrogen gases only, synthesis gas only or combinations thereof.

In the hydroformylation reactor, olefins may be hydroformylated using a continuous, semi-continuous or batch process. In case of a continuous mode of operation, the liquid
20 hourly space velocities may be in the range of about 0.1 h⁻¹ to about 10 h⁻¹. When operating the hydroformylation unit as a batch process, reaction times may vary from about 0.1 hours to about 10 hours or even longer.

Reaction temperatures in the hydroformylation reactor may
25 range from about 100°C to about 300°C. In certain embodiments, reaction temperatures in the hydroformylation unit ranging from about 125°C to about 250°C may be used. Pressure in the hydroformylation reactor may range from about 1 atmosphere (0.1 MPa) to about 300 atmospheres (30.4 MPa).

30 An amount of catalyst relative to the amount of olefin to be hydroformylated may vary. Typical molar ratios of catalyst to olefin may range from about 1:1000 to about 10:1. A ratio of between about 1:10 and about 5:1 may be used in certain

embodiments. The reaction mixture may include solvents that do not interfere substantially with the desired reaction. Examples of such solvents include, but are not limited to, alcohols, ethers, acetonitrile, sulfolane and paraffins.

5 Mono-alcohol selectivities of at least 90 percent and even of at least 92 percent may be achieved in the hydroformylation reactor. In addition, olefin conversions to aliphatic alcohols may range from about 50 percent by weight to greater than 95 percent by weight. In certain embodiments, olefin conversion
10 to aliphatic alcohols may be greater than 75 percent by weight. In some embodiments, olefin conversion to aliphatic alcohols may be greater than 99 percent by weight.

Isolation of aliphatic alcohols produced from the hydroformylation reaction product stream may be achieved by
15 generally known methods. In an embodiment, isolation of the aliphatic alcohols includes subjecting the produced aliphatic alcohols to a first distillation, a saponification, a water washing treatment and a second distillation.

The hydroformylation reaction mixture stream may enter a
20 separator wherein C₄₋₆ saturates and unreacted olefins are separated from the C₅₋₆ alcohols which are mainly linear alcohols but may include some branched byproduct. In the separator, the hydroformylation reaction product stream may be subjected to a first distillation step (e.g., flash
25 distillation or a short path distillation). In an embodiment, a short path distillation may be used to produce at least two streams, a bottom stream and a top stream. At least a portion of the bottom stream may be recycled to the hydroformylation reactor in certain embodiments. The top stream may include,
30 but is not limited to, paraffins, unreacted olefins and a crude aliphatic alcohol product.

Any suitable dehydration process may be used to convert the alcohol with the increased carbon chain length to 1-pentene

and 1-hexene. The dehydration process may be controlled to produce α -olefinic compounds. A small amount of double bond isomerization may occur. For 1-pentene this is not a problem because both 1-pentene and 2-pentene hydroformylate to mainly
5 1-hexanol.

Many different dehydration processes are known and several are described in GB797989, GB1225559, U.S. 5,130,287, U.S. 6,627,782 and U.S. 2005/0065389, all of which are herein incorporated by reference in their entirety. The dehydration
10 may be out under low acidity conditions and a low acidity catalyst support such as Al_2O_3 , SiO_2 , TiO_2 , or ZrO_2 may be employed to afford a dehydration reaction at temperatures from about 200 to about 450°C, typically from about 250 to about 350°C, and at pressures from about 0 to about 3 MPa, typically
15 from about 0 to about 0.5 MPa. The catalyst may comprise a gamma-alumina catalyst or a promoted alumina catalyst, for example $\text{CaO} \cdot \text{Al}_2\text{O}_3$, $\text{Ca}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$.

Fig. 1 is a flow diagram of one embodiment of the process of the present invention. Raffinate-1 is directed through line
20 1 into MTBE reactor 3. C_{5-6} olefins in recycle stream 2 are also directed to reactor 3. Raffinate-1 is combined with methanol which enters through line 15 from decomposition reactor 4 and is reacted to form MTBE.

The product MTBE is directed to decomposition reactor 4
25 through line 14 wherein the MTBE is cracked to produce high purity isobutylene (line 5). Line 6 contains C_{5-6} branched olefins and heavy materials.

