Production of Biofuels by 5-Hydroxymethylfurfural Etherification Using Ion-Exchange Resins as Solid Acid Catalysts †

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Abstract: In this work, acidic ion-exchange resins with strong Brönsted sulphonic groups were assessed in the catalytic etherification of the platform molecule 5-(hydroxymethyl)furfural (HMF) to 5-(ethoxymethyl)furfural (EMF), a biofuel with an energy density close to that of gasoline (30 MJ/L) which also reduces emissions of NO_x and SO_x and solid particles respect to fossil-derived fuels. Catalytic performance was optimized modifying experimental parameters such as reaction time, temperature, and concentration of reagent employed. This process was carried out in batch reactors using ethanol 96% as solvent. Among different cation-exchange resins tested, Purolite CT275DR provided the fastest HMF conversion together with Purolite PD206, and the highest selectivity to EMF, achieving above 70% selectivity at 100 °C. Over time, strong acid sites favoured product hydrolysis opening the furan ring originating ethyl levulinate (EL) to the detriment of EMF selectivity. Purolite CT275DR was also utilised to realize the transformation from sugars directly to EMF in the same reaction medium, in a one-pot process, obtaining relevant results from fructose (37% HMF yield, 21% EMF yield after 5 h), but originating selectively ethylglucosides and ethylgalactosides in the presence of glucose and galactose, respectively, due to the absence of necessary Lewis acid sites to isomerize aldose and proceed with dehydration.

Keywords: 5-(hydroxymethyl)furfural; 5-(ethoxymethyl)furfural; ethyl levulinate; ethanol; biofuel; monosaccharides; hexoses; etherification; ionic exchange resins

1. Introduction

Currently, fossil resource depletion as well as climate change produced by their exploitation are major concerns [1]. Biomass is receiving increasing attention due to its renewable nature, abundance, and worldwide availability. Lignocellulose is the most abundant renewable source [2] since it appears in nature with structural function in plants and constitutes an important part of their dry weight. Approximately 45% of lignocellulosic biomass corresponds to cellulose, 27.5% to hemicellulose, and 17.5% to lignin [3]. Cellulose is the most abundant biopolymer in earth, and this makes glucose, its only monomer, a key compound for valorisation processes into high value-added chemicals and fuels.

Hexose triple dehydration in the presence of Brönsted acid leads to the formation of HMF, a versatile platform molecule with applications in polymer science and biofuel production [4]. EMF is a potential biofuel derived from HMF, which is produced from the simple etherification with ethanol of the hydroxyl group present in the HMF molecule. EMF is a substance with similar properties to

those of common fuels currently employed. It has an energy density of 30.3 MJ/L (94% of that of gasoline) [5], improves kinematic properties in cold and reduces particle formation, NO_x and SO_x production respect to common fuels [6].

Under acidic media, saccharides and their valuable derivatives can produce a wide range of by-products, as well as soluble oligomers and insoluble polymers (humins) that reduce selectivity [7–9]. EMF synthesis has been reported by using ionic liquids [10], heteropoly acids [11], ion exchange resins [6], or metal salts [12] accompanied by Lewis acid sites to promote isomerization of glucose to fructose when it was required [6,13]. However, difficulties remain still in the transformation of fructose to EMF, or specially starting from glucose.

Aiming to improve results and achieve more selective production from different sources, this work evaluates the behaviour of several ion exchange resins in the catalytic etherification of HMF to EMF, including the one-pot transformation of saccharides. Thus, cation exchange resins with different nature, both macroreticular (Purolite CT275DR, CT269DR, and Amberlyst 15) and a gel type resin (Purolite PD206), were tested for EMF production.

2. Materials and Methods

Catalysts employed were commercially available ion exchange resins. Purolite CT275DR, Purolite CT269DR and Purolite PD206 were acquired from Purolite®, Amberlyst 15 from Fluka®.

