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COYAL SOCIETY

ARTICLE

Journal Name

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Synthesis of high-density aviation fuels with methyl benzaldehyde and cyclohexanone

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A new two-step process was developed for the synthesis of high-density jet fuel range tricyclic alkanes with methyl benzaldehydes and cyclohexanone which can be derived from lignocellulose. In the first step, C_{14} oxygenates (*i.e.* 2-(2-methylbenzylidene)cyclohexanone) were obtained by the solvent-free aldol condensation of 2-methyl benzaldehyde (or 4-methyl benzaldehyde) and cyclohexanone. Among the investigated catalysts, EAOAc ionic liquid (a renewable catalyst which was prepared with ethanolamine and acetic acid) exhibited the highest activity and good stability for this reaction. Over it, high carbon yields (~85%) of C_{14} oxygenates were acheived under mild reaction conditions (353 K, 6 h). In the second step, the C_{14} oxygenates were selectively converted to 1-methyldodecahydro-1*H*-fluorene and 3-methyldodecahydro-1*H*-fluorene by the aqueous phase hydrodeoxygenation (APHDO) over a commerical Pd/C catalyst. According to our measurement, the 1-methyldodecahydro-1*H*-fluorene and 3-methyldodecahydro-1*H*-fluorene as obtained have high densities (0.99 g mL⁻¹ and 0.96 g mL⁻¹ at 298 K). As a potential application, they can be used as additives to improve the volumetric heat values of current bio-jet fuels.

Introduction

Because of the great social concerns about the renewable energy and sustainable development, the catalytic conversion of renewable and CO₂ neutral biomass to fuels¹ and chemicals² has become a research hotspot. Jet fuel (includes kerosenetype jet fuel and naphtha-type jet fuel) is a refined petroleum product used in jet aircraft engines.³ Globally, jet fuels account for 12% of current used liquid transportation fuels.⁴ During the past decade, tremendous efforts have been devoted to the production of jet fuel range hydrocarbons with the feedstocks which can be obtained from biomass.⁵ So far, three routes (including Fischer-Tropsch process of bio-synthesis gas, hydroprocesses of bio-derived esters and fatty acids, or hydrogenation of farenene from the fermentation of sugars) have been approved by ASTM D7566 for the production of sustainable aviation fuels with biomass.⁶ However, the bio-jet fuels produced by these routes are mainly composed of straight or branched chain alkanes which have lower density $(0.76 \text{ g mL}^{-1} \text{ vs. } 0.8 \text{ g mL}^{-1})$ or volumetric heat values than conventional jet fuel (mixture of chain alkanes and cyclic hydrocarbons). Compared with chain alkanes, cycloalkanes have higher density or volumetric heat values due to strong ring strain. In recent years, the synthesis of jet fuel range highdensity cycloalkanes with lignocellulosic platform compounds has attracted a lot of attention.^{7, 8, 9}

Methyl benzaldehyde is a lignocellulosic platform compound which can be obtained by the self-terminated cascade reactions of biomass derived ethanol and acetaldehyde over calcium hydroxyapatite catalyst.^{10, 11} As we know, ethanol can be obtained from the fermentation of cellulose, hemicellulose, sugar cane, sugar beet, sugar palm, cassava, corn, potatoes or other sugar plants.¹² Acetaldehyde can be obtained by the selective oxidation or dehydrogenation of ethanol. Likewise, cyclohexanone can be produced by the selective hydrogenation of phenol which can be obtained from the Pd/C catalyzed hydrogenolysis of Kraft lignin in choline-derived ionic liquids¹³ or the pyrolysis of lignocellulose.¹⁴ It has been found by Han et al.¹⁵ that phenol can be selectively hydrogenated to cyclohexanone over a dual supported Pd-Lewis acid catalyst. In this work, it was reported for the first time that jet fuel range tricyclic alkanes can be selectively produced in ~80% overall carbon yield by the solvent-free aldol condensation of methyl benzaldehyde and cyclohexanone, followed by the aqueous phase hydrodeoxygenation over a commercial Pd/C catalyst. The strategy for this process was illustrated in Scheme 1. Compared with the commodity chemicals that are used today as additives in kerosene-type jet fuels and the biomass-derived jet fuel rang cycloalkanes which have been reported in some recent literature,^{7, 8, 9, 16} the tricyclic alkanes obtained in this work have higher density or lower freezing points (see Table S1 in supporting information). These characters are advantageous in real application.

