Production of Biodiesel from Dairy Waste Scum

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Abstract - **Dairy factory waste scums are increasingly being considered a valuable resource. However, these wastes may also contain contaminants, natural or artificial, that may adversely affect the land or water to which they are discharged. The study investigates the potential of using dairy waste scum as a feed stock for bio-diesel production. Present study optimized the parameters involved in the alkali catalysed transesterification process of dairy waste scum oil. The effects of methanol to oil ratio, temperature and amount of KOH were investigated. The yield of bio-diesel reached 84% at 1.2 wt. % of Potassium Hydroxide, reaction temperature of 60°C, 90 min of time and 100% excess methanol oil ratio. The fuel properties viz., specific gravity, viscosity, flash point, pour point, cloud point were studied. It was found that the properties were quite comparable and some even superior to the properties of petroleum diesel. The present study found that biodiesel from dairy waste scum is quite suitable as an alternative to petroleum diesel with recommended fuel properties as per ASTM standards. By using dairy waste scum as a feed stock for biodiesel production reduces the cost of production of bio-diesel and the environmental impact related to the disposal of dairy scum.**

Keywords-biodiesel; dairy waste; scum oil; waste oil

I. INTRODUCTION

Worldwide energy crisis due to the gradual depletion of resources and impact of environmental pollution, has led to the exploration for a sustainable and environment friendly alternative fuel. Bio-diesel is a cleaner fuel than petroleum diesel and a clear substitute for existing diesel engines [1]. Biodiesel is defined as a fuel comprised of mono alkyl ester of long chain fatty acids derived from vegetable oils or animals fats.

The current feed stock for biodiesel production is vegetable oil, animal fats and micro algal oil etc., throughout the world [2]. It is believed that the world food crisis may occur as the result of using food crops for the production of biodiesel. This lead to search for new feed stocks for bio-diesel production from unconventional, non-edible oil and fats like, waste grease, waste cooking oil, waste tallow, tobacco seed oil, rubber seed oil etc., and other animal fats [3]. Bio-diesel is more costly than petro-diesel since the cost of raw materials accounts for 75– 85% of the production cost of bio-diesel. By using waste materials as a feed stock for biodiesel production, the higher price of bio-diesel can be reduced [4]. And also waste oils pose a very serious environment challenge because of their disposal problems all over the world. In this context, waste oils are currently receiving renewed interest. The present study reveals that bio-diesel from Dairy Waste Scum Oil is a suitable alternative for petro-diesel.

Milk is the natural & complete food for all human as well as mammalian animals. It contains complete nutrients such as fats, proteins, vitamins & carbohydrate [5]. There are number of dairy industries producing drinking milk & associated products such as Cheese, Yogurt, Milk Powder, Ice-Cream, Ghee, Paneer & Other Products. Dairy industries are handling number of equipment for processing, handling, storing, packing & transportation of milk & its products. In large dairy industries while cleaning the equipment, the residual butter & related fats which are washed and get collected in effluent treatment plant as a dairy waste scum. Scum is a less dense floating solid, white in texture and usually formed by the mixture of fats, proteins, lipids and some other packing materials. Most of the dairies dispose this scum in solid waste disposal site or by incinerating [6]. By doing so it economically wastes fuel & generates pollutants thus contaminating water and discarding of this waste can be challenging. One possible solution is to convert this waste scum in to biodiesel and use it as an alternative fuel.

There are mainly four different methods used for production of biodiesel, viz. blending, micro emulsification, pyrolysis, and transesterification. Table II shows the problems and probable cause of direct blending. The major problems of using pyrolysis are the equipment for thermal cracking and pyrolysis is expensive. In addition, while the products are chemically similar to petroleum-derived gasoline and diesel fuel, the removal of oxygen during the thermal processing also removes any environmental benefits of using an oxygenated fuel. It produced some low value materials and, sometimes, more gasoline than diesel fuel. Transesterification is a well-established and most commonly used method for biodiesel production. It also improves fuel property of oil. For this reason, this method was chosen for the current study. Transesterification is the displacement of alcohol from an ester by another alcohol. Overall transesterification reaction is given by three consecutive and reversible reactions. This reaction is widely used to reduce the viscosity of triglycerides derived from renewable feedstock such as vegetable oil and waste oil for use in compression engine.

