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(54) **Title**: SUCCINIC ACID FROM BIOMASS

(57) **Abstract**: Disclosed is a method that allows obtaining succinic acid or succinic anhydride from biomass, with good yield, under mild conditions and yet avoiding fermentative processes. The method comprises obtaining levulinic acid from biomass, and converting the levulinic acid into succinic acid. According to the invention, the latter process is conducted by subjecting succinic acid to elevated temperature in the presence of nitric acid. Preferably vanadium pentoxide is added as a catalyst.

Title: SUCCINIC ACID FROM BIOMASS

Field of the Invention

The invention pertains to the synthesis of succinic acid, or carboxylic acid derivatives thereof, from biomass. Particularly, the invention pertains to a chemical route of converting levulinic acid into succinic acid, or a corresponding conversion of a carboxylic acid derivative of levulinic acid.

Background of the invention

It is desired for the world to become less dependent on fossil feedstock. Particularly, with fossil feedstock prices increasing and in view of the need to reduce greenhouse gas emissions, there is an increasing interest to make better use of biomass. Whilst this has long been investigated with a view to obtaining biofuels, an increasing demand exists for obtaining biobased bulk chemicals.

One such potential biobased bulk chemical is succinic acid (IUPAC name: butanedioic acid). Succinic acid can be used for a multitude of biobased products. E.g., it can serve as a platform chemical for the production of chemicals like 1,4-butanediol, THF (tetrahydrofuran), γ-butyrolactone, 2-pyrrolidone, succinate esters and the like. Next to this succinate has potential to be used in polymers such as PBS (polybutylene succinate) also known as Bionolle®.

Recently fermentative routes for the production of succinic acid, starting from varying fermentable sugars, have received considerably increased attention. A 2008 review by Stevens et al. (A. Cukalovic, C.V. Stevens, "Feasibility of production of succinic acid…; Biofuels, Bioprod. Bioref.

2; 505-529, 2008) describes various processes for the fermentative production of succinic acid. Productivities are approximately within the range of 3 grams/liter/hour resulting in concentrations of approximately 20-30 gl^{-1} of succinate. These are low productivities (space time yields) compared to many chemical processes and on top of that the relatively low concentrations make product recovery a significant challenge. Furthermore the process is not fully selective towards the formation of succinic acid and, depending on the microorganism and conditions, besides succinic acid also non volatile components such as pyruvic acid, acetic acid and malic acid are formed during the fermentation process (ref e.g. Meynial-Salles et al. Biotechnology and Bioengineering, 99, 2008. p. 13-135).

As advantages of fermentative processes above thermo-chemical ones, the much milder conditions are usually advocated. In contrast, however, fermentative processes frequently require much longer reaction times and the necessity to work under diluted aqueous conditions. These conditions impose significant challenges on the down stream processing of the reaction products.

It is therefore desired to provide a suitable thermo-chemical route for the production of succinic acid from biomass, that can operate under highly concentrated aqueous biomass conditions, at relatively low temperatures. A potential starting material for this is levulinic acid (4-oxopentanoic acid), which can be obtained from biomass. Reference is made to US 6,054,611 which discloses a method for the production of levulinic acid by an acid catalyzed conversion of (hemi)cellulosic material.

US 6,054,611 mentions that the production of levulinic acid via the described process also allows for recovery of certain by-products, to be separated by chromatography, viz. furfural, 5-HMF, succinic acid, maleic acid, or fumaric acid. The patent aims at producing levulinic acid and no yields of succinic acid are given.

In a 1952 patent (US 2,676,186) a process is described for the synthesis of succinic acid from levulinic acid. The described method uses an

ammonium metavanadate catalyst; at temperatures as high as 275- 400 °C, levulinic acid is converted into succinic acid, in 48 % yield at 275 °C and 81 % yield at 400 °C.

The high temperatures required form a severe limitation to the economical use of this process. Moreover, the very desire to produce succinic acid from biomass is related to providing environmentally better sustainable chemistry. It will be apparent that this should not be outbalanced by a need for high energy input, such as the high temperatures as used in US 2,676,186.

The aforementioned chromatographic separation of succinic acid as a by-product of the synthesis of levulinic acid as disclosed in US 6,054,611 clearly does not serve to provide an economically viable, energy-attractive, method of producing succinic acid.

