



Short Communication

Highly controllable and selective hydroxyalkylation/alkylation of 2-methylfuran with cyclohexanone for synthesis of high-density biofuel

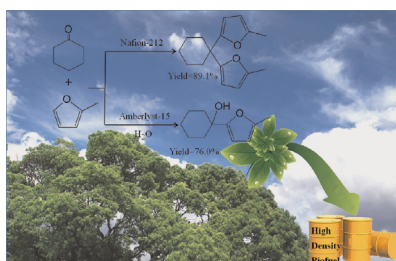


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GRAPHICAL ABSTRACT



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ABSTRACT

Catalytic hydroxyalkylation/alkylation of hemicellulose-derived 2-methylfuran with lignin-derived cyclohexanone yields high-density biofuel precursor (FCF) with high yield of 89.1% over nafion-212. The reaction can also be controlled at the hydroxyalkylation stage to produce another precursor (FC) with yield of 76.0% with amberlyst-15 catalyst, low FC/cyclohexanone ratio and the presence of water solvent. After hydrodeoxygenation, two high-density biofuels with density of 0.804 g/ml and 0.825 g/ml were produced, respectively.

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1. Introduction

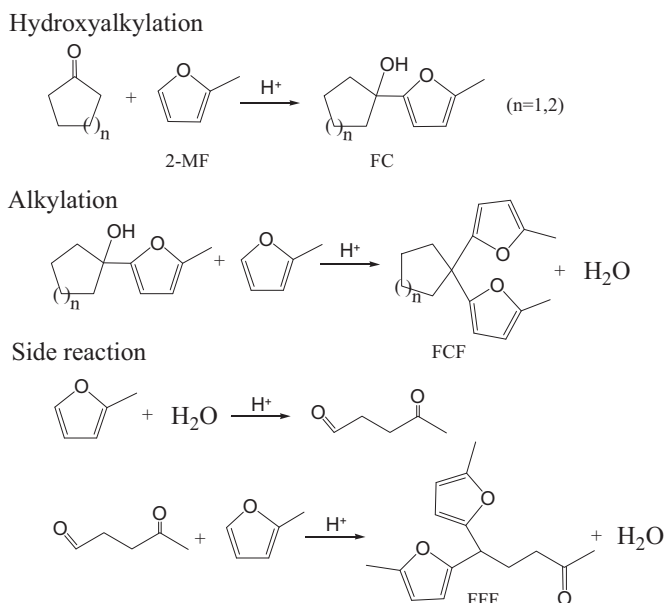
High-density liquid fuel composed of cyclic hydrocarbons can provide more volumetric energy than conventional jet fuel mainly consisting of linear alkanes, and is particularly important for volume-limited aircraft, missile and rocket. (Chung et al., 1999; Ma et al.,

2013; Wang et al., 2012; E et al., 2015; Zou et al., 2007a, 2007b, 2008) It can also be blended with common jet and diesel fuels to increase the mileage per litre. Currently, high-density fuel is synthesized using chemicals derived from petroleum, but the conversion of biomass to high-density biofuel is attracting increasing interest from the perspective of sustainable development.

Synthesis of jet fuel using lignocelluloses-derivatives has been intensively studied (Huber et al., 2005; Olcay et al., 2013; Yang et al., 2013; Bond et al., 2010; Corma et al., 2011, 2012; Li et al., 2012, 2013), but the obtained linear and branch alkanes have relative low density (< 0.79 g/ml). Cyclic hydrocarbons with higher density can be

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Scheme 1. Reaction pathway for synthesis of FC and FCF.

synthesized by C–C coupling of cyclic C–C ring compounds, if necessary, followed by hydrodeoxygenation. (Meylemans et al., 2011, 2012, 2013, 2014; Harvey et al., 2010, 2014, 2015; Zou et al., 2012; Nie et al., 2014) Liquid fuel with a density of 0.94 g/ml has been synthesized by the dimerization of turpentine derivatives, (Harvey et al., 2010; Meylemans et al., 2012, 2013; Zou et al., 2012; Nie et al., 2014) but the fuel has high viscosity at low temperature and the resource of turpentine is relatively limited. A more versatile way is to use cyclic biomass platform compound as reactant, such as aldol self-condensation of cyclic ketones, (Yang et al., 2014; Deng et al., 2015) aldol condensation of furfural (or 5-hydroxymethylfurfural) with cyclopentanone, (Hronec et al., 2014) alkylation of 5-hydroxymethylfurfural with oil refinery aromatics, (Arias et al., 2015) and hydroxyalkylation/alkylation of 2-methylfuran (2-MF) with cyclopentanone. Li et al. (2014)

In particular, hydroxyalkylation/alkylation of 2-MF with cyclopentanone produces monocyclic hydrocarbon (FCF, Scheme 1) that can be hydrodeoxygenated to high-density fuel. The hydroxyalkylation step proceeds via attack of 2-MF on the electropositive carbonyl carbon of cyclopentanone, but the low electrophilicity of this reactive site makes the reaction takes place slowly and branched product via trimerization reaction (FFF, Scheme 1) are formed. Compared with cyclopentanone, lignin-derived cyclohexanone is a better electrophile and more active. (Zhao et al., 2012; Laube, 1999) Moreover, cyclohexanone can produce C16 hydrocarbons with higher density compared with cyclopentanone. Besides FCF, the hydroxyalkylation product (FC, Scheme 1) is also a good fuel candidate with good low-temperature properties, but the amount of FC is extremely low because it is quickly converted to FCF. Taking these into consideration, herein, we report the hydroxyalkylation/alkylation of 2-MF with cyclohexanone. This reaction is highly controllable and selective toward FC and FCF, respectively, which provides an efficient route for synthesis of high-density biofuel.

