Bioresource Technology 196 (2015) 217–224

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Synergetic deoxy reforming of cellulose and fatty acid esters for liquid hydrocarbon-rich oils

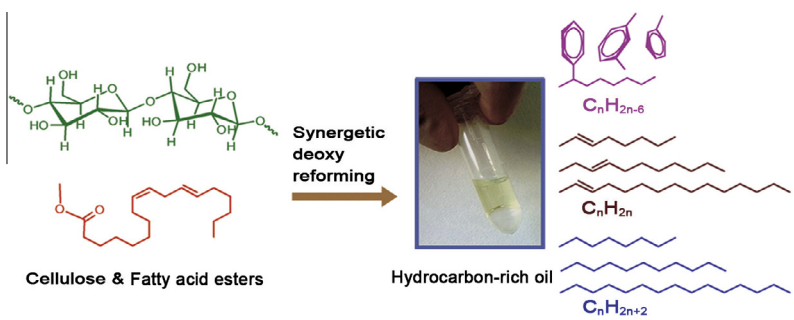
Chao Wang [a], Jingjing Sui [b], Weipeng Lu [a], Baopeng Li [a], Guoxing Li [a], Yihong Ding [b], Yong Huang [a], Jianxin Geng [a,*]

[a] Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, 29 Zhongguancun East Road, Haidian District, Beijing 100190, China
[b] A State Key Laboratory of Theoretical and Computational Chemistry, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, China

HIGHLIGHTS

- A synergetic deoxy reforming was developed to produce hydrocarbon-rich oil.
- Alkylbenzenes instead of phenols were detected in the hydrocarbon-rich oil.
- A radical pathway was proposed on the base of quantum chemical calculations.
- The synergetic interactions between the intermediates of cellulose & LAME for H_2O formation is the key point.
- Raw materials can be extended to cellulose and plant oils.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 April 2015
Received in revised form 21 July 2015
Accepted 22 July 2015
Available online 28 July 2015

Keywords:
Cellulose
Hydrocarbons
Fatty acid esters
Alkanes
Alkylbenzenes

ABSTRACT

A series of liquid hydrocarbons (alkylbenzenes, alkanes, and alkenes) were obtained by a synergetic deoxy reforming (SDR) process of cellulose and linoleic acid methyl ester (LAME) at 350 °C and 4–6 MPa in a closed system without external source of hydrogen. The liquid product was obtained with a yield of 15 wt% at a LAME/cellulose ratio of 0.2. In contrast, the direct deoxy reforming of cellulose produces oil that contains plenty of phenols and oxygen-containing compounds. Due to the insufficiency of water employed (30 wt%), a radical reaction pathway was proposed. Quantum chemical calculations indicate that the radicals from LAME interfere with the reactions of the intermediate products from cellulose, being responsible for the removal of phenols and the formation of hydrocarbons. The SDR process offers an embryonic insight in an alternative technique for preparation of hydrocarbon fuels.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Due to the limited reserves and non-renewability of fossil fuels, coal and fossil oil cannot satisfy the requirement for continuous industrial growth. Great efforts have been concentrated on searching for renewable fuels and chemicals for a sustainable economy (Suckling, 2014). The ultimate objective is that the fuel produced from biomass comprises of longer-chain alkanes, like gasoline and diesel oil, which is in line with the demand of the prevailing automotive combustion engines. It is well known that the vehicle fuel is composed of dominating hydrocarbons (C_8–C_{22}) and a certain amount of benzenes (toluene and xylene). However, such components are not very prevailing in the bio-based oils formed through pyrolysis or high pressure

* Corresponding author. Tel.: +86 10 8254 3416; fax: +86 10 6255 4670.
E-mail address: jianxingeng@mail.ipc.ac.cn (J. Geng).

http://dx.doi.org/10.1016/j.biortech.2015.07.079
0960-8524/© 2015 Elsevier Ltd. All rights reserved.

liquefaction of biomass, as well as in the biodiesel prepared through conversion of vegetable oils without additional hydrogenation upgrading (Nguyen et al., 2013).

To date, there are several technologies aiming at the conversion of biomass or biomass derivatives into transportation fuels. A well-established process for producing methanol and hydrocarbon (light alkanes) fuels starts with gasification of biomass to produce CO and H_2, followed by the Fischer–Tropsch synthesis (Huber et al., 2004). But, this is a multi-step and energy-consuming process. A high-profile aqueous-phase reforming of biomass-derived oxygenates such as glucose, sorbitol, and glycerol was proposed by Dumesic and co-workers, offering a simple route for the production of hydrocarbons (Han et al., 2014). Recently, Beeck et al. presented a biphasic catalytic approach to directly transform cellulose into straight-chain alkanes under a hydrogen pressure of 5 MPa, which was an improved procedure in comparison to the aqueous-phase reforming (de Beeck et al., 2015).

In addition, pyrolysis of biomass toward obtaining a mixture of various organic compounds is an alternative way for fuel production. The advantage of the pyrolysis process is its high yield (30–60 wt%), which was predicted by Van de Velden through designing a model of circulating fluid bed for biomass pyrolysis (Van de Velden et al., 2008). But, the major compounds in the biomass-based oil were levoglucosan and its isomers, as well as furans, alcohols, aldehydes, esters, and carboxylic acids (Venkatakrishnan et al., 2014). This product also contained a fraction of water commonly ranging from 15−50%, forming a single phase with the oxygen-containing compounds. The fast pyrolysis liquid with an oxygen content of 30–40 wt% delivered a higher heating value (HHV) ca. 17 MJ kg^{-1} (Bridgwater, 2012). Therefore, catalytic hydrodeoxygenation was developed to upgrade the biomass-based oil to high-calorific fuels (Elliott, 2007). For example, Grilc et al. have developed a series of catalytic systems, including Mo, W, $NiMo/Al_2O_3$, the oxides and sulphides of Ni, Mo, and Pd, to upgrade the solvolysis oil (Grilc et al., 2014, 2015). Lu et al. demonstrated the feasibility to convert biomass such as wheat straw, soybean stalk, and poplar leaves to liquid oils containing alkanes, benzenes, and phenols through one-pot deoxy-liquefication process (Lu et al., 2010). In this process, a small amount of water was accompanied with the liquid oil, forming separated oil and water phases; as a result, the two phases could be readily separated using a separation funnel. The oil with low oxygen content (<6 wt%) delivered a HHV higher than 40 MJ kg^{-1}. However, the presence of phenols could decrease the heating value of the resultant oil and limit its practical applications.

