Tandem Reactions for the Synthesis of High-Density Polycyclic Biofuels with a Double/Triple Hexane Ring

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ABSTRACT: Synthesizing high-density fuels from non-food biomass is of great interest in the field of biomass conversion because they can increase the loading capability and travel distance of vehicles and aircraft as compared to conventional low-density biofuels (<0.78 g/cm^3). In this work, we reported a new and facile strategy for the synthesis of high-density biofuels with polycyclic structures from lignocellulose-derived 5,5-dimethyl-1,3-cyclohexanedione and different aldehyde derivatives in two steps under mild reaction conditions, including a developed tandem reaction and a hydrodeoxygenation reaction. Theoretical approaches were used to estimate the fuel properties, which indicate that the obtained biofuels have a high density of $0.78-0.88$ g/cm^3 and high net heat of combustion (NHOC) values of $44.0-46.0$ MJ/kg. A representative biofuel **3c** was measured to have a high NHOC of 43.4 MJ/kg, which matched well with the calculated NHOC value of 44.4 MJ/kg, indicating the high accuracy of the theoretical approaches. This work is expected to provide a green strategy for the synthesis of polycyclic high-density biofuels with platform chemicals.
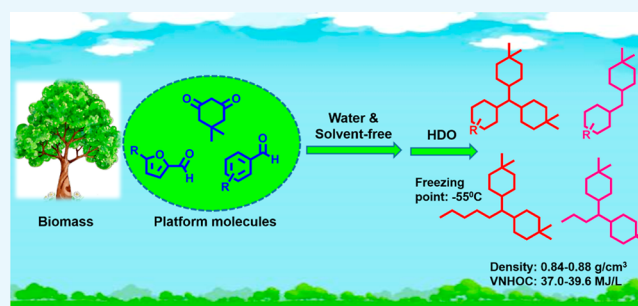
INTRODUCTION

Biofuel is sustainable green energy, which is considered as an alternative liquid fuel for fossil fuels.[1,2] However, it is very challenging to obtain high-density jet and diesel range biofuels because the direct degradation and subsequent hydrodeoxygenation (HDO) of biomass typically offer small molecules with C5 and C6, wherein the carbon number is far behind the prerequisite of gasoline and diesel fuels.[3,4] In order to produce long-chain alkanes, a range of catalytic approaches have been developed, such as Fischer−Tropsch synthesis.[5] In these processes, light molecules are converted to biofuels, which match the gasoline/diesel range through formation of C−C chains. However, the Fischer−Tropsch transformation process is unable to give good selectivity toward specific products.[6] Multifunctional heterogeneous catalysts, such as zeolites, are able to catalyze the formation of C−C bonds in a controlled process, but the inherent instability in hot water and the site blocking in the vapor phase reduce the efficiency of catalysts.[7−9]

Constructing ring-structure biofuels with increased carbon numbers is one of the most popular strategies for jet and diesel range biofuels because ring-structure biofuels typically have higher densities than chain-structure biofuels with the same carbon numbers.[10,11] Moreover, ring-structure biofuels generally have a higher energy content than linear or branched chain-structure biofuels[12,13] because the release of ring strain of ring-structure biofuels often generates extra energy. Therefore, it is of great interest for researchers in academia and industry to synthesize high-energy ring-structure biofuels, which can

offer a higher loading capacity or longer travel distance of trucks and aircraft with limited oil tank volume.

However, it is a challenge to achieve ring-structure molecules from biomass-derived chemicals with simple and low-cost processes. Lignocellulose is the most abundant carbon source on the earth, which is typically segregated into glucose monomers with C5 and C6.[3] These small molecules can be directly converted into biofuels by the HDO reaction.[14,15] The obtained biofuels are often gas-range biofuels with a low density (<0.77 g/cm^3) and a low volumetric net heat of combustion (NHOC) (<34 MJ/L), which might not be suitable for heavily loaded transport vehicles and aircrafts. Connecting the biomass-derived platform chemicals is a popular strategy to increase the density and energy content, especially connecting ring-structure biomass-derived molecules.[16−18] Harvey[19] and Zou[20] used pinene as the raw material to synthesize a pinene dimer-based biofuel with a high density of 0.94 g/cm^3. Zhang et al. reported that isophorone can be dimerized to a biofuel with a high density of 0.86 g/cm^3.[21] However, these starting materials are generally obtained

from some specific woods and plants, the resource of which is limited in nature.

