

Physico-chemical and tribological studies of *Argemone* biodiesel synthesized using microwave technique

Shilpi Agarwal^{1*}, Vijay K. Chhibber²,
Ajay K. Bhatnagar³, Bhawana Srivastav⁴,
Amit Kumar¹, Shailey Singhal¹ and
Amit K. Sharma¹

¹Department of Chemistry, University of Petroleum and Energy Studies, Dehradun 248 007, India

²BFIT, Dehradun 248 007, India

³Indian Institute of Petroleum, Dehradun 248 001, India

⁴Quality Control Department, Panipat Refinery,

Indian Oil Corporation Limited, Panipat 132 140, India

Microwave technique was applied for the synthesis of *Argemone* biodiesel from *Argemone* oil under defined experimental conditions. The method presented has the potential to synthesize quality biofuel in time-efficient manner. It also results in higher yield of biodiesel while decreasing the reaction time by almost 75% when compared with conventional heating method. The biodiesel produced was tested for various physico-chemical properties and found to maintain the quality as recommended by various specifications. Reduction in the wear scar diameter of low-sulphur diesel from 432 to 256 μm at a very low concentration of biodiesel (1.0%) was an additional advantage to produce biofuel.

Keywords: *Argemone*, biodiesel, microwave technique, physico-chemical properties, tribological behaviour, wear scar.

BODIESEL has emerged as one of the most energy-efficient and environment-friendly alternatives in recent times to satisfy the future energy needs. It can be directly used as a fuel with some engine modifications, or blended with petroleum diesel for use in diesel engines with few or no modifications¹⁻⁶. The European Union has issued a directive (2003/30/EC), which mandates the use of biofuels ranging from 5.75% in 2010 to 20.00% in 2020 (calculated on the basis of energy content) for all transportation fuels marketed within the member states⁷. Biodiesel can be produced from the various edible and non-edible feedstocks as rapeseed⁸⁻¹⁰, soybean^{11,12}, oil palm^{13,14}, coconut^{15,16}, sunflower^{17,18}, *Jatropha curcas*^{19,20} and *Argemone maxicana*²¹. In India, non-edible oils are the most suitable feedstock for biodiesel since the demand for edible oil exceeds the domestic supply. Much of the work has been carried out with *J. curcas*, but *A. maxicana* is comparatively less studied. *A. maxicana* plant is widely distributed in many parts of the world and is tolerant to drought and poor soil. Its seeds contain 22–36%

of non-edible oil. Therefore, it has the potential to be utilized as a major feedstock for the biodiesel programme.

Although trans-esterification of oils to produce biodiesel by conventional heating is a well-established method, it requires longer reaction times with higher energy inputs and losses to the ambient²², which result in the higher cost of biodiesel. Microwave-assisted trans-esterification, is, however, a relatively new, energy-efficient and quick technology to produce biodiesel from different feedstocks²³⁻²⁵. Patil *et al.*²⁴ produced biodiesel from *Camelina sativa* oil using different methods of heating such as conventional, supercritical and microwave. Among these, the microwave method proved to be superior due to its inherent advantages of shorter reaction time and lower energy requirements. Along with reducing the reaction time and increasing the biodiesel yield, the microwave method also significantly reduced the product separation time. The present study is focused on the utilization of inexpensive *A. maxicana* oil for biodiesel (ABD) synthesis using microwave energy in order to overcome the problem of longer reaction time. Attempts were also made to compare the results with the conventional method to ascertain the competence of the process. The quality of biodiesel was evaluated by measuring the various physico-chemical properties. The tribological behaviour was monitored and estimated by blending it with low-sulphur diesel (LSD) in various concentrations.

A. maxicana seeds were purchased from JDG Seeds, Madhya Pradesh, India. HPLC-grade methanol (99.8%), anhydrous KOH pellets and concentrated H₂SO₄ were used without any further purification.

Scientific microwave oven (Raga Scientific Microwave Systems, model RG31L) and conventional biodiesel reactor were used to synthesize biodiesel from *Argemone* oil. The oil was extracted mechanically from *A. maxicana* seeds using a screw press expeller (Azad-made, Ghaziabad).

