# Microwave Assisted Esterification and Transesterification of Dairy Scum Oil for Biodiesel Production: Kinetics and Optimization Studies

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**Abstract:** In the present study, a lab scale microwave reactor was used to conduct the esterification and transesterification of Dairy Scum Oil (DSO). The optimum parameters for acid catalysed esterification were: Microwave power-600 W, molar ratio of methanol to FFA-30:1, Temperature of reaction-60°C, concentration of sulphuric acid-8% by wt. while the optimum parameters for transesterification were: Temperature-60°C, Microwave power-600 W, molar ratio of methanol to DSO-7:1, concentration of KOH-1% (by wt.). Experiments conducted under optimum conditions both in microwave reactor and conventional electrically heated reactor revealed that, a highest conversion of FFA was 93.63% (reaction time-16 min) while a highest yield of FAMEs in transesterification was 93.47 (reaction time-5 min) in microwave reactor. Kinetic studies conducted in microwave reactor showed that, esterification and transesterification followed pseudo first order kinetics.

## INTRODUCTION

Among the various biofuels, biodiesel has gained more attention recently as it is biodegradable with superior lubricity, renewable, nontoxic, contains low sulphur content. Further it is eco-friendly and leads to lower carbon dioxide emissions. Since, it has point is >110°C, it is safer[1]. Biodiesel is produced from transesterification and it is basically monoalkyl esters of long chain fatty acids. The fatty acids may be derived from non-edible vegetable oil or animal fats[2]. Presently, biodiesel is being produced from nonedible oils such as Jatropha oil[3], Pongamia oil[4], waste cooking oil[5], Soyabeen[6], Sunflower[7], Rapeseed oil[8] etc. However, the quantity of biodiesel produced from these sources is not able to meet the demand. Hence, there is need to search for alternative sources having high oil content, economically viable and which do not impart any influence on food security.

In this connection, dairy waste scum can provide a solution. A large quantity of water is used for washing the equipment and housekeeping in a dairy industry which produces large amount of scum per day that is difficult to dispose. Scum oil consists of fat, proteins, lipid, unsolicited materials, etc.[9]. From this waste scum, oil can be obtained by removing suspended particles and water.

This oil can be valuable feedstock for the production of biodiesel. Unlike other agricultural feedstocks which are seasonal, dairy scum oil is abundantly available throughout the year.

There are few reports in literature on biodiesel production from daily waste scum using conventional electrical heating[10-13]. However, to the best knowledge of authors, there were no reports for biodiesel production using microwave irradiation. Hence, in the present work, a low cost microwave reactor was used to conduct esterification and transesterification experiments of dairy waste scum.

## MATERIALS AND METHODS

**Collection of dairy waste scum and pre-treatment:** The dairy scum was collected from Karnataka Milk Federation (KMF), Tumakuru Milk Union (TMU), Tumakuru, Karnataka (Fig. 1). It was heated to 100°C for 30 min, cooled and transferred to separating funnel. The bottom aqueous layer consisting of solid particles was separated and the top oil layer was further centrifuged at 8000 rpm in cooling centrifuge (REMI c-24 bl) for 10 min to separate fine solid particles. The clear Dairy Scum Oil (DSO) was used for esterification and transesterification experiments. The physical properties of DSO are depicted in Table 1.

Table 1: Physical properties of DSO

| Property | Values |
|---|---|
| Free fatty acid (%) | 8.82 |
| Saponification value (mg KOH/g ) | 183.6 |
| Specific gravity | 0.924 |
| Kinematic viscosity @40°C (cSt) | 31.78 |
| Flash point (°C) | 295 |
| Fire point (°C) | 304 |
| Pour point (°C) | 12 |
| Cloud point (°C) | 15 |



Fig. 1: Dariy scum

**Construction of microwave reactor:** The design and fabrication details of microwave reactor used in the present study have been described in our previous work[14].

**Construction of conventional electrically heated reactor for esterification and transesterification experiments:** The apparatus consisted of a 3 L round bottom reactor placed on a basket heater, Two spiral condensers for efficient methanol recovery, an agitator with rpm indicator cum controller and iv) a platinum RTD temperature sensor (Pt-100) connected to digital temperature indicator. Proportional Integral Derivative (PID) controller was used to maintain the temperature of the reaction mixture.