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Electronic Supplementary Information (ESI) available: [Preparation and purification method of **1A** and **2A**; GC chromatogram, NMR spectra and mass spectrogram of products]. See DOI: 10.1039/x0xx00000x

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Scheme 1. Strategy for the synthesis of jet fuel range high-density tricyclic alkanes with lignocellulose and other biomasses.

Experimental

Materials. All of the chemicals used in this work were purchased from Energy Chemicals and were directly used as their received. The acetic acid based ionic liquids were synthesized according to the method developed by Guo and Ying *et al.*.¹⁷ Typically, 0.1 mol ethanolamine was put in a round bottom flask which was immersed in an ice-water bath. Under violently stirring, 0.1 mol acetic acid was added dropwise into the ethanolamine by a constant pressure funnel. By controlling the addition speed, the system temperature was maintained in the range of 283-288 K. After the completely introduction of acetic acid, the mixture was stirred for 24 h at room temperature. The yellowish viscous liquid as obtained was denoted as EAOAc. For comparison, we also prepared other acetic acid based ionic liquids (See Scheme 2) by the same method using corresponding amines and acetic acid.



Scheme 2. Chemical structures of acetic acid (HOAc) based ionic liquids and ethanolamine (EA) used in the aldol condensation tests.

The Pd/C catalyst used in the aqueous phase hydrodeoxygenation process is commercial available. According to the information from supplier, the Pd content in the catalyst is 5% by weight (denoted as 5 wt.%).

Aldol condensation. The solvent-free aldol condensation of methyl benzaldehydes and cyclohexanone was carried out in a 35 mL glass batch reactor. The temperature of the reactor was controlled by a water bath. Typically, 10 mmol 2-methyl benzaldehyde, 10 mmol cyclohexanone and 1 mmol ionic liquid were used for each test. After being magnetically stirred at 353 K for 4 h, the reaction system was quickly cooled down to room temperature with ice water. Subsequently, isophorone was added into the system as internal standard. The mixture was diluted with tetrahydrofuran and analyzed by Agilent 7890A GC equiped with a flame ionization detector (FID). The **1A** and **2A** as obtained were purified from the aldol condensation products (according to the method described in supporting information) and used in the subsequent aqueous phase hydrodeoxygenation tests.

Aqueous phase hydrodeoxygenation. The aqueous phase hydrodeoxygenation (APHDO) of **1A** and **2A** were carried out in a 100 mL stainless steel batch reactor (Parr Company). Typically, 1 g purified **1A** or **2A**, 0.1 g Pd/C catalyst and 35 mL water were sealed into the reactor. Before the tests, the reactor was purged with hydrogen for 3 times to remove the air in it. Subsequently, 6 MPa H₂ was charged into the reactor at room temperature. After being heated to 453 K and electromagnetically stirred at that temperature for 4 h, the reaction system was quenched to room temperature with ice water. 1.0 g tridecane was added into the system as internal standard. The mixture was extracted by CH_2Cl_2 (20 mL) for 3 times. The CH_2Cl_2 phases were combined together and analyzed by GC-MS and an Agilent 7890A GC equiped with a

FID. The densities and freezing points of cycloalkane products were determined by a DMA 4500M digital densitometer and a PFA-70Xi freezing point analyzer, respectively.

Results and discussion

Aldol condensation. In this work, a series of acetic acid based ionic liquids were found to be effective catalysts for the solvent-free aldol condensation of 2-methyl benzaldehyde and cyclohexanone. From the analysis of GC and NMR spectra (see Figures S1-S3 in supporting information), both 2-(2-methylbenzylidene)cyclohexanone (*i.e.* **1A** in Scheme 3) and 2-(2-methylbenzyli)-6-(2-methylbenzylidene)cyclohexanone (*i.e.* **1B** in Scheme 3) were identified in the product. According to Scheme 3, **1A** and **1B** were generated from the aldol condensation of one cyclohexanone molecule with one or two 2-methyl benzaldehyde molecule(s). As the potential applications, the **1A** and **1B** as obtained can be used as precursors for the production of jet fuel and lubricant range cycloalkanes, respectively.



Scheme 3. Reaction pathways for the generation of 1A and 1B from the aldol condensation of 2-methyl benzaldehyde and cyclohexanone.



Figure 1. Conversions of 2-methyl benzaldehyde and the carbon yields of **1A** or **1B** over ionic liquid catalysts. Reaction conditions: 10 mmol 2-methyl benzaldehyde, 10 mmol cyclohexanone, 1 mmol ionic liquid; 333 K, 4 h.

