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ScienceDirect

Procedia Environmental Sciences 31 (2016) 26 – 30

Procedia Environmental Sciences

The Tenth International Conference on Waste Management and Technology (ICWMT)

Biodiesel production from sewage sludge by using alkali catalyst catalyze

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Abstract

Sewage treatment produces sewage sludge, which is in large amount and continue to increase. The sludge contains considerable lipid and they can react with methanol to produce biodiesel. Normally acid catalyst was used in the transesterification reaction with sludge as a raw material, because sewage sludge contains a lot of free fatty acid which is an inhibition factor for transesterification reaction by alkali catalyst. However, alkali catalyst has other advantages such as easy to separate and fast reaction speed. As a result, in this research in-situ transesterification by alkali catalyst with sewage sludge as raw material was discussed. KOH/activated carbon as solid base catalysts were prepared by using wet impregnation method, which were used as catalysts in sewage sludge in-situ transesterification reaction. The influence of the catalyst mass fraction (15%,20%,25%,35%,45%), and dosage of catalyst (0.1g,0.2g,0.3g,0.35g,0.4g,0.5g,0.6g,0.7g), on the in situ-transesterification has been examined. The results show that: 25% (mass fraction, the same below) KOH/activated carbon was used as catalyst in the reaction process. When the mass ratio of alcohol and sludge was 10:1, reaction temperature was 60℃, catalytic amount (3wt%)and reaction time was 8h,the yield of FAME was 6.8%.Those were the optimum conditions. The surface features of catalyst were analysed by BET.

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Keywords: KOH/activated carbon; Sewage sludge; Biodiesel

1. Introduction

Fatty acid alkyl esters, also known as biodiesel, is a renewable fuel that is commonly produced by the reaction of refined pre-extracted vegetable oil and a simple aliphatic alcohol in the presence of a alkaline or acid catalyst[1,2]. It provides a similar energy density to petrodiesel and can be used in most diesel engines in pure form (B100) or may be blended with petroleum diesel at any concentration[3-7].However, because 70–85% of the overall biodiesel production cost is associated with the raw materials, sewage sludge is more competitive when the lipid concentration in it is more than 10% [4 ,8, 9].Sewage sludge is abundant and can get continuous yield. The higher value of the food products, more competitive the sewage sludge as the raw material for biodiesel. Therefore, the worldwide research in

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doi:10.1016/j.proenv.2016.02.004

the biodiesel industry has currently focused on how to convert low cost feedstock especially renewable wastes such as sewage sludge into biodiesel products via low cost technology i.e. cheap catalyst, simple processes, economic and environmentally friendly, etc. [10-12]. Sewage sludge normally has a large amount of free fatty acid (FFA), which is an obstacle for biodiesel production when alkaline catalyst is used. Because FFA will react with alkaline catalysts as a kind of acid which lead to yield of water and finally lead to soap production, so it will need much more consumption of catalyst and it also lead to lower yield of biodiesel. However, comparing with acid catalyst, alkaline catalyst is easier to be separated from the final product and it reacts much faster. Thus, developing new efficient alkaline catalyst for producing biodiesel by sewage sludge is still of interest.

Yongtao An et al, as to alkaline catalyst, supported solid alkaline catalysts are more widely used and faster for biodiesel production [13]. They can be filtered easily from the liquid products and be reused, and it also can be designed to give higher activity, selectivity and longer catalyst lifetime [14-16]. Therefore, research of heterogenous catalysts for biodiesel production is now taken more and more seriously. Shaotong Jiang et al. provided result on FAMEs yields from cottonseed oil by transesterification (95.3%) is the highest of all methods (several extraction strategies, different dosage of Na_3PO_4/MgO, and transesterification) tried [17].

The main objective of this paper is to determine the optimal parameters of in-situ transesterification of sewage sludge for maximizing the yield of biodiesel by alkaline catalyst, which are the catalyst mass fraction, dosage of catalyst.

