



Hydrodeoxygenation of angelica lactone dimers and trimers over silica-alumina supported nickel catalyst



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ARTICLE INFO

Article history:

Received 10 March 2015
Received in revised form
30 August 2015
Accepted 3 September 2015
Available online xxx

Keywords:

Angelica lactone
Levulinic acid
Di/trimerization
Biogasoline
Bifunctional catalyst

ABSTRACT

Fractionation of biomass to furan derivatives followed by hydrodeoxygenation could provide an efficient route for bioalkanes production. A simple catalytic process to obtain fuels rich in alkanes with 8–12 carbons via hydrodeoxygenation of biomass-derived angelica lactone dimers/trimers was investigated. Dimers and trimers obtained by C–C coupling of α - and β -angelica lactones were hydrodeoxygenated over a bifunctional catalyst, nickel supported on silica-alumina (Ni/SiO₂–Al₂O₃). Reaction conditions such as hydrogen pressure, temperature and time were considered and it was observed that changes in reaction conditions had significant effect on product distributions. Effective conversion of di/trimers of angelica lactone was achieved over Ni/SiO₂–Al₂O₃ with highly branched alkanes and aromatics being selectively produced. The hydrogenated products which are similar in composition to fossil-derived gasoline could further encourage research into more efficient processes to produce bioalkanes on an industrial scale.

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1. Introduction

The uncertainties surrounding fossil fuel have necessitated research into alternative sources such as nuclear power, hydro-power, and lignocellulosic biomass [1]. However, lignocellulosic biomass has been recognized as the only source of renewable fuel [2].

Lignocellulosic materials can be converted into a versatile organic compound, levulinic acid (LA; 4-oxopentanoic acid) via acid hydrolysis [3]. LA could be produced from microcrystalline cellulose (MCC), cotton, cornstalk, fructose, glucose and starch in the presence of a mineral acid, HCl with concomitant production of equimolar amount of formic acid [4]. Hydrogenation of levulinic acid produces γ -valerolactone, GVL, which can be used as a blending agent (10% v/v) in conventional gasoline [5] or as a co-solvent in splash blendable diesel fuel [6]. Alternatively, GVL can undergo decarboxylation to produce butene in the presence of an

acid catalyst (e.g. SiO₂/Al₂O₃). The butene produced can then be passed to the oligomerization reactor in the presence of Amberlyst or ZSM-5 to produce larger alkenes suitable as transportation fuels [7]. Xin and co-workers [8] also reported the production of high octane number gasoline from GVL. Recently, a range of linear alkanes suitable for use as transportation fuels has been produced from biomass of diverse functional groups [9]. Their approach was based on organocatalyzed aldol condensation of isolable furfuraldehyde-based derivatives under mild conditions to produce only linear alkanes with $n \geq 9$. However, most of the reports on C–C coupling reactions are carried out in the presence of organic solvent leading to difficulties in products separation.

Recently, our research groups discovered solvent-free C–C formation between angelica lactones (4-Hydroxy-3-pentenoic acid γ -lactone). Angelica lactones (ALs) could be produced by acid-dehydration of LA which itself could be derived from renewable source. Although ALs does not undergo aldol–condensation reaction to form ring structures of appropriate molecular weight for liquid fuel production because it does not possess an α -H atom. Alternatively, angelica lactone can undergo di/trimerization reaction to give a product with increased number

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of carbon atoms. This process was catalyzed by K_2CO_3 and the reaction completed within a short time (~5 min) [4]. The dimer and trimer produced were then hydrogenated over expensive metal catalyst (Pd/C) to mainly C_6 – C_{12} alkanes and aromatics. Thus, we have extended our studies on the use of cheap heterogeneous catalyst (Ni/SiO₂–Al₂O₃) for the production of bioalkanes and aromatics suitable for gasoline application through hydrodeoxygenation of angelica lactone dimer and trimer. The process yields organic stream which spontaneously separates from the aqueous phase. With the appropriate mix of reaction conditions such as hydrogen pressure, temperature and time; liquid products suitable for transportation fuels was obtained.

2. Experimentals

2.1. Materials and methods

α -angelica lactone (reagent grade) was supplied by Wuhan Chi-Fei Chemical Co. and used without further purification. K_2CO_3 (purity 99.0%) and acetone (purity 99.5%) were provided by Beijing Chemical Works, China. The commercial catalyst, nickel on silica-alumina (B.E.T surface area = 181.498 m²/g) was obtained from Alfa Aesar, China.

Di/trimerization of α -angelica lactone was carried out in a batch reactor heated with the aid of thermostatically controlled oil bath (± 273 K). Initially, 3 g of K_2CO_3 (3 wt.% of the feed) was crushed, dried at 393 K and added into the pre-heated (353 K) reactor containing 100 g of α -angelica lactone. The reaction proceeded for 5 min, cooled to room temperature to obtain a highly viscous liquid with the following compositions; dimers (65 wt.%), trimers (33 wt.%) and tetramer (2 wt.%). Since the di/trimers formed is stable in aqueous medium, lukewarm distilled water was used to extract the catalyst from the di/trimerized products.

