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CA 2697717 C 2016/11/22

(11)(21) **2 697 717**

(12) **BREVET CANADIEN
CANADIAN PATENT**

(13) **C**

(86) **Date de dépôt PCT/PCT Filing Date:** 2008/09/05
(87) **Date publication PCT/PCT Publication Date:** 2009/03/12
(45) **Date de délivrance/Issue Date:** 2016/11/22
(85) **Entrée phase nationale/National Entry:** 2010/02/24
(86) **N° demande PCT/PCT Application No.:** EP 2008/007423
(87) **N° publication PCT/PCT Publication No.:** 2009/030509
(30) **Priorités/Priorities:** 2007/09/07 (EP07075777.8);
2008/05/19 (EP08075504.4)

(51) **Cl.Int./Int.Cl.** **C07D 307/42** (2006.01),
C10L 1/00 (2006.01), **C10L 1/02** (2006.01)
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(54) **Titre : 2-(ALCOXYMETHYL) FURANES 5-SUBSTITUES**
(54) **Title: 5-SUBSTITUTED 2-(ALKOXYMETHYL)FURANS**

(57) **Abrégé/Abstract:**

The present invention concerns a method for the manufacture of a 5-substituted 2-(alkoxymethyl)furan (or a mixture of such furans) by reacting a starting material comprising at least a 5-substituted furfural with hydrogen in the presence of an alcohol and a catalyst system



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
12 March 2009 (12.03.2009)

PCT

(10) International Publication Number
WO 2009/030509 A2

(51) International Patent Classification:

C07D 307/42 (2006.01) *C10L 1/00* (2006.01)
C10L 1/02 (2006.01)

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(21) International Application Number:

PCT/EP2008/007423

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(22) International Filing Date:

5 September 2008 (05.09.2008)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

07075777.8 7 September 2007 (07.09.2007) EP
08075504.4 19 May 2008 (19.05.2008) EP

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

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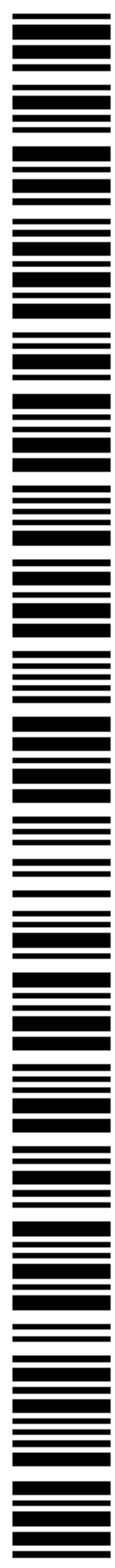
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Published:

— *without international search report and to be republished upon receipt of that report*

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Title: 5-substituted 2-(alkoxymethyl)furans

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Technical Field

The present invention concerns a method for the manufacture of a 5-substituted 2-(alkoxymethyl)furan (or a mixture of such furans) by reacting a starting material comprising at least a 5-substituted furfural with hydrogen in the presence of an alcohol and a catalyst system. The invention also concerns a method for the manufacture of mixtures of 5-substituted 2-(alkoxymethyl)furan(s) and 2-(alkoxymethyl)furan(s) by reacting a starting material further comprising furfural. The invention also concerns the use of the products or product mixtures obtained by the method according to the invention as a fuel or a fuel additive. The invention also relates to the use of 2-(alkoxymethyl)furan(s) as a fuel or fuel additive.

Background Art

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.

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. 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.

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
5 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-
10 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
15 hydrogenolysis process step to convert HMF into dimethylfuran (DMF), which is assumed to be an interesting gasoline additive.

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.
20 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. A similar case is co-pending patent application PCT/EP2007/002146, which describes the manufacture of HMF esters, such as
25 acetylmethylfurfural (AMF).