Efforts have been made on exploring new synthesis strategies to produce ring-structure high-density biofuels with biomass-derived chemicals from common bioresources such as agricultural wastes and forest residues. Lignocellulose is a typical biomass, which comprises lignin, hemicellulose, and cellulose. Lignin can be degraded into benzene derivatives, which can be converted into cycloalkanes and bicycloalkanes.[22,23] They can also be converted into fused-ring structure biofuels with a high density up to 0.99 g/cm³.[12] Hemicellulose and cellulose can be degraded into various chemicals with carbonyl and hydroxyl groups. Among them, furfural and its derivatives have been the most investigated molecules for ring-structure high-density biofuels because they can be subsequently converted to cyclopentanone. A series of bi-(cyclopentane)- and tri(cyclopentane)-based biofuels have been synthesized from cyclopentanone by Zhang[24,25] and Zou.[11] However, coupling methods (such as aldol condensation and hydroxyalkylation/alkylation) of the C−C bond of cyclopentanone, cyclohexanone, and furfural/benzaldehyde derivatives are catalyzed by solid base or solid acid catalysts.[24−27] Generally, reactions catalyzed by a solid base need more amounts of catalyst (>0.1 equiv) and a high reaction temperature (>100 °C), and more byproducts would be produced, resulting in a low yield of products. Highly efficient methods under green reaction conditions are desired for the synthesis of high-density ring- structured biofuels.

Green reactions have become critical objectives in modern organic chemistry to improve the reaction efficiency, avoid toxic reagents, and reduce wastes.[28−31] Reactions occurring in water[32−34] or under solvent-free conditions[28,35] accord with the green chemistry concept in modern organic synthesis. A tandem reaction is a powerful method to meet the demands of modern synthesis with high efficiency in terms of minimization of synthetic steps.[36−38] A cascade sequence often can lead to the target molecules by combining a series of reactions in one synthetic operation. For example, 5,5-dimethyl-1,3-cyclohexanedione, with a highly active methylene and a six-membered ring skeleton, has been used in synthesis of heterocyclic compounds through a multistep tandem reaction.[39−42] Herein, new synthesis strategies have been reported to produce high-density biofuels with furfural/benzaldehyde derivatives and 5,5-dimethyl-1,3-cyclohexanedione in two steps including a catalyst-free tandem reaction in water or a solvent-free tandem cyclization reaction and the following HDO reaction. The catalyst-free tandem reaction comprises a Knoevenagel condensation, followed by a Michael addition reaction. The solvent-free tandem cyclization reaction contains a Knoevenagel condensation, a Michael addition reaction, and an intramolecular cyclization reaction. These reactions are performed under green conditions, which represent clean, economical, efficient, and safe procedures. More importantly, the reactants furfural/benzaldehyde derivatives and 5,5-dimethyl-1,3-cyclohexanedione can all be obtained at the industrial scale from biomass. For example, furfural was obtained at the industrial scale from agricultural wastes and forest residues.[43] Benzaldehyde was prepared by oxidation of cinnamaldehyde or cinnamon oil, and cinnamaldehyde or cinnamon oil can be obtained directly from biomass.[44−46] 5,5-Dimethyl-1,3-cyclohexanedione was obtained with a common reaction from acetone and malonic acid (shown in Figure S1) that was produced from the glucose fermentation process.[47,48]

Therefore, a series of polycyclic high-density biofuels with two or three cyclohexane structures and alkyl chains were synthesized from the above raw materials as shown in Scheme 1.

