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Biodiesel production from *Argemone mexicana* seed oil using crystalline manganese carbonate

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This communication explores the feasibility of biodiesel production from a weed plant Argemone mexicana seed oil and an efficient catalyst crystalline manganese carbonate. To the best of the authors' knowledge, this is the first study making use of pure, crystalline, ash colored manganese carbonate as a heterogeneous catalyst for the production of methyl esters as fuel from Argemone mexicana seed oil. The optimum process conditions for the conversion of Argemone mexicana oil to its methyl ester by transesterification required 1% manganese carbonate as catalyst with alcohol to oil ratio 5:1 at 60ºC to yield biodiesel of 99.99% purity. The methyl esters obtained were examined by Gas chromatography analysis.

Keywords: Biodiesel, Fatty acid methyl esters, *Argemone mexicana* seed oil, crystalline Manganese carbonate, Heterogeneous catalyst

INTRODUCTION

Biodiesel, an alternate fuel has attracted considerable attention during the past decade as a renewable, biodegradable and non-toxic fuel[1–4]. As a future prospective fuel, biodiesel has to compete economically with petroleum diesel fuels. One way of reducing the biodiesel production costs is to use the less expensive feedstock containing fatty acids. The availability and sustainability of sufficient supplies of less expensive feedstock will be a crucial determinant delivering a competitive biodiesel price. Recent food verses fuel controversy makes edible oil not an ideal feed stock for biodiesel production. In this competition the non edible oil sources are preferred as feed stock for the production of biodiesel. The use of non-edible oils as alternative feedstock is picking up as the demand for biodiesel is expected to increase sharply in the near future[2]. The oil from the seeds of weed plant like *Argemone mexicana* can become the main source of feedstock due to a profuse growth and availability of this plant. The economic viability of biodiesel depends on the price of the feedstock used for biodiesel production. In a recent study[5] biodiesel was synthesized from *Argemone mexicana* seed oil having more than 3% FFA in a single step sodium methoxide catalyzed transesterification in 90% yield[5,6]. Since sodium methoxide is corrosive, keeping in view the industry, an attempt is made here with crystalline manganese carbonate a non corrosive, versatile and low cost catalyst which brings about 90% conversion of oil to fatty acid methyl esters (FAME).

In many research publications, biodiesel is produced from the refined edible oil using methanol and alkaline catalysts[7]. Alkaline hydroxides are the most effective transesterification catalysts as compared to acid catalysts. However, the problem with alkaline catalyzed transesterification of vegetable oils is possible only if the acid value of oil is less than four[7]. High percentage of free fatty acid in the oil reduces the yield of esterifiction process; such oils are mainly used for making low cost soap. Therefore, it is considerably more costly to separate the catalyst from the produced monoesters. It is difficult to transesterify these higher FFA vegetable oils using common alkaline catalysts[8,9]. The purpose of this study is to develop a method for transesterification of high FFA vegetable oils as it is considered as potential feedstock for biodiesel production. Heterogeneous pure manganese carbonate base catalyst has many advantages in biodiesel production, with vegetable oils containing high FFA.

Petroleum sourced fuels is now widely known as nonrenewable due to fossil fuel depletion and environmental degradation[10,11]. Renewable, carbon neutral, transport fuels are necessary for environmental and economic sustainability. The rising prices of petroleum fuels, depletion of oil reserves and stiff regulations on exhaust emissions have necessitated the substitution of fossil fuel with the less polluting and easily available renewable fuels for the use of internal combustion of engines. Development of biodiesel as an alternative and renewable source of energy for the mechanized agricultural and transportation sector has become critical in the national efforts towards the maximum self reliance for the corner stone of energy security strategy. Biodiesel fuel is considered to be the environmentally friendly fuel because of its renewability, high biodegradability, low pollutant emission, high flash point and excellent lubricity. It is well known that 3.2kg of CO_2 could be reduced by 1kg of biodiesel fuel atomization, incomplete combustion and carbon deposition on the injector and valve seats leading to severe engine problems, all this is due to the viscosity of vegetable oil that is greater than the viscosity of diesel. This problem is overcome by lowering the viscosity of vegetable oil[12]. There are three well known procedures such as pyrolysis, cracking and transesterification processes to lower the viscosity of vegetable oil[12,13].

