



## Carbon–carbon bond formation for biomass-derived furfurals and ketones by aldol condensation in a biphasic system

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### ABSTRACT

Production of liquid alkanes in the range of C<sub>8</sub>–C<sub>15</sub> from renewable sources, such as xylose and fructose (C<sub>5</sub> and C<sub>6</sub>), requires the formation of C–C bonds between the carbon chains. We have investigated aldol condensation as a catalytic route for this conversion in a biphasic system between various furfurals (furaldehyde (FUR), methyl furfural, and 5-hydroxymethyl furfural (HMF)) and ketones (acetone, acetol, dihydroxyacetone, 2-hexanone, and 3-hexanone) derived from biomass. This system employs a reactive aqueous phase containing a basic NaOH catalyst, an organic extracting phase to remove the aldol-adducts from the homogeneous catalyst, with the addition of salt (NaCl) to the aqueous phase employed to expand the miscibility gap between the aqueous and organic phases. The effect of reagent ratios and reaction conditions on the final product distribution, such as ketone to furfural and base to furfural ratio, was investigated and a simple first order model was used to gain insight into the reaction network. High yields to single and double condensation products can be achieved for acetone condensation with furfural compounds by proper choice of reagent ratios. Degradation of HMF appears to be catalyzed by base, leading to the formation of organic acids that subsequently neutralize the base catalyst. This degradation process limits the recycling of the aqueous phase and also decreases the condensation yield of species such as hexanones that do not readily dissolve in the aqueous phase. FUR, which does not readily degrade, is more completely condensed to form products; however, because FUR is less soluble in the reactive aqueous phase compared to HMF, high concentrations of base must be used to increase the rate of reaction.

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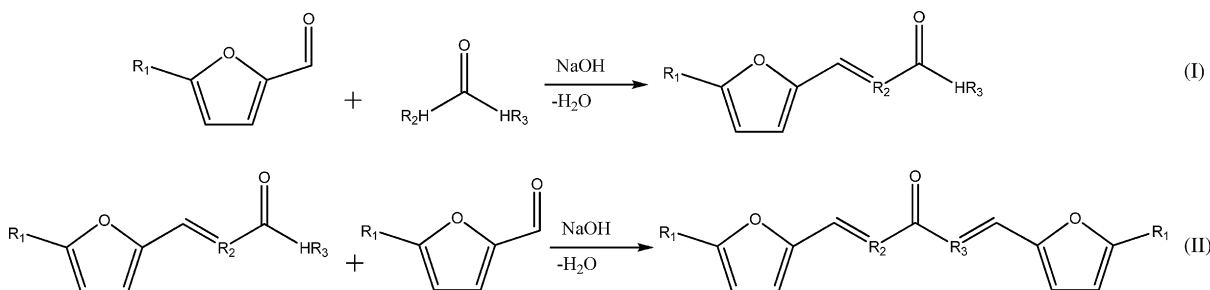
### 1. Introduction

The amount of biomass that can be grown globally on a sustainable basis could provide approximately 100EJ of energy per year [1], a value comparable to the annual worldwide use of energy by the transportation sector [2]. While it is currently possible to convert a hexose to *n*-hexane with high yields [3], this molecule is at the lower limit of molecular weight for use in liquid alkane transportation fuels [4,5]. In a recent paper, it was shown that the targeted synthesis of specific alkanes with molecular weights higher than hexane can be achieved from fructose by first dehydrating the sugar to produce furfurals, followed by the formation of C–C bonds via aldol condensation with ketones, and completed by subsequent removal of oxygen atoms to form alkanes by a combination of hydrogenation and dehydration reactions [6]. The first step in this process, the formation of furfurals such as 2-furaldehyde (FUR) and hydroxymethylfurfural (HMF), can be accomplished using chemical catalysts by acid-catalyzed dehydration of xylose and fructose

in high yields [6–9]. In addition, the final two steps in this alkane production process, hydrogenation and dehydration, are readily performed in flow reactors over solid catalysts with high yields [6]. In the present paper, we focus on the critical intermediate process involving C–C coupling reactions via aldol condensation.

The formation of C–C bonds by aldol condensation occurs between two carbonyl groups with reactive  $\alpha$ -hydrogens on at least one of the carbonyls, catalyzed under acid or basic conditions, although the present paper focuses on the latter. Scheme 1 shows reactions between the aldehyde group of furfural compounds (F) and the  $\alpha$ -hydrogen of ketone molecules (K). A single condensation occurs when the enolate form of the ketone created via base-catalyzed  $\alpha$ -hydrogen abstraction attacks the aldehyde of the furfural compound. These C–C coupling reactions are accompanied by dehydration, leading to the formation of conjugated systems of C=C and C=O double bonds, as shown in Scheme 1, (I). For ketones with a reactive  $\alpha$ -hydrogen on either side of the carbonyl group, a second condensation with the furfural is possible producing an F–K–F compound (Scheme 1, (II)). This formation of F–K and F–K–F compounds can be carried out with high selectivity versus the formation of F–F and K–K adducts. In particular, F–F bonds are not formed because furfural compounds do not possess a hydrogen

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**Scheme 1.** Single and double condensation of a furfural and ketone model. (I) Formation of single condensation, F–K molecule. (II) Formation of double condensation, F–K–F molecule.

atom that is alpha to the carbonyl group, and reactions between two ketone molecules to form K–K compounds are slower compared to reactions of an aldehyde with a ketone [10].

