

(19)



(11)

**EP 2 199 366 A1**

(12)

**EUROPEAN PATENT APPLICATION**

(43) Date of publication:

**23.06.2010 Bulletin 2010/25**

(51) Int Cl.:

**C10G 1/00 (2006.01)**

**C10G 1/02 (2006.01)**

(21) Application number: **08171260.6**

(22) Date of filing: **10.12.2008**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT  
RO SE SI SK TR**

Designated Extension States:

**AL BA MK RS**

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(54) **Conversion of biomass to bio-oil using inorganic carbonates and decomposition and regeneration of inorganic carbonates**

(57) A process is disclosed for the catalytic conversion of biomass to form a bio-oil. Controlled amounts of inorganic carbonates are used in the process. At least some of the carbonate is converted to the corresponding

oxide or hydroxide during the conversion reaction. The oxide or hydroxide is regenerated to the carbonate, which is recycled to the biomass conversion reaction.

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**Description**

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

**[0001]** The invention relates generally to the use of inorganic carbonates in the conversion of biomass, and more specifically to the decomposition and regeneration of such inorganic carbonates.

## 2. Description of the Related Art

**[0002]** Inorganic carbonates, in particular sodium carbonate and potassium carbonate, have been proposed as catalysts for the conversion of biomass. It is also known that carbonates, in particular potassium carbonate, are formed as a byproduct of the conversion of certain types of biomass. However, the role of inorganic carbonates in biomass conversion has been poorly understood, which has led to on the one hand a sub-optimal use of these carbonates and, on the other hand, to an undesirable accumulation of carbonates in biomass conversion reactors due to the formation of carbonates as a byproduct.

**[0003]** Thus, there is a particular need for an optimized process for the catalytic conversion of solid biomass material making use of the catalytic properties of inorganic carbonates.

## BRIEF SUMMARY OF THE INVENTION

**[0004]** The present invention addresses these problems by providing a process for the catalytic conversion of solid biomass material, said process comprising the steps of:

(i) reacting the solid biomass with an inorganic carbonate, whereby a bio-oil is formed and at least part of the inorganic carbonate is converted to the corresponding hydroxide;

(ii) regenerating the hydroxide to the corresponding carbonate; and

(iii) recycling the carbonate obtained in step (ii) to step (i).

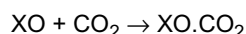
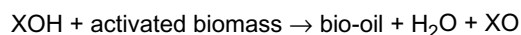
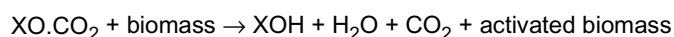
**[0005]** Another aspect of the invention comprises a method for recovering heat from char and coke that are formed during the biomass conversion. Suitably, the step of regenerating the hydroxide to the corresponding carbonate is combined with the step of recovering heat from char and coke.

## DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

**[0006]** The present invention is based on the discovery that inorganic carbonates decompose to the corresponding metal oxide and carbon dioxide under conditions that are suitable for their catalytic conversion of biomass material to a bio-oil.

**[0007]** This discovery has led to the development of a catalytic conversion process for solid biomass material, said process comprising the steps of (i) reacting the solid biomass with an inorganic carbonate whereby a bio-oil is formed and at least part of the inorganic carbonate is converted to the corresponding hydroxide; (ii) regenerating the hydroxide to the corresponding carbonate; and (iii) recycling the carbonate obtained in step (ii) to step (i).

**[0008]** Schematically, this can be represented as follows:



**[0009]** The temperature in step (i) is generally in the range of from 200°C to 500°C, more preferably in the range of from 350°C to 450°C. These temperatures are normally not considered high enough to cause the decomposition of inorganic carbonates. However, due to interactions that exist between the carbonate and the biomass material, at least partial decomposition of the organic carbonates occurs at these temperatures.

**[0010]** In addition, bio-oil that is formed in the conversion of biomass is highly acidic, due to the presence of organic

acids such as carboxylic acids. Typically, bio-oils produced in these reactions have a pH of less than 3. This is low enough to convert an inorganic carbonate to the corresponding hydrogen carbonate, or bicarbonate. The bicarbonates are thermally considerably less stable than the carbonates from which they derive.