TABLE I Known problems and probable cause for using straight oil in diesels (Direct blending)

Problem	Probable cause
Cold weather starting	High viscosity, low cetane, and low flash point of oils
Plugging and gumming of filters, lines and injectors	Natural gums (phosphatides) in oil. Other ash
Engine knocking	Very low cetane of some oils. Improper injection timing
Coking of injectors on piston and head of engine	High viscosity of oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils
Carbon deposits on piston and head of engine	High viscosity of vegetable oil, incomplete combustion of fuel. Poor combustion at part load with vegetable oils
Excessive engine wear	High viscosity of oil, incomplete combustion of fuel. Poor combustion at part loads with oils. Possibly free fatty acids in oil. Dilution of engine lubricating oil due to blow-by of oil
Failure of engine lubricating oil due to polymerization	Collection of polyunsaturated oil blow-by in crankcase to the point where polymerization occurs

A catalyst is required to initiate the transesterification reaction. Catalysts that can be used for the trans-esterification reaction includes base, acid or enzyme. The acid catalyst is not used as they are generally considered to be too slow for industrial processing. Enzyme catalyst is not used for this reaction process, on a commercial basis, as the cost is too high and rate of reaction is slow. KOH is used as an alkali catalyst because it is used widely in large industrial scale biodiesel production [7]. Alkali catalyst such as Potassium Hydroxide (KOH) easily gets dissolved in methanol. In methanolysis, formations of emulsion were quick and easily break down to form glycerol rich bottom layer and methyl ester rich upper layer. Transesterification occurs approximately 4000 times faster in the presence of alkaline catalyst than the same amount of acid catalyst. Application of base catalysts may cause problems due to the side saponification reaction which creates soap and consumes catalyst. These problems occur because of higher content of fatty acids and water in waste oil. Notwithstanding these drawbacks, transesterification process using alkali catalyst has some benefits like low production cost, faster reaction speed and mild reaction conditions. The transesterification reaction is strongly influenced by several factors including molar ratio of alcohol, catalyst, presence of water, free fatty acid in oil samples, reaction temperature, reaction time and agitation speed [8].

Economic reason have been one of the major obstacles in the use of biodiesel. Diesel fuel derived from vegetable oils is more expensive than petroleum-based Diesel. The feedstock for biodiesel is already more expensive than conventional Diesel fuel and it can be reduced by using dairy waste oil as a feed stock. In the case of conversion of dairy waste scum to their esters, the resulting glycerol co-product, which has a potential market of its own, may offset some of the costs. Nevertheless, biodiesel is attractive for other reasons. Besides being a renewable resource and therefore creating independence from the imported commodity petroleum and not depleting natural resources, health and environmental concerns are the driving forces overriding the economic aspects in some cases.

II. MATERIALS AND METHODS

A. Materials

The scum was collected from the skimming tank of dairy effluent treatment plant, Milma Cochin. The other materials used in the study were Hexane, KOH and Methanol (99.8% pure). The equipment used were water bath, conical flask, stirring equipment, gravity separator, thermometer, flash and fire point apparatus, bomb calorimeter, viscometer, cloud point apparatus.

B. Production of Biodiesel

The first step before producing a batch of biodiesel is to determine the most suitable catalyst by titration and determination of the presence of water in the feedstock. Titration is conducted to determine the amount of catalyst needed and for choosing the best route for transesterification, whether acid or base catalysed or a combination of processes. Titration shows that alkali catalyst transesterification is the best method due to its low free fatty acid content. Determination of water may be quickly accomplished by boiling a small sample of oil and checking for spattering, which will occur violently even in the presence of very small amounts of water due to rapid vaporization caused by the extreme difference in boiling points [9].

The transesterification reaction was carried out in a system which consists of a 1 L conical flask put inside a water bath. Thermostat in water bath maintains the temperature of the reactant at the desired value. Methanol has a boiling point of 65°C, which vaporizes at elevated temperature during the reaction. In order to achieve perfect contact between the reagents and the oil during transesterification, they must be stirred well at constant rate; stirring was done by glass rod manually.

Transesterification is the process of reacting triglyceride with alcohol in the presence of a catalyst to produce fatty acid esters and glycerol. The transesterification process was studied at six catalyst loadings (0.4%, 0.6%, 0.8%, 1%, 1.2%, and 1.4% KOH wt/wt) at 60 ± 2˚c and 75% excess of stoichiometric ratio of the alcohol to oil. The stoichiometric ratio of methanol-oil ratio is 12.5 % of the oil. The excess methanol required can be studied at six alcohol-to-oil ratios (25%, 50%, 75%, 100%, 125%, 150% excess of stoichiometric oil ratio v/v) at a reaction time (0.5–3 h), temperature 60 ˚c and catalyst ratio of 1.2%. The required temperature can be studied at five temperatures varying from 40 to 80 ˚c keeping other parameters at optimum condition. Care was taken to make bio feed free from water, as any water or moisture in the system will consume some of catalyst and slowdown the transesterification reaction. Scum oil was preheated at 110 ˚C in order to ensure complete removal of water; if present.

