

Acid and Base Catalyzed Transesterification of Animal Fats to Biodiesel

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ABSTRACT: *The present study has been focused on the acid and base transesterification of animal fats (dairy cow and beef) to produce biodiesel by varying process parameters such as catalyst amount, catalyst nature, reaction time and temperature. The maximum biodiesel yield after acid catalysis was 94.1 ± 2.43 and 98.4 ± 2.3 percent for dairy cow and beef tallow, respectively. The quantity of biodiesel obtained after base catalysis was comparatively lower than obtained in case of the acid catalysis. The optimum conditions for biodiesel production using acid catalysis were: 2.5 g of conc. H_2SO_4 , 24 h of reaction time and 50 °C for dairy cow fat and 2.5 g of conc. H_2SO_4 , 6 h of reaction time and 60 °C for beef fat. The amount of biodiesel obtained from beef tallow in the present study was much higher than earlier reported yields. The evaluation of transesterification process was followed by gas chromatographic analysis of tallow fatty acid esters (biodiesel) at optimal conditions. The fuel properties of biodiesel thus obtained accomplished the requirements of both the American and European standards for biodiesel.*

KEY WORDS: *Biodiesel, Fat, Transesterification, Methanolysis, Fuel.*

INTRODUCTION

The use of fats and oils as diesel engine fuels has been recognized since the advent of the diesel engine [1-5]. However, their relatively high viscosities forced their conversion into their simple alkyl derivatives to improve their viability as more suitable replacement of convention diesel fuel [6-10]. The main driving forces behind the implementation of the biodiesel in any country are rural economy, energy self-sufficiency and environmental concern [11].

Biodiesel can be used in any concentration with petroleum-based diesel fuel with little or no modification to existing diesel engines. These blended fuels are referred to as “biodiesel blends”, and include the

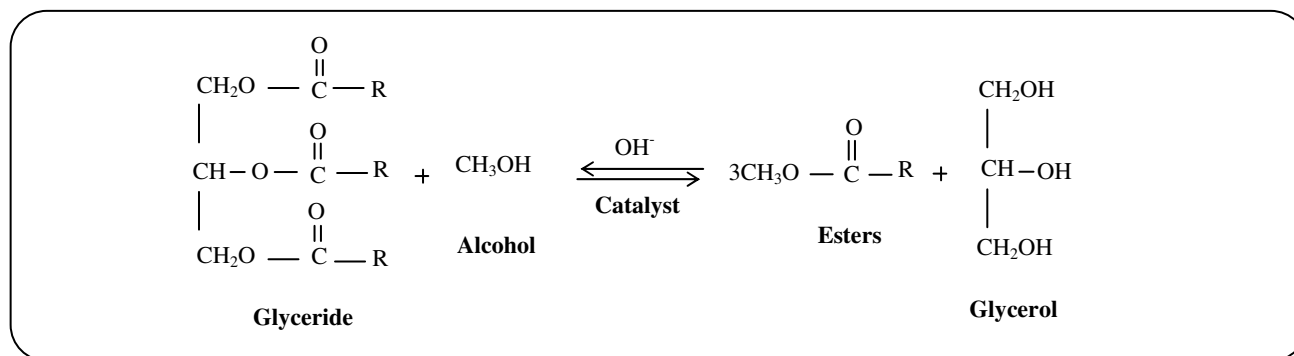
percentage of biodiesel in the blend, such as B2 (2 percent), B5 (5 percent) or B20 (20 percent). Biodiesel offers economic, energy security, fuel quality, and environmental benefits versus petroleum-based diesel. Domestic production of biodiesel not only helps to prolong the depleting fossil fuel resources but also ensure the dependence on foreign fuel. In addition to micro-economic benefits of biodiesel it also offers positive fuel performance attributes such as an increased cetane rating, high fuel lubricity, and high oxygen content. This is not all about biodiesel. Biodiesel is a pollution free, cleaner-burning fuel than petroleum diesel as it doesn't contain sulfur or aromatics [12-16].

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8/\$2.80



Scheme 1.

