IJE TRANSACTIONS C: Aspects Vol. 26, No. 12, (December 2013) 1545-1550

International Journal of Engineering

Journal Homepage: www.ije.ir

TECHNICAL NOTE

An Optimized Process for Biodiesel Production from High FFA Spent Bleaching Earth

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PAPER INFO

Paper history:
Received 24 April 2013
Received in revised form 25 May 2013
Accepted 20 June 2013

Keywords:
Spent Bleaching Earth Oil
Free Fatty Acids
Biodiesel
Esterification

ABSTRACT

Biodiesel may be economical if produced from inexpensive feedstock which commonly contains high level of free fatty acids (FFA) as an inhibitor in production of methyl ester. In this study a two-step process for biodiesel production from high FFA oil in a batch stirred tank reactor (BSTR) is developed. Oil sample extracted from spent bleaching earth (SBE) was utilized for biodiesel process. In the first step, FFA of the SBE oil was reduced to 3.01% through acid catalyzed esterification following by another reduction to less than 2%. Triglycerides resulted from both steps were transesterified with methanol (molar ratio 6:1) using an alkaline catalyst (1% wt/wt) to produce biodiesel. Major fuel properties of SBE biodiesel were measured to comply with ASTM and EN standards. Therefore, an optimized process for production of biodiesel from a low cost high FFA source was accomplished.

doi: *10.5829/idosi.ije.2013.26.12c.15*

1. INTRODUCTION

The price of fossil diesel has been continuously rising in the last ten years. A serious continuity and disruptions in the supply of energy is also a challenging issue to be considered. Thus, looking for an alternative way to develop a substitute for diesel fuel is an imperious task for the future world. Biodiesel is an additive or even a substitute to diesel which is commonly derived from oil plants, animal fats and oil containing wastes [1]. It must be carefully noted that most of the feedstock are essentially edible and usable in food chain. Few attempts have been made for producing biodiesel with non-edible oils such as waste cooking oils, agricultural wastes and industrial waste oils.

Currently, compared to petroleum-based diesel, the high cost of biodiesel is a major barrier to its commercialization. It is reported that approximately 70 to 85% of the total biodiesel production cost arises from the cost of the raw material. Use of low-cost feedstock helps to make biodiesel competitive in price with petroleum diesel. Most of the current challenges are targeted to reduce its production cost, as the cost of biodiesel is still higher than its petro-diesel counterpart [2]. To lower the production cost of biodiesel and to expand its usage, use of less expensive raw materials is desired. Waste vegetable oil adsorbed in spent bleaching earth (SBE) during the crude oil refining process is a potential candidate that has been overlooked in the past [3].

SBE is an industrial waste generated at the vegetable oil refining industry after the discoloration (bleaching) of crude oil. The annual world generation of SBE is between 1.5 and 2.0 million tons based on the world edible oil production of 128.2 million metric tons in 2007 [4] and 1.2–1.6 kg of SBE generation per metric ton of edible oil production. SBE contains 20–40% by weight of oil, fat and colored pigments [5]. It is estimated that about 600,000 metric tons or more of bleaching earth are utilized worldwide in the refining process based on the worldwide production of more than 60 million tons of oils. The SBE serves as by-product, which contains high percentage of oil [6]. The oil from spent bleaching earth has low production cost and is quite available rather than refined or recycled oils. There are three primary methods of transesterification to make biodiesel from oils of spent bleaching earth including alkali catalyst, acid catalyst and enzymatic transesterification [7].

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The recovery of residual oils adsorbed in SBE has been studied by many researchers. Huang and Chang, [3] extracted oil from SBE with n-hexane (1:4 wt/wt ratio) in a soxhlet extractor. Lye-extraction is also reported by Chang et al. [8]. Only a small fragment of SBE generated throughout the world is recovered and most of them are disposed at landfills.

Park et al. [9] used as an organic solvent for the transesterification of triglycerides embedded in the waste activated bleaching earth. When 1% (w/w) lipase was added to waste activated bleaching earth, the fatty acid methyl ester content reached 97% (w/w) after reaction for 12 h at 25°C with an agitation rate of 30 rpm.

