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(54) Title: PROCESS FOR THE PRODUCTION OF ETHYLENE GLYCOL

(57) Abstract: The present invention provides a process for the production of monoethylene glycol, said process comprising the steps of: (a) reacting ethylene oxide with a ketone in the presence of a solid acidic catalyst to form a ketal; and (b) hydrolysing the ketal with water to form monoethylene glycol, wherein the ketone contains in the range of from 4 to 20 carbon atoms.



WO 2011/000830 A1

PROCESS FOR THE PRODUCTION OF ETHYLENE GLYCOL

Field of the Invention

This invention relates to a process for the production of ethylene glycol.

Background of the Invention

5 Ethylene glycol, also known as mono-ethylene glycol (MEG), is widely used as an antifreeze, e.g. in the automotive industry, and as a raw material in the manufacture of polyethylene terephthalate (PET) resin and fibres.

10 Ethylene glycol is generally produced from ethylene oxide (EO), which itself may be produced by direct oxidation of ethylene in the presence of a silver catalyst. Direct conversion of EO to MEG can be carried out via hydrolysis with water under pressure or catalytic
15 conditions. Such processes use a greater than stoichiometric amount of water, which must then be removed from the product MEG.

 The selective synthesis of ethylene glycol via the intermediate ethylene carbonate has been described in US
20 6,080,897 and US 6,187,972. Ethylene carbonate can be obtained by reaction of ethylene oxide with carbon dioxide and can be selectively hydrolysed to form MEG in high yield.

 US 5,072,059 describes a two-step reaction process
25 for converting ethylene oxide to MEG by first reacting the ethylene oxide with acetone and then hydrolysing the resultant 2,2-dimethyl-1,3-dioxolane with water to provide MEG. The hydrolysis step, in particular, was found to proceed with high selectivity and only a
30 slightly greater than stoichiometric amount of water was

required for the hydrolysis step. However, the overall process is affected by UV and odour problem resulting from the formation of by-products such as 1,4-dioxane, diacetone alcohol and mesityl oxide.

5 A process for the production of 1,2-alkanediols by reaction of a 1,2-epoxyalkane, specifically those containing 6 to 24 carbon atoms, with an aldehyde or ketone and subsequent hydrolysis is described in JP 2005126357 A2. The disclosed process uses a much higher
10 than stoichiometric quantity of water in order to effect hydrolysis.

 It would be advantageous to develop a process for the production of MEG that avoided the use of large amounts of water, which must then be removed from the
15 product. A process in which the production of noxious by-products is avoided would also be advantageous.

 Further, it would be beneficial to be able to integrate the process for the production of MEG from EO with the process for the production of the starting
20 material EO. In the conventional process for the production of EO, after reaction of ethylene with oxygen over a silver catalyst, the resultant EO is absorbed from the product mixture in a separate absorber using water, which has relatively low solubility for ethylene oxide,
25 as the absorbent and is then stripped from the water at increased temperature.

Summary of the Invention

 The present invention provides a process for the production of monoethylene glycol, said process
30 comprising the steps of:

- (a) reacting ethylene oxide with a ketone in the presence of a solid acidic catalyst to form a ketal;
and

(b) hydrolysing the ketal with water to form monoethylene glycol, wherein the ketone contains in the range of from 4 to 20 carbon atoms.

5 Brief Description of the Drawings

Figure 1 shows a schematic reactor set-up suitable for the process of the present invention;

Figure 2 shows a schematic reactor set-up suitable for an embodiment of the process of the present
10 invention;

Figure 3 shows a schematic reactor set-up suitable for a further embodiment of the process of the present invention;

Figure 4 is a plot of the production of ketals vs
15 time for the Examples.

Figure 5 is a table showing the by-product make for the Examples.

Figure 6 is a plot of the production of ketals vs time for further Examples.

Figure 7 is a table showing the by-product make for the further Examples.

Detailed Description of the Invention

The present invention relates to a method suitable for the production of monoethylene glycol. The inventive
25 process is a two-step process carried out by first reacting EO with a ketone selected from the group consisting of those ketones containing in the range of from 4 to 20 carbon atoms and then hydrolysing the ketal thus formed in order to provide the desired MEG in high
30 selectivity, without the formation of malodorous mesityl oxide. In a preferred embodiment of the present invention, the process can be integrated with the process used to form the starting material, EO.