**Methodology:** Experiments were conducted in two stages namely:

- Acid catalysed esterification: the process reduces the FFA of oil to about 2% using acid catalyst
- Base catalysed transesterification: the oil is transesterified to mono-esters of fatty acids using alkaline catalyst

For esterification experiments, 150 g of DSO was transferred to reactor and preheated to the desired reaction temperature. Specified amount of sulphuric acid and anhydrous methanol (99.5% purity) were added and the reaction time and microwave power were set on the control panel of reactor. Following the reaction, the contents were transferred to separating funnel and phases were allowed to separate. The top layer consisting of excess alcohol, acid and impurities was removed. The acid value of bottom layer consisting of DSO was measured as per ACOAS titration method and the conversion of esterification was calculated as:

$$\text{Conversion of esterification reaction } (\%,\text{ w/w}) = \frac{AV_0 - AV}{AV_0} \times 100$$

where to $AV_0$ and AV refer to initial and final acid values of DSO. The effect of operating variables of esterification (molar ratio of methanol to FFA, temperature of reaction, concentration of acid catalyst, reaction time and microwave power) on conversion were studied by conventional method of optimization (one factor at a time).

For base catalyzed transesterification, 100 g of pre-treated DSO having FFA content of <2% was transferred to microwave reactor and preheated to desired reaction temperature. Known quantity of KOH dissolved in calculated amount of methanol was added to it and time of reaction and microwave power were set in control

panel. Following the reaction, the contents of reactor were transferred to and allowed for phase separation for 7 h, resulting into separation of two layers. The top layer consists of mainly DSO methyl esters while the lower layer comprises of glycerol as a major component. The excess methanol in both layers was recovered by distillation. The upper biodiesel layer was washed twice with warm distilled water (10%, v/v) and dried. The Fatty Acid Methyl Esters content (FAME content) of biodiesel was measured as described in the study.

**Analytical methods**
**Average molecular weight of DSO:** The average molecular weight of DSO ($M_{DSO}$) calculated based saponification value and acid value as:

$$M_{DSO} = \frac{3 \times 56100}{(\text{Saponifica tion value-Acid value})} \quad (1)$$

**Acid value of DSO:** The 5 mL of sample was transferred to 250 mL conical flask. The 50 mL of freshly neutralized hot ethanol and 1 mL of phenolphthalein TS were added. The mixture was boiled for 5-10 min and titrated against KOH as hot as possible until the pink colour persists for at least 30 s. Acid value of sample was calculated as:

$$\text{Acid value (mg KOH/g lipid)} = (56.1 \times V_{KOH} \times N_{KOH}) / (\text{weight of lipid in sample in g})$$

where, $V_{KOH}$ is volume of KOH run down (mL) and NKOH is normality of KOH (0.1N).

**FAME content in biodiesel:** For FAME analysis, Agilent 7890B equipped with HP-5 column (30.0×0.32 mm×0.25 µm) was used along with FID detector. The injector and detector temperatures were set at 250°C and nitrogen was used as carrier gas at a flow rate at 2 mL$^{-1}$ min. The oven temperature was programmed to start at 60°C and increased to 175°C at a rate of 25°C min$^{-1}$ and then to 240°C at a rate of 4°C min$^{-1}$ and held constant for 20 min$^{-1}$. The 1 mg of internal standard solution of methyl heptadecanoate was added. The analysis was performed by injecting 1 mL of sample solution into the gas chromatograph. FAMEs were quantified by comparing the peak areas between the samples with those of the standard compounds. The percentages of each peak/FAME were calculated. Based on these values, the FAME conversion was calculated.

**Calculation of yield of transesterification reaction and purity of biodiesel:**

$$\text{Yield of DSO FAMEs} = \frac{\text{g of FAMEs in biodiesel}}{\text{g of DSO added to reactor}} \times 100 \quad (2)$$

$$\text{Purity of DSO biodiesel} = \frac{\text{g of FAMEs in biodiesel}}{\text{g of biodiesel}} \times 100 \quad (3)$$

**RESULTS AND DISCUSSION**

**Physical properties of DSO:** The physical properties of DSO are depicted in Table 1. The FFA% was 8.74, indicating that a two-step procedure involving acid catalysed esterification followed by base catalysed transesterification was required for biodiesel production.

