VOL. 11, NO. 11, JUNE 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

PRODUCTION OF BIODIESEL USING TANNERY FLESHING AS A FEEDSTOCK: AN INVESTIGATION OF FEEDSTOCK PRE-TREATMENT VIA SOLID-STATE FERMENTATION

Santhana Krishnan, Zularisam A. Wahid, Lakhveer Singh and Mimi Sakinah,
Faculty of Engineering Technology, University Malaysia Pahang (UMP), Lebuhraya Tun Razak, Gambang, Kuantan, Pahang, Malaysia
E-Mail: zularisam@ump.edu.my

ABSTRACT

Depleting fossil fuel resources, increasing cost and the effect of GHGs has signalled the exploration alternative fuels for diesel engines. This study focused on transesterification using tannery fleshing as a feedstock and sodium hydroxide as a homogenous catalyst. The tannery fleshing was pre-treated via solid-state fermentation in order to reduce the free fatty acids present in it. The optimum conditions for the transesterification were: time 3 h; methanol to oil ratio 6:1 and catalyst amount 1% with highest methyl ester content at 89 wt. %.

Keywords: biodiesel, catalyst, transesterification, solid-state fermentation.

1. INTRODUCTION

Recently, the increase of petroleum consumption in industrial, transportation and technology developments has been leading to scarcity of the limited fossil fuel resources in the world [1,2]. Because of this, researchers have been putting more attention finding alternative energy such as biodiesel which is believed can lower the dependency of fossil fuel and to support the environmental sustainability [3]. Biodiesel is renewable,non-toxic, biodegradable, environmental friendly and acts as a source domestic energy [4]. Starting from last quarter of this year, the Malaysian government decided to implement the B10 biodiesel programme using crude palm oil (CPO) because of resources and also demand of energy [5]. Chemically, it is a mono alkyl ester of long chain fatty acids and can be produced from vegetable oils or animal fats. Biodiesel can be produced from various vegetable oils and animal fats. However, the feedstock types, availability and material cost are the obstacles to the commercialization of biodiesel production [6]. A wide range of low-cost feedstock such as waste frying oils [7] and new vegetable species [8] have been investigated. Presently, biodiesel from tannery waste has drawn interest for biodiesel production by the researchers. A typical representative of such wastes is abundant fat and fleshing's which however, usually contains a significant amount of free fatty acids, proteins and other impurities. Pre-treatment was suggested as a means of processing this acidic feedstock, thus enabling the reduction of the free fatty acid content under the limit value of 0.5% w/w when the alkali catalyst is then appropriate for transesterification. The feedstock pre-treatment process involved the refining of tannery wastes and subsequent extraction using a methanol or methanol solution with an equimolar amount of alkali [9-10]. Encinar et al. [10], studied the effects of homogeneous base and acid catalysts at different concentrations on the biodiesel yield from beef tallow and concluded that NaOH was a more efficient base catalyst than sodium methoxide for the transesterification of beef tallow. They obtained optimum yield of biodiesel at a 9% catalyst concentration. This research aimed to reveal the utilization of tannery fleshing as feedstock and sodium hydroxide as a catalyst. The pre-treatment of feedstock study using solid-state fermentation was also studied. The optimization of methanol to oil ratio, catalyst amount and time was investigated.

2. METHODS

a) Materials

Tannery fleshing was collected from Long Lai Tannery Sdn. Bhd, Selangor, Malaysia. Sodium hydroxide, methyl heptadecanoate of chromatographic grade (internal standard) and methanol were purchased from obtained from Sigma–Aldrich (USA).

b) Pre-treatment using solid-state fermentation

In the 5 L reactor, 250 grams of sized 0.20 cm tannery fleshing (working height of 15 cm) were inoculated with 500 grams of sand silica immobilized with microbacterium species and incubated for 72 hours at 37°C, pH 6.5 with 95% humidified air [28]. The small amount of trace elements 0.59 g/L magnesium sulphate ($MgSO_4$), 0.065 g/L ferrous sulphate ($FeSO_4$), 0.038 g/L cobalt chloride ($CoCl_2$), 0.029 g/L manganese di chloride ($MnCl_2$), 0.247 g/L calcium chloride ($CaCl_2$) and 0.223 g/L ammonium molybdate ($(NH_4)_6Mo_7O_{24}$ were also added. The fermentation was performed for 3-4 days at suitable time intervals, samples of substrates were randomly sampled and analysed in GC-MS instrument (Thermo scientific GCMS 51872, mobile phase- methanol 2ml/ml flow rate) and separated compounds were determined using library match.