In the process of the present invention, the EO is reacted with a ketone selected from the group consisting of ketones containing 4 to 20 carbon atoms. Preferably, the ketone contains from 5 to 12 carbon atoms. The ketone may be a mono-ketone (containing one ketone functional group), a di-ketone (containing two ketone functional groups) or a poly-ketone (containing multiple ketone functional groups). The ketone may be cyclic or acyclic and the ketone carbon chain may be substituted or unsubstituted and branched or unbranched. Specific examples of suitable non-cyclic ketones include methyl ethyl ketone, diethyl ketone and acetophenone. Preferably, the ketone is a cyclic mono- or di-ketone. Specific examples of suitable cyclic ketones include, but are not limited to, cyclopentanone, cyclohexanone and 1,4-cyclohexandione.

The EO is reacted with the ketone in the presence of a solid acidic catalyst. The solid acidic catalyst, to be employed in the process according to the invention, is preferably one or more acid activated clay. Especially important clays are those of the montmorillonite series, such as montmorillonite, beidellite, nontronite, hectorite, saponite and sauconite. Acid activated clays are the clays which have been treated with mineral acids, such as hydrochloric acid or sulphuric acid. The acid activated clays are prepared by mixing crushed raw material with water to form a slurry to which the mineral acid amounting to about 35% of the total dry weight of the clay is added. The mixture is then treated with live steams for 5 to 6 hours, after which the whole mixture is dumped into fresh water and then washed, until it is substantially free of acids.

In the reaction of the EO with the ketone according to the present invention, the molar ratio of ketone to ethylene oxide may suitably range from 1:1 to 8:1, preferably from 1:1 to 5:1, although higher ranges are not excluded.

The reaction of the ketone and EO is preferably carried out at a temperature of at least 20 °C, more preferably at least 30 °C, most preferably at least 40 °C. The upper limit for the temperature of the reaction of the ketone and EO is at most 120 °C, more preferably at most 100 °C, most preferably at most 80 °C.

After reaction of the EO with the ketone, the thus-formed ketal is then hydrolysed with water in order to form the desired MEG.

Before hydrolysis, the ketal may be separated from the product mixture. Alternatively, the product mixture from the reaction of the EO with the ketone may be used without further purification.

The hydrolysis may be carried out in the presence of an acidic catalyst. Preferably, the acidic catalyst is selected from the group consisting of acid activated clays and acidic ion exchange resins. Suitable acid activated clays are those listed above as suitable for the catalysis of the reaction of EO with the ketone.

There are three types of acidic ion exchange resins, i.e. the strongly acidic ion exchange resins of the sulfonic type, the acidic ion exchange resins of the acrylate type and the weakly acidic ion exchange resins of the methacrylate type.

Examples of commercially available weakly acidic ion exchange resins of the methacrylate type are those known by the trade marks AMBERLITE IRC-50, AMBERLITE GC-50, AMBERLITE IRP-64 and AMBERLITE IRP-88.

Examples of commercially available acidic ion exchange resins of the acrylate type are those known by the trade marks AMBERLITE IRC-86, AMBERLITE IRC-76, IMAC HP 336 and LEWATIT CNP 80.

5 Preferably, the acidic ion exchange resin used in the process of the present invention are of the sulfonic type. Suitable, commercially available examples of such are those known by the trademarks AMBERLYST 15, AMBERJET 1500H, AMBERJET 1200H, DOWEX MSC-1, DOWEX 50W, DIANON
10 SK1B, LEWATIT VP OC 1812, LEWATIT S 100 MB and LEWATIT S 100 G1. These strongly acidic ion exchange resins are available in H^+ form and in salt form, such as the Na^+ form. The H^+ form is catalytically active in the process of the present invention. When this material is used in
15 this process, the product stream having passed through the ion exchange resin may become acidic. Using a mixture of the strongly acidic ion exchange resin in its H^+ form and its salt form has the advantage that the pH of the product stream, having passed through the ion exchange
20 resin, remains close to neutral.

 If an acidic ion exchange resin is used as the hydrolysis catalyst then, in order to allow for possible exhaustion of the acidic ion exchange resin during operation, it is advantageous to operate the ion exchange
25 resin reactor bed in two or more separate vessels, to allow the process to be switched between the two vessels, maintaining continuous operation.

