



US 20120304529A1

(19) **United States**

(12) **Patent Application Publication**
O'Connor et al.

(10) **Pub. No.: US 2012/0304529 A1**

(43) **Pub. Date: Dec. 6, 2012**

(54) **TEMPERATURE-OPTIMIZED CONVERSION
OF LIGNOCELLULOSIC BIOMASS**

(75) Inventors: **Paul O'Connor**, Hoevelaken (NL);
Jacobus Cornelis Rasser, Redondo
Beach, CA (US)

(73) Assignee: **KiOR, Inc.**, Pasadena, CA (US)

(21) Appl. No.: **13/391,720**

(22) PCT Filed: **Sep. 1, 2010**

(86) PCT No.: **PCT/US2010/047507**

§ 371 (c)(1),
(2), (4) Date: **Aug. 17, 2012**

Related U.S. Application Data

(60) Provisional application No. 61/238,728, filed on Sep.
1, 2009.

Publication Classification

(51) **Int. Cl.**
C10L 1/00 (2006.01)

(52) **U.S. Cl.** **44/307**

(57) **ABSTRACT**

A process is disclosed for converting lignocellulosic material to liquid fuels. In the process the cellulose is dissolved in an Ionic Liquid. The conversion process may comprise pyrolysis, thermal cracking, hydrocracking, catalytic cracking, hydrotreatment, or a combination thereof. Undissolved lignin is removed from the Ionic Liquid medium, and is converted in a separate conversion process. The Ionic Liquid preferably is an inorganic molten salt hydrate.

TEMPERATURE-OPTIMIZED CONVERSION OF LIGNOCELLULOSIC BIOMASS

RELATED APPLICATIONS

[0001] This application claims benefit under 35 U.S.C. §119(e) of the U.S. provisional patent application Ser. No. 61/238,728, filed Sep. 1, 2009, the content of which is incorporated herein by reference in its entirety.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The invention relates generally to the conversion of lignocellulosic biomass, and more particularly to such a conversion process comprising use of an Ionic Liquid medium.

[0004] 2. Description of the Related Art

[0005] Several processes have been proposed for converting lignocellulose to hydrocarbons. One such process comprises gasification of cellulose to synthesis gas (“syngas”, a mixture of carbon monoxide and hydrogen), and conversion of the syngas in a Fischer-Tropsch reaction to hydrocarbons. This process is inherently inefficient, because long-chain polymeric materials are first broken down to small molecules, which are subsequently built back up to larger molecules. It is inefficient also because the oxygen content is first increased (syngas has higher oxygen content than cellulose), and subsequently reduced or eliminated.

[0006] Another process is the pyrolysis, in particular fast or flash pyrolysis. High liquid yields have been reported, but the pyrolysis liquids have high oxygen content. The liquids are highly acidic and corrosive. They are unstable, due to their propensity to polymerization. Moreover, the liquids contain large amounts of water, which is difficult to separate from the organic components due to the hydrophilic nature of the organic compounds. The liquids need to be subjected to a separate upgrading to provide usable hydrocarbon products. Upgrading processes reported in the prior art generally comprise two hydrotreatment steps. In a first step, which is carried out in the presence of the water component of the pyrolysis liquid, the organic compounds are deoxygenated to the point that they become sufficiently hydrophobic to cause phase separation into an aqueous phase and an oil phase. The oil phase is further deoxygenated to form hydrocarbons. The three-step process has a rather poor overall yield.

[0007] It has been known to dissolve cellulose in Ionic Liquids. S. Fischer et al., “*Inorganic molten salts as solvents for cellulose*”, Cellulose 10: 227-236, 2003, discloses the use of various molten salt systems as solvent media for cellulose. Upon dissolution, cellulose can be derivatized by carboxymethylation or acetylation. The derivation reactions leave the cellulose polymer backbone in tact.

[0008] Sheldrake and Schleck, “*Dicationic molten salts (ionic liquids) as re-usable media for the controlled pyrolysis of cellulose to anhydrosugars*”, Green Chem 2007, pp 1044-1046, reports on low temperature pyrolysis of cellulose in ionic liquid media. The pyrolysis temperature is low enough that the ionic liquid can be recovered and re-used after the pyrolysis reaction. The pyrolysis products are anhydrosugars. The reported conversion yields are 3.5 wt % or less.

