

(19)



(11)

EP 2 034 005 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

11.03.2009 Bulletin 2009/11

(51) Int Cl.:

C10L 1/14 (2006.01)

C10L 1/185 (2006.01)

(21) Application number: **07075779.4**

(22) Date of filing: **07.09.2007**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE
SI SK TR**

Designated Extension States:

AL BA HR MK RS

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(54) **Fuel additive concentrate derived from a biomass resource**

(57) The current invention concerns a process for preparing a fuel additive concentrate from a renewable resource (biomass), and to the fuel additive concentrate

comprising a fuel and fuel additives which are made from a renewable resource

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Description

Technical Field

[0001] The current invention concerns a process for preparing a fuel additive concentrate from a renewable resource (biomass), and to the fuel additive concentrate comprising a fuel and fuel additives which are made from a renewable resource.

Background Art

[0002] Fuel, fuel additives and various chemicals used in the petrochemical industry are derived from oil, gas and coal, all finite sources. Biomass, on the other hand, is considered a renewable source. Biomass is biological material (including biodegradable wastes) which can be used for the production of fuels or for industrial production of e.g. fibres, chemicals or heat. It excludes organic material which has been transformed by geological processes into substances such as coal or petroleum.

[0003] Production of biomass derived products for non-food applications is a growing industry. Bio-based fuels are an example of an application with strong growing interest.

[0004] Biomass contains sugars (hexoses and pentoses) that may be converted into value added products. Current biofuel activities from sugars are mainly directed towards the fermentation of sucrose or glucose into ethanol or via complete breakdown via Syngas to synthetic liquid fuels. EP 0641 854 describes the use of fuel compositions comprising of hydrocarbons and/or vegetable oil derivatives containing at least one glycerol ether to reduce particulate matter emissions.

[0005] More recently, the acid catalysed reaction of fructose has been re-visited, creating HMF as an intermediate of great interest. Most processes investigated have the disadvantage that HMF is not very stable at the reaction conditions required for its formation. Fast removal from the water-phase containing the sugar starting material and the acid catalyst has been viewed as a solution for this problem. Researchers at the University of Wisconsin-Madison have developed a process to make HMF from fructose. HMF can be converted into monomers for plastics, petroleum or fuel extenders, or even into fuel itself. The process by prof. James Dumesic and co-workers first dehydrates the fructose in an aqueous phase with the use of an acid catalyst (hydrochloric acid or an acidic ion-exchange resin). Salt is added to salt-out the HMF into the extracting phase. The extracting phase uses an inert organic solvent that favors extraction of HMF from the aqueous phase. The two-phase process operates at high fructose concentrations (10 to 50 wt %), achieves high yields (80% HMF selectivity at 90% fructose conversion), and delivers HMF in a separation-friendly solvent (DUMESIC, James A, et al. "Phase modifiers promote efficient production of Hydroxymethylfurfural from fructose". Science. 30 juni 2006, vol.312, no.

5782, p.1933-1937). Although the HMF yields from this process are interesting, the multi-solvent process has cost-disadvantages due to the relatively complex plant design and because of the less than ideal yields when cheaper and less reactive hexoses than fructose, such as glucose or sucrose, are used as a starting material. HMF is a solid at room temperature which has to be converted in subsequent steps to useful products. Dumesic has reported an integrated hydrogenolysis process step to convert HMF into dimethylfuran (DMF), which is assumed to be an interesting gasoline additive.

[0006] In WO 2006/063220 a method is provided for converting fructose into 5-ethoxymethylfurfural (EMF) at 60 °C, using an acid catalyst either in batch during 24 hours or continuously via column elution during 17 hours. Applications of EMF were not discussed.

[0007] Also in copending patent application PCT/EP2007/002145 the manufacture of HMF ethers are described, including the use of such ethers as fuel or fuel additive. Indeed, both the methyl ether and the ethyl ether (methoxymethylfurfural, or MMF; ethoxyethylfurfural or EMF) were prepared and tested.

[0008] Indeed, there is a growing interest in the preparation of the so-called furanics, wherein the expression furanics is used to include all derivatives of furan and tetrahydrofuran, which are derived from biomass and are used as fuel additive.

[0009] These interesting fuel additives, however, still have to be isolated in a separate process step from the polar solvent used, which thus increases the overall costs of their production, before they can be used as fuel additive. The inventors have therefore set out to overcome this shortfall.