The catalyst was dissolved in methanol by stirring. 50 ml of the oil was introduced into the reaction flask. After the appropriate temperature was reached, KOH previously dissolved in methanol was added and the mixture was continuously stirred by means of a stirrer. This mixture was carefully transferred to a separating funnel and allowed to stand there around 24 hrs. Lower value of the specific gravity of the final product is an indication of completion of reaction and removal of heavy glycerine. The separated methyl ester is washed to remove the entrained glycerol, catalyst, soaps and excess methanol and heated to a temperature 105 ˚C to remove the water content in the biodiesel [10].

C. Biodiesel Testing

The physical properties of biodiesel derived from dairy waste scum oil such as specific gravity, calorific value, viscosity, flash point, and fire point are tested by using a hydrometer, a Bomb calorimeter, Brufill viscometer, and closed cup apparatus [11].

III. RESULTS AND DISCUSSION

A. Factors Affecting the Yield of Biodiesel

Alkaline catalyst transesterification of scum oil was carried out and following factors affecting yield of biodiesel, were studied.

1) Effects of methanol content

The important parameter affecting the yield of biodiesel is ratio of methanol to oil (dairy scum oil) (v/v) basis. The ratio of methanol to scum oil also affects the conversion efficiency as well as production cost of biodiesel. The conversion efficiency is defined as the yield of the process represented in terms of weight percentage.

In the present study, methanol was the used alcohol for transesterification process due its low cost and physical chemical advantageous. The effect of methanol in the range of 25% to 150% excess of stoichiometric ratio of scum oil (v/v ratio) at 60 ± 2 ˚C was studied, keeping other process parameters constant. Fig.1 shows the effect of methanol oil ratio on biodiesel production. Presence of sufficient amount of methanol during transesterification is essential to break glycerine, fatty acid linkages. But when the ratio increased to 100%, high methanol amounts interfere with the separation of glycerine because of an increase in solubility. The glycerine remaining in the solution drives the equilibrium back to the left side of reaction, resulting in the lower yield of esters. Fig 5.1 shows the variation of yield vs methanol ratio. The maximum conversion (optimum condition) to the methyl ester is achieved at a ratio (methanol/dairy scum oil) of 100 %(v/v). Furthermore increasing alcohol amount beyond the optimal ratio will not increase the yield, but will increase cost for alcohol recovery. Also the methanol scum oil ratio is associated with the type of catalyst used.

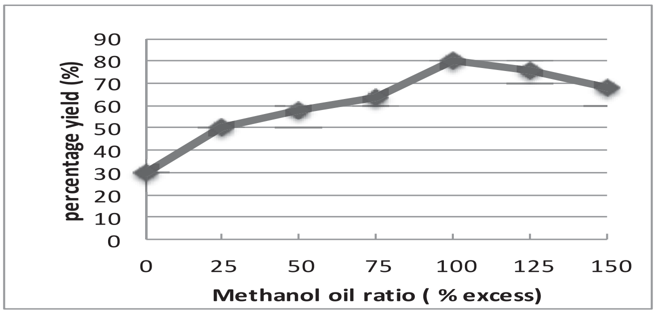

Fig. 1. Effect of methanol- oil ratio to biodiesel yield

2) Effect of catalyst

Biodiesel formation is also affected by the concentration of catalyst. The effect of catalyst loading (KOH) on methyl ester conversion was studied for scum oil in the range of 0.2-1.4 wt./wt. % at 60 ± 2 ˚C and 100% excess stoichiometric ratio of oil (v/v). It is noted that during the present study, the excess addition of KOH increased the yield. The effect of the catalyst amount on the yield is shown in Fig.2 It was observed that the yield of the methyl esters was small at lower catalyst concentration due to incomplete reaction, and then increased as the catalyst concentration was increased. The optimum yield was observed at 1.2 wt. % and maximum yield produced is 80%. However, using higher catalyst concentrations than 1.2 wt. %, the yield decreased and resulted in no clear separation during settling, while during washing with warm de-ionized water more soap was observed, due to the excess catalyst favouring the process of saponification. It can be easily concluded that the concentration of KOH is strongly dependent on the type of oils used.

