Catalytic conversion of furfural towards fuel biocomponents

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Introduction

The climate change, the perspective of finishing oil resource and its rising prices led the world to search for an alternative ways of acquiring valuable chemicals and fuels. In recent years technologies of production the most important chemicals for chemical and automotive industries are developed, especially these which use a renewable source of biomass (biodegradable fraction of products, waste and residues from agriculture, forestry and related industries, as well as the biodegradable fraction of industrial and municipal waste) [12, 14, 17]. From chemical point of view a lignocellulosic biomass is composed of cellulose (30-45%), hemicellulose (20-35%) and lignin (10-20%) [1, 12]. Currently, the main attention is paid to furan derivatives and to catalytic processes for production them from the sugars contained in biomass [12]. Furans in the latest "Technology road map, biofuels for transport", compiled by the International Energy Agency, were classified as prospective biofuels [15].

Compounds such as furfural and 5-hydroxymethylfurfural (HMF) can be obtained with good yield through dehydration of monosaccharides, such as hexoses (e.g. fructose) or pentoses (e.g. xylose) in the presence of various catalysts [14].

Furfural

Furfural (FF) is a heterocyclic aldehyde with the molecular formula C_5H_4O. The name of this compound comes from the Latin name of one of the feedstock from which furfural is produced (latin furfur - bran). FF at room temperature is a colorless oily liquid with a characteristic 'almond-benzaldehyde' odor. When exposed to air changes color to red / brown due to auto-oxidation [16, 21]. Furfural is known for a long time and its industrial production started in the U.S. in the early 30s of the 20th century [1]. The commercial process of Furfural production based on the Quaker Oast Technology. In this process FF is obtained though catalyzed mineral acid (H_2SO_4) dehydration of xylose. Furfural, as a relatively inexpensive aldehyde, is considered as one of the most important intermediates for the synthesis of valuable chemicals and biofuels. The main paths using furfural derivatives are shown in Figure 1.
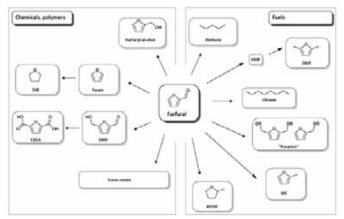

Fig. 1. Furfural derivatives

Currently China is at the forefront of production and consumption of furfural (over 80% of global capacity and 72% of world consumption – in 2010) [20]. 88% of the furfural produced is used for the synthesis of furfuryl alcohol, which has many important industrial applications. FF is used also as a solvent in lubricating oils and butadiene extractions (5% of total use). Furfural is not miscible with gasoline and diesel fuel, is not chemically stable but its derivatives obtained through catalytic conversion can be used as alternative fuels and fuel components [20].

Selected derivatives of furfural, their synthesis and applications into biofuels
2-Methyltetrahydrofuran - component of the P-Series fuels

Furfural can be catalytically hydrogenated to 2-methyltetrahydrofuran (2-MTHF) which is used in innovative P-series fuels [7, 12]. These fuels, contain methyltetrahydrofuran, and includes as well: ethanol, butane, pentane and higher alkanes. Depending on the composition, P-Series fuels can contain from 60 to 100% of biocomponents, where MTHF and ethanol can be produced from lignocellulosic biomass. MTHF is an oxygenated fuel additive with high oxygen content (20% w/w), with similar octane number MON to regular gasoline (about 87) and a higher heating value (32 MJ/kg) than ethanol (26.7 MJ/kg).

Furfuryl alcohol

So far, from the commercial point of view, the most important derivative of furfural is a furfuryl alcohol ($C_5H_6O_2$). This amber liquid (at 20 °C) with a faint odour of burning, is a very important feedstock for the polymer industry [21]. More than 85% of the world produced furfuryl alcohol (in 2010) was used for the production of furan resins. Furfuryl alcohol has been used in solvents, flavor and fragrance chemicals, and pesticide and pharmaceutical products [20]. FA also has been used as a rocket fuel: together with an oxidant - white fuming nitric acid (WNFA) or red fuming nitric acid (RNFA) forms a hypergolics mixture (self ignition mixture) [18].

Furfuryl alcohol is manufactured by the pressure and non-pressure method in the catalytic hydrogenation of furfural [9]. Installations, which are operating under pressure, can achieve relatively high efficiency, but it requires the use of special, expensive solutions for the design of the reactor. The non-pressure technology is successfully used by the Quaker Oats Company (US).

