Syringa (Melia azedarach L.) Berries Oil: a Potential Source for Biodiesel Fuel

CARMEN EUGENIA STAVARACHE1*, JOHN MORRIS2, YASUAKI MAEDA1, IKUKO OYANE1, MIRCEA VINATORU1

1 C. D. Nenitescu’ Institute of Organic Chemistry, Spl. Independenței, 2028, 060023 Bucharest, PO-Box 15-254, Romania
2 Syringa Bioscience (Pty) Ltd, Unit 8, Ferndale Industrial Park, 18 Lyn Road, Ferndale Ext. 4, Randburg, 2195, South Africa
3 College of Engineering, Osaka Prefecture University, Gakuen-cho 1-2, Sakai, Osaka 599-8570, Japan

The ultrasonically assisted transesterification of oil extracted from Melia azedarach L. berries, using base catalyst, in order to obtain biodiesel fuel, was investigated. The parameters that affect the yield and purity of the product include the oil quality, type of catalyst, type of alcohol and reaction temperature. The best results were obtained for the transesterification of purified oil with methanol in a 1:9 molar ratio, at 36°C, using 1% NaOH as catalyst. The time to complete the reaction was less than 40 minutes when methanol was employed and only 20 min when ethanol was employed. The product is characterized by specific parameters used to describe the biodiesel quality. The results presented in this paper show that this tree could be considered as a potential source for renewable biodiesel fuel, especially in South Africa where it is an alien invasive plant meant for destruction.

Keywords: biodiesel, ultrasounds, methyl esters, ethyl esters, Melia azedarach L

Syringa tree (Melia azedarach L.), also known as Indian or Persian lilac is an alien invasive plant in South Africa. Known as syringa on popular name, or Melia azedarach L. on its botanical Latin name, is a small to large tree and is spread around the country. It was first introduced as an ornamental tree, but it escaped to the wild and it became naturalized in many areas where it has replaced the indigenous vegetation and disturbed the natural ecosystem. It is known to be of Indian or Persian origin probably due to its other name: Indian or Persian lilac. Another variety (Melia azedarach japonica) is a common tree in Japan. This tree has green leaves that turn yellow in the autumn and fall in the winter. The flowers are produced in large, sparse clusters in the spring and have a strong scent resembling the lilac scent (Syringa vulgaris). The fruits are cherry-like shape, yellowish to brown in colour and persist longer after the leaves have fallen.

M. azedarach has numerous defences against insects and other plant pathogens, giving a competitive advantage over many native African species [1]. Syringa berries are known as poisonous especially for children, due to numerous toxins such as limonoids, tetra-nortriterpene or meliatoxins, with a steroidal structure. Almost all compounds isolated from different parts of the tree shown biological activities such as: insect antifeedant [2], grown regulator properties [3], cytotoxic [4], antiviral activities [5] as well as proteolytic activities of berries extract from Melia azedarach L. var. japonica [6]. 12 new limonoids from the roots bark were isolated [7].

According to the South Africa Working for Water Program, this tree, an invader of South African flora should be destroyed.

The berries contain up to 10% vegetable oil. The oil could be extracted from dried and milled berries, by using organic solvents. After solvent removal, the crude oil could be used further for the production of biodiesel (an environmentally friendly replacement of Diesel fuel).

The term “biodiesel” refers to the mono alkyl esters of long chain fatty acids derived from renewable lipid feedstocks, such as vegetable oils or animal fats, for use in compression ignition (diesel) engines [8]. Numerous vegetable oils have been tested as biodiesel feed stocks [9-14]. Often the oils investigated are those that occur abundantly in the country of testing. Biodiesel is produced from vegetable oils by a chemical reaction, namely transesterification. The transesterification of vegetable oils with an alcohol leads to the formation of a mixture of esters of fatty acids and glycerol. The alcohol usually employed in the transesterification is methanol, but ethanol is also suitable for this purpose. Base catalysis such as sodium or potassium hydroxide with reagents is preferred [15].

Our group extensively studied the transesterification of vegetable oils under ultrasonic irradiation and found that ultrasounds can enhance the mixing efficiency and speed up the transesterification reaction [16, 17]. In this paper the transesterification of syringa oil by means of ultrasounds, with the purpose of potential biodiesel feedstock was investigated.

This study could allow the South African decision factors to develop a new strategy to destroy this tree, namely when the fruits are fully ripened and have maximum oil content that can be used for biodiesel production.

Experimental part
Reagents and materials
Sodium hydroxide (>95%) and potassium hydroxide (>95%) were purchased from Wako Chemicals and used after milling, to facilitate the dissolution in alcohol. The methanol and ethanol employed in the reactions purchased from Wako Chemicals had more than 99.8% purity and were used as received.