Summary of the invention

In order to better address the foregoing desires, the invention, in one aspect, presents a process for the preparation of succinic acid or succinic anhydride,, or a carboxylic acid derivative thereof, by thermo-chemical conversion of levulinic acid, or a carboxylic acid derivative thereof, the process comprising heating levulinic acid, notably at mild temperatures, in the presence of nitric acid.

In another aspect, the invention presents the use of vanadium pentoxide as a catalyst in the thermo-chemical conversion, in the presence of nitric acid, of levulinic acid into succinic acid.

In a still further aspect, the invention provides a method for the production of succinic acid from biomass, the method comprising (a) obtaining levulinic acid from biomass, and (b) subjecting heating the levulinic acid, notably at mild temperatures, in the presence of nitric acid.

In yet another aspect, the invention puts to use nitric acid as an oxidizing agent in the thermo-chemical conversion of levulinic acid into succinic acid.

Detailed description of the invention

From a chemical point of view the invention, in a broad sense, is based on the choice of nitric acid as an agent in the thermo-chemical conversion of levulinic acid into succinic acid. Effectively, this reaction involves an oxidative process in which levulinic acid is converted into succinic acid or a mixture of succinic acid (generally as a major amount) and oxalic acid, the amount of oxalic acid usually not exceeding 30%.

The foregoing is equally applicable to the conversion of carboxylic acid derivatives of levulinic acid. Where the term "carboxylic acid" is used, in the context of the invention this can apply to either the free carboxylic acid, or a carboxylic acid derivative. The term "carboxylic acid derivatives" is known to the skilled person, and refers to any carboxylic compound in which the hydroxyl group is replaced by a group that can be split-off so as to yield the acid again. Such groups typically include acid halides, acid anhydrides, esters, and amides. Preferred carboxylic acid derivatives of levulinic acid as used in the invention are esters and amides. It will be understood that if the starting compound is a carboxylic acid derivative of levulinic acid, the resulting product can be either a free acid or the anhydride (i.e. succinic acid or anhydride), or the corresponding carboxylic acid derivative of succinic acid, e.g. succinic acid amide.

The invention relates to thermo-chemical conversion. In contrast to biological conversion such as fermentative processes, this refers to chemical reactions that are basically induced by subjecting reactants to an effective

combination of temperature and time conditions, optionally under the influence of a catalyst.

In the process of the invention, nitric acid is used in an amount effective to establish the formation of succinic acid. This will generally be more than 0.1 equivalent of nitric acid calculated on levulinic acid, preferably more than 0.5 equivalent, and more preferably a stoichiometric or excess amount of nitric acid. Generally, the nitric acid will be present in an amount of at least 100 gram/liter. Preferably nitric acid is present in excess and, most preferably, it is used as the reaction medium. To this end the nitric acid preferably has a concentration of at least 200 gram/liter, more preferably at least 250 gram/liter.

For the production of succinic acid from levulinic acid, in the presence of nitric acid, the reaction is conducted at elevated temperature. Although higher heating temperatures are possible, it will be clear that the advantages of the invention will be most pronounced if the heating is conducted at relatively mild elevated temperatures. The heating in the process of the invention refers to a temperature above ambient temperature (generally above 18°C), at atmospheric pressure. It will be understood by the skilled person that lower temperatures can be used, and would be regarded "elevated" if the reaction is conducted under elevated (i.e. above atmospheric) pressure. It is preferred that the reaction temperature, calculated on the basis of atmospheric pressure, is below 100°C Preferably, also with a view to optimally benefit from the energy-attractiveness of the process of the invention, the reaction is conducted at a temperature between 20°C and 80°C and more preferably between 40°C and 60°C.

It will be understood that the reaction is conducted, for a sufficient period of time to obtain the reaction product. In general, the reaction will be conducted for half an hour to one day, preferably one hour to half a day, and more preferably for 2 to 6 hours.

When apprised of the reactants to be chosen, and being informed of the favorable reaction conditions obtainable with the process of the invention, the skilled person will be able to select the best suited reaction conditions (pressure, temperature, time) and reaction equipment.