Etherification reactions were carried out in batch reactors (Ace pressure 15 mL). Typical conditions employed were 5 mL of solvent (ethanol 96%, VWR Chemicals, Leuven, Belgium), 0.1 g of HMF (99.9%, Sigma-Aldrich, St. Louis, MO, USA), 0.05 g of catalyst and 100 °C, unless otherwise specified. Reactors were purged before reaction with N_2 to avoid secondary reactions related to O_2 presence and heated under magnetic stirring in a temperature regulated aluminium block. Reaction time started counting once it was submerged in the aluminium block, previously heated at the desired temperature. Once the reaction time finished, the reactor was extracted from the aluminium block and cooled with water. For the analysis, samples were diluted in water and analysed through a JASCO high performance liquid chromatography (HPLC). The instrument employed a Phenomenex REZEX Ca^{2+} Monosaccharide (300 × 7.8 mm) column heated in a column oven (CO-2065) at 70 °C with 0.4 mL/min of deionized water flow provided by a quaternary gradient pump (PU-2089). The instrument is equipped with a multiwavelength detector (MD-2015) as well as a refractive index detector (RI-2031-PLUS) for qualitative and quantitative measurement.

$$\text{Conversion}_{HMF} = ((\text{mol}_{initialHMF} - \text{mol}_{finalHMF}))/\text{mol}_{initialHMF}) \cdot 100 \tag{1}$$

$$\text{Selectivity}_X = (\text{mol}_{finalX}/(\text{mol}_{initialHMF} - \text{mol}_{initialHMF})) \cdot 100 \tag{2}$$

$$\text{Yield}_X = (\text{Selectivity}_X \cdot \text{Conversion}_{HMF})/100 \tag{3}$$

3. Results and Discussion

Firstly, these cation exchange resins were submitted to catalytic screening under aforementioned conditions (100 °C, 0.1 g HMF, 0.05 g catalyst, 5 mL ethanol) at different reaction times (Figure 1a). HMF conversion followed a first order reaction (Figure 1b) with very high conversion values after 24 h of reaction for all studied resins. Purolite CT275DR and Purolite PD206 seemed to be slightly more active than the others. Regarding the selectivity, resins could produce EMF with selectivities above 70%, concretely Purolite CT275DR in a time below 9 h or Purolite CT269DR after 9 h reaction. EMF selectivity values become increasingly worse as time progresses, decreasing due to secondary reactions (Figure 1c). Therefore, reaction time is a factor that unfavourably affects EMF selectivity. HMF and EMF rehydration are known to produce levulinic and formic acids, or their respective esters, in alcohol media [14]. Over time, EL selectivity increased in agreement with this statement (Figure 1d). While Purolite CT275DR, Purolite CT269DR and Amberlyst 15 presented similar values of EL selectivity at all times, Purolite PD206 particularly showed the highest EL selectivity among the resins studied, up to 26%, after 24 h. It should be noted that purolites provided the best selectivity results towards EMF surpassing that of Amberlyst 15.
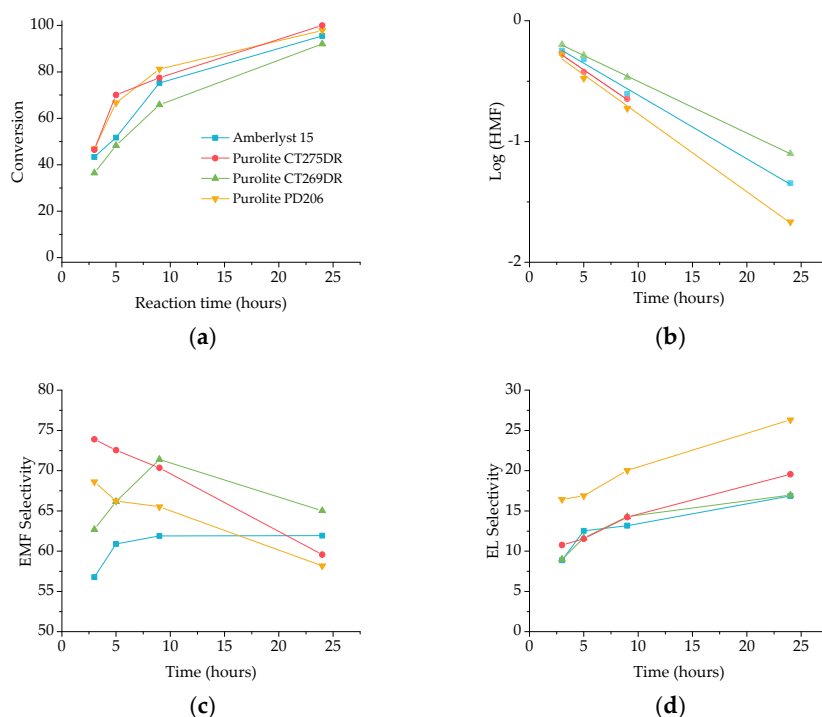
Figure 1. (**a**) Conversion of HMF at 100 °C. (**b**) Logarithmic representation of HMF concentration respect to time. (**c**) Measured selectivity towards EMF production. (**d**) Measured selectivity towards EL formation. (100 °C, 0.1 g HMF, 0.05 g catalyst, 5 mL ethanol at different reaction time).

