Renewable Energy 111 (2017) 764–770

Contents lists available at ScienceDirect

Renewable Energy

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

A non-catalytic *in situ* process to produce biodiesel from a rice milling by-product using a subcritical water-methanol mixture

Siti Zullaikah, Ph.D. [a,*], Yulia T. Rahkadima, MT [a], Yi-Hsu Ju Professor [b]

[a] *Institut Teknologi Sepuluh Nopember, Indonesia*
[b] *National Taiwan University of Science and Technology, Taiwan*

A R T I C L E I N F O

Article history:
Received 12 August 2016
Received in revised form
23 January 2017
Accepted 19 April 2017
Available online 22 April 2017

Keywords:
Biodiesel
Rice bran
Subcritical water-methanol
In situ process
Non-catalytic process

A B S T R A C T

A non-catalytic method to produce biodiesel *in situ* from a rice milling by-product, i.e. rice bran, using subcritical water-methanol mixture has been investigated. The method was found to be unaffected by initial moisture and free fatty acids (FFA) contents in rice bran so that no pretreatment was required. The yield and purity of biodiesel were higher under CO_2 atmosphere than those under N_2 atmosphere due the ability of the gas to acidify water-methanol mixture. Oil extraction from the bran was identified as the limiting step and complete oil extraction could be achieved in 3 h at 200 °C, 4 MPa (under CO_2 atmosphere) and 43.8 wt% methanol concentration. Consequently, the highest biodiesel yield was also achieved at those operating conditions. The experimental data suggested that hydrolysis of rice bran oil into FFA followed by methyl-esterification of FFA into biodiesel could be the preferred reaction path to direct transesterification of oil. Subcritical water-methanol mixture was also able to break down complex carbohydrates in rice bran into simple sugars soluble in aqueous phase so that it could be separated easily from biodiesel.

1. Introduction

Human activities, especially the burning of fossil fuels that emits greenhouse gasses into atmosphere, have been identified as the main cause of recent climate change [16]. The use of renewable fuels which can be considered carbon neutral can mitigate this issue. One kind of renewable fuel which is currently produced in industrial scale is biodiesel or fatty acid methyl esters (FAME). It can be blended with petrodiesel and requires practically no changes in the fuel distribution infrastructure [17]. Unfortunately, most biodiesel currently in use is produced from edible feedstocks, such as palm oil, soy oil and rapeseed oil [17,35], which can drive food price higher. Ideally, the feedstock should be available in large quantity, relatively cheap and inedible, such as rice bran.

Rice bran is produced during the milling of husked rice as a by-product and is traditionally used as cattle feed despite of its rich nutrient content. Husked rice contains about 8–12% rice bran while rice bran itself contains about 10–26% oil [5,19,24,35]. The potential of annual rice bran oil (RBO) production in China alone is about 6 million tonnes [23] while worldwide production could reach 8 million tonnes if all rice bran produced is harnessed for oil extraction [1,17]. RBO is rather unsuitable for human consumption due to higher free fatty acids (FFA), acetone-insoluble contents and darker appearance [6,23]. Complicated refining and stabilization process is required to transform RBO into edible oil suitable for human consumption, making it economically uncompetitive against other edible oils, such as palm, soy and rapeseed oils [17].

Since RBO has high FFA content, conventional biodiesel production method using base catalyst is unsuitable since the base reacts with FFA forming soap making FAME yield lower and purification process more complicated [17]. Various methods to produce biodiesel from crude and refined RBO have been proposed in the literature involve multiple steps. Zullaikah et al. [35] developed a two-step acid-catalyzed methanolysis method to produce FAME under atmospheric condition from dewaxed/degummed RBO with high FFA content (up to 76%). The first step was carried out at 60 °C mainly to convert FFA to FAME while the second step was carried out at 100 °C to convert the remaining triglycerides (TG) to FAME with a total reaction time up to 8 h. While [23] developed a three-step method to produce FAME from crude RBO. The first two pretreatment steps were carried out at 50 °C using acid catalyst to reduce FFA content to below 1 mg/g while the third step was carried out at 60 °C using base catalyst to convert TG into FAME. The total reaction time can be reduced to less than 3 h however, a

* Corresponding author.
E-mail address: szulle@chem-eng.its.ac.id (S. Zullaikah).

http://dx.doi.org/10.1016/j.renene.2017.04.040

Abbreviation

DRB	deffated rice bran
FAME	fatty acid methyl esters
FFA	free fatty acids
GC	gas chromatography
MS	mass spectrometry
RBO	rice bran oil
TG	triglycerides
V	volume

separation step was required between acid catalyzed steps and base catalyzed step. Although FFA contents in the feedstock and the methods were different, both of them reported that more than 98% of FFA and TG were converted into FAME under optimum conditions.