The common method to produce biodiesel is by transesterification of vegetable oils or animal fats with short chain alcohols. Along with biodiesel, commercially valuable by-product glycerol is also obtained. High purity of biodiesel can be achieved by transesterification of fresh vegetable oils with methanol in the presence of an alkaline catalyst. Transesterification is the chemical reaction between triglycerides and alcohol in the pres-

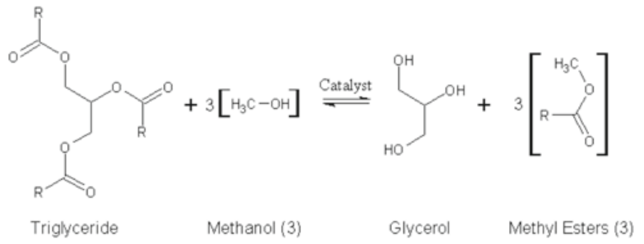

Figure 1. Transesterification of triglycerides with alcohol

ence of the catalyst to produce monoesters. The long and branched chain triglyceride molecules are transformed to monoesters and glycerides[14]. Transesterification process consists of three consecutive reactions. That is, conversion of triglycerides to diglycerides followed by the conversion of diglycerides to monoglycerides. The overall transesterification reaction can be represented by the following

The glycerides are converted into glycerol and yielding one ester molecule in each step. The major factors affecting the conversion efficiency of the process are molar ratio, amount of catalyst, and reaction time.

Recent literature shows that production of biodiesel is well studied and established, especially using acids or alkali catalysts like H_2SO_4 and NaOH[15–19]. However, these catalytic systems have some technological problems, as the acid system is corrosive and basic one with emulsification. To minimize these problems attempts have been made to use heterogeneous catalysts systems in alcoholysis of *Argemone mexicana* oil. The heterogeneous manganese carbonate base catalyst is active for high molecular weight alcohol achieving conversion to 90% and produces neither corrosion nor emulsion making it easier to separate the product obtained. The activity of manganese carbonate is similar with the traditional NaOH and H_2SO_4 catalysts under the reaction conditions studied. Another way to reduce the biodiesel production cost is to use the less expensive feedstock containing fatty acids such as non-edible oils, animal fats, waste food oil and byproducts of the refining vegetable oils[20].

In this paper the focus is on the use of noncorrosive versatile catalyst and the low cost feedstock for high biodiesel production in optimized condition. The manganese carbonate was found to be an environmentally friendly catalyst and *Argemone mexicana* is an annual herbaceous plant and is found all throughout the world as the weed plant. The plant grows to a height of 0.5–1.5 m and matures in 110 to 120 days. It requires moderate rainfall and temperate and tropical areas. The plant prefers all types of soil. The seeds are black in appearance and are heavy in weight. The seeds contain about 30% oil with 25% oleic and 55% linoleic acid in fatty acid composition. In the present work *Argemone mexicana* is evaluated as the potential feed stock for biodiesel with heterogeneous pure manganese carbonate as a versatile catalyst.

EXPERIMENTAL

Materials

The *Argemone mexicana* seeds were collected from the forest of Araku, Vizag, Koraput Orissa, hilly regions of Karnataka and Maharashtra states of India. Methanol, chloroform and sodium sulphate were purchased from Sarabhai Division of Chemicals, Mumbai. India. Fine Chemicals, Mumbai, India. Pure ash colored crystalline manganese carbonate was purchased from ICI Chemical India.

Extraction of Oil

Prior to the extraction process *Argemone mexicana* seeds were dried at 50°C for 12 hours in the oven to remove the excess moisture. The dried seeds were then weighed and powdered. The fine seed powder was then subjected to Soxhlet extraction using n-hexane as a solvent. The duration of each batch was 10 hrs for complete extraction. The solvent required for extraction of per kg seeds was in the ratio of 5:1 (5L solvent for 1kg seeds). The oil was recovered from the solvent by rotary evaporator. The extracted oil was then measured to calculate the percentage oil in the seeds.