Whilst nitric acid is known as an oxidizing agent, in the art the use of an oxidizing agent, e.g. hydrogen peroxide, does not *per se* result in the formation of succinic acid. The inventors, without wishing to be bound by theory, believe that in the specific conversion of levulinic acid into succinic acid, with the formation of oxalic acid, it not only acts as an oxidative agent, but also as a catalyst or co-catalyst for this conversion. Without this combined action, as an oxidative agent and as a catalyst, it would not be well-explicable that so much milder reaction conditions can be employed than in the aforementioned process of US 2,676,186.

The relatively mild reaction conditions, and good yields obtainable, render the process of the invention a favorable choice not only to avoid the drawbacks of fermentative processes, but still have desirably mild conditions.

To this end, in one aspect the invention further provides the use of nitric acid as an oxidative agent in the thermo-chemical conversion of levulinic acid into succinic acid.

The nitric acid will preferably be used in a concentration of at least 200 g/liter. Preferably, the nitric acid (in aqueous solution at 200 to 650 g/liter) is used as a reaction medium.

In addition to nitric acid small amounts (0.1 to 0.5% by weight, preferably 0.2-.0.25 % by weight compared to nitric acid) of sodium nitrite ($NaNO_2$) are optionally present. This is a preferred embodiment, which serves to accelerate the reaction.

The term nitric acid also includes the usual nitrogen oxides such as NO and NO_2, that are present in nitric acid. In addition to nitric acid, other acids and/or oxidizing agents can be present.

Compared to fermentative processes, the process of the invention presents an advantage in that it immediately results in the production of succinic acid instead of its salts. Furthermore the nitric acid further oxidizes unstable components into e.g. gaseous products that are easily removed. In contrast to this (see examples 6 and 7) the succinic acid formed, is stable under reaction conditions applied. Overall this leads to a much simpler and improved down stream processing.

In order to be able to employ even milder conditions, it has also been found, in accordance with another aspect of the invention, that the foregoing reaction can be advantageously conducted in the presence of vanadium pentoxide as a catalyst.

In this respect, the invention in a still further aspect presents the use of vanadium pentoxide as a catalyst in the thermo-chemical conversion, in the presence of nitric acid, of levulinic acid into succinic acid. Vanadium pentoxide (V_2O_5) will generally be used in a catalytic amount, preferably 0.5 - 2.0 wt %. Its use is particularly preferred if it is desired to increase the rate and the selectivity of the reaction.

The reaction processes of the invention, with or without vanadium pentoxide as a catalyst, can be conducted in any reaction equipment normally used in thermo-chemical process chemistry. It will be understood that, with reference to the presence of nitric acid, the equipment is to be chosen such as to sustain the oxidative actions of nitric acid. Such equipment is well-known and available to the skilled person, and does not require any elucidation here.

The foregoing reaction most advantageously can be employed for the purpose of producing succinic acid from biomass. The term biomass is defined as any organic matter that is available on a renewable basis, including dedicated energy crops and trees, agricultural food and feed crop residues, (recycled) paper residues, aquatic plants, wood and wood residues, animal wastes and other waste materials.

In accordance with the invention, in order to use lignocellulosic biomass for the production of succinic acid, the levulinic acid used as a starting material can be obtained from such biomass. This can be done, e.g., by a process as described in US 6,054,611. Levulinic acid can, e.g., be produced by mixing biomass containing cellulose and hemicellulose with a solution of approximately 25-90 % sulfuric acid. By dilution of the gel thus obtained and separating the liquid portion, levulinic acid can subsequently be obtained by heating the liquid mixture at 80-100 °C for 7-42 hours. In an alternative procedure, levulinic acid efficiently can be obtained from cellulose as previously published by Efremov. Without further purification, the so obtained levulinic acid can be transformed into succinic acid by means of the process of the invention (examples 10 and 11).

It will be understood that the step of obtaining levulinic acid does not require isolation of levulinic acid. Whilst the latter is not excluded, it is in fact preferred – as a more economical way of operation – to use a (e.g. converted as above) biomass mixture that comprises levulinic acid, and subject that to the nitric acid reaction of the invention.

In this respect the invention, according to one aspect thereof, also resides in a method for the production of succinic acid from lignocellulosic biomass, the method comprising (a) obtaining levulinic acid from biomass, and (b) subjecting the crude levulinic acid, optionally after isolation and/or purification thereof, to elevated temperature in the presence of nitric acid.