Among the investigated catalysts, EAOAc ionic liquid catalyst which was prepared with ethanolamine and acetic acid exhibited the highest activity for the solvent-free aldol condensation of 2-methyl benzaldehyde and cyclohexanone (see Figure 1). Over it, high 2-methyl benzaldehyde conversion (62.5%) and good carbon yields (38.5% and 16.2%) of **1A** and **1B** were achieved under mild conditions (333 K, 4 h). As we know, acetic acid can be obtained as by-product from the furfural production by the acid catalyzed hydrolysis-dehydration of hemicellulose.¹⁸ In the recent work of our group,¹⁹ it was also found that ethanolamine can be produced

with cellulose by a two-step process. Taking into consideration of the high activity and renewability of EAOAc ionic liquid, we believe that it can be considered as a promising catalyst in future application.

From Figure 1, we can see that the chemical structures of ionic liquids have evident influence on its activity in the aldol condensation of 2-methyl benzaldehyde and cyclohexanone. For example, the activity of EAOAc is evidently higher that of EOAc under the same reaction conditions. This result means that the presence of hydroxyl group is favorable for the aldol condensation, which can be explained by the hydrogen bond between the catalyst and reactants. The activity of ionic liquid catalysts which have only one hydroxyl group decrease in the order of EAOAc > 3-PAOAc > 4-BAOAc. This result indicates that the closer interaction of hydroxyl group and amino group is beneficial for the aldol condensation. Finally, we also studied the effect of hydroxyethyl group number on the activity of catalyst. From Figure 1, we can see that DEAOAc which has two hydroxyethyl groups has lower activity than that of EAOAc. This can be rationalized by steric effect.



Figure 2. Conversions of 2-methyl benzaldehyde and the carbon yields of **1A** or **1B** over EAOAc, EA and HOAc catalysts. Reaction conditions: 10 mmol 2-methyl benzaldehyde, 10 mmol cyclohexanone, 1 mmol ionic liquid; 333 K, 4 h.

To get deeper insight into the excellent performance of the EAOAc ionic liquid catalyst, we also studied the activity of ethanolamine (EA) and acetic acid (HOAc) under the same reaction conditions. From Figure 2, it is noticed that ethanolamine can also catalyze the aldol condensation of 2methyl benzaldehyde and cyclohexanone. However, its activity is evidently lower than that of EAOAc. In contrast, the acetic acid is inactive under the investigated conditions. The 2-methyl benzaldehyde conversion and the carbon yields of 1A or 1B over the EAOAc ionic liquid are evidently higher than the sums of those over ethanolamine and acetic acid. Based on this result, we think that there is some synergetic effect between ethanolamine and acetic acid in the aldol condensation of 2methyl benzaldehyde and cyclohexanone. According to the literature about similar reaction system, 17, 20 the reaction mechanism for the aldol condensation of 2-methyl

DOI: 10.1039/C8GC01628C

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benzaldehyde and cyclohexanone was proposed in Scheme 4. Firstly, EAOAc ionic liquid reacts with cyclohexanone and generates a corresponding imide ion. Subsequently, the acetic acid molecule is released from EAOAc to form an enamine structure. The enamine structure is unstable. Therefore, it can attack the carbonyl group of 2-methyl benzaldehyde which is activated by hydroxyl group on enamine structure through hydrogen-bond. By this way, a new C-C bond and a new ionic compound are formed. This compound will decompose to ionic liquid EAOAc and **1C**. Finally, **1C** is dehydrated into **1A** which is more stable due to its conjugated chemical structure. Analogously, we can also obtain **1B** by the further reaction of **1A** with another 2-methyl benzaldehyde molecule.



Scheme 4. Reaction mechanism for the generation of **1A** from the aldol condensation of 2-methyl benzaldehyde and cyclohexanone.

The effects of reaction conditions (such as reaction temperature, initial cyclohexanone/2-methyl benzaldehyde molar ratio in the feedstock, reaction time and catalyst dosage) on the catalytic performance of EAOAc ionic liquid were investigated (see Figures 3-6). Under the optimum reaction conditions (353 K, 6 h, 2 mmol EAOAc ionic liquid catalyst, at an initial cyclohexanone/2-methyl benzaldehyde molar ratio of 3:1), up to 85% carbon yield of **1A** was achieved.



Figure 3. Conversions of 2-methyl benzaldehyde and the carbon yields of 1A or 1B over EAOAc ionic liquid catalyst. Reaction conditions: 10 mmol 2-methyl benzaldehyde, 10 mmol cyclohexanone, 1 mmol EAOAc ionic liquid; 4 h.



Figure 4. Conversions of 2-methyl benzaldehyde and the carbon yields of 1A or 1B over EAOAc ionic liquid catalyst. Reaction conditions: 10 mmol 2-methyl benzaldehyde, 1 mmol EAOAc ionic liquid; 353 K, 4 h.



