

Research article

Efficient synthesis of high-density aviation biofuel via solvent-free aldol condensation of cyclic ketones and furanic aldehydes



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ABSTRACT

Transferring lignocellulose-derived compounds to cyclic hydrocarbons via aldol condensation has great potential in synthesizing high-density biofuel. But current synthesis involves large amount of solvent that inevitably affects the production efficiency. Herein, we synthesized high-density biofuel efficiently using solvent-free condensation of cyclopentanone/cyclohexanone and furfural/5-hydroxymethylfurfural. It is found that the solvent-free reaction gives much higher conversion than the diluted one does, for example 86.7% vs 62.7% for cyclopentanone/furfural condensation, and the selectivity of condensed product is above 90.0%. The reaction rate slows down when the reactant is changed from cyclohexanone to cyclopentanone or from furfural to 5-hydroxymethylfurfural, but can be improved by simply increases the dosage of catalyst or reaction temperature. As a result, the yield over 85.0% is obtained for the condensation reactions. Subsequently, the condensed products were converted to branched cyclic hydrocarbons with selectivity of about 70–80%. Their density increases from 0.815 g/ml to 0.826 g/ml with the increase of carbon number, with the freezing point increasing from $-24.6\text{ }^{\circ}\text{C}$ to $-9.5\text{ }^{\circ}\text{C}$. They have very low viscosity and can be used as liquid fuels alone or blended with other fuels.

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1. Introduction

High-density aviation fuel, generally consisting of cyclic hydrocarbons, can provide more energy than conventional fuel composed of linear hydrocarbons, and is advantageous in extending the flight range of volume-limited aircrafts like missile and rocket [1–8]. An critical property of this fuel is high density. Generally, high-density fuel can be used as fuel alone, but many of them have relatively high viscosity and high freezing point, and a more practical way is blending them with conventional fuel to get high density and acceptable cold temperature properties. High-density aviation fuel is mainly derived from petroleum, like JP-10 (with *exo*-tetrahydrodicyclopentadiene as major component) [1–3], RJ-7 and HDF-T1 (with *exo*-tetrahydrotricyclopentadiene as major component) [1,4–7], but currently the conversion of biomass to high-density aviation fuel is attracting increasing interest. The synthesis of aviation biofuel has been widely studied [9–15], but the obtained linear and branch alkanes have relative low density ($<0.79\text{ g/ml}$).

Actually, many biomass-derived compounds have cyclic C–C rings and are ideal feedstock for high-density biofuel because the cyclic structure brings up higher density than linear structure. For example, liquid fuel with density close to synthetic fuel JP-10 can be obtained by dimerization of pinene and turpentine followed by hydrogenation [16–20]. Linalool can be used to synthesize high-density fuel RJ-4 via olefin

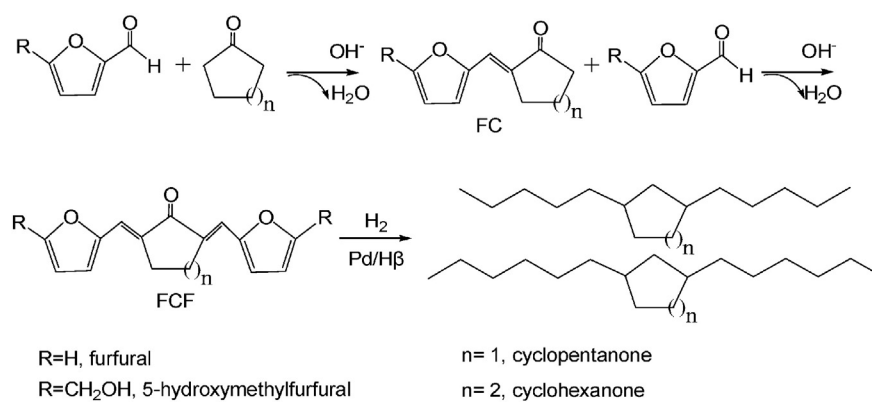
metathesis, dehydration reaction and dimerization [21]. However, these feedstocks are relatively limited because they are obtained only from specific woods and plants.

An alternative is to use cyclic biomass platform compounds as reactant. Recently, hemicellulose-derived cyclopentanone and lignin-derived cyclohexanone are converted to bi-cyclic biofuels by aldol self-condensation followed by hydrodeoxygenation [22–27]. Some monocyclic alkanes are obtained through aldol condensation of hemicellulose-derived furfural (or cellulose-derived 5-hydroxymethylfurfural) and cyclopentanone [28,29], hydroxyalkylation/alkylation of 2-methylfuran with cyclopentanone or cyclohexanone [30,31]. Actually, the aldol condensation involving furfural/5-hydroxymethylfurfural as reactant has many advantages because these compounds are primary derivatives of lignocellulose and thus produced with low-cost. Although solvent-free condition has been used in aldol reaction of furfural and methyl isobutyl ketone/3-pentanone [32,33], mostly a lot of water are used as solvent/diluent in these aldol reactions of furanic aldehydes and cyclic ketones [28,29], which inevitably affects the production efficiency and cost of biofuels. Compared with diluted reaction, the solvent-free reaction is more efficient for scale-up and saves cost for solvent purification and recycling. In addition, cyclohexanone can also react with furanic aldehydes via aldol condensation [34], and produces cycloalkane with density higher than the case of cyclopentanone due to the increase of carbon number in molecule.

In this work, we explored the solvent-free aldol condensation of cyclic ketones (cyclopentanone, cyclohexanone) and furanic aldehydes

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Scheme 1. Synthesis of biofuel using cyclic ketones and furanic aldehydes as feedstock.

