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Commercially attractive process for production of 5-hydroxymethyl-2-furfural from high fructose corn syrup

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ABSTRACT

5-Hydroxymethyl-2-furfural (HMF) was prepared with high fructose corn syrup (HFCS) manufactured directly from industry. Equipped industrial process and cheaper availability considered HFCS-90 as a competitive starter for production of HMF. Readily evaporable solvent, 1,4-dioxane was found as a promising reaction media from the screening of various solvents and readily available cation exchange resin, Amberlyst-15 was used as a solid acid catalyst. Parametric variation studies including amount of catalyst, concentration of HFCS-90, and reaction temperature were performed to achieve a maximum HMF yield of 80% at 100 °C within 3 h. In particular, use of readily evaporable solvent and heterogeneous catalyst allowed highly practical purification of HMF, which still remains as a major obstacle to the commercialization of HMF. With filtration, evaporation, and extraction, HMF was simply isolated in 72% yield and ^{1}H NMR spectra of the isolated HMF confirmed that its purity was sufficient for use in next step of reactions. In addition, all solvents could be recycled with distillation and catalyst was reused up to 5 cycles without a significant loss of activity.

1. Introduction

In the mission of replacing fossil resources based on carbon feedstocks by renewable biomass, for production of fuels and chemicals, many efforts were underway throughout the globe using carbohydrate biomass regenerated most abundantly on earth via photo-synthesis [1–6]. Among carbohydrate-derived platform compounds, 5-hydroxymethyl-2-furfural (HMF) is promisingly considered as a versatile intermediate leading to a variety of applications in a post-petroleum world [7–11]. With this regard, a large number of studies on preparation of HMF from various carbohydrate resources have been performed using potentially fascinating methods [12–20], however, industrial-scale production of HMF is still limited due to unaffordable costs on materials and process, insufficient supply of starters, especially difficulties in isolation.

Many efforts were dedicated to the conversion of fructose into HMF using homogeneous or heterogeneous acid catalysts in various reaction media. However, high boiling solvents like *N*,*N*-dimethylformamide (DMF) [21,22], *N*,*N*-dimethylacetamide (DMA) [23], *N*-methyl-2-pyrrolidone (NMP) [24], dimethyl sulfoxide (DMSO) [25–31], sulfolane [32] could encounter difficulties in separation and purification. Cost-burdened reaction conditions using microwave heating [33–35], ionic liquid [36–43], supercritical water [44–46] are not suitable for commercialization for the time being. Focusing on the manufacture of HMF in a volatile solvent, Lai et al. recently reported the production of HMF (isopropyl etheric derivatives of HMF were also obtained as co-products) from fructose using isopropanol solvent and homogeneous HCl as a catalyst; product was purified using flash column chromatography [47]. Attempts were also tried using volatile tetrahydrofuran (THF), however in biphasic system [48,49].

Herein, we report a commercially attractive process to produce HMF from industrially available high fructose corn syrup (HFCS) in readily evaporable solvent, 1,4-dioxane (abbreviated as dioxane in the following) using heterogeneous catalyst, Amberlyst-15 (Fig. 1).

Established technology for industrial production and cheaper availability in market can consider HFCS as an attractive starter of HMF in a realistic point of view. HFCS is a less expensive sweetener made from starch, used as alternative for sucrose in 1977 [50]. Two classes of HFCS are manufactured through 3 step enzymatic catalytic process followed by fractionation process, namely HFCS-42 and HFCS-90, which contain 42% and 90% of fructose, respectively [51,52]. HFCS-55 is produced by combining

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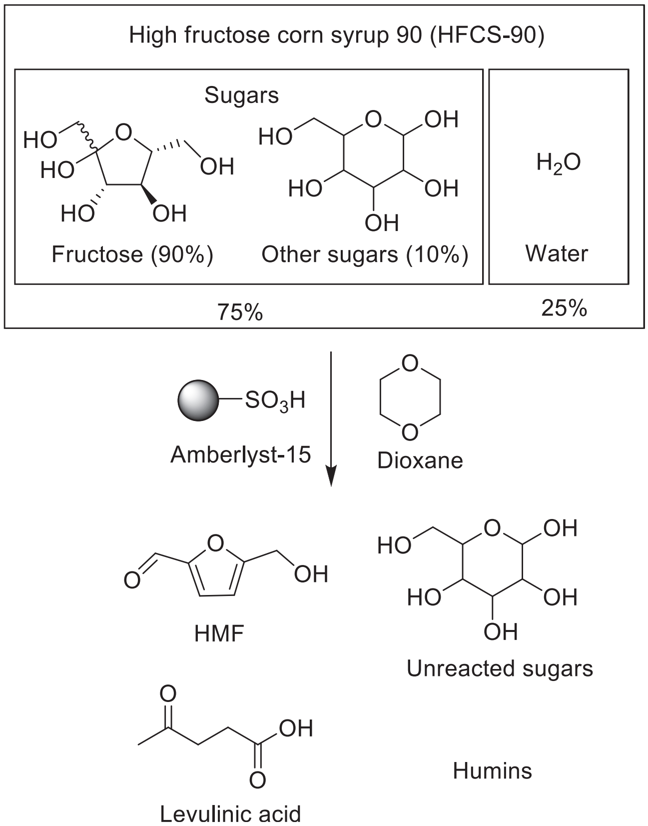

Fig. 1. Production of HMF from HFCS.

