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An integrated approach for obtaining biodiesel, sterols, gossypol, and raffinose from cottonseed on a biorefinery concept

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ABSTRACT

This study outlined an integrated approach for obtaining several products, such as biodiesel, gossypol, sterols, raffinose, and nontoxic cottonseed meal from cottonseed via modified two-phase extraction (TPE), supercritical methanol transesterification and other technologies. The modified TPE could not only simplify the steps of separating substances, but also improve the quality of cottonseed oil and cottonseed meal. The suitable conditions of modified TPE were as follows: the petroleum ether/methanol volume ratio of 1:3, the extraction temperature of 40 °C, and the extraction time of 20 min. The supercritical methanol transesterification had a favorable yield of biodiesel with shorter time. The conversion of cottonseed oil was up to 97.5% with the temperature of 270 °C, the molar ratio of methanol to oil of 40, and a reaction time of 40 min at 10 MPa. Meanwhile, with the suitable conditions, the purity of the obtained gossypol, sterols and raffinose could be got to 92.1%, 89.8% and 94.2%, respectively. This integrated biorefinery could be useful for comprehensive development and utilization of cottonseed with fewer steps and lower cost.

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1. Introduction

Nowadays, with the rapid increase of world's energy consumption and concerns about environmental pollution, some useful measures have been taken to improve the conditions of the world energy crisis and environment problems. On one hand, new and renewable resources of energy should be explored, such as geothermal energy, solar energy, wind energy and biological energy. On the other hand, biomass, as an interesting alternative and renewable energy sources, can be stored and converted to energy on-demand. Biomass includes virgin wood, energy crops, agricultural residues, food waste, industrial waste and co-products. It is considered that a lower-carbon recycling society can be established to mitigate global warming, because the carbon dioxide released into atmosphere by using biomass is recovered again by growth of new biomass. Biomass has attracted significant attention as feedstocks for industrial production, addressing not only the non-energy sector but also the energy needs. Since the price of food

has been pushed up for the competition between energy and food crops, the inedible biomass resources such as cottonseeds, castor seeds should be developed and utilized in a rational manner.

Cottonseeds as by-products of the cotton contain a lot of useful substances, such as cottonseed meal, cottonseed oil, gossypol [1,2], raffinose [3], sterols, flavonoid [4], tocopherols [5] and other trace substances which are of great interest as high value-added products because of their bioactivities. Cottonseed meal, as a protein source, is only slightly inferior to soybean [6], and part of it is used to feed livestock and poultry. Gossypol has been used as a male oral contraceptive in China, and it also has antimalarial and proapoptotic properties [7], additionally, it can inhibit the replication of HIV-1 virus [8]. However, the gossypol molecule contains 6 hydroxyl and 2 aldehyde groups which easily react with other chemicals. Gossypol acetic acid, contains an equimolar ratio of gossypol and acetic acid, is more stable than gossypol. Furthermore, the antifertility activity of gossypol acetic acid is not less than that of gossypol [9]. Raffinose is beneficial for protecting against colonic diseases such as ulcerative colitis, colon cancer [10,11]. Raffinose also has been used as a pharmaceutically acceptable carrier or stabilizer for pharmaceuticals and biopharmaceuticals [12]. Tocopherols, widely used as an inexpensive antioxidant in cosmetics and foods, can alleviate oxidative stress and defend the body by quenching free radicals. Furthermore, tocopherols are also good for

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preventing cancer, coronary heart disease and other diseases [13,14]. Cotton oil can be used in both food industry and biodiesel production [5,6].

It is considered that the biorefinery is an integrated system and a sustainable process to produce a spectrum of bio-based products (chemicals, materials, food and feed) and energy (biofuels, power, heat) from biomass [15]. The biorefinery concept is similar to the traditional petroleum refinery, which produces multiple fuels and products from petroleum. A biorefinery takes advantage of various components in biomass and maximizes the value derived from the biomass feedstock. Furthermore, it should be feasible not only from the perspective of energy, but also from the points of view of economy and environment [16].

Biodiesel, an environmentally friendly and renewable diesel fuel, can be prepared from vegetable oils [17], waste oil [18] and other fats by extraction–transesterification, hydrolysis–esterification, direct methanolysis–transesterification or some other methods. Biodiesel is also regarded as one of the most promising alternatives fuel for the automobile [19]. The traditional method of biodiesel production from plant seeds includes oil extraction, oil refining, transesterification with catalysts and the purification of biodiesel [20]. However, there are some disadvantages in the traditional method of production. On one hand, more than 70% of the total biodiesel production costs are used in the multiple process of oil purification [21]. On the other hand, this kind of production can produce some by-products due to the presence of water and alkali catalyst, which would cause a lot of complication in the separation of biodiesel and glycerin [22]. To sum up, most of the existing biodiesel are currently produced in a single production chain and not within a biorefinery concept. And their exploitation is thereby limited. Therefore, a biorefinery processing which can lead to better energy, environmental and economic performances are needed.

