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(54) Title: PROCESS FOR THE PREPARATION OF LEVULINIC ACID
(57) Abstract: The invention relates to a process for the preparation of levulinic acid and more particularly to a selective conversion of fructose to levulinic acid in a mixture of glucose and fructose.

FIGURE 1

Sucrose → Fructose + Glucose

Selective Reaction → Fructoside → Glucoside

No reaction → Levulinate → Hydrolysis

→ Glucose

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DESCRIPTION

TITLE: PROCESS FOR THE PREPARATION OF LEVULINIC ACID

FIELD OF INVENTION

The invention relates to a process for the preparation of levulinic acid and more particularly to a selective conversion of fructose to levulinic acid in a mixture of glucose and fructose.

BACKGROUND

10 Levulinic acid, a keto-acid is prepared from renewable biomass. It is used to prepare esters of LA generally used as octane booster for gasoline and as a fuel extender for diesel. It is also a substrate for a variety of condensation and addition reactions involving the ester and keto groups with alkyl amines to form various polymers which have applications in various industrial processes like coatings, plastic, films, etc as well as a reactant in many chemical preparation processes to create various chemical substances that are used in consumer or pharmaceutical products.

Conversion of glucose and other hexose sugars to levulinic acid by treating hexose sugar containing streams with mineral acids appeared in the patent literature as early as 1960 (Canadian patent no. CA594974A). This method was adapted later to the direct transformation of biomass using mineral acids at high temperatures. Besides, PCT application WO2005070867 discloses reactive extraction of levulinic acid by means of esterification of C5 to C12 un-branched aliphatic alcohols with yields of levulinate esters as high as 85%. However, most of these methods require the use of corrosive acids and hazardous chemicals during the conversion of sugars to levulinates.

The major issues with conversion of sugars to levulinic acid relate to the selectivity of the conversion, the yields obtained, and the associated high cost of production of levulinic acid. Thus, there is still a need for a process to produce levulinic acid that is
economically viable, energy efficient, environment friendly and yet capable of producing the desired product with enhanced purity and significantly increased product yields.

BRIEF DESCRIPTION OF THE INVENTION

The present invention provides a process for converting sugars to levulinic acid. It specifically provides for selective conversion of fructose to levulinic acid in a mixture of hexose sugars like a mixture of glucose and fructose.

The present invention provides a process for the preparation of levulinic acid comprising: providing a feedstock comprising fructose; mixing methanol and an acid with said feedstock and allowing insoluble matter to separate forming a first stream; subjecting said first stream to solid-liquid separation forming a reaction mixture free of said insoluble matter; maintaining said reaction mixture at an effective temperature for a specific time period forming in a second stream; subjecting said second stream to pH correction using an alkali forming a third stream; distilling said third stream forming a fourth stream and a forming a first distillate stream; filtering said fourth stream forming a fifth stream; extracting said fourth stream with an organic solvent to get a mixture of aqueous and organic phases; separating said mixture by liquid-liquid separation forming an organic stream and an aqueous stream; subjecting said organic stream to distillation to remove said organic solvent and get a product stream comprising methyl levulinate; and recovering levulinic acid from said methyl levulinate by hydrolysis and removal of methanol.

DESCRIPTION OF DRAWINGS

These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings, wherein:

FIGURE 1 depicts a general scheme of the process of invention in that a feedstock comprising fructose and other sugars like glucose is subjected to the innovative and
specific reaction conditions in that firstly fructose and glucose are covered to their respective methyl glycosides. Then in the second step, only methyl fructose side is converted selectively to methyl levulinate and methyl glucoside remains as it is which is further used to recover glucose on hydrolysis. Herein said methyl levulinate may be hydrolysed to obtain levulinic acid.

FIGURE 2 depicts a process flow diagram of the production of levulinic acid from a feedstock comprising a mixture of fructose and glucose such as molasses or invert syrup. Different elements of the process are identified and directional movement of different streams and components formed during the process are shown to describe the features of one embodiment of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

Feedstock comprising fructose may be converted in accordance with one aspect of the present invention to form levulinic acid useful for applications such as polymers, bulk chemicals, solvents, fuel additives, detergents, antifreeze agents, pharmaceutical ingredients, herbicides, plasticizers, lubricants, cleaning chemicals or resins. Examples of fructose containing feed stock include sugarcane or sugar beet or sweet sorghum juice or syrup or molasses, dates, honey, corn, potato, cassava, sago, rice, wheat, barley, sorghum or millet wherein if only glucose is present it is inverted to fructose by enzymes.