The raffinate-2 formed as a result of the MTBE reaction is directed through line 7 with the C_{5-6} linear olefins into
30 separation unit 8. The C_6 olefins are separated from the other materials which are mainly linear butenes and pentenes with C_4 saturates. The C_6 olefins are directed to separation unit 9

wherein the 1-hexene (line 10) is separated from the other C₆ olefins (line 16).

The linear butenes and pentenes are directed through line 17 to hydroformylation reactor 11 wherein they are reacted with
5 syngas from line 18 to produce alcohols. The product alcohols are separated in separator 12 which produces mainly primary linear C₅₋₆ alcohols with some branched byproduct (line 19). These alcohols are directed through line 20 to dehydration unit 13 wherein they are dehydrated to produce the C₅₋₆ olefins which
10 are recycled in recycle stream 2.

In another embodiment of the present invention, the olefins from the dehydration reactor are recycled to the hydroformylation reactor rather than to the MTBE reactor. In this embodiment, the branched alcohols are separated from the
15 linear alcohols, preferably by distillation. This is possible because the difference in boiling points is much greater for the alcohols than for the olefins. 1-pentene and its isomers 2-methyl-1-butene, 2-pentene(cis) and 2-pentene(trans) boil at 30°C, 31.2°C, 36.9°C and 36.3°C, respectively, whereas 1-
20 pentanol and 2-methyl-1-butanol boil at 137.8°C and 128.7°C. Similarly, 1-hexene, 2-methyl-1-pentene, 2-hexene(cis) and 2-hexene(trans) boil at 63.5°C, 62.1°C, 68.9°C and 67.9°C, respectively, and 1-hexanol and 2-methyl-1-pentanol boil at 157.4°C and 148°C. Both 1-pentene and 2-pentene hydroformylate
25 to mainly 1-hexanol.

This separation is preferably carried out in three steps. The branched C₅ alcohols are removed in step 1. The 1-pentanol is removed in step 2 and is directed to the dehydration reactor. Then in step 3, the branched C₆ alcohols are removed
30 from the 1-hexanol which is directed to the same dehydration reactor or a separate one.

In Fig. 2, raffinate-1 is directed through line 1 into MTBE reactor 3. Raffinate-1 is combined with methanol (line 22 from decomposition reactor 4) and reacted to form MTBE. The product MTBE is directed through line 23 to decomposition reactor 4 wherein the MTBE is cracked to produce high purity isobutylene in line 5. Line 6 contains any C₅₋₆ branched olefins and heavy materials.

The raffinate-2 formed as a result of the MTBE reaction is directed through line 7 into the hydroformylation reactor 11. Recycle stream 2 containing the C₅ olefins (the C₆ olefins are not recycled in this embodiment) is also directed to hydroformylation reactor 11. The linear butenes and pentenes are reacted with syngas (line 24) to produce C₅ and C₆ alcohols. The product alcohols are separated in separator 12 from the C₄₋₆ saturates and unreacted materials (line 25). The alcohols are then directed through line 26 to separator 14 wherein the branched C₅ alcohols (line 27) are separated from the other alcohols, preferably by distillation. The other alcohols are then directed through line 28 to separator 15 wherein 1-pentanol is separated from the C₆ alcohols, preferably by distillation, and is directed through line 29 to the dehydration unit 13. The C₆ alcohols are directed through line 30 to separator 16 wherein the branched C₆ alcohols are separated from the 1-hexanol, preferably by distillation, which is then directed to the dehydration unit 13 through line 31.

The C₅₋₆ olefins produced in dehydration unit 13 are then directed to separator 17 wherein the 1-pentene (there should be no other compounds in this stream) is separated out and recycled in stream 2 to the hydroformylation reactor 11. The 1-hexene and trace impurities are directed to separator 18 wherein 1-hexene (line 32) is separated from said impurities if needed.

Fig. 3 illustrates an option wherein a portion of raffinate-2 is used to make 1-butene. The description of the elements of the figure are the same as in the preceding paragraph except that a portion of raffinate-2 is directed through line 19 to separator 20 wherein 1-butene is separated off as a relatively pure stream 21. The remaining materials, called raffinate-3, are directed through line 33 to the hydroformylation reactor 11.