Furfural alcohol from furfural in gas phase hydrogenation reaction at atmospheric pressure using a Cu-Zn with various admixtures of Al, Mn and Fe as a catalyst were carried out in Poland [9]. Process was successfully run in the temperature range of 150 – 180 °C. For the hydrogenation was used hydrogen interchangeable with a mixture of hydrogen and nitrogen. The best results were obtained for copper-zinc catalyst having the following composition (% in weight): CuO - 62.0, ZnO - 21.0; Al_2O_3 - 12.2, MnO_2 -2.2 and Fe_2O_3 - 0.2. Better selectivity and the highest conversion (more than 98%) were obtained in the temperature range of 160…180 °C when hydrogen was used.

Recently, Sitthisa and Resasco developed a method for conversion of furfural to furfuryl alcohol using a Cu catalyst supported by SiO_2 [13].

Reaction of hydrogenation was carried out in continuous-flow quartz reactor under atmospheric pressure of hydrogen in the 210…290°C temperature range. The best yield (71%) of furfuryl alcohol was obtained at 270 °C with 77% conversion of furfural. One of by-products was

2-methylfuran (2-MF), which because of its high research octane number RON (131), can be used as an octane number improver. Interestingly, when catalyst was changed into Pd/SiO$_2$, at the same reaction conditions, the main product of hydrogenation obtained another valuable derivative of furfural - furan. Further hydrogenation of furan leads to tetrahydrofuran (THF), which is used as popular commercial solvent.

Production of liquid alkanes from furfural

Furfural produced from biomass is promising material for the synthesis of alkanes, which are the basic components of fuels. Dumesic and co-wokers developed method for producing of liquid alkanes with the number of carbon atoms ranging from C7 to C15, which can be used as a fuel component [6, 17]. This method is based on three processes: aldol condensation of furfural or HMF with dimethyl ketone (acetone), or a possible self-condensation or condensation of intermediate products with substrates, hydrogenation of obtained aldols to alcohols and then further dehydratation/ hydrogenation to liquid alkanes. Reactions were run in the presence of solid catalysts Pt/SiO$_2$ or Pd/MgO-ZrO$_2$ at high pressure and temperature (5.2-6 MPa, 250…260°C). This process has some side effects, by-products such as coke poisoning the catalyst. It was because of shorter-chain alkanes formation due to hydrogenolysis of C-C bonds at high temperature and pressure.

Researchers are looking for ways to obtain alkanes from furfural with good selectivity, yield and under mild conditions. The new method was described in paper [17]. Two, new bifunctional catalysts Pt/Co$_2$AlO$_4$ and Pt/NbOPO$_4$ were used in this process. That allowed to produce octane from furfural with a high yield (76%) at lower temperatures and pressures. Idea of the process is shown in Figure 2.
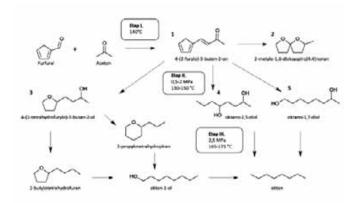

Fig. 2. Synthesis of octane from furfural [17]

The first step of the process was aldol condensation of furfural with dimethyl ketone over Pt/Co$_2$AlO$_4$ or NaOH as catalyst. Then, the hydrogenation of the resulting aldol

(4-(2-furyl-3-buten-2-one) was performed. The hydrogenation gave mixture of four products (compounds (2),(3),(4) and (5) show in Figure 2). The resulting diols are converted to octane in the dehydration/ hydrogenation reaction over Pt/NbOPO$_4$ as a catalyst. It has been proven that by using Pt/NbOPO$_4$ as a catalyst also part of the

4 - (2-tetrahydrofurylo)-butane-2-ole (3) was converted to octane, which additionally has increased the efficiency of the process.

The other method of preparation from furfural different aliphatic hydrocarbons – pentane was developed in China [19].
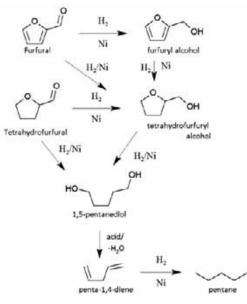

Fig. 3. Synthesis of pentane from furfural [19]

In this process pentane was obtained by a series of catalytic hydrogenation and dehydration reactions carried out in an aqueous-phase (Fig. 3). The bifunctional Ni/SiO$_2$-Al$_2$O$_3$ or Ni/γ-Al$_2$O$_3$ catalyst was used. The advantage of synthesis is that it runs in a single reactor under mild conditions (3MPa, 110…220°C). The resulting pentane can be used as a component for biofuels (when being added directly to fossil gasoline).