Scheme 1. Synthesis Routes of Polycyclic High-Density Aviation Biofuels from Furfural/Benzaldehyde Derivatives and 5,5-Dimethyl-1,3-cyclohexanedione
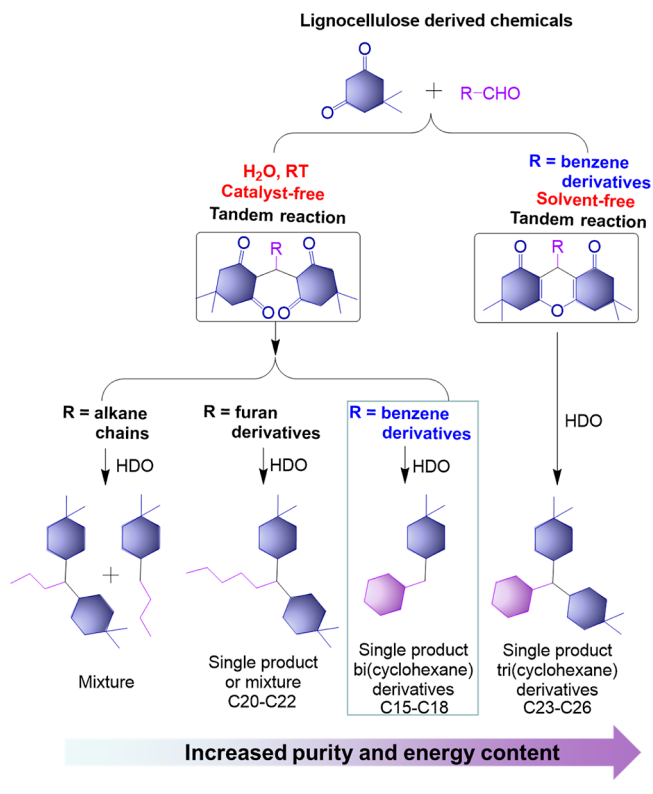

