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(54) Title: THE DEHYDROGENATION OF MIXED ALCOHOLS

(57) Abstract: The present invention relates to a process for the production of alkene(s) from a feedstock comprising of at least ethanol and/or propanol(s).

THE DEHYDROGENATION OF MIXED ALCOHOLS

The present invention relates to a process for the production of alkene(s) from a feedstock comprising of at least one monohydric aliphatic paraffinic alcohol.

5 Olefin(s) have traditionally been produced by steam or catalytic cracking of hydrocarbons. However, inevitably as oil resources are decreasing the price of oil is increasing; which makes light olefin(s) production a costly process. Thus there is an ever-growing need for non-petroleum routes to produce C₂ and C₂+ olefin(s), essentially ethylene and propylene. Such olefin(s) are useful starting materials for numerous chemical
10 products including polymeric products such as polyethylene.

In recent years the search for alternative materials for C₂+ olefin(s) production has led to the use of alcohols such as methanol, ethanol and higher alcohols. The said alcohols may be produced by the fermentation of, for example, sugars and/or cellulosic materials.

15 Alternatively, alcohols may be produced from synthesis gas. Synthesis gas refers to a combination of hydrogen and carbon oxides produced in a synthesis gas plant from a carbon source such as natural gas, petroleum liquids, biomass and carbonaceous materials including coal, recycled plastics, municipal wastes, or any organic material. Thus, alcohol and alcohol derivatives may provide non-petroleum based routes for the production of olefin(s) and other related hydrocarbons.

20 Generally, the production of oxygenates, primarily methanol, takes place via three process steps. The three process steps are: synthesis gas preparation, methanol synthesis, and methanol purification. In the synthesis gas preparation step, an additional stage may be employed by where the feedstock is treated, e.g. the feedstock is purified to remove sulfur and other potential catalyst poisons prior to being converted into synthesis gas. This
25 treatment can also be conducted after syngas preparation; for example, when coal or biomass is employed.

Processes for producing mixtures of carbon oxide(s) and hydrogen (synthesis gas) are well known. Each has its advantages and disadvantages and the choice of using a particular reforming process is dictated by economic and available feed stream
30 considerations, as well as by the desired mole ratio of H₂:CO in the feedstock resulting from the reforming reaction. The synthesis gas may be prepared using any of the processes known in the art including partial oxidation of hydrocarbons, steam reforming, gas heated

reforming, microchannel reforming (as described in, for example, US 6,284,217 which is herein incorporated by reference), plasma reforming, autothermal reforming and any combination thereof. A discussion of these synthesis gas production technologies is provided in "Hydrocarbon Processing" V78, N.4, 87-90, 92-93 (April 1999) and "Petrole
5 et Techniques", N. 415, 86-93 (July-August 1998). It is also envisaged that the synthesis gas may be obtained by catalytic partial oxidation of hydrocarbons in a microstructured reactor as exemplified in "IMRET 3: Proceedings of the Third International Conference on Microreaction Technology", Editor W Ehrfeld, Springer Verlag, 1999, pages 187-196. Alternatively, the synthesis gas may be obtained by short contact time catalytic partial
10 oxidation of hydrocarbonaceous feedstocks as described in EP 0303438. Preferably, the synthesis gas is obtained via a "Compact Reformer" process as described in "Hydrocarbon Engineering", 2000, 5, (5), 67-69; "Hydrocarbon Processing", 79/9, 34 (September 2000); "Today's Refinery", 15/8, 9 (August 2000); WO 99/02254; and WO 200023689.

Typically, for commercial syngas production the pressure at which the synthesis
15 gas is produced ranges from approximately 20 to 75 bar and the temperature at which the synthesis gas exits the reformer ranges from approximately 700 DEG C. to 1100 DEG C. The synthesis gas contains a molar ratio of hydrogen to carbon oxide which is dependent on the syngas feedstock - ranging from 0.8 to 3.