Few researchers have worked with feedstocks having higher FFA levels using alternative processes [10, 11]. Canakci and Gerpen [10] used a two-step pretreatment to reduce the FFAs of yellow grease from 12% and brown grease from 33% to less than 1%. Transesterification reaction was completed with an alkaline catalyst to produce biodiesel. Felizardo et al. [12] described a possible method for the pre-treatment of oils with a high content of FFA (20 to 50%) by esterification with glycerol. In order to reduce the FFA content, the reaction between these FFA and an esterification agent is carried out before the transesterification reaction.

Waste SBE oil generally contains about 9% FFAs and a procedure for converting this oil to biodiesel seems extremely promising. This study discusses the findings of experiments carried out to optimize the pretreatment process for reducing the FFA content of SBE oil below 2% with two-step esterification reaction for maximum biodiesel production.

2. MATERIALS AND METHODS

2. 1. .Spent Bleaching Earth SBE for this study was provided by Naz Company in Esfahan, Iran. At the first step, oil adsorbed in SBE was obtained by extraction with solvent hexane (1:2 wt/wt ratios) in a soxhlet extractor. The extraction was continued for 1 h and 3000 rpm at the room temperature. Solid particles in solvent containing oil were removed by paper filters. Finally, solvent was removed from the oil by vacuum evaporation. Fatty acid profile of SBE oil is given in Table 1. Its FFA content was determined by gas chromatography method.

2. 2. Esterification Reaction SBE oil had an initial acid number of 18mg KOH/g corresponding to a FFA level of 9%, which is above the 2% limit for sufficiently transesterification reaction using alkaline catalyst. Hence, FFAs were first converted to esters in a two-step pretreatment process using an acid catalyst (H_2SO_4 1% v/v) to reduce the FFA of SBE oil below 2%. Experiments were directed in a laboratory-scale setup which consisted of 1000 ml glass flasks with air tight caps that retained any vaporized methanol to the reacting mixture and hot plate to provide temperature and stirrer. In each step, various methanol to oil ratios (0.1, 0.2, 0.3 and 0.4), reaction times (15, 30, 45 and 60 min) and different catalyst to oil ratios (0.5, 1, 1.5 and 2) were used to investigate their influence on the FFA of SBE oil. After completing the reaction in each step, the product was allowed to settle for 30 min into a separating funnel and the methanol–water fraction that separated at the top was removed. The esterification product was then titrated with potassium hydroxide to ensure that the concentration of FFA was below 2%. In cases that the FFA concentration was above 2%, the esterification process had to be repeated. The final product with minimal FFA concentration was subjected to transesterification process.

2. 3. Transesterification Reaction The transesterification reaction was carried out with 6:1 methanol to oil molar ratio and 1% wt/wt KOH as an alkaline catalyst. The reaction was conducted at 60 C° and 20 min in batch stirred tank reactor (BSTR). After separation of glycerin from biodiesel, soap and other impurities were removed through washing and heating and finally pure biodiesel was obtained. The fuel properties of SBE biodiesel were determined and matched with ASTM D6751 and EN14214 standards.

3. RESULTS AND DISCUSSION

3. 1. Effect of Methanol to Oil Ratio on Acid Value Reduction of the acid value of the mixture at the first step of esterification is illustrated in Figure 1.

TABLE 1. Fatty acid profile of SBE oil

Fatty acid	Formula	Structure [a]	Fatty acid composition (%)
Palmitic	$C_{16}H_{32}O_2$	16:0	12.245
Stearic	$C_{18}H_{36}O_2$	18:0	4.565
Oleic	$C_{18}H_{34}O_2$	18:1	22.4
Linoleic	$C_{18}H_{32}O_2$	18:2	53.445
Linolenic	$C_{18}H_{30}O_2$	18:3	7.345

[a] Carbons in the chain: double bonds

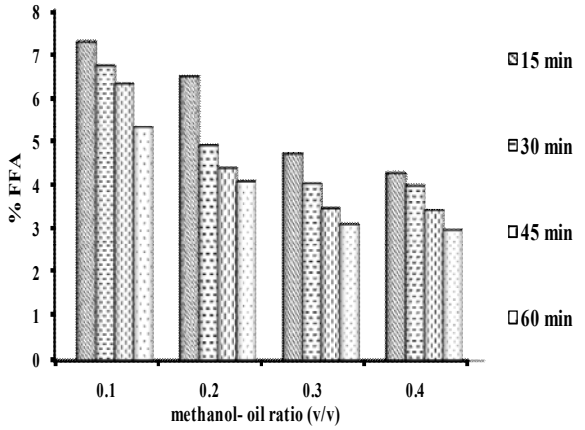

Figure 1. Effect of methanol amount and reaction time on reduction of FFA during the first step of esterification; initial FFA was 9%.