Utilization of biodiesel in many countries is still not very established. The major obstacle in implementation of biodiesel as a local automatic fuel in any country is its higher cost than the petroleum diesel. Openshaw estimated the selling price of Jatropha and other plant oil might be 2.5 times more than diesel price [12]. However the effect of cost factor may be reduced by taking the following important steps: (i) increasing the percentage yield of biodiesel, (ii) discovering the local low cost biodiesel feed stock, (iii) use of glycerine and cake as valuable by products which further reduce the cost of biodiesel, (iv) reduction of tax on biodiesel. Beef is the most extensively used meat all-around the world. The fat from beef can be used as a very low cost renewable source to produce biodiesel of comparable price to conventional petroleum diesel.

In this scenario, the present study was focused on the beef tallow (dairy cow and beef) as a low cost feed stock for biodiesel production using acid and base transesterification process. The effect of different experimental parameters such as catalyst amount, catalyst nature, reaction time, and temperature on integrated biodiesel production was evaluated. Gas chromatographic analyses were carried out to test the methyl esters produced during methanolysis of beef tallow. The quality of thus produced biodiesel had also been assessed using standard methods and reported.

EXPERIMENTAL

Reagents

All chemicals and reagents including sodium thiosulphate, sodium hydroxide, hydrochloric acid, sulphuric acid, nitric acid and methanol were of analytical grade, purchased from Fisons, Loughbrough, England.

Biomass

Dairy cow and beef fats used in the present study were collected from main slaughter house of Faisalabad, Pakistan. To remove the waxy materials and other suspended matters and residues, the collected animal fats were melted by slowly heating up to 60 °C. Melted fats were then filtered and decanted. Thus obtained fats were homogeneous in nature, which were stored in air tight opaque plastic jars to prevent oxidation.

Esterification

Transesterification of animal fat for the production of fatty acid methyl esters was carried out in the presence of acidic and basic catalysts as shown in scheme 1.

Acid catalyzed transesterification

Beef fats were transesterified using three levels of concentrated sulfuric acid catalyst (25, 50 and 100 percent of fat) at four different temperatures (30, 40, 50 and 60 °C) on a shaker at uniform speed of 130 rpm. 5 g of fat and 150 mL of methanol were taken in 250 mL flasks for all experiments. The reaction mixture was heated for specified period of time, cooled and was distilled to remove excess methanol. The obtained mixture consisted of glycerol and methyl esters (biodiesel). It was separated into two layers using a separating funnel. The upper oil layer (biodiesel) was separated and washed with hot water (50 °C) until the washing was neutral. The biodiesel product was obtained by separating water. Biodiesel yield (wt. percent) relative to the weight of fat was estimated.

Base catalyzed transesterification

Ireland method 1

Base catalyzed transesterification was carried out in a

250 mL conical flask equipped with a magnetic stirrer. Fat (50 g) was taken in flask and potassium hydroxide (1 percent of fat's weight) dissolved in methanol (22.5 percent of fat's weight) was added to flask. Stirring was continued for 2h at room temperature, the mixture was transferred to a separatory funnel and glycerol was allowed to separate and washed up to one week [17].

Ireland method 2

Potassium hydroxide (1.8 g) dissolved in 33.5 mL methanol was added to 120 g melted fat. Stirring was continued for 1 h at room temperature, the mixture was transferred to a separatory funnel and glycerol was allowed to separate for a minimum of 3 h. After draining off the glycerol, methyl ester was washed twice with 1:1 volume of water for 1 h to remove excess methanol [8].

Third method

Potassium hydroxide (2.5 g) dissolved in 24 mL methanol was added to 120 g melted fat. Stirring was continued for 1 h at room temperature, the mixture was transferred to a separatory funnel and glycerol was allowed to separate for a minimum of 3 h. After draining off the glycerol, methyl ester was washed twice with 1:1 volume of water for 1 h to remove excess methanol [18].