However, it is important to attain the direct transformation of saccharides to EMF instead of utilizing HMF as feedstock, given that these saccharides can be easily accessible from lignocellulose. Hence, Purolite CT275DR was tested by using fructose, glucose, and galactose to obtain EMF in a one-pot reaction (Figure 2). Fructose was readily dehydrated in the presence of strong Brönsted acid sites present on the resin, giving rise to a HMF yield of 39% after 5 h. Moreover, EMF was detected from fructose, so HMF was etherified to EMF, obtaining an EMF yield of 20% after 5 h. Nevertheless, aldoses need the presence of Lewis acid sites to isomerize to ketoses and proceed with dehydration to form HMF. As expected, neither glucose nor galactose produced HMF, EMF, or EL. Both reagents were transformed selectively to a single unidentified product, which, according to previous works dealing with the treatment of glucose with Brönsted acidic solids in the presence of ethanol [11], could be ethyl glucoside and ethyl galactoside, respectively.
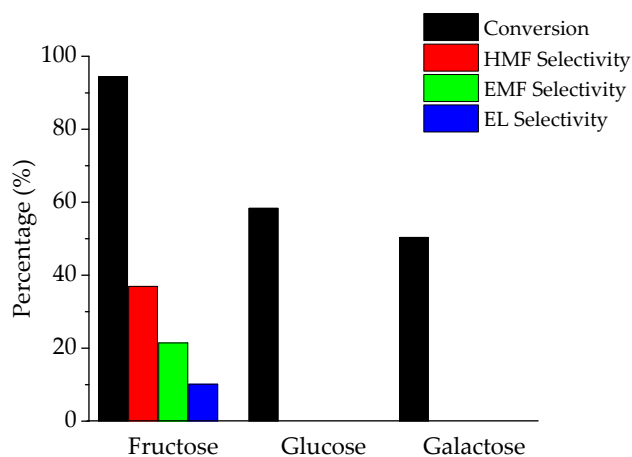

Figure 2. Conversion and selectivities towards HMF, EMF and EL (100 °C, 0.15 g hexose, 0.05 g Purolite CT275DR, 5 mL ethanol for 5 h).