RESULTS AND DISCUSSION

Butyraldehyde and 5,5-dimethyl-1,3-cyclohexanedione were used as starting materials for the synthesis of high-density biofuels (Figure 1a). Butyraldehyde can be obtained from butanol produced from the fermentation of lignocellulose at the industrial scale.[49−51] It is interesting to notice that when butyraldehyde was mixed with 5,5-dimethyl-1,3-cyclohexanedione, the reaction spontaneously occurred at room temperature, and no catalyst was necessary. Briefly, butyraldehyde (1 equiv) and 5,5-dimethyl-1,3-cyclohexanedione (2 equiv) were stirred in a round-bottom flask with water as the solvent for 4 h. The products precipitated in the solution without adding any precipitants, which were purified by simple filtration, washing, and drying to afford **2a** at a modest isolated yield of 76%. Then, **2a** was hydrodeoxygenated by Pd/C (purchased by Beijing InnoChem Science & Technology Co. Ltd.) at 220 °C to afford **3a** with a yield of 86%. The obtained final product **3a** was a mixture composed of C20 and C12 with carbon yields of 80 and 6%, respectively. In the process, the yields of intermediates and the yields of HDO products were calculated according to the following equations. For intermediates, isolated yield was used, which is the ratio of the mass of the target compound obtained after post-treatment to the theoretical mass: isolated yield (%) = (actual quality of target product/theoretical quality of target product) × 100%.
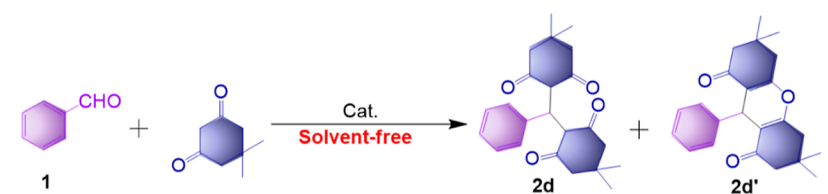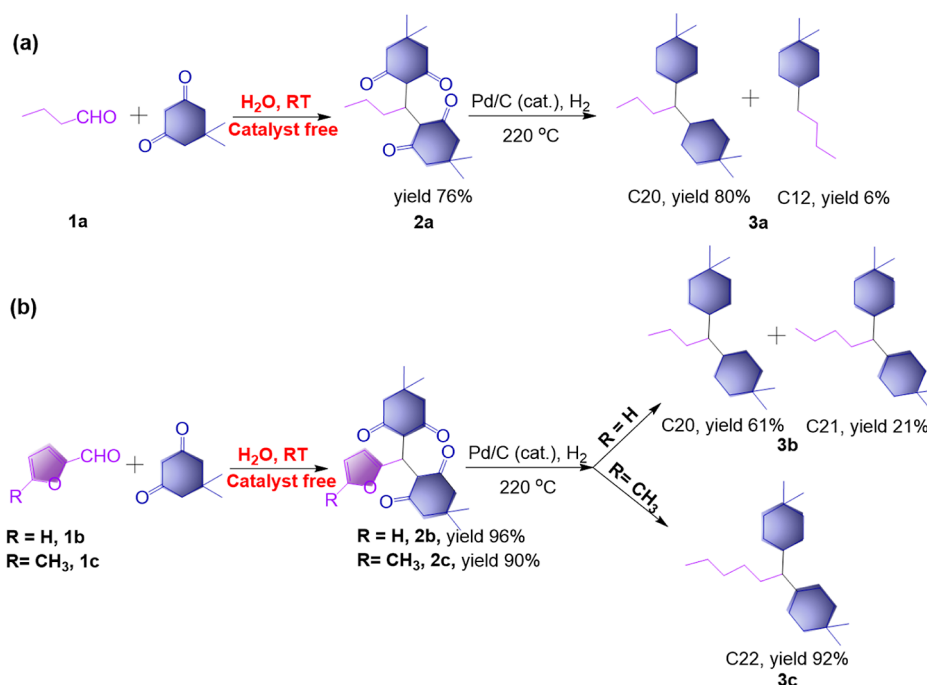
Figure 1. Synthesis process of dicyclohexane biofuels from (a) butyraldehyde or (b) furfural/5-methyl furfural and 5,5-dimethyl-1,3-cyclohexanedione. Catalyst-free tandem reaction in water, reaction conditions: 5,5-dimethyl-1,3-cyclohexanedione (2 mmol, 2.0 equiv), butyraldehyde or furfural derivatives (1 mmol, 1.0 equiv), H_2O (5 mL), rt, 2 h, isolated yield; (b) HDO, reaction conditions: precursors (0.5 mmol), Pd/$C_{10\%}$ (50 mg), Hf(OTf)$_4$ (0.025 mmol), AcOH (1 drop), cyclohexane (5 mL), H_2 (4 MPa), 220 °C, 24 h, carbon yield.
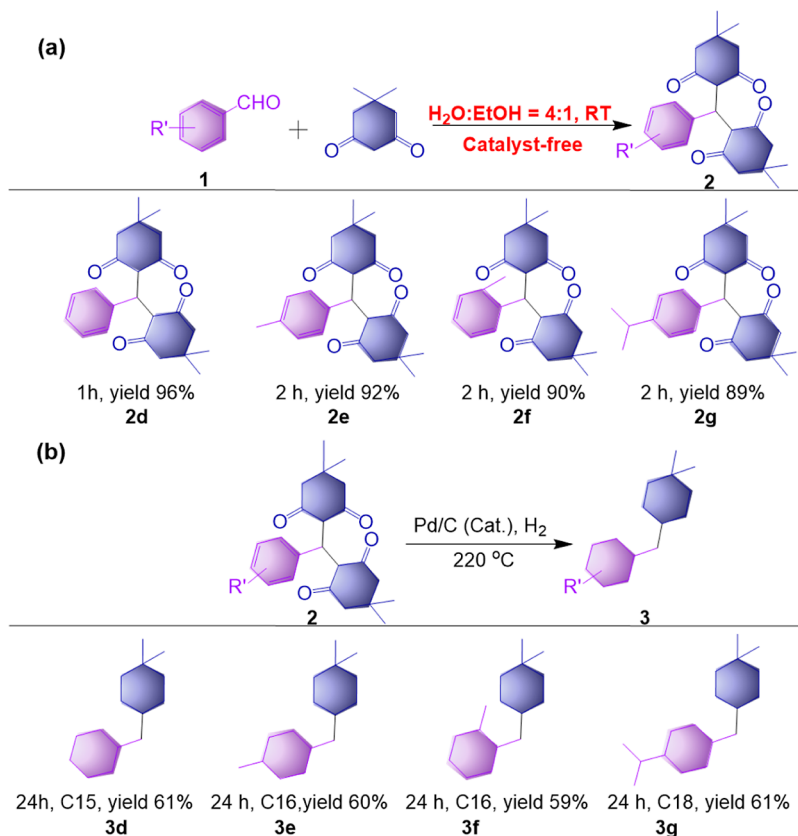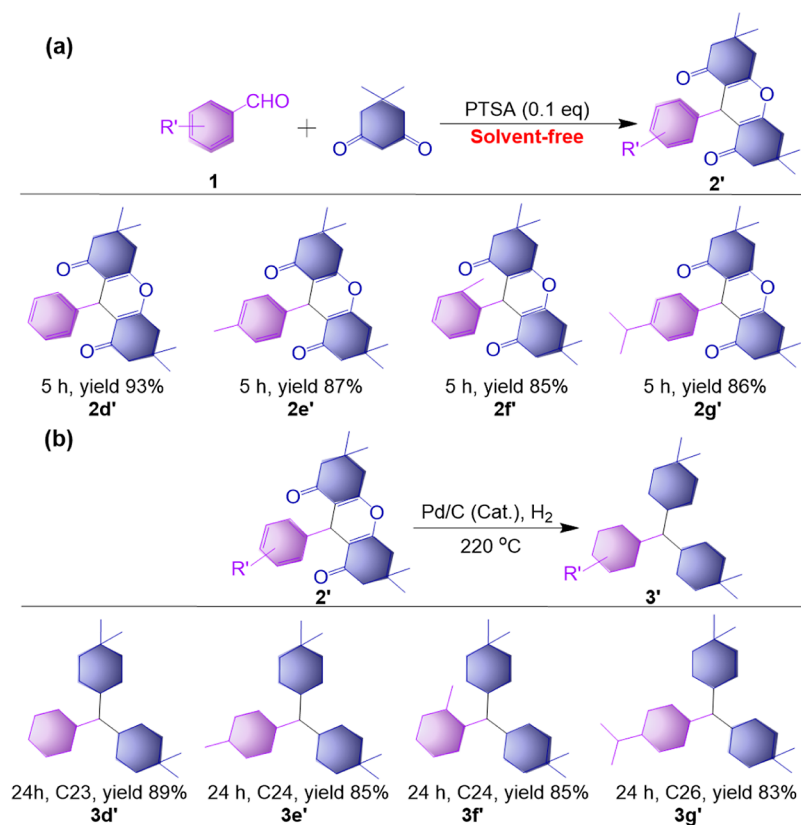

