



Process for preparing ketene in the presence of a fluidized bed material with a surface area of up to 600 m²/g

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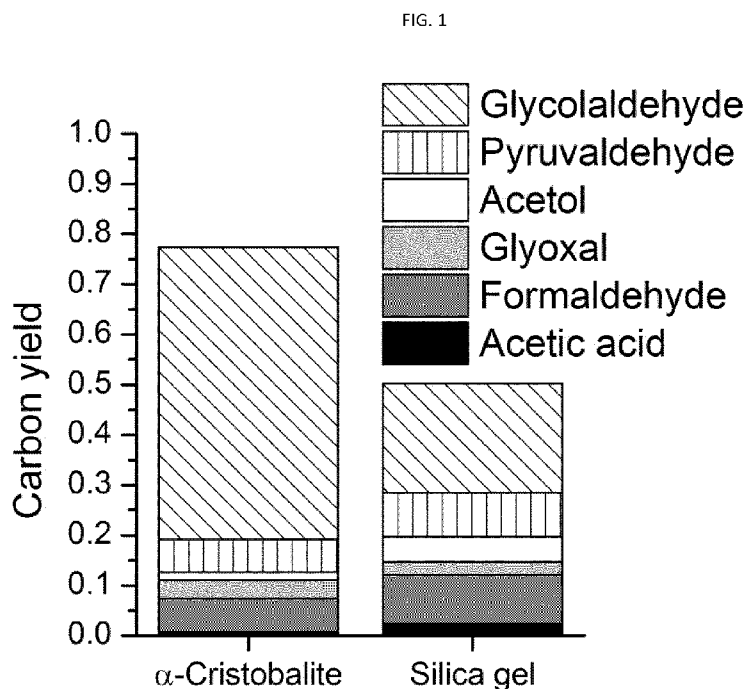
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[Continued on next page]

(54) Title: PROCESS FOR PREPARING KETENE IN THE PRESENCE OF A FLUIDIZED BED MATERIAL WITH A SURFACE AREA OF UP TO 600 M2/G



(57) Abstract: A Process for preparing ketene in the presence of a fluidized bed material with a surface area of up to about 600 m²/g. The process is further defined as a process for preparing ketene from a sugar or glycolaldehyde feedstock.

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Title: Process for Preparing ketene in the presence of a fluidized bed material with a surface area of up to 600 m²/g.

Ketene (ethenone) is a highly volatile, reactive compound that has a tendency to react with other species, such as water, therefore making it difficult to detect and quantify.

Symposium on thermal uses and properties of carbohydrates and lignins (1976) 261-273, discloses the formation of ketene from the pyrolysis of glucose via trapping experiments with deuterated water (deuterium oxide) and alkyl amines. A yield of 16% of ketene from the pyrolysis of glucose at 700 °C is disclosed; at lower reaction temperatures, such as 500 and 600 °C, the yield is 2.4 and 4.2 % respectively.

US 7,094,932 discloses the pyrolysis of an aqueous solution of glucose via a fluidized bed of sand. The condensable products are quantified; the aim of the experimental is to provide an improved process for preparing a glycolaldehyde-rich solution. Although US 7,094,932 cites 'Symposium on thermal uses and properties of carbohydrates and lignins (1976) 261-273' as disclosing the formation of ketene from glucose, no ketene product is observed in the products of the reactions disclosed in US 7,094,932, supporting the fact that pyrolysis reaction temperatures below 700 °C are not optimal for ketene (ethenone) formation.

Ind. Eng. Chem. Res. (1994) 2904 - 2912, discloses the use of chromatographic grade silica, i.e. high surface area silica, to increase the selectivity of ketene formation from acetates pre-adsorbed onto silica. At lower tempera-

tures, 573 -673 K (300-400 °C), the selectivity for ketene formation from acetic acid (0.48-0.41) is higher than at higher temperatures, 773 - 973K (500-700 °C), (0.34-0.16). Reaction temperatures of 750 K were essential for steady state catalysis. When longer chain carboxylic acids are subjected to the reaction conditions, the longer chain ketene is formed; i.e. valeric acid forms propylketene. Smaller carbon chain compounds, e.g. propionic acid, provide the corresponding ketonisation product as the greatest yielding product.