„Furanics" - fuels of the future

In recent years the company Avantium, appreciating the possibility of using furan as fine chemicals, has developed a new method (YXY Technology), which allows to produce valuable chemicals, polymers, as well as higher-generation alternative fuels. This method is based on the catalytic conversion of biomass-derived monosaccharides (pentoses and hexoses mixture) to furan compounds in the presence of alcohol and their further transformation in the hydrogenation and/or etherification reaction [4, 23]. The idea of YXY fuels production is shown in Figure 4.
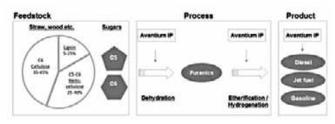

Fig. 4. Schematic of YXY production process (for fuels) [24]

In the first stage of synthesis in presence of acid catalyst and ethanol, pentoses undergo dehydratation reaction and are transformed to furfural. In the same step hexoses are converted into alkoxymethylfurfural (RMF) ethers.

One of the furan compounds obtained in this step is ethoxymethylfurfural (EMF) with a boiling point equal 235 °C and the energy density of 8.7 kWh/l . From of energetic point of view EMF is a better fuel than ethanol (6.1 kWh/l), similar to regular gasoline (8.8 kWh/l) and slightly worse than diesel (9.7 kWh/l) [8]. EMF due to the high boiling point is especially attractive as an additive to the diesel fuel.

RMF ethers can be used as components of fuel in appropriate composition but the resulting in the same processes furfural is not mixed with gasoline or diesel fuel. It is necessary to continue transformation of furfural. The second step of the process was furfural further conversion

into ethers which can be successfully used as bio-component fuel. In this reaction hydrogen, acid catalyst and alcohol was used. Under these conditions also the RMF are catalytically converted into dieters by hydrogenation/ etherification reaction. Depending on the type of alcohol used at this stage was obtained different diethers with better miscibility than the RMF ethers. The process efficiency was improved. Examples of ethers and diethers which can be obtained at first and second step of the YXY process are shown in Figure 5.
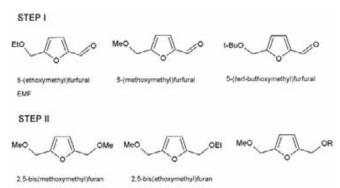

Fig. 5. Examples of ethers and diethers obtained in YXY process [4]

Research of biofuels containing EMF and other derivatives of furan (to 30% vol. of ethers) were conducted by the Avantium company [8]. The independent engine test was performed by Intertek (in Geleen, The Netherlands). Blends of Furanics with regular diesel were tested using a Citroën Berlingo with a diesel engine. Results for all biofuels studied by Avantium were encouraging. The engine ran for 90 minutes without any problems. The car exhaust gas analysis showed decrease in the amount resulting soot by 16% and SO_2 emissions by 17% compared to conventional fuel oil (Tab.1).

Table 1

Results of the engine test of fuel oil and RMF mixtures [8]

Fuel	Time (min.)	SO_2	NO_x (ppm)	Total particulate matter (mg/Nm³)	O_2 (%)	CO_2 (%)
Fuel oil	30	1	160	6.1	17.8	2.4
4% w/w RMF	30	0.96	160	5.7	17.7	2.4
17% w/w RMF	30	0.83	162	5.1	17.7	2.5

The advantage of this process is the ability to obtain components of furan, which can be used as fuel for aircraft engines. Aviation fuels, due to the specific working conditions and safety of passengers, has to meet several requirements [22]. That fuel must have a sufficiently high calorific value, both mass and volumetric. Weight and volume of fuel is very important in the aircraft, fuel can not be too heavy and takes a large volume. Aviation fuel should have also a low freezing point. The temperature decrease on an average of 0.65°C per 100 m of the altitude, so on the flight-level of passenger aircraft (10 000 m) is about -50° C. Figure 6 shows the cyclic tetrahydrofuran ethers produced in YXY technology, which have a high potential for use in aviation fuels. These ethers have high energy density, low freezing point (up to -47°C) and flash point above 38°C [4].

Fig. 6. Examples of tetrahydrofuran ethers for aviation fuels [4]

Tetrahydrofuran ethers are obtained similarly as diethers in the second stage of the process, only the catalyst is changed. The use of other catalyst allows to perform etherification reaction of furfural and products from the first stage of the process combined with ring hydrogenation.

Dimethylfuran (DMF) as a new competitive fuel for ethanol

2,5-dimetylofuran (DMF) is a derivative of furan with the molecular formula C_6H_8O and a molar mass 96.13 g / mol [3]. It can be used as an organic solvent, bio-component of fuel and as an independent biofuel. DMF is classified as second generation biofuel due to the fact that in the process of its production requires raw materials rich in lignocellulose, starch and other polysaccharides, which can be found in industrial waste and biomass [3, 5].