Moreover, it is known to make furfural from the polysaccharide hemicellulose, a polymer of sugars containing five carbon atoms each. When heated with sulphuric acid, hemicellulose undergoes hydrolysis to yield these sugars, principally xylose. Under the same conditions of heat and acid, xylose and other five carbon sugars undergo dehydration, losing
30 three water molecules to become furfural:



Although MMF, EMF, AMF and other ethers and esters of HMF and furfural are useful as fuel or fuel additives, the inventors found that these ethers and esters leave room for improvement, in particular when used in higher concentration blends with fuels such as
35 gasoline, kerosene, diesel, biodiesel or green diesel. The inventors have therefore set out to overcome this shortfall. It is known that HMF may be converted into 2,5-dimethylfuran. For instance, in "Production of dimethylfuran for liquid fuels from biomass-derived

carbohydrates", Nature, vol. 447 (21 June 2007), pp. 982-985, James Dumesic et al. describes the conversion of fructose into HMF, which is subsequently converted into several hydrogenation steps via 2,5-dihydroxymethylfuran and 2-methyl-5-hydroxymethylfuran into DMF. Thus, a large amount of hydrogen is required to generate a liquid fuel suitable for the transportation sector.

Surprisingly, the current inventors found that the conversion of HMF into DMF is not required in order to prepare a product with a high energy density, suitable boiling point and suitable solubility. Moreover, suitable fuel or fuel additives may even be made from furfural, HMF, HMF ethers and HMF esters such as EMF and AMF and/or mixtures containing these components with much smaller amounts of hydrogen and without losing molecular mass but with adding molecular mass to the products. This would therefore provide a route to an alternative fuel or fuel additive from a renewable (and hence CO₂ neutral) source.

Disclosure of Invention

Accordingly, the current invention provides a method for the manufacture of ethers of 5-substituted furfural via the corresponding alcohol by reacting 5-substituted furfural with hydrogen in the presence of an alcohol and a catalyst system, comprising of one or more catalysts. Within the scope of the current invention is the use of 5-substituted furfural, and in particular 5-hydroxymethylfurfural and the ethers or esters thereof, which may be obtained from C₆ sugars. The synthesis of furfural (from C₅ sugars) and/or of the 5-substituted furfural are not part of the current invention. It is noted, however, that the current process is ideally suitable for the manufacture of fuel components or additives from feed containing 5-substituted furfural and optionally unsubstituted furfural, which in turn was obtained from a pentose and hexose containing biomass source. The current invention relates also to the use of 2-alkoxymethyl furan as a fuel or fuel additive, which may be obtained from furfural (pure or in a mixture as described herein elsewhere), hydrogen, alcohol in the presence of a catalyst.

When the reaction product of the above method is used as such or when it is used as an intermediate for a subsequent conversion, the selectivity of the reaction is preferably high as the product is preferably pure. However, when the reaction product of the above method is used as a fuel, a fuel additive or as a fuel or a fuel additive intermediate, the reaction product does not necessarily need to be pure. Indeed, in the preparation of fuel and fuel additives from biomass, which in itself is a mixture of various pentoses and hexoses is an advantage. Next to the 5-substituted 2-(alkoxymethyl)furan and 2-(alkoxymethyl)furan, the reaction product may contain additional non-interfering components such as levulinic acid derivatives and/or products of non-selective hydrogenation such as 5-substituted 2-methylfuran, 2-methylfuran, dimethylfuran, tetrahydrofuran derivatives and the like. For ease of reference,

however, the method and the reaction product of the current invention are described in terms of the reaction of a 5-substituted furfural starting material to the di-ether 5-substituted 2-(alkoxymethyl)furan. Also within the scope of the invention is the reaction of HMF and mixtures of HMF and HMF ethers or esters which may contain furfural with hydrogen in the presence of an alcohol and a catalyst system, since HMF is believed to be produced as intermediate from the fructose and/or glucose-containing starting material during the synthesis of HMF ethers and esters.

The current invention also provides for the use of the reaction product made according to the present invention as fuel or as fuel additive. Fuels for blending with the product of the present invention include but are not limited to gasoline and gasoline-ethanol blends, kerosene, diesel, biodiesel (refers to a non-petroleum-based diesel fuel consisting of short chain alkyl (methyl or ethyl) esters, made by transesterification of vegetable oil, which can be used (alone, or blended with conventional petrodiesel), 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). The product is a premium diesel fuel containing no sulfur and having a cetane number of 90 to 100). 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

The synthesis of HMF from fructose, glucose and sucrose as a biomass source is a hot topic. HMF has been obtained in processes using both homogeneous and heterogeneous catalysts, using different diluent systems such as water, 2 phase systems for extracting the HMF into an organic phase after its formation, or using diluent systems such as acetone, dmso or ionic liquids.

