



# Lignin-derived multi-cyclic high density biofuel by alkylation and hydrogenated intramolecular cyclization



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## ABSTRACT

Biofuels are important alternative for fossil-based fuel but they have either relatively low density or high freezing point and viscosity. Here we reported a simple and efficient route to synthesis biofuel with density comparable to widely used JP-10 fuel as well as good low-temperature properties. Substituted diphenyl methane was synthesized by acid catalytic alkylation of lignin-derived phenols (phenol, anisole, guaiacol) with benzyl ether or benzyl alcohols, and MMT-K10 exhibits better activity than HPW, Amberlyst-15, and Al-MCM-41, due to the modest acid strength and open lamellar structure. High selectivity along with good-to-excellent conversion was obtained under optimized conditions regardless of different reactant used. Then the alkylated product was subjected to hydrogenation with the presence of Pd/C and HZSM-5, and interestingly, intramolecular cyclization reaction occurred to produce a large amount of perhydrofluorene as well as dicyclohexylmethane. Subsequently, biofuel with density as high as 0.93 g/mL and freezing point as low as  $-40.0\text{ }^{\circ}\text{C}$  was obtained, which surpasses the state-of-art of biofuel reported.

## 1. Introduction

As response to increasing concerns on sustainable development and environmental issues, carbohydrate-derived substrates from lignocellulose and fatty acid esters have been converted into transportation fuel such as gasoline, diesel and jet fuel (Alonso et al., 2010; Chheda et al., 2007; De et al., 2015; Willems, 2009; Zakzeski et al., 2010). Nevertheless, for some specific applications like space-limited air vehicles, these biomass-derived jet fuels with mostly linear hydrocarbons have relative low density and volumetric heating value especially (Harvey and Quintana, 2010; Yang et al., 2015). Multi-cyclic hydrocarbons have evidently higher densities and volumetric heating values compared with linear and mono-cyclic hydrocarbons (Osmond et al., 2008). In particular, many multi-cyclic fuels such as JP-10 (*exo*-tetrahydrodicyclopentadiene as major component, density of 0.93 g/mL), RJ-5 (*endo-endo*-dihydrodi(norbornadiene) as major component, density of 1.08 g/mL), RJ-7 and HDF-T1 (*exo*-tetrahydrotricyclopentadiene as major component, density of 1.02 g/mL), called high density fuel, have been developed using chemicals derived from petroleum industry (Arias-Ugarte et al., 2015; Chung et al., 1999; Wang et al., 2012; Zou et al., 2007a, 2007b). Additionally, terpene dimer fuel and sesquiterpanes from metabolic product of plants also arouse much attention due to their high density (Harvey, et al., 2014, 2015; Liang,

et al., 2015). In terms of the source issue, lignin is richer far than terpene. Therefore, synthesizing multi-cyclic biofuel from lignin as alternative to fossil-based high density fuel has been attracting particular interest recently.

Generally, biomass-derived molecules have less than one ring along with unsaturated carbon bond and/or oxygen containing groups, so multi-reaction synthesis is needed to obtain multi-cyclic hydrocarbons. Firstly, C–C coupling is necessary to construct multi-cyclic precursor. Then, hydrogenation is performed to remove oxygen and saturate the C=C bond. According to biomass molecules used, different C–C coupling reactions can be used like aldol condensation, oligomerization, Diles-Alder addition, and alkylation (Arias-Ugarte et al., 2015; Corma et al., 2007, 2011; Deng et al., 2016). A pool of substitutional multicyclic hydrocarbons has been synthesized by dimerization of terpenes (Harvey et al., 2010; Meylemans et al., 2012, 2014; Nie et al., 2014; Zou et al., 2012;), which has the highest density of 0.94 g/mL among the reported biofuels. Unfortunately, the extremely high viscosity along with the limited source of terpenes limits its application. Recently, platform chemicals derived from abundant biomass, such as cyclohexanone, cyclohexanol, cyclopentanone and cyclopentanol have been converted to high density biofuel. For example, bicyclic hydrocarbons such as 1,1'-bi(cyclohexane) (0.88 g/mL) and 1,1'-bi(cyclopentane) (0.87 g/mL) are synthesized from cyclohexanone and cyclo-