Example 1

Hydroformylation of either 1-butene or 2-butene (10 milliliters) was carried out in a 250 milliliter autoclave reactor at 160°C and a pressure of about 80 bar (the autoclave was charged with hydrogen pressure of 40 bar and a carbon monoxide pressure of 20 bar at room temperature) employing 2-ethylhexanol as the solvent (30 milliliters) and a homogeneous phosphine modified cobalt-based catalyst (ligand:cobalt ratio of 2; 10 millimoles of cobalt; ligand--9-eicosyl-9-phospha-bicyclo-[3.3.1]nonane and 9-eicosyl-9-phospha-bicyclo-[4.2.1]nonane in a ratio of about 55:45 by weight).

The hydroformylation reaction was fast and completed within 1 to 2 hours. A regioselectivity to 1-pentanol of about 85 to 87 percent was achieved in some experiments and in others a higher regioselectivity of about 92 to 93 percent was achieved. In all cases butane was formed as the main side product.

Example 2

Example 1 was repeated using alternative ligand di-dimethylamide propanone-9-phospha-bicyclo-[3.3.1]nonane. The linearity of the pentanol produced was about 94 percent and only about 6 to 8 wt% of paraffin was made.

Example 3

1-pentene (99.15 wt% alpha olefin and 0.85 wt% internal olefins) was hydroformylated in 2-ethylhexanol using a cobalt

octoate catalyst. The syngas had a volumetric hydrogen/carbon monoxide ratio of 1.882 in experiments 4 and 5, 2.067 in experiments 8, 12, and 15-17, and 1.849 in experiments 18 and 19.

5 The hydroformylation was carried out in a 300 milliliter Hastelloy autoclave equipped with a hollow shaft stirrer (speed about 100 rpm). The autoclave was filled with an internal standard (n-nonane), 2-hexanol and potassium hydroxide as a 5 wt% solution in 2-ethylhexanol. The air present in the
10 autoclave was removed with a vacuum pump and purged the first three times with nitrogen and then carbon monoxide. After carbon monoxide purging, the reactor was filled with the calculated amount of carbon monoxide gas at 6 to 8 bar. Then the olefin was transferred separately via a high pressure pump.
15 The autoclave was finally pressurized with syngas at 44-45 bar and heated to the desired conditions (shown in Table 1). The start of the experiment was when the catalyst mixture was injected in the autoclave with a dedicated injection system.

After submission of carbon monoxide, the hydrogen/carbon
20 monoxide ratio of the syngas feed to the reaction was about 2 moles per mole. The syngas was made up to maintain a constant reactor pressure using a constant pressure valve.

Gas chromatography was used to quantify the olefin compound and paraffin make, the formation of intermediary
25 structures such as aldehydes and acetals, internal standard nonane, solvent 2-ethylhexanol, branched and linear alcohols and heavy ends such as dimer-aldehydes and dimer-alcohol. The main experimental conditions and results are shown in Table 1. RM17 is 9-Eicosyl-9-phosphabicyclo[3.3.1/4.2.1]nonane (mixture
30 of isomers); sym-PhN is 9-Phosphabicyclo[3.3.1]nonane-9-propanamide, N,N-dimethyl-; and sym-RM17 is 9-Eicosyl-9-phosphabicyclo[3.3.1]nonane.

Table 1. Experimental conditions and main results of the hydroformylation reactions^(a,b)

No.	Ligand	T (°C)	[Co] (wt%)	Ligand/Co (mol/mol)	KOH/Co (mol/mol)	Conversion (%)	Linearity	Paraffin (mol%)	Acetal ^c (mol%)	HE (mol%)
5	RM17	160	0.18	1.0	0.9	98.3	93.3	6.3	9.4	4.7
8	sym-PhN	165	0.18	1.0	0.9	99.9	94.3	8.2	5.1	1.9
4	RM17	170	0.18	1.0	0.9	99.8	92.1	7.0	5.6	1.7
12	RM17	170	0.21	2.0	0	99.9	93.3	6.5	3.1	0.1
17	sym-PhN	171	0.12	1.5	0	100	93.7	6.8	3.8	0.4
19	sym-RM17	170	0.10	1.5	0	99.8	93.1	6.1	4.2	0.1
15	RM17	170	0.20	1.3	0.5	99.8	93.0	6.0	4.2	0.6
16	sym-PhN	170	0.12	1.5	0.5	99.8	94.3	5.7	2.9	1.2
18	sym-RM17	169	0.12	1.5	0.5	99.8	93.9	5.8	5.7	2.1