The synthesis gas preparation, also known as reforming, may take place in a single-
20 step wherein all of the energy consuming reforming reactions are accomplished in a single tubular steam reformer. The single-step reformer results in a production of surplus hydrogen. In a preferred alternative, the synthesis gas preparation may take place in a two-step reforming process wherein the primary reforming in a tubular steam reformer is combined with an oxygen-fired secondary reforming step which produces a synthesis gas
25 with a deficiency in hydrogen. With this combination it is possible to adjust the synthesis gas composition to obtain the most suitable composition for methanol synthesis. As an alternative, autothermal reforming -wherein a stand-alone, oxygen-fired reformer produces synthesis gas having a hydrogen deficiency followed by the downstream removal of carbon dioxide to restore the desired ratio of hydrogen to carbon oxide - results in a simplified
30 process scheme with lower capital cost. The burner design is an important part of either oxygen-fired step. The burner mixes the hydrocarbon and oxygen and by combustion in the flame, heat is provided for conversion of the hydrocarbons.

The reaction from synthesis gas to oxygenates such as methanol is an exothermic equilibrium limited reaction which is favored by low temperatures. It also requires high pressures over a heterogeneous catalyst as the reactions which produce methanol exhibit a decrease in volume. As disclosed in U.S. Pat. No. 3,326,956, low-pressure methanol synthesis is based on a copper oxide-zinc oxide-alumina catalyst that typically operates at a nominal pressure of 5-10 MPa and temperatures ranging from approximately 150 DEG C. to 450 DEG C. over a variety of catalysts, including CuO/ZnO/Al₂O₃, CuO/ZnO/Cr₂O₃, ZnO/Cr₂O₃, Fe, Co, Ni, Ru, Os, Pt, and Pd. Catalysts based on ZnO for the production of methanol and dimethyl ether are preferred. The low-pressure, copper-based methanol synthesis catalyst is commercially available from suppliers such as BASF, ICI Ltd. of the United Kingdom, and Haldor-Topsoe. Methanol yields from copper-based catalysts are generally over 99.5% of the converted CO+CO₂ present. Water is a by-product of the conversion of the synthesis gas to oxygenates. A paper entitled, "Selection of Technology for Large Methanol Plants," by Helge Holm-Larsen, presented at the 1994 World Methanol Conference, Nov. 30-Dec. 1, 1994, in Geneva, Switzerland, and herein incorporated by reference, reviews the developments in methanol production and shows how further reduction in costs of methanol production will result in the construction of very large plants with capacities approaching 10,000 metric tonnes per day.

U.S. Pat. No. 4,543,435 discloses a process for converting an oxygenate feedstock comprising methanol, dimethyl ether or the like in an oxygenate conversion reactor into liquid hydrocarbons comprising C₂-C₄ olefin(s) and C₅+ hydrocarbons. The C₂-C₄ olefin(s) are compressed to recover an ethylene-rich gas. The ethylene-rich gas is recycled to the oxygenate conversion reactor. U.S. Pat. No. 4,076,761 discloses a process for converting oxygenates to gasoline with the return of a hydrogen-rich gaseous product to a synthesis gas plant or the oxygenate conversion reaction zone. U.S. Pat. No. 5,177,114 discloses a process for the conversion of natural gas to gasoline grade liquid hydrocarbons and/or olefin(s) by converting the natural gas to a synthesis gas, and converting the synthesis gas to crude methanol and/or dimethyl ether and further converting the crude methanol/dimethyl ether to gasoline and olefin(s). International Patent Application No. 93/13013 to Kvisle et al. relates to an improved method for producing a silicon-alumino-phosphate catalyst which is more stable to deactivation by coking. The patent discloses that after a period of time, all such catalysts used to convert methanol to

olefin(s) (MTO) lose the active ability to convert methanol to hydrocarbons primarily because the microporous crystal structure is coked; that is, filled up with low volatility carbonaceous compounds which block the pore structure. The carbonaceous compounds can be removed by conventional methods such as combustion in air.

5 EPO publication No. 0 407 038A1 describes a method for producing dialkyl ethers comprising feeding a stream containing an alkyl alcohol to a distillation column reactor into a feed zone, contacting the stream with a fixed bed solid acidic catalytic distillation structure to form the corresponding dialkyl ether and water, and concurrently fractionating the ether product from the water and unreacted materials.

