Green Process without Thinning Agents for Preparing Sebacic Acid via Solid-Phase Cleavage

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ABSTRACT: A green and environmentally friendly route of no thinning agent was designed to prepare sebacic acid. Sodium ricinoleate was selected as the raw material to carry out solid-phase cleavage in a tubular furnace. The reaction parameters including catalyst, ratio of sodium ricinoleate/KOH, reaction time, reaction temperature, and absolute pressure were optimized to obtain a high yield of sebacic acid. A satisfactory yield (70.2%) of sebacic acid was received in the presence of 1% catalyst (Fe₂O₃) by weight (w/w), with 5:4 (w/w) ratio of sodium ricinoleate/KOH at 543 K under the absolute pressure of 0.09 MPa in 60 min. Sebacic acid was identified by gas chromatography analysis, and the purity (98.1%) of the product was further assessed by its melting point (306.3 K). Alkaline enhancement generates a better cracking effect. The yield of sebacic acid can be improved by a certain absolute pressure as a result of avoiding oxidation of sodium ricinoleate as well as reducing the residence time of hydrogen.

INTRODUCTION

Castor oil is a fatty oil obtained by extracting and refining from the mature seeds of the castor plant (Ricinus communis L.). Due to high content of ricinoleic acid, it is used in a variety of applications including medicine, chemicals industry, and other technologies. Alkali fusion is one of the unit processes involved in converting castor oil to chemical intermediates with 8–10 carbon atoms. Sebacic acid (C₁₀H₁₈O₄) is the main product of alkali fusion. As a saturated aliphatic dicarboxylic acid containing ten carbon atoms, with the chemical similarity of saturated dibasic acid, this important chemical raw material⁹ has been widely used in producing higher-temperature-resistant lubricant, high-temperature lubricating oil such as isopropyl sebacate, artificial perfume such as diethyl sebacate, high-quality engineering plastics such as nylon-610, and biodegradable polyesters for the medical industry.¹⁰–¹⁴

Sebacic acid remained the highest castor oil derivatives consumed in 2015 and held more than 20% of the global market revenue. China is a major producer of sebacic acid, and the production capacity of sebacic acid in some Chinese factories including Hebei Kaide Biomaterials Co., Ltd. and Hebei Hengshui Jinghua Chemical Co., Ltd. has reached over 40 000 tons per year. They produce sebacic acid by alkali fusion of castor oil in a tank reactor using phenol as a thinning agent, which is detrimental to the environment and hard to be separated. Although many new methods to prepare sebacic acid have been developed recently, including microwave-induced and electrolytic adipic acid, these are too difficult to apply to large-scale industrial production. Therefore, the improvement of the cracking process is particularly important.

Different reactions occur as temperature changes, which is accomplished with NaOH or KOH at elevated temperatures and in the presence of catalysts to split the ricinoleate molecule in either a batch or a continuous process. For example, upon heating at 523 K in the presence of NaOH, sebacic acid is produced. To explain the reaction, a detailed reaction mechanism has been proposed (Figure 1). In this reaction, because alkaline soaps resulting from alkali fusion are relatively hard, poor heat conductors, and practically impossible to be mixed by mechanical agitation, it is common practice to carry out the cracking process in the presence of a thinning agent. Logan et al. used certain isocarboxylic acids, isoaldehydeys, and isoalcohols as thinning agents in the alkali fusion of ricinoleic acid. Dou et al. obtained sebacic acid by using a multicomponent acid diluent containing more than two types of organic C₇−C₁₄ acids. In addition, mineral oils have been used by Shen as thinning agents.

Splitting decomposition can be carried out in a tubular furnace. Compared with liquid-phase cleavage in a tank reactor, tubular furnace can be used for the solid-phase cleavage to avoid the addition of thinning agent, which generates better effect of heat preservation, higher uniformity of temperature, and higher heat efficiency caused by larger heat transfer per unit volume as a result, temperature can be controlled precisely and stably in the tubular furnace. So, a green reaction without the thinning agent for preparing sebacic acid by solid-phase cleavage was carried out in the tubular furnace.
The present study aims at designing a green process without a thinning agent for obtaining a high yield of sebacic acid and, simultaneously, investigating and optimizing reaction parameters of solid-phase cleavage including catalyst, ratio of sodium ricinoleate/KOH, reaction temperature, reaction time, and absolute pressure. Furthermore, the effect of alkaline strength on yield is also explored.

