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INVESTIGATING POSSIBILITY OF USING LEAST DESIRABLE EDIBLE OIL OF *ERUCA SATIVA* L., IN BIO DIESEL PRODUCTION

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Abstract

Eruca sativa Miller of the family Brassicaceae is grown in West Asia and Indo-Pakistan as poor quality oilseed crop at marginal land under poor rainfall. Studies have shown that it is salt tolerant as well. When crushed for oil, glucosinolates in the seeds are hydrolyzed by myrosinase, yielding isothiocyanates which make the oil pungent. Due to its bitterness, the oil has almost negligible value in the food market. However, its fatty acid profile shows that it has the potential to be used as an alternative fuel for the transport sector. In the present study, its bio diesel was found possessing more or less similar storing, handling and combustion properties as bio diesel formed from edible oils of soya bean or canola. In addition, due to lower sulphur content, its bio diesel is expected to be environment friendly in comparison to petroleum based diesel fuel.

Introduction

Eruca sativa Miller (commonly known as taramira) belongs to the Brassicaceae family of plants, grown in parts of the Middle East, India and Pakistan as a minor oil crop and for the preparation of some traditional medicines and remedies (Flanders & Abdul Karim, 1985). It can be grown on marginal and barren land as well as in areas where rainfall and soil fertility are low. It is also known to be drought resistant and has some degree of salt tolerance (Shannon and Grieve, 1999). The seeds can yield up to 35% of oil (Yadava *et al*., 1998) and 27% of protein (Flanders & Abdul Karim, 1985). Market for taramira oil and cake is yet to be identified (Das *et al*., 2001). Due to its pungent smell, the oil is unlikely to find any market in the food industry. Hence, it would be ideal if it can be converted to a suitable fuel for the transportation industry in an environment friendly manner.

Bio diesel is produced by a chemical reaction between triglycerides present in vegetable oils and alcohol (Harun *et al*., 2006). It is essentially a fatty acid mono alkyl ester. Bio Diesel has almost negligible impacts upon the environment. It can be used as a pure fuel or blended in different percentages with petroleum diesel with negligible impacts upon the ecological environment in comparison to mineral diesel fuel (Harun *et al*., 2006). In addition, the production of greenhouse gases and the level of most vehicle exhaust emissions, including those associated with asthma are reduced considerably (Chakrabarti & Ali, 2008b). It has also been reported that the growth of energy crops for bio diesel production produces a positive energy balance of approximately 250% to 300% as output of energy from the use of bio diesel exceeds that of the energy input for manufacturing the fuel (Harun *et al*., 2006). Hence bio diesel can be used in the transportation sector as well as for electricity generation due to its positive energy balance (Nwafor, 2004; Labeckahs *et al*., 2006).

So far, bio diesel has been produced from edible oil feedstocks all over the world. Bio diesel produced from non-edible oil extracted from plants grown on marginal land, such as jatropha (Berchmans & Hirata, 2008), jojoba (Selim *et al*., 2003), mahua (Raheman & Ghadge, 2007), tobacco seed (Veljkovic' *et al*., 2006) and castor bean (Chakrabarti & Ahmad, 2008) has shown some encouraging results. However other oils from plants that can sustain growth in marginal lands are yet to be searched and converted to bio diesel.

Since taramira oil bears lowest acceptable value among edible vegetable oil, its utility for production for Bio diesel could raise economically feasible value up to a great extent. The present work has been undertaken to explain its suitability for conversion in to bio diesel to run vehicles.