10 U.S. Pat. No 5,817,906 describes a process for producing light olefin(s) from a crude oxygenate feedstock comprising alcohol and water. The process employs two reaction stages. Firstly, the alcohol is converted using reaction with distillation to an ether. The ether is then subsequently passed to an oxygenate conversion zone containing a metal aluminosilicate catalyst to produce a light olefin stream.

15 There is one well known chemistry that can be employed to produce olefin(s) from alcohol(s), i.e. the one called Methanol to olefin(s)- MTO- process.

This method - MTO Process - can be described as the dehydrative coupling of methanol to olefin(s). This mechanism is thought to proceed via a coupling of C1 fragments generated by the acid catalysed dehydration of methanol, possibly via a
20 methyloxonium intermediate. However the main disadvantage of the said MTO process is that a range of olefin(s) are co-produced together with aromatic and alkane by-products, which in turn makes it very difficult and expensive to recover the desired olefin(s).

Molecular sieves such as the microporous crystalline zeolite and non-zeolitic catalysts, particularly silicoaluminophosphates (SAPO), are known to promote the
25 conversion of oxygenates by methanol to olefin (MTO) chemistry to hydrocarbon mixtures. Numerous patents describe this process for various types of these catalysts: U.S. Pat. Nos. 3,928,483, 4,025,575, 4,252,479 (Chang et al.); 4,496,786 (Santilli et al.); 4,547,616 (Avidan et al.); 4,677,243 (Kaiser); 4,843,183 (Inui); 4,499,314 (Seddon et al.); 4,447,669 (Harmon et al.); 5,095,163 (Barger); 5,191,141 (Barger); 5,126,308 (Barger);
30 4,973,792 (Lewis); and 4,861,938 (Lewis).

This reaction has a high activation energy, possibly in the methanol or dimethylether activation step so in order to achieve high conversion there is often a need

for high temperatures e.g. 450°C, to drive the reactions forward. Conventionally various means such as a heated catalyst recycle, and downtherm heating systems have been implemented in such systems in order to obtain these high temperature conditions.

5 However, unfortunately operating at these said high temperatures leads to major problems such as catalyst deactivation, coking and by-product formation. In order to avoid these problems the reactions may be operated at lower temperatures, but this necessitates an expensive recycle of intermediates and reactants.

Another major disadvantage associated with this method is that the aromatic and alkane by-products are co-produced together with the olefin(s) and are both difficult and
10 expensive to separate from the desired products e.g. separating ethylene and ethane is an expensive process.

These and other disadvantages of the prior art show that there is a need for an improved and/or alternative process for the production of C2+ olefin(s) from alcohols.

The solution is provided by the present invention which relates specifically to a
15 new non-MTO process and which proceeds via the dehydration of the C2+ alcohol(s) into olefins.

The present invention relates to a process for the production of alkene(s) from a feedstock comprising at least one monohydric aliphatic paraffinic alcohol(s) having from 2 to 3 carbon atoms wherein the monohydric aliphatic paraffinic alcohol(s) containing 2 to 3
20 carbon atoms are dehydrated into the corresponding same carbon number alkene(s), characterised in that the alcohol(s) present in the feedstock consist of ethanol and propanol(s), preferably ethanol and n-propanol and/or iso-propanol, and most preferably ethanol and n-propanol. That is to say, the feedstock does not comprise C3+ alcohols, e.g. butanols or higher carbon number alcohols..

25 According to a preferred embodiment, the present invention provides a process for the conversion of hydrocarbon to alkene(s) comprising the steps of

- a. converting in a syngas reactor hydrocarbon into a mixture of carbon oxide(s) and hydrogen,
- b. converting the said mixture of carbon oxide(s) and hydrogen from step a in the
30 presence of a particulate catalyst in a reactor under a temperature comprised between 200 and 400°C and a pressure of 50 to 200 bar into a feedstock comprising at least one monohydric aliphatic paraffinic alcohols having from 2 to 3 carbon

atoms alcohols,

- c. treating the said feedstock from step b in order to remove the C3+ alcohols and/or the methanol thereof, and
- d. dehydrating the treated feedstock of step c into the corresponding same carbon number alkene(s).

5

According to a preferred embodiment of the present invention, the dehydration step is performed in a vapour phase or liquid phase reactor e.g. batch, flow, semi-continuous batch reactors, reactive distillation column at elevated pressure and temperature to produce the corresponding same carbon number alkene(s) and, optionally ether(s).