Argemone oil with FFA 6.5 was used for the process. FFA was determined by using standard titrimetric method using phenolphthalein as an indicator. Microwave and conventional, both methods were used to produce biodiesel under similar conditions in order to study the effectiveness and competence of microwaves for the process.

Biodiesel was produced in the scientific microwave oven having ten power levels ranging from 140 to 700 W, 2.45 GHz, a magnetic stirrer with selectable speeds and a temperature meter with flexible probe/IR sensor to control the temperature up to 500°C. Acid value was reduced by heating it with concentrated H₂SO₄ and 20% methanol (by weight of oil) in the microwave at 280 W using 420 rpm for 10 min. The resulting oil had FFA value of 1.54. For trans-esterification, 1% anhydrous potassium hydroxide (by weight) was dissolved in 25% methanol (by weight of oil) and then added to 250 g pretreated oil. The mixture was heated for 20 min in the microwave at 280 W using 420 rpm for better dispersion of reactants.

*For correspondence. (e-mail: shilpi.upes86@yahoo.in)

The product was cooled at room temperature and then poured into a separating funnel to separate biodiesel from glycerol. After 2 h, the glycerol layer was withdrawn from the bottom of the funnel and the crude biodiesel layer was washed with warm distilled water to remove KOH and glycerol, until the washing water had a pH value equal to that of distilled water. The washed ABD was then dried over silica gel and characterized. The yield of ABD was 91.6% (by weight of oil).

Keeping the conditions constant as for microwave, biodiesel was also synthesized in the conventional biodiesel reactor. The produced biodiesel was transferred in separating funnel; which took 10 h to separate from another layer. Biodiesel was then washed with warm distilled water and dried over silica gel. The yield of ABD was found to be 48% (by weight of oil).

In another experimental set-up using conventional method, oil was heated with methanol in acidic medium for 2 h to reduce the acid value. The esterified oil was then subjected to trans-esterification for 1.5 h to get the maximum conversion (88%).

The fatty acid composition of *Argemone* oil was determined using gas chromatograph (GC; Nucon 5700 series with EOX column; serial no. 5061; 30 m length, 0.25 mm ID and 0.27 mm outer diameter). Helium (99.9% purity) was used as the carrier gas with a column flow rate of 1 ml/min and a pre-column pressure of 49.7 kPa. The column temperature regime was 40°C for 3 min, followed by a 5°C/min ramp up to 230°C, and then by 40 min at 230°C. The injection volume and temperature were 0.2 µl and 240°C respectively, and the split ratio was 1/30. FAME (fatty acid methyl ester) peaks were identified by comparison of their retention times with authentic standards by GC and quantified by area normalization.

GC of ABD produced under microwave radiation indicated the presence of a number of esters (Table 1).

In Table 1, the figures in parenthesis show the carbon number and number of double bonds present in the fatty acid.

Quality assessment of microwave-assisted biodiesel, produced under optimized conditions, was performed using various physico-chemical properties according to

standard methods. The lubricity test of neat ABD and LSD was done on a high frequency reciprocating rig (HFRR) according to CEC F-06-A-96, ASTM D6079 and ISO 12156. To find the efficiency of biodiesel to enhance the anti-wear property of LSD, tests were repeated using blends of LSD with different amounts of ABD.

In conventional biodiesel reactor, the trans-esterification process took 1.5 h to complete and yield was 88%. In the present study, biodiesel was synthesized using microwave-assisted method, which reduced the reaction time to 20 min, i.e. by more than 75% in contrast to the conventional method. During the synthesis of biodiesel, the mixture of *Argemone* oil, methanol, and potassium hydroxide contains both polar and ionic components; therefore, rapid heating is observed upon microwave irradiation, which increases the reaction rate and so higher yield is obtained in short times compared to conventional heating^{26,27}. Also, the separation of biodiesel from glycerol layer in the microwave method took much shorter time than using the conventional method; thus making the overall process more speedy. The yield of biodiesel obtained under microwaves was 91.6% by weight of oil. However, when biodiesel was produced in the conventional biodiesel reactor under similar conditions, the yield was only 48% which again reflects the direct and positive impact of microwaves on the process.