In one embodiment of the present invention, a process for selectively converting fructose to levulinic acid comprises mixing methanol with a feedstock comprising fructose creating a reaction mixture. The mass percentage of total fructose in the reaction mixture is in a range from about 5 percent to about 25 percent. The mass percentage of water in the reaction mixture may be in a range from about 2.5 percent to about 10 percent.

In accordance with an embodiment of the present invention, the reaction mixture is contacted with an acid catalyst like sulphuric acid, hydrochloric acid or an organic acid like methane sulphonic acid. A contact between the reaction mixture and the
acid catalyst is maintained at an effective temperature and pressure to cause a desired reaction forming a product stream.

In one embodiment of the present invention, the contact between the reaction mixture and the acid catalyst is maintained at a temperature in the range from about 90 °C and 120 °C. In another embodiment of the present invention, the contact between the reaction mixture and the acid catalyst is maintained for a time-period ranging from about 20 minutes to about 300 minutes.

In one embodiment of the present invention, the reaction results in a product stream comprising methyl levulate, and other by-products. The said methyl levulinate may be hydrolysed in the presence of an acid to get levulinic acid as a final product.

In one embodiment of the present invention, alkali is added to the liquid stream to adjust pH in a range from about 6 to about 8. The alkali used may include, but are not limited to aqueous solution of ammonia, metal and alkaline metal hydroxides, such as hydroxides of sodium, potassium, calcium, lithium, and their carbonates and bicarbonates.

In a process according to one embodiment of the present invention, methyl levulinate is selectively prepared from fructose as detailed below in a system of modules, wherein each module has a specific function leading to conversion of said sugar to the methyl levulinate with high specificity and selectivity. In another embodiment of the present invention, the system may be used to recover and recycle of the methanol used in the process.

In one embodiment of the present invention, efficient conversion of fructose to methyl levulinate is obtained using a system comprising three modules namely: 1] feed preparation module; 2] reaction module; and 3] downstream processing module. Each module has one or more elements/ means for performing specific or optional functions as required for achieving the selective production of ethyl levulinate at higher amounts. A person skilled in the art may appreciate different variations and/or combinations of these elements that may be used to perform the objects of the invention disclosed herein.
FEED PREPARATION MODULE

Feed preparation module is used for mixing a feedstock comprising fructose with methanol and adjusting moisture content to a desired level if necessary. This is followed by conditioning leading to the formation of a reaction mixture of feedstock and methanol in a desired ratio. After a period of about 30 min to 5 h of conditioning, solid insoluble matter such as salts, settle out of said reaction mixture. These salts are removed by filtration to obtain a clarified reaction mixture. Further, it is sent to the next module called the reaction module.

In one embodiment of the present invention, a feedstock comprising liquid glucose obtained from corn starch is inverted to with enzymes to contain about 50 % fructose by volume and then mixed with in the feed preparation module leading to the creation of a reaction mixture for the preparation of methyl levulinate at higher amounts and glucose obtained as the by-products is recycled to produce fructose upon inversion, or converted ethanol by fermentation.

REACTION MODULE

The second module of the system is a reaction module characterized by one or more high temperature and pressure vessels, capable of holding the reaction mixture, acid catalyst and a product stream and allowing a desired reaction to occur at a condition of high pressures up to 40 bars and high temperatures up to 200 °C. These vessels may be one or more of stirred tanks, plug-flow reactors, accelerated plug-flow reactors, recirculation reactors or fluidized-bed reactors. These vessels may operate in batch mode, fed-batch mode or continuous mode in parallel or in series or a combination thereof. The reaction module has means for controlling temperature and pressure at a desired level during the reaction for extended time-periods. In another embodiment of the present invention, the reaction mixture and the acid catalyst are fed into the reaction module and contact between the catalyst and the reaction mixture is maintained at an effective temperature and pressure for a specific retention time-period in the vessel to achieve a desired reaction resulting in formation a product stream, which is fed to the next module called downstream processing module.
In one embodiment of the present invention, the vessel is an autoclave vessel wherein the reaction mixture is subjected to an elevated temperature and pressure for a desired time-period in the presence of a acid catalyst held in place in the autoclave such that it optimally contacts the reaction mixtures leading to efficient production of desired products.