It is therefore desirable to provide a high yielding, improved one-step catalytic process for the preparation of ketene (ethenone) from a feedstock comprising one or more sugars or glycolaldehyde. In particular, it is desirable to provide an improved process wherein ketene is obtainable in its free form and is suitable for subsequent transformations. In particular, the improved process provides a yield of ketene (ethenone) suitable for commercial viability of the process.

The process of the present invention is further defined as a process for preparing ketene from a feedstock, wherein the feedstock is pyrolysed in the presence of a fluidized bed material with a surface area of up to about 600 m²/g.

In an embodiment of the invention the feedstock may be one or more sugars or glycolaldehyde. In a preferred embodiment of the present invention the feedstock is a monosaccharide. In a more preferred embodiment of the present invention the feedstock is one or more sugars selected from the group consisting of glucose, fructose, galactose, xylose, sucrose and mannose. Preferably the feedstock is glucose.

In a preferred embodiment of the present invention the fluidized bed material has an average particle size suitable for achieving a fluidized bed.

In a preferred embodiment of the present invention the fluidized bed material has a surface area of up to about 600 m²/g. In a further preferred embodiment of the present invention the fluidized bed material has a surface area of between 200 and 600 m²/g, preferably between about 300 and 550 m²/g, more preferably between about 400 and 600 m²/g.

In a preferred embodiment of the present invention the fluidized bed material has a pore volume of up to about 0.80 ml/g, preferably between about 0.40 and 0.75 ml/g, preferably between about 0.50 and 0.70 ml/g, preferably about 0.60 and 0.70 ml/g.

In a preferred embodiment of the present invention the fluidized bed material has a silanol concentration of up to about 4.0 M, preferably between about 2.0 M and 4.0 M, preferably between about 3.0 and 4.5 M, preferably about 3.5 M and 4.0 M.

In a preferred embodiment of the present invention the fluidized bed material is silicon oxide. In a more preferred embodiment the fluidized bed material is selected from the group consisting of high surface area silica.

In a preferred embodiment of the present invention the fluidized bed material is selected from the group consisting of SiC, silica gel and silica gel calcined at 500 °C.

In a preferred embodiment of the present invention the fluidized bed material is colloidal silica mixed with an oxide selected from the group consisting of Nb_2O_5 , TiO_2 , ZrO_2 , CeO_2 and BaO .

In a preferred embodiment of the present invention the temperature of the reaction is less than about $700\text{ }^\circ\text{C}$, preferably less than about $600\text{ }^\circ\text{C}$, more preferably between about 500 and $600\text{ }^\circ\text{C}$.

In a preferred embodiment of the present invention the reaction chamber contains a fluidized catalyst. More preferably the reaction chamber contains a fluidized catalyst and the residence time of the feedstock in the reaction chamber of the fluidized bed is between about 50 to about 150 ms .

In a preferred embodiment of the present invention the percentage yield of ketene is greater than 16% .

In a preferred embodiment of the present invention the process is run as a continuous process.

In a preferred embodiment of the present invention the feedstock is introduced into the fluidized bed reaction chamber as an aqueous solution. In a further preferred embodiment the feedstock is introduced into the fluidized bed reaction chamber as an aqueous solution comprising up to 60% by weight of the feedstock, as disclosed in US $7,094,932$. In a further preferred embodiment the feedstock is introduced into the fluidized bed reaction chamber as an aqueous solution comprising between about 10% to about 60% by weight of the feedstock. In a further preferred embodiment the feedstock is introduced into the fluidized bed reaction chamber as an aqueous solution comprising between

about 10% to 30% by weight of the feedstock. In a further preferred embodiment the feedstock is introduced into the fluidized bed reaction chamber as an aqueous solution comprising about 10% by weight of the feedstock.

In a preferred embodiment of the present invention the feedstock is introduced into the fluidized bed reaction chamber as an atomized solution with a particle size of less than 10 μm .

In a preferred embodiment of the present invention the process is carried out under an inert atmosphere, e.g. an atmosphere of nitrogen.

