

Leather processing industry waste (lime fleshing): A prospective substrate for production of biodiesel

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Abstract

Production of biodiesel using leather industry solid wastes (leather lime fleshing) containing high fats and proteins was developed, which benefitted both the ways to manage waste along with generation of renewable energy. Oil from this waste was obtained using solvent extraction process. Acid catalyzed esterification followed by transesterification using KOH was used in this biodiesel production process. Extracted oil containing high free fatty acid of 11.19 % was subjected to acid catalyzed esterification using 80% methanol, 2.5 % H₂SO₄ at 70 °C for 60 min. The esterified oil than trans esterified into biodiesel using 60% methanol and 0.8% KOH at 60 °C for 120 min. Biodiesel yield was 95.81%. Characteristics of produced biodiesel like flash point (145 °C), acid value (2.7 mg KOH/g), density (0.870 g/cc), pour point (-12 °C) and viscosity (5.79 and 1.2 cSt at 40 and 100 °C respectively) etc. were determined. These characteristics were very close to the commercial biodiesel standards. The renewable leather industry waste could be a potential sources of biodiesel production and would protect environment and contribute to energy demand.

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Introduction

Leather industry and leather goods is one of the most important export sectors in Bangladesh and around 3% of country's export amounting US\$ 250 m yearly since past decade (Basak *et al.*, 2014). At the same time these industries are one of the most pollutant producing sector (Rouf *et al.*, 2013). These industries generate a large volume of solid wastes containing protein, fats and residual chemicals (Thangamani *et al.*, 2009). Volatile fatty acids (VFAs) are produced from the fatty ingredients in fleshing by bacterial hydrolysis (Shanmugam and Horan, 2009). Hydrogen sulphide (H₂S) generating from fleshing was expedite by produced VFAs, exposure of which can cause irritates the eyes, skin and creates respiratory problems (Kump *et al.*, 2005). Waste biomass is one of the important sources to produce fuels and chemicals (Islam *et al.*, 2017 and 2021).

Leather lime fleshing can be an alternative source for biodiesel production and would be environment friendly to utilize this waste.

Most of the energy used these days are from fossil sources: petroleum, coal, and natural gas. Energy requirements in the world is ever increasing and this problem cannot be avoided but need to find alternative sources of energy. It is necessary to find a sustainable solution in future energy scenario to overcome the drawbacks of fossil sources and petroleum reserve depletion, rise of energy price and greenhouse gas emission as byproducts while using fossil fuels which has undesirable impact on the environment. Biodiesel is a suitable alternative substitute which is renewable and it can decrease the dependency of diesel from fossil fuel (Banik *et al.*, 2015).

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The main sources of feedstock to produce biodiesel are vegetable oil, animal fats, used cooking oil and used greases. Most commonly used vegetable oil for biodiesel production are oils from soybean, rapeseed, sunflower seed, palm oil etc. (Dripan, 2020). It can be used as it is or in the form of mixture without any engine modifications. The use of biodiesel can reduce the CO₂ emissions and there are no requirements of current refueling setup for wider range of implementation (Mehmet, 2021).

Leather industries are working to minimize the volume of waste generated by utilizing these to produce value added products. The efficient use of leather lime fleshing, which is renewable resources in leather industry. The objective of this work is to use this renewable leather industry waste as substrate to produce biodiesel which is substantially reduce the environmental pollution and to contribute to the fuel sector.

Materials and methods

Sample collection and oil extraction

Wet salted cow limed fleshing was collected from Samina tannery at Hamayetpur, Savar, Dhaka, Bangladesh. Collected sample then chopped and sun dried followed by oven dried at 100 °C before grinding into powder using mortar and pestle. Oil extraction was done from the grounded sample in Soxhlet equipment and petroleum ether as solvent. 50 g powder fleshing sample was taken with 400 mL of solvent in Soxhlet apparatus and extraction was performed for 2.5 h at 60 °C. The extracted fleshing oil and solvent was separated by distillation. The distillate, pet-ether recovered was reused in the oil extraction process. Extracted oil was characterized using ASTM and IP standard methods.