4. Conclusions

Several resins were assessed in the etherification reaction of HMF to EMF by using ethanol as solvent. The resins showed relevant conversion values. The use of purolite resins resulted in good values of EMF selectivity, particularly the use of Purolite CT275DR, which also showed the best conversion values together with Purolite PD206. To prove the applicability of the resin to saccharide conversion, fructose, glucose, and galactose were employed as feedstock, under similar experimental conditions instead of HMF, as reagent. As expected, the resin failed to convert satisfactorily aldoses to HMF in the absence of Lewis acid catalyst, but Purolite CT275DR successfully transformed fructose with a HMF yield of 39% and an EMF yield of 20% after 5 h.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. IPCC. *Global Warming of 1.5 °C*; Masson-Delmotte, P.V., Zhai, H.O., Pörtner, D., Roberts, J., Skea, P.R.S., Pirani, W.A., Moufouma-Okia, C., Péan, R., Pidcock, S., Connors, J.B.R., et al., Eds.; World Meteorological Organization: Geneva, Switzerland, 2018.
2. Zhou, C.H.; Xia, X.; Lin, C.X.; Tong, D.S.; Beltramini, J. Catalytic conversion of lignocellulosic biomass to fine chemicals and fuels. *Chem. Soc. Rev.* **2011**, *40*, 5588–5617.
3. Menon, V.; Rao, M. Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept. *Prog. Energy Combust. Sci.* **2012**, *38*, 522–550.
4. Mika, L.T.; Cséfalvay, E.; Németh, Á. Catalytic Conversion of Carbohydrates to Initial Platform Chemicals: Chemistry and Sustainability. *Chem. Rev.* **2018**, *118*, 505–613.
5. Liu, X.; Wang, R. Upgrading of Carbohydrates to the Biofuel Candidate 5-Ethoxymethylfurfural (EMF). *Int. J. Chem. Eng.* **2018**, *2018*, doi:10.1155/2018/2316939.
6. Lew, C.M.; Rajabbeigi, N.; Tsapatsis, M. One-pot synthesis of 5-(Ethoxymethyl)furfural from glucose using Sn-BEA and Amberlyst catalysts. *Ind. Eng. Chem. Res.* **2012**, *51*, 5364–5366.
7. Holm, M.S.; Saravanamurugan, S.; Taarning, E. Conversion of Sugars to Lactic Acid Derivatives Using Heterogeneous Zeotype Catalysts. *Science* **2010**, *328*, 602–605.
8. Zhang, J.; Weitz, E. An in situ NMR study of the mechanism for the catalytic conversion of fructose to 5-Hydroxymethylfurfural and then to levulinic acid using 13c labeled d -fructose. *ACS Catal.* **2012**, *2*, 1211–1218.
9. van Putten, R.-J.; van der Waal, J.C.; de Jong, E.; Rasrendra, C.B.; Heeres, H.J.; de Vries, J.G. Hydroxymethylfurfural, A Versatile Platform Chemical Made from Renewable Resources. *Chem. Rev.* **2013**, *113*, 1499–1597.
10. Guo, H.; Duereh, A.; Hiraga, Y.; Qi, X.; Smith, R.L. Mechanism of Glucose Conversion into 5-Ethoxymethylfurfural in Ethanol with Hydrogen Sulfate Ionic Liquid Additives and a Lewis Acid Catalyst. *Energy Fuels* **2018**, *32*, 8411–8419.
11. Yang, Y.; Abu-Omar, M.M.; Hu, C. Heteropolyacid catalyzed conversion of fructose, sucrose, and inulin to 5-ethoxymethylfurfural, a liquid biofuel candidate. *Appl. Energy* **2012**, *99*, 80–84.
12. Liu, B.; Zhang, Z.; Huang, K.; Fang, Z. Efficient conversion of carbohydrates into 5-ethoxymethylfurfural in ethanol catalyzed by AlCl3. *Fuel* **2013**, *113*, 625–631.
13. Mahmoud, E. Glucose Conversion to Furans in Alcohols Catalyzed by Lewis Acidic Beta Zeolites and Brønsted Acidic Resins. *Chem. Sel.* **2017**, *2*, 10336–10339.

14. Flannelly, T.; Dooley, S.; Leahy, J.J. Reaction Pathway Analysis of Ethyl Levulinate and 5-Ethoxymethylfurfural from d -Fructose Acid Hydrolysis in Ethanol. *Energy Fuels* **2015**, *29*, 7554–7565.