**Effect of operating variables on FFA conversion in microwave reactor**
**Effect of molar ratio of methanol to FFA:** One of the parameters affecting the FFA reduction in esterification is the molar ratio of methanol to FFA. Stoichiometrically, one mole of FFA requires one mole of methanol to produce one mole FAME and one mole water. However, in order to shift the equilibrium to product side, an excess methanol is needed. Using excess methanol also facilitates dissolution of water during the reaction and avoids hydrolysis. Among the constituents of reaction mixture (methanol, sulphuric acid and fatty acids), methanol has ability to strongly absorb microwave irradiation due to presence of -OH group. Under the changing electric field, the dipole rotates at very high speed which results in molecular friction and local superheating that further accelerates the reactions to complete faster[15]. In this regard, quantity of methanol in reaction mixture plays an important role in the microwave assisted esterification of FFA. In the present work, esterification experiments were conducted with various ratios of methanol to FFA in the range of 20:1-60:1. The temperature of reaction mixture was maintained at 60°C and the reaction time of 16 min was set for these trails. As depicted in Fig. 2a, %FFA reduction increased with increasing molar ratio of methanol to FFA and reached a highest level of 58.49% at an optimum molar ratio was 30:1. The FFA reduced to 5.11 mg KOH/g from an initial value of 8.75 mg KOH/g DSO under these conditions. However, further increase in molar ratio to 60:1 led to decrease in %FFA reduction (56.25%). Thus, a large excess methanol decreases the conversion of esterification. This may be due to the fact that, in the presence of excess methanol, the concentration of FFA in reaction mixture decreases and this combined effect of concentration change of reactants is not conductive for the balance of esterification to move in forward direction. Hence, a molar ratio of 30:1 was maintained in all further trails.

**Effect of temperature:** Temperature is also one of critical parameter affecting the conversion of esterification reaction. In practice, biodiesel manufacturers need to balance the reaction time and temperature to obtain both high yield and low energy
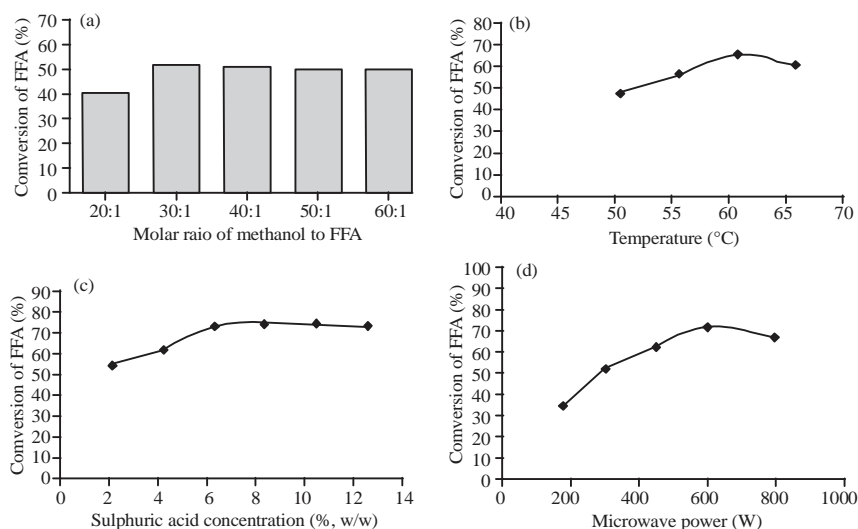
Fig. 2(a-d):  (a) Effect of molar ratio of methanol to FFA, (b) Effect of temperature, (c) Effect of acid concentration and (d) Effect of microwave power

consumption. In the present work, the temperature was optimized in the range of 50-65°C. As illustrated in Fig. 2b, %FFA reduction increased with rising temperature and reached a maximum of 67.76% at 60°C. With further increase of temperature to 65°C, the %FFA reduction decreased to 62.39%. This decrease in %FFA conversion might be due to evaporation of methanol at its boiling point, thus decreasing the amount available for reaction.

**Effect of concentration of sulphuric acid:** The effect of sulphuric acid concentration of conversion of FFA is depicted in Fig. 2c. Basically, $H^+$ species from sulphuric acidare released to protonate the carboxylic moiety of the fatty acid, increasing the electrophilicity of the carbonyl carbon atom and facilitating the second step which is the nucleophilic attack of the alcohol, forming a tetrahedral intermediate. In the last step, proton migration and breakdown of the intermediate occurs to form FAME. In the present work, the concentration of sulphuric acid was varied from 2 wt.-12%/w). As illustrated in Fig. 2c, the %FFA reduction was meagre at an acid concentration of 2 wt.% (58.97%). Increased catalyst dosage favoured the conversion of reaction till an optimum of 8 wt%( 81.49%). Further increase in catalyst concentration to 10 and 12% reduced the FFA conversion to 80.25 and 79.17%, respectively. Similar result has also been observed by another study where the conversion rate was reducedwith further addition of sulphuric acid after the maximumconversion ratewas achieved at a certain sulphuric acid amount[16]. This may be due to the excess quantity of sulphuric acid consumes more KOH during neutralization. Also, in a commercial scale, excess sulphuric acid may be corrosive to reactor. Hence, a concentration of 8 wt.% was selected as optimum.