Esterification of extracted oil

Esterification of oil was done using alkaline catalyst in 500 mL two neck round bottom flask reactors with continuous stirring of 400 rpm which reduced free fatty acid content in the oil below 2%. Acid catalyzed methanol esterification of oil was done in hotplate magnetic stirrer for 2 h. Glycerin was also produced along with methyl ester. High FFA contained oil is not suitable for transesterification and hence esterification was necessary to reduce FFA (Atadashi *et al.*, 2013).

Transesterification

The base catalyzed transesterification utilizes the same setup that was used for acid esterification. Methanolic KOH solution was prepared then used for transesterification reaction. The pretreated oil from the acid esterification step was heated to 40 °C and methanolic KOH solution was added into the flask. Heating was continued at the required temperature along with the stirring at 400 rpm until the reaction was completed. The reaction mixture was settled in separatory funnel for 16 h. Upper layer in the funnel mainly consisting of methyl ester and glycerol and other impurities was in the bottom layer. Methyl ester was collected by drawing off the bottom layer.

The impurities present in methyl ester along with some unreacted materials like triglyceride (TG), residual catalyst and alcohol was separated in the biodiesel purification process. As intermediate monoglyceride and diglyceride are also produced along with biodiesel (Takase *et al.*, 2014).

Biodiesel purification

Hot water (10 vol.% of biodiesel) was sprayed over the methyl ester layer and this was repeated until clear water was found in the lower layer. Collected biodiesel from top layer then distilled to clear from the traces amount of methanol. Fig. 1 shows the biodiesel production from limed leather fleshing waste.