Fuel Properties

The properties of methyl esters were determined by methods specified in Handbook of Analytical Methods for fatty acid methyl esters as diesel substitute [19] or by equivalent standard methods. Acid value, viscosity, density, iodine value, saponification value, moisture content and ash contents were determined according to ISO 660, 3104, 3675, 3961, 3657, 662 and 6884, respectively. Cloud point and pour point were measured using ISO 3016 and ISO 3015, respectively, and iodine value using ISO 3961. Fatty acid compositions of biodiesel were determined by gas chromatography. Cetane number (CN) of biodiesel was empirically determined according to the method described by *Krisnangkura* [20].

Determination of fatty acid composition

Each fraction of oil was analyzed to determine triglycerides in term of determining fatty acid components as described earlier [21]. A 100 μ L of the test sample was

thoroughly mixed with 1 mL of n-hexane and 1 μ L of sodium methoxide in a 2 mL vial, and then shaken vigorously. The clear upper layer of methyl ester was pipetted off and injected into a GC column (methyl lignoserate coated (film thickness 0.25 μ m) SP-2330 polar capillary column (30 m \times 0.32 mm; Supelco Inc., Supelco Park Bellefonte, PA). A gas chromatograph (Model, G-3000, HITACHI) was used to determine the fatty acids profile. The oven temperature was set at 190 $^{\circ}$ C, the detector and injector temperature held constant at 250 $^{\circ}$ C. Carrier gas flow rate was 1 mL/min with a split ratio of 1:100. Chromato-integrator (HITACHI, D-2500) and an auto injector (AI-1000) were used.

Statistical Analysis

All experiments were performed in triplicate ensure the reproducibility of results. These obtained data was statistically analyzed using Microsoft excel 2004, version, office XP. The error was shown in figures represents mean \pm SD values.

RESULTS AND DISCUSSION

Acid catalyzed transesterification

The acid catalyzed transesterification reaction was carried out at the constant amount of fat (5 g) and methanol (150 mL) and varying other experimental parameters such as reaction temperature, catalyst quantity, and reaction time.

Effect of reaction temperature

The yield of biodiesel product under different temperatures at various catalyst quantities (on oil basis) is shown in Fig. 1a-c. Maximum biodiesel yield was obtained at 50 $^{\circ}$ C for dairy cow fat and 60 $^{\circ}$ C for beef fat. The increased yield of biodiesel with temperature suggested the endothermic nature of the process. The requirement of different temperature for dairy cow and beef fat was due to difference in their fatty acid composition (table 1). From results it can be seen that beef fat has more percentage of saturated fatty acid in comparison to dairy cow fat. Higher the percentage of saturated fatty acid, higher the reaction temperature needed for biodiesel production. Reaction temperature beyond 60 $^{\circ}$ C was not studied because at too high temperature H_2SO_4 could burn some of oil and can reduce biodiesel yield [17].

