Bioresource Technology 247 (2018) 51–57

Contents lists available at ScienceDirect

Bioresource Technology

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

Optimization and kinetic study of ultrasonic assisted esterification process from rubber seed oil

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ARTICLE INFO

Keywords:
Biodiesel
Rubber seed oil
Ultrasonic reactor
Response surface methodology
Esterification kinetics

ABSTRACT

Recently, rubber seed oil (RSO) has been considered as a promising potential oil source for biodiesel production. However, RSO is a non-edible feedstock with a significant high free fatty acid (FFA) content which has an adverse impact on the process of biodiesel production. In this study, ultrasonic-assisted esterification process was conducted as a pre-treatment step to reduce the high FFA content of RSO from 40.14% to 0.75%. Response surface methodology (RSM) using central composite design (CCD) was applied to the design of experiments (DOE) and the optimization of esterification process. The result showed that methanol to oil molar ratio was the most influential factor for FFA reduction whereas the effect of amount of catalyst and the reaction were both insignificant. The kinetic study revealed that the activation energy and the frequency factor of the process are 52.577 kJ/mol and 3.53×10^8 min^{-1}, respectively.

1. Introduction

Recently, larger scale biodiesel production has increased globally, resulting in demand for more innovative, cost saving and efficient processes (Tabatabaei et al., 2015). Regarding feedstock sources for biodiesel production, edible oils have been utilized to produce biodiesel with high quality that complies with international fuel standards. However, feedstock cost is reported to be 70–95% of total biodiesel production cost and thus plays the most crucial factor in the commercial viability of biodiesel (Banković-Ilić et al., 2012). Besides, food versus fuel crisis has risen due to the detrimental impact of biofuel production on price and availability of food (Bokhari et al., 2016). These problems can be overcome by using low-cost non-edible oils such as Rubber seed oil (RSO), Jatropha oil and Ceiba pentandra oil. Among them, rubber seed which found abundant in many countries and normally considered as waste has attracted more and more attention from researchers (Zhu et al., 2014). It has a high content of oil (40% to 50% oil) (Eka et al., 2010). Moreover, previous works have reported that biodiesel derived from RSO was in reasonable agreement with international standards (Ramadhas et al., 2005; Ahmad et al., 2014). Nonetheless, the main drawback of non-edible oils is their high content of free fatty acid (FFA). The presence of high FFA causes soap formation, yield loss, difficulty in separation and purification of the products as well as increase in the production cost (Leung et al., 2010; Sharma and Singh, 2009). FFA level in RSO varies depending on extraction methods and has been found to be significantly high. It can reach up to 45% (Morshed et al., 2011). Besides, owing to a high composition of unsaturated fatty acids, FFA level in RSO is unstable and increases depending on storage duration and condition (Chuah et al., 2016a,b). In order to solve this limitation, esterification process is applied as a pre-treatment step for biodiesel production. In generally, esterification is the reaction between FFA and alcohol in the presence of acid catalyst (typically sulfuric acid) (Issariyakul and Dalai, 2014). The FFA level should be reduced to less than 1% prior to transesterification process (Banković-Ilić et al., 2012). Nevertheless, conventional esterification process is slow, leading to low conversion and high energy consumption (Leung et al., 2010). The low reaction rate is mainly caused by immiscibility of reactants.

Ultrasonic irradiation can dramatically increase the interface mixing and thus enhance the reaction rate (Ramachandran et al., 2013). In ultrasonic method, the collapse of cavitation bubbles simultaneously provides the mixing and heating to carry out the reaction. Andrade-Tacca et al. (2014) investigated the esterification pre-treatment of Jatropha oil with high FFA using direct ultrasonic irradiation with auto-induced temperature-rise. A 0.92 wt% of sulfuric acid was used as catalyst for the process. In the esterification without temperature control, the FFA conversions of 56.73% and 83.23% obtained at 10 min and 30 min for ultrasonic irradiation process were much higher than 36.76% and 42.48%, respectively, obtained for mechanical stirring (MS). Mootabadi et al. (2010) conducted an ultrasonic-assisted transesterification process from palm oil, using alkaline earth metal

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http://dx.doi.org/10.1016/j.biortech.2017.09.075
Received 17 July 2017; Received in revised form 8 September 2017; Accepted 9 September 2017
Available online 12 September 2017
0960-8524/