**Effect of microwave power:** Trials were conducted with varying microwave power levels (180, 300, 450, 600 and 800 W) to analyse the influence of microwave power on conversion of FFA. As shown in Fig. 2d the %FFA reduction was least at 180 W (45.17%). This might be contributed to poor microwave efficiency at lower power level. Also, the reaction times are longer at lower microwave power due to extremelyslower heating rates. In the present work, optimum power level was 600 W (resulting in FFA conversion of 93.63%,w/w). Microwave power influences the rates of reaction basically bylowering it's activation energy through dipolar polarization effect. This occurs due to molecular level interactions of themicrowaves in the reaction mixture (mainly with methanol) which results in dipolar At 100% power level (800 W), reactants attain set temperature in a very short time. However, power losses are high. Also, with increasing microwave power level, methanol evaporation losses increase which results in the reduction of quantity of methanol for reaction. Hence, 600 W was found to be adequate level of microwave power. Increasing the power beyond this level had negative effect on yield of FAMEs.

**Kinetics of esterification under optimum operating conditions:** The kinetics of esterification of DSO was studied at three temperatures (50, 55, 60 and 65°C) both in microwave and electrically heated reactor. Molar ratio of methanol to DSO, microwave power and the sulphuric acid concentration were maintained at 30:1,600 W and 8%, respectively (as optimized in the previous sections). The results are depicted in Table 2 . As expected, the rate constants increased with increasing temperature as

Table 2: Kinetics of esterification of fatty acids in microwave reactor under optimized conditions (Reaction conditions: Sulphuric acid concentration = 8%, Molar ratio of methanol to lipid = 30:1, Microwave power = 600 W, initial FFA = 12.41%)

| Temperature (°C) | Rate constant $K_{est}$ | FFA in reaction mixture after (%): Time (min) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 |
| 50 | 0.321 | 10.52 | 8.76 | 7.41 | 6.91 | 6.47 | 6.23 | 6.11 | 6.05 |
| 55 | 0.342 | 9.87 | 8.55 | 7.77 | 6.52 | 5.41 | 4.56 | 4.33 | 4.25 |
| 60 | 0.387 | 9.21 | 8.54 | 6.79 | 5.13 | 2.17 | 1.21 | 0.94 | 0.79 |
| 65 | 0.462 | 9.58 | 8.98 | 7.45 | 6.69 | 4.42 | 3.89 | 3.74 | 3.57 |

expected in both reactors. Maximum reduction in FFA was recorded at 60°C (Final FFA of reaction mixture = 0.79%) after 16 min in microwave reactor, corresponding to a FFA conversion of 93.63%. However, a higher reaction time was required (80 min) in electrically heated reactor to reduce FFA to 1.82% (conversion of FFA = 85.33%). Thus, microwave heating could considerably reduce the reaction time (by nearly 5 times) as compared to conventional electrically heated reactor. This is due to differences in the mechanism of heat transfer taking place in the reactors. In the conventional heating, heat is transferred to the reactants from the surface and then towards the center of the material by conduction, convection and radiation. This increases the temperature of the surface of the vessel[17]. As a result, vast amounts of energy supplied are lost to the environment, leading to the increase of reaction time. On the other hand, microwaves transfer heat through the interaction of electromagnetic waves with the materials at molecular level. Since, it is a volumetric heating process such interactions in microwave heating can affect molecular actions at a very fast rate, contributing to localized and rapid superheating of the sample. This leads to heating of the sample in the whole volume at similar rate due to internal thermal dissipation of the vibrational energy of the particles. Therefore, under microwave irradiation, esterification occurs by even heating, short reaction time and being environmentally friendly.

**Determination of order and rate constants of esterification:** The reaction for esterification of FFA is a reversible represented as:

$$RCOOH + CH_3OH \Leftrightarrow RCOOCH_3 + H_2O \qquad (4)$$

The rate equation for above is $-r_A = k_1 C_A a C_B b - k_2 C_R C_S s$ (5)

where, $C_A$, $C_B$, $C_R$ and $C_S$ represent concentrations of FFA, methanol, FAME and water, respectively. $k_1$ and $k_2$ represent the rate constants of forward and reverse reactions, respectively. a, b, r and s are the reaction orders with respect to A, B, R and S, respectively.