The current method provides for the conversion of 5-substituted furfural into 5-substituted 2-(alkoxymethyl)furan and as furfural may be present when pentoses were present in the sugar dehydration step or when furfural is formed during hexose dehydration, the current method also provides for the concurrent conversion of the furfural into furfuryl

alcohol and its etherification with the added alcohol. Surprisingly, little or no ethers are found derived by the etherification of the added alcohol with itself.

The alcohol used in the method of the current invention preferably bears a single hydroxyl group, which may be in a primary, secondary or even tertiary position. Diols and polyhydric compounds may be used, but provide little benefit. The alcohol may comprise from 1 to 20 carbon atoms, preferably from 1 to 8 carbon atoms. Examples include methanol, ethanol, 2-propanol, 2-butanol, 2-methyl-1-propanol (isobutanol), 2-methyl-2-propanol (*tert*-butanol), 2-pentanol (s-amyl alcohol); 2-methyl-1-butanol (p-amyl alcohol); 2-methyl-2-butanol (t-amyl alcohol); 3-methyl-1-butanol (isoamyl alcohol); 2,2-dimethyl-1-propanol (neopentyl alcohol); 2-hexanol; 2-ethyl-1-hexanol (isooctyl alcohol). Preferred alcohols used in the method of the current invention include methanol, ethanol, propanol, *iso*-propanol, isobutanol, *tert*-butanol, isoamyl alcohol, isooctyl alcohol. Also blends of alcohols may be used, e.g., of methanol and ethanol.

The amount of alcohol used during the manufacture of the HMF ether is preferably at least equimolar on the furfural, 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 furfuryl ether.

The catalyst system used in the method of the present invention may comprise one or more (co)catalysts, and preferably comprises a single catalyst having hydrogenation and etherification functionality or a combination of (a) hydrogenation catalyst(s) and (an) etherification catalyst(s), for the hydrogenation and for the etherification steps. The single catalyst may for instance be used in the form of an acidic hydrogenation catalyst, or a combination of 2 or more catalysts can be used, for the hydrogenation and for the etherification steps.

The hydrogenation catalyst (or the single hydrogenation/etherification catalyst) is preferably a heterogeneous (meaning solid) catalyst. Suitably, it is a granular catalyst which may be formed into any suitable shape, e.g. pellets, rings or saddles.

Hydrogenation catalysts for aldehydes are known and believed suitable in the method of the current invention. Typical aldehyde hydrogenation catalysts include copper-containing catalysts and Group VIII metal-containing catalysts. Examples of suitable copper-containing catalysts include copper-on-alumina catalysts, reduced copper oxide/zinc oxide catalysts, with or without a promoter, manganese promoted copper catalysts, and reduced copper chromite catalysts, with or without a promoter, while suitable Group VIII metal-containing catalysts include platinum, rhodium, ruthenium and palladium catalysts, preferably on a refractory support such as carbon, silica, alumina, aluminasilica, a carbonate such as barium carbonate, diatomaceous earth and the like.

Suitable copper oxide/zinc oxide catalyst precursors include CuO/ZnO mixtures wherein the Cu:Zn weight ratio ranges from about 0.4:1 to about 2:1. Promoted copper oxide/zinc oxide precursors include CuO/ZnO mixtures wherein the Cu:Zn weight ratio ranges from about 0.4:1 to about 2:1 which are promoted with from about 0.1% by weight up to about 15% by weight of barium, manganese or a mixture of barium and manganese. Suitable copper chromite catalyst precursors include those wherein the Cu:Cr weight ratio ranges from about 0.1:1 to about 4:1, preferably from about 0.5:1 to about 4:1. Promoted copper chromite precursors include copper chromite precursors wherein the Cu:Cr weight ratio ranges from about 0.1:1 to about 4:1, preferably from about 0.5:1 to about 4:1, which are promoted with from about 0.1% by weight up to about 15% by weight of barium, manganese or a mixture of barium and manganese. Manganese promoted copper catalyst precursors typically have a Cu:Mn weight ratio of from about 2:1 to about 10:1 and can include an alumina support, in which case the Cu:Al weight ratio is typically from about 2:1 to about 4:1. Other catalysts which can be considered for use include Pd/ZnO catalysts of the type mentioned by P. S. Wehner and B. L. Gustafson in Journal of Catalysis 136, 420-426 (1992), supported palladium/zinc catalysts of the type disclosed in U.S. Pat. No. 4,837,368 and U.S. Pat. No. 5,185,476, and chemically mixed copper-titanium oxides of the type disclosed in U.S. Pat. No. 4,929,777.