 Exhausted acidic ion exchange resin can be regenerated by treatment with an acid, which is stronger
30 than the acid groups in the resin matrix, such as HCl and H_2SO_4 . Hot sulfuric acid of 0.1 to 2 N has been proven to be effective.

In the hydrolysis reaction, the molar ratio of the water added to the ketal present is at least 1:1 and is preferably as close to stoichiometric as possible.

However, a molar ratio of water to ketal in the range of
5 from 1:1 to 5:1, preferably in the range of from 1:1 to 4:1, more preferably in the range of from 1:1 to 3:1, most preferably in the range of from 1:1 to 2:1 may be used.

The hydrolysis of the ketal may take place at any
10 suitable temperature. The hydrolysis is preferably carried out at a temperature of at least 20 °C, more preferably at least 40 °C, most preferably at least 60 °C. The upper limit for the temperature of the hydrolysis reaction is preferably at most 200 °C, more preferably at
15 most 120 °C, even more preferably at most 100 °C, most preferably at most 80 °C.

The process of the invention may be carried out in batch operation. However, in particular for large scale
20 embodiments it is preferred to operate the process continuously.

Such a continuous process may be carried out in a fixed bed reactor, operated in up-flow or down-flow. Down-flow operation is preferred. The reactors of the present invention may be maintained under isothermal,
25 adiabatic or hybrid conditions. Isothermal reactors are generally shell- and tube reactors, mostly of the multi-tubular type, wherein the tubes contain the catalyst and a coolant passes outside the tubes. Adiabatic reactors are not cooled, and the product stream leaving them may
30 be cooled in a separate heat exchanger.

In order to accommodate any swelling of an Ion Exchange Resin that may occur during operation, the reactor volume can advantageously be greater than the

volume occupied by the catalyst therein, for example in the range of from 10 to 70 vol% greater.

After hydrolysis, the product mixture may then be subjected to a purification step in which the MEG is separated from any contaminants, including the ketone. Such a process is generally carried out by distillation. However, as MEG is highly water-soluble, if a ketone which has very low water solubility, such as cyclopentanone, is used, then a simple organic/aqueous phase separation procedure may be applied.

Alternatively, the hydrolysis reaction may be carried out in a reactor operating under reactive distillation conditions. In such a reactor, the catalyst will preferably be contained in vertically stacked trays or in the packing of a packed column. The ketal and water are fed in to the reaction zone of the reactive distillation reactor or column. The ketone produced during hydrolysis, as well as any excess ketone remaining in the reaction mixture, is removed as the lowest boiling fraction of the reaction mixture as the reaction progresses. This results in an MEG-rich high boiling fraction which is removed as the bottom product as it is formed.

In an embodiment of the present invention wherein a ketone with a higher boiling point than water is used, such a reactive distillation set up may also be suitable if the ketone forms a low boiling azeotrope with water and excess water is used in the hydrolysis reaction. In such an embodiment, the azeotrope of ketone and water will form the lowest boiling fraction and be removed as the hydrolysis reaction progresses.

Following the hydrolysis reaction and separation of the MEG from the ketone, further purification steps, e.g. by distillation, may be carried out in order to provide the MEG product of the necessary purity.

5 A schematic drawing of a reactor set-up suitable for use in the present invention, in combination with the preparation of EO and the purification of the product MEG is shown in Figure 1.

10 In a particularly preferred embodiment of the present invention, the process for making MEG is integrated with the process used to form the starting material, EO. As stated above, in the process for the production of EO, after reaction of ethylene with oxygen over a silver catalyst, the resultant EO is absorbed from
15 the product mixture in a separate EO absorber using water as the absorbent and is then stripped from the water at increased temperature.

 In this embodiment of the process of the present invention, the ketone to be reacted with the EO may be
20 used as the absorbent in the EO absorber. Using the ketone as an absorbent removes the need for using water, which has relatively low solubility for ethylene oxide, and also removes the requirement for a separate stripping step. The EO and ketone are then in place for carrying
25 out the reaction to form the ketal. A schematic drawing of a reactor set-up suitable for use in this embodiment of the present invention is shown in Figure 2.

 In a further preferred embodiment, termed herein 'reactive absorption', the EO absorber may be replaced by
30 a ketalisation reactor in which both the ketone and catalyst are present under conditions such that the EO reacts with the ketone and the need for a separate absorption step is avoided entirely.