For the various embodiments of step (b), viz. the conversion of levulinic acid into succinic acid, reference is made to the above-mentioned conditions. As above, it is preferred to use vanadium pentoxide as a catalyst.

In all of the foregoing aspects and embodiments, it will be understood that not only succinic acid can be readily produced, but also carboxylic acid derivatives thereof. Such derivatives include, but are not limited to, succinic anhydride, succinic esters, and succinic amides. Generally, these carboxylic acid derivatives can be produced in accordance with the

invention from the corresponding carboxylic acid derivatives of levulinic acid. Esters can be made up of any alcohol, e.g. C_{1-30} alcohol, preferably C_{1-10} alcohol, and more preferably C_{1-6} alcohol. For amides, the analogous amines are preferably employed. The amount of water in the reaction system can be used to steer the reaction towards the production of succinic acid or, in the event of a relatively low water-content, succinic anhydride.

The succinic acid produced by the method of the invention can be isolated and purified in accordance with standard methods in the art.

From the above it follows that the conversion of levulinic acid into succinic acid, which goes in near quantitative conversion yield (generally over 90% conversion, and particularly capable of over 95% conversion, typically approximately 99%), involves the co-production of oxalic acid. The skilled person will not have any difficulties beyond normal chemical work-up in separating, isolating and purifying both the chemicals obtained.

In this respect, the invention also pertains to the combined production of succinic acid and oxalic acid, including carboxylic acid derivatives thereof as indicated above.

It is to be understood that the invention is not limited to the embodiments as described hereinbefore. It is also to be understood that in the claims the word "comprising" does not exclude other elements or steps. Where an indefinite or definite article is used when referring to a singular noun e.g. "a" or "an", "the", this includes a plural of that noun unless something else is specifically stated.

The invention will be illustrated with reference to the following, non-limiting Examples. Parts and percentages in the following examples are by weight.

Methods

Materials

Levulinic acid (98%) and vanadium(V)oxide (98+%) were purchased from Sigma-Aldrich. Nitric acid (p.a., 65wt%) and Sicapent from Merck, and sodium nitrite (>99%) from Fluka.

NMR

NMR spectra were recorded on a Bruker Avance III spectrometer operating at 400.17 MHz (^{1}H) and 100.62 MHz (^{13}C). DMSO-d_6 (99.9 atom % D, Aldrich) was stored on dried molecular sieves 4Å.

GC

Gas chromatography was performed on a Hewlett-Packard 5890 Series II Gas Chromatograph equipped with an automatic injection system (HP7673 GC/SFC Injector and Controller). Injection volume 1µl. Split ratio 1:20. Column pressure 150kPa Helium. GC column: Varian CP-FFAP (free fatty acids), 25m x 0.32mm x 0.30µm. Detector; FID at 280°C. Injection port temperature 250°C. GC program; Hold 1 min. at 50°C, ramp 7°C/min. to 150°C, then ramp 4°C/min. to 240°C.

Methylation method; typical procedure for acid products

A sample of 5mg of material was weighed into a 2 ml GC vial and dissolved in 1ml of a 1:1 mixture of chloroform (Merck, p.a.) and methanol (Merck, p.a.). To 200µL of this solution was added 100µL of a 0.25M trimethylsulphonium hydroxide solution in MeOH (Fluka). These vials are manually shaken and directly used for GC analysis without further treatment.

Experimental

Percentages in the following examples are by weight.

Example 1

A 100ml 3-neck round bottom flask was equipped with a reflux condenser, a pressure-equalizing dropping funnel, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (34ml, 0.49mol). Under stirring at room temperature, sodium nitrite (86mg, 1.2mmol) was added. Brown fumes appeared and after 10 min. the temperature was increased to 40°C.

A solution of levulinic acid (4.6g, 39.6mmol) in demineralized water (2.3ml) was added drop wise under stirring at such a rate that the increase in temperature did not exceed 5°C, but within a time span of 15 min. Little gas formation was observed during the addition. The resulting clear yellow solution was subsequently stirred for 4h at 40°C.