According to Le Chatelier's principle, any change to the concentration of a chemical will shift the equilibrium to the side that minimizes the change in concentration. As mentioned earlier in the presence of excess methanol, the reaction is considered irreversible. The reaction rate equation can be simplified to pseudo-homogeneous equation with 'a' as the reaction order:

$$-r_A = kC_A a \qquad (6)$$

For a system of constant density, the fractional conversion of FFA and concentration of FFA are related as:

$$C_A = C_{A0}(1 - X_A) \qquad (7)$$

where $C_{A0}$ is the initial concentration of FFA. Inserting Eq. 6 and 7 in Eq. 5 and rearranging:

$$\frac{dX_A}{dt} = kC_{A0}^{a-1}(1 - X_A)^a = K_E(1 - X_A)^a \qquad (8)$$

Thus, by plotting $dX_A/dt$ versus $(1 - X_A)$, the order of the reaction was evaluated. The variation of $dX_A/dt$ as a function of $(1 - X_A)$ at three temperatures (50, 55, 60 and 65°C) is depicted in Fig. 3a. As can be observed as the temperature increases, the rate constant increased and a highest value was obtained at 60°C (0.462 $min^{-1}$). Further, at all temperatures, the reaction order was 1. Hence, it was confirmed that, esterification followed a pseudo first order kinetics.

**Arrhenius plots and activation energy:** A plot of ln K as a function of 1/T is depicted in Fig. 3b, c. The activation energy was determined to be 14.087 and 19.859 kJ $mol^{-1}$ in microwave reactor and electrically heated reactor, respectively. Thus, the activation energy for the reaction was reduced in the presence of microwave field by nearly by a factor of 1.409. The rate constant of esterification obtained in microwave reactor was 16.64 times the value obtained in conventionally heated reactor. The frequency factor (Arrhenius constant) was 69.45 higher in microwave reactor than the corresponding value in conventional electrically heated reactor. The values of Arrhenius constants have been compared with various studies as shown in Table 3.

Table 3: Kinetics of esterification of fatty acids in electrically heated reactor (Reaction conditions: Sulphuric acid concentration = 8%, Molar ratio of methanol to lipid = 30:1, initial FFA = 12.41%)

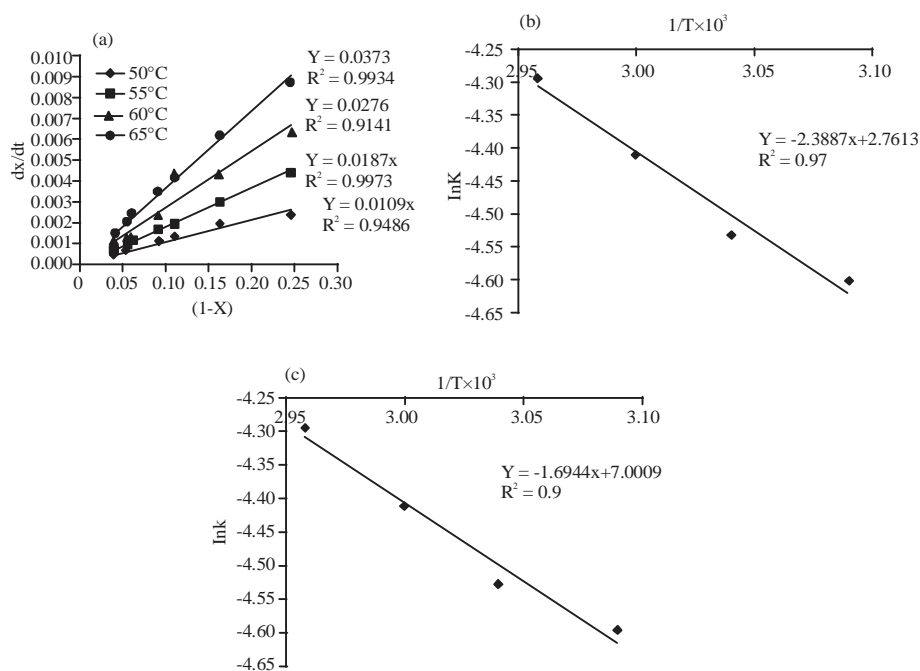| Temperature (°C) | Rate constant $K_{est}$ | FFA in reaction mixture after (%): Time (min) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | 10 | 20 | 30 | 40 | 50 | 60 | 70 | 80 |
| 50 | 0.027 | 10.79 | 8.42 | 7.97 | 7.25 | 6.84 | 6.77 | 6.71 | 6.68 |
| 55 | 0.034 | 10.32 | 8.25 | 7.55 | 7.14 | 6.54 | 6.36 | 6.21 | 6.15 |
| 60 | 0.045 | 9.460 | 7.12 | 6.07 | 4.56 | 2.89 | 2.17 | 1.96 | 1.82 |
| 65 | 0.041 | 9.810 | 7.81 | 6.55 | 5.47 | 4.13 | 3.77 | 3.64 | 3.55 |



Fig. 3(a-c): (a) Determination of order of esterification, (b) Arrhenius plot for esterification in electrical reactor and (c) Arrhenius plot of esterification in microwave reactor

## Effect of operating variables on transesterification

**Effect of temperature:** The effect of temperature on yield of biodiesel is depicted in Fig. 4b. Similar to esterification, 60°C was optimum temperature for transesterification of DSO resulting in FAME yield of 88.67%. The FAME yield at 65°C decreased to 86.25%. At 65°C, the boiling point of methanol is reached and excessive methanol losses occur. Hence, the quantity of methanol available for reaction decreases which might have resulted in the reduction of conversion of transesterification.

