Fuel Processing Technology 137 (2015) 186–193

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

A two-step biodiesel production process from waste cooking oil via recycling crude glycerol esterification catalyzed by alkali catalyst

Zi-Zhe Cai [a], Yong Wang [b,c,*], Ying-Lai Teng [b], Ka-Man Chong [b], Jia-Wei Wang [b], Jie-Wen Zhang [b], De-Po Yang [a,**]

[a] School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China
[b] Department of Food Science and Engineering, Jinan University, Guangzhou 510632, China
[c] Guangdong Saskatchewan Oilseeds Joint Laboratory, Jinan University & University of Saskatchewan, Guangzhou 510632, China

ARTICLE INFO

Article history:
Received 30 April 2014
Received in revised form 31 March 2015
Accepted 4 April 2015
Available online 4 May 2015

Keywords:
Biodiesel
Waste cooking oil
Alkali catalyst
Crude glycerol
Esterification

ABSTRACT

A novel biodiesel production process using waste cooking oil (WCO) as feedstock was developed in this work. Free fatty acids (FFAs) from WCO were esterified by crude glycerol catalyzed by NaOH, which lowered the content of free fatty acids of WCO. The conversion of FFA in the WCO (acid value: 124.9 mg KOH/g) to acylglycerols is 99.6% under the optimal conditions (1.4:1 molar ratio of glycerol to FFA, 4 h, 210 °C, catalyst loading 0.5 wt.% based on WCO weight). After the transesterification of esterified WCO with methanol catalyzed by NaOH, the yield of the final product is 93.1 wt.% with 98.6 wt.% of fatty acid methyl ester (FAME). The crude glycerol and the catalyst from transesterification were recycled as reactant for esterification during the biodiesel production. Soap formed from the subsequent processes maintained a high catalyzing activity for FFA esterification after being recycled for 13 times. This new glycerol esterification process using alkali (soap) catalyst provides a promising solution to convert feedstock with high FFA levels to biodiesel. This biodiesel production process has distinct advantages compared with traditional two-step methods, including lower cost of catalyst for both esterification and transesterification processes, less energy consumption for methanol recovery, recycling of the glycerol byproduct and catalyst (soap), and no requirement of anti-corrosive equipment.

1. Introduction

With the boost of global economy, the increasing demand of energy is challenged by the depletion of fossil fuels. In addition, the use of fossil fuels brings environmental hazards such as the emission of greenhouse gases and pollutants. So it is urgent to find clean and renewable energy sources to substitute fossil fuels. Biodiesel, which is defined as "a substitute for or an additive to diesel fuel that is derived from the oils and fats of plants and animals" [1], has advantages in being sustainable, carbon neutral and less polluting [2]. Thus it is considered to be one of the most promising alternatives to fossil fuels.

Various types of edible oil are being used as feedstock for biodiesel production, including soybean oil (U.S.), rapeseed oil (Europe), coconut oil and palm oil (Southeast Asia) [3–6]. However, some developing countries such as India are not self-sufficient in the production of edible oils [7,8]. This means that using edible oil as feedstock would not be feasible because of the short supply and the high price. Previous studies suggested that the cost of feedstock contributes nearly 80% of the biodiesel price [9]. To enable the economical production of biodiesel in populous countries such as China, the ideal feedstock should meet the criteria of having a low feedstock cost and a large volume available for production.

In small cities of China (population < 200 k), waste cooking oil (WCO) is often discharged directly into environment because of the lack of processing facilities. Meanwhile, some illegal oil producers can recycle WCO and sell it back to restaurants, bringing both environmental and health issues. In bigger cities, like Guangzhou, most of the restaurants are equipped with an oil separation tank where WCO can be trapped and accumulated. WCO is then collected by the environmental protection agency authorized by the local government. The price of WCO is about 40–70% cheaper than edible vegetable oils. If it can be used to manufacture biodiesels, the feedstock cost can be significantly reduced [10]. Furthermore, the increasing food consumption in China will result in a large production of WCO. The annual WCO production of a city with a population larger than 10 million (e.g. Guangzhou) is estimated to be more than 20 thousand tons [11], suggesting that WCO is an economical and sustainable resource for biodiesel production. With proper processing, biodiesel from WCO can also meet the ASTM D 6751 standard [12]. Compared with discarding it directly into

* Correspondence to: Y. Wang, Department of Food Science and Engineering, Jinan University, Huangpu Rd. West 601, Guangzhou 510632, China. Tel.: +86 20 85224358; fax: +86 20 85226630.
** Correspondence to: D. Yang, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China. Tel./fax: +86 20 39943043.
E-mail addresses: twyong@jnu.edu.cn (Y. Wang), lssydp@mail.sysu.edu.cn (D.-P. Yang).

http://dx.doi.org/10.1016/j.fuproc.2015.04.017
0378-3820/

the drainage system or illegally recycling the WCO to restaurants, this is socially and environmentally friendly.

The traditional way to produce biodiesel is by catalytic transesterification of vegetable oil with an alcohol to yield fatty acid alkyl esters and glycerol. The alkali-catalyzed transesterification is considered to be efficient and can achieve high purity and yield, but it requires feedstock with high purity. For example, Freedman et al. studied the influence of free fatty acid (FFA) in the biodiesel production and found that the acid value of the feedstock should be less than 1.0 mg KOH/g, or the yield of FAME would be reduced due to the deactivation of the catalyst and hydrolysis of triacylglycerol caused by the soap formed [13]. As WCO has a high acid value, it is impossible to achieve such a high yield and efficiency through a direct alkali-catalyzed transesterification. In such case, a one-step acid-catalyzed process can be applied, but this method requires more alcohol, higher reaction pressure, and more costly stainless steel facilities, and the yield is relatively low (82% of fatty acid conversion rate with 200% excess of ethanol when sulfuric acid is used as the catalyst) [14,15].

