

Research article

Synthesis of high-density biofuel with excellent low-temperature properties from lignocellulose-derived feedstock



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ARTICLE INFO

Article history:

Received 14 February 2017

Received in revised form 29 March 2017

Accepted 10 April 2017

Available online xxxx

Keywords:

High-density biofuel

Alkylation

Hydrodeoxygenation

Furfural alcohol

Lignocellulose-derived feedstock

ABSTRACT

Converting chemicals that can be derived from lignocellulose to cyclic hydrocarbons is a promising route for the synthesis of high-density biofuels. But the low-temperature properties of most synthesized fuels are not good, with high viscosity and freezing point. Herein, we presented the synthesis of cyclohexane derivatives by the alkylation of aromatic oxygenates (anisole, guaiacol and phenol) with furfural alcohol (furfuryl alcohol and 5-hydroxymethylfurfural), followed with hydrodeoxygenation. It is found that FeCl_3 exhibits relatively high activity and selectivity for the alkylation of anisole (guaiacol), and AlCl_3 is the best catalyst for phenol. The selectivity of mono-alkylation product is 71.0%, 92.4% and 84.3% for the alkylation of anisole, guaiacol and phenol with furfuryl alcohol when the reactant ratio is 10, respectively. A semi-continuous operation was adopted for the alkylation of furfuryl alcohol to improve the conversion of aromatic oxygenates. When furfuryl alcohol is replaced by 5-hydroxymethylfurfural, the selectivity reaches almost 100%, but the reaction is a little slower and longer time is needed to get full conversion. After hydrodeoxygenation by combination of Pd/C and HZSM-5, the alkylation product was converted to branched cyclohexane with density of 0.804 g/cm^3 at 20°C , kinematic viscosity of $34.4 \text{ mm}^2/\text{s}$ at -60°C and freezing point lower than -80°C , which shows great potential as additive to promote the low-temperature properties of other fuels.

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1. Introduction

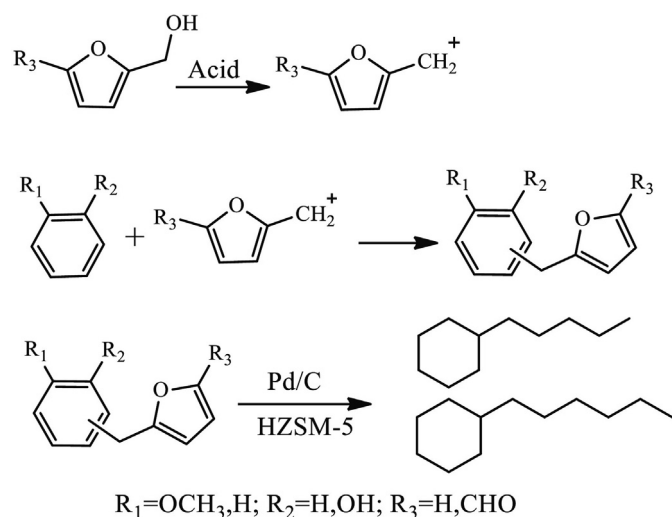
High-density jet fuels, generally with density higher than 0.8 g/cm^3 , composed of cyclic hydrocarbons have great potential to improve the flight distance, flight speed and loading capacity of aerospace vehicles [1,2]. Usually high-density fuels are synthesized using petroleum intermediates as raw feedstock [3–5]. As response to the exhaustion of traditional fossil fuels, the synthesis of them using biomass-derived resources is attracting increasing interests [6–8]. To synthesize high-density biofuels, a versatile method is to convert the platform molecules into multi-cyclic intermediates via C–C coupling reactions (e.g. alkylation, aldol condensation, Diels-Alder addition, Michael reaction, oligomerization and ketonization), and then transform the intermediates to alkanes by hydrodeoxygenation (HDO) [8–13]. For example, some high-density biofuels have been synthesized by aldol self-condensation of cyclohexanone [14,15], aldol cross-condensation of cyclic ketones and furanic aldehydes [16], hydroxyalkylation/alkylation

of 2-methylfuran with cyclic ketones [17], hydroxyalkylation/aldol condensation of furanics and phenolics [18], oligomerization/rearrangement of cyclopentene [19], and alkylation of phenols (phenol, anisole, guaiacol) with benzyl ether or benzyl alcohols [20]. Although the obtained cycloparaffins have high density, their freezing point is relatively high (mostly $> -35^\circ\text{C}$) and the viscosity is high, which hinders the utilization of these biofuels in practical application.