Analysis of Vegetable oil

The extracted oil was then subjected to Gas chromatography to find out the fatty acid composition (Table-1). The samples were analyzed with a Shimadzu GC-2010 gas chromatograph equipped with a split-split less injection system. Helium was used as a carrier gas the conditions of instrument were: Column oven temperature 75°C, injection temperature set at 280°C, the Flow control mode in the linear velocity with 26.0 cm/Sec, the total flow 14.0 ml/min, column flow 1.0 ml/min, purge flow 3.0 ml/min, pressure 131.6 Kpa, where as the split ratio 10.0. 1 % solution of oil in hexane was used for analysis.

Transesterification reaction

Optimum conditions for catalyst to oil ratio and methanol to oil ratio were investigated. The crude *Argemone mexicana* oil was taken into the reaction flask and heated at 50°C. The catalyst mixed in methanol at different concentrations was used for the conversion of extracted *Argemone mexicana* oil to fatty acid methyl esters (FAME). The reaction conditions such as the amount of catalyst and the oil-methanol ratio were optimized. The transesterification reactions were performed in a 25 ml round bottom flask 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 catalyst was mixed in the required amount of methanol and was heated separately to the desired temperature. This methanolic catalyst was then added to the round bottom flask containing oil. At that point, the reaction was kept under reflux conditions. The molar ratio of methanol /oil ratio was fixed at 5:1. Formation of methyl esters from vegetable oil was monitored by thin layer chromatography using petroleum ether a as solvent system. After the completion of reaction the product was extracted with chloroform, dried over sodium sulphate and concentrated under vacuum to afford FAME.

Analysis of Fatty Acid Methyl Esters

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[21]. The samples were analyzed with a Shimadzu GC-2010 gas chromatograph equipped with a split-split less injection system. Helium was used as a carrier gas. The conditions of the instrument were: Column oven temperature 75ºC, injection temperature set at 280ºC, Flow control mode in linear velocity with 26.0 cm/Sec, total flow 14.0 ml/min, column flow 1.0 ml/min, purge flow 3.0 ml/min, 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. The samples were prepared for analysis by adding approximately 0.05 g of FAME to 5 ml of n-Hexane. About 1ml of this mixture was put in to GC auto sampler vials. Two micro liters of the sample were injected into the column.

Recovery of the catalyst

In the present work, the catalyst was recovered from the reaction and washed with distilled water thoroughly 4–5 times. Then the catalyst was dried at 50ºC for 35 hrs. The recovered catalyst was studied for its efficiency and was found to bring about 95% conversions.

Fuel properties of fatty acid methyl esters

Fatty acid methyl esters obtained from transestrification reaction was analysed as per the specifications of biodiesel as fuel. The following properties of the biodiesel produced were determined: atmospheric liquid density was calculated by measuring the sample mass in a 10ml graduated cylinder. The viscosity measured which defines this property as the resistance to flow of a fluid under gravity at 40ºC. The testing device used was a Redwood viscometer which measures viscosity within the limits of precision given in the standards. The apparatus performs at least three measurements to guarantee correct results. The flash point was measured; the testing device was a Cleveland's open cup apparatus, which automatically determines empirical flash point of flammable liquids according to standardized test procedures. The saponification value, peroxide value and acid value were determined and these values of the biodiesel were compared with the standards. The cloud point and Pour point determined by following the standard procedures. The obtained results were compared with the standards. Most of these parameters comply with the limits prescribed in the ASTM Standards for biodiesel. Each experiment was conducted in triplicate and the data is reported as mean.