Further catalysts of interest for use in the process of the invention include the rhodium/tin catalysts reported in A. El Mansour, J. P. Candy, J. P. Bournonville, O. A. Ferrehi, and J. M Basset, Angew. Chem. 101, 360 (1989).

Any recognised supporting medium may be used to provide physical support for the catalyst used in the process of the invention. This support can be provided by materials such as zinc oxide, alumina, silica, aluminasilica, silicon carbide, zirconia, titania, carbon, a zeolite, or any suitable combination thereof. Particularly preferred are catalyst systems comprising a Group VIII metal ("noble metal") on a carbon support, since such catalysts systems may be used to perform the hydrogenation and etherification.

The acid etherification catalyst system in the method of the present invention 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.

The protonic acid may be organic or inorganic. For instance, the organic acid can be selected from amongst oxalic acid, levulinic acid, maleic acid, trifluoro acetic acid (triflic acid), methansulphonic acid or para-toluenesulphonic acid. Alternatively, the inorganic acid can be

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selected from amongst (poly)phosphoric acid, sulphuric acid, hydrochloric acid, hydrobromic acid, nitric acid, hydroiodic acid, optionally generated in situ.

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.

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. If elevated reactions temperatures are used, as defined hereafter, then the catalyst should be stable at these temperatures.

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.

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 (substituted) furfural content of the feed, preferably from 0.1 to 30 mole %, more preferably from 1 to 20 mole %.

In the preferred embodiment, the catalyst is a heterogeneous catalyst.

The temperature at which the reaction is performed may vary, but in general it is preferred that the reaction is carried out at a temperature from 0 to 200 degrees Celsius, preferably from 10 to 150 degrees Celsius, more preferably from 20 to 120 degrees Celsius. Also, the hydrogenation reaction is most selective at low temperatures such as e.g. between 20 and 80 degrees Celsius, depending on the selected catalyst. The reaction of the invention can also be carried out in a system with 2 reactors in series, whereby the hydrogenation step and the etherification step are carried out in the first and second reactor at lower and higher temperature, respectively. The reaction may be performed in a single reactor, at a temperature from 20 to 140 degrees Celsius, or in two reactors, where in the first reactor the hydrogenation is performed at a temperature from 20 to 80 degrees Celsius, and where in the second reactor the hydrogen is removed for the etherification at a temperature from 40 to 160 degrees Celsius, preferably from 60 to 120 degrees Celsius. The operation in one batch reactor can start with a low temperature hydrogenation, followed by increasing the temperature and removing the hydrogen gas.

Hydrogen is supplied in sufficient abundance, and either bubbled through the reaction medium introduced concurrently or counter currently with one of the feed streams or dissolved using another form of mixing. Depending on the catalyst and the selected process temperature, the reaction is carried out at a hydrogen pressure from 1 to 100 bars, preferably from 2 to 25 bars, more preferably from 2 to 10 bars. In general, pressures higher than 100 bars are less preferred as the selectivity of the reaction reduces and too much hydrogen is consumed for by-products formation.

The furfural, HMF and HMF ether and ester containing starting material is typically dissolved in a solvent or more preferably in the alcohol reactant, in order to facilitate the reaction. The non-alcohol solvent may be selected from the group consisting of organic solvents such as, ketones, ethers, alkanes and the like.

The alcohol solvent is the alcohol selected for the etherification. The amount of solvent is preferably sufficient to dissolve or suspend the starting material and to prevent certain side-reactions.

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, one or two homogenous catalysts may be used and the residence time of the reactants in the flow process is between 0.1 second and 10 hours, preferably 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, or when a heterogeneous hydrogenation catalyst is used in combination with a homogeneous acidic etherification catalyst, 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.

The above process results in stable furan ethers, which can then be used as such or be converted into a further derivative before being used as fuel and/or as fuel additive. The inventors are of the opinion that some of the products prepared by the method of the current invention are actually new. Thus, the ethers made from alkoxymethylfurfural with C1 to C20 alcohols, preferably C1 to C8 alcohols are new and are excellent fuel components or fuel additives. Since these alcohols may be made from biomass, this might open a class of products that are fully biomass-derived. Accordingly, these new ethers are claimed as well.