Using a low boiling ketone, such as acetone, in such a set-up would be entirely unsuitable due to the temperatures necessary for the absorption step.

This embodiment of the process of the present invention may be carried out in batch operation. However, in particular for large scale embodiments it is preferred to operate the process continuously.

Such a continuous process for reactive absorption will preferably be carried out in a fixed bed reactor, operated in up-flow or down-flow. Down-flow operation is preferred. The reactor may be maintained under isothermal, adiabatic or hybrid conditions. Isothermal reactors are generally shell- and tube reactors, mostly of the multi-tubular type, wherein the tubes contain the catalyst and a coolant passes outside the tubes. Adiabatic reactors are not cooled, and the product stream leaving them may be cooled in a separate heat exchanger.

In this embodiment, the ketone is reacted with the EO in the presence of a solid acidic catalyst and in the presence of the product mixture from an EO reactor. A schematic drawing of a reactor set-up suitable for use in this embodiment of the present invention is shown in Figure 3.

The invention will be illustrated by the following non-limiting examples.

Examples

General Procedure

The ketalisation reactions were carried out with EO and a number of different ketones (acetone (comparative), cyclohexanone, cyclopentanone, diethylketone (DEK), methylethylketone (MEK), acetophenone) in a 500 ml Medimex autoclave batch reactor. The progress of the ketalisation reactions was followed with the aid of GC-

analysis. During sample-taking the sample containers were cooled with solid CO₂ so that almost all the EO still present can be trapped.

At the start of each experiment, the reactor was charged with the ketone, 3g of catalyst (K10; montmorillonite) and toluene (to an overall reaction volume of 275 ml) and then flushed with He at 15 bar. After flushing, 15 bar He-pressure was applied to the vessel and the temperature was raised to 40 °C (60 °C in the case of acetone). When the required temperature had been reached, 22 g of EO was added with the aid of an ISCO pump (10 minutes at a rate of 150 ml/hr) to and the EO to ketone ratio was maintained at 1:2.5. A series of samples were taken at specific time intervals.

The results of these Examples are shown in Figures 4 and 5.

The Examples demonstrate the successful use of a range of ketones in the ketalisation of EO at 40 °C. Although the ketones do not have as high a rate of ketalisation as the comparative example, acetone, at this temperature, they are higher boiling and, thus, higher temperatures may be used in order to increase the reaction rate. Further Examples were run according to the above general procedure, but at the temperatures and EO:ketone ratios shown in Figures 6 and 7. The results of these Examples are shown in Figures 6 and 7.

Also due to their higher boiling points, the ketones shown may be applied in the preferred embodiments of the present invention in which the ketone replaces water as an absorbent for EO. Further, some of these ketones are suitable for use in the reactive distillation and phase separation embodiments described herein, simplifying the process for the production of MEG.

Close to stoichiometric levels of water may be used in the hydrolysis of the ketals formed, lowering the energy required for the stripping of water from the resultant MEG.

- 5 Using a non-gaseous ketone reactant removes the requirement for expensive and complex equipment which is necessary when using a gaseous reactant, such as CO₂.

C L A I M S

1. A process for the production of monoethylene glycol, said process comprising the steps of:

(a) reacting ethylene oxide with a ketone in the presence of a solid acidic catalyst to form a ketal;

5 and

(b) hydrolysing the ketal with water to form monoethylene glycol,

wherein the ketone contains in the range of from 4 to 20 carbon atoms.

10 2. A process as claimed in claim 1, wherein the ketone contains in the range of from 5 to 12 carbon atoms.

3. A process as claimed in claim 1 or claim 2, wherein the solid acidic catalyst is an acid activated clay.

15 4. A process as claimed in claim 3, wherein the acid activated clay is selected from the group consisting of montmorillonite, beidellite, nontronite, hectorite, saponite and sauconite.

20 5. A process as claimed in any one of claims 1 to 4, wherein hydrolysing the ketal is carried out in the presence of a catalyst selected from the groups consisting of acid activated clays and acidic ion exchange resins.

25 6. A process as claimed in any one of claims 1 to 5, wherein hydrolysing the ketal is carried out in the presence of water in a ratio of water to ketal in the range of from 1:1 to 4:1.