10

According to an embodiment of the present invention the pressure at which the dehydration step is operated is more than 0.5 MPa but less than 4.0 MPa and preferably more than 1.8 MPa but less than 2.7 MPa. The temperature employed during this dehydration step is controlled by the boiling point of the specified components at the given pressure, and it is preferably less than 300°C and more preferably less than 250°C.

15

Temperatures and pressures outside of the stated limits are not excluded, however they do not fall under the preferred embodiments of the present invention.

20

According to the present invention the method for the production of alkene(s) from alcohol(s) proceeds via the dehydration of C2 and C2+ alcohols; for this to occur one or more alpha hydrogen(s) must be present e.g. Phenol, neo-pentyl glycol, for example 2,2-dimethyl-propan-1-ol will not dehydrate via this mechanism whereas ethanol, n-propanol and t-butanol will. These dehydration reactions are distinguished from the aforementioned MTO process in that although no coupling of carbon fragments is required in the dehydration process a C-C double bond is formed during the elimination of water and as a result very high selectivity can be achieved. In general the conditions employed in

25

MTO process are much more severe than those employed in alcohol dehydration. Advantageously, according to our preferred embodiment, the process of the present invention i.e. the conversion of the feedstock to alkene(s) and, optionally ether(s) is conducted in a single reactive distillation column thereby reducing the capital and energy costs.

30

The dehydration of the feedstock is believed to proceed by either the direct dehydration to alkene(s) and water;

Equation 1



5 or via an ether intermediate;

Equation 2



10 Equation 3



where R and R' are an ethyl, propyl, butyl or pentyl group.

15 All of the main reactions occurring in the dehydration vessel shown above are catalysed by acid catalysts. Equation 1, shows the endothermic direct elimination of alcohol to alkene(s) and water. Competing with Equation 1 are Equations 2 and 3; the exothermic etherification reaction (Equation 2), and the endothermic elimination of ether(s) to produce alkene(s) and alcohol (Equation 3). However, the overall dehydration of alcohols to alkene(s) is an endothermic process.

20 Equations 1, 2 and 3 are all equilibrium limited. However, according to an embodiment of the present invention, as all three reactions occur in a reactive distillation column and, there is increased conversion for equilibrium limited reactions as a result of the continuous removal of products via distillation. This benefit is expected based on Le Châtelier's Principle, which states that if any disturbance is imposed on a system at
 25 equilibrium, the system will adjust itself to regain the equilibrium. Therefore according to this embodiment the conversion of an equilibrium limited reaction is increased beyond its thermodynamic limitation because of the continuous removal of the products via distillation and as a result there is an increased concentration of the reactants. Hence, the olefin product becomes concentrated at the top of the reactive distillation column together

with the ether(s) and is termed the head product; and the water is concentrated in the base of the reactive distillation column as

is known as the base product. The alcohol(s) and ether(s) having water azeotropes are of intermediate boiling point and are concentrated in the reaction zone of the reactive
5 distillation column.

It is well known that when using a heterogeneous catalyst in the vapour phase ethanol inhibits the elimination of diethyl ether by virtue of its stronger catalyst interaction. This can lead to a sequence of reactions. For example, when Ethanol is fed into a flow reactor with a dehydration catalyst, Equations 1 and 2 predominate until the ethanol
10 concentration drops to a level where the ether can effectively compete for the catalytic sites. The competition of two reactants for an active site can be described by Langmuir Hinselwood mechanism (e.g. Chemical Kinetics 3rd edition author K.J.Laidler P 249 - 251, Harper and Row publishers New York). An effect of this interaction for batch or
15 flow reactors has been found to reduce the rate of ethylene production until the ethanol has been mostly consumed e.g. Collection of czechoslovak chemical comms 1986 51 (4) p763-73 V.Moravek and M.Kraus

However, according to this preferred embodiment, the present invention through a combination of reaction and distillation this limitation can be overcome. For example in the reactive distillation column the ether(s) and alcohol(s) are separated accordingly by
20 their azeotropes and by their boiling points. So ether(s) are concentrated onto the catalyst at positions different from the alcohol(s) and hence this will result in decreased alcohol inhibition of the reaction.