The HMF ethers of the invention can also be used as or can be converted to compounds that can be used as solvent, as monomer in a polymerization (such as 2,5-furan dicarboxylic acid or FDCA), as fine chemical or pharmaceutical intermediate, or in other applications. Oxidation of the HMF ethers using an appropriate catalyst under appropriate conditions such as for example described for p-xylene with a $\text{NHPI}/\text{Co}(\text{OAc})_2/\text{MnOAc}_2$ catalyst system in Adv. Synth. Catal. 2001, 343, 220-225 or such as described for HMF with a Pt/C catalyst system at $\text{pH} < 8$ in EP 0 356 703 or or such as described for HMF with a Pt/C catalyst system at $\text{pH} > 7$ in FR 2 669 634, all with air as an oxidant, resulted in the formation of 2,5- Furan dicarboxylic acid (FDCA).

The invention further concerns the use of the HMF ethers prepared by the method of the current invention as fuel and/or as fuel additive. Of particular interest is the use of the ethers in diesel, biodiesel or "green diesel", given its (much) greater solubility therein than ethanol. Conventional additives and blending agents for diesel fuel may be present in the fuel compositions of this invention in addition to the above mentioned fuel components. For example, the fuels of this invention may contain conventional quantities of conventional additives such as cetane improvers, friction modifiers, detergents, antioxidants and heat stabilizers, for example. Especially preferred diesel fuel formulations of the invention 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.

Examples are enclosed to illustrate the method of the current invention and the suitability of the products prepared therefrom as fuel. The examples are not meant to limit the scope of the invention.

Example 1. Formation of 2,5-di(ethoxymethyl)furan

In a 7.5 ml batch reactor, 0.06 mmol 5-(ethoxymethyl)furfural (EMF) in ethanol/ H_2O (90/10) and 3.3 mmol H_2 was reacted for 2 hours at a temperature of 150 or 80 degrees Celsius with 5 mg heterogeneous hydrogenation catalyst and in some cases with 5 mg acid catalyst. Four furan peaks were observed in the UV spectrum. Mass spectrometry (LC-MS CI) identified these products as 5-(ethoxymethyl)furfural (EMF; starting material), 2,5-di(ethoxymethyl)furan (DEMF), 2-(ethoxymethyl)-5-(hydroxymethyl)furan (EMHMF) and 2-(ethoxymethyl)-5-methylfuran (EMMeF).

Conversion of substrate, selectivity and yield of furan derivatives were calculated according to the following formulae:

$$X = 100 \cdot m_{\text{r substrate}} / m_{\text{0 substrate}}$$

X conversion (%)

$m_{\text{r substrate}}$ amount of reacted substrate (mg)

$m_{0 \text{ substrate}}$ amount of substrate in feed (mg)

$S_{\text{compound}} = 100 \cdot n_{r \text{ substrate}} / n_{0 \text{ substrate}}$

S_{compound} selectivity to compound (%)

5 $n_{r \text{ substrate}}$ moles of substrate reacted

$n_{0 \text{ substrate}}$ moles of substrate in feed

$\text{Yield} = 100 \cdot n_{\text{product}} / n_{0 \text{ substrate}}$

Yield yield (%)

10 n_{product} moles of product formed

Selectivities and conversions for catalysts used in this example can be found in table below.

Table 1. Conversion and selectivities for the hydrogenation of 5-(ethoxymethyl)furfural in the presence of ethanol at different temperatures and reaction times.