A new method for obtaining 2.5-DMF for fuel was developed by a team of Roman-Leshkova [10, 11]. The conversion process is illustrated in Figure 7.
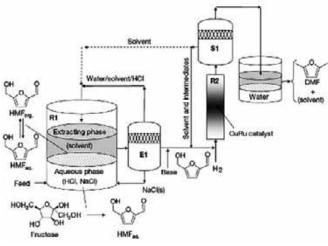

Fig. 7. The conversion of D-fructose into 2,5-DMF [11]

The synthesis is carried out in two steps in the biphasic reactor. The first step is acid-catalyzed dehydration of D-fructose towards hydroxymethylfurfural HMF (also 5-(hydroxymethyl)-2-furaldehyde) (R1 in Fig. 7). The reactive aqueous phase in the biphasic reactor contains an acid catalyst and a sugar, and the extracting phase contains a partially miscible organic solvent (for example, butanol) that continuously extracts the HMF product. the addition of a salt to the aqueous phase improves the partitioning of HMF into the extracting phase, and leads to increasing yields of HMF without the use of high boiling point solvents. 5-HMF is extracted in the organic phase and is subsequently converted to 2,5-DMF by hydrogenolysis of C-O bonds over copper-ruthenium (CuRu/C) catalyst (R 2 in Fig. 7). The final step involves the separation of DMF from the solvent and the reaction intermediates (S1 in Fig. 7). The more volatile components (that is DMF and water) can be separated from the solvent and the intermediates. The final stream can be then recycled to the hydrogenolysis reactor. The hydrophobic product (DMF and 2-methylfuran) separate spontaneously from water after condensation stage. Depending on the final fuel composition requirements a distillation process may be used to control more precisely the distribution of components and to recycle a fraction of the solvent to the dehydration reactor. It was noted that the energy required to evaporate the stream containing DMF and

n-butanol, leading to product separation, is approximately one-third of the energy required to evaporate an aqueous solution of ethanol produced by fermentation [3, 10, 11].

Dimethylfuran is defined as a prospective replacement for bioethanol, which is currently used as biofuel. DMF compared to ethanol has a better physicochemical properties in terms of its use as a fuel (Tab.2) [3].

Table 2

Properties of DMF and ethanol comparison [3]

Name	DMF	ETHANOL	Gasoline
Molecular Formula	C6H8O	C2H6O	C2-C14
H/C ratio	1.333	3	1.795
O/C ratio	0.167	0.5	0
Oxygen mass contents	16.67	34.7	0
State of matter	liquid	liquid	liquid
Safety	flammable	flammable	flammable
Density (20 °C) [g/cm³]	0.888	0.789	0.720-0.775
Boiling Point [°C]	92-94	78	32
Water Solubility [mg/ml]	<1	100	0
Energy density [MJ/l]	31.5	23	35
Research Octane Number (RON)	119	106	95-98
Air–fuel ratio	10.7	9.0	14.5

As shown in the table, DMF has several important advantages over ethanol as a gasoline-alternative biofuel. The solubility of DMF in water is close to zero, which makes it easier to store. It is completely soluble in hydrocarbons and other compounds of oxygen used in the composition of motor fuels. The volumetric calorific value of DMF (31.5 MJ / l) is similar to gasoline (35.0 MJ / l) and higher than ethanol (23,0 MJ/l) by 40% [2, 10, 11, 14]. The boiling point of dimethylfuran is higher over 15% than boiling point of ethanol, which makes it less volatile and more practical as a liquid fuel for transportation. Moreover dimethylfuran is chemically stable and can by storage for a long time. DMF also has several other advantages: it is non-toxic and does not contain any sulfur, phosphorus, metals, benzene and polycyclic aromatic hydrocarbons. DMF has a high resistance for knocking effect during combustion, his octane number (RON) equals 119 and is higher than the octane number of bioethanol and petrol. The use of DMF in the composition of engine petrol (as a component for improving the octane number of fuel) does not require any changes in engine design, power systems and distribution systems. The problem occurs when DMF is used as a pure fuel. The existing, recently exploited traction combustion engines with spark ignition, which use gasoline with an octane number in the range 95-98 (E95 or E98), are not suitable for pure DMF because of its very high octane number [3, 5].

Summary

This article presents selected derivatives of furfural, which may become future bio-components, or self-contained biofuel. In most examples, the processes discussed here are catalytic conversions of furfural derived from biomass and can be found in the stage of research and development. First engine test of new compounds are being carried out by the research teams. However, common availability of biomass (especially the non-food waste type), caused the trend for reduction of dependency from petroleum resources and increased responsibility for the environment. This factors can be the driving forces behind the development of technologies that use derivatives of furfural, which are called, not without a reason, the "sleeping giants". One might assume that a lot of interest in furan compounds may contribute to the development of new catalytic conversion processes of furfural and its derivatives, which in the future can lower the cost of their production. This could increase the scale of production, which will result in the launch on the market beneficial alternative fuels for spark ignition engines, which are forward-looking replacement for conventional gasoline.

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