Methyl ester of palmitic acid, oleic acid and linoleic acid were observed in the major amounts, i.e. 12.2%, 28.6% and 53.28% respectively. The composition of ABD was found to be in close agreement to the existing literature²⁸.

The quality of biodiesel was established through various physico-chemical properties. In Table 2, the fuel properties of *Argemone* oil, ABD and diesel are compared and summarized. From the various properties, it can be found that the calorific value of ABD is 37,720 kJ/kg, which is more than the corresponding oil. Flash point is high, which is advantageous for fuel transportation. The various properties of *Argemone* oil methyl ester were found to be comparable with those of diesel fuel.

All the properties of ABD were found to be within the limits of ASTM standards, which confirms the suitability of microwave-assisted biodiesel as engine fuel.

In tribological studies, LSD was found to have the maximum WS 1.4 of 431.66 µm due to the presence of less amount of polar compounds and showed a decrease in value upon the addition of ABD (Figure 1).

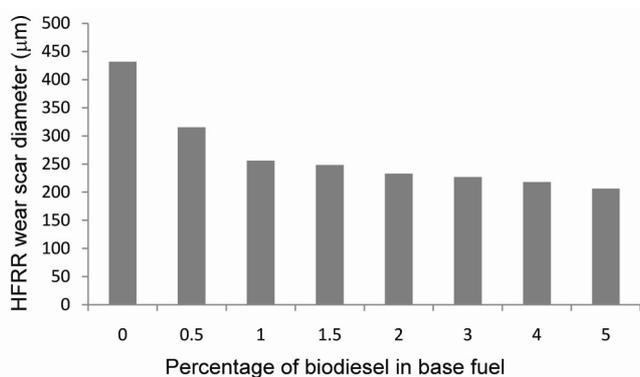
A significant improvement in lubricity was observed when the concentration of ABD in LSD was increased up to 1.0%. This can be attributed to the presence of long-chain methyl esters present in ABD as major components. The polar end of the compounds adsorbs over the metal surface while non-polar tail remains soluble in LSD, thereby preventing any wear when the two surfaces to come in direct contact with each other. Results of the analysis (Table 1) suggest that esters with one (C18 : 1 = 28.6%) and two (C18 : 2 = 53.28%) double bonds between

Table 1. Fatty acid composition of *Argemone* biodiesel (ABD) synthesized using microwave technique

Fatty acid methyl ester	Molecular formula of fatty acid	% Composition in ABD
Methyl palmitate (16 : 0)	C ₁₆ H ₃₂ O ₆	12.2
Methyl palmitoleate (16 : 0)	C ₁₆ H ₃₀ O ₆	0.32
Methyl stearate (18 : 0)	C ₁₈ H ₃₆ O ₂	4.42
Methyl oleate (18 : 1)	C ₁₈ H ₃₄ O ₂	28.6
Methyl linoleate (18 : 2)	C ₁₈ H ₃₂ O ₂	53.28
Methyl linolenate (18 : 3)	C ₁₈ H ₃₀ O ₂	0.16
Methyl eicosanoate (20 : 0)	C ₂₀ H ₄₀ O ₂	0.15

Table 2. Comparison of physico-chemical properties of ABD with *Argemone* oil, diesel oil and the standard limits

Properties	Diesel oil standard limits (EN 590)	<i>Argemone</i> oil	ABD	ASTM D6751-12
Density (g/cm ³) at 15°C	0.82–0.845	0.9274	0.8756	0.860–0.900 (D 4052)
Kinematic viscosity (mm ² /s) at 40°C	2.0–4.5	21	3.94	1.90–6.00 (D 445)
Flash point (°C)	55 minimum	224	156	130°C minimum (ASTM D93)
Cloud point (°C)	–	+15	+5	(D2500)
Pour point (°C)	–	+9	+3	(ASTM D97)
Acid value (mg of KOH/g)	–	6.5	0.41	<0.5 (ASTM D664)
Calorific value (kJ/kg)	–	35,875	37,720	–
Oxidation stability (IP, at 140°C)	–	–	6.03 h	3 h minimum (ASTM D7545, EN 15751)
Lubricity	460 µm maximum	–	170 µm	<520 µm (ASTM D6079)
Water and sediments (% volume)	200 ppm maximum	–	0.02	0.05 maximum (ASTM D2079)
Copper strip corrosion (3 h/50°C)	No. 1, maximum	–	No. 1	No. 3 maximum (ASTM D130)