[0011] In a sense, the reaction is self catalyzed. The formation of a small amount of a bio-oil lowers the pH, thereby accelerating the decomposition of the carbonate. The metal hydroxide resulting from the decomposition of the carbonate access a sink for the acidic bio-oil compounds that are formed. The presence of the metal hydroxide thereby facilitates the formation of the acidic bio-oil.

[0012] An important corollary to the above described reaction mechanism is the fact that the inorganic carbonates are not true "catalysts" in that they are themselves converted in the reaction that is catalyzed by them. As a consequence, they need to be converted back to the original carbonate before they can be utilized again in the biomass conversion reaction.

[0013] To some extent, regeneration of the hydroxide to the carbonate may take place *in situ*, as sufficient CO<sub>2</sub> may be formed in the biomass conversion to react at least some of the hydroxide back to the corresponding carbonate. This may be a reason why the need for regeneration is not generally recognized by those active in this field.

[0014] The picture is complicated further by the fact that biomass material from most sources contains considerable amounts of inorganic materials, which form a solid byproduct generally referred to as "ash". Depending on the reaction conditions, at least part of the ash will be in the form of inorganic carbonates.

[0015] As a result of these complicating factors, prior art processes tend to operate with uncontrolled amounts of inorganic carbonates. On the one hand, unknown quantities of carbonate are lost to conversion to the corresponding hydroxide. On the other hand, equally unknown quantities of carbonate may be formed from the inorganic materials present in the biomass feedstock.

[0016] The process of the present invention addresses the former issue by providing a regeneration step in which hydroxide is converted to the corresponding carbonate. In a preferred embodiment the process of the invention addresses the latter issue by recovering carbonates present in the ash by-product and recycling them back into the process to the extent required.

[0017] The process of the invention is suitable for conversion of any type of solid biomass material to form a bio-oil. The process is particularly suitable for the conversion of biomass comprising cellulose. The biomass feedstock used in the process may further comprise lignin.

[0018] An important aspect of the process of invention is the formation of bio-oil. In addition, part of the biomass is converted to non-condensable gases. During the conversion reaction to a solid residue is formed as well. The solid residue may contain any unconverted solid biomass material. The solid residue further comprises solid reaction products of the biomass conversion reaction, in general coke and char. The inorganic materials present in the biomass feedstock to some extent end up in the gas phase in the form of fly ash; for the most part, however, the ash is present in the solid residue, generally embedded in the char.

[0019] Any inorganic carbonate that was added to the reaction mixture will also find its way to the solid residue of the biomass conversion reaction. For reasons explained above, at least some of the inorganic carbonate may be present in the solid residue in the form of the hydroxide.

[0020] It is desirable to burn the char and/or coke present in the solid residue by heating the solid residue in an oxygen containing gas. A suitable example of an oxygen containing gas is air. Heat generated by burning the char and/or coke can be used to supply heat to the biomass conversion step. Significant amounts of CO<sub>2</sub> are formed during the burning of the char and coke. Any metal hydroxide or metal oxide present in the solid residue is converted to the corresponding carbonate during this regeneration step. A suitable regeneration temperature is in the range of from 550°C to 800°C, typically around 650°C.

[0021] Regenerated carbonate is recycled back into step (i). Suitably, the carbonate particles may be used to carry heat from the regeneration reaction to the biomass conversion step.

[0022] Any inorganic carbonate is suitable for use as a catalyst in step (i) of the process. Particularly suitable are the carbonates of the monovalent and divalent metals. The monovalent alkali metals are particularly preferred, especially sodium and potassium.

[0023] The ash formed in the solid residue of the biomass conversion reaction may comprise the oxide, the hydroxide or the carbonate of alkali metals and earth alkaline metals. The ash can be converted to the carbonate ash in step (ii), and the carbonate ash can be recycled to step (i).

## Claims

1. A process for the catalytic conversion of solid biomass material, said process comprising the steps of:

(i) reacting the solid biomass with an inorganic carbonate, whereby a bio-oil is formed and at least part of the

inorganic carbonate is converted to the corresponding hydroxide;  
(ii) regenerating the hydroxide to the corresponding carbonate; and  
(iii) recycling the carbonate obtained in step (ii) to step (i).