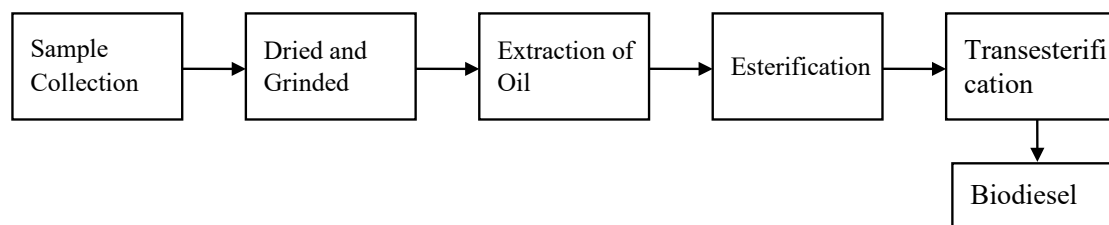


Fig. 1. Flow diagram of biodiesel production from limed leather fleshing waste

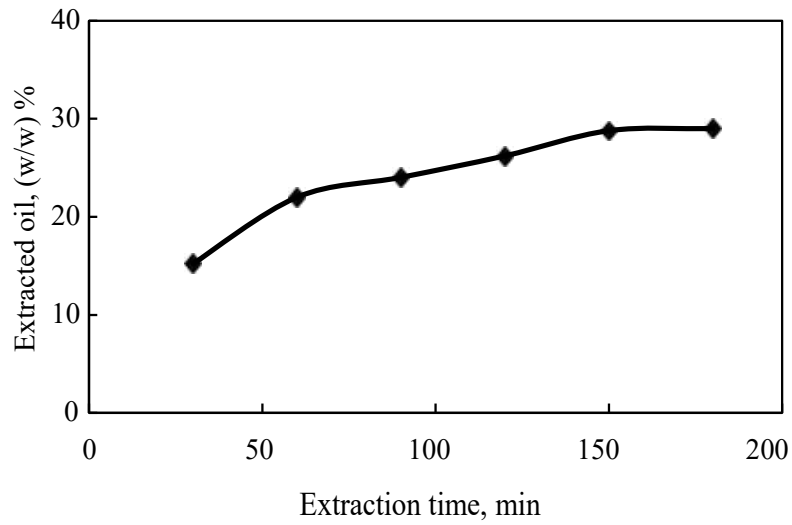


Fig. 2. Variation of Oil Content with Extraction Time

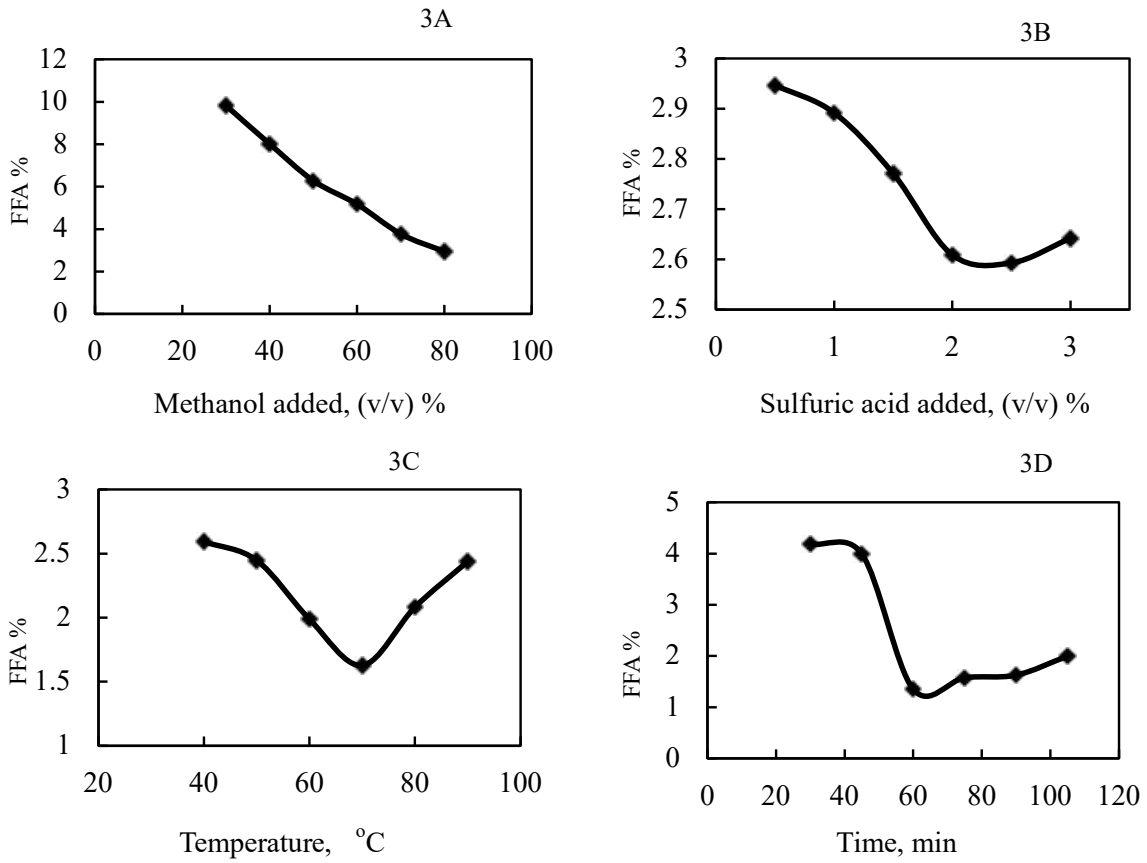


Fig. 3. A. Variation of FFA Content with the Volume of Methanol; B. Volume of Sulfuric Acid; C. Temperature and D. Reaction Time

Results and discussion

Extraction of the oil

The extraction of oil was optimized by changing the extraction duration from 30 to 180 min at 60 °C using petroleum ether as solvent. The oil content was about 15.2% when the extraction was carried out for 30 min. With the increasing of extraction time to 60 min there was drastic increase in extraction to 22% (Fig. 2). During the extraction period of 60 to 150 min there were a steady rise of extracted oil which was attributed to increase the rate of internal mass transfer with consequent increase in efficiency of extraction. While the extraction duration was increased to 180 min, oil content was not that significantly increased, being 28.77% for 150 min and 28.98% for 180 min.