c) Transesterification reaction

Transesterification process was performed using 1L reaction flask equipped with reflux condenser, magnetic stirrer and thermometer. The pre-treated tannery fleshing was introduced into the reaction flask. The process was experimented in three catalyst loadings such as (0.5%, 1.0% and 1.5% sodium hydroxide) and three methanol-to-oil molar ratios (3:1, 6:1 and 9:1). The reaction temperature was maintained at 60 ± 1°C for 1 to 3 hours. After completion of reaction time, the mixture was transferred to a separating funnel and allowed to stand for overnight separation. The lower layer was separated from an upper layer and using solvent evaporation using a rotary evaporator, the pure methyl ester was obtained. C_{13} NMR analysis was conducted for the preliminary analysis to observe the resultant methyl ester according to Silverstein et al. [11].

3. RESULTS AND DISCUSSION

a) Tannery fleshing characterisation

From the composition, the moisture and ash content of the tannery fleshing was found to be 78.5 ± 5.5% and 51.9 ± 2.5% respectively. The C: H: N ratio was 15: 1: 1. Among the various elements studied by the atomic sorption spectrophotometer, no elements were found higher than other elements with the absence of chromium and manganese. The acid and saponification values were 13 and 202 mg KOH/g respectively (Table-1). All the experiments were performed on the basis of dry weight and the standard deviations are based on triplicate readings.

Table-1. Properties of raw tannery fleshing.

Properties	Unit	Raw tannery fleshing
Dry matter	(wt. % ± S.D.)	92.02 ± 0.48
Acid value	(mg KOH/g ± S.D.)	13.70 ± 0.10
Saponification value	(mg KOH/g ± S.D.)	202.90 ± 0.99
Water content	(wt. % ± S.D.)	7.98 ± 0.58

b) Solid-state fermentation

The free fatty acid content in tannery fleshing residues under investigation was reduced using solid-state fermentation from 1.65–6.55% to less than 0.5% to avoid an unfavourable condition. Table-2 shows properties of pre-treated tannery fleshing used as feedstock after solid-state fermentation.

Table-2. Fatty acids composition of tannery fleshing after solid-state fermentation.

Fatty acid	Composition (%)	
	Present study	Previous study [13]
C14:0	1.4	1.5-1.6
C16:0	22.5	23.7-29.1
C16:1	3.7	1.2- 3.2
C18:0	11.3	11.2-21
C18:1	49.1	26-51
C18:2	5.5	7.2-11.9
C18:3	0.5	0.4-1.5
C20:0	0.4	0.1-0.6
C20:1	1.5	0.7-1.6
Total	95.2	-

During the pre-treatment, microbial loading capacity on sand silica matrix was 1 mg/g of microbacterium with 5.5 mg/g silica support. The silica matrix provided the uniform mat for the microbacterium to adhere and hydrolyse tannery fleshing effectively. The scanning electron microscopy investigation of the hydrolyzed tannery fleshing samples allowed the visualization of hydrolysis of the solid fat and protein present in it (Figure-1 a and b). After fermentation, the micro structural arrangements of fleshing fibres has been completely altered and damaged. Similarly, Ferrarezi et al. [12] immobilized microbe Thermomucor *indicae* on loofah sponges for transesterification reactions in their studies. The main fatty acids in the tannery fleshing were around 48.5% oleic acid, 5.5% linoleic acid and 22.5% palmitic acid, totalizing 40-45% saturated, 55–60% unsaturated fatty acids. From this amount, 40–43% was monounsaturated that are much more stable than polyunsaturated fatty acids [3]. The lipid profile was similar with the results Shahidi et al. [13]. They investigated the optimum conditions for methyl ester production using waste lards.