Recently, alkyl naphthenic kerosene with very low freezing point has been produced by the alkylation reaction of petrochemicals (toluene, mesitylene and *o*-xylene) with 5-hydroxymethylfurfural [21,22]. Biofuel (mainly composed by pentylcyclohexane) with good low-temperature properties has also been synthesized by hydroxyalkylation of 2-methylfuran with cyclohexanone [17]. Although these feedstocks can be derived from biomass, a complex procedure is needed to produce them [23–25]. So it is preferable to synthesize biofuel using molecules that can be derived from biomass via relatively simple treatment and/or procedure. Bio-oil produced by pyrolysis of lignin contains abundant aromatic oxygenates such as guaiacol, phenol and anisole [26–29]. For example, guaiacol and phenol can be produced by thermal pyrolysis of lignins (oak wood, organosolv lignin and Kraft lignin) followed by selective hydrodeoxygenation [30,31]. Phenols and guaiacols can be produced from catalytic fast pyrolysis of torrefied biomass [32]. Anisole,

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Scheme 1. Synthesis of biofuels using aromatic oxygenates and furfural alcohol.

phenol and guaiacols can be obtained by catalytic depolymerisation of Kraft lignin in near-critical water [33]. So they are more suitable as feedstock for the synthesis of cyclic hydrocarbons.

With these considerations, the goal of this study was to produce high-density biofuel with excellent low-temperature properties by Friedel-Craft alkylation using easily available chemicals. Branched cycloalkanes were synthesized by the alkylation of aromatic oxygenates with furfural alcohol, followed by hydrodeoxygenation. The obtained biofuel has low freezing point and kinematic viscosity and thus can be used as additive to promote the low-temperature properties of other high-density fuels.

2. Experimental section

2.1. Materials

All the chemicals were used without further purification and the purity was more than 98% except trifluoromethanesulfonic acid (97%), sulphuric acid (95–98%), phosphoric acid (85%), sodium hydroxide (96%). Nafion-212 film from Dupont Co. was cut into about 1×1 cm pieces and used for the reaction. Amberlyst-15 (pore size 29 nm) was purchased from Shanghai Crystal Pure Reagent Co., China. Pd/C (5 wt%) were obtained from Shaanxi Rock New Materials Co., Ltd.

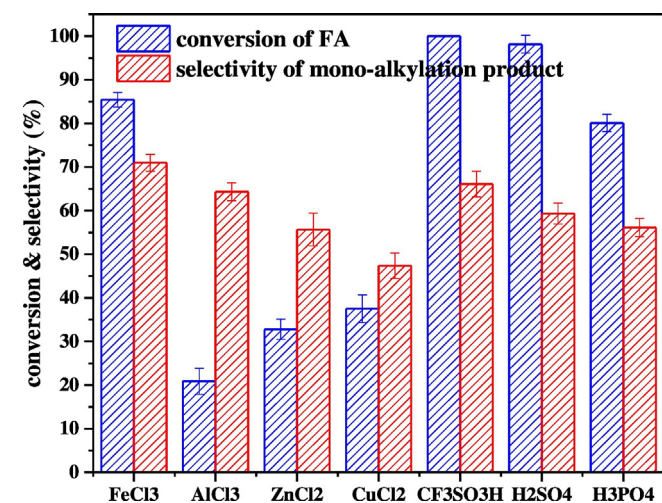


Fig. 1. Alkylation of anisole with FA by different catalysts. Reaction conditions: 100 mmol anisole, 10 mmol FA, 100 °C, 15 min, 0.05 g solid catalyst or 0.5 mmol H⁺.