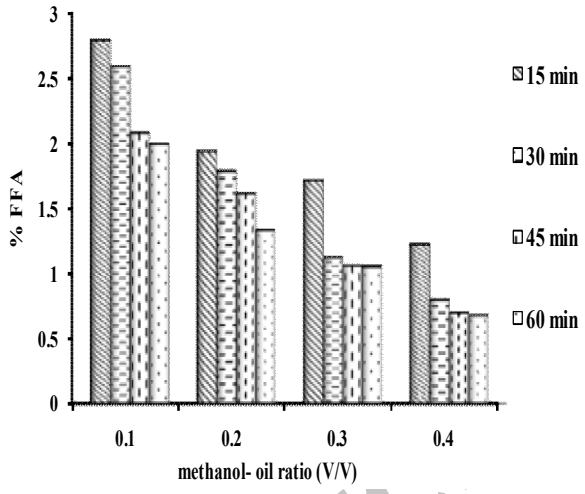

Figure 2. Effect of methanol amount and reaction time on reduction of FFA during the second step of esterification. The initial FFA from the first stage pretreatment was 2.8%.

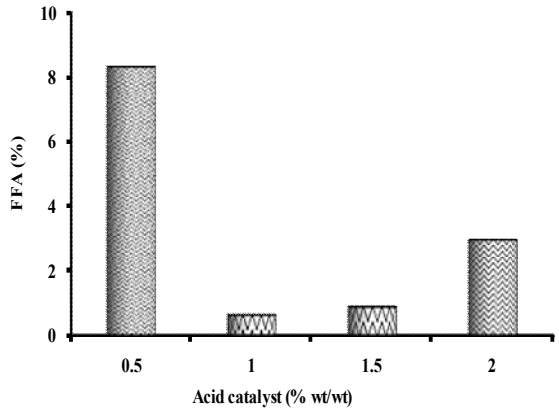

Figure 3. Effect of catalyst values on decreased FFA in the esterification reaction during both stages.

Figure 1 shows that methanol-oil ratio had a significant effect on FFA reduction. In the first 45 min and high levels of methanol, more than 80% reduction of FFA was observed. Between 0.3 and 0.4 v/v methanol- oil ratios, there was no significant difference in FFA values. At the first stage, minimum amount of FFA was 3.01% and optimal condition for decreasing FFA was 0.3 methanol– oil ratio and 45 min. After 45 min, there was no significant reduction in FFA. This might be due to the effect of water produced during the esterification of FFAs, which prevented further reaction [13-17].

Figure 2 indicates that within the second step, the amount of FFA reduces to less than 2%. Result shows that at the second step of the experiments, less amount of methanol was required for lowering the FFA content. This can be explained by the fact that some of the FFAs were already esterified during the first step and lower amount of water was produced during the second step reaction [17]. 0.2 methanol–oil ratio and 45 min reaction time were detected as optimum conditions for the second step.

In these two steps, high amount of methanol was consumed which is not affordable. To get it economically justified, methanol can be recycled by water removal making it possible for reusability. Additionally, continuous removal of water from the mixture during the reaction provides a further reduction of methanol consumption [17].

3. 2. Effect of Catalyst on FFA The amount of catalyst used in the esterification reaction in both stages and variations are shown in Figure 3. According to Figure 3, the amount of optimized catalysts for both reactions is 1% wt/wt. various quantities of acid catalyst for biodiesel production from high FFA feedstocks have been reported in the literature.