[0010] Surprisingly, the inventors have found that the aforementioned furanics and in particular the ethers of HMF and subsequent derivatives thereof may be effectively and efficiently isolated from the solvents wherein they are produced using fuel as extractant. The extraction provides a fuel additive which can be further concentrated, diluted or added as such to the fuel.

Disclosure of Invention

[0011] Accordingly, the current invention provides a fuel additive concentrate and a method for the manufacture of a fuel additive concentrate comprising a biomass-derived furan derivative and/or tetrahydrofuran derivative dissolved in a fuel, by extracting said derivative from the polar solvent wherein the derivative is produced, using a fuel as extractant. The method is of particular interest in the extraction of ethers of 5-hydroxymethyl-2-furfural and/or further derivatives thereof.

[0012] The current invention also provides for the use of the fuel additive concentrate.

[0013] Fuels for extracting and forming the fuel component of the fuel additive concentrate include but are not limited to gasoline and gasoline-ethanol blends, kerosene, diesel, biodiesel (all renewable fuels combustible

in a diesel engine), Fischer-Tropsch liquids (for example obtained from GTL, CTL or BTL gas-to-liquids/coal-to-liquids/biomass to liquids processes), diesel-biodiesel blends and green diesel and blends of diesel and/or biodiesel with green diesel (green diesel is a hydrocarbon obtained by hydrotreating biomass derived oils, fats, greases or pyrolysis oil; see for example the UOP report OPPORTUNITIES FOR BIORENEWABLES IN OIL REFINERIES FINAL TECHNICAL REPORT, SUBMITTED TO: U.S. DEPARTMENT OF ENERGY (DOE Award Number: DE-FG36-05GO15085)). Fuels for blending with the product of the present invention may also include one or more other furanics, wherein the expression furanics is used to include all derivatives of furan and tetrahydrofuran. The invention also provides a fuel composition comprising a fuel element as described above and the reaction product made according to the present invention.

Mode(s) for Carrying Out the Invention

[0014] Biomass resources are well known. The components of interest in biomass are the mono-, di- or polysaccharides (hereinafter referred to as hexose-containing starting material). Suitable 6-carbon monosaccharides include but are not limited to fructose, glucose, galactose, mannose and their oxidized, reduced, etherified, esterified and amidated derivatives, e.g. aldonic acid or alditol, with glucose being the most abundant, the most economic and therefore the most preferred monosaccharide albeit less reactive than fructose. On the other hand, the current inventors have also succeeded to convert sucrose, which is also available in great abundance. Other disaccharides that may be used include maltose, cellobiose and lactose. The polysaccharides that may be used include cellulose, inulin (a polyfructan), starch (a polyglucan) and hemi-cellulose. The polysaccharides and disaccharides are converted into their monosaccharide component(s) and dehydrated during the manufacture of the 5-HMF ether.

[0015] The current inventors and various other researchers have succeeded in the conversion of the hexose-containing starting material. By way of example hereafter is described the preparation of 5-HMF ethers by reacting a hexose-containing starting material with an alcohol in the presence of an acid catalyst. It should be noted, however, that similar ethers may be made by conversion of the hexose-containing starting material with an olefin in the presence of a suitable catalyst system.

[0016] Alcohols used in the manufacture of 5-HMF ethers are typically monoalcohols, having a primary hydroxyl group. The alcohol may, however, be branched, containing some unsaturated carbon-carbon double bonds, and bear more than one hydroxyl group. Also, rather advantageously mixtures of alcohols may be used; the product which is used as fuel additive does not need to be pure.

[0017] Preferred are alcohols having 4 carbon atoms

or more, although methanol, ethanol and (iso)propanol may be used as well.

[0018] The amount of alcohol used during the manufacture of the HMF ether is preferably at least equimolar on the hexose content of the feedstock, but typically is used in much greater excess. Indeed, the alcohol may be used as solvent or co-solvent. In such a case, a sufficient amount of alcohol is present to form the HMF ether.

[0019] The acid catalyst used in the preparation of an HMF ether can be selected from amongst (halogenated) organic acids, inorganic acids, Lewis acids, ion exchange resins and zeolites or combinations and/or mixtures thereof. It may be a homogeneous catalyst, but heterogeneous catalysts are preferred for purification reasons. The HMF ethers can be produced with a protonic, Brønsted or, alternatively, a Lewis acid or with catalysts that have more than one of these acidic functionalities.

