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Congeneration biodiesel, ricinine and nontoxic meal from castor seed

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ABSTRACT

Castor seed, as non-edible energy oilseed, was used to obtain several products, such as biodiesel, ricinine, and non-toxic castor seed meal through ultrasonic-assisted two-phase extraction (UATPE), alkaline transesterification, and recrystallization. The products with higher quality could be obtained by UATPE in shorter extraction time. The optimum conditions for UATPE were as follows: the extraction time of 60 min, the corresponding temperature of 55 °C, the ratio of castor seed meal, petroleum ether and deionized water was 1:4:6 (mg/mL/mL). Castor oil which was obtained by UATPE was used to produce the biodiesel. And the yield of biodiesel could come up to 95.7% with the temperature of 60 °C, the molar ratio of methanol to oil of 7:1, the amount of the catalyst of 0.7%, and the reaction time of 60 min. Meanwhile, with the trichrolomethanol as re-extraction agent, and ethanol as the recrystallization agent, the purity and recovery of the ricinine could be got to 97.7% and 93.8%, respectively. In addition, the structural characterizations of the obtained ricinine and biodiesel were carried out by UV, FITR, ESI-MS and other analytical methods.

1. Introduction

The growing awareness of world's energy crisis and environmental pollution had stimulated people to explore renewable resources of energy, and to take a holistic approach for development and utilization inedible biomass resource, such as cottonseed [1], castor seed, jatropha. Castor, as one of the most important non-edible oilseed crops, was mainly cultivated in India, Brazil and China [2]. Castor seed contained castor oil, protein and several undesirable substances such as ricinine, allergen and ricin. Castor oil was hydroxyl oil which had widespread application in the industry, such as biodiesel production, food, bio-lubricant, pharmaceuticals, cosmetics, and plastics. Castor seed meal would be a significant source of high protein if there were not any toxic components—ricinine, ricin and allergen. Therefore, it was necessary for castor seed to reduce ricinine to a permissible level at which castor seed meal could be used as animal protein feed resources. Ricinine, as a poisonous alkaloid, which was derived from castor could cause nausea, emesis, and even death of animals. Although ricinine was toxic, it was the important natural active ingredients of castor meal. It exhibited significant biological activities, such as insecticidal action, analgesic action, hepatoprotective action and the central nervous excitatory action [2]. Furthermore, it might be useful for the treatment of human amnesias [3], and it could perform its bioactivities to against some insect pests efficiently and environment-friendly. To sum up, castor seed was very useful, and it was necessary to exploit and utilize castor seed resources extensively and rationally.

Biodiesel, as a part of substitute for petroleum-based diesel fuel, was a biodegradable, clean, renewable and nontoxic diesel fuel which was usually made from vegetable oils, animal fats [4], waste cooking oil [5–8], and microalgae [9,10]. Biodiesel production from edible vegetable oil had a negative effect of its high cost of the feedstock. Therefore, non-edible vegetable oil as the raw material could be benefit for the biodiesel production. Castor oil was typical non-edible oil with a lot of advantages such as short growing duration, low planting cost, large planting area, and good yields [11,12]. In addition, castor oil as the major ingredient of castor seed, was better soluble in both methanol and fatty methyl esters than other non-edibles, therefore, it was benefit for biodiesel production [13]. In a word, castor oil was the good choice as the feedstock of biodiesel production.

So far, there had been several studies on the subject of obtaining biodiesel or ricinine from the castor [14–17]. Most of them focused on the effects of catalyst, reaction temperature and pressure, reaction time, and separation on the biodiesel or ricinine production from castor oil. Although the integrated production of some useful substances from castor plant was not a new topic [18,19], a holistic

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approach on how to obtain biodiesel as well as ricinine from castor seed had not been found in the literature. Therefore, the aim of this study was to obtain biodiesel, ricinine and nontoxic castor seed meal from castor bean through several simple procedures, such as ultrasonic-assisted two-phase extraction (UATPE), alkaline transesterification, recrystallization, and so on.

2. Materials and method

2.1. Materials

Castor beans were purchased from Jiangsu province. The powder was obtained from the castor beans, which were milled by an electric grinder. Petroleum ether (60–90 °C), acetonitrile, potassium hydroxide, methyl salicylate, and trichloromethane were purchased from Nanjing Huaqingnanfang Chemical Ltd. (Nanjing, China). Deionized water was prepared in the laboratory.

2.2. Method

The whole process was composed of the following steps: ultrasonic-assisted two-phase extraction (UATPE), biodiesel (methyl ricinoleate) production, and purification of ricinine. The schematic drawing of the procedure was described in Fig. 1. The detail operational procedures were described below.