Di/trimers of α -angelica lactone were hydrodeoxygenated in a stainless steel batch reactor (100 mL) capable of withstanding a high pressured reaction. The reactor was charged with the feed (5 g) and Ni/SiO₂–Al₂O₃ catalyst (0.25 g). The reactor was purged to remove any trapped air, followed by addition of H₂ to 10–50 bar, stirred at 1000 rpm and heated to 573–648 K for 12–30 h. The reactor pressure was maintained with additional H₂ until the completion of the reaction.

2.2. Product analyses

The liquid (organic) phase was analyzed using a gas chromatography (Agilent 6980N, USA) with a mass spectrometer and HP-5MS 5% phenyl methyl siloxane column (30 m \times 0.25 mm \times 0.25 μ m). The sample (0.2 μ L) was injected into the column and the initial oven temperature was set at 50 °C, holds for 2 min, then ramped at 5 °C/min until 165 °C, 15 °C/min to 250 °C and then finally hold for 4 min at 250 °C. N₂ (purity 99.999%) was used as carrier gas and product identification was done by comparing the spectra of the compounds with those in the NIST library.

Gas phase alkanes (C_1 – C_4) were analyzed using a GC (SP-6890, China) connected to a flame ionization detector (FID) and HP-PLOT column with N₂ (purity 99.99%) as the carrier gas while CO/CO₂ gases were detected with GC (SP-6890, China) with thermal conductivity detector (TCD) and TDX-01 column with Ar (purity 99.999%) as the carrier gas. The gas phase samples were obtained with a gas bag, injected into the GC with the appropriate column and were identified and quantified by comparing with known standards. The total carbon detected in the gaseous was less than 10% for all the experiments.

3. Results and discussion

3.1. Di/trimerization reaction

α -angelica lactone (molecular weight; 98.10 g mol⁻¹) can be constructed to yield higher molecular weighted compound by coupling of C–C bonds in the presence of K_2CO_3 [4].

The produced di/trimers contain 10–15 carbon numbers which are within a suitable range for biogasoline production. Building C–C linkages directly from smaller molecules to form larger molecules are of great importance in renewable energy parlance. Dumesic and his co-workers employed aldol–condensation reaction in building C–C bonds between HMF and acetone [10]. Also, Corma et al. [11] increased the carbon chain of 2-methylfuran, 2 MF by hydroxylalkylation/alkylation reaction. In our reaction, we found that the carbon atoms of α -angelica lactone can be increased from five to either ten (dimers) or fifteen (trimers).

The hypothesis of the reaction as illustrated by Zhang's group [4] showed that α -angelica lactone, derived by acid dehydration of levulinic acid, firstly isomerized to β -angelica lactone (BAL) in the presence of a basic catalyst, K_2CO_3 , and then C–C coupling occurred between the carbon terminal ends of β -angelica lactone to form products of not more than three furan moieties fused together. These di/trimers were of the appropriate molecular weight for hydrogenation reaction to produce hydrocarbons suitable as transportation fuels application [4]. During the construction of the di/trimers, the reaction was exothermic leading to evolution of CO₂. However, the carbon yield of this process is 100% because the reaction can be carried out in a closed vessel where the CO₂ produced can be sequestered appropriately [12]. Unlike the fermentation of glucose for bioethanol production, where the CO₂ produced is lost to the environment [13] leading to loss of carbon.

3.2. Hydrodeoxygenation of angelica lactone dimers and trimers

The conversion of angelica lactone di/trimers to the corresponding hydrocarbons by hydrodeoxygenation must proceed via the controlled rate of C–C and C–O bond cleavage [2,14,15]. It has been noted that high rates of C–O bond scission produce hydrocarbons [14], whereas C–C bond cleavage lead to the formation of CO, CO₂ and H₂ [14]. In addition, undesired reaction pathways such as dehydrogenation–hydrogenation leading to alcohols and dehydrogenation–rearrangement to form acids can take place in solution and on the support aided by metal catalyst [16]. These intermediates can then react in solution or on the catalyst to make more hydrocarbons. Hence good catalyst for the production of hydrocarbons by hydrodeoxygenation reactions must be highly active for C–O bond cleavage and less active for C–C bond scission.

Since angelica lactone di/trimers are composed of fused furan moieties, its conversion to alkanes proceeds via ring opening reaction. Under elevated pressure and temperature, ring opening of the furan moieties readily occur on an acid [17] while hydrogenation takes place on the metal surface [16]. Therefore, we varied the conditions that affect conversion of angelica lactone di/trimers to hydrocarbon over Ni/SiO₂–Al₂O₃.

3.2.1. Effect of H₂ pressure on product distributions and carbon selectivities

Table 1 and Fig. 1 show the carbon selectivities and product distribution in the organic phase for hydrodeoxygenation of angelica lactone di/trimers to fuel over Ni/SiO₂–Al₂O₃ catalyst respectively. At low pressure (10 bar), oxygenated species dominate while alkanes were not detected in the organic phase (Fig. 1A). On an acid site, ring opening followed by aromatization can occur even at atmospheric pressure [18]. This phenomenon was observed

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