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A novel process for the production and separation of heavier hydrocarbons from sorbitol-derived oil

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HIGHLIGHTS

- Production process for heavier hydrocarbons from sorbitol was developed.
- A novel separation process for eliminating 2-iodohexane byproduct with zinc powder was developed to get pure hydrocarbons.
- The reaction conditions for 2-iodohexane removal were studied and optimized.
- The obtained heavier hydrocarbons are mainly C_{12} and C_{18} hydrocarbons including alkanes, alkenes, and aromatics.
- The high heating value of the obtained heavier hydrocarbons is 43.5 MJ/kg, suitable for being used as transportation fuel.

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ABSTRACT

A novel process for the production and separation of heavier hydrocarbons from sorbitol-derived oil was studied. 2-Iodohexane, the by-product of the reduction of sorbitol into hydrocarbons, was successfully removed by transforming it into hexane and hexenes after reacting with zinc. The eliminating reaction was completed in 45 min at the conditions of: a zinc/2-iodohexane molar ratio of 6:1, a reaction temperature of 120 °C, and an agitation speed of 1200 rpm. The heavier hydrocarbons obtained were mainly C_{12} and C_{18} alkanes, alkenes, and aromatics, which have a water content of 0.1% and a high heating value of 43.5 MJ/kg. Other physico-chemical properties of the heavier hydrocarbons were characterized with GC–MS, FT-IR and ^1H NMR. The approach developed in this work for the production and purification of heavier hydrocarbons from sorbitol-derived oil is relatively simple yet promising, which we believe could possibly become a new way for the production of transportation fuels from biomass sources.

1. Introduction

As one of the top value-added chemicals from biomass, sorbitol has drawn a lot of attentions over the past decades because the utilization of biomass-derived sorbitol has great merits such as being renewable and abundance [1]. Sorbitol can be obtained from the hydrolysis of biomass accompanied by simultaneous hydrogenation [2–5], and can be used for the synthesis of isosorbide [6] and lactic acid [7]. It is also widely used in drugs, cosmetics, food, and toothpaste, etc. [8]. Meanwhile, as an important platform chemical, sorbitol can also be transformed into downstream products such as hydrogen or methane [9,10]. Most importantly, liquid fuels derived from sorbitol were renewable and considered as potential substitutes for the traditional petroleum-based fuels in view of the increasing depletion of fossil oil [11].

To convert sorbitol into liquid hydrocarbons, it is necessary to get rid of the oxygen it contains and transform its molecular structure. Currently, alcoholic dehydration and decarbonylation are the two most frequently used methods for sorbitol deoxygenation and transformation [12,13]. Huber et al. [14–16] demonstrated that alkanes can be generated from sorbitol via aqueous-phase reforming (APR) over Pt or Pd bifunctional catalysts at 225 °C under H_2 pressure of 3.9 MPa. The products were mainly C_9–C_{15} hydrocarbons. However, the separation of alkanes from the products mixture was a big challenge because many different compounds existed in the intermediates [17]. Zhang et al. [18,19] investigated the conversion of sorbitol into pentane and hexane over the Ni/HZSM-5 in the presence of hydrogen at 240 °C and 4.0 MPa. Although the catalyst used by them is cheaper than that by Huber, the generated C_5 and C_6 alkanes have lower boiling points than the heavier hydrocarbons, which are not safe for storage and transportation. Additionally, a large amount of hydrogen is consumed and an appreciable amount of water is generated in the process. Therefore, all the above mentioned conversion

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processes have their own limitations, and are not ideal for commercialization.

Robinson [20,21] proposed a new strategy for the production of hydrocarbons from biomass-derived polyols such as sorbitol. In his work, polyols were reduced into hydrocarbons and halocarbons via reaction with hydroiodic acid under a co-reducing agent such as phosphorous acid, which simultaneously reduced I_2 back to HI. To overcome the drawbacks of dealing with phosphate wastes from HI regeneration, Robinson further developed a system in which metal ions were capable of converting I_2 back to HI [22,23]. The method developed by Robinson was considered highly innovative and economical because the reaction took place at relatively mild conditions that did not need any precious metal catalysts and is under atmospheric pressure.

Inspired by Robinson's work, the authors of this paper developed a similar process to produce hydrocarbons from sorbitol. The details of the process were already reported in our previous work [24], in which the effects of reaction conditions (molar ratio of reactants, water content, and reaction time) on the yield and selectivity of hydrocarbons were investigated, and the possible reaction mechanisms were proposed for the sorbitol transformation. However, the separation of the heavier hydrocarbons from the generated products mixture and the characterization of the intermediates and final products have not yet been studied in detail. Therefore, more work in this area is needed. The present study will focus on the separation and purification of the heavier hydrocarbons from the mixture of sorbitol-derived oil (which is generated by reducing sorbitol with hydroiodic acid). According to the literature [25], iodoalkane can be removed via a reaction with alkali in an alcohol solution, but this method requires additional steps such as extraction and distillation after reacting with alcohol, making it not suitable for sorbitol-derived oil, because alcohol (if used) is soluble with hydrocarbons and has a boiling point similar to those of C_6 hydrocarbons or C_{12}, C_{18} hydrocarbons. Thus, other more effective methods need to be explored.