Catalyst 1	Catalyst 2	T [°C]	Conversion					s Further hydrogenate products[%]
			[%]	sEMHMF [%]	sDEMF [%]	sEMMeF [%]	sEMHMF+DEMF [%]	
1.85%Ru on silica	None	80	29.0	92.5	0.1	0.0	92.6	7.4
1.85%Ru on silica	CrCl ₂	80	42.4	13.8	28.7	0.2	42.5	57.3
5% Ru on alumina	None	150	92.4	52.5	0.2	0.0	52.7	47.3
5% Ru on alumina	None	80	73.3	85.0	0.8	0.1	85.8	14.2
5% Ru on alumina	Amberlyst36Wet	80	91.1	33.1	27.7	0.4	60.8	38.9
5% Ru on alumina	CrCl ₂	80	70.8	15.9	28.5	0.3	44.3	55.4
5%Pt/0.5%V	None	80	99.5	65.5	5.2	3.6	70.7	25.8
5%Pt/0.5%V	CrCl ₂	80	70.7	13.0	21.8	3.4	34.8	61.9
5%Rh on active C	Bentonite	80	66.9	32.4	6.3	7.9	38.7	53.4
Ni on silica	None	150	93.2	33.0	0.1	0.8	33.2	66.1
Ni on silica	None	80	98.6	51.1	0.0	0.0	51.1	48.9
Ni on silica	Amberlyst36Wet	80	99.3	22.3	21.5	0.1	43.8	56.2
15 Ni on silica	CrCl ₂	80	31.0	98.5	0.7	0.5	99.2	0.3

Analytical Method

The reaction products were quantified with the aid of HPLC-analysis with an internal standard (saccharine, Sigma Aldrich). An Agilent 1100 series chromatograph, equipped with UV and
20 ELSD detectors, was used. Stationary phase was reverse phase C18 (Sunfire 3.5 µm, 4.6x100mm, Waters) column. A gradient elution at a constant flow 0.6 ml/min and temperature 40 °C was used according to the following scheme.

Time	H ₂ O(vol%)	MeOH (vol%)	MeCN (vol%)	Flow (ml/min)	T (°C)
Initial	95	0	5	1	40
1	89	3	8	1	40
8	25	3	72	1	40

C.I. Mass spectrum of DEMF (MW=184.2 g/mol)

Example 2. Batch experiment with hydrogenation/etherification of 5-(ethoxymethyl)furfural

In a 7.5 ml batch reactor, 0.06 mmol 5-(ethoxymethyl)furfural (EMF) in 1 mL ethanol and 5 bars of hydrogen was reacted with 3 mol% of a Pt/C catalyst for 4 days at room temperature. The starting material was completely converted in 100% selectivity to 5-(ethoxymethyl)-2-hydroxymethyl)furan. Subsequently, the mixture was heated to 75 °C for 1 day without hydrogen. The 5-(ethoxymethyl)-2-hydroxymethyl)furan was fully converted and 2,5-bis(ethoxymethyl)furan was obtained in 80% yield. 20% Side products are ring opened levulinate derivatives. The experiment was successfully repeated on a 20 gram scale.

Example 3. Batch experiment with hydrogenation/etherification of 5-(tert-butoxymethyl)furfural

In a 7.5 ml batch reactor, 0.06 mmol 5-(tert-butoxymethyl)furfural (tBMF) in 1 mL ethanol and 2 bars of hydrogen was reacted with 3 mol% of a 5% Rh on alumina catalyst for 4 hours at room temperature. The starting material was completely converted in 100% selectivity to 5-(tert-butoxymethyl)-2-(ethoxymethyl)furan. The experiment was successfully repeated on a 20 gram scale.

No reduction of the furan ring could be detected.

Example 4. Batch experiment with hydrogenation/etherification of 5-(hydroxymethyl)furfural

In a 7.5 ml batch reactor, 0.06 mmol 5-(hydroxymethyl)furfural (HMF) in 1 mL ethanol and 5 bars of hydrogen was reacted with 3 mol% of a Pt/C catalyst for 2 days at room temperature. The starting material was completely converted in 100% selectivity to 2,5-di(hydroxymethyl)furan. Subsequently, the mixture was heated to 75 °C for 1 day without hydrogen. The 2,5-di(hydroxymethyl)furan was fully converted and 2,5-bis(ethoxymethyl)furan was obtained in 75% yield. 25% Side products are ring opened levulinate derivatives. The experiment was successfully repeated on a 20 gram scale.

Example 5. Diesel fuel applications

Fuel solubility

Fuel solubility is a primary concern for diesel fuel applications. Not all highly polar oxygenates have good solubility in the current commercial diesel fuels. Results show that 2,5-di(ethoxymethyl)furan and 5-(tert-butoxymethyl)-2-(ethoxymethyl)furan are miscible in all blend ratio's with commercial diesel. In a comparative set of experiments it was shown that

ethoxymethylfurfural (EMF) is completely miscible in a 5 vol% blend with commercial diesel, but that phase separation occurs with the 25 vol% and with the 40 vol% blends of EMF and diesel.