General Experimental:

The thermolytic conversion of carbohydrates was investigated in a fluidized bed setup. The setup consists of a stainless steel reactor (i.d.: 22 mm, length: 80 cm) fitted with a gas atomizing nozzle (Spraying Systems Co.), capable of delivering the liquid feed as a fine mist into the reactor (droplet size: $<10 \mu\text{m}$). The reaction temperature was monitored with a thermocouple extending from the top of the reactor into the bed. The top of the reactor was fitted with a disengager to prevent elutriation of the bed particles. Immediately after the outlet, the gas stream was directed through a condenser kept at 1 °C to collect the liquid product. The gas phase product may be passed into a subsequent reactor and transformed into further products as illustrated in 'Ketenes' Ullman's Encyclopedia of Industrial Chemistry (2002) 171-185.

In a typical experiment, the reactor was charged with 10 ml of the bed material, having a particle size from 90 to 150 μm . A nitrogen flow of 3.5 Nl/min was used to fluidize the bed, while the reactor temperature was raised to the desired reaction temperature of between 550-600 $^{\circ}\text{C}$. When the reactor reached the desired temperature water was pumped to the nozzle, using a tube pump, at a flow rate 0.5 ml/min and injected into the bed. The liquid flow was maintained for at least 20 min to obtain a stable temperature in the bed.

The experiment was started by changing the liquid to a 10 wt % aqueous solution of the substrate, at which point the time was set as $t = 0$. The dead time from the feed flask to the nozzle was approx. 20 min. Collection of the liquid product was started at $t = 30$ min. The condensed liquid was collected over the entirety of the experiment to calculate mass balances. Each experiment was run for at least 6 hr.

Liquid products were quantified by HPLC analysis (Agilent, 1200 Series). The analytes were separated on a BioRad Aminex HPX-87H column operating at 65 $^{\circ}\text{C}$. The eluent was a 0.005 M aqueous H_2SO_4 , at a flow rate of 0.6 ml/min. The analytes were quantified using a RI detector against standard samples. Products were identified either by matching retention time with a known standard, or if possible by GC-MS analysis on an Agilent Technologies 6890 Plus series gas chromatograph with an Agilent Technologies 5973A series mass selective detector.

Analysis of the gas phase products was performed by directing part of the gas stream, after the condenser, into a

mass spectrometer (IPI, GAM 200 Multi Component Gas Analyser).

Measurement of fluidized bed material silanol concentration:

The dehydroxylation behavior of silica was measured on a Mettler TGA/DSC 1; the sample was dehydrated at 150 °C for 60 min in a flow of 20% O₂, 26% He and 54% Ar at 50 ml/min; this gas flow was maintained for the duration of the analysis. The temperature was lowered to 40 °C and then increased to 1500 °C at 5 °C /min, while monitoring the weight of the sample.

	BET surface area (m²/g)	Pore volume (ml/g)	Silanol concentration (M)
Silica gel (SG60)	517	0.68	3.60
Silica gel (calcined at 1000 °C)	4	0.01	0.20
alpha-cristobalite	4	0.01	0.00

The first two parameters (BET surface area and Pore Volume) are determined by N₂ sorption. The silanol concentration is measured by a combination of TGA and Hg porosimetry.

Example 1:

The experimental procedure was followed according to the general experimental, where the fluid bed material was a

silica compound [α -cristobalite; Sigma Aldrich named as Silicon dioxide (quartz, cristabolite), product number: 84878], the substrate was glucose (D-glucose monohydrate; Sigma Aldrich). The reactor temperature was 550 °C.

Example 2:

The experimental procedure was followed according to the general experimental, where the fluidized bed material was a silica compound [silica gel; SG60 from Merck], the substrate was glucose (D-glucose monohydrate; Sigma Aldrich). The reactor temperature was 560 °C

Example 3:

The experimental procedure was followed according to the general experimental, where the fluidized bed material was a silica compound [silica gel; SG60 from Merck) calcined at 500 °C], the substrate was glucose (D-glucose monohydrate; Sigma Aldrich).