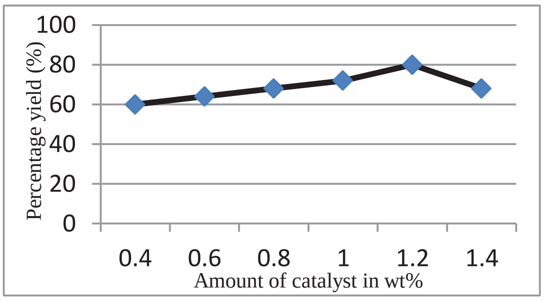

Fig.2. Effect of catalyst on biodiesel yield

3) Effect of Temperature

The effect of reaction temperature was found at the obtained optimum amounts of catalyst and methanol to oil ratio. It was observed that increase in temperature favours methyl ester conversion, but the operating temperature higher than boiling point of methanol (65 ˚C), will evaporate the alcohol and thus result in less yield and also higher reaction temperature accelerates the saponification of triglycerides. The effect of temperature on the yield is shown in fig.3 The optimum temperature for the reaction is found to be in the range of 60°C and the maximum yield at 60°C was found to be 84%. A higher reaction temperature can decrease the viscosities of oils and results in an increased reaction rate, and a shorter reaction time. However, high reaction temperature may decrease biodiesel yield because it accelerates the saponification reaction of triglycerides.

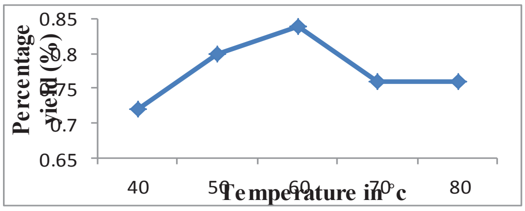

Fig.3. Effect of Temperature on Percentage Yield

A. Characteristics of dairy scum biodiesel

The physical properties of biodiesel derived from dairy scum oil, such as Density, Kinematic viscosity, Flash point, Pour point, and Heat of combustion were found and are shown in Table I. The physical properties of scum biodiesel were similar to those of diesel fuel. Also the comparison of biodiesel from different wastes is given in the Table III.

TABLE II Characteristics of dairy scum biodiesel

Sl no	Characteristics	Biodiesel obtained from scum oil	ASTM Standard for biodiesel	Petro-Diesel standard
1	Viscosity in cSt at 40˚c	3.8	1.9-6.0	1.3 - 4.1
2	Density in kg/mm^3	0.86	0.875	0.850
3	Flash point in ˚c	105	100.0 (minimum)	50
4	Fire point in ˚c	120	130	56
5	Acid value	0.53	0.80 (maximum)	0.12
5	Colour	Light golden	Light golden	Golden
6	Solubility in water	Insoluble	Insoluble	Insoluble
7	Odour	Light soapy order	-	-
8	Cloud point in ˚c	9	-3 to 12	-15 to 5
9	Pour point in ˚c	56	-10 to 12	-35 to -15
10	Calorific value in kj/kg k	40129	-	43500

1) Density

Density represents the ratio of mass of the biodiesel to the volume at constant standard temperature. The density of scum oil is 0.939 whereas the density of scum biodiesel is 0.875, thus there is decrease in density of biodiesel. This indicates that the product obtained is lighter than the feed. The density of Diesel fuel is 0.850, which is just matching the density of biodiesel obtained from the dairy waste scum oil. Density limit in European EN norm is in the range of 0.86 – 0.9 kg/mm^3. The ASTM norms include no regulation on this parameter. Fuel density affects the mass of fuel injected in to the combustion chamber and thus the air fuel ratio.

2) Viscosity

Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when an increase in viscosity affects the fluidity of the fuel. Here kinematic viscosity of scum oil biodiesel is found to 3.8 cSt. Kinematic viscosity at 40 °C is limited to 3.5-5.0 (cSt) in the European biodiesel standard norms. The American specifications allow a broader range of values (1.9-6.0 cSt). The corresponding limit for petro-diesel fuel is considerably low (1.3 - 4.1). The viscosity of dairy scum biodiesel is slightly near to the standard viscosity of biodiesel. But it is higher than that of petro – diesel and the high viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The lower the viscosity of the biodiesel, the easier it is to pump and atomize and achieve finer droplets. The conversion of triglycerides into methyl or ethyl esters through the transesterification process reduces the molecular weight to one third that of the triglyceride and reduces the viscosity. The increased viscosity may be due to the increased acid and alcohol segment in the dairy scum biodiesel. Also the viscosity increases with higher contents of high molecular compounds like unreacted glycerides found in scum oil biodiesel.

3) Flash Point and Fire Point

The obtained value of flash and fire point of scum oil biodiesel is much lower than pure vegetable oil biodiesel and higher than diesel. The flash and fire point of scum biodiesel are 105˚C and 120 ˚C respectively, and it is higher than conventional diesel fuel (55 ˚C). Biodiesel with a higher flash point can prevent auto ignition and fire hazard at high temperature during transportation and storage periods. Hence, higher the flash point, the higher is the safety during handling, transportation, and storage.