**RESULTS AND DISCUSSION**

**Calculation of Theoretical Yield of Sebacic Acid.** Ricinoleic acid (82.8 wt %) was determined as the main fatty acid component of castor oil by gas chromatography (GC) analysis. Hence, after saponification, sodium ricinoleate (82.8 wt %) was determined as the main content of saponified castor oil. Theoretical yield of sebacic acid was calculated according to the reaction mechanism (Figure 1) using the relative percent of sodium ricinoleate content of the saponified oil.

**Reaction Parameters of Solid-Phase Cleavage.** The function of a catalyst is to oxidize the aldehyde of decanoic acid to form more sebacic acid, thereby inhibiting the formation of 10-hydroxydecanoic acid. Catalysts with different oxidizabilities were selected to investigate their effect on the yield of sebacic acid.

Table 1 shows the effect of different catalysts on the yield of sebacic acid using KOH/sodium ricinoleate in the ratio of 5:4 at 563 K under 0.09 MPa absolute pressure in 60 min. As seen in Table 1, metal oxides of high chemical valence such as Pb3O4 generate better catalytic effect than the inferior counterparts such as CuO. Although the color value of the product can be increased by the bleaching effect of ZnO, a yield of just 62.2% was obtained. Cu2O, as a metal oxide of intermediate valence, has both oxidizability and reductibility and was mainly used for absorbing hydrogen instead of catalyzing, thereby promoting the chemical equilibrium transfer in the direction of forming sebacic acid. The reaction
processed in a certain absolute pressure; hydrogen, once generated, was extracted by the pump immediately, and there was no obvious influence of adding Cu2O on the yield. Although a higher yield of sebacic acid can be obtained by using PbO2 compared with Fe2O3 under the same cracking condition, the improvement is limited. Compared with Fe, Pb is a highly polluting heavy metal. Hence, Fe2O3, an environmentally friendly and nontoxic oxide, is determined as the environmentally friendly catalyst with satisfactory catalytic performance. As the oxidizability of the catalyst increased, the yield of the final product was improved. Fe2O3 was considered to be the most optimum catalyst.

According to Table 1, the yield was influenced by different additive amount of Fe2O3. The yield of sebacic acid was improved obviously with the increase of additive amount and reached the peak at 1%, beyond which the yield nearly remained stable (1.5 and 2%). Therefore, the most suitable ratio of Fe2O3 was determined (1%).

The results represented in Table 2 show the effect of sodium ricinoleate/alkali ratio on the yield of sebacic acid in the presence of 1% Fe2O3 at 563 K under 0.09 MPa absolute pressure. As presented in Table 3, 17.7% increase of sebacic acid was observed with the increase of reaction time from 30 to 60 min because the reactants cannot be completely pyrolyzed over a short period. The obtained result showed that 60 min is the optimum reaction time, beyond which the yield of sebacic acid gradually decreases, which may be attributed to the degradation and volatilization of sebacic acid. Larger heat transfer area of tubular furnace ensures a higher heat efficiency, which makes reactants to react rapidly. Heat loss is avoided because of better air tightness under vacuum system and no need of stirring. Hence, tubular furnace has a better temperature-controlling system compared with tank reactor, ensuring the stability of the reaction. Because of higher heat efficiency and better heat transfer, reaction time is reduced dramatically. The extension of reaction time causes the mass formation of various side-products. Therefore, controlling the reaction time is quite necessary to obtain a high yield of sebacic acid.

Reaction temperature has an important influence on the yield of sebacic acid because different reactions occur in different temperature ranges. Table 4 shows the effect of reaction temperature using sodium ricinoleate/KOH ratio of 5:4, 1% Fe2O3, 0.09 MPa absolute pressure, and 60 min reaction time. Low reaction temperature such as 513 K cannot obtain a high yield of sebacic acid due to the formation of large amount of side product (10-hydroxydecanoic acid). The yield of sebacic acid increased rapidly with the increase of reaction temperature up to 543 K and changed little at a further increase of 20 K. With the increase of temperature to 593 K, the yield of the final product decreased to some extent. Charred and polymerized oil molecules are the possible reasons for the decreased yield. Therefore, the most suitable reaction temperature was determined to be 543 K.