Example 4:

The experimental procedure was followed according to the general experimental, where the fluidized bed material was a silica compound [silica gel; SG60 from Merck], the substrate was glucose (D-glucose monohydrate; Sigma Aldrich). However, the reactor temperature was 515 °C.

Example 5:

The experimental procedure was followed according to the general experimental, where the fluidized bed material was a silica compound [silica gel; SG60 from Merck], the substrate was glucose (D-glucose monohydrate; Sigma Aldrich). However, the reactor temperature was 590 °C.

Example 6:

The experimental procedure was followed according to the general experimental, where the fluidized bed material was a silica compound [silica gel; SG60 from Merck], the substrate was glucose (D-glucose monohydrate; Sigma Aldrich). However, the liquid feed was a 30 wt % aqueous solution of the substrate, i.e. the concentration of the substrate in water was 30 wt % of glucose.

Example 7:

The experimental procedure was followed according to the general experimental, where the fluidized bed material was prepared from a mixture of colloidal silica with a colloidal metal oxide selected from the group consisting of Nb₂O₅, TiO₂, ZrO₂, CeO₂ and BaO₂ (all colloidal metal oxides were obtained from Alfa Aesar). The colloidal silica and colloidal metal oxide mix [TiO₂, ZrO₂ or CeO₂] was prepared by mixing colloids of the desired oxides with colloidal silica (Ludox AS-30 from Sigma-Aldrich) in a ratio of 1:9 oxide to silica, and evaporating to dryness, followed by calcination at 1000 °C. An aqueous solution of BaNO₃ was used to prepare the BaO/colloidal silica mix. Nb₂O₅ was

prepared by impregnation of NbCl_5 onto silica gel [SG60, Merck] by incipient wetness impregnation and calcined at 1000 °C.

Table 1: Carbon yield and composition of the liquid condensate.

Liquid Condensate Composition	Example				
	1	2	4	5	6
Glyoxal	0.037	0.026	0.029	0.028	0.028
Pyruvaldehyde	0.065	0.088	0.110	0.080	0.090
Glycolaldehyde	0.582	0.217	0.292	0.213	0.385
Formaldehyde	0.067	0.098	0.090	0.092	0.072
Acetic Acid	0.007	0.024	0.018	0.021	0.011
Acetol	0.016	0.050	0.044	0.033	0.027

Table 2: Comparison of the MS signal of the gas phase components for Examples 1, 2, 4, 5 and 6 where the intensity of the MS signal of Examples 2, 4, 5 and 6 are normalized to the signal obtained in Example 1.

Table 2 illustrates that an increase in surface area of the fluidized bed material increase the amount of acetone and ketene produced.

Gas Phase MS signal	Example				
	1	2	4	5	6
Acetone (m/z = 58)	1	6.25	2.9	5.3	7.6
Ketene (m/z = 42)	1	3.17	1.6	3.4	4.8

Figures:

Figure 1: Carbon yield and product composition of liquid condensate of pyrolysis of 10 wt% aqueous solution of glucose according to Examples 1 and 2 wherein α -cristobalite or silica gel are used as fluidized bed material.

Figure 2: Carbon yield of condensed liquid products of Examples 2 [Silica gel as received] and 1 [silica gel calcined at 1000 °C is equivalent to α -cristobalite], as a function of time of the reaction.

Figure 3: Carbon yield and product composition of pyrolysis of 10 wt% aqueous solution of glucose according to Example 7 wherein colloids of acidic and basic oxides are mixed with colloidal silica and used as bed material.