Tiwari et al. [18] concluded that optimum amount of acid catalyst for reducing the FFA of jatropha curcas oil from 14% to less than 1% was found to be 1.43% v/v H_2SO_4. Also Hayan et al. [19] reported that the FFA of sludge palm oil (SPO) was reduced from 23.2% to less than 2% FFA using 0.75% wt/wt of sulphuric acid as acid catalyst.

3. 3. Transesterification Reaction With reducing FFAs of SBE oil from 9% to less than 1.34%, transesterification reaction was carried out. This reaction was conducted with methanol/oil molar ratio of 6:1 and 1% wt/wt KOH as an alkali catalyst [2, 20]. Also, biodiesel produced features the standards of Europe and US and results showed that the fuel is produced in accordance with these standards. Table 2 shows the properties of produced biodiesel.

TABLE 2. Fuel properties of SBE biodiesel

SBE biodiesel	EN14214 standard limits	EN14214 standard	ASTM D6751 standard limits	ASTM D6751 standard	Fuel property
177	>101	ISO CD 3679e	>130	D93	Flash point (˚C)
4.105	3.0282 – 4.3260	EN ISO 3104	1.6438 – 5.1912	D445	Dynamic viscosity (mPa.s in 40˚C)
0.876	0.860 – 0.900	EN ISO 3675/EN ISO 12185	-	-	density (g/cm^3 in 40˚C)
0.021	<0.050	EN ISO 12937	<0.050	D2709	Water content and sediment (% v)
0.425	<0.5	EN14104	<0.8	D664	Acid value (mg KOH/g)
0.017	0.02	EN14105m/EN14109	<0.02	D6584	Free glycerin (%wt)

4. CONCLUSION

The production of biodiesel from low-cost, high FFA raw materials is investigated. Feedstocks with high FFAs could not be an option for biodiesel with conventional alkali catalyst transesterification process. In this study, biodiesel was produced from SBE oil that contained high free fatty acid. Therefore, two-step esterification process was improved to reduce FFA value of the recovered oil. Diminishing the FFA content of the SBE oil to 3.01% was achieved using acid catalyzed (1% v/v H_2SO_4) reaction with methanol (0.30 v/v) at 60 °C and 45 min reaction time. In second phase of the research, FFA content was reduced from 3.01 to less than 2%. After each step, a settling time of minimum 1h was required for removal of methanol–water mixture. The molar ratio of 6:1 methanol to oil favors the completion of alkaline catalyzed transesterification process within 20 min at 60 °C. The principle properties of resulted biodiesel were compared with European and American Standards and most of properties matched the specifications.

5. ACKNOWLEDGMENT

The authors would thank Biofuel Research Team for their support in providing the bleaching earth oil.

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P A P E R I N F O

Paper history:
Received 24 April 2013
Received in revised form 25 May 2013
Accepted 20 June 2013

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چکیده

بیودیزل درصورتی اقتصادی خواهد بود که از مواد اولیه ارزان قیمت که حاوی مقدار زیادی اسید چرب آزاد (FFA) هستند و مانع تولید بیودیزل می‌شوند، تولید شود. در این مطالعه به فرایند دو مرحله‌ای برای تولید بیودیزل از روغن با درصد اسید چرب آزاد بالا در راکتور همزن دار بچ، پرداخته می‌شود. نمونه روغن از خاک رنگبر (SBE) استخراج گردید و برای تولید بیودیزل استفاده شد. در مرحله اول درصد FFA روغن تا ۳/۰۱ درصد با کاتالیزور اسیدی کاهش داده شد و در مرحله دوم به کمتر از ۲ درصد کاهش یافت. تری گلیسیرید تولید شده طی دو مرحله با متانول به نسبت مولی (۶:۱) مخلوط شد و در حضور کاتالیزور بازی به نسبت ۱ درصد وزنی روغن، واکنش ترانس استریفیکاسیون انجام گردید. مشخصات سوخت تولید شده از روغن خاک رنگبر اندازه‌گیری شد و با استانداردهای آمریکا و اروپا مورد مقایسه قرار گرفت. بنابراین فرایند بهینه تولید بیودیزل از منابع با درصد اسید چرب آزاد بالا انجام شد.

doi: *10.5829/idosi.ije.2013.26.12c.15*