So far, there are some studies on the subject of obtaining one or two substances from the cottonseeds. Bhattacharjee et al. [23] investigated the optimum conditions of pressure (550 bar), temperature (70–80 °C) and extraction time (2–3 h) to obtain the maximum oil yield with minimum gossypol by supercritical carbon dioxide technology. Dowd and Pelitire [24] recovered gossypol from cottonseed soapstock by a single recrystallization with the yield of gossypol acetic acid product of 99%, and the recovery of 58%. Qian et al. [6] obtained biodiesel and nontoxic cottonseed meal by in-situ alkaline transesterification. In the previous study [5], it had ever suggested that raffinose, gossypol, biodiesel and tocopherols could be obtained from cottonseed by two-phase extraction. The two-phase system (TPS) consisted of petroleum ether and a polar solvent phase (containing methanol, water, citric acid and ascorbic acid). According to the rule of similarity, cottonseed oil and other non-polar substances could be dissolved in petroleum ether, while methanol phase was beneficial for dissolving the raffinose, gossypol and others. Therefore, this TPS could not only improve the quality of cottonseed oil and meal, but also simplify the steps of separation these substances. However, there was not any detailed information for specifying how to purify these products, furthermore, the two-phase extraction could also be modified by ultrasound-assisted to reduce the extraction time. In conclusion, few studies which were focused on how to take a holistic approach to development and utilization in the biorefinery of cottonseeds resources have been appeared in the literature.

There are two aims in this study. Firstly, to extend an approach for getting several products from cottonseeds through a modified two-phase extraction process, supercritical methanol transesterification, recrystallization and other technologies. Secondly, to describe the emerging biorefinery concept through an overview of cottonseeds, technological processes and final products.

2. Materials and methods

2.1. Materials

Cottonseeds were obtained from Yancheng Jiangsu Province (Jiangsu, China). They were milled into powders by an electric grinder and sifted through a 60 mesh screen sieve to obtain particulates with particle sizes less than 0.3 mm. According to the ISO 659-1988 and GB/T 14489.1-2008/ISO 665:2000, the oil and the moisture content of the milled cottonseed were 32.2% (wet basis) and 6.9 wt%, respectively.

Methanol (>98%) and petroleum ether (60–90 °C) were purchased from Nanjing Huaqingnanfang Chemical Ltd. (Nanjing, China). The critical temperature, pressure and density of methanol were 239.4 °C, 8.09 MPa, and 0.27 g/cm³, respectively. Stigmasterol, raffinose, and gossypol of analytical reagent grade were purchased from Shanghai Aladdin Reagent Co., Ltd. (Shanghai, China). Methanol and acetonitrile of HPLC grade were purchased from Shandong Yuwang Chemical Ltd. (Shandong, China). The water used as the mobile phase of HPLC to determine the content of raffinose was purchased from Wahaha Company. All other chemicals used during this experiment were analytical reagent (AR) grade.

2.2. Method

The design process was comprised of several sections, including modified two-phase extraction, supercritical methanol transesterification, recovery of sterols by solvent crystallization, separation of raffinose and gossypol. The flow chart for the operations was summarized in Fig. 1. As shown in Fig. 1, the cottonseed meal was subjected by the TPS with ultrasound-assisted. After vacuum filtration, the obtained solution was divided into two layers by gravitation. The upper layer was used to obtain sterols, biodiesel and glycerin, while gossypol and raffinose could be got from the lower phase with several operation steps. The detailed experimental procedures were expanded in the following subsections.

2.2.1. Modified two-phase extraction

Extraction process with integrating high intensity ultrasound could enhance the molecular movement of solvent and sample, shortens extraction time and improves efficiency of extracting targeted produces. Ultrasound cavitation could prompt the diffusion of solvent to the cell because of the mechanical activity of the sound waves [25]. And this technology had been widely used in the chemical, pharmaceutical and food industries [26].

Cottonseed meal (50 g) was mixed with TPS. The mixtures were added to a 500 mL four-necked round-bottom flask, which was equipped with a thermostat, a reflux condense, a mechanical stirrer and a nitrogen duct which could prevent oxidation during the process. The flask was placed into an ultrasound water bath (UP3200HE, 40 KHz, 100 W) preheated to the set temperature before extraction, and then the stirrer was set at 600 rpm to make a good contact between the cottonseed meal and TPS. After certain minutes, the mixture was vacuum-filtered by a Buchner funnel, and the filter cake was washed with 25 ml of petroleum ether and 25 ml of methanol, respectively. The filtrate was transferred into a separatory funnel and divided into two layers. The lower layer was the methanol phase, which contained gossypol, raffinose, methanol, and other components. The excess methanol was recovered by a vacuum rotary evaporator. The upper layer included petroleum ether, vitamin E, cottonseed oil (triacylglycerols TAGs) and some others.

2.2.2. Supercritical methanol reaction

After two-phase extraction with ultrasound-assisted, the upper layer was evaporated under vacuum 40 °C to recover excess

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