The reactive distillation column in which the process is preferably conducted refers to a combined distillation column and reactor. The internals of the reactive distillation
25 column are arranged to provide a plurality of "theoretical plates" which assist the separation of the products from the reactants. The internals of the column are usually those used in conventional distillation for example, sieve plates, unstructured and structured packing, bubble cap and mixtures thereof. This particular apparatus is very effective at promoting vapor-liquid contacting and, therefore fractional distillation of the product(s)
30 from the reactants. The catalyst(s) employed can be either homogeneous or heterogeneous, homogenous catalyst(s) being the preferred option.

According to the present invention when using a heterogeneous catalyst(s), the

catalyst(s) are positioned so that they have maximum interaction with reactants and reaction intermediates; this can be achieved by supporting the catalyst(s) on the column internals, for example ion exchange resins have been supported; in cloth bales, on sieve plates, fibreglass bags, in methyl tertiary butyl ether (MTBE) reactive distillation plants.

5 The catalyst(s) can also provide the column packing, for example they can be coated, extruded, moulded into raschig rings or any other known type of column packing. The catalyst(s) can also be inter-dispersed with unmodified column packings. Heterogeneous catalyst(s) have an added advantage in that the separation of the reactants and products is trivial, that is it is done by physical separation e.g. filtration.

10 According to the present invention suitable heterogeneous catalyst(s) include but are not limited to insoluble heteropolyacids, sulphonated supports (e.g. Nafion and ion exchange resins) zeolites, metal modified zeolites, mordenites and mixtures thereof; preferably heteropolyacids and ion-exchange resins; more preferably heteropolyacids; and most preferably salts of 12-tungstosilicic acid and 18-tungstophosphoric acid.

15 The heteropolyacids of the present invention are complex, high molecular weight anions comprising oxygen-linked polyvalent metal atoms. Typically, each anion comprises 12-18, oxygen-linked polyvalent metal atoms. The polyvalent metal atoms, known as peripheral atoms, surround one or more central atoms in a symmetrical manner. The peripheral atoms may be one or more of molybdenum, tungsten, vanadium, niobium, 20 tantalum, or any other polyvalent metal. The central atoms are preferably silicon or phosphorus, but may alternatively comprise any one of a large variety of atoms from Groups I-VIII in the Periodic Table of elements. These include copper, beryllium, zinc, cobalt, nickel, boron, aluminium, gallium, iron, cerium, arsenic, antimony, bismuth, chromium, rhodium, silicon, germanium, tin, titanium, zirconium, vanadium, sulphur, 25 tellurium, manganese nickel, platinum, thorium, hafnium, cerium, arsenic, vanadium, antimony ions, tellurium and iodine. Suitable heteropolyacids include Keggin, Wells-Dawson and Anderson-Evans-Perloff heteropolyacids. Specific examples of suitable heteropolyacids are as follows:

18-tungstophosphoric acid	-	H ₆ [P ₂ W ₁₈ O ₆₂].xH ₂ O
30 12-tungstophosphoric acid	-	H ₃ [PW ₁₂ O ₄₀].xH ₂ O
12-molybdophosphoric acid	-	H ₃ [PMo ₁₂ O ₄₀].xH ₂ O
12-tungstosilicic acid	-	H ₄ [SiW ₁₂ O ₄₀].xH ₂ O

12-molybdosilicic acid - $H_4[SiMo_{12}O_{40}].xH_2O$
 Cesium hydrogen tungstosilicate - $Cs_3H[SiW_{12}O_{40}].xH_2O$

and the free acid or partial salts of the following heteropolyacids:

Potassium tungstophosphate - $K_6[P_2W_{18}O_{62}].xH_2O$
 5 Sodium molybdophosphate - $Na_3[PMo_{12}O_{40}].xH_2O$
 Ammonium molybdodiphosphate - $(NH_4)_6[P_2Mo_{18}O_{62}].xH_2O$
 Potassium molybdodivanado phosphate - $K_5[PMoV_2O_{40}].xH_2O$

The heteropolyacids employed in the present invention may have molecular weights of more than 700 and less than 8500, preferably more than 2800 and less than
 10 6000. Such heteropolyacids also include dimeric complexes.