In another embodiment of the present invention, the vessel is a batch-type stirred tank reactor wherein a mixture of fructose and glucose and methanol are subjected to an elevated temperature and pressure for a desired time period in the presence of a acid catalyst such that it optimally contacts the reaction mixture leading to efficient production of methyl levulinate and methyl glucoside. Levulinic acid and glucose is prepared on hydrolysis of respectively products.

In yet another embodiment of the present invention, the vessel is a plug-flow reactor wherein a mixture of fructose and methanol is subjected to an elevated temperature and pressure for a desired time period in the presence of a acid catalyst such that it optimally contacts the reaction mixture leading to efficient production of methyl levulinate.

In yet another embodiment of the present invention, the vessel is a recirculation reactor wherein a mixture of liquid glucose and methanol and is subjected to an elevated temperature and pressure for a desired time period in the presence of a acid catalyst such that it optimally contacts the reaction mixture leading to efficient production of methyl levulinate.

170 DOWNSTREAM PROCESSING MODULE

The downstream processing module comprises of various unit processes to enable efficient separation of the product and by-product streams. Typical unit processes include solvent extraction, filtration, neutralization and distillation units.

In one embodiment of the downstream module, the reaction mixture emerging out of the reaction module is pH corrected to a value between 6 and 8 and then subjected to distillation to remove a stream [first distillate stream] comprising methyl formate
from which formic acid and methanol is recovered on acid hydrolysis. After the distillation the remaining crude stream is subjected to filtration and the filtrate is subjected to solvent extraction with an organic solvent immiscible in water. Typical solvents employed are but not limited to alkyl ketones, halogenated solvents or higher alcohols having affinity for methyl levulinate. The organic stream resulting from solvent extraction is subjected to final distillation to obtain the final product. The aqueous stream is subjected to an acid to separate glucose from methyl glucoside, which is fermented to ethanol or isomerised to fructose and recycled back to prepare levulonic acid as disclosed herein.

The methyl levulinate or levulonic acid content at the various stages in the process is analyzed in test samples by known methods. Methyl levulinate or levulonic acid is analyzed by gas chromatography with flame ionization detector. Alltech ATT-wax column of size 60 m X 0.53mm ID and film thickness of 1 μm or any equivalent column is used. Helium is used as carrier gas with flow rate of 3 mL/min. Injector and detector temperatures are kept at 240°C and 260°C respectively. Temperature gradient program is used with total run time of about 24 minute. Retention time of ethyl levulinate is observed at about 10.63 minute. Sample injection volume is about 1 μL. Dimethyl formamide is used as a diluent for the sample preparation. Estimation of ethyl levulinate content in the test samples is done using calibration graph generated using at least five known concentrations of standard compound.

Glucose content is analyzed by liquid chromatography with refractive index detector. BioRad Aminex 87 H⁺ column of size 300 X 7.8 mm or any equivalent column is used with 0.005 M H₂SO₄ as mobile phase with flow rate of 0.6 mL/min. Column oven temperature is kept at 55 °C and injection volume at 20 pL. Deionised water is used as a diluent for the sample preparation. Retention time of glucose is observed at 8.9 minute. Estimation of glucose content in the test samples is done using calibration graph generated using five known concentration of standard compound.

EXAMPLES

Examples provided below give wider utility of the invention without any limitations as to the variations that may be appreciated by a person skilled in the art. A non-limiting
summary of various experimental results is given in the examples, which demonstrate the advantageous and novel aspects of the process of using methanol in the selective conversion of fructose to methyl levulinate of levulinic acid.