[0009] Thus, there is a need for a process in which lignocellulosic biomass is converted to liquid fuels at a high yield. There is a particular need for such a process in which cellulose and lignin are each converted at a feedstock-specific

conversion temperature. There is a further need for such a process that can be carried out in continuous mode.

BRIEF SUMMARY OF THE INVENTION

[0010] The present invention addresses these problems by providing a process for converting lignocellulosic biomass material to a liquid fuel, said process comprising the steps of:

[0011] (i) contacting the lignocellulosic biomass material with an Ionic Liquid to form a solution of at least part of the cellulose component of the biomass material;

[0012] (ii) separating undissolved lignin from the cellulose solution;

[0013] (iii) converting the dissolved cellulose material to a liquid fuel at a first temperature T_1 ;

[0014] (iv) converting the undissolved lignin to a liquid fuel at a second temperature T_2 ;

[0015] wherein $T_1 < T_2$.

DETAILED DESCRIPTION OF THE INVENTION

[0016] The present invention relates to a process for converting lignocellulosic biomass material to a liquid fuel, said process comprising the steps of:

[0017] (i) contacting the lignocellulosic biomass material with an Ionic Liquid to form a solution of at least part of the cellulose component of the biomass material;

[0018] (ii) separating undissolved lignin from the cellulose solution;

[0019] (iii) converting the dissolved cellulose material to a liquid fuel at a first temperature T_1 ;

[0020] (iv) converting the undissolved lignin to a liquid fuel at a second temperature T_2 ;

[0021] wherein $T_1 < T_2$.

[0022] Any lignocellulosic material can be used in the process of the invention. Preferred are lignocellulosic biomass materials, in particular forestry waste materials (wood chips, saw dust; tree bark; leaves); agricultural waste materials (straw; bagasse; corn stover; and the like); and energy crops (switch grass; coppice; fast-growing trees, such as eucalyptus, willow, poplar).

[0023] Lignin is insoluble in certain Ionic Liquid media, and partially soluble in others. It is an essential part of the process that undissolved lignin is removed from the Ionic Liquid in step (ii). Dissolved lignin is at least partially converted to hydrocarbon compounds during step (iii). The mixture of hydrocarbon compounds is more complex as a result when lignin is present in the Ionic Liquid medium during step (iii). This can provide a distinct advantage. For example, if the hydrocarbon products produced by the process are to be used as a gasoline mixing stock, the presence of lignin conversion products tends to increase the octane rating of the mixture.

[0024] In an alternate embodiment the operator of the process can select an Ionic Liquid medium in which lignin is substantially insoluble. As a general rule, lignin is insoluble in inorganic molten salt hydrates. It has surprisingly been found that nevertheless these materials are capable of dissolving the cellulose component of a lignocellulosic composite material. This makes it possible to unlock the cellulose portion of a lignocellulosic material, without requiring a separate process, such as the Kraft process, which involves the use of aggressive and environmentally undesirable chemicals. Accordingly, the process of the present invention permits separate processing of the cellulose (and hemicellulose) com-

ponents of a lignocellulosic biomass material, on the one hand, and the lignin component on the other.

[0025] Many sources of lignocellulosic material further contain inorganic materials. To the extent these materials are insoluble in the Ionic Liquid medium they are easily removed from the process prior to step (iii). Inorganic materials that are dissolved in the Ionic Liquid medium can be removed in a regeneration step, for example using solvent extraction.

[0026] It is desirable to at least partially hydrolyze dissolved cellulose and hemicellulose to the corresponding sugars. This can be accomplished by adding an acid catalyst, for example hydrochloric acid (HCl); by increasing the temperature of the Ionic Liquid medium to above about 70° C.; or by a combination of these two measures.

[0027] An important aspect of the process of the present invention is that the (hemi-)cellulose and cellulose component of the lignocellulosic biomass material are converted at one temperature, T_1 , whereas the lignin component is converted at a different temperature, T_2 . Generally, the (hemi-)cellulose conversion is carried out at a lower temperature than the lignin conversion. In other words, $T_1 < T_2$.

[0028] Preferably T_2 is at least 50° C. higher than T_1 , more preferably at least 100° C.; most preferably at least 200° C.

[0029] The conversion of the (hemi-)cellulose component takes place in solution, which permits the use of low conversion temperatures. Preferably, T_1 is less than 200° C.

[0030] The conversion of solid lignin generally requires a temperature greater than 200° C., preferably in the range of from 300° C. to 600° C.