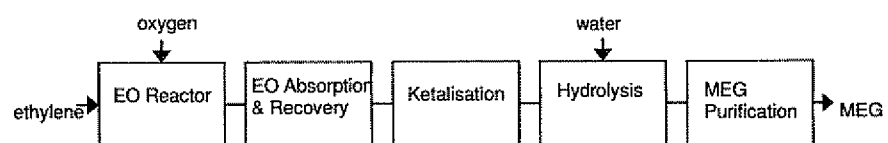
7. A process as claimed in claim 6, wherein hydrolysing the ketal is carried out in the presence of water in a ratio of water to ketal in the range of from 1:1 to 2:1.

8. A process as claimed in any one of claims 1 to 7, wherein the ketone has low water solubility and, after hydrolysis of the ketal, the ketone is separated from an aqueous solution of MEG by phase separation.

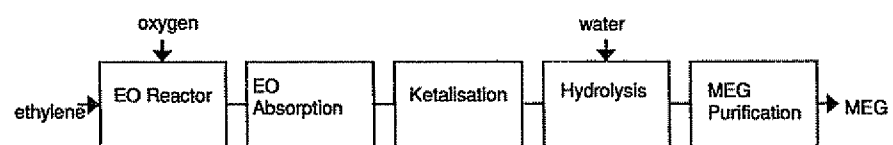
5 9. A process as claimed in any one of claims 1 to 8, wherein the ketone to be reacted with the ethylene oxide is first used as an absorbent in an ethylene oxide absorber.

10 10. A process as claimed in any one of claims 1 to 9, wherein the ketone is reacted with the EO in the presence of a solid acidic catalyst and in the presence of the product mixture from an EO reactor.