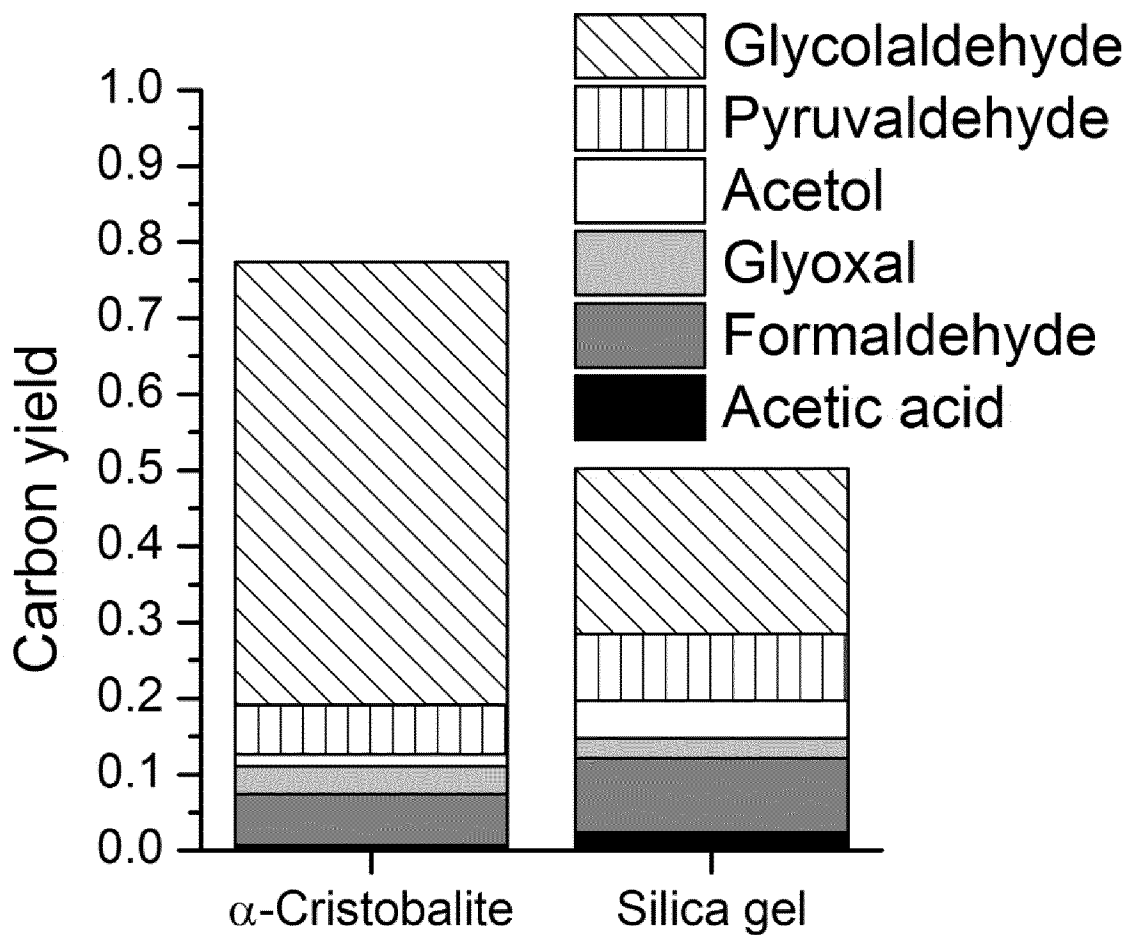
Figures 1 to 3 illustrate the increased yield of acetic acid produced as the surface area of the fluidized bed material increases. An increase in acetic acid yield correlates to an increase in ketene yield as ketene is hydrated to acetic acid.

Claims:

1. A process for preparing ketene from a feedstock wherein the feedstock is pyrolysed in the presence of a fluidized bed material, wherein the surface area of the fluidized bed material is up to 600 m² per gram and the feedstock is selected from one or more of the group consisting of glucose, fructose, galactose, xylose, sucrose and mannose and glycolaldehyde.
2. A process according to claim 1, wherein the fluidized bed material is selected from the group consisting of SiC, silica gel, and silica gel calcined at 500 °C.
3. A process according to claim 1, wherein the fluidized bed material is colloidal silica mixed with an oxide selected from the group consisting of Nb₂O₅, SiO₂, TiO₂, ZrO₂, CeO₂ and BaO.
4. A process according to claims 1 to 3, wherein the temperature of the reaction is less than 700 °C.
5. A process according to claims 1 to 4, wherein the reaction chamber is a fluidized bed.
6. A process according to claims 1 to 5, wherein the residence time of the material in the reaction chamber of the fluidized bed is up to 150 ms.
7. A process according to claims 1 to 6, wherein the percentage yield of ketene is greater than 16 %.