EXAMPLE 1

About 1000 g of molasses containing about 487 g of total sugar was mixed with about 500 g of methanol. The reaction mixture was allowed to stand for about 5 h for the insoluble matter to settle and resulting in a supernatant liquid stream containing about 390 g of sugar (about 378 g of sucrose, 59 g fructose and about 32 g of glucose) and having ash value below about 5 % by weight. Said supernatant liquid stream was cleared by filtration. The stream so obtained was transferred to a reactor wherein about 48 g of \( \text{H}_2\text{SO}_4 \) and about 4117 g of fresh methanol was added. Next, the reactor was heated under stirred condition and maintained at about 105 °C for about 12 h. After 12 h the reaction mass was flashed or distilled to separate methyl formate and methanol from it. Remaining reaction mass, without methyl formate and methanol, was treated with about 12 g NaOH dissolved in about 2220 g water before subjecting it to complete methanol removal by distillation. Then it was extracted with ethylene dichloride or methyl isobutyl ketone to separate methyl levulinate in the organic stream leaving behind methyl glucoside in the aqueous stream. The organic stream was subjected to final distillation to separate said organic solvent from methyl levulinate. Methyl levulinate was hydrolyzed to recover about 83 g of pure levulinic acid and methanol, whereas methyl glucoside remaining in the aqueous stream was hydrolyzed using acid to recover about 159 g of D-glucose. Additional about 93 g of sugars are obtained by extracting the insoluble matter separated in the first step of methanol wash of the molasses feedstock. Thus, about 252 g of total sugar was recovered. This sugar on fermentation using yeast yielded about 117 g of ethanol. This process afforded about 90 % efficiency of methyl levulinate production from fructose with recovery of about 90 % of unreacted sugars in the form of fermentable glucose. The methanol recovered at each of the above steps was recycled.
EXAMPLE 2

240 About 1000 g of low ash sugar stream, obtained as described in EXAMPLE 1, containing about 286 g of sugar was mixed with about 3450 g of methanol and about 75 g sulphuric acid. The reaction mixture was transferred to a reactor. Next, the reactor was heated under stirred condition and maintained at about 105 °C for about 8 h. Then the reaction mass was analyzed by gas chromatography for methyl levulinate formation. The analysis of reaction mass contained about 1.4 % methyl levulinate, which corresponded to about 31 % yield of theoretical value based on the input sugars.

EXAMPLE 3

250 About 529 g of low ash sugar stream, obtained as described in EXAMPLE 1, containing about 308 g of sugar was mixed with about 3270 g of methanol and about 40 g sulphuric acid. The reaction mixture was transferred to a reactor. Next, the reactor was heated under stirred condition and maintained at about 105 °C for about 4 h. Then the reaction mass was analyzed by gas chromatography for methyl levulinate formation. The analysed reaction mass contained about 1.65 % w/w methyl levulinate, which corresponded to a yield of about 27 % of theoretical value on the input sugars. The reaction was further continued for a period of 12 h. Analysis of reaction mass after 12 h showed that it contained about 2.2 % w/w of methyl levulinate, which corresponded to about 36 % yield of theoretical value based on input sugars.

EXAMPLE 4

About 60 g of low ash sugar stream, obtained as described in EXAMPLE 1, containing about 15 g of sugar was mixed with about 352 g of methanol and about 8 g sulphuric acid. The reaction mixture was transferred to a reactor. Next, the reactor was heated under stirred condition and maintained at about 95 °C for about 5 h. Then reaction mass was analyzed by gas chromatography for methyl levulinate
formation. The analysed reaction mass contained about 0.5 % methyl levulinate by weight, which corresponded to a yield of about 10 % of theoretical value on the input sugars. The reaction was further continued for a period of 23 h. Analysed reaction mass showed that it contained about 1 % w/w of methyl levulinate, which corresponded to about 18 % yield of theoretical value based on input sugars.

EXAMPLE 5

About 33 g of clarified cane syrup containing about 25 g of sugar was mixed with about 407 g of methanol and 4 g sulphuric acid. The reaction mixture was transferred to a reactor. Next, the reactor was heated under stirred condition and maintained at about 105 °C for about 4 h. After 4 h the reaction mass was analyzed using gas chromatography for methyl levulinate formation. The analysis of reaction mass contained about 1.36 % w/w methyl levulinate, which corresponded to a yield of about 33 % of theoretical value on the input sugars. The reaction was further continued for a period of 12 h. Analysed reaction mass showed that it contained about 7 % w/w of methyl levulinate, which corresponded to about 39 % yield of theoretical value based on input sugars.