[0031] Step (iii) can be carried out in the absence or of a catalyst. Dissolved cellulose, in particular when hydrolyzed to sugars, is far more reactive than cellulose in solid form, so that suitable conversion yields can be obtained even in the absence of a catalyst.

[0032] It can be advantageous to carry out step (iii) in the presence of a catalyst. The presence of a catalyst accelerates the conversion reaction of dissolved cellulose, which reduces the reaction time; or permits the reaction to be carried out at a lower temperature than the uncatalyzed reaction; or a combination of these two advantages. In addition, use of a catalyst generally results in a more selective hydrogenation reaction.

[0033] Examples of suitable catalysts include catalysts selected from the group consisting of hydrotreatment catalysts; hydrogenation catalysts; hydrocracking catalysts; and combinations thereof.

[0034] In one embodiment the catalyst comprises a hydrotreatment catalyst. Suitable examples include catalysts comprising one or more of the elements from the group consisting of Ni, Co, Mo, and W. Preferred are catalysts comprising Mo. More preferred are catalysts comprising Mo and Ni or Co.

[0035] In a specific embodiment the hydrotreatment catalyst is in a sulfided form. The catalyst may be converted to the sulfided form by contacting it with a feedstock that has been spiked with a sulfur-containing compound. The practice of sulfiding hydrotreatment catalysts is well known in the world of oil refining, and will not be further disclosed here.

[0036] As a general rule, hydrotreatment catalysts are more active when in a sulfided form, as compared to an oxide form. However, the use of sulfur results in consumption of hydrogen for the formation of H_2S . This is undesirable from a perspective of a loss of valuable hydrogen, as well as from the resulting need to remove H_2S from the reaction mixture. Moreover, as lignocellulosic feedstocks typically contain

little or no sulfur, it is necessary to spike the feedstock with sulfur in order to keep the catalyst in its sulfided form.

[0037] In many cases it is economically more attractive to forego sulfidization of the hydrotreatment catalyst, as the lower catalyst activity is more than outweighed by the advantage of being able to operate sulfur-free.

[0038] In an alternate embodiment the catalyst comprises a hydrogenation catalyst. Examples include catalysts containing Ni, Fe, or a metal from the Pt group in its metallic form. Particularly preferred are the noble transition metals.

[0039] In yet another embodiment the catalyst comprises a hydrocracking catalyst. For the purpose of the present invention the term "hydrocracking catalyst" refers to catalysts containing both a hydrogenation functionality and a cracking functionality. The hydrogenation functionality is generally provided by one or more of the typical hydrogenation metals (Ni, Fe, noble transition metals). The cracking functionality is generally provided by acidic sites in the catalyst material. Thus, a hydrogenation metal on a solid acid support, such as an acidic zeolite, is typically a very effective hydrocracking catalyst.

[0040] It should be recognized that many Ionic Liquids are strong Lewis acids, and can act as acidic catalysts. Thus, the combination of a hydrogenation catalyst in an Ionic Liquid medium that is a strong Lewis acid can show strong hydrocracking properties.

[0041] The Ionic Liquid medium can comprise an organic anion. In particular dicationic organic Ionic Liquids are excellent solvents for cellulose and hemicellulose. Several organic Ionic Liquids have been reported in the literature as being capable of (partially) dissolving the lignin component of lignocellulosic materials. Organic Ionic Liquids also have major disadvantages, the most important ones being high cost, and limited temperature resistance. Many have the additional disadvantage that they are poor solvents for cellulose when contaminated with water.

[0042] Step (iv) can, for example, be carried out in a cyclone reactor, a fixed fluidized bed reactor, or a transported fluidized bed reactor.

[0043] The process of step (iv) can be carried out in the absence of a catalyst, for example a pyrolytic conversion or a thermal cracking process.

[0044] Preferably step (iv) is carried out in the presence of a catalyst, for example a hydrocracking, catalyst, a cracking catalyst, or a hydrotreatment catalyst. The catalyst can be used as a heat transfer medium to apply heat to the endothermic conversion reaction.

[0045] In one embodiment the catalyst in step (iv) comprises a solid acid. Examples of suitable solid acids include acidic zeolites, such as zeolite-Y, ZSM-5 (in particular HZSM-5), and combinations thereof.

[0046] In an alternate embodiment the catalyst comprises a solid base.

[0047] Examples of suitable solid base materials include hydrotalcite; hydrotalcite-like materials; mixed metal oxides; layered hydroxy salts; clays; and the calcination products of any of these materials.