Material and Methods

Three litres of oil was extracted from about 8 kg of taramira seeds, using an oil expeller which would amount to 35% oil yield approximately. The crude taramira oil was first refined by adding caustic soda (Merck) following the procedures described by O'Brien *et al*., (2000). Bio diesel was prepared as follows: 1.5 litres of refined taramira oil was heated with stirring to 100°C for 60 min. The sample was then cooled down to 70 °C and 5 g Potassium hydroxide pellets (Merck) were added after 15 min., 420 ml methanol (Tedia) was added and the mixture was heated to 70°C for 30 min., after which, 4 g of Potassium hydroxide was added again. Methanol 300 ml was then added and the reaction was allowed to proceed at 70°C for one hour. A condenser was used to ensure that any methanol vapours were refluxed back into the reaction mixture. After reaction, the product was placed in a separating funnel and left overnight to settle. Glycerine settled to the bottom of the funnel and was removed. This impure bio diesel was then washed with 2.5% (w/w) Sulphuric acid (98%, Merck) followed by washing water, prior to drying at 150 °C for 2 h. After heat drying, about 0.5 kg of anhydrous grade Sodium sulphate (Merck) was added to the sample to remove traces of moisture.

The ester content (proportional to the yield of bio diesel) was determined by means of Gas Chromatography (GC) following the procedures adopted by Bhatti *et al*., (2008). The fatty acid composition of crude taramira oil was also determined by means of GC.

Density of bio diesel sample was determined at 15°C by a hydrometer as per American standard (ASTM D 1298). Kinematic viscosity was determined at 40°C. The time was measured for a volume of liquid to flow under gravity through the capillary of a calibrated viscometer under a reproducible driving head at controlled temperature (ASTM D 445). The kinematic viscosity was calculated from flow time and the calibration constant of the viscometer.

ASTM D-93 Standard Test Method was used for determining flash point of bio diesel samples by closed cup method. The test for measuring sulphur content involved the determination of total sulphur in bio diesel samples (ASTM D 5453). A fixed volume of bio diesel sample was burnt in a tubular resistance furnace at 1100°C. UV Fluorescence was used to analyze the SO_2 gas produced during combustion. The concentration of SO_2 determined was in direct proportion to the sulphur content in the bio diesel fuel.

Cetane index the relative measure of the interval between the beginning of injection and auto-ignition of the fuel was measured by means of a standard compression ignition engine using the procedure outlined in ASTM D 613. Water and sediment test method (ASTM D 2709) was used as an indication of water and sediment in bio diesel samples. Water content of bio diesel samples was determined by Coulometric Karl Fischer titration method. Based on stoichiometry of the reaction, one mole of iodine reacts with one mole of water, thus the quantity of water is proportional to the total integrated current according to Faraday's Law. Sediment content was determined by extracting the bio diesel sample using an Erlenmeyer extraction flask, block tin coil condenser, water cup and extraction thimble.

The copper strip corrosion test result was determined using the procedures outlined in ASTM D 130. The sample was placed in a pressure vessel immersed in a water bath at 100 °C and the copper corrosion result was determined. Total acid value was determined by means of titrimetric method as per ASTM D 974. Oxidation stability was determined by means of a rancimat according to the ASTM D 2274 procedures.

Results and Discussion

1. Fatty acid composition of taramira oil: Fatty acid composition of taramira oil as determined in the present investigation and profiles of some other members of Brassicaceae family reported by Dorado *et al*., (2006) and Chakrabarti & Ahmad (2008) are presented in Table 1 for discussion. Erucic and oleic acids of taramira oil were 40.8% and 22.3% of total fatty acid composition, respectively, which was found to be consistent with literature values (Yadava *et al*., 1998; Das *et al*., 2001). The fatty acid profile of taramira oil was closer to that of mustard seed oil than canola oil. High concentrations of erucic acid in taramira oil may be the reason for not using it as a cooking medium as erucic acid yields unpalatable flavour and also has links with cardiac problems.

2. Transesterification of taramira oil: The results obtained from testing taramira oil bio diesel under present investigation and those reported by Chakrabarti & Ali (2008a) in oil of canola are presented in Table 2 for the purpose of comparison and discussion.

