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Continuous production of biodiesel from soybean flakes by extraction coupling with transesterification under supercritical conditions: Original research article

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ABSTRACT

Biodiesel is regarded as one of the most promising alternatives for petroleum diesel. In this study, biodiesel continuous production with three kinds of reactor which are straight tube, coil and fixed bed reactor were compared, and the results showed that the fixed bed reactor needed a shortest stable time of 30 min, and with the condition of methanol to oil molar ratio 42:1, 18 MPa, 150 min and 300 °C, the highest yield: 80.11% of methyl ester was obtained. A continuous coupling process of supercritical extraction and non-catalytic supercritical methanol transesterification method for preparing biodiesel is put forward. Based on the investigation of process optimization, oil extraction was found to be the crucial step for the coupling process. The optimum reaction condition was the extraction and reaction temperature 40 °C and 300 °C, pressure 18 MPa, and the flow rate of CO_2 and *n*-hexane were 2 l/min and 0.4 ml/min, respectively. In these circumstances, the fixed bed reactor provided a yield of 83.84%.

1. Introduction

With the global energy strategy adjustment, green renewable energy plays a more and more important role in the development of energy industry, and will gradually replace the traditional fossil energy. Biodiesel is a typical renewable diesel replacement that is less emission and improving the environment. This type of fuel burns clean, which results in a significant reduction of the types of pollutants that contribute to smog and global warming and emits up to 85% fewer cancer-causing agents. The transesterification reaction using fats or vegetable oils and an alcohol like methanol is the most mature process for the production of biodiesel.

Biodiesel production from a batch process of supercritical transesterification has provided high conversion of oil. In 2001, Saka et al. [1] suggested the supercritical methanol transesterification of rapeseeds to biodiesel for the first time, they conducted the reaction in the condition of molar ratio 42:1, and temperature 350–400 °C, pressure in the range of 45–65 MPa. Within 240 s, the conversion of rapeseed oil reached 95%. Many Researchers [2] then studied the effects of different reaction conditions on the yields of biodiesel in supercritical methanol. Batch reactor is widely employed in the early research of biodiesel production. This kind of reactor can convert oil to biodiesel ranging from 73% to 98% in 20 min to 4.5 h [3]. Methanol is the feed stock and also the solvent of the reaction, which can be easily separated from the product, provides convenience for the post-treatment. But the supercritical process needs high temperature and pressure, leads to a high cost for the preparation [4]. Adding some catalyst [5,6] and co-solvent [7,8] can somehow intensify this reaction. Demirbas [9] used calcium oxide as the catalyst to improve the transesterification reation of sunflower seed oil in supercritical methanol, and found that calcium oxide had high catalytic activity in sub and supercritical transesterifications, the methyl ester's yield was greatly improved even when a little CaO was added.

The batch process is usually employed in the production with an annual capacity of ten thousand tons. Continuous flow process [10–13] can be brought so as to provide much bigger manufacturing scale, and cut the cost. Most of the feed stock of biodiesel includes vegetable oil, animal fats, algae and waste cooking oil was bought from manufacturer, which increased the biodiesel's cost due to the transportation and storage. Coupling with supercritical extraction which extracted the oil from raw material can solve this problem [14–17]. Supercritical fluid, as a typical green solvent, weighs in the green chemistry technology [18]. The extraction was affected by pre-treatment [4], temperature, pressure and operating time [19]. The density which determines the solvation of supercritical

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fluid varies directly with pressure [20], and changes inversely with temperature. But the diffusion coefficient determining the mass transfer is directly proportional to the temperature. High diffusivity promotes the extraction. Therefore, the optimum temperature and pressure should be selected.

Jackson [21] verified that the supercritical CO_2, an environmental benign solvent, can extract oil selectively. Using this oil as feed and enzyme as catalyst, the transesterification reaction was progressed. Friedrich [22] using $scCO_2$ to extracted full-fat soyflakes at pressures of 21–69 MPa, at the temperature of 50–60 °C. The soybean oil is lighter in color and contains less iron and phosphorus than that extracted by hexane. So the degumming step in the post treatment can be omitted. Casas [23] compared four extraction techniques, Soxhlet, orbital shaker extraction, ultrasonic-assisted extraction, and supercritical fluid extraction have been analyzed. The results show that the supercritical extraction process produces a better product for the subsequent transesterification reaction. Paiva et al. [24] studied the continuous production of biodiesel from chicken feather meal (CFM) carried out in supercritical carbon dioxide. The integrated extraction and enzymatic transesterification of CFM oil were then carried out at 40 °C and 250 bar, at solvent flow rates in the range 30–150 g/min, for oil: methanol molar ratios of 1:6–1:24, using Lipozyme RMIM (R) as biocatalyst, in a pilot plant unit. The lowest FAME yield obtained was 96.7%.