Physicochemical characterization of extracted oil

Characteristics of extracted oil are showed in Table-I, where all the parameters were determined by following standard ASTM and IP methods. Table-I shows that, extracted oil contained high acid value (22.38 mg KOH/g) because of higher content of FFA. The oil also had high moisture content

(0.28 vol%) and this may cause the hydrolysis of triglycerides to diglycerides and lead to the formation of free fatty acids. There was also a possibility that no transesterification reaction would occur due to high FFA content and therefore, refining of oils to reduce their acid value was necessary prior to transesterification. The viscosity of oil at 40 °C was exceptionally high (40.3 cSt) and oil pretreatment by esterification in presence of acid as catalyst was necessary to lower the viscosity. Calorific value was low may be due to higher oxygen presence of the triglycerides. Low flash point, high ash and carbon residue led to pretreatment followed by transesterification and purification in order to get rid of the impurities present in extracted oil.

Acid catalyzed esterification

The esterification reaction was done in acidic condition to decrease the FFA content below 2%, because more than this FFA content in Oil is not appropriate for transesterification to produce biodiesel (Thiruvengadaravi *et al.*, 2012). In the acid catalyzed esterification, the FFA react with alcohol in existence of H₂SO₄ catalyst and converted to biodiesel eliminating the problems associated with FFA in the base catalyzed transesterification. The acid catalyzed esterification was

Table I. Characteristics of extracted limed fleshing oil

Parameter	Method	Result
Density at 15 °C, g/cc	IP-160/57	0.890
Kinematic viscosity at 40 °C, cSt	ASTM-D 445-65	38.75
Kinematic viscosity at 100 °C, cSt	ASTM-D 445-65	11.97
Acid value, mg KOH/g	IP-1/58	22.38
Carbon residue, % (w/w)	ASTM-D 189-65	0.032
Water content, % (v/v)	IP-74/57	0.29
Flash point, °C	ASTM-D 93-62	190
Color index	ASTM & DIN 51900	1
FFA	Titration and 0.5 mg KOH/g of Acid Value	11.19

optimized by varying the methanol addition, catalyst addition, reaction temperature and reaction time and the condition for which the FFA content was the lowest and utilized for the pretreatment of the oil which was later used to produce biodiesel.

The acid value and FFA content was determined with the methanol addition of 30, 40, 50, 60, 70 and 80 (v/v)% of oil keeping the H_2SO_4 of 0.5 vol% at 60 °C for 90 min. Fig. 3A shows that, with the increase of methanol addition from 30 to 80%, the FFA was decreased from 9.8 % to 2.9% higher amount of methanol drives the reaction towards completion as well as decrease the viscosity of oil. The volume of methanol was not increased further as there was a chance of methanol acting as a co-solvent and leading to the hydrolysis of the free acid methyl esters and forming free fatty acids.

H_2SO_4 was used for acid pretreatment of oil. The FFA and acid value were determined using various amount of acid added from 0.5 to 3% (v/v) of oil keeping methanol addition of 80 vol% at 60 °C for 90 min. With the increase of sulfuric acid addition from 0.5 to 3.0% FFA decreased from 2.94% to 2.64% respectively (Fig. 3B). This was attributed to the dual role of sulfuric acid to increase the rate of reaction and acting as a dehydrating reagent, pushing the forward equilibrium and hence ester yield was increased. On carrying out at the esterification reaction using 3.0% (v/v) of sulfuric acid, the mixture became dark in color and it was not possible to separate the mixture into two layers because additional sulfuric acid added color of the product was dark. 2.5 vol% of H_2SO_4 was used as the optimum catalyst volume for the esterification reaction as maximum reduction in FFA content was observed at this volume.