[0048] The catalyst can comprise alumina.

[0049] The catalyst can be mixed with an inert heat transfer medium, such as silica sand. Mixing the catalyst with an inert heat transfer medium permits independent adjustment of the lignin/catalyst ratio and the lignin/heat carrier ratio.

[0050] Preferred Ionic Liquids are inorganic Ionic Liquids, in particular inorganic molten salt hydrates. As compared to

organic Ionic Liquids, inorganic Ionic Liquids are more temperature stable, and have a lower cost. In addition, in particular the inorganic molten salt hydrates are effective solvents for cellulose even in the presence of water. In fact, as their name indicates, a certain amount of water needs to be present for these materials to function as Ionic Liquid media.

[0051] Inorganic Ionic Liquids have an inorganic anion. The anion can contain a halogen atom. Examples include halides, oxyhalides and hydroxyhalides, in particular chloride, oxychlorides, and hydroxychlorides. The anion can also be hydroxide; for example, the hydroxide of the Cu/ammonia complex is a suitable Ionic Liquid medium for use in the process of the present invention.

[0052] The molten salt hydrate further comprises a cation, in particular Zn, Ba, Ca, Li, Al, Cr, Fe, or Cu.

[0053] Mixtures of inorganic salts can also be used, in particular eutectic mixtures. In general, any salt or salt hydrate that is liquid at a temperature of 200° C. or below, and is capable of dissolving cellulose, is suitable as the Ionic Liquid medium in the process of the present invention.

[0054] Particularly preferred are the hydrates of ZnCl₂, in particular ZnCl₂·4H₂O.

[0055] If step (ii) comprises reaction with hydrogen (hydrogenation, hydrotreatment or hydrocracking, this step is preferably carried out at a hydrogen partial pressure in the range of from 1 to 200 bar, more preferably from 5 to 60 bar. The temperature used in step (iii) to obtain the desired conversion of cellulose and/or sugars to hydrocarbons will depend on the amount and type of catalyst used, and on the contact time between the reactants and the catalyst. In general reaction temperatures in the range of from 150 to 400° C. are suitable, temperatures in the range of from 180 to 350° C. being preferred.

[0056] If step (ii) is carried out in the substantial absence of hydrogen (pyrolysis, thermal cracking, catalytic cracking), this step is generally carried out at a temperature in the range of from 200° C. to 600° C., preferably from 200° C. to 450° C.

[0057] Even when step (ii) is carried out in the presence of hydrogen, the reaction products obtained in step (ii) can still contain residual oxygen. The main objective of step (ii) is to convert cellulose, hemicellulose and their hydrolysis products (C₆ and C₅ sugars, respectively) to reaction products that do not dissolve in the Ionic Liquid medium.

[0058] In one embodiment the reaction products are a C₆ and C₅ hydrocarbon mixture that is oxygen-free, or has an oxygen content low enough for the mixture to be used as a blending stock for gasoline.

[0059] In an alternate embodiment step (ii) is operated such that the reaction products have oxygen content just low enough for them to be insoluble in the Ionic Liquid medium, and miscible with a refinery feedstock. The reaction products can be easily recovered from the Ionic Liquid medium, due to their insolubility therein. The reaction products can also easily be co-processed with a refinery stream, due to their miscibility therewith.

[0060] In yet another embodiment step (ii) is operated to produce primarily dry gas, in particular C₂ and C₃ hydrocarbons.

[0061] In a preferred embodiment at least part of the lignin present in the Ionic Liquid is converted to a liquid fuel.

[0062] Preferably the liquid fuel is insoluble in the Ionic Liquid.

[0063] The process can comprise the additional step (v) of removing the liquid fuel from the Ionic Liquid.

[0064] The process can comprise the additional step of upgrading the liquid fuel.

[0065] In a preferred embodiment the process comprises the additional step (vi) of regenerating the Ionic Liquid medium obtained in step (v). This additional regeneration step can comprise removing water from the Ionic Liquid medium. The regeneration step can comprise removing sludge from the Ionic Liquid medium. The term "sludge" as used herein refers to solid reaction products that are insoluble in the Ionic Liquid medium. The term encompasses such reaction products as coke and certain types of char. In general the process can be operated such that little or no coke and char are formed. However, it may be desirable to produce liquid hydrocarbons under conditions that promote cracking. Such reaction conditions can promote the formation of coke and/or char. The operator of the process may well accept a certain amount of coke yield as a price to pay for a high liquid yield, as coke is easily removed from the Ionic Liquid medium. In general, coke removal can be accomplished by passing the Ionic Liquid through a suitable filter medium, such as a bed of silica or alumina. The filter medium can be regenerated by burning off the coke and any other components of the sludge. Heat generated during this regeneration process can be used in the conversion process, in particular in step (iv).