2. Materials and Methods

2.1 Chemicals

Methanol (analytically pure), activated carbon (analytically pure), Anhydrous sodium sulfate(analytically pure),Sodium chloride (analytically pure),and n-hexane (analytically pure) were purchased from Xilong Chemical Co.,Ltd. Potassium Hydroxid(analytically pure)was purchased from Sinopharm chemical reagent Co. Ltd. All chemicals used in this process were at analytical pure level and used without further purification.

2.2 Sample preparation

Sewage sludge sample was collected from a municipal wastewater treatment plant in Beijing, China. The moisture content of the sludge sample is 83.3%, and the VSS of the sludge sample is 65.3%, and the average lipids content of the sludge sample is 9.4%. Sewage sludge was dried at 105 °C for 24 h and then was milled into fine powder by vibration mill. The sludge samples were stored in sealed plastic vials at 4 °C.

2.3 Catalysts preparation

In this research, alkali catalyst which was KOH/activated carbon prepared by using wet impregnation method was used. KOH/activated carbon preparation process: First, we had prepared KOH aqueous solution the mass fraction of which were 15%, 20%, 25%, 30%,35%,40%,45%. Then respectively got 30 ml KOH aqueous solution mixed with 6g activated carbon, impregnated for 30h, and then dried for 30h at 120 ℃.Finally, removed them and set aside.

2.4 Experimental design

Two factors(catalyst mass fraction, dosage of catalyst),and seven kinds catalysts of different mass fractions, and eight levels of catalyst dosage were shown in Table 1,the mass ratio of alcohol and sludge was 10:1,reaction temperature was 60℃,and reaction time was 8h,KOH/activated carbon was respectively taken as catalysts. The results were shown in Figure 1.The methanol to sludge mass ratio was 10:1 and the reaction temperature was 60℃.The reaction time and mechanical stirring speed were maintained at 8 h and 300 rpm, respectively.

Table 1. The factors of reaction process

The mass fraction of catalyst (%)	The dosage of catalyst(g)
15	0.1
	0.2
	0.35
20	0.1
	0.2
	0.35
	0.4
25	0.1
	0.3
	0.4
	0.6
35	0.4
	0.45
	0.6
	0.7
45	0.2
	0.35
	0.5

2.5 In situ transesterification

10 grams of dried sewage sludge was poured into a 500 mL rounded-bottomed flask with a reflux condenser. The mixture was heated to 60℃ at ambient pressure and stirred using a magnetic stirring bar at 300 rpm, and the assigned volume of methanol and catalysts were added to the flask. 50 mL volume of hexane was added to improve the lipid solubility in the reaction mixture. The reaction time was maintained at 8 h. After the reaction completed, the mixture was allowed to cool to room temperature. Then the flask contents were transferred into a 500 mL bottle, 10 mL of saturated NaCl solution and 100 mL of hexane were added and the mixture was stirred vigorously for three minutes. The mixture was then centrifuged at 3000 rpm for 5 minutes and the supernatant hexane phase was withdrawn and transferred into a 250 mL separatory flask. The extraction procedure was repeated two times. Afterwards, the total volume of the collected supernatant was washed with deionized water.The bottom layer was then discarded and the upper layer (hexane layer) was passed through a filter paper containing anhydrous sodium sulfate and collected into a 250mL flask. A 10 mL aliquot of the hexane phase was pipetted into a test tube for FAME analysis and the remainder was subjected to solvent removal using a vacuum rotary evaporator at 40 °C. After all the hexane was removed, the flask was flushed with nitrogen to remove any remaining hexane in the gas phase and then weighed to determine the weight of the residue.