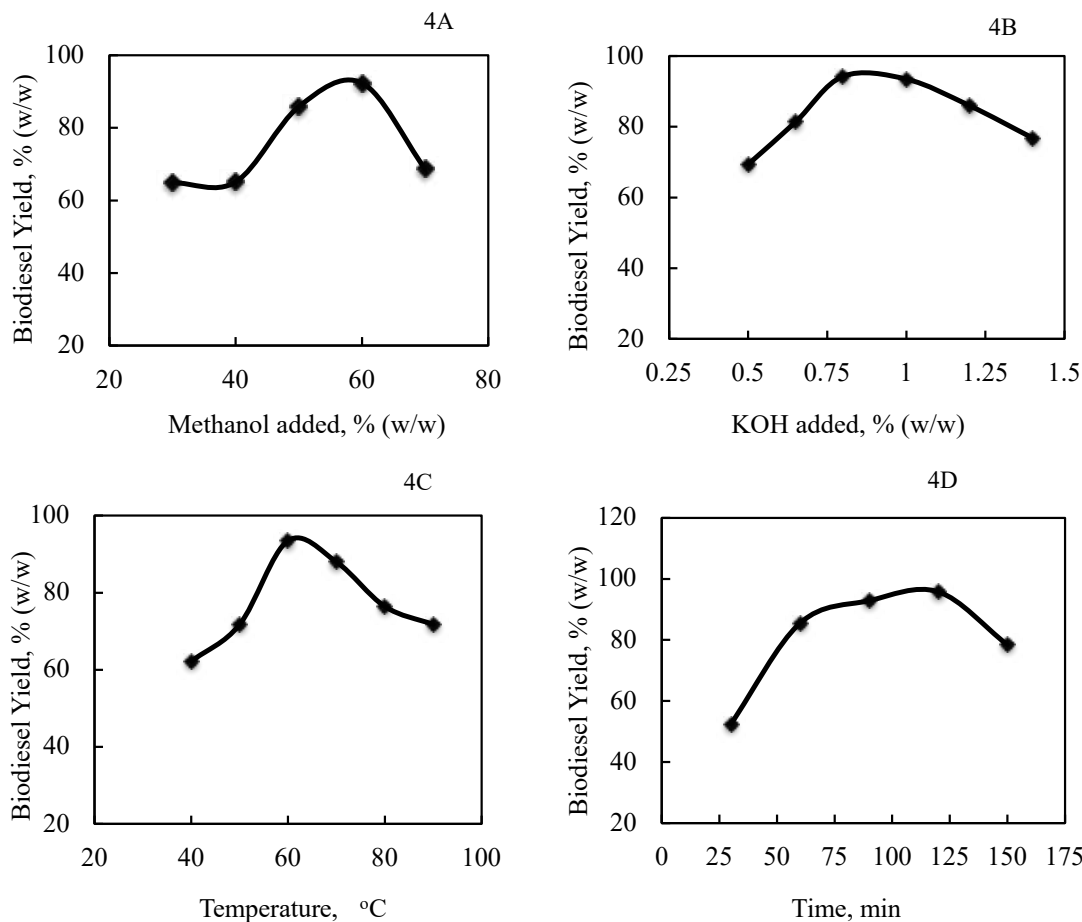


Fig 4. A. Effect of methanol addition; B. Effect of KOH; C. Effect of reaction temperature; D. Effect of reaction time on transesterification reaction

The FFA and acid value was measured at various reaction temperature from 40 to 90 °C keeping the methanol addition of 80 vol%, sulfuric acid addition of 2.5 vol% for the reaction time of 90 min. Fig. 3C shows that, FFA content was decreased from 2.59% to 1.62% with the increase of reaction temperature from 40 °C to 70 °C then started to increase again with higher temperature. Biodiesel conversion from free fatty acid was very low at lower temperature even with the long time stirring. Conversion rate was increased with the increasing the temperature. But as the temperature increased over 70 °C, FFA content was showed slightly higher probably due to methanol losses in the reaction and yield was also showed darker in color.

The FFA content was measured with the reaction time of 30 to 105 min at constant methanol added 80 vol%, sulfuric acid 2.5 vol% at the temperature of 70 °C. With the increased time of reaction from 30 to 60 min, FFA content was reduced from

4.18% to 1.35% and then started to increase again, because 60 min was required to complete conversion of FFA into methyl ester. After 60 min, the surge of FFA content may be because of ester decomposition as a consequence of longer stirring time (Fig. 3D).

Effect of methanol added, catalyst, reaction temperature and reaction time in transesterification

Esterified oil was separated using a separatory funnel while settled in 1 h time, the excess sulfuric acid, methanol and water moved up to the top layer and the bottom layer contained esterified oil. Lower amount of methanol present in esterified oil was removed by distillation and used for base catalyzed transesterification. The condition was used for transesterification followed by previous studies (Sivakumar *et al.*, 2011; Banik *et al.*, 2022).