Apart from biomass materials, lipid such as plant oil and fatty oil is another ideal source for making hydrocarbon oil. For example, Asomaning et al. studied the pyrolysis conversion of mono unsaturated fatty acids into hydrocarbon products (350–450 °C). Analysis of the liquid fraction revealed a series of n-alkanes, alkenes, and fatty acids (Asomaning et al., 2014a). Noble metal-catalyzed deoxygenation of fatty acid methyl esters was also developed to improve the selectivity of carbon distribution (Meller et al., 2014; Santillan-Jimenez et al., 2014). Additionally, the mixture of biomass and plant oil was used in co-deoxy-liquefaction (Chen et al., 2011), and the results showed that the co-deoxy-liquefaction of soybean stalk and sunflower oil (4.4:1) could greatly increase the content of alkanes and decreased the content of phenols, leading to an increased HHV of the resultant oil in comparison with the product of the deoxy-liquefaction of biomass alone.

Herein, a synergetic deoxy reforming (SDR) process of cellulose and linoleic acid methyl ester (LAME, one representative aliphatic ester) is reported to prepare hydrocarbon-rich oil comprising alkanes, alkenes, and alkylbenzenes. The significance of the SDR is that the phenols found in the deoxy reforming of cellulose were replaced by alkylbenzenes in the resultant oil of the SDR technique, leading to higher HHV and energy density of the resultant hydrocarbon-rich oil. Quantum chemical calculations gave a deep insight into the SDR process of cellulose and LAME.

2. Methods

2.1. Materials

The cellulose used was purchased from Sigma–Aldrich. The commercial brand is Sigmacell cellulose type 20, which has an average particle size of ca. 20 μm and an average molecular weight of 36–40 kDa. The LAME with purity of 99 wt% was purchased from Aladdin Reagent (Shanghai) Co., Ltd. The soybean oil and corn oil used in this study were produced by Shandong Luhua Group Co., Ltd. (China). The soybean oil contains 16.6 wt% of saturated fat, 23.6 wt% of monounsaturated fat, and 59.7 wt% of polyunsaturated fat. The corn oil contains 15.0 wt% of saturated fat, 30.8 wt% of monounsaturated fat, and 54.1 wt% of polyunsaturated fat.

2.2. Experimental methods

The cellulose and LAME were loaded into an autoclave for the SDR process. The autoclave was heated using a resistance coil wrapping outside the autoclave, and the heating rate was controlled using a booster. The temperature and the pressure in the autoclave were monitored using a thermocouple and a pressure gauge. In a typical reaction, cellulose (3.5 g), LAME (0.7 g, 20 wt% of cellulose), and water (1.26 g, 30 wt% of cellulose) were put into the autoclave. The autoclave was heated up to 350 °C at a rate of 10 °C min^{-1}, and then kept for 20 min at this temperature. The pressure in the autoclave was in a range of 4–6 MPa. Finally, the autoclave was naturally cooled down to room temperature after turning off the heating. The organic phase companied with water was collected by distillation (from 100 to 450 °C), where the organic phase and the water automatically separated into two phases. Then the water was removed by a separation funnel, and the oil (denoted as $Oil_{0.2}$) was measured to be 0.66 g. The hydrocarbon-rich oils obtained from LAME and cellulose with other mass ratios (0:1, 0.1:1, 0.3:1, 0.4:1, 1:0) were also investigated. The organic phases were designated as Oil_0, $Oil_{0.1}$, $Oil_{0.3}$, $Oil_{0.4}$, Oil_1, respectively, and analyzed by gas chromatography–mass spectrometry (GC–MC). The yield (wt%) of the hydrocarbon-rich oil was calculated using the following formula:

$$\text{Yield} = \frac{W3}{W1 + W2} \times 100\%$$

where $W1$ is the weight of cellulose (g), $W2$ is the weight of LAME (g), and $W3$ is the weight of the liquid oil (g). For the SDR of cellulose and plant oils (corn oil or soybean oil), the mixtures of cellulose and plant oil with ratio of 0.2 were employed to investigate the oil composition and component distribution.

2.3. Characterization

2.3.1. GC–MS analysis of liquid samples

A TRACE GC Ultra Thermo gas chromatograph equipped with a DSQ mass spectrometer (GC–MS) was used for analyzing the organic phases (Nelson et al., 1984). A fused-quartz capillary column coated with TR-5MS was used as the stationary phase (30 m × 0.25 mm × 0.25 μm). The temperature of the oven was programmed with an initial temperature of 50 °C for 1 min, which was followed by heating up to 250 °C with a heating rate of 10 °C min^{-1}, and held for 10 min. The full scan spectra were obtained after a 2 min solvent delay. The compounds in the organic

Download English Version:

https://daneshyari.com/en/article/7074100

Download Persian Version:

https://daneshyari.com/article/7074100

Daneshyari.com