To prepare the catalysts that can advantageously be used in the present invention, a catalyst support is impregnated with a non-aqueous solution of the heteropolyacid and the catalyst is precipitated by preparing a low solubility salt in situ. Such a solution is prepared by dissolving the heteropolyacid in a non-aqueous solvent. Suitable solvents
 15 include polar solvents such alcohols, ketones and aldehydes. Suitable alcohols include C_1 to C_8 alcohols, preferably, C_1 to C_4 alcohols and most preferably methanol and ethanol. Suitable ketones are C_2 to C_4 ketones e.g. acetone. The concentration of heteropolyacid in the solution is preferably 10 to 80 wt %, more preferably 20 to 60 wt % and most preferably 30 to 50 wt %.

20 The impregnation may be carried out using the incipient wetness technique, with a partial neutralization stage to prepare the insoluble catalyst. Any suitable drying technique may be employed, with evaporation in a standard bench-top rotary evaporator being preferred.

Alternatively, the catalyst support may be immersed in the aqueous solution and
 25 left to soak and then a solution of counter ion added to precipitate the HPA onto the support. The impregnated support may then be washed and dried. This may be achieved using any conventional separation technique, including, for example, decantation and/or filtration. Once recovered, the impregnated support may be dried, preferably by placing the support in an oven. Alternatively, or additionally, a desiccator may be employed. The
 30 amount of heteropolyacid impregnated on the support is suitably in the range of 10 wt % to 60 wt % and preferably 30 wt % to 50 wt % based on the total weight of the heteropolyacid and the support.

Suitable catalyst supports include silica supports, such as silica gel supports and supports produced by the flame hydrolysis of SiCl_4 . Preferred supports are substantially free of extraneous metals or elements which might adversely affect the catalytic activity of the system. Thus, suitable silica supports are at least 99% w/w pure. Impurities amount to less than 1% w/w, preferably less than 0.60% w/w and more preferably less than 0.30% w/w. The pore volume of the support is 0.3-1.2 ml/g, preferably 0.6-1.0 ml/g. The average pore radius (prior to use) of the support is 10 to 500Å, preferably 30 to 100Å. The support has a crush strength of at least 2 Kg force, suitably at least 5 Kg force, preferably at least 6 Kg and more preferably at least 7 Kg. The bulk density of the support is at least 380 g/l, preferably at least 440 g/l.

Suitable silica gel supports include Grace 57 and 1371, Grace No. 1371 being preferred. Grace No. 1371 has an average particle size of 0.1-3.5 mm. However, these particles may be crushed and sieved to smaller sizes of, for example, 0.5-2 mm, if desired.

Suitable supports produced by the flame hydrolysis of SiCl_4 may be prepared by the pelletisation of AEROSIL® 200 (ex Degussa). An example of such a support is Support 350. Suitable pelletisation procedures are described in US Patent 5,086,031, particularly in the examples. The average particle diameter of the pellets are 2 to 10 mm, preferably 4 to 6 mm.

A further embodiment of the said invention is where the catalyst support, as used in the present invention, is first treated with a fluorinating agent; it is believed that due to the highly electronegative nature of fluorine the resulting effect is that the electronic properties of catalyst support will be modified and it is believed that this allows the following advantages: inertness of support and/or improved acidity, thus improving the overall selectivity and/or activity of the catalyst.

Fluorinating agents that can be used to treat the support may comprise, but are not limited to; hydrogen fluoride, aqueous solutions of hydrofluoric acid, mixtures of hydrofluoric acid with lesser amounts of other acids such as hydrochloric or acetic acids or acid solutions to which certain aluminum salts have been added or weak solutions of hydrofluosilicic acid containing an aluminum salt. The treatment of the said catalyst support with aqueous hydrofluoric acid solutions may be performed by soaking the catalyst particles in a solution of the acid of between 1 to 8% acid for a period of between 1 to 24 hours. The fluorinated support can then be impregnated with the catalyst of choice.

According to the present invention homogeneous catalyst(s) can also be employed in the dehydration of the feedstock to alcohol(s).