The ester content of taramira bio diesel was above the international standard's minimum limit of 96% showing that almost complete conversion of the crude vegetable oil was achieved. However, it is still possible to achieve higher conversions by subjecting the crude oil to a process of refining, bleaching and deodorization (O'Brien *et al*., 2000). The density of both taramira bio diesel and canola bio diesel (Chakrabarti & Ali, 2008a) were close to the lower ASTM limit as well as the density for pure mineral diesel. This result indicated that the bio diesel fuels are likely to have comparable storage, handling and combustion properties as mineral diesel fuel.

Considering the fact that the viscosity of taramira bio diesel is close to the upper limit for the American standard for testing materials (Anon., 2008), it is likely to have less lubricating effects upon the engine in comparison to canola bio diesel or mineral diesel fuel. In addition, handling and storage of the fuel would be more cumbersome in comparison to the other fuel types shown in Table 2.

The flash point of taramira bio diesel is lower than the ASTM limit (Anon., 2008) indicating that it may cause a possible fire hazard when stored. However, its flash point is higher than that of mineral diesel and it is thus safer than its fossil fuel counterpart. However, high flash point may result in a relative inability of the bio diesel to combust desirably in the compression-ignition engine in comparison to mineral diesel fuel.

Table 1. Fatty acid composition of some members of Brassicaceae family (Dorado *et al.*, 2006) in comparison with that of taramira used in the present investigation.

Vegetable oil	Fatty acid composition of oil (% w/w)						
	Palmitic C16:0	Stearic C18:0	Oleic C18:1	Linoleic C18:2	Linolenic C18:3	Eicosenoic C20:1	Erucic C22:1
Taramira	10.2	1.6	22.8	6.4	11.9	6.4	40.8
Canola	3.5	0.9	64.4	22.3	8.2	0.0	0.0
Mustard	2.0	2.50	23.5	15.5	10.0	5.0	30.5

Low or almost negligible sulphur content is a common trait of bio diesel derived from any vegetable oil. Hence, taramira bio diesel is also showing no exception in terms of low sulphur content in comparison to mineral diesel fuel thus enabling it to be considered as a very environment friendly fuel. However, slightly higher sulphur content in comparison to canola bio diesel means that it may result in the release of more SO_X compounds in the compression-ignition engine in comparison to its canola cousin (Chakrabarti & Ali, 2008b).

Provided the test is performed on the base fuel without additive the carbon residue of diesel or bio diesel fuel correlates approximately with combustion chamber deposits in the compression-ignition engine (Anon., 2008). Both canola bio diesel and premium diesel fuel have negligible carbon residual potential but taramira bio diesel seems to have the tendency to cause some deposits in the combustion chamber of any diesel engine (Table 2). However, the good news is that its potential to cause deposits is below the limit specified by the international standard (Anon., 2008), thus enabling it to be considered for further testing.

The cetane number provides a measure of the ignition characteristics of diesel fuel or bio diesel fuel in compression ignition engines (Anon., 2008). The higher the cetane index the shorter the delay interval and the greater the fuel combustibility. Fuels with low Cetane Numbers will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate better on fuels with Cetane Numbers above 50. As per the results obtained in this research (Table 2), the best ignition characteristics can be obtained from canola bio diesel (Chakrabarti & Ali, 2008b) whereas taramira bio diesel is unlikely to match the performance of its cousin derivative. However, its ignition characteristics are likely to be better than that of mineral diesel in the diesel engine.

Appreciable amounts of water and sediment in a fuel oil tend to cause fouling of the fuel-handling facilities and to give trouble in the fuel system of a burner or engine (Anon., 2008). An accumulation of sediment in storage tanks and on filter screens can obstruct the flow of oil from the tank to the combustor (Anon., 2008). From the results obtained as shown in Table 2, mineral diesel is likely to provide better engine performance than both taramira or canola bio diesel as reported in the literature (Chakrabarti & Ali, 2008b). Taramira is unlikely to provide as much better engine performance in comparison to canola bio diesel, even though its water and sediment content meets the international limit (Anon., 2008).