1/7

Figure 1

2/7

Figure 2

3/7

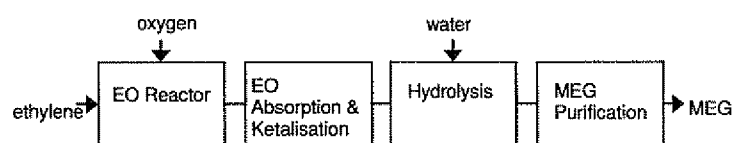
Figure 3

Figure 4

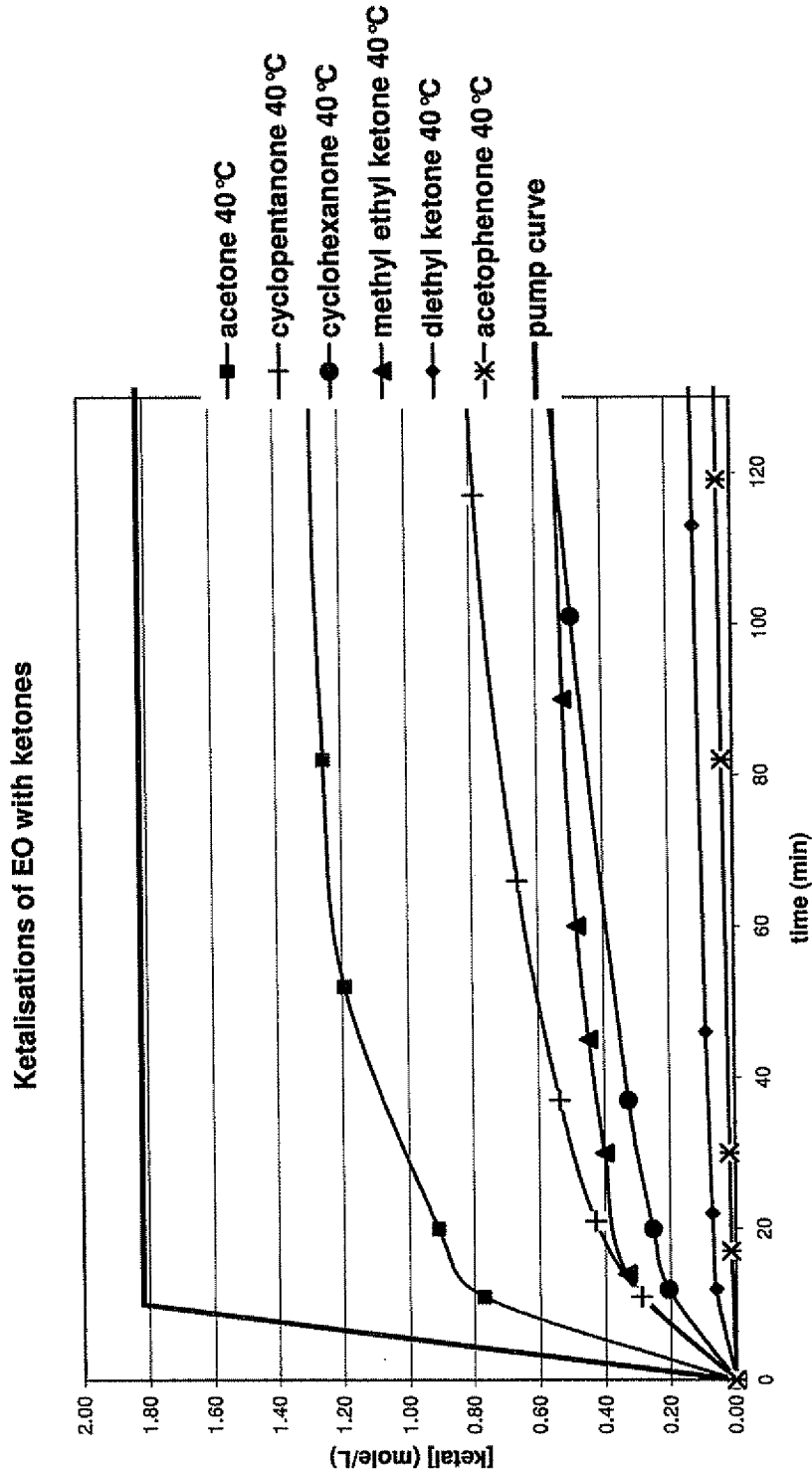


Figure 5

Product	EO-equivalents	product selectivity @ 100 % conversion (mole %)				
		acetone	MEK	DEK	cyclopentanone	cyclohexanone
ketal	1	60.79	35.71	8.44	50.14	2.76
dioxane	2	15.62	32.39	60.02	16.82	50.34
MEG	1	0.41	0.02	0.09	0.06	0.34
DEG	2	1.16	0.8	0.85	1.04	1.24
TEG	3	1.23	0.84	0.57	1.28	0.7
TTEG	4	2.96	2.1	1.88	3.39	2
2-methyl 1,3-dioxolane	3	1)	1.8	3.54	1.72	6.07
2-cyclopentyl-1,3,6-cyclooctane	2				1.3	
2-methyl-1,3,6-trioxacyclooctane	3					0.34
mesityl oxide (aldol)	0	0.12				
di acetone alcohol (aldol)	0	0.20				
aldol condensate	0		0.67	2)	3)	0.12
2-cyclohexyl-1,3,6-oxacyclooctane	2					0.77
crown ether	3-5	0.08	0.75	0.75	0.27	0.17
unknown						1.38