[0066] The removal of water can generally be accomplished by distillation. Step (iii) is generally carried out under increased pressure, at temperatures exceeding 100° C. By releasing the pressure while the temperature of the Ionic Liquid medium is maintained above 100° C., water is flashed off in a process sometimes referred to as flash-distillation.

[0067] After regeneration the Ionic Liquid medium may be recycled to step (i) of the process. This feature is particularly useful if the process is conducted in continuous mode. It will be understood, however, that the process can be conducted in batch mode as well.

[0068] It will be understood that steps (iii) and (iv) can be conducted independent from each other. For example, lignin recovered from step (ii) can be transported to a separate location for conversion in step (iv).

[0069] Even when steps (iii) and (iv) are carried out at the same location, they can be carried out at different points in time. For example, step (iii) can be carried out immediately after step (ii), while lignin from step (ii) can be stockpiled for conversion in step (iv) at a later time.

[0070] It can be advantageous to carry out steps (iii) and (iv) simultaneously, as this facilitates integration of the heat balances of the two process steps. For example, excess heat as may be generated during a catalyst regeneration step of (iv) can be used to fuel the reaction of step (iii).

1. A process for converting lignocellulosic biomass material to a liquid fuel, said process comprising the steps of:

- (i) contacting the lignocellulosic biomass material with an Ionic Liquid to form a solution of at least part of the cellulose component of the biomass material;
- (ii) separating undissolved lignin from the cellulose solution;
- (iii) converting the dissolved cellulose material to a liquid fuel at a first temperature T₁; and
- (iv) converting the undissolved lignin to a liquid fuel at a second temperature T₂;

wherein T₁ < T₂.

2. The process of claim 1 wherein T₂ - T₁ is at least 50° C., at least 100° C., or at least 200° C.

3. (canceled)

4. (canceled)
5. The process of claim 1 wherein T_1 is less than 200° C.
6. The process of claim 1 wherein T_2 is 200° C. or above.
7. The process of claim 1 wherein step (iii) is carried out in the presence of a catalyst, or wherein step (iv) is carried out in the presence of a catalyst or wherein steps (iii) and (iv) are carried out in the presence of a catalyst.
8. (canceled)
9. The process of claim 7 wherein step (iv) is carried out in a cyclone reactor, a fixed fluidized bed reactor, or a transported fluidized bed reactor.
10. The process of claim 7 the catalyst in step (iv) acts as a heat transfer medium.
11. The process of claim 7 wherein the catalyst in step (iv) comprises a solid acid.
12. The process of claim 11 wherein the catalyst comprises a zeolite.
13. The process of claim 12 wherein the zeolite comprises zeolite Y, ZSM-5, or a combination thereof.
14. The process of claim 7 wherein the catalyst of step (iv) comprises a solid base, hydrotalcite, a hydrotalcite-like material, a mixed metal oxide, a layered hydroxy salt, a clay, or a calcination product thereof.
15. (canceled)
16. The process of claim 7 wherein the catalyst in step (iv) comprises alumina.
17. The process of claim 7 wherein the catalyst in step (iv) is mixed with a particulate inert heat transfer medium.
18. The process of claim 7 wherein step (iv) is carried out at a temperature in the range of from 300° C. to 600° C.
19. The process of claim 1 wherein the liquid fuel produced in step (iii) is insoluble in the Ionic Liquid.
20. The process of claim 1 wherein the Ionic Liquid comprises an organic cation or molten salt hydrate.
21. (canceled)
22. The process of claim 21 wherein the molten salt hydrate comprises a halogen anion.
23. (canceled)
24. The process of claim 20 wherein the molten salt hydrate comprises a cation selected from the group consisting of Zn, Ba, Ca, Li, Al, Cu, Fe, $\text{Cu}(\text{NH}_3)_x$ and Cr.
25. The process of claim 20 wherein the Ionic Liquid is a molten salt hydrate comprising ZnCl_2 , CaCl_2 , LiCl , or a mixture thereof.
26. The process of claim 1 comprising the further step of upgrading the liquid fuel obtained in step (iii) and/or (iv).

* * * * *