To overcome these drawbacks, two-step biodiesel production methods have been developed: firstly FFAs are esterified catalyzed by acid as a pretreatment, and then the acylglycerols are transesterified using a homogeneous alkali catalyst (typically NaOH). For some methods using high acid value oils as feedstock (such as mahua oil, rubber seed oil, and tobacco oil), esterification of FFA and methanol is applied. However, among these methods, the methanol esterification step is time-consuming and requires large amounts of methanol and acid catalyst. It has been suggested that for high acid value feedstock, the molar ratio of methanol to oil needs to be up to 18:1 to achieve a higher conversion yield of FFA to FAME [16]. After the conversion, the unreacted methanol needs to be recovered and purified so as to be recycled in the production processes. Compared with conventional transesterification methods, more amount of methanol needed in the pretreatment (10–20:1 vs. 6:1) means more energy is required for its evaporation and rectification [3,17]. Dhar et al. suggested that, to achieve the standard purity of recovered methanol (94%), the reboiler heat duty to recycle higher amount of methanol (15:1, 4 MW) is 4 times that of the lower amount of methanol (6:1, 1 MW) [18]. To reduce the energy consumption of the biodiesel production, one can think of replacing the methanolysis step in the pretreatment with other reaction methods.

In our previous study, solid super acid was reported to act as a catalyst for the esterification of FFA with glycerol, but solid super acid catalyst is expensive, and additional separation of the catalyst and excess glycerol is required before transesterification [19]. To tackle this, soaps can be used to catalyze the esterification of glycerol with FFAs. Echeverri et al. used sodium oleate to catalyze the glycerolysis of methyl ester with glycerol to prepare monoglyceride [20]. Lithium soap can also serve as a catalyst in the production of monoglyceride and diglyceride [21]. Szelag and Zwierzykowski have studied the kinetics of fatty acids esterified with glycerol in the presence of sodium and potassium soaps, showing that sodium soap is capable of catalyzing the esterification of FFA and glycerol [22]. In the biodiesel production, this catalyzing method might be applied to esterify crude glycerol with WCO which is rich in FFAs, which has not been reported yet.

The purpose of this study is to develop a practical and economical method for biodiesel production from feedstock with high FFA content, such as WCO. Soap which is formed from FFA and NaOH is served as a catalyst in the esterification of crude glycerol with the FFAs in WCO. This new esterification process (Fig. 1) has several distinct advantages compared to the traditional esterification process, including the wide availability of NaOH catalyst, the recycling of inexpensive byproduct (crude glycerol from transesterification) and catalyst. As methanol is replaced with crude glycerol in the pretreatment, the energy required to recover and rectify methanol can be saved. Also, compared with the acid catalyzing method, it is not necessary to use corrosion resistant equipment. With a proper catalyst loading in the esterification and transesterification steps, our process can achieve recycling of catalyst (soap). As no subsequent addition of esterification catalyst is required, the cost of catalyst can be significantly lower.

2. Materials and methods

2.1. Materials

WCO from restaurants was provided by Guangzhou Balis Waste Treatment Co., Ltd (Guangzhou, China) under the authority of the

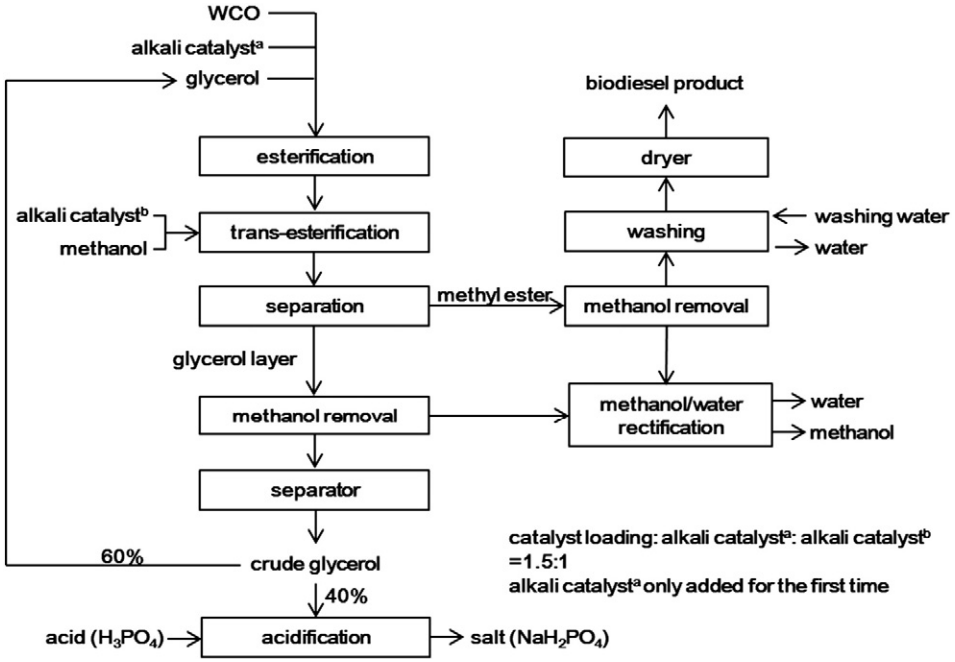

Fig. 1. Process diagram for biodiesel production from WCO catalyzed by alkali catalyst.