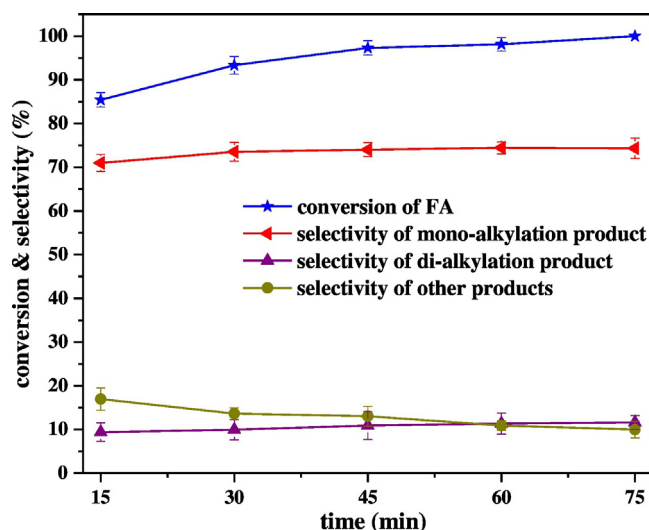


Fig. 2. Product distribution in alkylation of anisole with FA. Reaction conditions: 100 mmol anisole, 10 mmol FA, 100 °C, 0.05 g FeCl₃.

HZSM-5 (SiO₂/Al₂O₃ = 50) was purchased from Nankai Catalysts Company and calcined in air at 550 °C for 6 h before use.

2.2. Alkylation reaction

The alkylation conditions including temperature and reaction time were pre-optimized to get considerable conversion. For the alkylation of aromatic oxygenates (anisole, guaiacol or phenol) with furfuryl alcohol (FA), the reaction was conducted at 100 °C, 40 °C, or 50 °C for 15 min, respectively. For the alkylation of aromatic oxygenates with 5-hydroxymethylfurfural (5-HMF), FA was replaced by 5-HMF at the same temperature, but the reaction time was prolonged to 1 h to achieve relatively high conversion of 5-HMF.

In detail, alkylation reaction was performed under mechanical agitation in a three-necked round-bottom flask with N₂ atmosphere. Typically, 10 mmol furfural alcohol (FA or 5-HMF) and 100 mmol aromatic oxygenates (anisole, guaiacol or phenol) were heated to 100 °C, 40 °C, or 50 °C, respectively, and then 0.05 g solid catalyst (FeCl₃, AlCl₃, ZnCl₂, CuCl₂, MnCl₂, SnCl₂, Nafion, Amberlyst-15 or Al-MCM-41) or 0.5 mmol H⁺ liquid catalyst (CF₃SO₃H, H₂SO₄, H₃PO₄ or CH₃COOH) was added. The reaction was monitored by taking samples periodically,

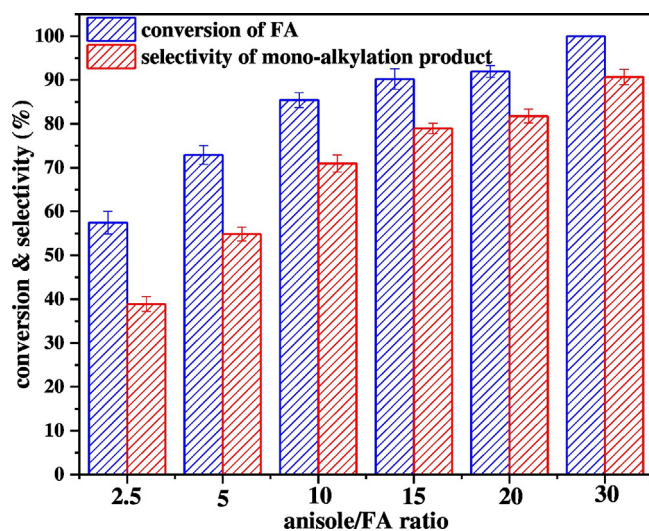


Fig. 3. Influence of the anisole/FA ratio on the reaction. Reaction conditions: 10 mmol FA, 100 °C, 15 min, 0.05 g FeCl₃.

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