Figure 2. Synthesis process of dicyclohexane biofuels from benzenaldehyde derivatives and 5,5-dimethyl-1,3-cyclohexanedione. (a) Catalyst-free tandem reaction in water, reaction conditions: 5,5-dimethyl-1,3-cyclohexanedione (2 mmol, 2.0 equiv), benzaldehyde derivatives (1 mmol, 1.0 equiv), H_2O/EtOH (4:1, 5 mL), rt, 2 h, isolated yield; (b) HDO, reaction conditions: precursors (0.5 mmol), Pd/$C_{10\%}$ (50 mg), AcOH (1 drop), cyclohexane (5 mL), H_2 (4 MPa), 220 °C, 24 h, carbon yield.

Table 1. Synthesis Conditions of 2d′

entry[a]	cat (0.1 equiv)	2d (%)[b]	2d′ (%)[b]
1	NaOH	76	0
2	DBU	84	0
3	DABCO	90	0
4	CaO	77	0
5	MgO	81	0
6	AcOH	87	trace
7	citric acid	77	trace
8	PTSA	0	93

[a]Conditions: 5,5-dimethyl-1,3-cyclohexanedione (2 mmol), benzaldehyde (1 mmol), PTSA (0.1 mmol), solvent-free, 80 °C, 2 h. [b]Isolated yield.


Figure 3. Synthesis process of tricyclohexane biofuels from benzenaldehyde derivatives and 5,5-dimethyl-1,3-cyclohexanedione. (a) PTSA-catalyzed tandem reaction under solvent-free conditions, reaction conditions: 5,5-dimethyl-1,3-cyclohexanedione (2 mmol, 2.0 equiv), benzenaldehyde derivatives (1 mmol, 1.0 equiv), PTSA (0.1 mmol, 0.1 equiv), solvent-free, 80 °C, 2 h, isolated yield; (b) HDO, reaction conditions: precursors (0.5 mmol), Pd/C$_{10\%}$ (50 mg), AcOH (1 drop), cyclohexane (5 mL), H$_2$ (4 MPa), 220 °C, 24 h, carbon yield.

For the HDO product, the carbon yield was used: carbon yield of specific product in the HDO reaction (%) = (carbon in the specific product obtained in the HDO reaction/carbon in the intermediates consumed during the HDO reaction) × 100%.

These reactions are powerful reactions that can be performed with furfural derivatives as the starting materials, which have been very popular as biomass-derived platform chemicals in the synthesis of biofuels.[52−54] When the furfural derivatives and 5,5-dimethyl-1,3-cyclohexanedione were mixed,

the reaction occurred spontaneously and provided the products 2b and 2c with high isolated yields of 96 and 90%, respectively. After that, 2b and 2c were hydrodeoxygenated by Pd/C and Hf(OTf)$_4$ at 220 °C to afford 3b and 3c with high carbon yields of 82 and 92%, respectively. The 5% of homogeneous Hf(OTf)$_4$ was loaded to promote the ring-opening process of cyclic ethers, which hydrogenated from the furan structure. Hf(OTf)$_4$ could mediate the rapid endothermic ether ⇌ alcohol and alcohol ⇌ alkene equilibria process, while the subsequent hydrogenation of alkene by Pd.[55−57] 3b
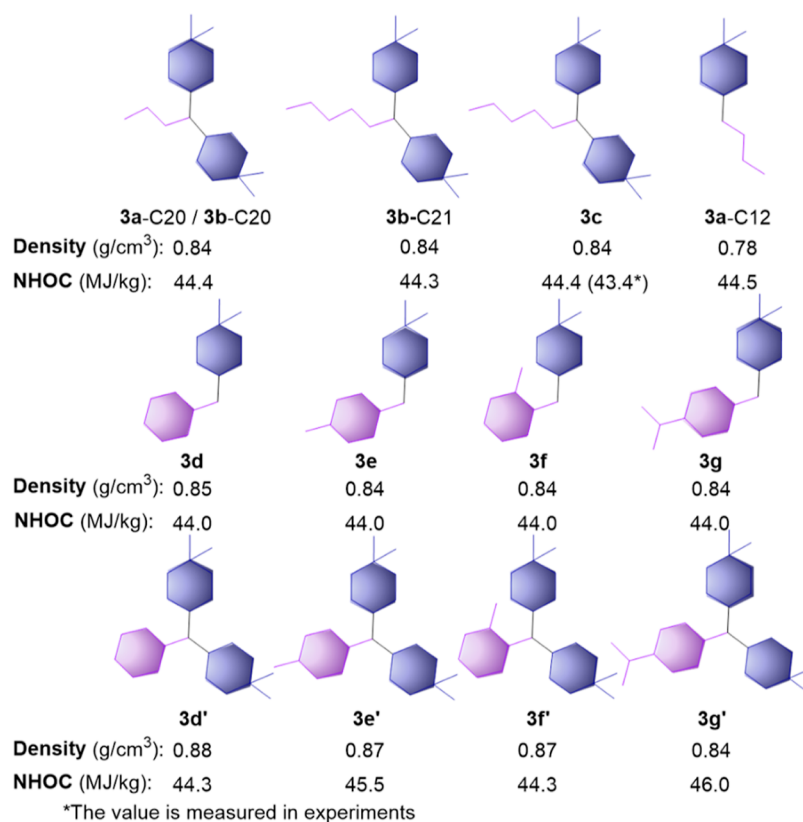
Figure 4. Calculated densities and NHOC values for the hydrocarbon products. The measured NHOC value of **3c** is 43.4 MJ/kg.