According to an embodiment of the present invention homogeneous catalyst(s) can also be employed in the reactive distillation column. The preferred homogeneous catalyst(s) are of a higher boiling point than the reactants and products and as result will predominately reside in the column liquid phase(s) and eventually concentrate in the reaction kettle. The interaction between these said catalyst(s) and reactants in the reaction zone can be controlled by varying the amount of catalyst(s) recycled into the reactive distillation column and by changing the columns' internals to increase the liquid hold up. The separation of the homogeneous catalysts from the water accumulating in the reboiler can be achieved by condensing above the reboiler a vapour stream of predominately pure water. An advantage of using homogeneous catalyst(s) is the concentration of catalyst can be altered freely. Also that the deactivated catalysts can easily be eliminated from the system and replaced by fresh catalyst. The recovered homogeneous catalyst solution from the reboiler is then recycled to the column. One or more addition points maybe employed to concentrate the catalyst where required.

Suitable homogeneous catalysts include but are not limited to sulphonic acids such as methane sulphonic acid, para-toluene sulphonic acid, triflic acid, sulphuric acids, heteropolyacids and phosphoric acid; phosphoric acid and organosulphonic acids are preferred.

When a reactive distillation column is used the said ether(s) that are produced are essentially C₂-C₃ alcohol derived ether(s) such as diethyl ether, n-propyl ether, iso-propyl ether and mixed ethers; such as ethyl-iso-propyl ether.

The thermodynamic studies have shown that the present invention allows the dehydration of a mixture of ethanol and propanol(s) into corresponding alkene(s) to be conducted with a much higher selectivity and an unexpected high conversion. This said higher conversion improves the economics of the process dramatically as due to a lack of by-products there is no longer a need to perform expensive separations of by-products and products as with the MTO process.

The crude oxygenate feedstock that is dehydrated into alkene(s) comprises of at least one C₂-C₃ alcohol which may be, for example, ethanol, n-propanol, iso-propanol, and mixtures thereof, the oxygenate feedstock can comprise homo and mixed ethers of these

alcohols. Typically, a mixture of at least two alcohols will be employed which will be selected from monohydric aliphatic paraffinic alcohols having from 2 to 3 carbon atoms, preferably a mixture of at least two alcohols selected from monohydric aliphatic paraffinic alcohols having from 2 to 3 carbon atoms will be used and most preferably a mixture of ethanol and n-propanol will be used.

A characterized feature according to the present invention is that the feedstock to be dehydrated does not comprise C3+ alcohols. For the purpose of the present invention and appending claims, "does not comprise C3+ alcohols" means that the total C3+ alcohols, i.e. the alcohols with more than 3 carbon atoms (e.g. n-butanol, iso-butanol, pentanol), content of the feedstock to be dehydrated is less than 1 wt%, preferably less than 0.1 wt%.

Indeed the Applicants have unexpectedly discovered that the presence of C3+ alcohols was detrimental to the alkene(s) production process according to the present invention. Conventional distillation can be used according to the present invention in order to reduce/eliminate the C3+ alcohols from the alcohols feedstock.

Another preferred embodiment according to the present invention is that the alcohol(s) feedstock does not comprise methanol. For the purpose of the present invention and appended claims, "does not comprise methanol" means that the methanol content of the alcohol(s) feedstock is less than 5 wt%, preferably less than 1 wt%, and most preferably less than 0.1 wt%.

Conventional distillation can be used according to the present invention in order to reduce/eliminate the methanol from the alcohols feedstock.

According to the present invention water is permissible in the crude oxygenate feedstock; in the preferred mode of operation the crude oxygenate feedstock may comprise up to 50 wt % of water. In another mode, that utilises the ability of a reactive distillation column to effectively separate water, crude bioethanol and other bioalcohol(s) which can comprise mostly of water may be used.

According to the most preferred embodiment of the present invention the C2-C3 alcohols together with the water represent at least 90 wt % of the crude oxygenate feedstock introduced into the reactive distillation column.

In a preferred embodiment, the reactive distillation can have as a co-feed a stream of ethers as previously defined hereabove.

