Short Communication

Thermodynamics and reaction pathways of furfuryl alcohol oligomer formation

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ABSTRACT

The acid-catalyzed transformation of furfuryl alcohol (FA) monomer to oligomers has been studied in the liquid phase to investigate the reaction mechanisms and intermediate species by using a combination of quantitative reaction product measurements and density functional theory calculations. FA monomer was converted into oligomers with a broad range of carbon number: C_9–C_{10}, C_{14}–C_{15}, C_{19}–C_{29}, $>C_{29}$. Based on the calculations, terminal CH_2OH dimer formation is both kinetically and thermodynamically favored, consistent with the experimental results. The order for dimer production in the C_9–C_{10} range follows terminal CH_2OH > ether bridged–methylene bridged dimer > OH-carbon bridge.

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1. Introduction

The conversion of lignocellulosic biomass into fuels and chemicals has been rigorously investigated as a response to the depletion of petroleum resources, increasing demand for oil, environmental concern over greenhouse gas emissions, and energy security [1–3]. Among the biomass derived chemicals, furfuryl alcohol (FA) is an attractive intermediate chemical for the production of levulinic acid [4], alkyl levulinate [5], and various useful polymer products [6–8]. FA can be obtained through the hydrogenation reaction of furfural and further converted into FA oligomers by the acid-catalyzed condensation reaction [9–11]. FA oligomers have been studied due to their application in fuel blending components [12] (Scheme 1). Buijtenen et al. have shown that after hydrogenation of FA oligomers with Ni/Al$_2$O$_3$, the fuel blend containing 10 vol.% of these C_9–C_{20} carbon coupled FA oligomers fulfills the European diesel specification [12]. The acid-catalyzed condensation of FA is the major source for the FA oligomerization [13,14]. Depending on the experimental conditions and method of analysis, different oligomer/polymer structures such as linear [9,15,16], cross-linked [17,18], and open ring [19] have been proposed from the results of XRD [20], NMR [15,21–23], UV–Vis [16,21,24,25], IR [16,20,21],

Raman spectroscopy [8–10,13,20], and DFT calculations [9]. We have recently shown that the FA monomer can dimerize in acidic solution and two possible structures can be produced through dehydration or deprotonation reactions (Eqs. (1) and (2), the changes in free energy are given in kcal/mol) [9].


(1)

(2)
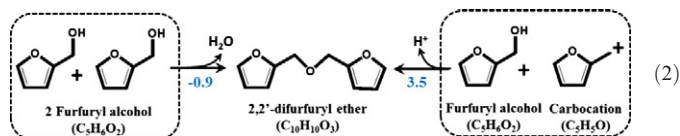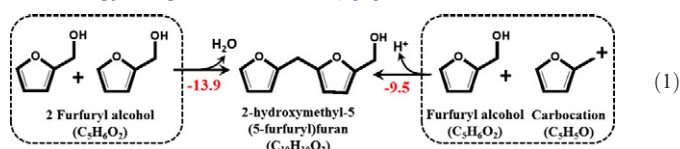
From the free energies formation of 2-hydroxymethyl-5(5-furfuryl) furan (HFF) is thermodynamically more favorable than 2,2′-difurfuryl ether (DFE). Even though, the formation of dimer from two FA monomers is thermodynamically favorable, because of the higher carbocation reactivity, dimer formation via the carbocation may be preferred for kinetic reasons. In addition to these two dimers, Khusnutdiv et al. reported that 2,2′-difurfurylmethane (DFM) can be also produced in the presence of the Rh(PPh$_3$)$_3$Cl catalyst using H$_2$O and CCl$_4$ as solvents [26]. The following mechanism for formation of DFM (Eq. (3)) was
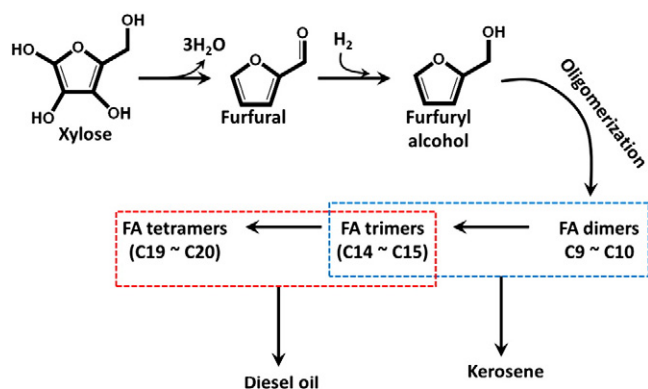
Scheme 1. Kerosene and diesel oil products from biomass by a combined dehydration, hydrogenation, and oligomerization reaction pathway.

proposed by Sunjic et al. [27] and Korneeva et al. [28]. DFM and formaldehyde are produced through decomposition of DFE derived from the condensation of two FA monomers.

$$(3)$$
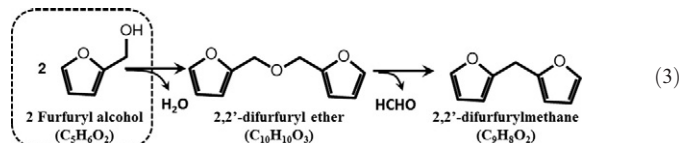
Using the ^{13}C NMR spectroscopy, Choura et al. proposed a similar reaction mechanism (Eq. (4)) for the conversion of 5-methylfurfuryl alcohol (MFA) to the bis[2-(5-methylfuryl)]methane (BMFM) [15]. 2,2′-dimethylfurfuryl ether is formed first, which then decomposes into formaldehyde and BMFM.