(furfural, 5-hydroxymethylfurfural), simply using NaOH as catalyst, as shown in [Scheme 1](#). It was found that the solvent-free reaction is more efficient than the diluted one, and the reaction conditions were optimized to maximize the yield (over 85%). After hydrodeoxygenation, four biofuels with density of 0.815 g/ml–0.826 g/ml were obtained.

2. Experimental section

2.1. Materials

Furfural (99%), cyclohexanone (99.5%), cyclohexane (99.5%), magnesium hydroxide, sodium hydroxide and palladium dichloride (99%) were obtained from Tianjin Guangfu Fine Chemical Research Institute. Cyclopentanone (99.5%) and sodium carbonate were purchased from Tianjin Jiangtian Chemical Technology Company. Calcium hydroxide was supplied by Tianjin Bodi Chemical Engineering Company. 5-hydroxymethylfurfural (5-HMF, 98%) was obtained from Beijing Ouhe Technology Company. All the chemicals were used without further purification. H β (SiO₂/Al₂O₃ = 25) was purchased from Nankai Catalysts Company and calcined in air at 550 °C for 6 h. 5wt% Pd/H β was prepared by the incipient wetness impregnation method.

2.2. Aldol condensation reaction

The aldol reaction was carried out in a round-bottom flask equipped with a reflux condenser and a mechanical stirrer. Typically, 0.208 mol furfural (or 5-HMF) and 0.104 mol cyclopentanone (or cyclohexanone) were heated to defined temperature and then defined amount of catalyst (molar ratio relative to cyclic ketones ranging from 3.6 mol% to 18.0 mol%) was added. The product (FCF, [Scheme 1](#)) is not dissolvable, so the reaction system gradually became slurry with the proceeding of reaction. The mixture was sampled periodically and dissolved in DMSO for analysis. The composition was analyzed by a gas chromatographs (Bruker 456GC, Bruker), equipped with FID detector and ZB-5HT column (60 m × 0.25 mm × 0.25 m). The structure of product was also determined by ¹³C and ¹H NMR spectra collected on a Varian Inova 500 MHz NMR.

2.3. Hydrodeoxygenation reaction and fuel property measurements

A reported procedure [[30,31](#)] was adopted for the hydrodeoxygenation of FCF produced via the aldol condensation in a 500 ml batch autoclave reactor (Parr Instrument Co.) equipped with mechanical stirring. 15.0 g of FCF, 300.0 ml of cyclohexane and 4.0 g of Pd/H β catalyst were sealed in, purged with H₂ and then heated to 280 °C for 24 h at 8 MPa of H₂. Biofuel was obtained by vacuum distillation of the hydrodeoxygenated product to remove the cracking byproduct.

The density of fuel was measured by Mettler Toledo DE40 density meter according to ASTM D4052. Freezing point was measured according to ASTM D2386, and kinematic viscosity was determined using capillary viscometer according to ASTM D445.

3. Results and discussion

3.1. Aldol condensation of cyclopentanone and furfural

The aldol condensation of cyclopentanone and furfural produces di-condensed 2,5-bis(2-furylmethylidene)cyclopentan-1-one (FCF), with small amount of mono-condensed 2-(2-furylmethylidene)cyclopentan-1-one (FC), as shown in [Scheme 1](#). The structure of FCF and FC is well illustrated by NMR spectra, see [Fig. 1a, e](#). Although cyclopentanone may take place self-condensation under acid and base catalysis [[22,23,27](#)], it does not happen in the present work because furfural reacts more quickly with carbon anion formed by cyclopentanone due to the smaller steric hindrance. Neither 2-furinic acid nor furfuryl alcohol presents in detectable amount, indicating furfural does not react with itself under these conditions although it is also a base catalytic reaction [[35](#)].

[Fig. 2](#) compares the reaction behavior under solvent-free and diluted conditions. Compared with the diluted reaction, the solvent-free one precedes more quickly due to the high concentration of reactant. Both cyclopentanone and furfural are converted almost equally, and the conversion of cyclopentanone reaches 87.7% at 2 h, whereas the diluted reaction gives a conversion of only 62.7%. And the selectivity of solvent-free reaction (87.9%) is just slightly lower compared with the case of diluted reaction (91.9%), which indicates that the reaction equilibrium can be easily reached in the solvent-free reaction. In previous literature, the use of solvent is aimed to improve the product separation [[28](#)]. Actually, the condensed product, namely FCF, is non-polar and not dissolved in either the reactant or in-situ produced water. After the reaction, FCF in form of yellow solid can be easily separated, see [Table 1](#).

Several base catalysts including NaOH, Mg(OH)₂, Ca(OH)₂ and Na₂CO₃ were tested in the solvent-free reaction. NaOH is very good catalyst but the others are nearly inactive (with conversion <2.0%). The alkalinity order of these catalysts is NaOH > Mg(OH)₂ > Ca(OH)₂ > Na₂CO₃, and weak base cannot activate cyclopentanone to form carbanion which is necessary for the condensation. [Table 2](#) shows that both the catalyst dosage and temperature have considerable effect on the reaction. The conversion increases from 12.4% to 96.5% when the catalyst dosage rises from 3.6 mol% to 10.8 mol% at 30 °C. Actually, the conversion approaches 94.0% in 30 min. Also, the selectivity of FCF increases slightly with the increase of catalyst dosage. As a result, after 2 h-reaction at 30 °C with 10.8 mol% catalyst, the conversion of cyclopentanone, selectivity and yield of FCF reach 96.5%, 95.3% and 92.0%, respectively. Alternatively, increasing the temperature can also improve the conversion and

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