^aP=65-67 bar, H₂/CO=1.4-1.5, τ =5.7-5.5 h^bConversion and selectivity calculated from GC data, istd method^cAcetals were almost exclusively linear aldehydes, 2-ethyl alcohol and product alcohol, reversible intermediates that give linear alcohol.

C L A I M S

1. A process for producing 1-hexene and isobutylene high purity from raffinate-1 which comprises:
- 5 (a) introducing raffinate-1 and a C₅₋₆ olefin recycle stream into an MTBE reactor and reacting the isobutylene in the raffinate-1 with methanol to produce MTBE, raffinate-2 and recycled C₅₋₆ olefins,
- (b) converting the MTBE to produce high purity isobutylene,
- 10 (c) separating the recycled C₆ olefins from the recycled C₅ olefins and raffinate-2,
- (d) producing 1-hexene by separating it from other C₆ olefins,
- (e) introducing raffinate-2 and the recycled C₅ olefins to a
- 15 hydroformylation reactor and reacting them with CO and H₂ to produce C₅₋₆ alcohols, and
- (f) dehydrating the C₅₋₆ alcohols to produce C₅₋₆ olefins which are recycled to the MTBE reactor.
- 20 2. A process for producing 1-hexene and isobutylene high purity from raffinate-1 which comprises:
- (a) introducing raffinate-1 into an MTBE reactor and reacting the isobutylene in the raffinate-1 with methanol to produce MTBE and raffinate-2,
- 25 (b) converting the MTBE to produce high purity isobutylene,
- (c) introducing raffinate-2 and recycled C₅ olefins to a hydroformylation reactor and reacting them with carbon monoxide and hydrogen to produce C₅₋₆ alcohols,
- (d) separating branched C₅ alcohols from the other alcohols
- 30 produced in step (d),
- (e) separating 1-pentanol from the C₆ alcohols,
- (f) separating 1-hexanol from the branched C₆ alcohols,

- (g) dehydrating the 1-pentanol and 1-hexanol to produce 1-pentene and 1-hexene, and
- (h) separating 1-hexene from 1-pentene to produce a 1-hexene stream, and
- 5 (i) recycling the 1-pentene to the hydroformylation reactor.

3. The process of claim 2 wherein a portion of raffinate-2 is directed to a separation unit and 1-butene is separated therefrom to produce a 1-butene stream and the remaining
10 material is directed to the hydroformylation reactor.