The solvent was removed with a rotary evaporator at 40°C, under vacuum. The product was further dried in a vacuum oven for 72h, over Sicapent at 200mbar, to give an orange solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The yield of the dry crude product amounted to 3.54g, consisting of 69% succinic acid (20.7mmol, 52% yield) and 27% oxalic acid (10.6mmol, 27% yield).

Example 2

A 100ml 3-neck round bottom flask was equipped with a reflux condenser, a pressure-equalizing dropping funnel, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (34ml, 0.49mol). Under stirring at room temperature, sodium nitrite (86mg, 1.2mmol) and vanadium(V)oxide (86mg, 0.5mmol) were added. Brown fumes appeared and after 10 min. the temperature was increased to 40°C.

A solution of levulinic acid (4.6g, 39.6mmol) in demineralized water (2.3ml) was added drop wise under stirring at such a rate that the increase in temperature did not exceed 5°C, but within a time span of 30min. Gas formation was observed during the addition. The resulting clear green solution was subsequently stirred for 4h at 40°C.

The solvent was removed with a rotary evaporator at 40°C, under vacuum. The product was further dried in a vacuum oven for 18h, over Sicapent at 200mbar, to give a green solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The yield of the dry crude product amounted to 1.76g, consisting of succinic acid (14.9mmol, 38% yield).

Example 3

A 100ml 3-neck round bottom flask was equipped with a reflux condenser, a pressure-equalizing dropping funnel, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (34ml, 0.49mol). Under stirring at room temperature, sodium nitrite (86mg, 1.2mmol) was added. Brown fumes appeared and after 10 min. the temperature was increased to 50°C.

A solution of levulinic acid (4.6g, 39.6mmol) in demineralized water (2.3ml) was added drop wise under stirring at such a rate that the increase in temperature did not exceed 5°C, but within a time span of 30 min. Gas formation was observed during the addition. The resulting clear light yellow solution was subsequently stirred for 1 h at 50°C.

The solution was cooled down to 40°C using a water bath. The solvent was removed with a rotary evaporator at 40°C, under vacuum. The product was further dried in a vacuum oven for 18h, over Sicapent at 200mbar, to give an orange solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The dry crude product mixture amounted to 2.14g, consisting of 13% oxalic acid (278mg, 3.1mmol, 8% yield) and 86% succinic acid (1.84g, 15.6mmol, 42% yield).

Example 4

A 100ml 3-neck round bottom flask was equipped with a reflux condenser, a pressure-equalizing dropping funnel, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (34ml, 0.49mol). Under stirring at room temperature, sodium nitrite (86mg, 1.2mmol) and

vanadium(V)oxide (86mg, 0.5mmol) were added. Brown fumes appeared and after 10 min. the temperature was increased to 50°C.

A solution of levulinic acid (4.6g, 39.6mmol) in demineralized water (2.3ml) was added drop wise under stirring at such a rate that the increase in temperature did not exceed 5°C, but within a time span of 30min. Gas formation was observed during the addition. The resulting clear green solution was subsequently stirred for 1h at 50°C.

The solution was cooled down to 40°C using a water bath. The solvent was removed with a rotary evaporator at 40°C, under vacuum. The product was further dried in a vacuum oven for 18h, over Sicapent at 200mbar, to give a black solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The yield of the dry crude product amounted to 2.29g, consisting of 98% succinic acid (20.7mmol, 48% yield).

Example 5

A 100ml 3-neck round bottom flask was equipped with a reflux condenser, a pressure-equalizing dropping funnel, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (34ml, 0.49mol). Under stirring at room temperature, sodium nitrite (86mg, 1.2mmol) and vanadium(V)oxide (86mg, 0.5mmol) were added. Brown fumes appeared and after 10 min. the temperature was increased to 60°C.

A solution of levulinic acid (4.6g, 39.6mmol) in demineralized water (2.3ml) was added drop wise under stirring at such a rate that the increase in temperature did not exceed 5°C, but within a time span of 30min. Gas formation was observed during the addition. The resulting clear green solution was subsequently stirred for 4h at 60°C.

The solution was cooled down to 40°C using a water bath. The solvent was removed with a rotary evaporator at 40°C, under vacuum. The product was further dried in a vacuum oven for 18h, over Sicapent at 200mbar, to give a black solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The yield of the dry crude product amounted to 1.76g, consisting of succinic acid (14.9mmol, 38% yield).