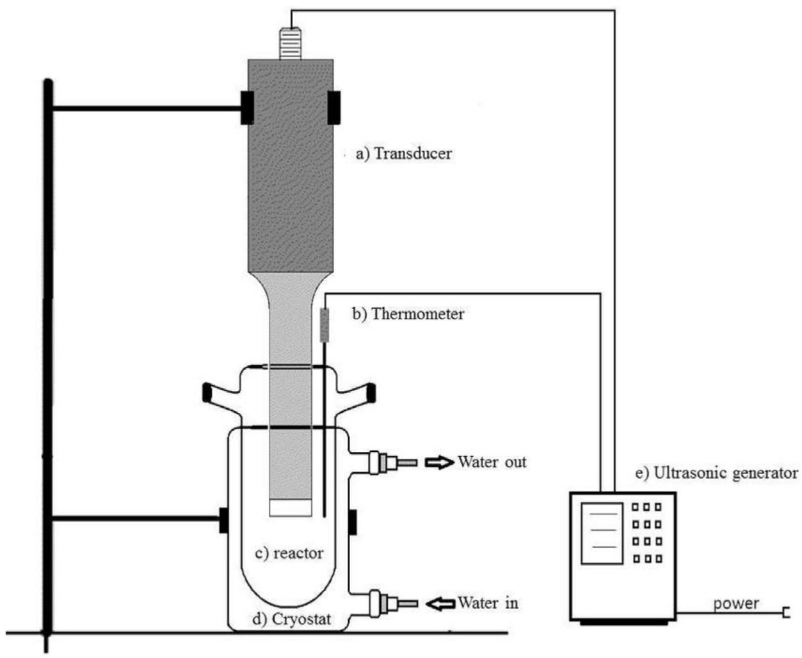

Fig. 1. Schematic diagram of batch ultrasonic system.

Table 1
Experiment design by central composite design for esterification process with reaction temperature = 50 ± 1 °C and ultrasonic amplitude = 50%.

Process Parameters	−α	−1	0	+1	+α
Methanol to oil ratio (mol:mol)	9.59	13	18	23	26.41
Catalyst amount (wt%)	5.80	7.5	10	12.5	14.20
Reaction time (min)	16.59	20	25	30	33.41

α = 1.68179.

Table 2
Detailed experimental results for esterification process with reaction temperature = 50 ± 1 °C and ultrasonic amplitude = 50%.

Run	A:Methanol:oil (mol:mol)	B:Catalyst (wt%)	C:Time (min)	Response:FFA (%)	predicted FFA (%)
1	13	7.5	20	2.40	2.47
2	23	7.5	30	0.72	0.72
3	23	12.5	20	1.02	1.12
4	23	7.5	20	0.87	0.80
5	13	7.5	30	2.29	2.24
6	13	12.5	20	2.38	2.45
7	18	5.80	25	1.35	1.42
8	18	10	25	1.39	1.38
9	26.41	10	25	0.69	0.71
10	18	10	25	1.73	1.38
11	13	12.5	30	2.03	2.16
12	18	10	16.59	1.61	1.54
13	18	10	33.41	1.24	1.23
14	18	14.20	25	1.77	1.62
15	23	12.5	30	0.99	0.98
16	18	10	25	1.29	1.38
17	9.59	10	25	3.20	3.10
18	18	10	25	1.29	1.38
19	18	10	25	1.29	1.38
20	18	10	25	1.28	1.38

oxides as catalysts. Among them, BaO catalyst showed the highest yield of 95.2%. Under ultrasonic irradiation, the optimum yield of 95.2% was obtained after 60 min while only 67% of biodiesel yield was achieved under MS in the same condition.

Parametric studies of esterification process for RSO using conventional stirring have been reported. Ahmad et al. (2014) conducted biodiesel production from RSO with high FFA value of 42% via conventional stirring. In the esterification step, the FFA value reduced from 42% to 0.82% at the optimized conditions of methanol to oil ratio of 15:1, sulfuric acid concentration of 10 wt% of the oil, reaction temperature of 45 °C and 90 min reaction time. A similar study was investigated by Chuah et al. (2016a,b) and the optimum conditions was obtained at 10:1 methanol to oil molar ratio, 10.74 wt% of sulfuric acid, 65 °C for 1 h with FFA conversion of 98%. Though many studies reported the pre-treatment of RSO via esterification reaction, very few optimization studies of the direct ultrasonic assisted esterification of RSO were reported. Widayat and Suherman (2012) reported use of bath ultrasonic reactor for improving RSO methyl ester yield. A predicted model of biodiesel yield was built to study the relationship between mesh sizes of rubber seed, oil to methanol ratio and types of catalyst (NaOH and H_2SO_4). The research stated that biodiesel yield and processing time were improved by using ultrasonic reactor. However, the reaction time was not given in the article. Recently, Reshad et al. (2017) employed a probe type ultrasonic reactor in pre-treatment of RSO (12.12% FFA content) before transesterification step. In order to minimize FFA concentration, optimization study was conducted using conventional optimization technique. Despite the fact that direct ultrasound was applied, the improvement in the optimum conditions were insignificant compared to conventional method. It took up 2 h for the pre-treatment of RSO. Other variables (15:1 methanol:oil and 1.5 wt% H_2SO_4) were similar to the conventional esterification of Malaysia RSO (23.2% FFA content) conducted by Chuah et al. (2016a,b).

In another attempt of pre-treatment of RSO prior to transesterification step, Chuah et al. (2016a,b) indicated that ultrasonic irradiation did not significantly enhance the esterification conversion. Thus conventional stirring was utilized for the esterification step instead of ultrasonic method. It can be seen that the use of ultrasonic method for esterification process of RSO still remains unclear. Therefore, the aim of this research is to study the parametric optimization of the esterification process of RSO using RSM. The interactions between three major parameters including methanol to oil molar ratio, acid catalyst concentration and reaction time were investigated. In addition, the present work also calculated the kinetic of the esterification process.

2. Materials and methods

2.1. Materials

RSO was imported from Vietnam by Kinetics Chemicals (M) Sdn.