- 5     **2.** The process of claim 1 wherein the solid biomass comprises cellulose.
- 3.** The process of claim 2 wherein the solid biomass further comprises lignin.
- 4.** The process of any one of the preceding claims whereby, in step (i), a solid residue is formed.
- 10    **5.** The process of claim 4 wherein the solid residue comprises the hydroxide, and solid reaction products of the biomass.
- 6.** The process of claim 5 wherein the solid reaction products of the biomass comprise char and ash.
- 15    **7.** The process of claim 6 wherein step (ii) comprises burning the char off the solid residue in an oxygen-containing gas.
- 8.** The process of any one of the preceding claims wherein the inorganic carbonate is the carbonate of a monovalent or divalent metal.
- 20    **9.** The process of claim 8 wherein the monovalent metal or divalent metal is an alkali metal or an earth alkaline metal.
- 10.** The process of claim 9 wherein the inorganic carbonate is sodium carbonate, potassium carbonate, or a mixture of sodium carbonate and potassium carbonate.
- 25    **11.** The process of claim 6 wherein the ash comprises the oxide, the hydroxide or the carbonate of an alkali metal and/or an earth alkaline metal.
- 12.** The process of claim 11 wherein the ash is converted to carbonate ash in step (ii), and the carbonate ash is recycled to step (i).
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## EUROPEAN SEARCH REPORT

Application Number  
EP 08 17 1260

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 2 581 130 A (MURPHREE EGER V) 1 January 1952 (1952-01-01) * claim 1; figure 1 *	1-12	INV. C10G1/00 C10G1/02
X	US 4 421 631 A (AMPAYA JAIME P [US] ET AL) 20 December 1983 (1983-12-20) * claims 1,9; figure 1 *	1-12	
X	EP 0 121 343 A (PENTANYL TECH INC [US]) 10 October 1984 (1984-10-10) * page 4, line 7 - page 6, line 11 * * page 10, line 19 - page 13, line 5 * * page 18, line 6 - page 25, line 15; claim 1; figure 1 *	1-12	
X	EP 1 970 425 A (BIOECON INTERNAT HOLDING N V [AN]) 17 September 2008 (2008-09-17) * paragraphs [0008], [0011], [0021] - [0023]; claims 1,3,4,10,11,14,15,14 *	1-12	
X	US 4 266 083 A (HUANG MAX W) 5 May 1981 (1981-05-05) * column 2, line 15 - line 65; claims 1,6; figure 1 *	1-12	TECHNICAL FIELDS SEARCHED (IPC) C10G
X	WO 2008/098358 A (RENDINA DAVID [CA]; HAUPTMANN EDWARD G [CA]) 21 August 2008 (2008-08-21) * page 10 - page 19; claims 1,2,5,8; figure 1 *	1-12	
X	US 3 553 279 A (BAWA MOHENDRA S) 5 January 1971 (1971-01-05) * claim 1; figure 1 *	1-12	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 14 May 2009	Examiner Deurinck, Patricia
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 08 17 1260

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
The members are as contained in the European Patent Office EDP file on  
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14-05-2009

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2581130	A	01-01-1952	NONE	
-----				
US 4421631	A	20-12-1983	CA 1178228 A1	20-11-1984
			GB 2106932 A	20-04-1983
			JP 1586121 C	31-10-1990
			JP 2011636 B	15-03-1990
			JP 58071989 A	28-04-1983
			NL 8203693 A	02-05-1983
-----				
EP 0121343	A	10-10-1984	AU 573573 B2	16-06-1988
			AU 2517184 A	13-09-1984
			AU 575872 B2	11-08-1988
			AU 3491384 A	09-05-1985
			CA 1262240 A1	10-10-1989
			DE 3471319 D1	23-06-1988
			GR 79531 A1	30-10-1984
			TR 21864 A	01-10-1985
			ZW 3684 A1	20-06-1984
-----				
EP 1970425	A	17-09-2008	WO 2008101949 A1	28-08-2008
-----				
US 4266083	A	05-05-1981	NONE	
-----				
WO 2008098358	A	21-08-2008	CA 2621673 A1	18-08-2008
			US 2008209797 A1	04-09-2008
-----				
US 3553279	A	05-01-1971	DE 1914710 A1	09-10-1969
			FR 2004996 A5	05-12-1969
			GB 1212811 A	18-11-1970
			NL 6901684 A	01-10-1969
-----				