Claims

1. Process for the production of alkene(s) from a feedstock comprising at least one monohydric aliphatic paraffinic alcohols having from 2 to 3 carbon atoms wherein the monohydric aliphatic paraffinic alcohol(s) containing 2 to 3 carbon atoms are dehydrated
5 into the corresponding same carbon number alkene(s), characterised in that the alcohol(s) present in the feedstock consist of ethanol and propanol(s).
2. Process for the conversion of hydrocarbon to alkene(s) comprising the steps of
 - a. converting in a syngas reactor hydrocarbon into a mixture of carbon oxide(s) and hydrogen,
 - 10 b. converting the said mixture of carbon oxide(s) and hydrogen from step a in the presence of a particulate catalyst in a reactor under a temperature comprised between 200 and 400°C and a pressure of 50 to 200 bar into a feedstock comprising at least one monohydric aliphatic paraffinic alcohols having from 2 to 3 carbon atoms alcohols,
 - 15 c. treating the said feedstock from step b in order to remove the C3+ alcohols and/or the methanol thereof, and
 - d. dehydrating the treated feedstock of step c into the corresponding same carbon number alkene(s).
3. Process according to claim 2 wherein both methanol and the C3+ alcohols are
20 removed from the feedstock of step b.
4. Process according to any of the preceding claims wherein the catalyst used for dehydrating the alcohols into alkene(s) is a heterogeneous catalyst chosen amongst insoluble heteropolyacids, sulphonated supports (e.g. Nafion and ion exchange resins) zeolites, metal modified zeolites, mordenites and mixtures thereof; preferably
25 heteropolyacids and ion-exchange resins; more preferably heteropolyacids; and most preferably salts of 12-tungstosilicic acid and 18-tungstophosphoric acid.
5. Process according to any of claims 1 to 3 wherein the catalyst used for dehydrating the alcohols into alkenes is a homogeneous catalyst, preferably a higher boiling point - than the reactants and products - catalyst.
- 30 6. Process according to claim 5 wherein the catalyst is chosen amongst sulphonic acids such as methane sulphonic acid, para-toluene sulphonic acid, triflic acid, sulphuric acids, heteropolyacids and phosphoric acid; phosphoric acid and organosulphonic acids.

7. Process according to any of the preceding claims wherein the alcohols present in the feedstock that is dehydrated into alkene(s) consist of ethanol and propanol(s), ethanol and n-propanol, or ethanol and iso-propanol.

8. Process according to any of the preceding claims wherein the feedstock that is dehydrated into alkene(s) also comprises homo and/or mixed ethers of ethanol and/or propanol(s).

9. Process according to any of claims 7 or 8 wherein the alcohols consist of a mixture of ethanol and n-propanol.

10. Process according to any of the preceding claims wherein the feedstock that is dehydrated into alkene(s) contains less than 1 wt%, most preferably less than 0.1 wt%, of methanol.

11. Process according to any of the preceding claims wherein the feedstock that is dehydrated into alkene(s) contains less than 1 wt%, preferably less than 0.1 wt% C3+ alcohols.

12. Process according to any of the preceding claims wherein an additional ether feed is added to the alcohol feed that is dehydrated.

13. Process according to any of the preceding claims wherein the pressure at which the dehydration step is operated is more than 0.5 MPa but less than 4.0 MPa and preferably more than 1.8 MPa but less than 2.7 MPa.

14. Process according to any of the preceding claims wherein the temperature employed during the dehydration step is less than 300⁰C, preferably less than 250⁰C

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INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2006/002430

A. CLASSIFICATION OF SUBJECT MATTER INV. C07C1/24 C07C11/02		
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, BEILSTEIN Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 398 050 A (HOFSTADT ET AL) 9 August 1983 (1983-08-09) the whole document	1-14
X	RAVI NARAYAN AND MICHAEL JERRY ANTAL JR.: "Influence of Pressure on the Acid-Catalyzed Rate Constant for 1-Propanol Dehydration in Supercritical Water" J. AM. CHEM. SOC., vol. 112, 1990, pages 1927-1931, XP002361367 the whole document	1-14
A	DE 30 05 551 A1 (SUED-CHEMIE AG) 20 August 1981 (1981-08-20) example 7; table I	1-14
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> 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 *E* earlier document but published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *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 *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *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 8 August 2006		Date of mailing of the International search report 17/08/2006
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Cooper, S

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Information on patent family members

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