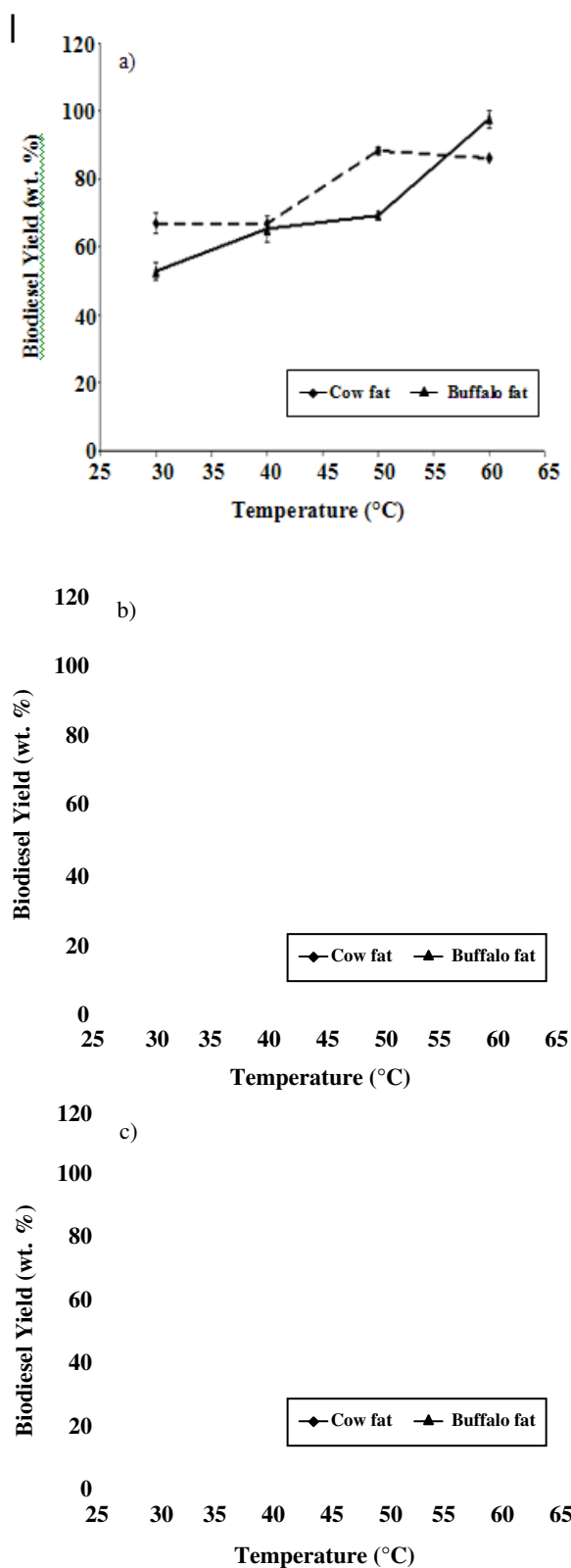


Fig. 1: Effect of temperature on the yield of biodiesel produced from dairy cow and beef fats at fixed amount of catalyst (a) 1.25 g of H_2SO_4 (b) 2.5 g of H_2SO_4 (c) 5 g of H_2SO_4 .