$$(4)$$
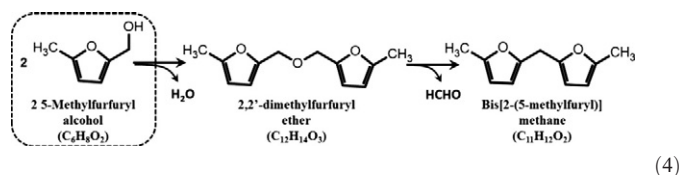
Although the oligomerization of FA appears in a number of literature citations, the detailed understanding of reaction mechanisms and thermodynamics for the oligomerization processes (multiple pathways) is not available. Such an understanding will substantially enhance the utilization of FA as a platform chemical for the formation of longer chain hydrocarbons used in liquid transportation fuels. The aim of the presented study is to understand the reaction mechanism of oligomer formation and provide an accurate analysis of oligomer products. Here we have determined the product distribution of dimers (C_9–C_{10}) in detail and employed density functional theory to provide a qualitative confirmation of the experimentally observed dimer distribution trends.

2. Experimental

2.1. Catalytic reaction

FA (98%) and sulfuric acid (99.999%) were obtained from Sigma-Aldrich and used without further purification. FA was mixed with dilute sulfuric acid (1 M) to catalyze the production of oligomers.

Initial GC/MS studies were undertaken to establish the identity of the major oligomeric species formed during the reaction (see Supporting information for the details of GC/MS experiment). Gas chromatographic analyses were performed using an Agilent 5890 Series II equipped with a flame ionization detector and a split/splitless injector. The column

had dimensions of 30 m × 0.25 mm and contained a 0.25 μm film of polymethylsiloxane stationary phase. The column oven temperature was linearly programmed from 100 °C to 300 °C at 6 °C/min after an initial hold of 4 min. The carrier gas was helium, and it was controlled at a constant pressure of 20 psi. The split flow was maintained at 150 mL/min. An injection volume of 0.4 μL was employed. Detector and injector temperatures were controlled at 250 °C. Samples were prepared for analysis by dissolving 0.1 g of sample into 2 mL of an internal standard solution (approximately 10 mg/mL 1,2,3,4-tetrahydro naphthalene in acetone). This was further diluted by addition of 2 mL acetone. The response factor for FA was determined directly from the analysis of a known blend with the internal standard, 1,2,3,4-tetrahydro naphthalene. Response factors for other components were estimated following an approach similar to that described by Scanlon and Willis [29]. The experimentally determined furfuryl alcohol response factor and that estimated by the Scanlon–Willis method were in close agreement. Smaller, unidentified peaks were added together and report as unidentified components. The response factor employed for these unknown components was taken as the average of the known components excluding that of furfuryl alcohol. The amount of non-eluted components (greater that the hexamer) was taken as 100% less the sum of all measured GC peaks including the unidentified components. For a batch system, the conversion, selectivity, and yield were calculated as follows:

$$\text{Conversion}\,(\%) = (W_{FAin} - W_{FAout})/(W_{FAin}) \times 100$$

$$\text{Selectivity of A}\,(\%) = W_{Aout}/(W_{FAin} - W_{FAout}) \times 100$$

where W_{FAin} and W_{FAout} are the masses of FA at time = 0 and time t, respectively; W_{Aout} is the outlet mass of A product formed.

2.2. Computational methods

The geometries, zero-point energies, and the thermal energies were computed using the B3LYP/6-31+G(2df,p) or B3LYP/6-31+G(d) levels of theory using the Gaussian 09 software [30]. To account for the effects of an aqueous environment, calculations were also performed in water dielectric using the solvation model (SMD) at the B3LYP level of theory. FA + one water complex is optimized and used as one of the starting structure. This model is used to include at least one discrete solvent molecule in the calculation in addition to the implicit dielectric model. The geometry of the lowest energy conformers for all molecular species was chosen from our recently published papers [9,31,32].

3. Results and discussions

3.1. Acid-catalyzed oligomerization of FA

Oligomerization of FA was performed with an aqueous solution containing 3.00 g FA and 0.03 g 1 M H_2SO_4 at 25 °C and ambient pressure, as shown in Fig. 1. During the reaction, the conversion values (mass basis) monotonically increase with increasing reaction time, and asymptotically reach ~32 wt.% in 24 h (Fig. 1a). Heavy oligomer ($>C_{18}$) formation monotonically increases, while FA monomer (C_5) wt.% decreases as a function of reaction time (Fig. 1b). It was found that up to 4 h, the wt.% of $>C_{18}$ was similar to the C_9–C_{15} wt.% values. After 4 h, however, the wt.% of $>C_{18}$ was higher than C_9–C_{15} values and after 24 h the heavier oligomers were favored significantly ($>C_{18}$ = ~20 wt.% and C_9–C_{15} = ~10 wt.%). The higher percentage of $>C_{18}$ heavy oligomers in the sulfuric acid catalyzed reaction is in agreement with the observed dark (black) color of the solution, which indicates FA degradation into humins [9].

To evaluate the product distributions, we investigated the FA oligomers in more detail (Fig. 1c). Oligomers larger than hexamers ($>C_{29}$) were the dominant product in $>C_{19}$ oligomers, whereas tetramer to hexamer (C_{19}–C_{29}) were only ~1 wt.% after 24 h. Dimer and trimer