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pentanone respectively, and tricyclic hydrocarbon like tricyclopentyl (0.91 g/mL) is also synthesized from cyclopentanone (Deng et al., 2015; Sheng et al., 2015; Yang et al., 2014;). Overall, compared with the widely used JP-10, these biofuels have either lower density or higher viscosity. So the synthesis of biofuel with both high density (comparable to conventional high density fuel like JP-10) and good low temperature properties is very necessary.

Anisole, phenol and guaiacol are the main products from pyrolysis of lignin which is an abundant biomass from agriculture wastes and forest residues (Jan et al., 2015; Xu et al., 2014). The hydroxyl (-OH) and methoxyl (-OCH<sub>3</sub>) groups in these compounds can donate electrons to the benzene ring and activate it for alkylation reaction with alkane, olefin, alcohol, ether and ketone (Kumar et al., 2014). This provides a way to synthesis high density biofuel precursor in more economical way because the feedstock is primary pyrolysis products of lignin that is different from the case of cyclic ketons that is obtained from biomass via several reaction steps.

Herein, we report a simple and efficient way to produce high density biofuel from lignin pyrolytic products involving acid-catalyzed alkylation of lignin-derived phenols (phenol, anisole, guaiacol) with benzyl ether or benzyl alcohols, followed with hydrodeoxygenation/intramolecular cyclization. The alkylation reaction builds C-C coupling of cyclic rings, and surprisingly the hydrogenation induces cyclization between two rings and finally affords perhydrofluorene instead of expected diphenylmethane. As a result, a biofuel with density comparable JP-10 fuel and low temperature property better than the state-of-art biofuel is obtained.

## 2. Experiment

### 2.1. Catalysts and chemicals

Benzyl ether (> 99%), phenylmethanol (> 99%), 2-phenylpropan-2-ol (> 99%) and 1-phenylethan-1-ol (> 99%) were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd. Montmorillonite K10 (MMT-K10), Amberlyst-15, and phosphotungstic acid (HPW) were purchased from Aladdin Co. HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=25) and Al-MCM-41 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>=12.5) purchased from Nankai Catalysts Co. were calcined in air at 580 °C for 3 h before use. Pd/C (5 wt%) was purchased from Shaanxi Rock New Materials Co., Ltd.

### 2.2. Alkylation reaction

Alkylation reaction was performed in a 50 mL flask equipped with a condensate reflux and mechanical agitation under N<sub>2</sub> atmosphere. Defined amount of phenols (phenol, anisole and guaiacol) and benzyl ether or benzyl alcohols (phenylmethanol, 2-phenylpropan-2-ol, and 1-phenylethan-1-ol) were mixed and heated to 110 °C in an oil bath, and then 0.1 g of catalyst was added to catalyze the reaction. The reaction was allowed to proceed 2 h and sampling was conducted at intervals for analysis. The compounds in the resulted mixture were determined qualitatively using an Agilent 6890/5975 GC-MS equipped with HP-5 capillary column (30 m×0.5 mm), and the corresponding concentrations were analyzed using internal standard method on Bruker 456 GC equipped with a flame ionization detector (FID) and a capillary column (ZB-5 HT, 60 m×0.25 mm×0.25 m) with flame ionization detector.

The alkylation reactions of phenol, anisole and guaiacol with benzyl ether or benzyl alcohols take place as shown in Scheme 1, and substituted diphenyl methane is the target products. GC/MS analysis shows that for the alkylation of anisole with benzyl ether, 1-benzyl-2-methoxybenzene (Fig. S1a) and 1-benzyl-4-methoxybenzene (Fig. S1b) are the main products (Fig. S2), the reaction of phenol with benzyl ether produces 2-benzylphenol (Fig. S1c) and 4-benzylphenol (Fig. S1d), and 2-benzyl-4-methoxyphenol (Fig. S1e) is produced from the alkylation of guaiacol with benzyl ether.

