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Heteropolyacid catalyzed conversion of fructose, sucrose, and inulin to 5-ethoxymethylfurfural, a liquid biofuel candidate

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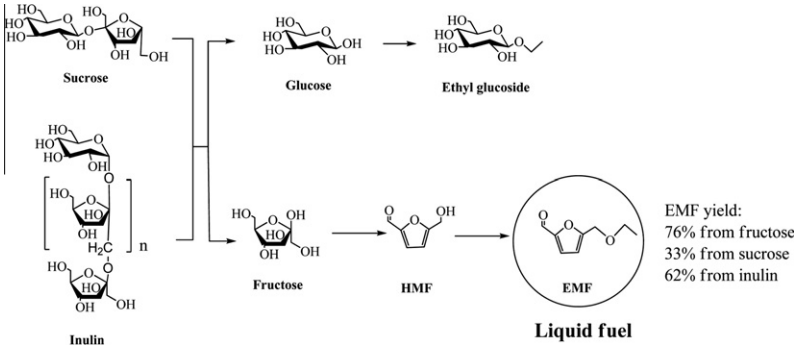
HIGHLIGHTS

- $H_3PW_{12}O_{40}$ was found to be an effective catalyst for 5-ethoxymethylfurfural synthesis.
- High 5-ethoxymethylfurfural yield of 76% was obtained from fructose.
- The fructose moieties in sucrose and inulin can also convert selectively.
- $H_3PW_{12}O_{40}$ can be reused without significantly loss of activity.

GRAPHICAL ABSTRACT



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ABSTRACT

The heteropolyacid $H_3PW_{12}O_{40}$ has been used as a catalyst for the production of 5-ethoxymethylfurfural (EMF), a viable liquid biofuel, from fructose, sucrose, and inulin. An EMF yield of 65% can be obtained from fructose within 30 min at 130 °C in ethanol under microwave heating. The introduction of tetrahydrofuran as a co-solvent improved the yield of EMF to 76%. Longer reaction time, higher reaction temperature and higher catalyst amount lead to the decomposition of EMF to ethyl levulinate. The fructose moieties in sucrose and inulin are converted to EMF selectively. However, glucose moieties cannot be converted to EMF by this heteropolyacid catalyst. Instead ethyl glucoside is formed.

1. Introduction

With diminishing fossil fuels, the production of biofuels from renewable biomass has been receiving much needed attention [1–10]. 5-Ethoxymethylfurfural (EMF), which can be synthesized from 5-hydromethylfurfural (HMF) [11] or 5-chloromethylfurfural (CMF) [12], has been proposed as a potential liquid biofuel for the future. It has high energy density of 8.7 kWh/L, which is comparable to that of standard gasoline (8.8 kWh/L) and diesel fuel (9.7 kWh/L). The blends test of EMF has "yielded positive results for all blends tested. The engine ran smoothly for several hours. Exhaust analysis uncovered a significant reduction of soot" [13].

In light of the high price of HMF and CMF, the preparation of EMF directly from pure HMF or CMF is limited. Using cheap and renewable fructose as the raw material, ethanol as solvent, and combining the dehydration of fructose to HMF followed by the etherification of HMF to EMF in one-pot is a more attractive reaction pathway [13–15]. This one-pot reaction avoids the isolation and purification of HMF, which saves time, energy and solvent.

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Moreover, ethanol is also renewable and can be obtained from biomass [16,17]. H_2SO_4 has been used for the production of EMF form fructose and an EMF yield of ca. 60% can be obtained at H_2SO_4 concentration of 1.8 M. However, using H_2SO_4 is limited by serious corrosion, safety concerns, and critical reaction conditions [14]. Using Amberlyst-15 resin can avoid the drawbacks associated with a strong Brønsted acid such as H_2SO_4. An EMF yield of 55% can be obtained from fructose within 20 h at 100 °C employing Amberlyst-15 resin as a catalyst. However, long reaction times and high catalyst amount (a typical mass ratio of fructose/Amberlyst-15 resin is 1/1) make this process less appealing [15]. Other acidic catalysts have been investigated. However, the EMF yield is often low (<40%) [13].

Heteropolyacids, such as $H_3PW_{12}O_{40}$ (HPW), have attracted considerable interest because of their well-defined structure, Brønsted acidity, possibility to modify their acid–base properties by changing their chemical composition, ability to accept and release electrons, and high proton mobility [18]. Heteropolyacids have been wildly used to catalyze the conversion of carbohydrates [19–22], and the etherification reaction [23]. In this paper, we report the use of HPW as a catalyst for the conversion of fructose to EMF in one-pot. The effect of reaction conditions and catalyst recycling were investigated. Moreover, fructose based di- and polysaccharides (sucrose and inulin) were used as raw material, which allowed access to hydrolysis, dehydration and etherification reactions all in one-pot (Fig. 1).