5 **Example 6. 5-substituted 2-(alkoxymethyl)furans**

10 A teflon lined, 7.5 mL stainless steel batch reactor containing 350 mg (2.3 mmol) of 5-(ethoxymethyl)furfural in 0.5 mL methanol, a hydrogenation catalyst (Ni on Silica) and an etherification catalyst (zeolite β- SAR 75) was pressurized to 12.5 bar with hydrogen and subsequently heated, under stirring, to 100 °C for 3 hours. After the reaction, de reactor is cooled quickly in an ice bath and depressurized. A sample is diluted with methanol and analysed of the products with GC and GC-MS. The results are shown in the below Table.

In this experiment, the selectivity was calculated slightly different, based on the formula:

Selectivity = 100 * n_t (product) / [n_0 (substrate) - n_t (substrate)]

Where:

- 15 n_0 - the initial number of moles
| n_t - the number the moles of a compound at time "t".

Table 1. Hydrogenation/etherification of EMF in MeOH to EMF alcohol and ethers

Cat. 1	Cat. 1 [mg]	Cat. 2	Cat. 2 [mg]	Conversion [%]	S-EMHMF [%]	S-DMMF [%]	S- EMMeF [%]	S-DMMF + EMMeF [%]
Ni on silica	50	Zeolite Beta (SAR 75)	50	92	3.8	47.9	30.1	78.0
Ni on silica	10	Zeolite Beta (SAR 75)	10	37	7.9	46.7	36.0	82.7

20 **Example 7. 5-substituted 2-(alkoxymethyl)furans using a mixture of EMF and Furfural**

Example 6, was repeated with 180 mg (1.9 mmol) of furfural and 180 mg (1.2 mmol) 5-(ethoxymethyl)furfural in 0.48 mL methanol. The batch reactor was pressurized to 20 bar of hydrogen and subsequently heated, under stirring, to 100 °C for 2 hours. The results are shown in Table 2.

Table 2. Hydrogenation/etherification of Furfural and EMF in MeOH

<u>Cat.</u> <u>1</u>	<u>Cat. 1</u> <u>[mg]</u>	<u>Cat. 2</u>	<u>Cat. 2</u> <u>[mg]</u>	<u>Conversion</u> <u>[%]</u>	<u>S-EMHMF</u> <u>[%]</u>	<u>S-DMMF</u> <u>[%]</u>	<u>S-</u> <u>EMMeF</u> <u>[%]</u>	<u>F-OH</u>	<u>F-</u> <u>OMe</u>
Ni on silica	20	Zeolite Beta (SAR 75)	20	(EMF) 31.6 (F) 64.7	24	6.3	36.5		
								32.3	29.7

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What is claimed is:

1. Method for the manufacture of a 5-substituted 2-(alkoxymethyl)furan by reacting a starting material comprising at least one 5-substituted furfural with hydrogen in the presence of an alcohol and a catalyst system.
2. Method according to claim 1, wherein said starting material further comprises furfural.
3. Method according to either one of claims 1 and 2, wherein the alcohol may comprise from 1 to 20 carbon atoms
4. Method according to claim 3, wherein the alcohol may comprise from 1 to 8 carbon atoms.
5. Method according to either one of claims 1 and 2, wherein the alcohol is selected from the group consisting of methanol, ethanol, 2-propanol, 2-butanol, 2-methyl-1-propanol (isobutanol), 2-methyl-2-propanol (tert-butanol), 2-pentanol (s-amyl alcohol); 2-methyl-1-butanol (p-amyl alcohol); 2-methyl-2-butanol (t-amyl alcohol); 3-methyl-1-butanol (isoamyl alcohol); 2,2-dimethyl-1-propanol (neopentyl alcohol); 2-hexanol; and 2-ethyl-1-hexanol (isooctyl alcohol).
6. Method according to either one of claims 1 and 2, wherein the alcohol comprises a blend of two or more of: methanol, ethanol, 2-propanol, 2-butanol, 2-methyl-1-propanol (isobutanol), 2-methyl-2-propanol (tert-butanol), 2-pentanol (s-amyl alcohol); 2-methyl-1-butanol (p-amyl alcohol); 2-methyl-2-butanol (t-amyl alcohol); 3-methyl-1-butanol (isoamyl alcohol); 2,2-dimethyl-1-propanol (neopentyl alcohol); 2-hexanol; and 2-ethyl-1-hexanol (isooctyl alcohol).
7. Method according to any one of claims 1-3, wherein the catalyst system is a heterogeneous acid hydrogenation catalyst
8. Method according to claim 7, wherein the heterogeneous acid hydrogenation catalyst comprises at least one noble metal on a carbon support.