**Figure 1.** HFRR lubricity evaluation for *Argemone* ABD mixed with LSD at various concentrations.

carbon atoms constitute a dominant group of compounds in ABD, which are responsible for enhanced lubricity. These observations are well supported by the studies made by Geller and Goodrum²⁹. After the formation of a complete film on the metal surface, extra amount of ABD added does not interact with the surface; therefore lubricity enhancement begins to level off, i.e. a dramatic increase in lubricity is no longer seen. The least wear occurred when 100% ABD (170 µm) was examined.

The results showed that application of microwave energy offers a fast and easy route for the synthesis of ABD. It reduced the reaction time by nearly 75% and at the same time maintained the quality of biodiesel as recommended by ASTM specifications, so as to meet the criteria to be used in engines as such or after blending with diesel fuel. Biodiesel also showed excellent behaviour towards improving the anti-wear property of LSD. Under similar conditions conventional heating method produced only 48% biodiesel in comparison to 91.6% yield using microwave method, indicating a significant correlation between the microwaves and the reaction rate enhancement.

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Isolation and structural elucidation of an isothiocyanate compound from *Indigofera tinctoria* Linn. extract

Veena Sharma* and Rashmi Singh

Department of Bioscience and Biotechnology, Banasthali University, Niwai 304 022, India

***Indigofera tinctoria* is a well-known medicinal plant that possesses several therapeutic activities. Isothiocyanate derivative from hydroethanolic extract of *Indigofera tinctoria* (HEIT) was isolated by means of chromatographic techniques, i.e. adsorption chromatography, thin layer chromatography and high-pressure liquid chromatography. Structural characterization of isolated compound was done using various spectroscopic techniques (liquid chromatograph–mass spectrometry, ¹H nuclear magnetic resonance and Fourier transform-infrared spectroscopy) and the possible structure was identified as 1-[1,2-Diisothiocyanato-2-(3-isothiocyanato-2,2-dimethyl-propylsulphonyl)-ethoxy]-3-isothiocyanato-2,2-dimethyl-propane (C₁₆H₂₂N₄OS₅; *m/z* 446.70; ITC-1). Maximum yield of ITC-1 was obtained as 22 mg/5 g HEIT with 97% purity.**

Keywords: Column chromatography, HPLC, *Indigofera tinctoria*, isothiocyanate compounds, LC–MS.

ISOTHIOCYANATE compounds (ITCs) belong to the category of organosulphur compounds, i.e. the compounds that contain sulphur moiety, possess R–N=C=S group¹. Brassicaceae and Fabaceae families are known to contain ITCs². These are weak electrophilic in nature. Some naturally occurring ITCs like PEITC (phenethyl isothiocyanate), BITC (benzyl isothiocyanate) have also been isolated from various cruciferous vegetables. ITCs are known for their various types of therapeutic activities³, hence have a great significance in medicine.

Indigofera tinctoria belongs to the family Fabaceae. It is found throughout South East Africa, tropical Africa as well as tropical America and is cultivated in Southern India, especially Tamil Nadu⁴. It is a deciduous shrub, reaching 1–2 m in height and may be annual, biennial or perennial. This plant has been reported to possess a wide range of therapeutic activities^{5–7}.

Keeping the need of naturally derived target specific drug to treat various health problems in medicine, the present study was designed to isolate and characterize the ITC from hydroethanol extract of *I. tinctoria* (Indigo).

Silica gel G and silica gel (60–120) were procured from Himedia, Mumbai, India. Solvents for HPLC were of HPLC grade and procured from RanKem, India. Ethanol, *n*-hexane, chloroform, methanol and petroleum ether

*For correspondence. (e-mail: drvshs@gmail.com)