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Full Length Research Paper

Melothria maderaspatna seed oil: A low cost feedstock for biodiesel production using crystalline manganese carbonate, a green catalyst

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This research focuses on the production of biodiesel from low cost feedstock such as *Melothria madraspatana* seed oil via $MnCO_3$ catalyzed transesterification process at 60°C, investigating the effects of process parameters such as molar ratio of feedstock to methanol, catalyst quantity, and reaction time on biodiesel yield. The biodiesel was successfully produced via transesterification process from low cost feedstock. The optimum parameters for maximum biodiesel yields were found to be methanol/oil molar ratio of 5:1, catalyst concentration of 1 wt% of oil, and reaction period of 75 min. The maximum biodiesel yield at the optimum condition was 93%. The fuel properties of biodiesel from *M. madraspatana* seed oil were also investigated and compared with those of American Society for Testing and Materials (ASTM) biodiesel standards. Crystalline manganese carbonate was found to be environmentally friendly, easy to handle and non-corrosive green catalyst for the production of biodiesel from *M. madraspatana*. The results demonstrated high potential of producing economically viable biodiesel from low cost feed stocks with proper optimization of the process parameters.

Key words: Biodiesel, *Melothria madraspatana* seed oil, $MnCO_3$, fatty acid methyl esters, green catalyst.

INTRODUCTION

In recent years many studies have investigated the economic and environmental impacts of biofuels, especially bio-ethanol, biodiesel, biogas and biohydrogen (Demirbas, 2009; Balat, 2009). Current research on bio renewable fuel is considerably focused on producing biodiesel from vegetable oils (Demirbas, 2002; Balat, 2008). Soaring prices of fossil fuels, geo-political issues and environmental pollution associated with fossil fuel use has led to a growing interest in the production and use of biofuels. However, the use of biodiesel has not expanded in developing countries mostly due to the high production which is associated with the expensive high quality oil feed stocks.

Several biodiesel production methods have been developed, among which transesterification, using alkali catalyst gives high level of conversion of triglycerides to

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their corresponding methyl esters in short reaction time (Fukuda et al., 2001).

Biodiesel production is a modern and technological area for researchers due to the relevance it is winning everyday because of the increase in the petroleum prices and its environmental advantages (Marchetti et al., 2005). In the present study, we looked at the new low cost feedstock, *Melothria maderaspatna* seed oil, with high free fatty acid (FFA) for biodiesel production. *M. maderaspatna* is an annual scandant or trailing herb of about 4 m long, of open not forested localities throughout the West African region and wide spread in tropical Asia. It belongs to the Cucurbitaceae family. All parts of the plants have medicinal used for as vermifuges, laxatives and febrifuges. The fatty acid profile of the *M. maderaspatna* oil showed that it composed primarily of oleic, palmitic, stearic, linoleic, myristic and benehic acids. The seeds contain 40% of oil.

MATERIALS AND METHODS

The *M. maderaspatna* seeds were purchased from a local seed store. Methanol and chloroform was purchased from SD fine chemicals, Mumbai, India. Pure crystalline, ash coloured manganese carbonate was purchased from chemical corporation of India.

Extraction of oil

Currently, there is no commercial production of *Melothria maderaspatna* seed oil in India; hence it was not available in the market. The collected seeds were extracted in laboratory scale and the procedure is as follows: The seeds were ground to a fine powder and dried for 2 h at 100 °C.

For the continuous extraction of the oil, the Soxhlet extraction apparatus was employed and hexane was used as a solvent in the extraction process. The soxhlet device temperature was kept at 65-70 °C and the overall process lasted 24 h. At the end of the process, the oil was separated from the organic solvent using a rotary evaporator, dried at 60 °C and weighed; yield was calculated on dry weight basis.

Fatty acid composition of *M. maderaspatna* oil

Fatty acid composition of *M. maderaspatna* seed oil methyl ester was also determined using gas-chromatography analysis. The fatty acid profile of the methyl ester was identified and quantified as shown in Table 1.

Table 1. Fatty acid composition of M. *maderaspatna* oil.

