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Conversion of glucose into furans in the presence of $AlCl_3$ in an ethanol–water solvent system

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ABSTRACT

Glucose was converted into furans (5-hydroxymethylfurfural and 5-ethoxymethylfurfural) in the presence of $AlCl_3$ in an ethanol–water solvent system. The system showed high activity for the conversion of glucose into furans but low activity for the subsequent formation of LAs (levulinic acid and ethyl levulinate). High furans yield of 57% with low LAs yield of 11% can be obtained at 160 °C within 15 min. Glucose-based disaccharides (sucrose, maltose and cellobiose) and polysaccharides (starch but not cellulose) can also be converted to furans effectively under the same condition. $AlCl_3$ can be used to prepare furans from biomass-derived compounds in ethanol–water, a green solvent system.

1. Introduction

Glucose, the monomer of cellulose and starch, is the most abundant and cheapest monosaccharide and extensive research is being conducted on the conversion of glucose into chemicals and biofuels. Different solvents have been used in the process of glucose conversion, such as water (Aida et al., 2007; Yang et al., 2010), dimethylsulfoxide (Yan et al. 2009), ionic liquids (Zhao et al., 2007; Zhang and Zhao, 2010), methanol (Tominaga et al., 2011) and ethanol (Peng et al., 2011; Hu et al., 2011). The use of alcohols as solvents for carbohydrate conversion has received increased attention because alcohols suppress humin formation (Hu et al., 2011) and afford biodiesel-like products, (the ether of 5-hydroxymethylfurfural (HMF) and/or the ester of levulinic acid (LA)), in one-pot reactions (Peng et al., 2011; Tominaga et al., 2011; Hu et al., 2011; Zhu et al., 2011; Saravanamurugan et al., 2011). Peng et al. (2011) used SO_4^{2-} as a catalyst for glucose conversion in ethanol to give ethyl levulinate (LAE) with a 30% yield. The use of Amberlyst-15 can give 80% LAE yield from glucose (Hu et al., 2011). Tominaga et al. (2011) used In $(OTf)_3$ in methanol for the conversion of glucose to afford methyl levulinate with a 58% yield after 5 h at 160 °C. The focus of these papers has been on the conversion of glucose to the esters of LA. Furans (HMF and its ethers) appear to be the intermediates in these reactions.

Compared to LAs (LA and its esters), furans are more valuable. HMF can serve as a platform chemical for liquid fuels and renewable polyesters (Corma et al., 2007). Furthermore, the ethers of HMF are excellent additive for diesel. For example, 5-ethoxymethylfurfural (EMF) has a high energy density of 8.7 kWh/L, similar to that of regular gasoline (8.8 kWh/L), nearly as good as that of diesel (9.7 kWh/L), and significantly higher than that of ethanol (6.1 kWh/L) (Gruter and Dautzenberg, 2007). A catalytic system that can convert glucose to furans selectively in alcohol solvents is highly desirable. In the present paper, the conversion of glucose into furans in the presence of $AlCl_3$ in an ethanol–water solvent system is reported. $AlCl_3$ is a cheap, nontoxic, and abundant chemical, and $AlCl_3$ in a water-tetrahydrofuran solvent system showed high activity for conversion of glucose into HMF (Yang et al. 2012). Ethanol was chosen because it is regarded as a green solvent and can be prepared from biomass (Saxena et al., 2009). The effect of the reaction conditions and possible reaction pathway are discussed. Some complex carbohydrates were also used as raw materials.

2. Methods

2.1. Materials

Ethyl glucoside (EGL) was purchased from Carbosynth (USA). All other chemicals were purchased from Sigma–Aldrich (USA). All reagents were of analytical grade and used as received.

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