Figure 5. Conversions of 2-methyl benzaldehyde and the carbon yields of 1A or 1B over EAOAc ionic liquid catalyst. Reaction conditions: 10 mmol 2-methyl benzaldehyde, 30 mmol cyclohexanone, 1 mmol EAOAc ionic liquid; 353 K.



Figure 6. Conversions of 2-methyl benzaldehyde and the carbon yields of 1A or 1B over EAOAc ionic liquid catalyst. Reaction conditions: 10 mmol 2-methyl benzaldehyde, 30 mmol cyclohexanone; 353 K, 6 h.

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For real application, we also checked the reusability of the EAOAc ionic liquid. From Figure 7, we can see that there is an evident decrease in the activity of catalyst after being used in the solvent-free aldol condensation of 2-methyl benzaldehyde and cyclohexanone. Such a phenomenon is normal for aldol condensation and can be explained by the negative effect of water which was generated during the reaction.²¹ To solve this problem, we dried the used EAOAc ionic liquid under vacuum condition. It was found that the activity of this catalyst can be recovered to its initial level by such a treatment.



Figure 7. Conversions of 2-methyl benzaldehyde and the carbon yields of 1A or 1B over EAOAc ionic liquid catalyst. Reaction conditions: 10 mmol 2-methyl benzaldehyde, 30 mmol cyclohexanone, 1 mmol EAOAc ionic liquid; 353 K, 4 h.



Scheme 5. Reaction pathways for the generation of 2A and 2B from the aldol condensation of 4-methyl benzaldehyde and cyclohexanone.



Figure 8. Conversions of methyl benzaldehyde and the carbon yields of C_{14} (*i.e.* **1A** and **2A**) and C_{22} (*i.e.* **1B** and **2B**) oxygenates over EAOAc ionic liquid catalyst. Reaction conditions: 10 mmol methyl benzaldehyde, 30 mmol cyclohexanone, 2 mmol EAOAc ionic liquid; 353 K, 6 h.

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To further check its stability, we also compared the NMR spectra of the fresh, used and regenerated EAOAc ionic liquids. From the results illustrated in the Figures S4-S6 in supporting information, no evident change in the chemical structure of EAOAc ionic liquid was observed, indicating that this catalyst is fairly stable under the reaction (or regeneration) conditions.

View Article Online DOI: 10.1039/C8GC016280

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In the recent work of Flaherty et al. about the selfterminated cascade condensation of ethanol and acetaldehyde to 2-methyl benzaldehyde, 4-methyl benzaldehyde was also obtained as a by-product.¹⁰ To increase the carbon economy of this route, we also explored the applicability of EAOAc ionic liquid to the solvent-free aldol condensation of 4-methyl benzaldehyde and cyclohexanone. According to the analysis of NMR and GC (see Figures S7-S9 in supporting information), 2-2,6-bis(4-(4-methylbenzylidene)cyclohexanone and methylbenzylidene)cyclohexanone (i.e. 2A and 2B in Scheme 5) were obtained from the aldol condensation of cyclohexanone and 4-methyl benzaldehyde. Under the same reaction conditions, the methyl benzaldehyde conversions and the carbon yields of C_{14} oxygenates (i.e. 1A or 2A) or C_{22} oxygenates (i.e. 1B or 2B) are very close to each other (see Figure 8), which means that the position of methyl group have no evidently effect on the reactivity of methyl benzaldehyde.

As the final aim of this work, we also explored the synthesis of jet fuel range cycloalkanes by the aqueous phase hydrodeoxygenation (APHDO) of 1A which was purified from the aldol condensation product according to the method described in supporting information. It was found that 1A can be selectively converted to 1-methyldodecahydro-1H-fluorene (i.e. 1D in Scheme 6) over the Pd/C catalyst. High carbon yield (92.5%) of 1D was achieved after the reaction was carried out at 453 K for 4 h. Besides 1D, small amount of 1E (carbon yield: 0.3%) was also identified in the HDO products. According to our measurements, the polycycloalkanes as obtained (i.e. a mixture of **1D** and **1E**) have high density (0.99 g mL⁻¹ at 298 K) and a low freezing point (251 K). Compared with the perhydrofluorene which has been claimed to be the highest density bio-jet fuel by Zou et al.,9 this fuel has higher density $(0.99 \text{ g mL}^{-1} \text{ vs. } 0.96 \text{ g mL}^{-1})$ and evidently lower freezing point (251 K vs. 330 K). These characters are advantageous in real application.