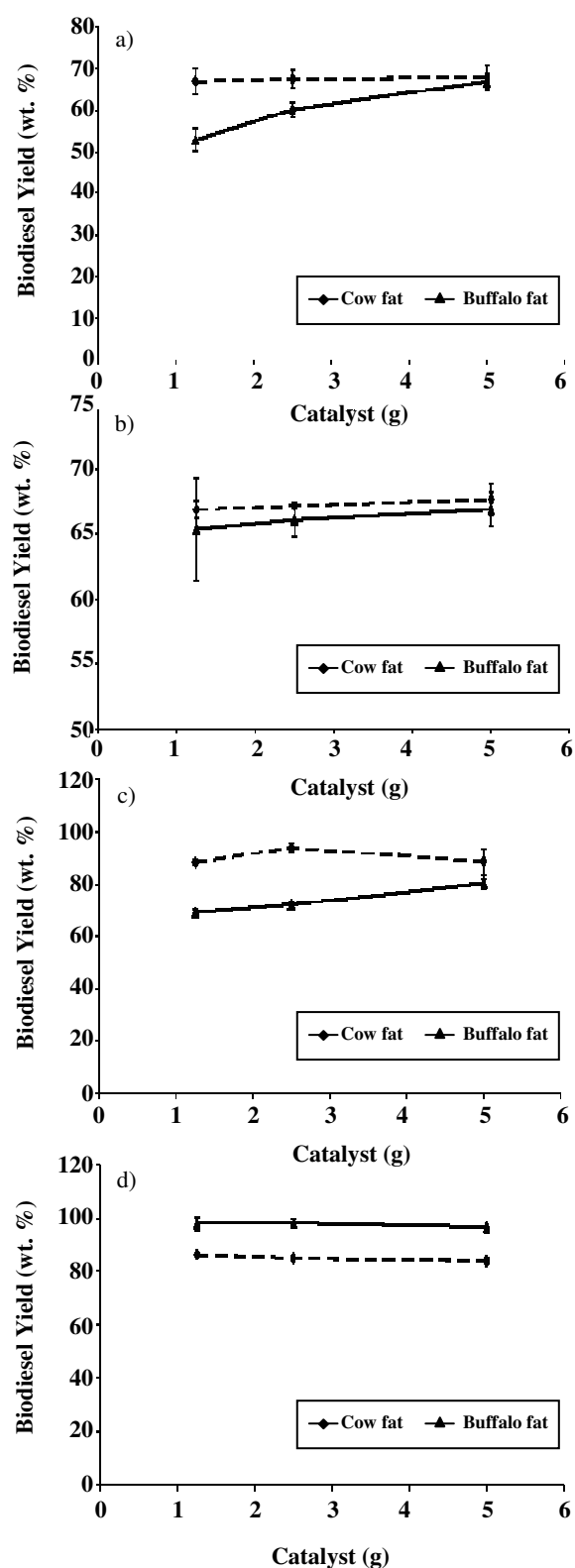


Fig. 2: Effect of catalyst quantity on the yield of biodiesel produced from dairy cow and beef fats at various temperatures (a) 30 °C (b) 40 °C (c) 50 °C (d) 60 °C.

Table 1: Fatty acid composition of biodiesel produced from dairy cow and beef fats.

Fatty acid	Dairy cow fat	Beef fat
Caprylic acid (%)	0.0689	0.1406
Capric acid (%)	0.1163	0.2185
Lauric acid (%)	3.1167	5.5816
Tridecanoic acid (%)	0.604	1.0609
Myristic acid (%)	0.0124	1.9435
Myristoleic acid (%)	0.4261	0.7332
Palmitic acid (%)	25.9862	34.2488
Palmitoleic acid (%)	1.1548	0.6789
Heptadecanoic acid (%)	0.1995	0.1526
Stearic acid (%)	31.1718	27.6372
Oleic acid (%)	29.1693	19.0228
Linoleic acid (%)	1.4015	0.7138
Linolenic acid (%)	0.0928	0.244
Arachidic acid (%)	0.1097	0.2631
Behenic acid (%)	0.1123	0.1442

Effect of catalyst

The effect of H₂SO₄ quantity on the yield of biodiesel was studied at four different temperatures (Fig. 2a-d). The percent yield of biodiesel increased with increase in H₂SO₄ quantity for both fats. At low temperatures, the kinetic energy of fat molecule was reduced, thus needed of more number of catalyst molecules to boost up the reaction [22].

Effect of reaction time

The yield of biodiesel produced after different reaction time is given in the Fig. 3. To evaluate the effect of reaction time on biodiesel yield, 5 g of each fat was thoroughly mixed at 130 rpm with 150 mL of methanol and 2.5 g of concentrated H₂SO₄ for 0.75-24 h. To achieve perfect contact between the reagents and the oil during reaction, the contents of the reaction were stirred well at constant rate for proper mixing. The optimum reaction temperature was 50 °C for dairy cow fat and 60 °C for beef fat. For dairy cow fat, the increase in biodiesel yield was almost linear as the time increased from 0.75-24 h. Whereas, in case of the beef fat the increase in biodiesel yield was linear up to 6 h and then

equilibrium was attained. Thus, it can be concluded that suitable reaction time for dairy cow and beef fats was 24 and 6 h, respectively. The results of present study are in accordance with the results of *Encinar et al.* [23] and *Freedman et al.* [24].

Base catalyzed transesterification

Methanolysis of dairy cow and beef fats was carried out with KOH as a catalyst using three different methods reported in literature (i.e. Ireland Method 1, Ireland Method 2 and Method 3). Fig. 4 shows the yield of methyl esters versus various reaction methods. Maximum biodiesel yield for dairy cow (88.0 ± 1.26 percent) and beef fat (2.06 ± 0.11 percent) was obtained by following Method 3. The significantly low yield in case of beef fat was due to higher percentage of saturated fatty acid (table 1). Saturated fatty acids are less reactive than unsaturated ones.

Dorado et al., [25] and *Mehu et al.*, [26] reported that with the increase in the concentration of catalyst, there was a decreased in the yield of methyl ester due to soap formation in the presence of high amounts of catalyst, which increased the viscosity of the reactants and lowered the yield. Thus, Method 3 was found more effective for biodiesel production as 1 percent of KOH was used to catalyze the reaction in comparison to Ireland method 1 (1.5 percent KOH) and Ireland method 2 (2 percent KOH), on fat weight basis.