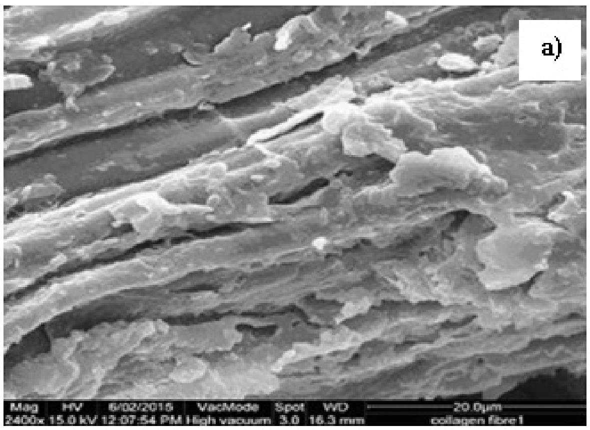
c) Transesterification

The conversion of pre-treated tannery wastes to methyl esters, under the conditions described in Section 2.3, was found to be 89 wt.%. The mass ratio of reactants such as methanol to oil ratio and catalyst loading and reaction time are the most significant variables to affect the conversion rate. It was confirmed from the experiment that fatty acids esters conversion increased from 50% to 89% with an increase catalyst loading percentage from 0.5 % to 1 wt. % (Figure-2b). In total, homogenous sodium hydroxide amount of 1.0 wt% was selected an optimal concentration for the transesterification because it was able to provide enough active sites between catalyst and the reactants hence drive the reaction kinetics. Further increase in catalyst ratio 1.5% shows the no improvement in conversion rate. The similar results were described by canoira et al., [14]. In the case of methanol/ oil mass ratio 6:1 was optimal as shown in Figure-2b. The excess methanol would shift the substrate- catalyst equilibrium towards the direction of methyl ester production and increase in methanol could dilute the oil resulting in slow reaction kinetics. The relationship between reaction time and the conversion rate showed that the reaction time had markedly significant effect on the transesterification process. The Triglycerides conversion increased from 71.2% to 97.9% with the increase of reaction time from 1 to 3 hours at 65°C (Figure-2c). However, further increasing reaction time, the conversion rate almost kept stable. A reaction time longer than 3 hours did not change the triglycerides conversion any more. It was possibly due to close equilibrium conversion achieved in the transesterification [15]. C_{13} NMR analysis was conducted for the preliminary analysis to observe the formation of functional group desired. C_{13}NMR spectrum shows the characteristic peaks of methylene carbons of the long carbon chain in fatty acid methyl esters at 22.2817-

VOL. 11, NO. 11, JUNE 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

31.9727 ppm. The carbonyl carbon of the ester molecules of methyl ester signals at 70.374 - 77.3942 ppm. The peak around the 42.3790 ppm indicated the methoxy carbon of esters. The terminal carbon of methyl groups and methylene and methyl carbons of fatty acid moiety are at 14.1932 and 20.851 ppm found respectively.



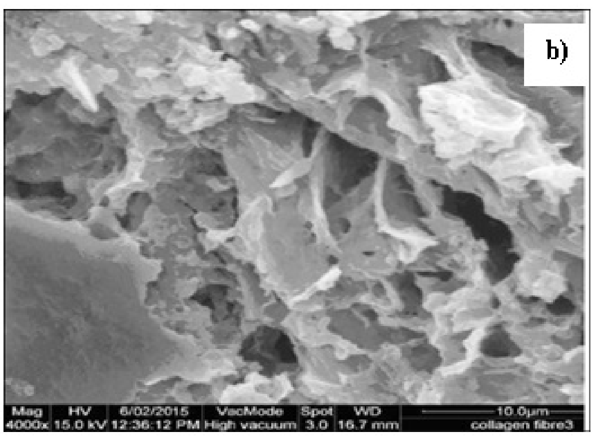
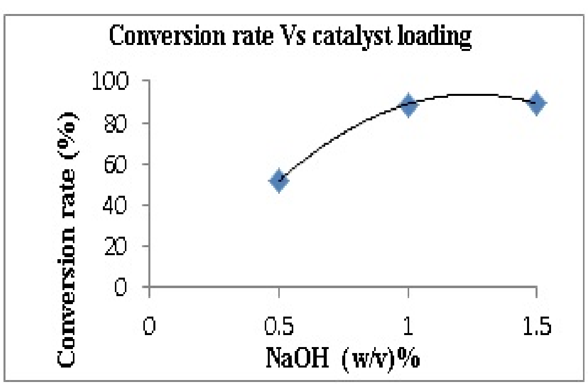
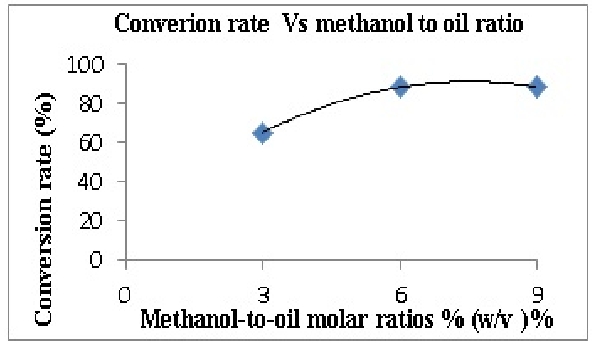


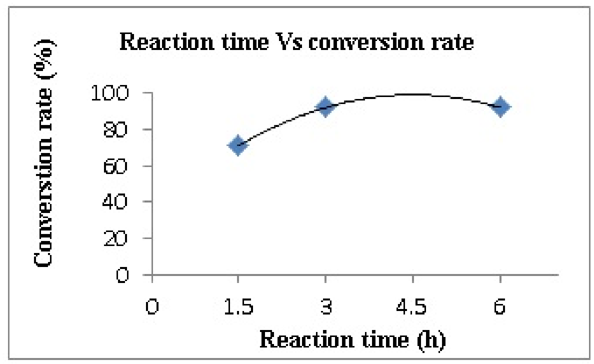
Figure-1. The Scanning electron microscopy images of tannery fleshing before and after solid-state fermentation. (a) Raw un-hydrolysed fleshing and (b) Hydrolyzed fleshing.