To further explore the effect of oxygen on the yield of sebacic acid, solid-phase cleavage was carried out on the ratio of sodium ricinoleate/KOH of 5:4 in the presence of 1% Fe2O3 at 543 K under standard atmosphere for 60 min; the yield was 61.1% of the theoretical value. As shown in Table 5, compared with that, adding 1% antioxidant MD-1024 at the same condition results in an obvious decrease of 7.7%. Air is inevitably left in the furnace. The larger the amount of heat needed for heating this air, the lower is the furnace efficiency; this results in a decrease of yield. Double bonds in sodium

### Table 2. Effect of Sodium Ricinoleate/Alkali Ratio

| alkali | sodium ricinoleate/alkali (g/g) | % of theoretical yield sebacic acid | temperature (K) | % of the theoretical yield sebacic acid |
|--------|-------------------------------|-------------------------------------|----------------|----------------------------------------|
| KOH    | 5:5                           | 66.9                                | 513            | 29.3                                   |
|        | 5:4                           | 68.8                                | 543            | 70.2                                   |
|        | 5:3                           | 44.6                                | 563            | 68.8                                   |
|        | 5:2                           | 18.6                                | 593            | 58.9                                   |
| NaOH   | 5:4                           | 52.1                                |                |                                        |

### Table 3. Effect of Reaction Time

| time (min) | % of the theoretical yield sebacic acid | absolute pressure (MPa) | antioxidant | % of the theoretical yield sebacic acid |
|------------|-----------------------------------------|--------------------------|-------------|----------------------------------------|
| 30         | 51.1                                    | 0                        | MD-1024     | 61.1                                   |
| 45         | 58.5                                    | 0.03                     | 1%          | 68.8                                   |
| 60         | 68.8                                    | 0.06                     | 1%          | 69.6                                   |
| 90         | 68.4                                    | 0.09                     | 1%          | 70.2                                   |
| 120        | 58.8                                    |                          |             |                                        |
ricinoleate (C═O and C═C) are easily oxidized by residual oxygen in the tubular furnace, especially when the temperature rises, and this circumstance can be prevented by adding antioxidant or vacuum system. Since the addition of antioxidant may cause an adverse effect on the quality of sebacic acid, vacuum environment is a better choice. The experiment concerning different absolute pressures was carried out on the ratio of sodium ricinoleate/KOH of 4:5 in the presence of 1% Fe₂O₃ at 543 K in 60 min. As presented in Table 5, with the increase of the absolute pressure, the yield of sebacic acid improved from 68.5% (0.03 MPa) to 70.2% (0.09 MPa). From Figure 1, after retro-aldol fission, C-10 aldehyde can either react with hydrogen to form 10-hydroxydecanoic acid or form sebacic acid under the action of excessive alkali. As the absolute pressure increases, the residence time of hydrogen is shortened because hydrogen generated by dehydrogenation of sodium ricinoleate is removed by the vacuum pump in time, which inhibits the formation of the side product 10-hydroxydecanoic acid, thereby promoting the reaction to proceed in the desirable direction.

Identification and Characterization. Sebacic acid was confirmed by GC analysis, affording the purity of 98.1%. High purity of sebacic acid was further assessed by its melting point (306.3 K).

CONCLUSIONS

The present study establishes a process of solid-phase cleavage without thinning agents to prepare sebacic acid using sodium ricinoleate and KOH as raw materials, Fe₂O₃ as catalyst, and tubular furnace as reactor. It is concluded that the optimum conditions for cracking are 5:4 ratio of sodium ricinoleate/KOH and 1% Fe₂O₃ at 543 K reaction temperature under 0.09 MPa absolute pressure and 60 min reaction time; this result in sebacic acid of 70.2% yield with 98.1% purity.

Sodium ricinoleate was selected as the raw material to replace other oleochemicals such as castor oil or ricinoleate acid because of its different physical property (solid at room temperature); this enables reactants (sodium ricinoleate, alkali and catalyst) to be ground into powder and premixed sufficiently to process solid-phase cleavage, thereby avoiding using thinning agents. However, in this process, the heat transfer is restricted to some extent, which means that the yield of sebacic acid cannot be improved further.