Quantification of methyl ester

Quantitative analysis of the methyl esters in the biodiesel was carried out using gas chromatography. Table 1 shows the percentage composition of dairy cow and beef fats. The results indicated that dairy cow fat has lower percentage of saturated fatty acid in comparison to beef fat which has higher percentage saturated fatty acid. The major fatty acid in both fats were palmitic acid (C_{16:0}), stearic acid (C_{18:0}) and oleic acid (C_{18:1}). These constitute about 92.09 and 87.20 percent of total fatty acid identified for dairy cow and beef fats, respectively. Previously *Gerpan et al.*, [27] reported that fats or oils containing fatty acids having carbon atom more than 15, produced biodiesel of superior quality.

Characteristics of biodiesel from beef fats

To assess the potential of biodiesel as a substitute of diesel fuel, the parameters such as density, viscosity, ash

Table 2: Fuel properties of biodiesel produced from dairy cow and beef fats.

Properties	Biodiesel from dairy cow fat	Biodiesel from beef fat	Biodiesel standards/Test methods
Density (kgL^{-1})	0.864	0.8612	0.86-0.9 (ISO 3675)
Viscosity ($\text{kgm}^{-1}\text{s}^{-1}$)	0.00425	0.00398	<0.005 (ISO 3104)
Cloud point ($^{\circ}\text{C}$)	-6	-5	- (ISO 3015)
Pour point ($^{\circ}\text{C}$)	-7	-7	- (ISO 3016)
Moisture contents (w/w percent)	0.045	0.045	<0.05 (ISO 662)
Ash contents (w/w percent)	0.016	0.019	<0.02 (ISO 6884)
Acid value (mg KOH g^{-1})	0.23	0.646	<0.8 (ISO 660)
Iodine value ($\text{gI}_2 100\text{g}^{-1}$)	118.5	115.1	<120 (ISO 3961)
Saponification value (mg KOH g^{-1})	228.88	241.23	<312.5 (ISO 3657)
Cetane number	59.2	58.7	58.0 (EN ISO 5165)

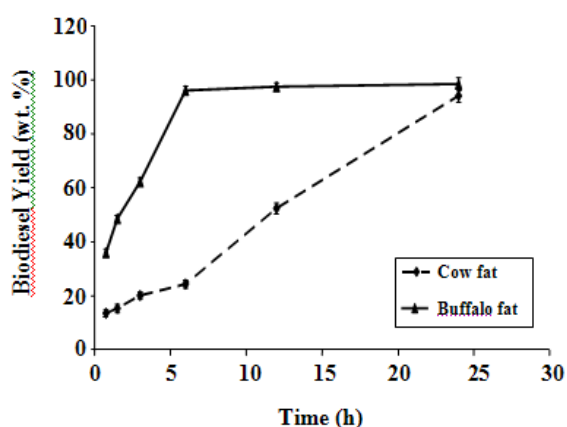


Fig. 3: Effect of shaking time on the yield of biodiesel produced from dairy cow and beef fats at constant temperature (50°C for dairy cow fat, 60°C for beef fat) and catalyst quantity ($2.5\text{ g of H}_2\text{SO}_4$).

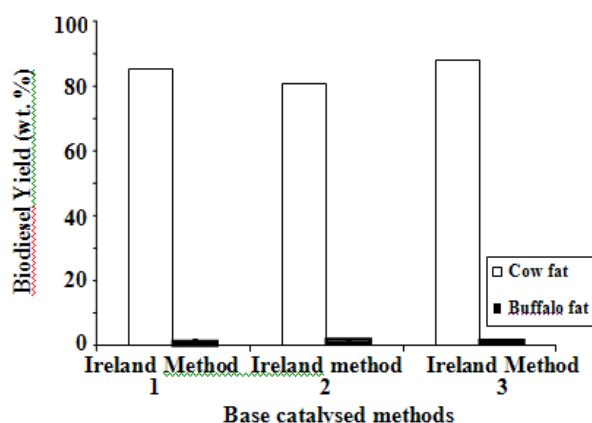


Fig. 4: Effect of different base catalysed methods on the yield of biodiesel produced from dairy cow and beef fats.

point, cloud point, pour point, acid value, iodine value and saponification number were determined [19].