**Effect of molar ratio of methanol to DSO:** Figure 4a illustrates the effect of molar ratio and temperature on biodiesel yield. The biodiesel yield increases with increasing molar ratio of methanol to DSO and a highest value of 88.67% was observed at 7:1. A further increase in molar ratio reduced the conversion of DSO. The reduction in yield may be because; the excess of methanol could interfere with the separation of ester product and by-products by increasing solubility of glycerol. Consequently, part of the diluted glycerol remains in the ester phase, leading to foam formation and therefore loss of ester product.

**Effect of KOH%:** The influence of concentration of KOH on methyl ester yield is depicted in Fig. 4c. A level of 1 wt.% was found to be adequate, resulting in highest biodiesel yield of 91.14%. However, at higher concentrations of KOH (above 1%), a decrease in yield was observed. This can be due to the fact that, at higher alkali concentrations, saponification of the triglycerides accelerates faster than transesterification resulting into decreased yield of methyl ester. Sinha *et al.*[18] reported that the yield of rice bran biodiesel decreased after 55°C. A similar observation was made by Dorado *et al.*[19].

**Effect of microwave power:** Microwave power affects the rates of transesterification basically by lowering it's
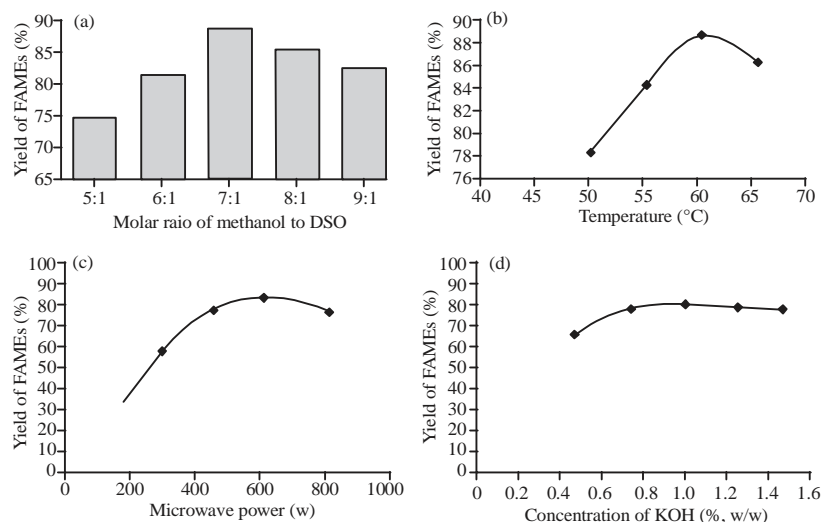
Fig. 4(a-d): (a) Effect of molar ratio of methanol to FFA, (b) Effect of temperature, (c) Effect of microwave power and (d) Effect of KOH%

activation energy by dipolar polarization effect. This occurs due to molecular level interaction of the microwaves in the reaction mixture resulting in dipolar rotation and ionic conduction. In order to optimize the power level, experiments were conducted at five levels (180, 300, 450, 600 and 800 W). A least yield of 38.47% was observed at 180 W which can be attributable to low heating rates and longer time required to attain the reaction temperature. With 100% power level, reactants attain desired temperature faster. However, higher power losses occur. Hence, 600 W was selected as adequate level of microwave power. At this level, FAME yields of 93.47% was observed (Fig. 4d). Increasing the power beyond this level had negative effect on yield of FAMEs.

**Kinetic modeling of transesterification of DSO in microwave reactor and conventional reactor:** After successful optimization of parameters, the kinetic modeling of transesterification of DSO was attempted to evaluate the kinetic rate constants in microwave as well as conventional reactor. The transesterification can be represented as:

$$TAG + 3CH_3OH \Leftrightarrow FAME + 3G \quad (9)$$

where, TAG refers to Tri acyl glycerol and G refers to glycerol. In transesterification process, TAG react with excess methanol to form FAMEs and glycerol. Hence, a pseudo-first order reaction can be considered suitable for this homogeneous catalytic reaction and kinetic model can be written as:

$$\text{Rate of transesterification} = -\frac{d[TAG]}{dt} \quad (10)$$

According to Eq. 9 and 10 can be modified as:

$$\text{Rate of transesterification} = -\frac{1}{3}\frac{d[FAME]}{dt} \quad (11)$$