1) = same retention time as ketal

2) = not identified with GC-MS

3) = unknown retention time

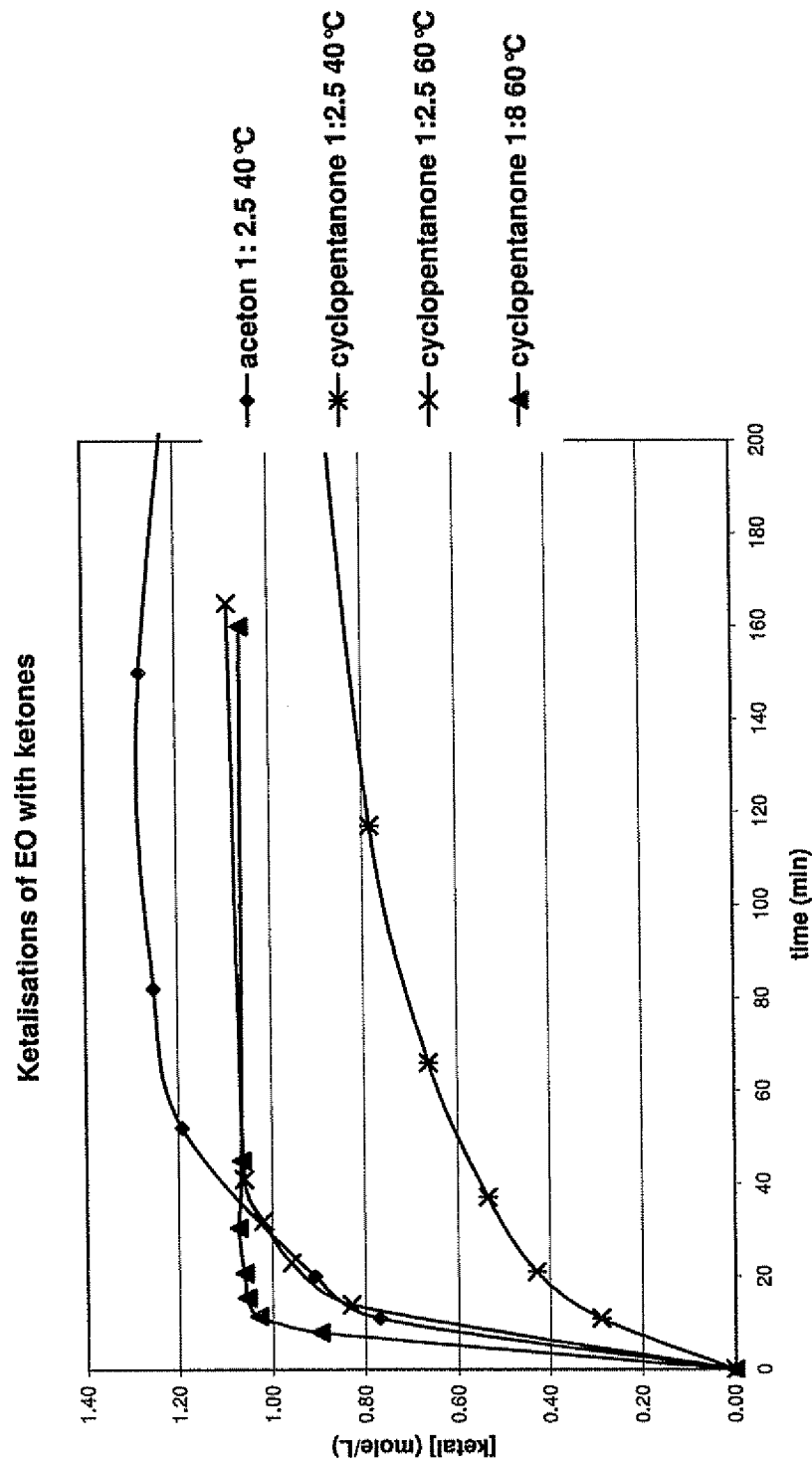


Figure 6

Figure 7

Product	EO-equivalents	product selectivity @ 100 % conversion (mole %)			
		acetone 40°C, 1:2.5	cyclopentanone 40°C, 1:2.5	cyclopentanone 60°C 1:2.5	cyclopentanone 60°C 1:8
ketal	1	60.79	50.14	59.8	80.5
dioxane	2	15.62	16.82	14.1	0.45
MEG	1	0.41	0.06	0.15	2.9
DEG	2	1.16	1.04	1.3	2.4
TEG	3	1.23	1.28	1.7	1.0
TTEG	4	2.96	3.39	3.6	0.54
2-methyl 1,3-dioxolane	3	1)	1.72	2.3	0.12
2-cyclopentyl-1,3,6-cyclooctane	2	0	1.3	0.88	0.07
mesityl oxide (aldol)	0	0.12	0	0	0
di acetone alcohol (aldol)	0	0.20	0	0	0
aldol condensate	0		2)	2)	2)
unknown		0.08	0.27	0.19	0.14

1) = same retention time as ketal

2) = unknown retention time

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2010/059209

A. CLASSIFICATION OF SUBJECT MATTER

INV. C07C29/10 C07D317/12 C07D317/72
 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 C07D

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, BEILSTEIN Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2005 126357 A (ASAHI DENKA KOGYO KK) 19 May 2005 (2005-05-19) cited in the application claims 1-3; examples 1,2	1-10
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Y	US 4 609 768 A (KNIFTON JOHN F [US] ET AL) 2 September 1986 (1986-09-02) claim 1; examples I,III	6,7
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Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

22 September 2010

Date of mailing of the international search report

06/10/2010

Name and mailing address of the ISA/

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2010/059209

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2004/175316 A1 (BOS ALOUISIUS NICOLAAS RENE [NL] ET AL) 9 September 2004 (2004-09-09) paragraphs [0024], [0025], [0028], [0035]; claims 4,16; figures 2,4,5 -----	8-10
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

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