Example 6

A 100ml 3-neck round bottom flask was equipped with a reflux condenser, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (34ml, 0.49mol). Under stirring at room temperature, sodium nitrite (86mg, 1.2mmol) was added. Brown fumes appeared and after 10 min. the temperature was increased to 60°C.

Succinic acid (4.3g, 36.4mmol) and demineralized water (2.3ml) were added. No temperature increase or gas formation was noticed. The resulting suspension was subsequently stirred for 4h at 60°C.

The solvent was removed with a rotary evaporator at 40°C, under vacuum. The product was further dried in a vacuum oven for 96h, over Sicapent at 200mbar, to give a white solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The yield of the dry crude product amounted to 4.38g, consisting of succinic acid (36.4mmol, 100% recovery).

Example 7

A 100ml 3-neck round bottom flask was equipped with a reflux condenser, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (34ml, 0.49mol). Under stirring at room temperature, sodium nitrite (86mg, 1.2mmol) and vanadium(V)oxide (86mg, 0.5mmol) were added. Brown fumes appeared and after 10 min. the temperature was increased to 60°C.

Succinic acid (4.6g, 39mmol) and demineralized water (2.3ml) were added. No temperature increase or gas formation was noticed. The resulting suspension was subsequently stirred for 4h at 60°C.

The solution was cooled down to 40°C using a water bath. The solvent was removed with a rotary evaporator at 40°C, under vacuum. The product was further dried in a vacuum oven for 18h, over Sicapent at 200mbar, to give a light orange solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The yield of the dry crude product amounted to 4.74g, consisting of succinic acid (39mmol, 100% recovery).

Example 8

A 500ml 3-neck round bottom flask was equipped with a reflux condenser, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

D-fructose (45g, 0.25mol) was dissolved at room temperature in 1N HCl (250ml) to give a colorless solution. The solution was heated to 95°C under stirring for 24h. The resulting black suspension was cooled down to room temperature using an ice bath.

The suspension was filtered over a type 3 glass filter. The filtrate was concentrated with a rotary evaporator at 60°C, under reduced pressure. Residual water was removed in a vacuum oven for 18h, over Sicapent at 200mbar, to give a black viscous liquid.

Product composition was determined by $^{1}H/^{13}C$ NMR.

The yield of the dry crude product amounted to 20.1g, consisting of levulinic acid (0.17mol, 69% yield).

Example 9

A 250ml 3-neck round bottom flask was equipped with a reflux condenser, a pressure-equalizing dropping funnel, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (48ml, 1.17mol). Under stirring at room temperature, sodium nitrite (157mg, 2.3mmol) and

vanadium(V)oxide (157mg, 0.9mmol) were added. Brown fumes appeared and after 10 min. the temperature was increased to 50°C.

A solution of (the in Example 8 prepared) crude levulinic acid (10g, 86mmol) in 10ml demineralized water was added drop wise under stirring, within a time span of 15min. Gas formation was observed during the addition. The resulting clear brown/green solution was subsequently stirred for 1h at 50°C.

The solvent was removed with a rotary evaporator at 60°C, under vacuum. The product was further dried in a vacuum oven for 18h, over Sicapent at 200mbar, to give a dark green solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The yield of the dry crude product amounted to 4.05g, consisting of 1% oxalic acid (41mg, 0.4mmol, 0.5% yield) and 86% succinic acid (3.48g, 29mmol, 34% yield).

Example 10

A 600ml Parr 4560 Mini Bench Top Reactor with a Parr 4843 Controller was charged with Avicel PH-101 cellulose (40g) and 400ml demineralized water. 37% HCl (2.75ml) was added and the reactor was closed.

Under stirring at 500rpm, the reactor was heated from 18°C to 250°C in 40min., reaching a pressure of 51bar. The reaction mixture was subsequently stirred for 2.5h at 250°C. During this period the pressure increased to 57bar. The reactor was allowed to cool down to room temperature in a time span of 2h. The residual pressure was 16bar. The pressure was released and the reactor was opened.

The resulting black suspension was filtered over a type 3 glass filter. The filtrate was concentrated with a rotary evaporator at 60°C, under reduced pressure. Residual water was removed in a vacuum oven for 18h, over Sicapent at 200mbar, to give a black viscous liquid.