(a)



(b)



(c)

Figure-2. Transesterification reaction: a) – Effect of catalyst b) Effect of methanol to oil ratio and c) Effect of reaction time on conversion rate.

4. CONCLUSIONS

In this work, pre-treated tannery fleshing was successfully utilized as a low-cost feedstock to produce methyl ester (biodiesel) via transesterification. The highest Methyl ester content of 89 wt. % was obtainable in 3 hour reaction time at 65 °C. Optimization of reaction parameters revealed that methanol to oil, 6:1 molar ratio; catalyst, 1 wt. % and reaction time of 3 hours as the optimal reaction conditions. Materials used in this work were derived from leather waste sources and it should be given a priority for sustainable production of biodiesel.

REFERENCES

[1] Singh L., and Wahid Z. A. 2015. Enhancement of hydrogen production from palm oil mill effluent via cell immobilisation technique. International Journal of Energy Research. 39(2):215-222.

[2] Silitonga A. S., Masjuki H. H., Mahlia T. M. I., Ong H. C., Kusumo F., Aditiya H. B., and Ghazali N. N. 2015. Schleichera oleosa oil as feedstock for biodiesel production. Fuel. 156: 63-70.

[3] Ferella F., Celso G.M., Michelis I., Stanisci V., and Veglio F. 2010. Optimization of the transesterification reaction in biodiesel production. Fuel. 89(1):36-42.

[4] Kolomaznik K., Barinova M., and Fuerst T. 2009. Possibility of using tannery waste for biodiesel production. The Journal of the American Leather Chemists Association. 104(5): 177-182.

[5] Silitonga A.S., Masjuki H.H., Mahlia T.M.I., Ong H.C., Atabani A.E., and Chong W.T. 2013. A global comparative review of biodiesel production from jatropha curcas using different homogeneous acid and alkaline catalysts: Study of physical and chemical properties. Renewable and Sustainable Energy Reviews. 24: 514-533.

[6] Kegl B. 2008. Effects of biodiesel on emissions of a bus diesel engine. Bioresource technology. 99(4): 863-873.

[7] Tomasevic A.V., and Marinkovic, S.S. 2003. Methanolysis of used frying oil. Fuel Processing Technology. 81(1): 1-6.

[8] Kulkarni M.G., Dalai A.K., and Bakhshi N.N. 2007. Transesterification of canola oil in mixed methanol/ethanol system and use of esters as lubricity additive. Bioresource technology. 98(10):2027-2033.

[9] Omar W.N. and Amin, N.A.S. 2011. Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology. Biomass and bioenergy. 35(3):1329-1338.

[10] Encinar J.M., Sanchez N., Martinez G., and Garcia L. 2011. Study of biodiesel production from animal fats with high free fatty acid content. Bioresoure Technology. 102:10907–14.

[11] Silverstein R.M., Bassler G.C., and Morrill T. C. 2001. Spectrometric identification of organic compounds. NY: John Wiley & Sons. p. 196.

[12] Ferrarezi A.L., Ohe T.H.K., Borges J.P., Brito R.R., Siqueira M.R., Vendramini P.H., and Gomes E. 2014. Production and characterization of lipases and immobilization of whole cell of the thermophilic Thermomucor indicae seudaticae N31 for transesterification reaction. Journal of Molecular Catalysis B: Enzymatic. 107:106-113.

[13] Shahidi F., & Zhong Y. 2010. Lipid oxidation and improving the oxidative stability. Chemical Society Reviews. 39(11): 4067-4079.

[14] Canoira L., Gamero R.M., Querol E., Alcantara R., Lapuerta M., and Oliva F. 2008. Biodiesel from low-grade animal fat: production process assessment and biodiesel properties characterization. Industrial & Engineering Chemistry Research. 47(21): 7997-8004.

[15] Rashid U. and Anwar F. 2008. Production of biodiesel through optimized alkaline-catalyzed transesterification of rapeseed oil. Fuel. 87(3): 265-273.