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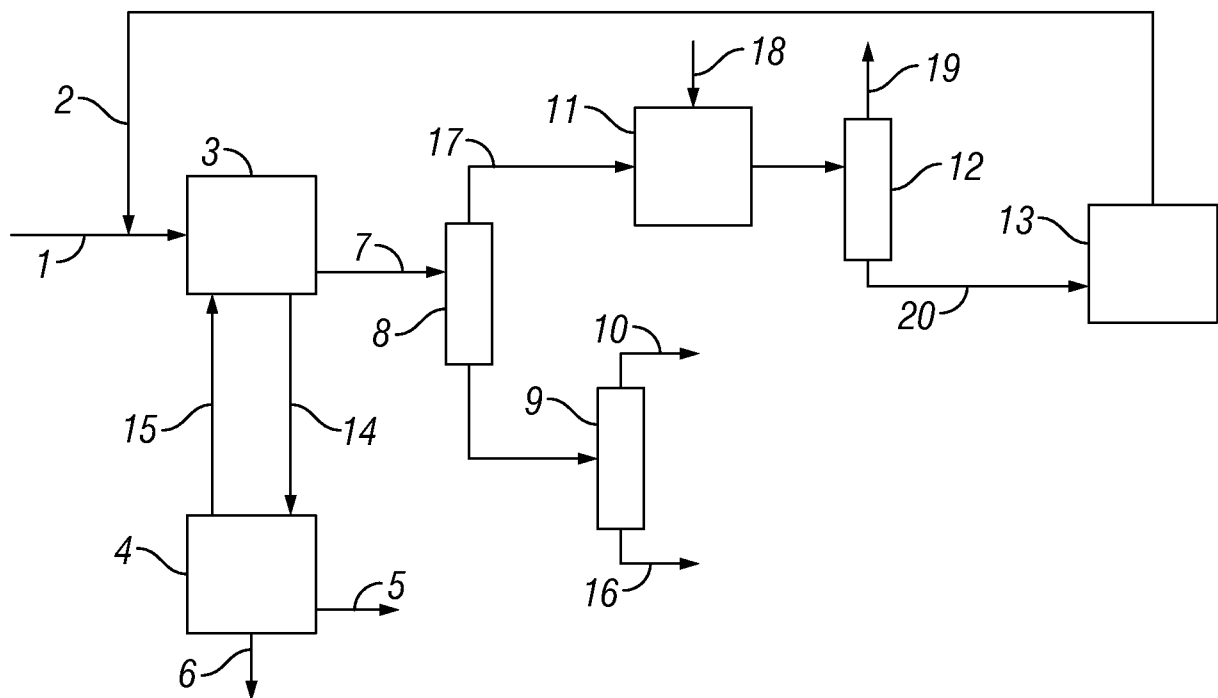