2. Results and discussion

First we compared the reactivity of cyclohexanone and cyclopentanone in the hydroxyalkylation/alkylation reaction (Fig. 1,

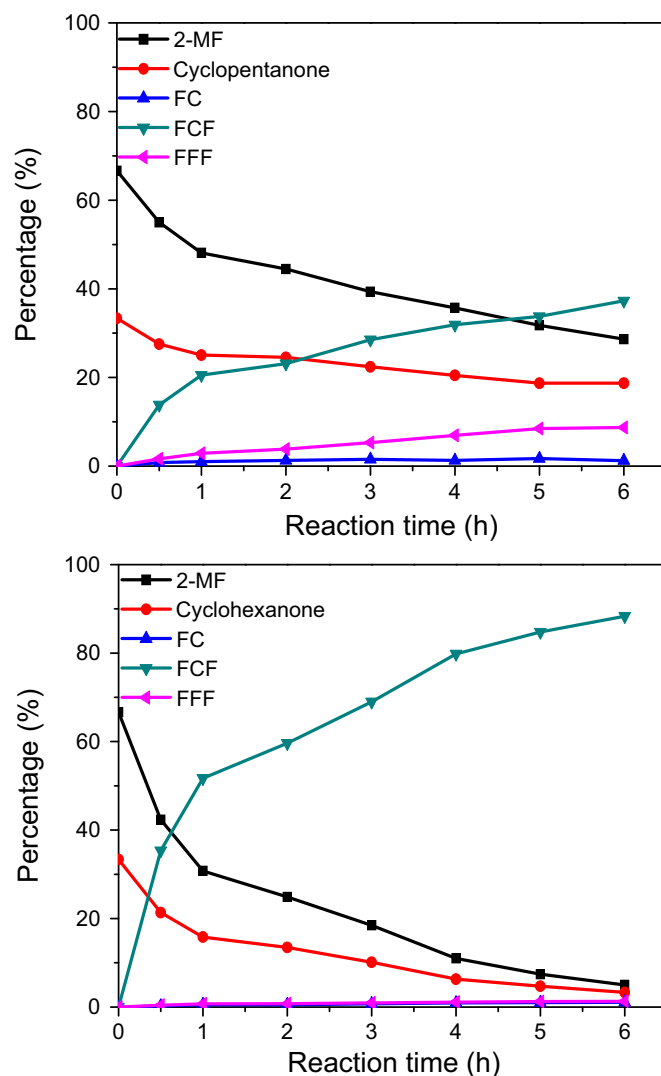


Fig. 1. Product distribution in hydroxyalkylation/alkylation of 2-methylfuran with cyclic ketones. Reaction conditions: 60 °C, 14.4 ml 2-MF, 2-MF/cyclic ketone=2:1, 0.6 g Nafion-212 film.

Scheme 1). This reaction produces hydroxyalkylation product (FC), hydroxyalkylation/alkylation product (FCF) and trimerized product (FFF). The formation of FC and FCF is verified by the ^{13}C and ^1H NMR (Fig. S1 and Fig. S2, SI). Using cyclohexanone to replace cyclopentanone brings up two obvious advantages. First, the reaction is significantly accelerated with the conversion of 2-MF increasing from 57.0% to 92.5% in 6 h, due to the stronger electrophilicity of cyclohexanone. Second, the formation of FFF is almost completely inhibited because 2-MF is quickly consumed, with the selectivity of FCF increasing from 70.9% to 96.3%.

Then we tested several catalysts for the reaction (Fig. 2A). Testing on three liquid acid shows the reactivity is dependent on the acid strength: H_2SO_4 (82.1%) > H_3PO_4 (10.5%) > CH_3COOH (0.5%). Microporous zeolites like HZSM-5, H β and HUSY are inactive due to the slow molecular diffusion in small channels. Layered MMT-K10 and mesoporous Al-MCM-41 are also inactive because the acidity is very weak in the presence of in-situ produced water. Harvey and Quintana (2010) Superacid like perfluorinated sulfonic acid resin (Nafion-212 and NR-50) and phosphotungstic acid (PTA), and relatively weak acid like sulfonic-acid-functionalized resin (amberlyst-15) show considerable activity. Nafion-212 film (1 × 1 cm × 51 μm piece) is much more active than NR-50 (2–3 mm pellet) because of the high surface area.

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