The copper strip corrosion results indicate that all fuel types are unlikely to have much corrosion effects on the compression-ignition engine. The results provide assurance that difficulties will not be experienced in deterioration of the copper and copper-alloy fittings and connections that are commonly used in many types of utilization, storage, and transportation equipment. Hence, taramira bio diesel has some potential if tested in the diesel engine.

Table 2. Comparison of results from taramira bio diesel found in present investigation against those of canola bio diesel reported by Chakrabarti and Ali (2008a).

Parameters	ASTM test method	ASTM Limits	Taramira oil bio diesel	Canola oil bio diesel	Premium diesel fuel
Ester content (%)	EN 14103	96.5, Min.	97	97	-
Density @ 15 °C (g/cm^3)	ASTM D 1298	0.875-0.900	0.8811	0.88	0.8503
Kinematic Viscosity @ 40 °C (cSt)	ASTM D 445	1.9-6.0	5.9	5.0	3.2
Flash Point (°C)	ASTM D 93	93°C, Min	52	170	37
Sulphur content (wt. %)	ASTM D 5453	0.0015, Max.	0.02	0.01	0.20
Carbon residue on 10% distillation (wt. %)	ASTM D 189	0.05, Max.	0.04	-	-
Cetane Number	ASTM D 613	47, Min	48	55	45
Water and sediment content (vol. %)	ASTM D 2709	0.050, Max.	0.05	0.02	Nil
Copper strip corrosion @ 100 °C	ASTM D 130	No. 3, Max.	1	1	1
Total acid value (mg KOH/g)	ASTM D 974	0.50, Max.	0.40	0.45	-
Oxidation Stability	ASTM D 2274	6, Min.	6	7	6

Total acid value is used as a guide in the quality control of lubricating oil formulations using mineral diesel or bio diesel. It is also sometimes used as a measure of lubricant degradation in service. In this respect, all fuels reported in Table 2 are likely to have good lubricating properties as they meet the international standard (Anon., 2008), with mineral diesel giving best performance.

Oxidation stability of a fuel is a measure of its shelf life. All tested fuel (as shown in Table 2) meet the international standard (Anon., 2008) but canola bio diesel seems to have the tendency of higher shelf life (suggesting that it can be stored for longer periods of time without deterioration in quality). Taramira bio diesel has similar shelf life as mineral diesel fuel.

From the physical-chemical properties of taramira oil (as shown in Table 2), it is clear that it has the potential to be a good bio diesel fuel. Even though its flash point is well below the desired limit of 93°C (low flash point can be beneficial in terms of storage safety of the fuel), it is still higher than that of mineral diesel, giving it a bit of an edge over its fossil fuel counterpart. One way of increasing the flash point may be attempted by blending with other non-edible bio diesel fuels (such as those produced from jatropha oil) or using some cheap and effective additives.

There appears to be limited work on the conversion of taramira oil to bio diesel in the literature, except in China (Chai *et al*., 2007), which focussed on the use of expensive heterogeneous catalyst. The economics of converting taramira oil to bio diesel needs to be assessed rigorously and the fuel is also recommended to be tested extensively in a compression-ignition engine (both environmental emissions testing as well as engine performance testing). In the economic evaluation, the growth of taramira plants on marginal lands of Pakistan may be taken into account (this can potentially bring down the price of producing bio diesel from this indigenous raw material). Encouragement in economical feasibility for growing four different cultivars of *Brassica* and that of *Eruca sativa* has been demonstrated at saline land (electrical conductivity of 11.0 dS m^{-1}) where growth of conventional crops is severely affected (Ashraf & Sarwar, 2002). Oil extracted from seeds of these salt tolerant cultivars belonging to family Brassicaceae and their conversion to bio diesel could bring a potential and gradual replacement of expensive mineral diesel fuel in Pakistan.

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