3.Results and Discussion

In this paper, in-situ transesterification was used for biodiesel production. The effects of different factors and levels of them were considered for optimization. The results were demonstrated in Figure 1. Figure 1 gives the test scheme and results of sewage sludge for biodiesel production , the evaluation index is the gravimetric yield (weight/dry weight of sludge) of the biodiesel. Each experimental result was three parallel samples' average and the

relative error was between 2%~7%. As Figure 1 shows, the in situ transesterification of sewage sludge have made effects under given conditions, the gravimetric yield is mainly between 3% and 7%

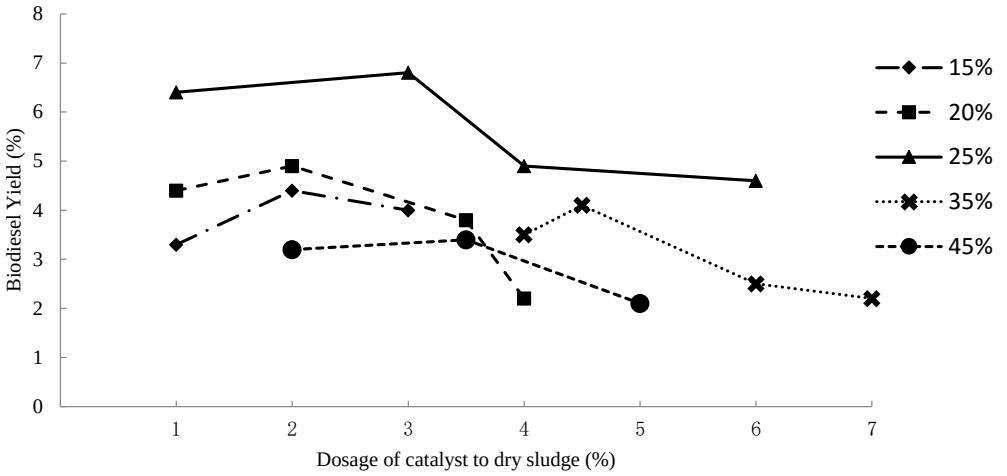

Figure 1 The tendency of biodiesel yield

From Figure 1 it can be found that the biodiesel yield increased with the increase of catalyst. The yield decreased after it reached the maximum.

We also have prepared biodiesel by using KOH as the catalyst. The yield of biodiesel (weight/dry weight of sludge) was about from 1% to 2%. The react conditions are the same with the Test1 besides the catalyst. As a result, we can conclude that KOH supported solid catalyst is better than pure KOH. Therefore we have tested the surface features of catalysts by BET.

Table 2 Surface features of catalysts

Items	15%	20%	25%	35%	45%	activated carbon
BET(m^2/g)	7.6	0.9	0.6	0.5	0.9	803.5
Aperture (nm)	6.15	21.2	25.5	23.4	50.3	2.9

BET of catalysts were analyzed by using 3H-2000PS2 static volume method with Specific surface &pore size analysis instrument which was made by BeiShiDE instrument-SAT .

In general, micropore of activated carbon is less than 2nm. However, the micropore of base catalyst is 6~51nm, which is much bigger than AC itself.

The activated carbon used here is mesopore. As the increase of KOH mass percentage, the aperture of the supported solid alkaline catalyst was gradually increased. So the original pores in AC were filled by KOH.

The minimum BET was 0.5m^2/g when the mass fraction was 35%. However, the highest yield of biodiesel was obtained when the mass fraction of KOH was 25%. It seems that if KOH was excessive, the yield was reduced. So we can conclude the best condition of supported alkaline catalyst for biodiesel process was the mass fraction of KOH was 25%.

4. Conclusions

Biodiesel production from sewage sludge catalyzed by alkali catalysts is feasible by using in situ transesterification. The suitable conditions were methanol to sludge mass ratio was 10:1(w/w), the mass fraction of KOH was 25%, the dosage of catalyst was 3% (wt/wt), and temperature was 65℃. The corresponding yield of

biodiesel is 6.8%. The mass fraction of KOH and dosage of catalyst had significance influence on the yield of FAMEs. With the different mass percent of KOH solution embedded with the same amount of AC, the structure of the base catalyst changed with bigger pore diameter and smaller BET.

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