Furanics: Versatile Molecules for Biofuels and Bulk Chemicals Applications

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Introduction

Furan derivatives obtained from renewable biomass resources have the potential to serve as substitutes for the petroleum-based building blocks used in the production of plastics and fine chemicals [1-3]. 5-Hydroxymethylfurfural (HMF), one of the important building-blocks, can be produced by the acid catalyzed dehydration of hexoses, such as glucose and fructose. Dumesic et al. has reported an improved process for the selective dehydration of fructose into HMF, where high fructose concentrations are used (10 to 50 weight %), achieving high yields (80% HMF selectivity at 90% fructose conversion) and HMF is delivered in a separation-friendly solvent [2]. The use of ionic liquids for an efficient conversion of glucose or fructose to HMF has also been reported. In ionic liquids, such as 1-alkyl-3-methylimidazolium chloride, metal halides showed a good performance as catalysts, among which chromium (II) chloride is found to be uniquely effective, leading to the conversion of glucose to HMF with a yield near 70% [4]. New kinds of Bronsted acidic ionic liquids, such as 3-allyl-1-(4-sulfobutyl)imidazolium trifluoromethanesulfonate, immobilized in silica gel have also been tested yielding 60-70% of HMF at 92-100% of fructose conversion after 4 minutes at 100 °C, using DMSO as solvent. Moreover, this new type of catalysts can be reused at least seven times without loss of HMF yields [5]. However, HMF itself is not a suitable candidate for biofuel applications because of its high melting point and instability. Recently, Mascal et al. have reported a way to prepare furan derivatives, mainly 5-chloromethylfurfural (CMF), directly from cellulose (71% yield) after 30 h of reaction using LiCl in concentrated hydrochloric acid [3]. In this paper we report a completely new and different approach to come to biofuels containing furan moieties.

Results and Discussion

By applying its advanced high-throughput R&D technology, Avantium is developing a next generation biofuels, called "Furanics", which can be produced on the basis of sugars and other, non-food, carbohydrates. The company is developing chemical, catalytic routes in batch and flow reactors to produce Furanics for a range of applications [6,7]. Next to its application as a biofuel, Furanics can also be used for the production of renewable polymers, bulk and specialty chemicals. Avantium targets to develop biofuels with advantageous qualities both over existing biofuels such as bioethanol and biodiesel as well as over traditional transportation fuels. The below reaction scheme shows the various possibilities that exist to develop fuel components suited for gasoline, diesel and/or jet fuels.

The energy density of ethoxymethylfurfural (EMF, a Furanics example) is 8.7 kWh/L. This is as good as regular gasoline (8.8 kWh/L), nearly as good diesel (9.7 kWh/L) and significantly higher than ethanol (6.1 kWh/L). This means that with a full tank of Furanics it is possible to drive almost as far as with a full tank of traditional fuels. The company successfully conducted engine tests to demonstrate the fuel potential of its novel biofuels (Table 1). The tests were carried out by Intertek, in Geleen, the Netherlands, an independent test center. Using a regular Citroën Berlingo with a diesel engine, Avantium tested a range of blends of its novel biofuels with regular diesel, with different concentrations of Avantium's novel biofuel. The tests yielded positive results for all blends tested. The engine ran for 90 minutes with each blend without any hick-up. The car exhaust analysis demonstrated a significant reduction of soot and sulphur oxide emissions when using Avantium's biofuels compared to oil-based diesel and has not the cold weather problems of conventional biodiesel. In addition the engine test results demonstrated that other exhaust levels were not affected. The compounds have higher cetane numbers than regular diesel and have good oxidation stability.

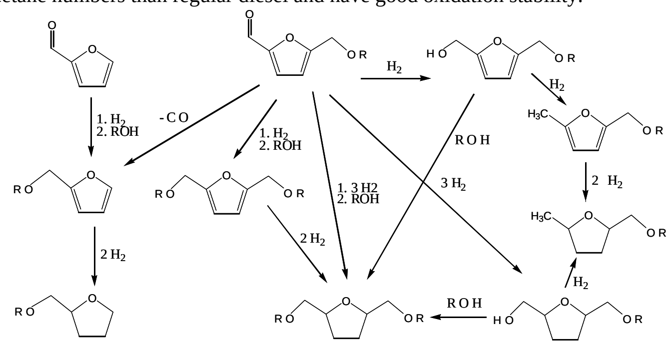

Table 1. Results of the engine tests of Diesel and RMF mixtures.

Fuel	Time (min)	SO_2 (normalized)	NOx (ppm)	Total particulate matter = Soot (mg/Nm3)	O_2 (%)	CO_2 (%)
Diesel	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

Significance

The high energy density of EMF, the fact that these HMF derivatives can now be obtained in high yields, in one step, from very cheap hexose or hexose-containing starting materials such as sucrose and glucose, and the physical properties of these ethers (liquids at room temperature, in contrast to HMF), make these very interesting biofuels. The excellent results of the engine tests support the proof of principle of our next generation biofuels, and are a valuable milestone for our biofuels development program. It is our intention to develop a next generation of biofuels that are regarding fuel quality and costs superior to existing biofuels and that can compete with oil-based fuels. The reduction of soot in the car exhaust is encouraging, since fine particulate matter is considered a major disadvantage of using diesel today, because of its adverse environmental and health effects. During the presentation the various routes to different fuel components, reaction mechanisms as well as catalyst properties will be discussed.

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