FIG. 1

2/2

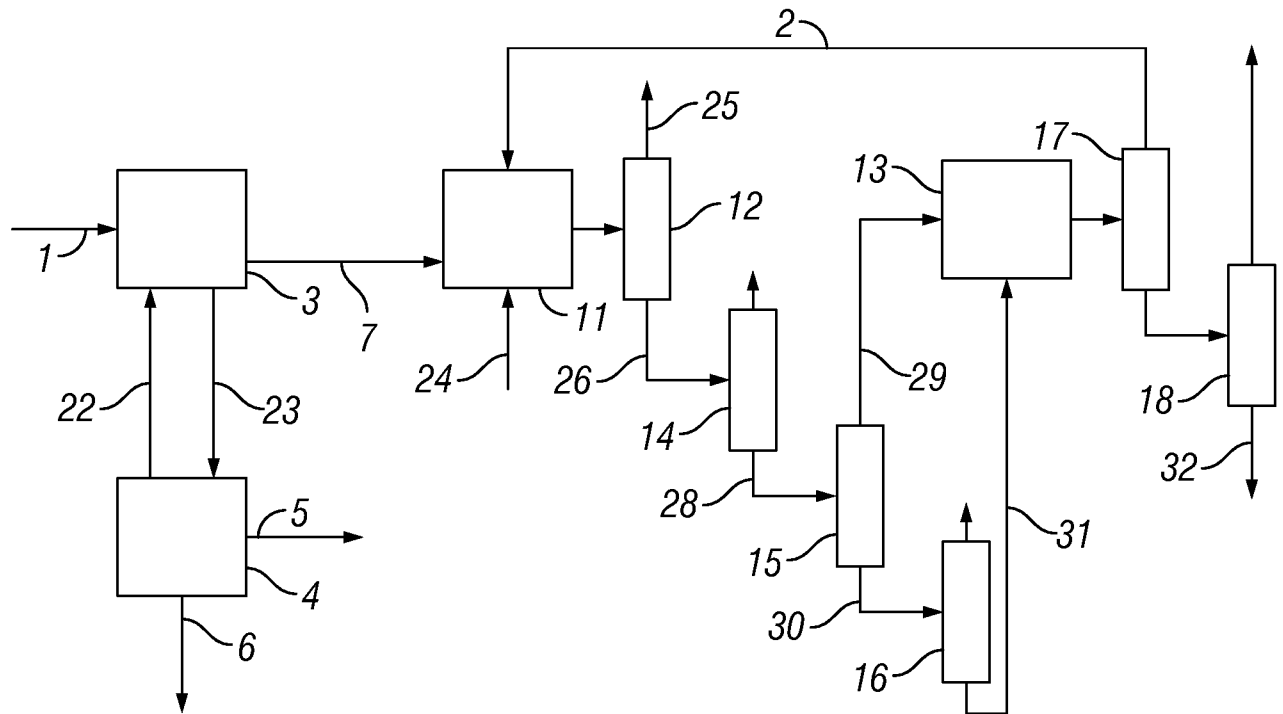


FIG. 2

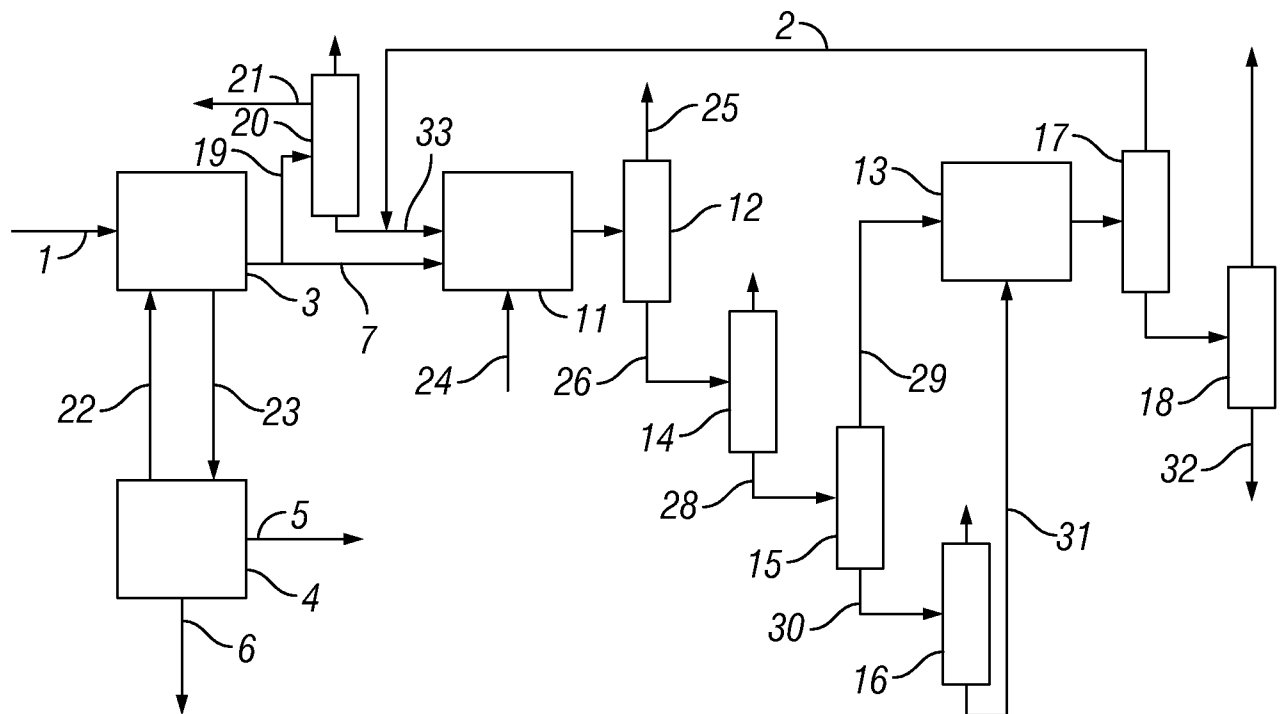


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/035907

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C11/09 C07C11/107
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 570 026 A (KEYWORTH DONALD A [US] ET AL) 11 February 1986 (1986-02-11) figure 1 column 7, line 23 - column 8, line 6 -----	1,2
A	US 2005/065389 A1 (DE BRUYN CORNELIS JOHANNES [ZA] ET AL) 24 March 2005 (2005-03-24) cited in the application examples 1-4 -----	1,2

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

22 June 2010

Date of mailing of the international search report

30/06/2010

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/035907

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4570026	A	11-02-1986	NONE
US 2005065389	A1	24-03-2005	CN
		WO	1555352 A
			03024910 A1
			15-12-2004
			27-03-2003