2. Experimental

2.1. Materials

Ethyl glucoside (EGL) and inulin were purchased from Carbosynth. HPW (keggin structure) was purchased from MP Biomedicals. Other chemicals were purchased from Sigma–Aldrich. All reagents were analytical grade and used without further purification.

2.2. General procedure for the reaction

Reactions were carried out in a Discover TM microwave batch reactor (CEM Corporation). In a typical experiment for the conversion of fructose in pure ethanol, a 10 mL reaction tube was charged with fructose (0.5 mmol), HPW (0.004 mmol), and ethanol (2.5 mL) and heated to 130 °C for 30 min. In a typical experiment for the conversion of carbohydrates in ethanol-tetrahydrofuran (THF), a 10 mL reaction tube was charged with carbohydrates (0.5 mmol based on monosaccharide units), HPW (0.004 mmol), ethanol (2.5 mL) and THF (1.5 mL) and heated to 130 °C for 30 min. All solutions were mixed at a maximum constant rate using a magnetic stir bar. Temperatures in the reactor were measured by a fiber optic sensor. The reaction vessel was pressurized due to the vapor pressure of the solution at the employed reaction temperatures. Time zero was taken when the set temperature was reached. After the desired reaction time, the reaction was stopped by nitrogen flow cooling and the reaction mixture was diluted, filtered with a 0.2 mm syringe filter before analysis.

2.3. Analytic methods

Quantitative analyses of fructose, HMF, EMF, glucose and EGL were performed by HPLC using a Waters 1525 pump, an aminex column HPX-87 column (Agilent) and Waters 2412 Refractive Index detector. 0.005 M H_2SO_4 solution was used as the mobile phase at a flow rate of 0.6 mL/min, and the column temperature was maintained at 338 K. The amounts of the above components were calculated based on external standard curves constructed with authentic samples. Ethyl levulinate (LAE) was determined by gas chromatography (Agilent 6890) equipped with DB-5 column and flame ionization detector (FID). The temperature of the injection was 270 °C. The temperature of the column was maintained at 120 °C for 3.3 min and then raised to 200 °C with a ramp rate of 80 °C/min. The amount of LAE was calculated using standard curves based on furfuryl alcohol as internal standard.

When using fructose as staring material, fructose conversion, fructose percent and products percents (yields) are defined as follows:

$$\text{Fructose conversion} = (\text{moles of starting fructose} - \text{moles of fructose unreacted})/\text{moles of starting fructose} \times 100\%$$

$$\text{Fructose percent} = \text{moles of fructose unreacted}/\text{moles of starting fructose} \times 100\%$$

$$\text{HMF percent(yield)} = \text{moles of HMF}/\text{moles of starting fructose} \times 100\%$$

$$\text{EMF percent(yield)} = \text{moles of EMF}/\text{moles of starting fructose} \times 100\%$$

$$\text{LAE percent (yield)} = \text{moles of LAE}/\text{moles of starting fructose} \times 100\%$$

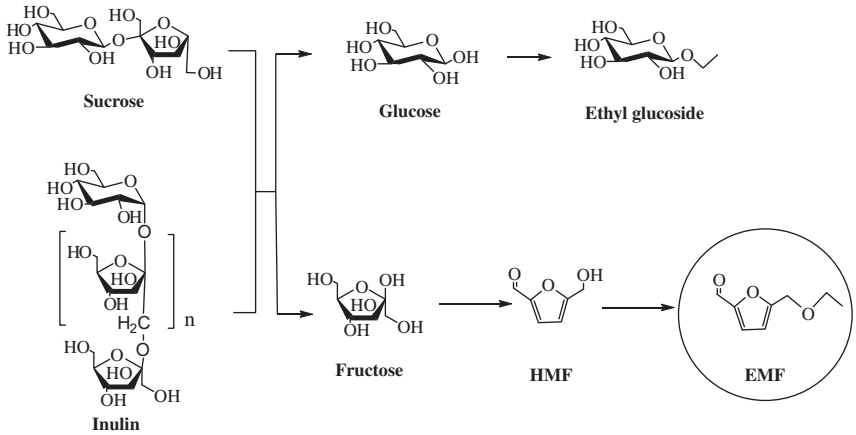

Fig. 1. Route for the synthesis of EMF from fructose, sucrose and inulin as catalyzed by HPW.