A comparison of these properties of biodiesel from dairy cow and beef fats with recommended properties is shown in table 2. Most of these parameters comply with the limits related to biodiesel quality. The physical and fuel properties of biodiesel from beef fat in general were comparable to those of recommended properties. The results suggested that the new process, which combined bioengineering and transesterification, could be a feasible and effective method for the production of high quality biodiesel from beef fats. The biodiesel from beef fats could be a competitive alternative to conventional diesel fuel.

CONCLUSIONS

Dairy cow and beff fats transesterified using acid catalysis were found more suitable in comparison to base catalysed reaction for biodiesel production. Effect of different experimental parameters such as amount of catalyst, temperature and time on production of biodiesel was investigated during the present study. Optimum amount of H_2SO_4 , temperature and time were 50 percent, 50°C and 24 h, respectively, for maximum production of biodiesel from dairy cow fat, while from beef fat these were 50 percent, 60°C and 6 h, respectively.

During optimization of experimental parameters one-at-a-time procedure has been used in this study. Results of the present study clearly demonstrated that biodiesel

can also be produced from waste animal fats and has similar performance with biodiesel produced from fresh vegetable oils.

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REFERENCES

- [1] Nouredin, H., Gao, X., Philkane, R.S., Immobilized *Pseudomonas Cepacia* Lipase Biodiesel Fuel Production from Soyabean Oil, *Bioresour. Technol.*, **96**, 769 (2005).
- [2] Balaco, V.M., Paiva, A.L., Malcata, F.X., Bioreactors with Immobilized Lipases: State of Art, *Enzyme Microb. Technol.*, **18**, 392 (1996).
- [3] Ali, Y., Hanna, M.A., Leviticus, L.I., Emissions and Power Characteristics of Diesel Engine on Methyl Soyate and Diesel Fuel Blends, *Bioresour. Technol.*, **52**, 185 (1995).
- [4] Schumacher, L.G., Borgelt, S.C., Fossen, D., Gocht, W., Hires, W.G., Heavy-Duty Engine Exhaust Emission Test Using Methyl Ester Soyabean Oil/Diesel Fuel Blend, *Bioresour. Technol.*, **57**, 31 (1996).
- [5] Mittelback, M., Tritthart, P., Diesel Fuel Derived from Vegetable Oil, III. Emission Tests Using Methyl Esters of Used Frying Oil, *J. Am. Oil. Chem. Soc.*, **65**, 1185 (1988).
- [6] Bruwer, J.J., Boshoff, B.V.D., Hugo, F.J.C., Fuls, J., Hawkins, C., Walt, A.N., Plessis, L.M., Agriculture Energy, ASAE Publication 4-81, American Society of Agriculture Engineers, St Joseph MI, **2**, 385 (1981).
- [7] Ali, Y., Hanna, M.A., Cuppett, S.L., Fuel Properties of Tallow and Soybean Oil Esters, *J. Am. Oil. Chem. Soc.*, **72**, 1557 (1995).
- [8] Natusch, D.F.S., Richardson, D.W., Joyce, R.J., Methyl Ester of Tallow as a Diesel Extender, In: *Proceedings of the VI International Symposium on Alcohol Fuels Technology*, May 21-25, Ottawa, Canada, **1**, 340-346 (1984).
- [9] Clark, S.J., Wagner, L., Schrock, M.D., Piennaar, P.G., Methyl and Ethyl Esters of Tallow As A Renewable Fuels for Diesel, *J. Am. Oil. Chem. Soc.*, **61**, 1632 (1984).
- [10] Wyatt, V.T., Hess, M.A., Dunn, R.O., Foglia, T.A., Haas, M.J., Marmer, W.N., Fuel Properties and Nitrogen Oxide Emission Levels of Biodiesel Produced from Animal Fats, *J. Am. Oil. Chem. Soc.*, **82**, 585 (2005).
- [11] Subramanian, K. A., Singal, S. K., Saxena, M., Singhal, S., Utilization of Liquid Biofuels in Automotive Diesel Engines: An Indian Perspective, *Biomass Bioenerg.*, **29**, 65 (2005).
- [12] Openshaw, K., A Review of *Jatropha Curcas*: An Oil Plant of Unfulfilled Promise, *Biomass Bioenerg.*, **19**, 1 (2000).
- [13] Nisworo, A. P., Biodiesel by Supercritical Transesterification: Process Design and Economic Feasibility, Twaio Graduation Project Thesis Report, Eindhoven University of Technology, Eindhoven, Netherland, (2005).
- [14] van Kasteren, J.M.N., Nisworo, A.P., A Process Model to Estimate the Cost of Industrial Scale Biodiesel Production from Waste Cooking Oil by Supercritical Transesterification, *Resour. Conserv. Recy.*, **50**, 442 (2007).
- [15] Zhang, Y., Dube, M.A., McLean, D.D., Kates, M., Biodiesel Production from Waste Cooking Oil, 1. Process Design and Technological Assessment, *Bioresour. Technol.*, **89**, 1 (2003).
- [16] Zhang, Y., Dube, M.A., McLean, D.D., Kates, M., Biodiesel Production from Waste Cooking Oil, 2. Economic Assessment and Sensitivity Analysis, *Bioresour. Technol.*, **90**, 229 (2003).
- [17] Rice, B., Frohlich, A., Leonard, R., Teagasc, Korbitz, W., Bio-Diesel Production Based on Waste Cooking Oil: Promotion of the Establishment of An Industry in Ireland, Altener Contract No. XVII/4.1030/AL/77/95/IRL. Final Report (1997).
- [18] Peterson, C. L., Reece, D. L., Hammond, B.J., Thompson, J.C., Processing Characterization and Performance of Eight Fuels from Lipids, *Appl. Eng. Agric.*, **13**, 71 (1997).
- [19] Bailer, J., Hödl, P., Mittelbach, M., Handbook of Analytical Testing Methods for Fatty Acid Methyl Esters Used as Diesel Fuel Substitute, ISBN: 3 9014 5700 3 (1994).