EXAMPLE 6

About 51 g of molasses containing about 26 g of sugar was mixed with about 260 g of methanol and about 6.4 g of sulphuric acid. The reaction mixture was transferred to a reactor. Next, the reactor was heated under stirred condition and maintained at about 95 °C for about 8 h. After 8 h the reaction mass was analyzed by gas chromatography for methyl levulinate formation. The analysed reaction mass contained about 2.5 % methyl levulinate, which corresponded to about 13 % yield of theoretical value based on the input sugars.
EXAMPLE 7

About 1000 g of dextrose powder containing about 95 g of moisture was mixed with about 6200 g of methanol and about 36 g of methane sulphonic acid. The reaction mixture was transferred to a reactor. Next, the reactor was heated under stirred condition and maintained at about 95 °C for about 5 h. After 5 h the reaction mass was analyzed by gas chromatography for methyl levulinate formation. The analysed reaction mass contained no methyl levulinate.

EXAMPLE 8

About 500 g of fructose powder was mixed with about 3400 g of methanol and about 20 g of methane sulphonic acid. The reaction mixture was transferred to a reactor. Next, the reactor was heated under stirred condition and maintained at about 95 °C for about 5 h. After 5 h the reaction mass was analyzed using gas chromatography for methyl levulinate formation. The analysed reaction mass contained about 2.6 % methyl levulinate, which corresponded to about 28 % yield of theoretical value based on the input sugars.

EXAMPLE 9

To about 400 g of the reaction product obtained from EXAMPLE 6, about 2.5 g of methane sulphonic acid was added and the resulting mixture was heated in a stirred autoclave reactor at about 105 °C for 7 h. After 7 h the reaction mass was analyzed by gas chromatography for methyl levulinate formation. The analysed reaction mass contained about 7 % methyl levulinate, which corresponded to a yield of about 71 % of theoretical value based on the input sugars.

EXAMPLE 10

To about 400 g of the reaction product obtained from EXAMPLE 6 about 2.5 g of methane sulphonic acid was added and the resulting mixture was heated in a stirred
autoclave reactor at 95 °C for 7 h. After 7 h the reaction mass was analyzed by gas chromatography for methyl levulinate formation. The analysed reaction mass contained about 3 % methyl levulinate, which corresponded to about 65 % yield of theoretical value based on the input sugars.

EXAMPLE 11

The reaction mass obtained in EXAMPLE 2, was further subjected to downstream treatment similar to that explained in EXAMPLE 1 and 100 g aqueous layer obtained post extraction with EDC was acidified with about 4.1 g HCl (30 % by weight) and heated on a oil bath maintained at about 135 °C for about 5 h. During this period methanol was continuously distilled out and simultaneous water was added drop wise to maintain reaction volume. After 5 h, the reaction mass was analyzed by HPLC and showed presence of about 4 % glucose and no presence of methyl glucoside. This corresponded to about 88 % yield of the theoretical value.

EXAMPLE 12

In a similar manner 551 g aqueous layer obtained post EDC extraction from EXAMPLE 2, containing 32 g of methyl glucoside was mixed with about 11.3 g of H₂SO₄, and about 0.8 g of sodium chloride. The mixture was heated in an oil bath maintained at about 135 °C for about 12 h. During this period methanol was continuously distilled out and simultaneous fresh water was added drop wise to maintain reaction volume. After 12 h, the reaction mass was analyzed by HPLC and showed presence of about 5.24 % glucose and without any methyl glucoside.

EXAMPLE 13

About 9.5 g methyl levulinate obtained from one of the above mentioned examples was mixed with 20 g about water and about 0.2 g H₂SO₄ and the mixture was refluxed with continuous removal of methanol 4 h. After 4 h, the reaction mass, on
analysis by GC technique, was found to contain about 39% of levulinic acid, which
corresponded to about 99% yield of theoretical value.

