



Water-promoted selective heterogeneous catalytic trimerization of xylose-derived 2-methylfuran to diesel precursors

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ABSTRACT

The catalytic trimerization of 2-methylfuran was performed to produce diesel precursors of C15 hydrocarbons using solid acid catalysts that can replace environmentally harmful sulfuric acid. The addition of water to the reaction system significantly increased the selectivity to the diesel precursor, which is a trimer, suppressing the formation of a tetramer. The selective production of a trimer increased the diesel fuel yield when hydrodeoxygenation was performed on the condensation products of 2-methylfuran.

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1. Introduction

The valorization of all of the carbon sources of biomass may help in the development of economically feasible biofuels. The use of lignocellulose, including wood and grass, is studied for the production of cellulosic bioalcohols from cellulose and hemicellulose, which compose 60–70% of lignocellulose. While glucose can be more easily converted into bioalcohols, xylose from hemicellulose is not readily fermented by common industrial yeast, although its valorization may improve the profitability of lignocellulose-based biofuels [1,2].

The valorization of xylose and the condensation of 2-methylfuran (2-MF), obtained by the dehydration and selective hydrogenation of xylose, to produce high-carbon-number hydrocarbons, are studied by means of the hydroxyalkylation/alkylation of 2-MF molecules, which are further converted into long-chain

diesel fuels [3–5]. Aqueous sulfuric acid is used as a homogeneous catalyst that efficiently produces high-carbon-number diesel precursors, including 5,5-bis(5-methylfuran-2-yl)pentan-2-one. Although it may be recovered after the reaction, this type of strong acid can damage the reactor and cause environmental issues. Thus, environmentally friendly catalysts exhibiting comparable activities will help in the development of economically benign processes.

In this study, we use Amberlyst-15 for the trimerization of 2-MF. Amberlyst-15, a macroreticular sulfonic-acid-based polystyrene ion-exchange resin, is commonly used as a commercial solid acid catalyst [6]. It is an environmentally friendly catalyst because of its high activity, non-toxicity, non-corrosiveness, and recyclability compared to sulfuric acid. Amberlyst-15 has also been demonstrated to be an effective catalyst for acetylation and aldol and cross-aldol condensation [7,8]. In aqueous media, Amberlyst-15 offers a simple and clean method for chemical synthesis with high selectivity and excellent yields [9,10].

In addition to replacing homogeneous acid catalysts with solid acid catalysts, the effects of the reaction media, water in this study, are investigated. Water is a common environmentally friendly solvent that can replace volatile, flammable, and toxic solvents for

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chemical synthesis. Additional benefits have been observed with regard to reactivity and selectivity when using water in organic synthesis applications, in which water became an efficient promoter and activating medium. For example, water improves the Diels–Alder reaction rate by 700-fold compared to the reaction using 2,2,4-trimethylpentane solvent [11]. A fast reaction rate with high selectivity is also observed when using water in the synthesis of a β -aminocarbonyl compound via the aza-Michael reaction [12]. However, the use of water in organic synthesis applications is also limited because most organic compounds have poor solubility in water and because many organic compounds are damaged by water. Solventless organic reactions are being developed for environmentally benign processes. The role of water in the solid-acid-catalyzed trimerization of 2-MF is discussed in this study. The hydrodeoxygenation of the condensation products is performed using Pd/charcoal and Ru/SiO₂–Al₂O₃ catalysts to obtain diesel hydrocarbons.

2. Experimental

2.1. Materials

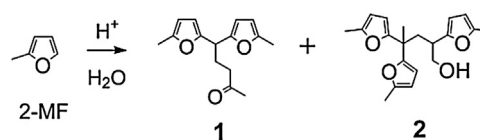
All materials were used without further purification. Amberlyst-15 (hydrogen form, 4.7 meq H⁺/g), p-toluenesulfonic acid (p-TosOH), Nafion-NR50, Nafion-SAC-13, 5 wt% Pd/charcoal, anhydrous RuCl₃, and silica–alumina support were purchased from Aldrich (Milwaukee, WI, USA). Amberlyst-15 was dried in a vacuum at 95 °C for 16 h prior to use. Sulfuric acid (H₂SO₄, 96%) was purchased from J.T. Baker (Central Valley, PA, USA). 2-Methylfuran (2-MF) was purchased from Alfa Aesar (Ward Hill, MA, USA). Ru/SiO₂–Al₂O₃ (5 wt% Ru) was prepared using a wet impregnation method by adding a silica–alumina support to an aqueous solution of ruthenium chloride. The produced mixture was stirred for 24 h at room temperature and dried using a vacuum evaporator. The mixture was further calcined in air for 2 h at 400 °C and reduced under a H₂ flow for 4 h at 400 °C. Deionized water (18.2 M Ω cm) was prepared using an aquaMAX Ultra 370 water purification system (Young Lin Instrument, Anyang, Korea).