2.2.1. Ultrasonic-assisted two-phase extraction (UATPE)

In this study, UATPE was applied to the step of castor oil and ricinine extraction. As an assistant method, ultrasound could markedly shorten the extraction time, enhance the extracts dissolve acceleratively and uniformly, and increase the extraction rates of products [20]. Therefore, this technology had been widely used in the chemical and other industries [21].

The castor seed meal (50 g) was mixed with two-phase system (TPS). And the TPS was composed of petroleum ether and deionized water. The mixtures were transferred into a 500 mL three-necked round-bottom flask, which was equipped with a mechanical stirrer, a thermostat, and a reflux condenser. Then, the flask was located at an ultrasound water bath (UP3200HE, 40 KHz, 300 W) with the different set desired temperatures for a certain time. After several minutes, the mixture was separated by the vacuum-filtered with the Buchner funnel. The filter cake was washed by 20 mL fresh petroleum ether and 20 mL deionized water, respectively. Then, the filter cake would be used to detect the amount of the residual ricinine. And the collected solvent was transferred into a separating funnel and separated into two layers. The upper layer was petroleum ether phase, which included the castor oil, petroleum ether, and some impurities. The lower layer was water phase, which would be prepared to obtain the ricinine.

2.2.2. Biodiesel production

The excess petroleum ether of the upper layer was recovered by a vacuum rotary evaporator. Then, transesterification of the extracted castor oil was conducted in a 500 mL three-necked flask, which was immersed in the water bath with magnetic stirring. The flask was equipped with a thermometer and a reflux condenser to control the reaction. The reaction was carried out with the extracted castor oil, desired amount of methanol (depending on the different molar rates of methanol to oil), and the suitable amount of catalyst (KOH), which had been dissolved in the methanol. At the end of the reaction, the reaction mixture was poured into a separating funnel and settled for a long time to form two phases completely by the gravity. The supernatant, which contained biodiesel (methyl ricinoleate), some methanol and catalyst, needed to be further purified. After removing extra methanol with reduced-pressure distillation, the biodiesel phase was washed by hot deionized water until the washing water became clear and transparent. And then, the crude biodiesel was treated in a vacuum drying oven to remove the volatile matters for achieving final biodiesel product.

2.2.3. Purification of ricinine

The lower phase separated from the UATPE contained ricinine, water, protein, polysaccharides and other impurities. Several purification steps should be taken to improve the purity of ricinine product. Trichloromethane, methanol, petroleum ether, and anhydrous ethanol were applied in the procedure to confirm the suitable solvent for ricinine purification.

Firstly, the lower phase solution was concentrated by reduce-pressure distillation to remove most of the water. After transferring, the paste-likes concentrate was divided into four equal parts. Every part of the concentrate was weighted and introduced into a Soxhlet apparatus, where a certain volume of extraction solvent was injected for the second extraction of ricinine. Several hours later, the extraction solvent was collected and concentrated by reduced-pressure distillation. Subsequently, the concentrate was dissolved in fresh anhydrous alcohol with ultrasound for crystallization several times, and the solution was stored in a fridge

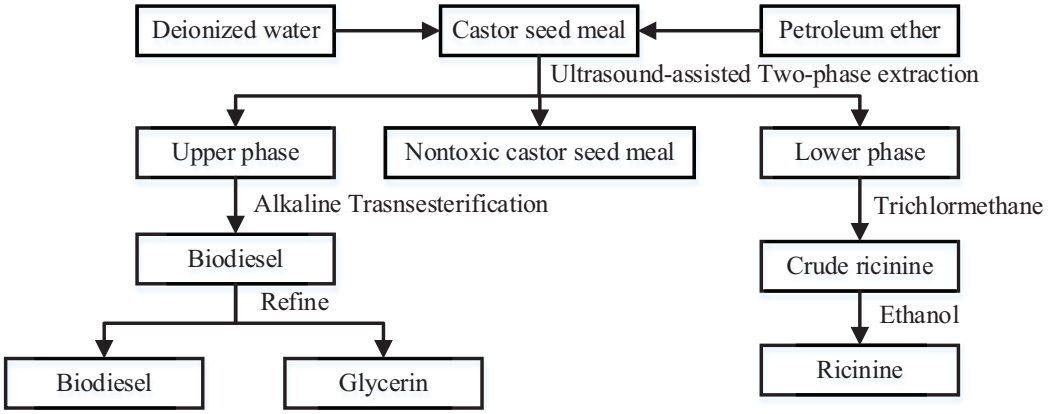

Fig. 1. Flow chart for the whole operations.