In this work, a novel process for the separation of heavier hydrocarbons from the sorbitol-derived oil (crude oil) was presented. Specifically, 2-iodohexane, the by-product of the reduction of sorbitol with HI, was eliminated from the heavier hydrocarbons by transforming it into hexane and hexenes via reaction with zinc, and the effects of the zinc/2-iodohexane molar ratio, temperature, agitation speed, and reaction time on separation efficiency were studied. Additionally, the composition and structure of the heavier hydrocarbons were characterized with GC–MS, FT-IR, and ^{1}H NMR. Finally, the physico-chemical properties of the hydrocarbons obtained were measured and compared. It is hoped that this work will be able to provide further theoretical basis for future applications of this innovative approach, so that liquid hydrocarbons can be produced from the biomass-derived polyols in a much cheaper, more effective, and cleaner way.

2. Experimental

2.1. Materials

Sorbitol was obtained from Aladdin Chemistry Co., Ltd, Shanghai, China. The other chemicals used, such as phosphorous acid, hydroiodic acid, dichloromethane, and zinc powder, were bought from Sinopharm Chemical Reagent Co., Ltd, Shanghai, China. All chemicals were used as received.

2.2. Methods

2.2.1. Preparation and separation of heavier hydrocarbons

The procedure for the preparation and separation of heavier hydrocarbons includes the following steps: (1) conversion of sorbitol into crude oil; (2) separation of the heavier hydrocarbons from the crude oil; and (3) purification of the heavier hydrocarbons. The details of the conversion of sorbitol into crude oil have already been elaborated on in our previous work [24]. Therefore, this work will focus on the second and third steps, that is, the separation and purification of heavier hydrocarbons from the sorbitol-derived oil (crude oil). To achieve this goal, the crude oil, which is the oil phase separated from the mixture of sorbitol reduction, was mixed with a metal powder (preferably zinc) and stirred with a magnetic stirrer in a 100 mL flask for a certain amount of time at a specific temperature. With such a treatment, 2-iodoalkane, which is the by-product of the reduction of sorbitol, was thus converted into C_6 alkenes. Then, dichloromethane was added to the mixture to extract hydrocarbons, followed by filtration to get rid of the solid zinc. The dichloromethane layer was then distilled in a rotary evaporator at the conditions of 20 °C and 0.05 MPa to recover the dichloromethane. Finally, vacuum distillation was used to separate the C_6 alkenes from the heavier hydrocarbons (C_{12}, C_{18}) at the conditions of 20 °C and 0.02 MPa. The detailed schematic of the separation is shown in Fig. 1.

2.2.2. Analysis

The products were characterized with a programmable GC–MS QP2010 from Shimadzu, which is equipped with an Rxi®-5 ms capillary column (5% diphenyl/95% dimethyl polysiloxane, 30 m × 0.25 μm × 0.25 mm) and a quadruple MS detector. Helium was used as the carrier gas at a flow rate of 1 mL/min. The column temperature was initially maintained at 30 °C for 4 min, then increased to 220 °C at a heating rate of 5 °C/min, and finally increased to 270 °C at a heating rate of 10 °C/min. The column continued to run at 270 °C for 3 min. The split ratio was 100:1, and the solvent delay time was 2.2 min. The mass of 2-iodohexane was determined

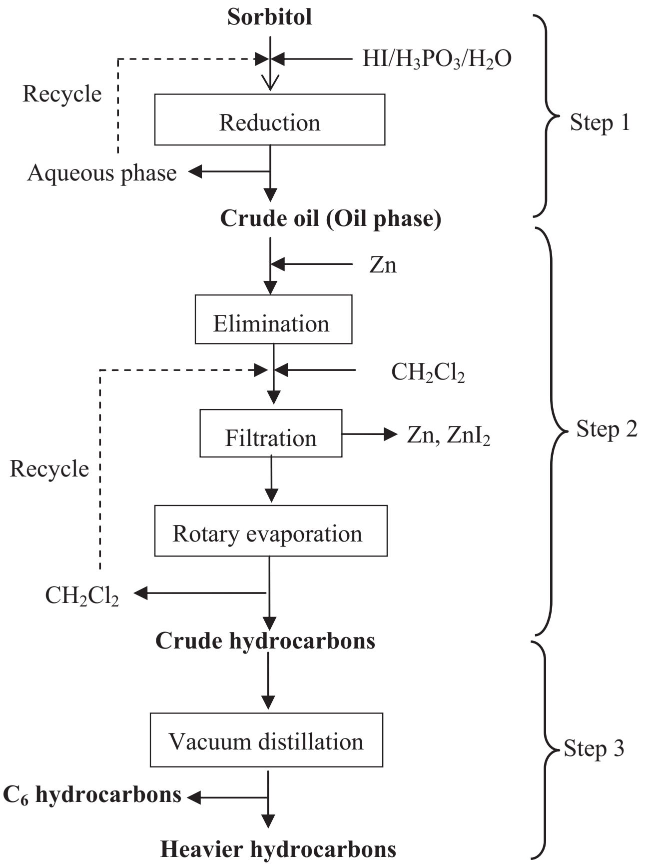

Fig. 1. Schematic for the production and purification of heavier hydrocarbons.