2.2. Trimerization of 2-methylfuran

The trimerization of 2-methylfuran was performed in a 100-mL round-bottomed flask. The catalysts and water (0–0.9 mL) were mixed with 2-MF (5.4 mL, 0.038 mol) at room temperature. The reaction mixture was refluxed at 85 °C for 3–56 h. The product was then analyzed using a GC–MS device (Agilent 5975C inert XL MSD with a triple-axis detector equipped with a HP-5 ms capillary column, 60 m \times 0.25 mm \times 0.25 μ m), ¹H NMR (Agilent spectrometer at 400 MHz), and a HPLC device (YL9100 equipped with a Zorbax SB-C18, 4.6 m \times 150 mm \times 5 μ m) for identification and quantification. The catalysts used in this study were Amberlyst-15 (0.15 g), sulfuric acid (aq, 0.7 and 24 wt%), p-TosOH (0.05, 0.15 g), Nafion-NR50 (0.15 g), and Nafion-SAC-13 (0.15 g).

2.3. Hydrodeoxygenation (HDO) of the condensed products

Hydrodeoxygenation (HDO) of the condensed products was performed in a two-step reaction process. In the first step, hydrotreated products were obtained from the trimerization product after unreacted 2-MF was removed by a vacuum evaporator at 70 °C for 20 min. The condensed products (40 mL) were then mixed with H₂ and Pd/charcoal (5 wt%, 4 g) in a batch reactor at room temperature. The reaction mixture was heated to 413 K and the reaction pressure was allowed to reach 60 bar [13]. The reaction continued for 24 h, while the reaction pressure was maintained at 60 bar by filling the reactor with H₂ during the reaction. In the second step,



Scheme 1. Condensation of 2-MF to its trimer and tetramer.

the hydrotreated products were filtered and HDO was performed at 553 K and 60 bar (H₂) for 16 h in a batch reactor filled with the hydrotreated liquid products (30 mL) and the Ru/SiO₂–Al₂O₃ catalyst (5 wt%, 3 g) [14,15]. The reaction pressure was adjusted to 60 bar by adding H₂ during the reaction. A mixture of final products was analyzed using a GC–MS device (Agilent 5975C inert XL MSD with a triple-axis detector) equipped with a HP-5 ms capillary column (60 m \times 0.25 mm \times 0.25 μ m) and a GC–FID gas chromatograph system (Clarus 600 series) equipped with an MXT-1HT SimDist column (60 m \times 0.25 mm \times 0.25 μ m) and a flame ionization detector (FID) for quantification.

3. Results and discussion

3.1. Trimerization of 2-MF

The trimerization of 2-methylfuran (2-MF) to produce C15 hydrocarbons was performed in a batch reactor at 85 °C for 3 h using sulfuric acid (aq, 24 wt%), p-toluenesulfonic acid (p-TosOH), and Amberlyst-15 (Scheme 1 and Fig. 1). Although 5,5-bis(5-methylfuran-2-yl)pentan-2-one (**1**, trimer) and 4,4-tris(5-methylfuran-2-yl)pentan-1-ol (**2**, tetramer) were obtained as major products for all of the catalysts at conversions of 37–46%, as confirmed by the HPLC and NMR results (Figs. S1–S4) [16], the selectivity characteristics with regard to **1** and **2** differed significantly depending on the catalysis system used. The formation of the tetramer was not reported in the previous reports of the aqueous-sulfuric-acid-catalyzed condensation of 2-MF [3]. The aqueous-sulfuric-acid-catalyzed condensation of 2-MF preferentially produced trimer **1** (86.8% selectivity), while catalysis using p-TosOH and Amberlyst-15 preferentially produced tetramer **2** (83.1 and 87.5% selectivity for p-TosOH and Amberlyst-15, respectively). In all cases, the formation of oligomers with molecular weight larger than that of tetramer was also observed as minor products. Because the possible hydrodeoxygenated products from **1** and **2** are 6-butylundecane (C15 hydrocarbon) and 6,8-dimethyl-6-pentyltridecane (C20 hydrocarbon), respectively, C15 hydrocarbon as a precursor is preferred as a HDO reactant, which is a desirable product in this study.

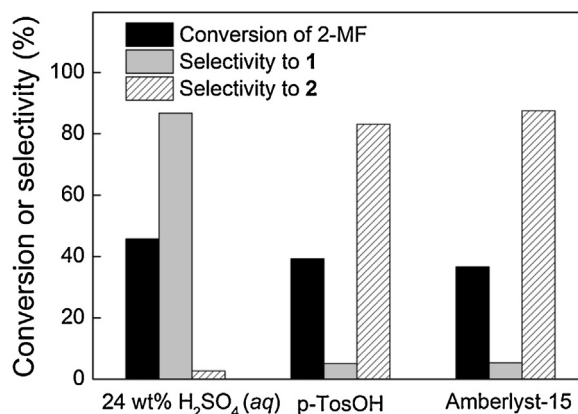


Fig. 1. Catalysis results of the condensation of 2-MF using 24 wt% H₂SO₄ (aq), p-TosOH, and Amberlyst-15. 2-MF (5.4 mL) was condensed using H₂SO₄ (aq, 24 wt%, 0.67 mL) or p-TosOH (0.05 g) or Amberlyst-15 (0.15 g) at 85 °C for 3 h.

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