[0020] The protonic acid may be organic or inorganic. For instance, the organic acid can be selected from amongst oxalic acid, levulinic acid, maleic acid, trifluoroacetic acid (triflic acid), methansulphonic acid or paratoluenesulphonic acid. Alternatively, the inorganic acid can be selected from amongst (poly)phosphoric acid, sulphuric acid, hydrochloric acid, hydrobromic acid, nitric acid, hydroiodic acid, optionally generated in situ.

[0021] Certain salts may be used as catalyst, wherein the salt can be any one or more of $(\text{NH}_4)_2\text{SO}_4/\text{SO}_3$, ammonium phosphate, pyridinium chloride, triethylamine phosphate, pyridinium salts, pyridinium phosphate, pyridinium hydrochloride/hydrobromide/perbromate, DMAP, aluminium salts, Th and Zr ions, zirconium phosphate, Sc and lanthanide ions such as Sm and Y as their acetate or trifluoroacetate (triflate) salt, Cr-, Al-, Ti-, Ca-, in-ions, ZrOCl_2 , $\text{VO}(\text{SO}_4)_2$, TiO_2 , V-porphyrine, Zr-, Cr-, Ti-porphyrine.

[0022] Lewis acids selected as dehydration catalyst can be any one of ZnCl_2 , AlCl_3 , BF_3 . ion exchange resins can be suitable dehydration catalysts. Examples include Amberlite™ and Amberlyst™, Diaion™ and Levatit™. Other solid catalyst that may be used include natural clay minerals, zeolites, supported acids such as silica impregnated with mineral acids, heat treated charcoal, metal oxides, metal sulfides, metal salts and mixed oxides and mixtures thereof.

[0023] An overview of catalysts that may be used in the method of the current invention may be found in Table 1 of the review article prepared by Mr. Lewkowski: "Synthesis, chemistry and applications of 5-hydroxymethylfurfural and its derivatives" Arkivoc. 2001, p.17-54.

[0024] The amount of catalyst may vary, depending on the selection of catalyst or catalyst mixture. For instance, the catalyst can be added to the reaction mixture in an amount varying from 0.01 to 40 mole % drawn on the hexose content of the biomass resource, preferably from 0.1 to 30 mole %, more preferably from 1 to 20 mole %.

[0025] In the preferred embodiment, the catalyst is a heterogeneous catalyst.

[0026] The temperature at which the reaction is per-

formed may vary, but in general it is preferred that the reaction is carried out at a temperature from 50 to 300 degrees Celsius, preferably from 125 to 250 degrees Celsius, more preferably from 150 to 225 degrees Celsius. In general, temperatures higher than 300 are less preferred as the selectivity of the reaction reduces and as many by-products occur, inter alia caramelisation of the sugar. Performing the reaction below the lowest temperature is also less preferable because of the low reaction rate.

[0027] The hexose-containing starting material is typically dissolved or suspended in a solvent which can be the alcohol reactant, in order to facilitate the reaction. The solvent may be selected from the group consisting of water, sulfoxides, preferably DMSO, ketones, preferably methyl ethylketone, methylisobutylketone and acetone or mixtures of two or more of the above solvents. Also so-called ionic liquids may be used. The latter refers to a class of inert ionic compounds with a low melting point, which may therefore be used as solvent. Examples thereof include e.g., 1-H-3-methyl imidazolium chloride, discussed in "Dehydration of fructose and sucrose into 5-hydroxymethylfurfural in the presence of 1-H-3-methyl imidazolium chloride acting both as solvent and catalyst", by Claude Moreau et al, Journal of Molecular Catalysis A: Chemical 253 (2006) 165-169.

[0028] Basically a sufficient amount of solvent is preferably present to dissolve or to suspend the starting material and to limit undesired side-reactions.

[0029] The method of the current invention may be carried out in a batch process or in a continuous process, with or without recycle of (part of) the product stream to control the reaction temperature (recycle via a heat exchanger). For instance, the method of the invention can be performed in a continuous flow process. In such method, homogenous catalysts may be used and the residence time of the reactants in the flow process is between 0.1 second and 10 hours, preferable from 1 second to 1 hours, more preferably from 5 seconds to 20 minutes. Alternatively, the continuous flow process may be a fixed bed continuous flow process or a reactive (catalytic) distillation process with a heterogeneous acid catalyst. To initiate or regenerate the heterogeneous acid catalyst or to improve performance, an inorganic or organic acid may be added to the feed of the fixed bed or reactive distillation continuous flow process. In a fixed bed process, the liquid hourly space velocity (LHSV) can be from 1 to 1000, preferably from 5 to 500, more preferably from 10 to 250 and most preferably from 25 to 100 min⁻¹.