Table II. Comparison of properties of biodiesel and biodiesel standard

Parameter	Produced biodiesel	Biodiesel Standard
Density at 15 °C, g/cc	0.870	0.880
Kinematic viscosity at 40 °C, cSt	5.79	1.9-6.0
Kinematic viscosity at 100 °C, cSt	1.2	1.1
Acid value, mg KOH/g	2.7	0.80 Max
Carbon residue, % (w/w)	0.03	0.05 Max
Ash content, % (w/w)	0.07	0.02 Max
Water content, % (v/v)	0.04	0.05
Flash point, °C	145	100-170
Sulfur content, % (w/w)	0.06	0.05 Max
Calorific Value, kcal/kg	9562.4	10027
Cetane Number	48.3	48-60
Pour point, °C	-12	-15 to 10

Methanol was used for transesterification of esterified oil. The yield of biodiesel was determined with the 40 to 70 % of methanol addition into the reaction maintaining catalyst KOH 1.0 wt% at 60 °C for 90 min. Methanol and triglyceride was non-miscible at ambient condition and hence reaction mixture was stirred mechanically at 400 rpm to expedite the mass transfer. During the reaction period, emulsions was developed and effortlessly broken down to bottom glycerol layer and top layer rich in methyl ester. The yield of biodiesel was increased from 64.89% to 92.35% with the increased amount of methanol from 30 to 60 wt% (Fig. 4A). Addition of more than 70 wt% of methanol into the reaction, biodiesel yield was decreased to 68.65% and this may be because the excess methanol acted as a solvent for methyl ester and glycerol that enhanced the contact between the molecules and favoured the backward reaction.

The biodiesel yield was determined for various KOH addition from 0.5 to 1.4 % (w/w) of oil with 60 % methanol at 60 °C for 90 min of reaction time. Fig. 4B shows that, lower yield of biodiesel at lower concentration of KOH may be due to incomplete conversion of the pretreated oil and no transesterification was observed below with 0.5% KOH. The biodiesel yield increased from 69.4% to 94.27% while KOH was increased from 0.5% to 0.8% and then yield decreased with the increasing of further KOH added. The decrease in the yield of biodiesel may be due to the emulsions formation which increased the viscosity and lead to gel development.

The yield of biodiesel was studied with reaction temperatures of 40 to 90 °C while methanol concentration was 60 %, KOH was 0.8 % of esterified oil and reaction time was 90 min. Fig. 4C. shows that, with the temperature increased from 40 °C to 60 °C, biodiesel yield was increased from 62.25 % to 93.52 % because rate of reaction was increased with the increased temperature but more than 60 °C there was a decrease in biodiesel yield. At higher temperature, yield was decreased may be because of the methanol evaporation loss (boiling point of methanol 64.7 °C).

When reaction time changed from 30 to 180 min with fixed methanol of 60%, KOH of 0.8% and temperature of 60 °C biodiesel yield increased with reaction time up to 120 min and at the peak the yield was 95.81% (Fig. 4D). This was due to perfect contact of reagents with increase in reaction time with continuous stirring. More than this reaction time yield was decreased because longer time of stirring caused difficulties in phase separation.

Physicochemical Characterization of Produced Biodiesel

Various physicochemical properties of the biodiesel were evaluated and compared with the standard values. Table-II assesses the standard biodiesel properties of produced biodiesel with commercial biodiesel. These results demonstrates that the characteristics of produced biodiesel would be an alternative option to commercial diesel.

Conclusion

The study showed that leather lime fleshing oil has great potential to be used as one of the feedstocks for biodiesel production owing to its higher oil content and yield potential. A two-stage acid-base process was needed for the biodiesel production from leather lime fleshing waste oil containing high FFA. Most of the properties of produced biodiesel was met with the standard values. Leather lime fleshing is generally dumped in Bangladesh rather than using it. Which is causing environmental pollution and it is increasing consequently. Using it as a raw material of biodiesel it will be a value-added product for the leather industry. Also, it's a good opportunity to use this waste as a feedstock of biodiesel and overcome the problems associated with environmental pollution and energy crisis.

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