- [20] Krisnangkura, K., A Simple Method for Estimation of Cetane Index of Vegetable Oil Methyl Esters, *J. Am. Oil. Chem. Soc.*, **63**, 552 (1986).
- [21] Bhatti, H.N., Hanif, M.A., Qasim, M., Rehman, A., Biodiesel Production from Waste Tallow, *Fuel*, **87**, 2961 (2008).
- [22] Miao, X., WU, Q., Biodiesel Production from Heterotrophic Microalgal Oil, *Bioresour. Technol.*, **97**, 841 (2006).
- [23] Encinar, J. M., Gonzalez, J.F., Sabio, E., Ramiro, M.J., Preparation and Properties of Biodiesel from *Cynara cardunculus* L., *Ind. Eng. Chem. Res.*, **38**, 2927 (1999).
- [24] Freedman, B., Pryde, E.H., Mounts, T.L., Variables Affecting the Yields of Fatty Acid Esters from Transesterified Vegetable Oil, *J. Am. Oil. Chem. Soc.* **61**, 1638 (1984).
- [25] Dorado, M.P., Ballesteros, E., Lopez, F.J., Mittelbach, M., Optimization of Alkali-Catalyzed Transesterification of *Brassica carinata* Oil for Biodiesel Production, *Energ. Fuel*, **18**, 77 (2004).
- [26] Meher, L. C., Dharmagadda, V. S. S., Naik, S. N., Preparation of Biodiesel from Crude Oil of *Pongamia pinnata*, *Bioresour. Technol.*, **96**, 1425 (2005).
- [27] Gerpen, J.H.V., Hammond, E.G., Johnson, L.A., Marley, S.J., Yu, L., Lee, I., Monyem, A., Determining the Influence of Contaminants on Biodiesel Properties, Final Report Prepared for: The Iowa Soybean Promotion Board, Iowa State University, USA (1996).