Aldol condensation of acetone with 2-furaldehyde has been studied in homogeneously catalyzed mono-phasic systems, using water, methanol/water or ethanol/water solution as solvent [11–13]. Mono-phasic homogeneously catalyzed systems have several drawbacks, including the eventual need to neutralize the catalyst and remove high volumes of water. Accordingly, in the present study we have employed a biphasic catalytic system consisting of a reactive aqueous phase and an organic extracting phase. The aqueous phase contains the basic catalyst (e.g. sodium hydroxide, NaOH), while the organic phase consists of a low boiling point organic solvent (e.g., tetrahydrofuran, THF) that continuously extracts the hydrophobic condensation products. Salt is added to the aqueous phase (e.g. sodium chloride, NaCl) to improve the miscibility gap between the two phases by salting-out organic components from the aqueous phase. The use of an organic solvent with a low boiling point and latent heat improves the energetics for removing and recycling the solvent from the aldol-adduct products. Compared to water, THF as a solvent has a lower boiling point (339 K compared to 373 K at atmospheric pressure) and lower latent heat of vaporization (30 kJ/mol compared to 41 kJ/mol at their normal boiling point temperatures).

## 2. Experimental

### 2.1. Reactive compounds

Acetone was chosen as a model compound for ketones, while FUR and HMF were chosen as furfural compounds. Acetone and FUR were purchased from Sigma–Aldrich, while HMF was produced by fructose dehydration in a biphasic system, as described in an earlier work [6]. The resulting solution of 6 wt% HMF in THF was used directly, or it was concentrated using a rotary evaporator. In addition to the aforementioned model compounds, we studied aldol condensation of 5-methyl-furfural (MeFur), which is formed from dehydration of methyl-pentoses that are present in varying concentrations with pentoses in biomass feedstocks used to make FUR [9]. In addition, we studied condensation of 2-hexanone and 3-hexanone, which can be made via the dehydration/hydrogenation of sorbitol [14]. We also investigated condensation of dihydroxyacetone, and glyceraldehyde, which can be formed by retro-aldol reactions of glucose [15]; and, we studied the condensation of acetol, which can be made from the dehydration of glycerol [16].

### 2.2. Experimental setup

Typical experiments for aldol condensation were carried out by mixing an organic feed solution and an aqueous feed solution in a 25 mL batch reactor. The organic phase was created by adding

the desired reactants (furfurals and ketones) to THF, or by adding the desired ketones to the solution of HMF in THF produced from the dehydration of fructose. The aqueous phase contained 6–27 wt% NaOH, and it was saturated with NaCl. The mass ratio of the organic and aqueous phase was kept at 2:1, except for several runs where a ratio of 20:1 was used. The stirring speed during reaction was set at 1180 rotations per minute (rpm), which was sufficient to achieve good mixing of the two phases, such that the results were not significantly affected by stirring speed.

Scaled-up reactions were performed in a 500-mL flask, employing 300 mL of solution. These experiments produced yields similar to those obtained using 25-mL reactors. These larger volumes of condensation products were then concentrated in a rotary evaporator, and subsequently hydrogenated over a Pd-based catalyst, and finally deoxygenated to produce alkanes by dehydration/hydrogenation over a bifunctional Pt/NbOPO<sub>4</sub> catalyst in tubular flow reactors. The alkane products were quantified by GC-FID detection, using standards obtained from Sigma. Because most of the condensation products were unavailable commercially for making standards, the composition of the final alkane products was used to back-calculate the relative amounts of single-step/double-step aldol condensation products [6].

### 2.3. Analysis method

The compositions of the aqueous and organic phases were analyzed using HPLC (Waters 2690 system equipped with PDA 960 UV (320 nm) detector) and GC (Shimadzu GC-2010 with an FID detector and a DB-5 column from Alltech). To monitor the progress of the reaction versus time, samples were taken more frequently at the beginning when the rate was most rapid and less frequently towards the end when the rate was slower. For other runs, only the feed and final solutions were analyzed. Hydrochloric acid was added immediately after sampling to neutralize the small amount of base catalyst and quench the reaction in all cases, except for studies of the change in pH with reaction for which the pH was measured before the sample was neutralized.

## 3. Results

### 3.1. Reactive system properties

#### 3.1.1. Biphasic system/salting out effect

The addition of a salt to the aqueous phase improves the separation of the two phases via the salting out effect. Without salt, THF and water are fully miscible. With concentrated salt, the two phases that form are not fully immiscible and contain small quantities of the other phase. Using water saturated with NaCl, it was determined that the THF layer contained  $0.079 \pm 0.009$  g water/g THF, while the water layer contained  $0.053 \pm 0.007$  g THF/g water at room temperature and pressure.

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