9. Method according to any one of claims 1 to 3, wherein the catalyst system comprises of two catalysts, one being a hydrogenation catalyst and the other being an etherification catalyst.
- 5 10. Method according to any one of the claims 1 to 8, wherein the reaction is performed in a single reactor, at a temperature from 20 to 140 degrees Celsius
- 10 11. Method according to any one of the claims 1 to 8, wherein the reaction is performed in two reactors, where in a first reactor the hydrogenation is performed at a temperature from 20 to 80 degrees Celsius, and where in a second reactor the hydrogen is removed for the etherification at a temperature from 40 to 160 degrees Celsius.
- 15 12. Method according to claim 10, wherein the reaction is performed in a batch reactor, and which method starts with a low temperature hydrogenation, followed by increasing the temperature and removing the hydrogen gas.
- 20 13. Method according to claim 11, wherein in the second reactor the hydrogen is removed for the etherification at a temperature from 60 to 120 degrees Celsius.
- 25 14. Method according to any one of the claims 1 to 13, wherein the starting material is selected from one or more of the group comprising 5-(hydroxymethyl)furfural and ethers and esters of 5-(hydroxymethyl)furfural.
- 30 15. Method according to claim 14, wherein the starting material further comprises furfural.
- 35 16. Method according to claim 15, wherein the starting material is 5-(hydroxymethyl)furfural.
17. Method according to any one of the claims 1 to 16, wherein a solvent is used, and wherein the solvent is selected from the group consisting of ketones, ethers, alkanes and aromatic hydrocarbons.
18. Method according to any one of the claims 1 to 16, wherein a solvent mixture is used, and wherein the solvent mixture comprises two or more solvents selected from the group consisting of ketones, ethers, alkanes and aromatic hydrocarbons.

19. Method according to any one of the claims 1 to 16, wherein a solvent is used, and wherein the solvent is alcohol.
- 5 20. Method according to any one of the claims 1 to 19, wherein the method is performed in a continuous flow process.
21. Method according to claim 20, wherein the residence time in the flow process is between 0.1 second and 10 hours.
- 10 22. Method according to claim 21, wherein the residence time in the flow process is between 1 second and 1 hour.
23. Method according to claim 22, wherein the residence time in the flow process is between 5 seconds and 20 minutes.
- 15 24. Method according to any one of claims 21 to 23, wherein the continuous flow process is a fixed bed continuous flow process.
- 20 25. Method according to claim 24, wherein the fixed bed comprises a heterogeneous acid hydrogenation catalyst as the catalyst system.
26. Method according to claim 24, wherein the continuous flow process is a reactive distillation process.
- 25 27. Method according to claim 24, wherein the continuous flow process is a catalytic distillation process.
28. Method according to claim 25, wherein in addition to the heterogeneous acid hydrogenation catalyst, an inorganic acid catalyst is added to the feed of the fixed bed continuous flow process.
- 30 29. Method according to claim 25, wherein in addition to the heterogeneous acid hydrogenation catalyst, an organic acid catalyst is added to the feed of the fixed bed continuous flow process.
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30. Method according to any one of claims 24 to 29, wherein the liquid hourly space velocity ("LHSV") is from 1 to 1000.
31. Method according to any one of claims 24 to 29, wherein the LHSV is from 5 to 500.
- 5 32. Method according to any one of claims 24 to 29, wherein the LHSV is 10 to 250.
33. Method according to any one of claims 24 to 29, wherein the LHSV is from 25 to 100.
- 10 34. A fuel composition comprising the ether produced by the method of any one of claims 1 to 33 as fuel component, blended with one or more of diesel, biodiesel, diesel-biodiesel blends and green diesel.