Several common metal oxides were used as catalysts, compared with Pb₃O₄, Fe₂O₃ was determined as a catalyst not only for high catalytic efficiency but also for its nontoxicity, ensuring that the entire route is environmentally friendly. Alkali plays an important part in the cracking reaction, and potassium hydrate generates better effect on yield than sodium hydrate due to stronger alkalinity. The reaction time was accelerated due to higher heat efficiency of tubular furnace. The yield of sebacic acid is further increased in the vacuum system, since the oxidation of sodium ricinoleate is avoided. Different absolute pressure experiments show that the process is influenced by the residence time of hydrogen, removing H₂ in time is beneficial for the formation of sebacic acid.

EXPERIMENTAL SECTION

Materials. Castor oil was purchased from Tian Xing biotechnology Co., Ltd (Shandong, China) and saponification castor oil was used in experiments. NaOH and KOH were purchased from Bodi chemical engineering Co., Ltd (Tianjin, China). Antioxidant MD-1024 was purchased from Bailingwei Technology Co., Ltd. (Beijing, China). All catalysts were purchased from Zhiyuan chemical reagent Co., Ltd (Tianjin, China). All chemicals used were of analytical grade.

Pyrolysis of Sodium Ricinoleate. Castor oil was presaponification with triple molar amount of NaOH to prepare sodium ricinoleate. Sodium ricinoleate, KOH (5:2, 5:3, 5:4, 5:5; sodium ricinoleate/alkali (w/w)), and catalyst such as Fe₂O₃ (0, 0.5, 1, 1.5%) were ground into powder. To prevent quartz (silicon dioxide) from reacting with alkali, a homemade cylindrical hollow sleeve of stainless steel (32 cm H × 3.2 cm D) was inserted in the quartz tube of tubular furnace (GL-1200-3, Si Yang precision equipment Co., Ltd) in which the reactants were placed. Two ends of tubular furnace were connected to the water spray device and the condensation recovery device, respectively. The vacuum pump was turned on before the furnace was heated up. The temperature of the tubular furnace was increased from room temperature to 373 K and maintained for 10 min to preheat the reactants and then rapidly reached the reaction temperature in 5 min. Superheated water steam of 453 K was ejected into the tubular furnace at a material flow of 0.5 g/min when reached reaction temperature, and lasting for the whole cracking process. Different reaction temperatures (513–593 K), reaction times (30–120 min), and absolute pressures (0.03–0.09 MPa) were set up to investigate the optimal parameters. After the reaction, the solid production was maintained in the stainless steel sleeve, 2-octanol and excessive H₂O were recovered by condensation, and a small amount of H₂ was evacuated by vacuum pump. The cracking setup is shown in Figure 2.

Separation of Sebacic Acid. The solid product was diluted with hot water in a glass container and acidified to pH 6.0 with 3 mol/L H₂SO₄, some insoluble monosodium salt of fatty acid suspended in the upper layer of the solution, and precipitated 10-hydroxydecanoic acid. After separation and filtration, the remaining solution was first decolorized by activated carbon and then acidified to pH 2.0 using 3 mol/L H₂SO₄. On the one hand, solid product was precipitated at the
bottom of the container, recovered by filtration, and dried in an air-dry oven at 353 K for 12 h to obtain the final sebacic acid. On the other hand, sulfate, the main content of the filtrate, is collected by distillation. The flow chart is shown in Figure 3.

Characterization of Castor Oil and Sebacic Acid. Fatty acid composition of castor oil was determined by gas chromatography (GC-9800, Shanghai Kechuang chromato-graphic instrument Co., Ltd.) of fatty acid methyl esters prepared according to the AOAC method. An CBP capillary column (50 m × 0.25 mm i.d., 0.25 μm film thickness) was used with nitrogen as a carrier gas (1.0 mL/min). The injection temperature was 553 K, the column temperature was started at 393 K and programmed to 513 K at a rate of 5 K/min, and the detector temperature was 553 K. High purity of sebacic acid was further confirmed by its melting point.

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Notes
The authors declare no competing financial interest.

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