EXAMPLE 14

Molasses of about 1000 g was mixed with about 6200 g of methanol and about 170
g of sulphuric acid. The mixture was heated under pressure at about 105 °C for 5 h
under stirring. After 5 h the reaction mass was cooled and centrifuged to effect solid-
liquid separation. The sludge obtained after centrifugation was stirred in about 200 g
of methanol followed by second solid-liquid separation. Supernatants of both solid-
liquid separations were mixed together and further 17 g sulphuric acid was added to
the mixture, and it was again heated under pressure at about 105 °C for about 12 h.
The reaction mass on analysis by GC showed formation of about 1.7% methyl
levulinate. This reaction mass was further downstream processed in a manner stated
above and the aqueous layer after solvent extraction was collected. This aqueous
layer on hydrolysis resulted in a glucose solution containing about 5% glucose by
weight.

While the invention has been particularly shown and described with reference to
embodiments listed in examples, it will be appreciated that several of the above
disclosed and other features and functions, or alternatives thereof, may be desirably
combined into many other different systems or applications. Also that various
presently unforeseen and unanticipated alternatives, modifications, variations, or
improvements therein may be subsequently made by those skilled in the art which
are also intended to be encompassed by the following claims. Although the invention
has been described with reference to specific preferred embodiments, it is not
intended to be limited thereto, rather those having ordinary skill in the art will
recognize that variations and modifications may be made therein which are within
the spirit of the invention and within the scope of the claims.
WE CLAIM:

1. A process for the preparation of levulinic acid comprising:
   (a) providing a feedstock comprising fructose;
   (b) mixing methanol and an acid with said feedstock and allowing insoluble matter to separate forming a first stream;
   (c) subjecting said first stream to solid-liquid separation forming a reaction mixture free of said insoluble matter;
   (d) maintaining said reaction mixture at an effective temperature for a specific time period forming a second stream;
   (e) subjecting said second stream to pH correction using an alkali forming a third stream;
   (f) distilling said third stream forming a fourth stream and a forming a first distillate stream;
   (g) filtering said fourth stream forming a fifth stream;
   (h) extracting said fourth stream with an organic solvent to get a mixture of aqueous and organic phases;
   (i) separating said mixture by liquid-liquid separation forming an organic stream and an aqueous stream;
   (j) subjecting said organic stream to distillation to remove said organic solvent and get a product stream comprising methyl levulinate;
   (k) recovering levulinic acid from said methyl levulinate by hydrolysis and removal of methanol; and
   (l) recovering glucose from said aqueous stream by hydrolysis and removal of methanol.
2. The process of claim 1, wherein said feedstock comprises molasses, cane sugar syrup or inverted glucose.

3. The process of claim 1, wherein said acid is one of sulphuric acid, hydrochloric acid or methane sulphonic acid,

4. The process of claim 1, wherein said specific time period in step [b] is between about 20 minutes to about 300 minutes.

5. The process of claim 1, wherein pH of said second stream is between about 6 and about 8.

6. The process of claim 1, wherein said alkali is one of ammonia, sodium hydroxide or sodium bicarbonate.

7. The process of claim 1, wherein methanol is recovered and recycled.

8. The process of claim 1, wherein said organic solvent is one of ethylene dichloride or methyl isobutyl ketone.

9. The process of claim 1, wherein said organic solvent is recovered and recycled.

10. The process of claim 1, wherein said effective temperature in step [d] is between about 90° C to about 120° C.

11. The process of claim 1, wherein said effective time-perid in step [d] is up to 20 h.

12. The process of claim 1, wherein formic acid is recovered from said first distillate stream.

13. The process of claim 1, wherein glucose recovered from said aqueous stream is fermented to ethanol.

14. The process of claim 1, wherein glucose recovered from said aqueous stream is enzymatically inverted to fructose.
15. The process of claim 1, wherein yield of levulinic acid is at least 60% by weight of fructose.

16. The process of claim 1, wherein recovery of unreacted glucose in the form of fermentable glucose at least 90% by weight of glucose.

17. A product comprising levulinic acid prepared according to claim 1.
FIGURE 1

Sucrose → Fructose + Glucose

Fructoside

Selective Reaction

Levulinate

Glucoside

No reaction

Hydrolysis

Glucose
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
C07C67/00, C07C5 9/185 Version=2016.01

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)
IPO INTERNAL, PATSEER

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US3267136 A Carlos Vincenty ET AL 16-08-1966 (16 Aug 1966) Example 1</td>
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<td>CN101781210 A XIUYANG LV ET AL 21-07-2010 (21 JULY 2010) CLAIMS</td>
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