The conversion and selectivity were calculated as follows:

$$\begin{aligned} \text{Conversion (\%)} &= \frac{\sum \text{reactant converted}}{\sum \text{original reactant}} \times 100 \text{Selectivity (\%)} \\ &= \frac{\sum \text{substituted diphenyl methane formed}}{\sum \text{phenols and benzyl ether converted}} \times 100 \end{aligned}$$

### 2.3. Hydrogenation reaction

The hydrogenation was performed in a 100 mL autoclave (EasyChem E100). 50 mL water as solvent, 18 g substrate, 0.8 g Pd/C and 8 g HZSM-5 were sealed in the reactor and hydrogenated under hydrogen pressure of 60 bar and 200 °C for 20 h. The alkylated compounds were purified by distillation before the reaction. After the reaction, the upper organic phase was collected and dewatered using anhydrous MgSO<sub>4</sub> overnight. The final biofuel was obtained by vacuum distillation.

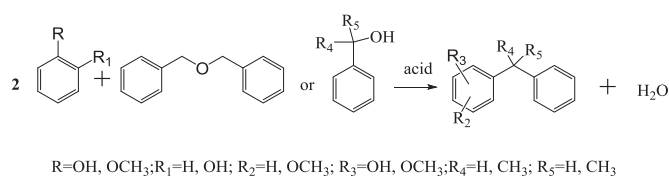
## 3. Results and discussion

### 3.1. Alkylation of anisole with benzyl ether

In this reaction (Scheme 1), one mole of benzyl ether can react with two moles of anisole, so ideally the conversion of benzyl ether should be half of that of anisole. Several commercial solid catalysts were invested here. As shown in Fig. 1, MMT-K10 exhibits the best catalytic performance, with the highest conversion of anisole (32.0%) and high selectivity of mono-alkylated product (68.0%). The conversion of benzyl ether is 0.63 times of that of anisole. For other catalyst tested, the conversion of benzyl ether is higher than that of anisole, and the selectivity is very low compared with the case of MMT-K10, suggesting a serious side reaction involving the conversion of benzyl ether. Overall, the activity sequence of catalysts is MMT-K10 > HPW > Amberlyst-15 > Al-MCM-41.

The properties of the catalyst tested are summarized in Table 1 to find out why these catalysts show different activity. MMT-K10 possesses a moderate acid amount, moderate average pore diameter and moderate surface area compared to others, but the unique lamella structure makes it easy for the molecules to contact with the acid sites. Actually, MMT-K10 is widely used in alkylation, dimerization and isomerization (Harvey et al., 2010; Meylemans et al., 2012). The reaction data show that the acid strength of MMT-K10 is strong enough for alkylation of anisole with benzyl ether but not enough for the side reaction. HPW has super-acidity (H<sub>0</sub> less than -12) (Kozhevnikov, 1998), but it shows lower activity because of the low surface area. Moreover, the conversion of benzyl ether is significantly higher than that of anisole, indicating the strong acidity induces more side reaction of benzyl ether. Amberlyst-15 resin possesses the highest acid concentration, but its acidity is relatively weak, so the activity is very low. Similarly, Al-MCM-41 is almost inactive in the reaction due to very weak acidity and small amount of active sites.

As mentioned above, the side reaction involves the converting of benzyl ether to other products and reduces the selectivity of mono-alkylated product. Several controlled reactions were conducted to check how the side reaction takes place. When anisole is heated with the presence of catalyst like HPW and MMT-K10, there are no any new products formed, even at temperature as high as 140 °C. When benzyl



Scheme 1. Alkylation reactions.

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