Rearranging and integrating the above equation:

$$\ln(FAME)_t - \ln(FAME)_0 = 3K_T t \quad (12)$$

where, $K_T$ (min$^{-1}$) refers to first order rate constant of transesterification, $(FAME)_t$ and $(FAME)_0$ refer to concentration of methyl esters at time 't' and time 't = 0'. The value of '$K_T$' can be evaluated with a linear plot of $(FAME)_t$ versus 't'. The rate constants were evaluated at 50, 55, 60 and 65°C and the activation energy of transesterification was evaluated (Fig. 5a, b). A comparison of results of kinetic studies between conventional heating and microwave heating along with values cited in literature is depicted in Table 4. A considerable increase in rate constant was observed in the presence of microwave irradiation (22.59 times). Further, the activation energy was nearly 5.1 times lower than the value obtained with conventional heating while the Arrhenius constant in microwave assisted transesterification was 11.1 times higher than corresponding value in conventional heating.

**Comparisons of DSO biodiesel with petroleum diesel:** The fuel properties of DSO biodiesel are depicted in Table 5. Almost all properties comply with standards specified by ASTM D6751 biodiesel. The neat biodiesel had a density of 0.862 g mL$^{-1}$ which was slightly higher than diesel whose density ranges between 0.825-0.835 g mL$^{-1}$. This may result in delivery of slightly greater mass of fuel in the engine.
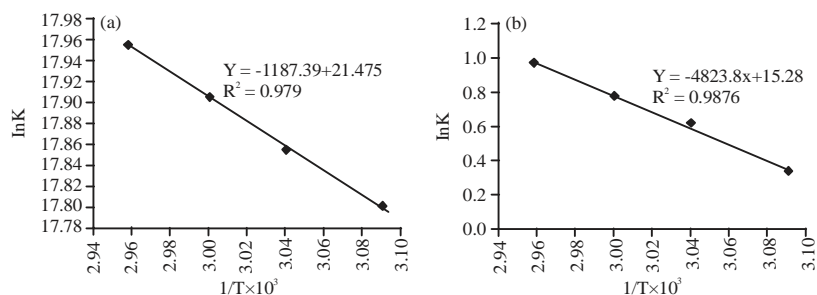
Fig. 5(a, b): (a) Arrhenius plot for transesterification in microwave heated reactor and (b) Arrhenius plot for transesterification in electrically heated reactor

Table 4: Comparison of activation energy, arrhenius factor and rate constant of microwave assisted esterification with literature

| Source | Ea (kJ mol$^{-1}$) | A | K (min$^{-1}$) | References |
|---|---|---|---|---|
| **Esterification in conventional heating** | | | | |
| Palm fatty acid distillate | 17.74 | 2.12 | 0.0299-0.0481 | Chongkhong et al.[20] |
| Jatropha | 11.37 | 101.02 | 0.0026 | Rathore et al.[21] |
| Karanja | 10.54 | 78.21 | 0.0025 | Rathore et al.[21] |
| Dairy scum oil | 19.859 | 15.79 | 0.045 | This study |
| **Microwave assisted esterification** | | | | |
| Ceiba pentandra seed oil | 53.717 | 3.98 | - | Lieu et al.[22] |
| Waste cooking oil | 45.4 | 7 | 0.913 | Mazubert et al.[23] |
| Dairy scum oil | 14.087 | 1096.63 | 0.462 | Present work |

Table 5: Comparison of activation energy, arrhenius factor and rate constant of microwave assisted transesterification with literature

| Source | Ea (kJ mol$^{-1}$) | A | K (min$^{-1}$) | References |
|---|---|---|---|---|
| **Esterification in conventional heating** | | | | |
| Sunflower oil | 47.03 | 1.9×105 | 0.006 | Marinkovic[24] |
| Dairy Scum oil | 67.21 | 5.182×108 | 0.0214 | Sivakumar[25] |
| Bombox ceiba oil | 35.99 | 11.06×103 | 0.031 | Hebbar et al.[26] |
| Dairy scum oil | 50.27 | 19.14×107 | 0.0254 | This study |
| **Microwave assisted esterification** | | | | |
| Waste cooking oil | 37.1 | 1.3×106 | 1.93 | Mazubert et al.[23] |
| Palm oil | 56.12 | - | 0.019 | Ding et al.[27] |
| Dairy scum oil | 9.87 | 212.27×107 | 0.574 | Present work |

The viscosity is the most important property of biodiesel because it affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors. The kinematic viscosity in the present work was found to be 4.6 mm$^{-2}$ s. Sadaf et al.[28] reported that the kinematic viscosities of soybean frying oil and the mixture of soybean and cotton seed frying oil were 4.76 and 4.45 mm$^{-2}$ s at 40°C, respectively. Ozsezen et al.[29] reported that the biodiesel from waste frying palm oil had a viscosity of 4.401 mm$^{-2}$. The value obtained in our case is comparable with these studies. The difference in the viscosities, however, may be because of different physical properties of frying oils and extent of conversion in transesterification. Further, the viscosity of biodiesel decreased nearly 7 times compared to original DSO.