RESULTS AND DISCUSSION

The seeds contained 25% moisture which was removed as explained in the experimental section. The seeds were dried and the dried seed powder of *Argemone mexicana* contains 40% oil. Oil was extracted by Soxhlet extractor using hexane as solvent. The fatty acid compositions determined for the *Argemone mexicana* oil in this work are shown in Table 1. Fatty acid composition of *Argemone mexicana* oil were determined as palmitic acid (14.1–15.3%), stearic acid (3.7–9.8%), oleic acid (34.3–45.8%), linoleic acid (29.0–44.2%), myristic acid (0–0.1%), linolenic acid (0–0.3%), Palmitoleic acid (0–1.3%) archidic acid (0–0.3%) and behenic acid (0–0.2%). As can be seen in Table 1, the nature of fatty acid present in *Argemone mexicana* oils does not vary significantly with the other vegetable oil sources that are already reported, variations in their proportions and their unsaturation degree, are noted. The comparisons of overall proportions of unsaturated fatty acids are similar to jatropha and pongamia oil.

The present study for the production of FAME from *Argemone mexicana* oil was investigated by changing catalyst concentration (0.2 to 3.0%), methanol/oil molar ratio (3:1 to 8:1), reaction time (20 to 90 min) and temperatures (25–75ºC). Volume of *Argemone mexicana* oil 10ml and methanol as alcohol was fixed as common parameter throughout the experiments. All the results obtained were compared with NaOH catalyzed transesterification reaction.

The amount of methanol required for transesterification was analyzed in terms of the methanol to oil molar ratio. The stoichiometric methanol to oil molar ratio required for the complete transesterification reaction is 3:1 but experimentally it is observed that this is not sufficient to complete transesterification reaction. A higher molar ratio is required to push the reaction at a faster rate. In the present work, transesterification of *Argemone mexicana* oil with 1v/w% manganese carbonate catalyst using alcohol /oil ratio between 3: 1 to 8:1 was carried out, and it was observed that the ester conversion increases with the increase in molar ratio up to the value of 5:1. Maximum biodiesel yield achieved at 5:1 molar ratio was 90%. It was observed that further increase in molar ratio show that conversion efficiency remains the same. But the biodiesel yield goes down because the excess alcohol makes glycerin separation difficult. Hence the methanol to oil molar ratio of 5:1was used for the remaining experiments. The methanol to oil molar ratio

Table 1. Fatty acid composition of crude *Argemone mexicana* oil

Fatty Acid	Formula	Systematic Name	Structure	Wt%
Myristic	$C_{14}H_{28}O_2$	Tetradecanoic	14:0	0.1
Palmitic	$C_{16}H_{32}O_2$	Hexadecanoic	16:0	14.7
Palmitoleic	$C_{16}H_{30}O_2$	cis-9-hexadecanoic	16:1	1.3
Stearic	$C_{18}H_{36}O_2$	octadecanoic	18:0	6.75
Oleic	$C_{18}H_{34}O_2$	cis-9-Octadecanoic	18:1	40.0
Linoleic	$C_{18}H_{32}O_2$	cis-9, cis-12-Octadecedianoic	18:2	36.6
Linolenic	$C_{18}H_{30}O_2$	cis-6,cis-9, cis-12-Octadecatrienoic	18:3	0.3
Arachidic	$C_{20}H_{40}O_2$	Eicosanoic	20:0	0.3
Behenic	$C_{22}H_{44}O_2$	Docosanoic	22:0	0.2

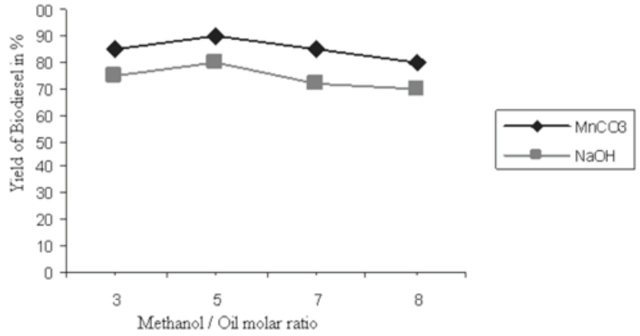

Figure 2. Effect of methanol to oil ratio

affects the yield as shown in Figure 2.

