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Direct production of aviation fuels from microalgae lipids in water

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HIGHLIGHTS

- Aviation fuels can be synthesized directly from microalgae lipids in water over Pt/C.
- Pt/C is capable for decarboxylation of all test model compounds of microalgae lipids.
- Pt/C keeps the catalytic activity on decarboxylation even at the third use.
- Mechanism of direct decarboxylation of fatty acid esters is proposed.
- Optimum reaction condition for decarboxylation of methyl stearate is obtained.

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ABSTRACT

In this contribution, we confirmed that aviation fuels could be synthesized directly from microalgae lipids in water over a Pt/C catalyst without additional hydrogen. After decarboxylation at 330 and 370 °C for 120 min, the oxygen content in the microalgae lipids was significantly reduced and the heating value of produced aviation fuels was greatly increased. The reaction mechanism of direct decarboxylation of microalgae lipids to aviation fuels was further investigated using each of the representative compounds in microalgae lipids, such as methyl laurate, methyl eicosanoate, methyl stearate, ethyl stearate, and tristearin as the starting material in separate reactions under the same conditions. Those reaction conditions, solvent, water loading, catalyst loading and reactant loading, were optimized. It was concluded that among the tested solvents, water was the most favorable for the selective decarboxylation of methyl stearate, that the catalytic decarboxylation rate of fatty acid esters with larger carbon numbers in water was faster than those with smaller carbon numbers, and that the Pt/C catalyst retained its activity through its third use. These results provide new insights for the direct decarboxylation of microalgae lipids to aviation fuels.

1. Introduction

Aviation fuel, a mixture of C8-16 alkanes, alkenes, and aromatic hydrocarbons derived from crude oil, is a special kind of liquid oil that has a higher heating value and greater energy density than conventional fuels. Although biofuels such as ethanol have demonstrated their compatibility with land transportation vehicles, the high heating value and high energy density required of aviation fuels are still properties difficult to achieve in biofuels. From an environmental and economic standpoint, the direct synthesis of aviation fuels from renewable biomass is of great interest in both academic research and industrial application. Microalgae has been regarded as a promising feedstock for biofuels because of their rapid growth rate, low land-area requirements, and high oil content [1–3]. The lipids of microalgae mainly consist of triglycerides, free fatty acids, phospholipids and glycolipids [4–6]. All these properties make microalgae lipids a competitive feedstock for the production of renewable bio-fuels such as biodiesel [7,8] and aviation fuels [9]. Direct conversion of microalgae lipids to aviation fuels or biofuels, however, is a challenge due to the complicated components found in microalgae. Hydrothermal liquefaction [10] and pyrolysis [11] of microalgae have been reported to produce bio-fuels, but the quality and properties of the resulting biofuels do not meet standards for aviation fuels.

At present, hydrodeoxygenation of vegetable oils followed by further cracking and isomerization is the main approach to producing aviation fuel from biomass [12,13] – a method that has been developed to the commercial scale. These technologies, however,

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require refined oil as the raw material and cannot utilize more complicated raw materials such as microalgae lipids. Moreover, the high cost of hydrogen in the hydrodeoxygenation process [14] and the use of refined oil as the starting material increases the overall cost of producing aviation fuel. These barriers limit the large-scale development and application of hydrodeoxygenation technology.

Recently, hydrothermal decarboxylation of fatty acids and its derivatives without additional hydrogen was reported as a new approach for producing aviation fuel at a lower cost [15–17]. The hydrothermal approach first converts phospholipids and glycolipids to fatty acids via hydrolysis, and then decarboxylates the fatty acids to alkanes. The major advantage of this strategy is that the decarboxylation step does not require any hydrogen. In our previous research [15,18,19], we determined the decarboxylation behaviors, kinetics and mechanisms of saturated and unsaturated fatty acids to alkanes over heterogeneous noble metal catalysts. It was found that hydrothermal decarboxylation is feasible for the production of aviation fuels. Further research, however, is necessary to apply this technique broadly to the other complicated compounds present in raw microalgae lipids.

In this article, the direct synthesis of aviation fuels from raw microalgae lipids in water was performed over a Pt/C catalyst without additional hydrogen. The reaction mechanism of direct decarboxylation of microalgae lipids to aviation fuels was further investigated using each of the representative compounds in microalgae lipids, such as methyl laurate, methyl eicosanoate, methyl stearate, ethyl stearate, and tristearin, as the starting material in separate reactions under the same conditions. Reaction conditions, such as solvent, water loading, catalyst loading and reactant loading, were optimized.

2. Experimental section

2.1. Materials

Microalgae (Chlorella) powders were obtained from Shandong Tianjian Biotechnology Co. Ltd, China. Methyl stearate (>99%), ethyl stearate (>99%), stearic acid (>99%), tristearin (>99%), methyl laurate (>99%), and methyl eicosanoate (>99%) were all purchased from Sigma–Aldrich, USA. Acetone (analytic reagent grade) was obtained from Hangzhou Chemical Reagent Co., Ltd, China. 5% Pt/C catalyst was purchased from Sigma–Aldrich, USA. Methylene chloride was obtained from Sinopharm Chemical Reagent Co. Ltd, China. Deionized water was purchased from Hangzhou Wahaha Co., Ltd, China. All above chemicals and catalysts were used as received.