The flash point was well above the required standard of minimum 100°C. The flash point is the measure of the tendency of a substance to form flammable mixtures when exposed to air. The higher value obtained in the present study indicates that the biodiesel produced from DSO is safer to handle.

Cold-flow properties of biodiesel are important indicators of commercial applicability of the fuel. There is no limitation for cloud and pour points of biodiesel in the ASTM D 6751 biodiesel standard. They must be reported to the customers by the producers to make them be prepared for any implications due to weather conditions. The cloud point and the pour points in the present work were found to be 3 and -4°C, respectively which are much higher than of conventional diesel. Hence, the performance of DSO in cold climatic conditions can be expected to be inferior compared to petroleum diesel. The gross calorific value obtained (41.2 MJ kg$^{-1}$) is much closer to that of diesel fuel which has a calorific value of 44.8 MJ kg$^{-1}$.

**FAME analysis:** Table 6 and 7 depicts FAME composition of DSO biodiesel The total FAME content DSO biodiesel was 94.34% which indicates the high purity of biodiesel. Out of total FAME constituents, saturated fatty acids (C14:0,C16:0,C18:0,C21:0 and C24:0) were 38.14, monosaturated fatty acids (C18:1,

Table 6: Comparison of fuel properties of DSO biodiesel with ASTM biodiesel standard

| Fuel property | Test procedures | DSO biodiesel | ASTM D 6751 specifications |
|---|---|---|---|
| Acid value (mg KOH/g oil) | ASTM D 664 | 0.44 | 0.5 max |
| Density @15°C (g mL$^{-1}$) | ASTM D 287 | 0.862 | 0.86-0.9 |
| Kinematic viscosity@40°C (mm$^{-2}$ sec) | ASTM D445 | 4.6 | 3.5-6 |
| Flash point (°C) | ASTM D93 | 173 | Min.100 |
| Higher heating value (MJ kg$^{-1}$) | ASTM D 240 | 43.2 | - |
| Pour point (°C) | ASTM D 97 | -4 | - |
| Cloud point (°C) | ASTM D2500 | 3 | - |

Table 7: Fatty acid composition of DSO methyl esters

| Fatty acid | FAME composition (wt.% in final biodiesel) |
|---|---|
| Myristic (14:0) | 2.87 |
| Palmitic (C16:0) | 22.71 |
| Stearic (C18:0) | 7.14 |
| Oleic (C18:1) | 39.04 |
| Linoleic (C18:2) | 13.14 |
| Linolenic (C18:3) | 0.98 |
| Arachidonic (C20:4 ω6) | 1.87 |
| Ocosanoic acid (C21:0) | 2.37 |
| Erucic acid (22:1) | 1.17 |
| Lignoceric acid (C24:0) | 3.05 |
| Σ Total | 94.34 |
| Σ Saturated | 38.14 |
| Σ monosaturated | 40.21 |
| Σ Polyunsaturated | 15.99 |

C22:1) were 40.21% and polyunsaturated fatty acids (C18:2, C18:3, C20:4ω6) were 15.99%. Oleic acid was the most abundant FAME in DSO biodiesel with a content of 39.04%. Further, it is well known that, low amounts of PUFAs (polyunsaturated fatty acids) and high oleic acid concentration favour e oxidation stability. On the other hand, higher amounts of saturated fatty acids produce biodiesel with high cetane number and low iodine value. Further, the presence of double bonds favours the Cold Filter Plugging Point, thus, avoiding the formation of crystals at low temperature which otherwise may clog engine filters and nozzles.

## CONCLUSION

A low cost lab scale kitchen modified microwave reactor with essential controls (Temperature, time, microwave power and stirring capacity) was used in the present work to conduct esterification and transesterification of DSO. The operating parameters affecting conversion of esterification and transesterification were optimized. A highest overall yield of biodiesel (87.51%) was obtained under optimum conditions. Both esterification and transesterification followed pseudo first order kinetics. The rate constants of esterification and transesterification were significantly higher in microwave reactor than in electrically heated reactor. The fatty acid profile of biodiesel indicated the presence of: C14:0, C16:0, C18:0, C24:0, C18:1, C22:1, C18:2, C18:3 and C20:4ω6. The most abundant FAME is the oleic acid methyl ester with a content of 39.04%.

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