Scheme 6. Reaction pathways for the generation of polycycloalkanes from the APHDO of 1A and 2A over the Pd/C catalyst.

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DOI: 10.1039/C8GC01628C

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Analogously, we studied the APHDO of 2A over the Pd/C catalyst. Under the same reaction conditions as we used for the APHDO of 1A, high carbon yield (82.3%) of 3methyldodecahydro-1H-fluorene (i.e. 2D in Scheme 6) and small amount of 1-(cyclohexylmethyl)-4-methylcyclohexane (carbon yield: 1.1%) were achieved. The density and freezing point of the polycycloalkane mixture were measured as 0.96 g mL⁻¹ (at 298 K) and 270 K (also lower than that of perhydrofluorene), respectively. Compared with the 2-methyl benzaldehyde route, the 4-methyl benzaldehyde route has disadvantages at two aspects: 1) Lower feedstock availability. In the previous work of Flaherty et al.,¹⁰ the carbon yields of 4methyl benzaldehyde are evidently lower than those of 2methyl benzaldehyde, which makes 4-methyl benzaldehyde less available than 2-methyl benzaldehyde. 2) Lower density and higher freezing point of final product. However, it is feasible to produce 1D and 2D simultaneously and save the energy for the separation of 2-methyl benzaldehyde and 4methyl benzaldehyde from the self-terminated cascade reactions of ethanol and acetaldehyde.

To figure out the reaction pathway for the generation of **1D** from the APHDO of 1A, we investigated the effect of reaction time on 1A conversion and the carbon yields of different products. From Figure 9, we can see that the APHDO of 1A is a fast reaction. During the heating process (0.5 h) from room temperature to 453 K (or reaction temperature), 1A was completely converted. 2-(2-Methylbenzyl)cyclohexanone, 2-(2methylbenzyl)cyclohexanol (i.e. 1F and 1G in Scheme 7) and 1D were obtained as the products. With the extension of reaction time, the carbon yields of 1F and 1G decreased. In contrast, the carbon yield of 1D increased. Meanwhile, small amount of **1E** appeared in the product. The reaction finished after 1 h. With the further increment of reaction time to 4 h, no evident change was observed. Based on the results we observed in this work and some recent literature about similar reaction systems,^{7,9} the reaction mechanism for the APHDO of **1A** to **1D** was proposed in Scheme 7.



Figure 9. Conversion of 1A and the carbon yields of different products over the commercial Pd/C catalyst as the functional of reaction time. Reaction conditions: 453 K, 6 MPa H_2 ; 1 g 1A, 35 mL H_2O , 0.1 g Pd/C.



Scheme 7. Reaction mechanism for the generation of different products from the APHDO of **1A** over the Pd/C catalyst.

Conclusions

The solvent-free aldol condensation of methyl benzaldehyde and cyclohexanone. followed by aqueous phase hydrodeoxygenation was found to be an effective method for the synthesis of jet fuel range high-density tricycloalkanes. Among the investigated catalysts, EAOAc ionic liquid exhibited the highest activity and good stability for the solvent-free aldol condensation of methyl benzaldehyde and cyclohexanone. The excellent performance of EAOAc ionic liquid can be explained by its special chemical structure and/or the synergetic effect of ethanolamine and acetic acid. Under the optimized reaction conditions, high carbon yields (~85%) of C₁₄ oxygenates can be obtained from the solvent-free aldol condensation 2-methyl benzaldehyde (or 4-methyl benzaldehyde) and cyclohexanone. By the aqueous phase hydrodeoxygenation over a commercial Pd/C catalyst, the C14 oxygenates as obtained can be selectively converted to tricycloalkanes which have high density (\geq 0.96 g mL⁻¹). As a potential application, these tricycloalkanes can be used as additive to improve the volumetric heats value of current bio-jet fuels.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (no. 21603221; 21690082; 21776273), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDB17020100), the National Key Projects for Fundamental Research and Development of China (2016YFA0202801), Dalian Science Foundation for Distinguished Young Scholars (no. 2015R005), Department of Published on 12 June 2018. Downloaded by Hacettepe Universitesi on 12/06/2018 04:25:47

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Science and Technology of Liaoning Province (under contract of 2015020086-101). Dr. Xu appreciates the Postdoctoral Science Foundation of China (2015M580235) and the dedicated grant for methanol conversion from DICP for funding this work.

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Table of contents entry



Synthesis of high-density aviation fuels with methyl benzaldehyde and cyclohexanone

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Jet fuel range tricyclic alkanes were first selectively synthesized with methyl benzaldehyde and cyclohexanone which can be derived from lignocellulose.