2.2. Experimental procedure

The hydrothermal decarboxylation of microalgae lipids and fatty acid esters were carried out in a micro batch reactor (1.67 mL volume), which was assembled from one 3/8-inch tube and two 3/8-inch caps purchased from Swagelok, USA. 0.1 mmol of reactant and 5 mg of 5% Pt/C catalyst were added and then a certain amount of water was loaded into the reactor. Afterwards, the sealed reactor was placed in a fluidized sand bath (Techne SBL-2) under the controlled reaction temperature. After the desired reaction time had elapsed, the reactor was placed in cold water to quench the reaction. The reaction mixture in the reactor was centrifuged to remove the solid catalyst and the liquid products were rinsed and diluted in a 10 mL volumetric flask with acetone for analysis.

2.3. Analysis method

The liquid products in acetone were analyzed with a gas chromatograph (GC, Agilent 7890A) equipped with a 30 m × 0.25 mm × 0.33 μm HP-5 capillary column and a flame ionization detector. 1 μL samples were injected into the GC with a split ratio of 10:1, and the carrier gas (nitrogen) flow rate was 11 mL/min. The temperature of the injector and detector were 280 and 300 °C, respectively. The programmed column temperature consisted of a 4 min soak at 40 °C followed by a 10 °C/min ramp up to 280 °C, which was held for 5 min. The reaction products were identified by fragmentation patterns from an Agilent 5970 Mass Spectrometric (MS) detector and by calibrated with known standards. Quantitative analysis was performed using calibration curves for each compound in the mixture. The elemental analysis of microalgae oil and the decarboxylation samples were carried out on a Elementar Analyzer (Vario EL, Germany).

In subcritical water, the fatty acid esters can be completely hydrolyzed to fatty acids [20]. Thus, the molar conversion of the esters were calculated as follows: (1 − the number of moles of corresponding fatty acid detected divided by the initial number of moles of ester added into the reactor) × 100%. Selectivity was calculated as the number of moles of product recovered divided by the number of moles of reactant that had reacted (i.e., yield/conversion). Each data point represents the mean result from at least three independent experiments. Uncertainties reported herein are standard deviations, which were determined by replicate experiments.

The heating values of raw microalgae lipids and decarboxylated samples were calculated using the Dulong formula [21]:

$$\text{heating value}(\text{MJ/kg}) = 0.338\text{C} + 1.428(\text{H}-\text{O}/8)$$

where C, H and O are the wt.% composition of each element in the organic material.

3. Results and discussion

3.1. Decarboxylation of microalgae oil over Pt/C

Raw microalgae lipids used in this experiment were extracted from microalgae by methylene chloride. Direct decarboxylation of microalgae lipids was carried out at 330 and 370 °C for 120 min. The loading of lipids was 30 mg and catalyst loading was 5 mg. The microalgae lipids the Elementar Analyzer detected contained 72.6% C, 9.9% H, 16.1% O and 1.4% N, and had a heating value of 35.8 MJ/kg. After hydrothermal decarboxylation at 330 °C, the elemental composition in the produced oil changed to 78.5% C, 11.1% H, 9.6% O and 0.8% N with a heating value of 40.7 MJ/kg. At 370 °C, the results of direct decarboxylation were similar with that at 330 °C, as shown in Table 1. Microalgae lipids extracted by methylene chloride contain many oxygen containing compounds except fatty acid esters and fatty acids. These oxygen containing compounds might not be deoxygenated by Pt/C, causing the remains of oxygen content in the sample after decarboxylation. Moreover, oxidative decarboxylation [22,23] might occur and contribute the oxygen content to the sample after decarboxylation since there was a certain amount of oxygen inside the reactor. Fig. 1 shows the GC chromatogram of microalgae lipids and the products of decarboxylation at 330 °C. It was found that those compounds (such as fatty acids) in microalgae lipids with high boiling points exhibit significant conversions to low boiling point compounds (alkanes and alkenes). These low boiling point compounds were identified as heptadecane, pentadecane, hexadecane, 2,6,11-trimethyl-dodecane, 4-methyl-dodecane, 2-methyl-octadecane, 2,6,10,14-tetramethyl-hexadecane, 2-methyl-Z-7-hexadecene, 2-ethyl-1,3-dimethyl-benzenne, 1,2,3-trimethyl-benzene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-naphthalene. When microalgae lipids were decarboxylated at 370 °C, more alkanes such as eicosane, octadecane, tetradecane, tridecane, 4-methyl-decane, 2-methyl-8-propyl-dodecane, 4-methyl-hexadecane were identified in the range