The effect of catalyst concentration was studied in the range of 0.2 to 3 wt% and maximum biodiesel yield of 90% was obtained with 1wt% catalyst. All the reactions were carried out with 5:1 alcohol to *Argemone mexicana* oil molar ratio, under reflux conditions. It was observed that the production of biodiesel decreases with the increase in manganese carbonate concentration, because of emulsification. According to Boocock, the yield of biodiesel increases proportionately with catalyst concentration at lower methanol to oil mass ratio[22,23]. But, in practice it was also observed that transesterification could not proceed well with an insufficient amount of catalyst. The effects of manganese carbonate catalyst concentration on transesterication are presented in Figure 3.

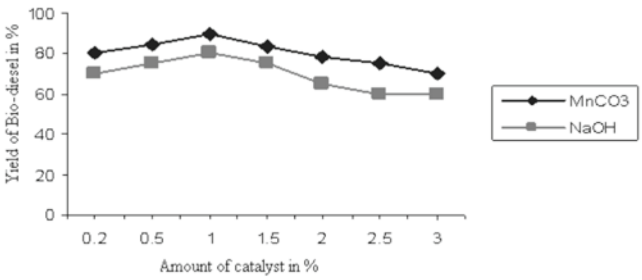

Figure 3. Effect of catalyst concentrations

For the complete conversion of oil to biodiesel during transesterification reaction, it must be stirred well at constant rate. The experiments were carried out at various speeds for 30–120 min. The experiments revealed that conversion of *Argemone mexicana* oil to biodiesel yield of 90% was achieved within 45 min at reflux condition. The effect of reaction time on biodiesel yield is given in Figure 4.

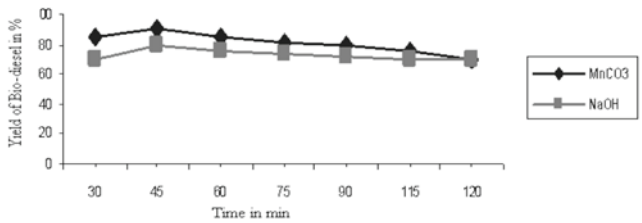

Figure 4. Effect of reaction time

The physical and chemical properties of FAME obtained from Argemone mexicana oil were determined in laboratory were found to be as shown in Table-2

Saponification, peroxide value and acid value parameters in A.mexicana oil is high compared to A. mexicana methyl ester as shown in Table 2. Acid value is high in the A. mexicana oil and so we have opted for two step

Table 2. The physical and chemical properties of methyl ester of *A. mexicana* oil

Fuel properties	A. mexicana oil	A. mexicana methyl ester	ASTM Diesel Standards
Saponification value (mg KOH /g)	202.5	167.5	187
Peroxide value (meq/kg sample)	150	131.4	0.2
Acid value (mg KOH/g)	76.2	0.95	0.02
Density(40° C)	910	860	780
Viscosity(40°C)	29.6	11.1	4.3
Flash point(°C)	235	171	66
Cloud point(°C)	12	8	1
Pour point(°C)	-12	-14	-23

transesterification. The acid value and peroxide value were determined to evaluate the storage ability of biodiesel. Acid values of methyl ester were determined as the percentage of free fatty acid present in oil which is estimated by titrating it against KOH in presence of phenolphthalein as indicator[24,25]. Peroxide value is the peroxide present in oil[26] that is determined by titrating against sodium thiosulphate in presence of KI and starch as indicator. Viscosity was determined by Redwood viscometer. The obtained results were compared with the standards. The measured viscosity of oil is much more as compared to biodiesel standards. The flash point determined in oil was very high as compared to its methyl ester and diesel. The blending of *A. mexicana* seed oil with petroleum diesel is known to bring down the flash point[26]. Biodiesel obtained was found to have higher cloud and pour points compared to conventional diesel. The special additives whichever routinely used to improve the cold flow properties of diesel fuels are perhaps also necessary for biodiesel. The cloud point and pour point of fatty methyl ester produced from this oil will be lower and their use as methyl ester will not bother even under cold conditions[5,21]. The present results obtained show that the transesterification process improved the fuel properties of the oil with respect to viscosity, flash point and acid value.