Product composition was determined by $^{1}H/^{13}C$ NMR.

The yield of the dry crude product amounted to 19.8g, consisting of levulinic acid (0.17mol, 69% yield based on a MW of 162.14 for cellulose monomers).

Example 11

A 250ml 3-neck round bottom flask was equipped with a reflux condenser, a pressure-equalizing dropping funnel, a thermocouple and a stirring bar. The round bottom flask was heated on a magnetic stirring plate with an oil bath.

The round bottom flask was charged with nitric acid (48ml, 1.17mol). Under stirring at room temperature, sodium nitrite (157mg, 2.3mmol) was added. Brown fumes appeared and after 10 min. the temperature was increased to 50°C.

A solution of (the in Example 10 prepared) crude levulinic acid (10g, 86mmol) in 10ml demineralized water was added drop wise under stirring, within a time span of 30min. Gas formation was observed during the addition. The resulting clear yellow solution was subsequently stirred for 1h at 50°C.

The solvent was removed with a rotary evaporator at 60°C, under vacuum. The product was further dried in a vacuum oven for 18h, over Sicapent at 200mbar, to give an orange solid.

Product composition was determined by $^{1}H/^{13}C$ NMR and GLC.

The yield of the dry crude product amounted to 5.11g, consisting of 17% oxalic acid (0.87g, 9.6mmol, 11% yield) and 74% succinic acid (3.78g, 32mmol, 37% yield).

The conditions and results of the examples are presented in Table 1 below.

Table 1

	Conditions			Products (yield mol%)			
Experimental	St. Mater	Temp	Time (h)	V2O5	Succinic	Oxalic	Lev
1	Lev.	40	4	-	52	27	
2	Lev.	40	4	2%	38	-	
3	Lev.	50	1	-	42	8	
4	Lev.	50	1	2%	48	-	
5	Lev.	60	4	2%	38	-	
6	Suc.	60	4	-	100	-	
7	Suc.	60	4	2%	100	-	
8	Fructose	95	24	-	-	-	69
9	Prod 8	50	1	2%	34	0.5	
10	Cellulose	250	2.5	-	-	-	69
11	Prod 10	50	1	-	37	11	

Claims

1. A process for the preparation of succinic acid or succinic anhydride, by thermo-chemical conversion of levulinic acid, the process comprising heating levulinic acid in the presence of nitric acid.

2. A process according to claim 1, wherein the heating temperature is in the range of from 20°C to 80°C, preferably of from 40° to 60°C.

3. A process according to claim 1 or 2, wherein vanadium pentoxide is added as a catalyst.

4. A process according to any one of the preceding claims, wherein 0.1 to 0.5 % by weight, calculated on the basis of nitric acid, of sodium nitrite is added, preferably in an amount of 0.2-0.5 % by weight.

5. A process according to any one of the preceding claims, wherein the levulinic acid and/or the succinic acid is in an acyl form selected from the group consisting of free carboxylic acid and carboxylic acid derivatives, said derivatives preferably selected from the group consisting of esters and amides.

6. A method for the production of succinic acid or succinic anhydride from biomass, the method comprising (a) obtaining levulinic acid from biomass, and (b) converting the levulinic acid into succinic acid by a process as defined in any one of the claims 1 to 5.

7. The use of nitric acid as an oxidizing agent in the thermo-chemical conversion of levulinic acid into succinic acid or succinic anhydride.

8. The use of vanadium pentoxide as a catalyst in the thermo-chemical conversion, in the presence of nitric acid, of levulinic acid into succinic acid or succinic anhydride.

INTERNATIONAL SEARCH REPORT

International application No
PCT/NL2011/050659

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C51/27 C07D307/60 C07C55/10
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, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2 676 186 A (DUNLOP ANDREW P ET AL) 20 April 1954 (1954-04-20) cited in the application claim 1	1,7,8
A	US 3 833 625 A (BERTRAND J ET AL) 3 September 1974 (1974-09-03) example 12	1,7,8
A	DE 753 781 C (HENKEL & CIE GMBH) 23 August 1951 (1951-08-23) claim 1	1,7,8

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

☒ See patent family annex.

* Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/NL2011/050659

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