In situ methods to produce biodiesel from rice bran have also been proposed to reduce production cost since oil extraction and its conversion into FAME occur simultaneously. *In situ* method using methanol and sulfuric acid (1.5–5 vol%) at low temperature (60–65 °C) has been investigated by Özgül-Yücel and Türkay [27,28] and Gunawan et al. [9]. This method showed efficient esterification of FFA but transesterification of triglycerides (TG) was poor and therefore FAME yield increased with FFA content [17]. Shiu et al. [32] investigated a two-step *in situ* method where acid catalyst was used in the first step followed by basic catalyst in the second step. They found that lipid extraction from rice bran was a slow process that could take 4–5 h to extract most lipids in the bran using Soxhlet with n-hexane as solvent. *In situ* method under supercritical methanol at 300 °C and 30 MPa with CO_2 as the pressurizing gas was reported by Kasim et al. [20]. However, the result was rather disappointing with an overall conversion of 51.3%. Our preliminary experiment also showed that supercritical methanol featuring high temperature and pressure caused rice bran to char hindering oil extraction. Therefore, although *in situ* method could potentially reduce biodiesel production cost, there are still a lot of problems to be solved.

Another method to produce biodiesel *in situ* is by using subcritical water. It has been used widely for extraction of organic compounds [10,29] and has been employed to produce biodiesel *in situ* from algae [34], activated sludge [14] and Jatropha curcas seed kernels [8]. One advantage of this method is that it can be carried out without acid or base catalyst. Besides that, subcritical water is able to hydrolyze complex carbohydrates into soluble sugars which can be utilized as a medium to grow yeast [8], feedstock for bioethanol production and other industrial applications [29].

In this work, subcritical water-methanol mixture was employed to produce biodiesel *in situ* from rice bran. The effects of reaction time, pressurizing gas type, temperature and methanol concentration were investigated. The composition of deffated rice bran (DRB) was also analyzed. Since this method requires no catalyst, it is expected that this work could provide an economical and environmentally friendly method to produce biodiesel from cheap, abundant and inedible feedstock to meet the requirement of renewable fuel in the future.

2. Experimental

2.1. Materials

Rice bran (from IR 64 rice variety) was obtained from local rice mill (Lamongan, East Java, Indonesia). The moisture and oil contents of the rice bran were 12.9 ± 0.1% and 14.9 ± 0.2%, respectively. The moisture content was determined by the drying method while the oil content was determined by the Soxhlet extraction method with n-hexane as solvent for 8 h. The rice bran oil content found in this work is in good agreement with those reported in the literature, i.e. between 10 and 26% depending on rice variety and degree of milling [5,9,10,19,23,35]. The FFA content in the RBO was found to be 37.6 ± 0.2% determined by using the titration method according to [30]. The fatty acid composition in the RBO was determined by using a gas chromatography (GC) analyzer after methanolysis of RBO and the results are comparable to those reported in the literature as summarized in Table 1.

Pressurizing gas, either CO_2 or N_2, was supplied by Genta Prima Gas (Surabaya, Indonesia). Standard of methyl linoleate and phenol was obtained from Sigma-Aldrich (St. Louis, MO, USA). Analytical grade NaOH, sulfuric acid, phenolphthalein (PP) indicator and glucose were purchased from Merck (Kenilworth, NJ, USA). Methanol, n-hexane and 96% ethanol were purchased from Brataco (Surabaya, Indonesia). In all experiments, distilled water was used.

2.2. In situ biodiesel production

Rice bran (5 g) was mixed with a water-methanol mixture (40 ml) in a hydrothermal reactor (V = 86 ml) made of seamless 316 stainless steel tubing (SS-T12-S-083-6ME, Swagelok, Solon, OH, USA). The volume ratio of methanol to water was varied from 5/35 to 35/5 ml/ml, corresponding to methanol concentration from 10.0 to 84.5 wt%, respectively. Pressurizing gas (either CO_2 or N_2) was

Table 1
Composition of fatty acids in rice bran oil (RBO) determined by using a gas chromatography (GC) analyzer.

Fatty acid	Composition (%)		
	Current study	Zullaikah et al. [35]	Bello and Oluboba [2]
Palmitic acid (C16:0)	22.8	17.7	15.0
Linoleic acid (C18:2)	29.5	35.6	38.7
Oleic acid (C18:1)	46.1	40.6	41.5
Arachidic acid (C20:0)	0.8	0.2	0.8
Myristic acid (C14:0)	0.8	0.8	0.1
Others	–	5.1	4.0
Details of GC analysis			
GC type	Agilent HP 6890	Shimadzu GC-17A	Agilent HP 6890
Column	HP 1 crosslinked methyl siloxane	DB-5HT (5%-Phenyl-) methylpolysiloxane	HP inno wax
Detector	Flame ionization detector	Flame ionization detector	Flame ionization detector
Initial temperature	125 °C	80 °C	60 °C
Temperature ramp	15 °C/min for 10 min	15 °C/min for 20 min	10 °C/min for 20 min + 15 °C/min for 4 min
Final temperature	275 °C	380 °C	320 °C