Fatty acid	Formula	Structure	Weight %
Oleic	$C_{18}H_{34}O_2$	18:1	45.1
Palmitic	$C_{16}H_{32}O_2$	16:0	28.8
Stearic	$C_{18}H_{36}O_2$	18:0	8.10
Linoleic	$C_{18}H_{32}O_2$	18:2	16.8
Linolenic	$C_{18}H_{30}O_2$	18:3	0.70
Myristic	$C_{14}H_{28}O_2$	14:0	0.25
Behenic	$C_{22}H_{44}O_2$	22:0	0.16

Pre-treatment of *M. maderaspatna* oil

Acid catalyzed pre-treatment of *Melothria maderaspatna* oil with an initial acid value of 2.20 mg KOH/gm was carried out in a 500 ml three necked round bottom flask connected to a reflux condenser and a mechanical magnetic stirrer. Initially *Melothria maderaspatna* seed oil and methanol were added to the flask, followed by dropwise addition of sulphuric acid. The contents were heated at reflux for 4 h. Upon cooling to room temperature, the phases were separated. The oil phase was washed with distilled water until a neutral pH was achieved, followed by rotary evaporation to remove residual methanol. Finally, treatment with anhydrous sodium sulphate (Na_2SO_4) provided *Melothria maderaspatna* seed oil with a final acid value 0.40 mg KOH/gm, which was subjected to transesterification process.

Transesterification

Transesterification of *Melothria maderaspatna* oil was conducted in a 500 ml three-necked round bottom flask connected with a reflux condenser, stirring was provided with a magnetic stirrer. This was set at a constant speed throughout the experiment. Initially, the oil was heated at a desired temperature. A known amount of manganese carbonate was mixed in the required amount of methanol.

This methanolic manganese carbonate was then added to the round bottom flask containing oil. At that point, the reaction was kept under reflux condition. The molar ratio of methanol/oil ratio was fixed at 5:1. Formation of methyl esters from *Melothria maderaspatna* oil was monitored by thin layer chromatography. The methyl esters of *Melothria maderaspatna* oil were extracted with chloroform. The product methyl esters were dried over sodium sulphate. The chloroform was then removed by rotary evaporator.

Recovery of catalyst

The catalyst was thoroughly washed 4-5 times with water for 35 h. After complete drying, the catalyst was re-used for transesterification reaction. The obtained results showed a catalytic efficiency even after seven times of use.

Analysis of *M. maderaspatna* oil methyl ester

Gas chromatography has been to date, the most widely used method for the analysis of biodiesel due to its higher accuracy in quantifying minor components (Schneider et al., 2004). The samples were analyzed with a Shimadzu GC-2010 gas chromatograph equipped with a splitless injection system. Helium gas was used as a carrier gas.

The conditions of the instrument were: column oven temperature 75°C, injection temperature set at 280°C, flow control mode in linear velocity with 26.0 cm/s, total flow 14.0 ml/m, column flow 1.0 ml/m, purge flow 3.0 ml/m, pressure 131.6 kpa where as the split ratio 10.0, methyl palmitate was used as an internal standard.

A stock solution of hexane with a known amount of methyl palmitate was prepared a priori and used for analysis. Samples were prepared for analysis by adding approximately 0.05 g of oil to 5 ml of *n*-hexane. About 1ml of this mixture was put into GC sampler vials. 2 µl of the sample were injected into the column. The analytical results of components of fatty acid methyl esters (FAME)

Table 2. The components of FAME from *M. maderaspatna* oil.

Methyl ester	*M. maderaspatna* %
Methyl oleate	43
Methyl palmitate	27
Methyl stearate	7.5
Methyl linoleate	15.1
Methyl linolenate	0.65
Methyl myristate	0.20
Methyl behenate	0.15

from *Melothria maderaspatna* oil using manganese carbonate are shown in Table 2.

RESULTS AND DISCUSSION

M. maderaspatna oil characterization

The oil content of *M. maderaspatna* seed is 42% on dry weight basis. This may result in lower operation costs compared to some other oil seeds such as soybeans and cottonseeds which have average oil contents of only 20% and 14% respectively. Lower operation costs result from higher oil percentage mainly due to less capacity needed for the extruder and oil seed press.

Effect of *M. maderaspatna* oil properties on the transesterification reaction

The two major quality parameters that influence the production process of biodiesel are the FFAs and water content. Several studies showed that the raw oil acid value should be less than KOH 1.0 mg/g and that all raw materials should be anhydrous (water content <0.3%) (Haas, 2005; Leung and Guo, 2006) If the above requirements are not met, it is still possible to produce biodiesel, but the overall yield of the reaction is significantly reduced due to the deactivation of the catalyst and the formation of soaps. From the GC analysis, it was observed that no soaps or other impurities were produced during the reaction process.