is a mixture of 61% C20 and 21% C21 hydrocarbons. It is common to see some fragments in the HDO process at high temperature. However, **3c** is a single product of a C22 hydrocarbon. The HDO reaction conditions (220 °C, 4.0 MPa H_2) are milder than some of the similar HDO reaction conditions reported in previous works (300 °C, 5.5 MPa H_2).[14]

This new procedure was then extended to other lignocellulose-derived aldehydes for the synthesis of biofuels with higher density. Benzaldehyde derivatives were chosen because they may increase the ring numbers and density of the biofuels. A mixed solvent of water and ethanol at a ratio of 4:1 was used because benzaldehyde derivatives have poor solubilities in water. As shown in Figure 2, the reaction was also performed at room temperature without a catalyst to afford the products **2d**–**2g** at high isolated yields of 89–96% (Figure 2a). The yields are strongly related to the size and the position of the substituted groups on the benzene ring of benzaldehydes, which should be due to the steric hindrance effects. **2d** was obtained at a high isolated yield of 96% in 1 h from **1d** with no substituting group. While **2g** was obtained at a lower isolated yield of 89% in 2 h from **1g**, which had an isopropyl group.

It is unfortunate to see that the final products were not biofuels with three rings after the HDO reaction. The hydrocarbons have only two rings as shown in Figure 2b. One hexane ring from 5,5-dimethyl-1,3-cyclohexanedione was missing. No difference was observed when reducing the HDO reaction temperature to 200 or 150 °C. The reason for the missing of one hexane ring should be mainly attributed to the fact that the Michael addition reaction is a reversible reaction that may go backward at high temperature. The proposed

mechanism has been illustrated according to the experimental results and literature reports (Figure S2).[58,59] The carbon yields of **3d**–**3g** are in the range of 59–61% (Figure 2b).

Reverse Michael addition was prone to occur in the HDO reaction of compound **2**, resulting in bicyclohexane hydrocarbons **3**. It is a huge waste to lose one molecule of 5,5-dimethyl-1,3-cyclohexanedione for synthesis of biofuels. The result goes against the concept of atomic economics. In order to inhibit the inverse Michael addition process of **2**, thermodynamically more stable octahydroxanthene-1,8-diones were synthesized by a one-step process. The react condition was optimized with a model reaction of benzaldehyde and 5,5-dimethyl-1,3-cyclohexanedione. There was no **2d** when the base was used as a catalyst (Table 1) such as NaOH, DBACO (1,4-diazabicyclo[2.2.2]octane), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), CaO, and MgO. When weak protonic acid AcOH and citric acid were used at 80 °C for 2 h under solvent-free conditions, the product was still **2d** with a trace amount of **2d′**. No obvious difference was observed when increasing the temperature to 100 °C and elongating the reaction time to 5 h with weak protonic acid as a catalyst. A high isolated yield of 93% was obtained for **2d′** at 80 °C for 2 h under solvent-free conditions when 4-methylbenzenesulfonic acid (also known as PTSA) was used as a catalyst (entry 8). The high yields of **2d′** should be attributed to the higher catalytic ability of strong acid PTSA (pK_a = 1.7) than weak acid AcOH (pK_a = 4.75) and citric acid (pK_a = 4.80). According to the experimental results and previous literature,[60,61] the proposed mechanism is illustrated in Figure S3 in the Supporting Information. This reaction is a green tandem reaction including a Knoevenagel condensation, a Michael addition reaction, and a dehydration reaction.