The GC analysis was performed to determine the composition of fatty acid methyl esters; using the gas chromatography it is easy to specify the biodiesel purity. The maximum biodiesel percentage yield achieved was 90%. The big difference in the composition of linoleic and linolenic acids is observed in the oils of other seed plants as well, for example Cucurbita pepo L[27]. The qualitative and quantitative analysis and the results of methyl ester components in *Argemone mexicana* oil are presented in Table-3. As it is obvious from the Table, the FAME (fatty acid methyl ester) from *Argemone mexicana* oil contained mainly methyl linoleate (47.43%) and methyl stearate (32.49%), methyl oleate (14.96), methyl palmitate (3.85), methyl palmitoleate (1.10), methyl myristate (0.10) and methyl laurate (0.06) which are comparable to fatty acid composition of same feedstock. The GC analysis data show that the fatty acid methyl ester (FAME) ranged between C14:0 and C24:1. Elution times for: methyl palmitate, methyl linoleate, methyl stearate, methyl oleate were consistent with selective retention times. Thus GC- MS analysis confirmed the formation

Table 3. The analytical results of the components of FAME from Argemone mexicana oil using manganese carbonate catalyst

Methyl ester	*Argemone mexicana* %
Methyl laurate	0.060
Methyl myristate	0.100
Methyl palmitate	3.85
Methyl palmitoleate	1.10
Methyl stearate	32.5
Methyl oleate	15.0
Methyl linoleate	47.4

of methyl esters of acids present in the feed stock used.

The purity of Biodiesel is reflected in the percentage of methyl esters as seen in the gas liquid chromatography analysis presented in Table 3, which is 99.93%. The other components less than 0.1% (0.07%) are negligible, they may be the unreacted diglycerids. The other advantages of manganese carbonate as a heterogeneous catalyst include its reuse, require no neutralization step, easy to handle and exhibits low toxicity. These attributes are expected to lower the production cost of biodiesel for commercial exploitation of the process as the main problem in biodiesel production is high cost of feedstock and catalyst which increase the cost of biodiesel[28]. New low cost oil crops are needed to produce economical oils suitable for biodiesel production. For the cost effective biodiesel production both the feedstock and the catalyst have an important role to play. It is important to note that the critical factor in biodiesel production is not the chosen production process but the cost of the catalyst and the feed stock, which adds up to 70% of the total[24]. Production of biodiesel from Argemone mexicana a weed plant does not affect the edible oil production like palm oil, sunflower oil, corn oil and rapeseed oil. On the other hand, cultivation of Argemone mexicana weed plant has the following advantages:

– grows wild,
– thrives on waste land,
– easy to propagate,
– seeds not eaten by animals and birds,
– Opens up employment opportunities for tribal's living in tropical countries.

CONCLUSION

In this paper, we have evaluated the catalytic activity of the crystalline manganese carbonate in heterogeneous phase in the transesterification of *Argemone mexicana* oil for biodiesel production, as an alternative low cost catalyst. Manganese carbonate efficiently promotes the transesterification in methanol solutions and in the presence of low cost *Argemone mexicana* oil. The high yields achievable under mild reaction conditions are comparable to those obtained with a common catalyst such as acid and base. Therefore it is demonstrated that manganese carbonate is a potential catalyst for the production of biodiesel which is a low-cost raw material. The advantage of this protocol is the use of an available low-cost catalyst, which is easy to manipulate and potentially less corrosive. The results of this work suggest manganese carbonate as a promising alternative catalyst for the production of biodiesel. *Argemone mexicana* oil as feedstock for the production of biodiesel coupled with a versatile catalyst manganese carbonate used in this study is expected to bring down the production cost of biodiesel. The process offers advantages in terms of mild conditions, high conversion and practical viability and may find commercial application.

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