4) Pour Point and Cloud Point

Two important parameters for low-temperature applications of a fuel are cloud point (CP) and pour point (PP). The CP is the temperature at which wax first becomes visible when the fuel is cooled. Pour point of oil is defined as the lowest temperature at which the oil just fails to flow when cooled and examined under prescribed conditions. The obtained value of CP and PP are 9 ˚c and 6 ˚c respectively and the CP occurs at a higher temperature than the PP. The obtained scum biodiesel has a higher CP and PP compared to conventional diesel which is in the range of -15 to 5 and -35 to -15 respectively as per ASTM standard. Due the higher value of CP and PP the obtained biodiesel is difficult to operate in the cold conditions. This higher value of CP and PP is may be due to the presence of long chain fatty acid in the dairy waste scum oil since transesterification cannot alter the fatty acid composition of the dairy scum oil.

5) Heat of Combustion

It measures the energy content in a fuel. It is an important property of biodiesel that determines its suitability as an alternative to diesel fuel. The Calorific value of biodiesel obtained from dairy waste scum is approximately 10 % less than that of petro-diesel (40.2 MJ/kg compared to ~ 43.5 MJ/kg). Therefore compression ignition of the dairy scum biodiesel as an alternative fuel should not be a problem. The biodiesel obtained from dairy scum oil was considerably less volatile than petro-diesel fuel. Biodiesel fuels do not contain aromatics, but they contain methyl esters with different levels of saturation. The obtained calorific value for biodiesel is slightly near to the standard value of petro-diesel as per ASTM standard.

TABLE III Comparison of characteristics of biodiesel from different waste

Characteristics	Biodiesel from dairy waste scum	Biodiesel from waste cooking oil	Biodiesel from waste lubricating oil	Biodiesel from waste plastic oil
Viscosity in cSt at 40˚c	3.8	1.81	3.49	2
Density in kg/m^3	860	807.3	818	840
Flash point in ˚c	105	53	57	50
Fire point in ˚c	120	58	62	56
Calorific value in kj/kg k	40129	42347	42500	46500

6) Acid Value

The acid value is defined as the milligrams of potassium hydroxide necessary to neutralize the free acids in 1 g of sample. The evaluated acid value of scum biodiesel is 0.53, and within the recommended range. The respective limit in the European norm is < 0.5 mg KOH/g sample, whereas the American standard is allowing slightly higher values. The ASTM standard for pure biodiesel sets the maximum acid value at 0.8 mg KOH/g. In 2006, the ASTM biodiesel acid-number limit was harmonized with the European biodiesel value of 0.50. Conventional diesel fuels generally possess a very low acid value of less than 0.12. High fuel acidity causes corrosion and the formation of deposits within the engine, particularly in fuel injectors.

IV. CONCLUSION

Bio-diesel has become alternative fuel recently because of its environmental benefits and the fact that it is made from renewable resources. The remaining challenges are its cost and limited availability of fat & oil resources. Present utilization of dairy waste scum as a feed stock reduces the cost of biodiesel. The base catalysed trans-esterification reaction for biodiesel production is often the method selected owing to its lower cost of production and simple processing conditions yielding higher conversion of oil to biodiesel. Biodiesel fuel also has its own advantages and disadvantages. The biggest advantage of biodiesel is that it can play a significant role in reducing the harmful hydro carbon emissions. However, there are still some drawbacks of biodiesel which may become a hindrance in the introduction of biodiesel as an alternative to the harmful carbon emitting fossil fuels. Biggest advantage of biodiesel fuel is that it is non-toxic and biodegradable, which makes it one of the most environment friendly alternatives of power generation.

The transesterification of dairy scum oil to biodiesel using KOH as a catalyst was studied. The effect of operating parameters such as methanol content, catalyst amount, and reaction temperature were found on biodiesel production. The optimum feed conversion and biodiesel yield were obtained at 100 % excess over the stoichiometric ratio (12.5%) of methanol/scum oil ratio, 1.2wt% KOH, and 60°C reaction temperature and the optimum biodiesel yield is 84% and $480x10^3$ litre of biodiesel can be produced from 1 million litre of waste oil. Analyses of characteristics of biodiesel produced from dairy waste scum, revealed that were comparable with that of petro-diesel. Most of the dairies dispose dairy waste scum in solid waste disposal site or by incinerating and it economically wastes fuel & generates pollutants. Dairy industries can use these kinds of projects to solve their ecological problems in scum disposal and to improve their economy.

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