With the optimized reaction conditions (Table 1, entry 8), the alkyl substituted benzaldehydes were used as starting materials. High isolated yields of 87, 85, and 86% were obtained for **2e′**, **2f′**, and **2g′**. When hydrogenated with Pd/C as the catalyst, tricyclohexane hydrocarbons were obtained at high carbon yields of 89, 85, 85, and 83% for **3d′**, **3e′**, **3f′**, and **3g′** (Figure 3), respectively. It is speculated that the activation energy of the reverse dehydration process of **2d′** formation was much higher than the activation energy of the reverse Michael addition reaction of **2d**. Because of the high activation energy, the reverse process was difficult to happen, so that it was hard to convert **2d′** into **2d**.

The density and NHOC of all the products were estimated with theoretical methods, which have high accuracy as demonstrated in our previous works.[62−64] As shown in Figure 4, the densities are in the range of 0.78−0.88 g/cm^3, which are close to those of state-of-the-art high-density artificial fuels such as JP-10 (0.94 g/cm^3) and RJ-5 (0.94 g/cm^3). The estimated NHOC values are in the range of 44.0−46.0 MJ/kg, which are also among the values for top-level petroleum based fuels (JP-4, JP-5, and RJ-4).[65] The NHOC of a representative product **3c** was practically measured to evaluate the accuracy of the calculation methods. The measured NHOC is 43.4 MJ/kg, which matches well with the calculated NHOC of 44.4 MJ/kg for **3c** (relative error <2%). In addition, the measured freezing point of **3c** is −55 °C, which is lower than those of many commercial petroleum-based fuels such as JP-7 (−44 °C), JP-8 (−51 °C), and so forth.[65] Meanwhile, compared with synthetic bio-based paraffinic kerosenes, such as HEFA-Jet (a mixture of hydrotreated fatty acids and esters, 0.76 g/cm^3), 5-MU (5-methylundecane, 0.75 g/cm^3, −50 °C), and DMO (2, 6-dimethyloctane, 0.73 g/cm^3, −53 °C), **3c** has a higher density (calculated density: 0.84 g/cm^3) and a lower freezing point (−55 °C).[66]

CONCLUSIONS

This work is expected to provide a green strategy for synthesis of polycyclic high-density biofuels from biomass-derived 5,5-dimethyl-1,3-cyclohexanedione and different aldehydes including linear-chain aldehyde, furfural aldehyde, and benzaldehyde. A catalyst-free tandem reaction in water and a solvent-free tandem cyclization reaction are developed to produce high-density aviation biofuels with dicyclohexane and tricyclohexane structures. The theoretical calculations show that the obtained hydrocarbons have a high density of 0.78−0.88 g/cm^3 and a high NHOC of 44.0−46.0 MJ/kg, which are higher than those of the commonly used commercial jet fuels such as JP-7, JP-8 and bio-based paraffinic kerosenes such as HEFA-Jet, 5-MU, and DMO. The freezing point of **3c** is −55 °C, which is much lower than those of biofuels (e.g., bicyclohexane, 1.2 °C and bicyclopentane, −38 °C)[24,67] and satisfying the requirement for jet fuels (generally <−50 °C). This work provides an efficient, promising way for production of polycyclic high-density aviation biofuels under mild conditions, which might be used for the synthesis of advanced aviation fuels or fuel additives.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c07241.

General information; measurement of fuel properties; general procedures; spectral data of intermediates; copies of ^{1}H NMR and ^{13}C NMR spectra of intermediates; copies of ^{1}H, ^{13}C, and DEPT-135 NMR and GC−MS spectra of products; and ^{1}H, ^{13}C, and DEPT-135 NMR spectra and GC−MS spectra of **3b** after vacuum distillation (PDF)

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Notes

The authors declare no competing financial interest.

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