[0030] The above process results in a stable HMF ether, which may be converted into a further derivative before being used as fuel and/or as fuel additive.

[0031] The characterizing feature of the current invention is that the fuel additives (plus some additional combustible by-products) may be extracted by liquid-liquid extraction using a fuel as extraction solvent. The extraction itself may be performed cross-currently or counter-currently using conventional equipment (e.g., a series of

mixers/settlers). The fuel additive concentrate will therefore comprise a fuel component and a biomass-derived furan derivative and/or tetrahydrofuran derivative dissolved in the fuel. The latter component may be present in amounts ranging from a 1 vol% upwards, preferably 5 vol% upwards to 80 vol% or less, preferably 50 vol% or less.

[0032] The polar phase (comprising the reaction solvent) may be -and preferably is- recycled for use in subsequent conversion of hexose-containing starting material.

[0033] No extraordinary temperature or pressure conditions apply. Obviously, using a fuel as extractant, the conditions should be selected such that none of the components (fuel, the furanics, the reaction solvent or the preceding reactants, if any) evaporate.

[0034] Having isolated the fuel additives in the fuel, the fuel additive concentrate may be further concentrated by removing (some) of the fuel. The concentrate may contain conventional quantities of conventional additives such as cetane improvers, friction modifiers, detergents, antioxidants and heat stabilizers, for example. Especially preferred fuel additive concentrates are diesel fuel formulations that comprise diesel fuel hydrocarbons and HMF ether as above described together with peroxidic or nitrate cetane improvers such as ditertiary butyl peroxide, amyl nitrate and ethyl hexyl nitrate for example.

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[0035]

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Claims

1. Method for the manufacture of a fuel additive concentrate comprising a biomass-derived furan derivative and/or tetrahydrofuran derivative dissolved in a fuel, by extracting said derivative from the polar solvent wherein the derivative is produced, using a fuel as extractant. 5
2. Method according to claim 1, wherein the biomass-derived furan derivative and/or tetrahydrofuran derivative is an ether of 5-hydroxymethyl-2-furfural and/or a further derivative thereof, prepared by reacting a hexose-containing starting material with an alcohol in the presence of an acid catalyst, or with an olefin in the presence of a catalyst system. 10 15
3. Fuel additive concentrate, obtainable by the method according to claim 1 or 2. 20
4. Fuel additive concentrate according to claim 3, comprising a fuel component and a biomass-derived furan derivative and/or tetrahydrofuran derivative dissolved in the fuel, wherein the biomass-derived derivative or derivatives is/are present in amounts ranging from a 1 vol% upwards, preferably 5 vol% upwards to 80 vol% or less, preferably 50 vol% or less. 25
5. Fuel additive concentrate according to claim 3 or 4, comprising conventional quantities of conventional additives such as cetane improvers, friction modifiers, detergents, antioxidants and heat stabilizers. 30
6. Fuel additive concentrate according to any one of the claims 3 to 5, comprising diesel fuel hydrocarbons and an ether of 5-hydroxymethyl-2-furfural and/or a further derivative thereof together with peroxidic or nitrate cetane improvers such as ditertiary butyl peroxide, amyl nitrate and ethyl hexyl nitrate. 35 40
7. A fuel or fuel composition comprising the fuel additive concentration produced by the method of any one of claims 1 or 2 or as defined in any one of claims 3-5, blended with one or more of gasoline and gasoline-ethanol blends, kerosene, diesel, biodiesel, Fischer-Tropsch liquids, diesel-biodiesel blends and green diesel and blends of diesel and/or biodiesel with green diesel and other furanics. 45 50

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EUROPEAN SEARCH REPORT

Application Number
EP 07 07 5779

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The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 6 February 2008	Examiner Bertrand, Samuel
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EPO FORM 1503 03.82 (P04C01)



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Application Number
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Place of search Munich		Date of completion of the search 6 February 2008	Examiner Bertrand, Samuel
CATEGORY OF CITED DOCUMENTS 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 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 & : member of the same patent family, corresponding document			

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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