8. A process according to claims 1 to 7, wherein the feedstock is introduced into the fluidized bed reaction chamber as an aqueous solution.
9. A process according to claims 1 to 8, wherein the feedstock is introduced into the fluidized bed reaction chamber as an aqueous solution comprising up to 60% by weight of feedstock.
10. A process according to claims 1 to 9, wherein the feedstock is introduced into the fluidized bed reaction chamber as an atomized solution with a particle size of less than 10 μm .
11. A process according to claims 1 to 10, wherein the process is carried out under an inert atmosphere of nitrogen.
12. A process according to claims 1 to 11, wherein the ketene is ethenone.

FIG. 1



2/3

FIG.2

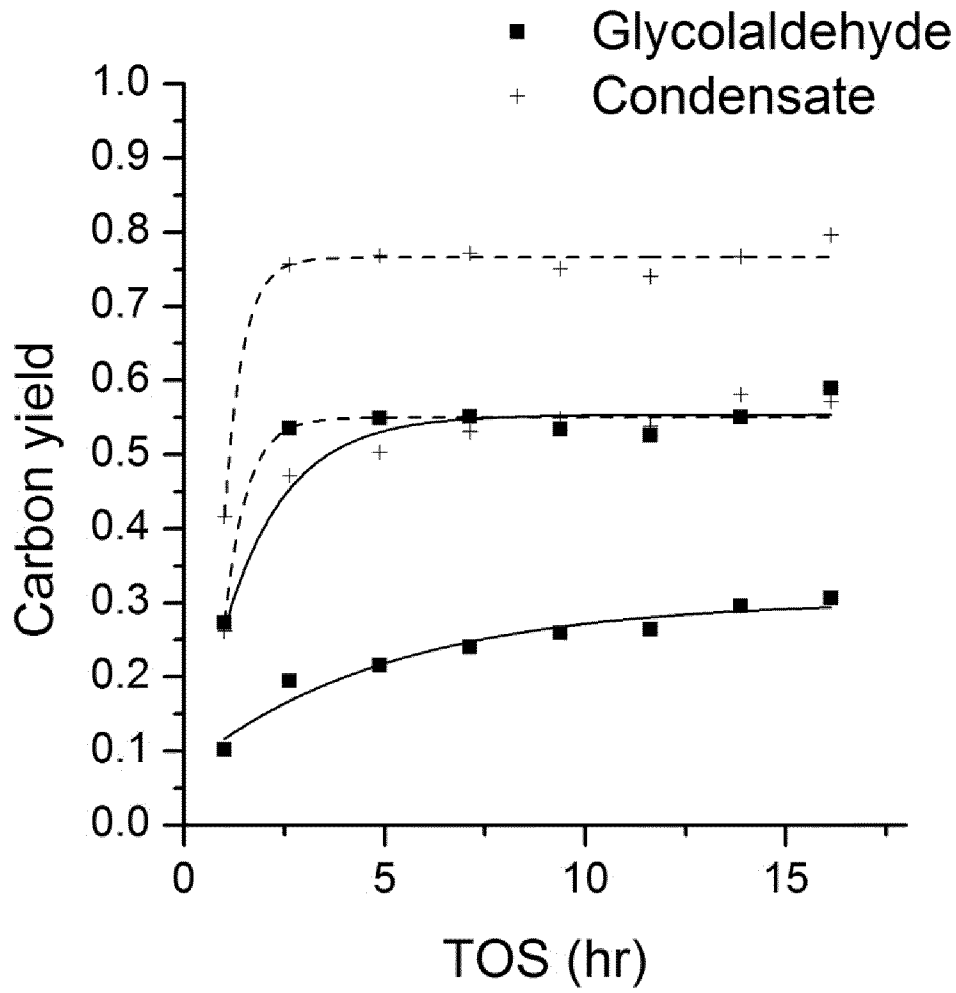
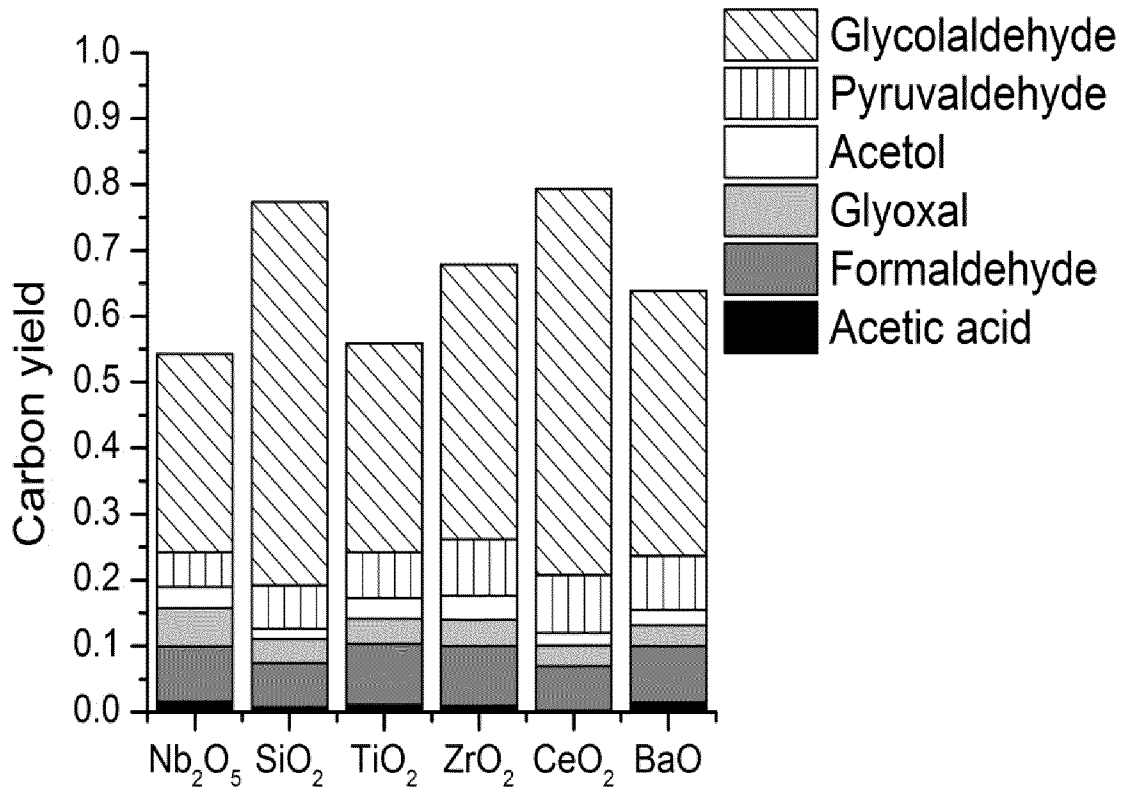


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2014/053644

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C45/87 C07C49/88 C07C49/90
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 practicable, search terms used)
EPO-Internal, 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.
Y	JOHN C KAIG ET AL: "Ketene Formation from the Pyrolysis of Carbohydrates", SYMPOSIUM ON THERMAL USES AND PROPERTIES OF CARBOHYDRATES AND LIGNINS: PAPERS FROM THE SYMPOSIUM HELD AT THE 172ND NATIONAL MEETING OF THE AMERICAN CHEMICAL SOCIETY, ACAD. PRESS, USA; SAN FRANCISCO, CALIFORNIA, USA, 1 January 1976 (1976-01-01), pages 261-273, XP008166493, ISBN: 0-12-637750-2 the whole document	1-12
Y	GB 691 352 A (HERBERT BOOKER; RICHARD JOHN YOUNG; ICI LTD) 13 May 1953 (1953-05-13) claims 1,12 page 2, column 1, line 40 - line 44 page 2, column 2, line 75 - line 76	1-12

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 12 May 2014	Date of mailing of the international search report 11/06/2014
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Delanghe, Patrick
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2014/053644

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 691352	A	13-05-1953	NONE