EFFECT OF REACTION PARAMETERS ON BIODIESEL YIELD

Effect of methanol/oil molar ratio

The methanol/oil molar ratio is considered to be one of the most important factors affecting the yield of biodiesel. Since the transesterification reaction was a reversible reaction, methanol was used in excess with respect to *M. maderaspatna* oil in order to drive the reaction towards the formation of fatty acid methyl esters.

As can be seen from Figure 1, the fatty acid methyl esters yield increased with increasing of the molar ratio of methanol to oil over the range from 3:1 to 8:1. The highest yield (93%) was obtained at the molar ratio 5:1 for 75 m. With further increasing of the molar ratio, a little decrease in the fatty acid methyl esters yield was observed. Therefore the optimal molar ratio of methanol to oil was to be 5:1.

Effect of catalyst concentrations

The effect of the amount of catalyst on the fatty acid methyl esters yield was investigated within the range 0.5-3.0% $MnCO_3$ (based on the oil weight) and the results are illustrated in Figure 2.

The highest yield of biodiesel was obtained at the catalyst concentration of 1% weight of oil. This amount resulted in the yield of 93%. However, the biodiesel yield declined significantly at the catalyst quantity higher than 1%, due to the formation of fatty acid salts (soap), *via* Saponification process. The produced soap prevented a clear separation of biodiesel from glycerine formation, which increased the viscosity of the biodiesel and thus lowering the yield.

Effect of reaction time

The effect of reaction time on the yield of fatty acid methyl esters at the catalysis of $MnCO_3$ was studied and the results are shown in Figure 3. The reaction time was varied within the range of 30 to 120 m. A gradual increase in the fatty acid methyl esters yield was observed with increasing the time from 30 to 75 m and then remained nearly constant. The optimum reaction time was 75 m, at which the highest *M. maderaspatna* methyl ester yield was to be 93%.

Fuel properties

The result obtained was within the specification limits. The fuel properties of produced biodiesel are summarized in Table 3. The standard for biodiesel states that the fuel should have a density between 860-900 kgm^{-3}. Density has very important influence on the engine fuel injection system (Lee et al., 2002). *M. maderaspatna* methyl ester had a density of 890 kgm^{-3}. The results obtained showed that the produced *M. maderaspatna* oil methyl ester was within the specification limits. Viscosity represents flow characteristics and tendency of fluids to deform with stress. The high viscosity interferes with the injection process and leads to insufficient fuels atomization.

Moreover, the mean diameter of the fuel droplets from

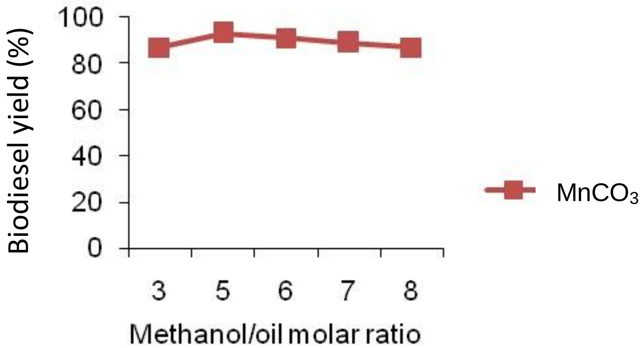

Figure 1. Effect of methanol/oil molar ratio.

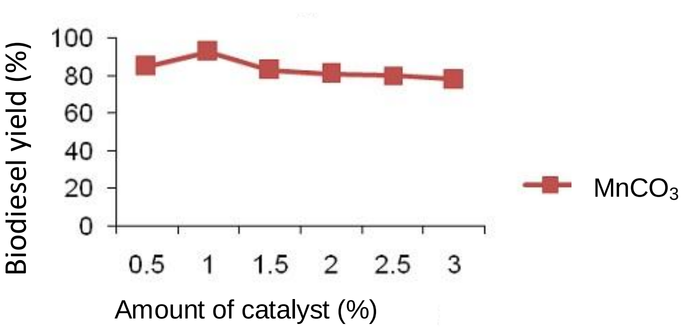

Figure 2. Effect of catalyst concentration.