Reactor is the key of the preparation process. To further improve biodiesel's yield and lower the cost, the reactor's structure should be optimized. The common equipment used by continuous process is tank, tube, tower and fixed bed reactor. Leevijit [25] designed a 6-stage continuous reactor for transesterification of palm oil, and found that the reactor had a residence time distribution equivalent to 5.98 ideal CSTRs in series and a production performance equivalent to a plug flow reactor. Zhu et al. [26] investigated the continuous transesterification of vegetable oil and supercritical methanol using a tube reactor with an outside diameter of 6 mm and length of 6 m. With the system, the methyl esters yield can be obtained more than 96%. He et al. [27] conducted the continuous biodiesel production from acidic oil containing soybean oil and oleic acid with methanol in two fixed bed reactors, the fixed stuffing were NKC-9 cation and D261 anion-exchange resin all showed high catalytic activity.

The continuous supercritical esterification coupling with supercritical extraction without catalyst was investigated. In order to enhance the continuous process, different reactors were studied and compared. The form of tube reactor includes coil and straight tube. The straight tube reactor has been applied in the research of continuous production, and some gratifying results have been achieved. This work aimed to give comparative study about coil and straight tube reactor, and the transformation of straight tube: fixed bed reactor. Then the reactor with good performance was selected to carry out the coupling process which combined the continuous transeserification and supercritical carbon dioxide extraction.

2. Experimental

2.1. Materials and instruments

Soybean oil and flakes were purchased from Riqing China Agri-Industries Co., Ltd. Methanol and *n*-hexane with the purification of analytical grade were obtained from Beijing chemical works. N_2 and CO_2 were supplied by Dalian Guangming Special Type Gas Co., Ltd. The quality of biodiesels is analyzed by Agilent 6890 gas chromatography.

2.2. Analysis

The FAME content of the samples was determined by an Agilent 6890 N gas chromatograph, equipped with a HP-5 capillary column (30m × ϕ0.32mm × 0.25 μm). The column temperature program was set at a starting temperature of 160 °C followed by an initial rate of 3 °C/min to 225 °C, held at 225 °C for 0.5 min, and then it was ramped at 15 °C/min to 270 °C, held at this temperature for 4 min. Nitrogen was used as carrier gas. The inlet pressure was 43.4 kPa. The split ratio was 40:1. The injector and detector temperatures were set at 270 °C and 290 °C, respectively. The FAME content of the products was determined by external standard method and the standard sample was prepared using potassium hydroxide catalysis method which yield is nearly 100%.

2.3. Experimental procedure

2.3.1. Continuous supercritical methanol transesterification process

Soybean oil and methanol were pumped into reactor through the high-pressure constant flow pump at the flow set beforehand. The temperature of the pre-heater and the reactor were controlled and adjusted by the temperature controller, meanwhile the pressure was regulated by the back pressure valve. Opened the outlet valve, when the temperature and pressure reached what we needed, collected the products carefully and started the timer. The methyl ester and soybean oil mixture in the upper layer were obtained from the products after static stratification and vacuum distillated. The mixture samples diluted by *n*-hexane were analyzed by gas chromatography (Agilent 6890). Three types of reactors were compared in this paper, a coil reactor (CR) (Φ3 × 0.51 mm, 2000 mm, volume 6.2 ml), a straight tube reactor (STR) (Φ18 × 5 mm, 250 mm, volume 12.6 ml), and a straight tubular fixed bed reactor (FBR). The packing weighed 6.5 g, and its volume was 1.5 ml. The fixed bed reactor is a straight tube reactor improved by filling wire mesh packing. Adding the wire mesh can restrain back mixing and increase the contact area of the feed stock.

2.3.2. Continuous production for coupling process

The raw material soybean oil can be extracted from soybean flakes using supercritical CO_2 extraction. In the beginning, some soybean flakes were settled in an extractor, and then CO_2 and a little *n*-hexane was pumped into extractor until a certain pressure was reached. Keep the pressure for 3 h so that CO_2 and the flakes can contact enough. Then the reaction system was switched on. The material in the extractor was heated by the thermostatic water bath, and the pre-heater and reactor were heated at a certain temperature. Methanol was pumped into reactor through the high-pressure constant flow pump at the flow set beforehand, timing when the pressure and temperature needed were reached after the outlet valves were regulated to a proper position and the products were accumulated in the collector. The flow of the tail gas CO_2 was measured by the wet type gas flow meter. Products were processed by the approach which has been mentioned in Section 2.2.

3. Results and discussion

3.1. Comparative study of different reactors

The tube reactor, as an ideal plug flow reactor, is used widely in chemical process. Lower the diameter of tube lead to a high yield of biodiesel [10], and the most convenient approach is adding some stuffing into the reactor to physically diminish the diameter and enhance mass transfer. Wire mesh had been selected. Through this modification, the straight tube reactor was transformed to a

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