HFCS-42 and HFCS-90, used in sweetened beverages and all of them contain 25% of water. Recent study revealed that HMF is formed on long storage of HFCS, causing a controversy on HFCS as a food additive [53]. In this study, HFCS-90 obtained directly from industry was used as a starter for production of HMF and, in particular, readily evaporable dioxane was selected as a reaction medium. For industrial production of HMF, use of dioxane was quite beneficial in many aspects: (1) it is easily removable and recyclable; (2) readily available solvent often used for a variety of practical applications as well as in the laboratory; (3) relatively nontoxic substance with an LD50 of 5170 mg/kg; (4) potentially obtained as a bio-based version from bioethanol (via bioethylene then bioepoxide).

2. Methods

2.1. Materials

High fructose corn syrup 90 (HFCS-90) was supplied by SK Chemicals Co. Ltd. (Manufacturer: Daesang corporation, Korea). Amberlyst-15 (hydrogen form, 4.7 mmol of SO_3H per gram resin) was purchased from Sigma–Aldrich (USA). Amberlyst-15 was washed by 2 N NaOH, deionized water, 3 N HCl, water by turns and dried under vacuum overnight prior to use. Solvents including dimethyl sulfoxide (DMSO, $\geq$99.9%), N,N-dimethylformamide (DMF, anhydrous, 99.8%), acetonitrile (CH_3CN, anhydrous, 99.8%), 1,4-dioxane (dioxane, anhydrous, 99.8%), tetrahydrofuran (THF, anhydrous, $\geq$99.9%), 2-propanol (isopropanol, anhydrous, 99.5%) were purchased from Sigma–Aldrich (USA) and directly used without any further purification. All other general chemicals including acetone, ethyl acetate, magnesium sulfate ($MgSO_4$), sodium hydroxide (NaOH), hydrochloric acid (HCl, 37%) were obtained from Fisher Scientific (USA) and Samchun chemicals (Korea).

2.2. Experimental procedures

2.2.1. Solvent screening procedures

Solvent screening reactions were carried out in Carousel 12 Plus Reaction Station (12 tubular reactors), HFCS-90 (430 mg and 860 mg each to 6 reactors) and Amberlyst-15 (300 mg each) were placed individually. Then solvents to be screened including DMSO, DMF, CH_3CN, dioxane, THF, isopropanol (3 mL each) were added to each reactor. After all reactors were installed into Carousel 12 Plus Reaction Station, the mixtures were heated to 100 °C and stirred at 700 rpm for 4 h. After reaction, they were cooled to room temperature, diluted with deionized water (100×) for HPLC analysis.

2.2.2. Experiments for parametric variation study

In the 250 mL round bottomed flask equipped with overhead stirrer were placed the designated amounts of HFCS-90 and Amberlyst-15 and then dioxane (100 mL) was added. The mixture was heated and stirred in a temperature-controlled oil bath. An aliquot of reaction mixture was pipetted out at intervals and diluted with deionized water (100×). The samples were analyzed using HPLC. For the study of temperature effect, into the ~38 mL glass thick walled pressure tubes with Teflon cap (25.5 mm of O.D. and 20.3 cm of length) were placed the HFCS-90 (715 mg) and Amberlyst-15 (500 mg) and then dioxane (5 mL) was added. The mixture was heated to the designated temperature and stirred. Reaction mixture for the designated time was diluted with deionized water (10×). The samples were analyzed using HPLC. (*Note*: Dioxane vapor can irritate the eyes and respiratory tract and thus make sure no-leak when temperature is higher than boiling point of dioxane. Also a radical stabilizer can be used in large-scale operation to inhibit the possible peroxides formed during the reaction.)

2.2.3. Experiments for recyclability of catalyst

In the 250 mL round bottomed flask equipped with overhead stirrer, HFCS-90 (14.3 g), Amberlyst-15 (10 g), and dioxane (100 mL) were placed and the mixture was heated to 100 °C and stirred in a temperature-controlled oil bath for 3 h. After reaction, they were cooled to room temperature and Amberlyst-15 was filtered, washed, and dried under vacuum overnight. Then the resulting Amberlyst-15 was reused for next reaction.

2.3. Analytic methods

Reactions were monitored by HPLC (Agilent 1200 series) equipped with auto sampler (G1329A, Agilent), column temperature controller (G1316A, Agilent), detector (G1315D for UV and G1362A for RID, Agilent) using ion-exclusion column (Bio-Rad Aminex HPX-87H 300 mm × 7.8 mm) and processed by ChemStation software. Synthetic HMF was characterized by HPLC and confirmed by ^{1}H and ^{13}C FT NMR (400 MHz, JNM-AL400, Jeol) processed by Delta program (ver. 4.3.6).

3. Results and discussion

3.1. Solvent screening

As an initial attempt for efficient conversion of HFCS-90 into HMF, various solvents which are completely miscible in water (HFCS-90 contains 25% water) with a range of polarities and boiling points (Table 1) including DMSO, DMF, acetonitrile, dioxane, tetrahydrofuran (THF), and isopropanol were screened (Fig. 2). Commercially available cation-exchange resin, Amberlyst-15 was used as a heterogeneous catalyst for dehydration of HFCS into HMF. Amberlyst-15 has been known as a suitable solid acid