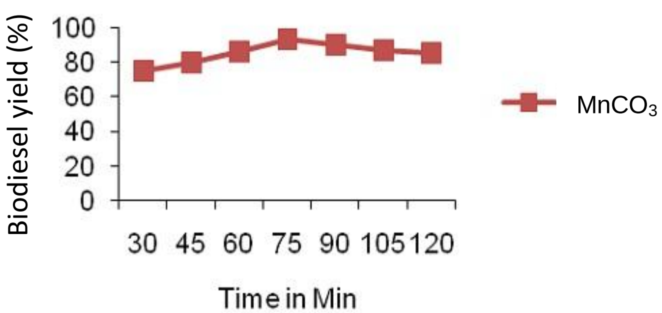

Figure 3. Effect of reaction time.

the injector and their penetration increases with increasing fuel viscosity (Choi and Reitz, 1999). Viscosity of the biodiesel affects the performance of the fuel supply system including fuel pump, fuel filters and air-fuel mixing behaviour (Tesfa et al., 2010). The viscosity must be between 1.9 to 6.0 mm^2s^{-1}. *Melothria maderaspatna* oil methyl ester had a viscosity 3.9 mm^2s^{-1}. The results obtained were within the specification limits.

The acid number of a biodiesel can be used to indicate the content of free fatty acids of the fuel. The acid number of a biodiesel increases 3 mg KOH/g/1 wt % water content in its raw oil state (Cvengros and Cengrosova, 2004). Biodiesel with a low acid value is considered “safe” for storage and transportation. *Melothria maderaspatna* oil methyl ester had an acid value 0.40 mg KOH/g. The results obtained were within the specification limits.

The flash point is the temperature at which the fuel will start to burn when it comes in contact with fire (Ali et al., 1995). It is an important parameter from the safety point of view during storage and transportation. The combination of high viscosity and low volatility of a fuel causes bad cold engine start up, misfire and ignition delay (Szybist et al., 2007). A fuel with high flash point may cause carbon deposits in the combustion chamber. The flash point must be a minimum of 120°C, but *M. maderaspatna* oil methyl ester had a flash point of 130°C. The result obtained was within the specification limits and is safe for transport.

Cold-flow quality of a fuel is determined by the cloud point and pour point. The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid when cooled. The pour point is the lowest temperature at which the fuel will still flow and can be pumped. The cold flow problem of biodiesel can be overcome using branched chain alcohols such as iso-propanol, 2-butanol in transesterification (Ali et al., 1995, Lee et al., 1995). The cloud point and pour point must be between the range -3-12 and -15-10 respectively. The *Melothria maderaspatna* oil methyl ester had a cloud point and pour point of 2 and 1 respectively.

Conclusion

Two factors, the cost of feed stock and catalyst affect the cost of production of biodiesel. The cost of seed oil obtained from *Melothria madraspatana* is low. Crystalline manganese carbonate was found to be a green catalyst in the production of biodiesel. Catalyst can be recovered and requires no neutralisation.

Manganese carbonate as a catalyst is easy to handle and exhibits low toxicity levels. Catalyst used is in the process were environmentally friendly. *M. madraspatana* plant grows in sandy and river bed soil, requiring no special care. Production of biodiesel from *M. madraspatana* generates employment opportunities for the poor and unemployed in countries like Argentina, China, Mexico and India.

The aim of this study was to evaluate *M. maderaspatna* seed oil as a potential raw material for biodiesel production via a transesterification reaction. The experimental results are described thus: *M. maderaspatna* seeds were found to be rich in oil with an average yield of approximately 42%. *M. maderaspatna* seed oil as low cost feedstock makes it an attractive alternative application of existing feed stocks for biodiesel production. The optimum parameters for maximum

Table 3. The fuel properties of *M. maderaspatna* oil methyl esters.

Fuel properties	Unit	Melothria maderaspatna oil methyl ester	ASTM biodiesel standard
Kinematic viscosity	Mm^2s^{-1}	3.9	1.9-6.0
Density	Kgm^{-3}	890	860-900
Acid value	mgKOH/g	0.40	0.80 max
Flash point	°C	130	130 min
Cloud point	°C	2	-3-12
Pour point	°C	1	-15-10

biodiesel yields were found to be methanol/oil molar ratio of 5:1, catalyst concentration of 1 wt% of oil, and reaction time of 75 minutes. The maximum biodiesel yield at the optimum conditions was 93%.

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