Syringa Bioscience, from South Africa, provided the syringa oil employed in the present study. One sample was treated with active carbon and heated for 10 min at 100°C. The oil was filtered off and regarded as “purified” oil. Usually, the treatment of oil with active carbon is applied for the removal of bad odour, some mucilage that still persists into the oil and for bleaching. The other sample was used as received and it will be regarded as “crude” oil.

* email: stavarache@yahoo.com

672

REV. CHIM. (Bucuresth) ♦ 59 ♦ Nr. 6 ♦ 2008
Procedure

The methyl or ethyl esters were synthesized using sodium or potassium hydroxide (NaOH or KOH) as catalyst. The ester preparation involved a one-step transesterification reaction, followed by gravimetric separation of the glycerol layer from esters layer, washing and drying of the esters layer. The one-step reaction used a total molar ratio of alcohol to oil of 9:1. The quantity of catalyst was 1.0% (wt/wt) to the oil. The hydroxide was dissolved into the alcohol prior to the addition of vegetable oil. All experiments were performed in an Erlenmeyer type flask having 100 ml total volume.

The ultrasonic reactions were performed using Honda Electronics Ultrasonic Cleaner WS 1200-40, with a total power of 1200 W, working power being set at 70%. The reaction temperature was maintained constant by circulating water through the bath.

The flask was immersed into the water filled ultrasonic bath, over one of the transducers, in order to maximize the coupling between the ultrasounds and the reacting mixture. Due to the complexity of the reaction mixture, no ultrasonic power measurement was possible in order to furnish a figure about how much ultrasonic power was really introduced into the reaction mixture.

In a dry Erlenmeyer type flask, equipped with stopper, 0.30 g milled NaOH or KOH were dissolved in 12.5 mL methanol or 18.0 mL of ethanol respectively. To this mixture 30 g vegetable oil (about 0.0343 moles) were added and sonicated until the completeness of the reaction. The progress of the reaction was monitored by TLC, method described in previous papers [16, 17]. When unreacted oil, determined by TLC has not been detected, the reaction was stopped.

The analytical yield, calculated according to this formula

\[
C_{tg} = \left( \frac{a \cdot A_{tg} / AIS + b \cdot C_{is}}{M} \right) \times 100
\]

where:
- \(a\) = slope of calibration function;
- \(b\) = intercept of calibration function;
- \(C_{tg}\) = mole percentage of triglycerides in the sample;
- \(A_{tg}\) = sum of peak area of individual triglycerides;
- \(A_{is}\) = peak area of internal standard;
- \(C_{is}\) = concentration of internal standard in the sample, moles;
- \(M\) = total number of moles of sample.

The analytical yield, calculated according to this formula is higher than isolated yield, the latter including the material lost during purification stage.

The compositions of the methyl and ethyl esters were analysed using a Shimadzu GC-MS Model QP-2010, equipped with a DB-225ms capillary column (0.25 mm 30 m) J&W Scientific.

A solution of approximately 1% methyl or ethyl esters mixture in hexane was prepared and 1 µL of this solution was injected into the GC-MS.

The analyses were carried out under the following conditions: the carrier gas was helium, the injector temperature was 220°C with a split ratio of 1:100 and the temperature of the detector was 220°C. Oven temperature started at 150°C for 3 min, increased at 220°C at a rate of 3°C/min and held for 5 min.

The quality of the product was determined according to ASTM specifications for biodiesel fuels (acid value, saponification value, iodine value, peroxide value). The density was estimated by using a pycnometer. The kinematic viscosity was determined by using an Oswald viscometer.

Results and discussions

An approximate characterization of a vegetable oil is given by its basic properties (i.e. acid value, saponification value, iodine value). Since syringa oil has no use in industry, almost no information about its composition is known. The

<table>
<thead>
<tr>
<th>Property</th>
<th>“Purified”</th>
<th>“Crude”</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Value (mg KOH/g oil)</td>
<td>5.58</td>
<td>5.75</td>
</tr>
<tr>
<td>Saponification Value (mg KOH/g oil)</td>
<td>175.06</td>
<td>168.83</td>
</tr>
<tr>
<td>Iodine Value (g l₂/100g)</td>
<td>130.73</td>
<td>126.58</td>
</tr>
<tr>
<td>Peroxide Value (nmol/µL)</td>
<td>7.00</td>
<td>9.94</td>
</tr>
<tr>
<td>Density (g/ml)</td>
<td>0.929</td>
<td>0.902</td>
</tr>
<tr>
<td>Kinematic viscosity (at 40°C, mm²/s)</td>
<td>33.54</td>
<td>15.46</td>
</tr>
<tr>
<td>Phosphorus (ppm)</td>
<td>19.07</td>
<td>39.72</td>
</tr>
</tbody>
</table>
The basic properties of the two types of syringa oil were determined and are given in Table 1.

The oils employed in the base-catalysed processes usually contain small amounts of free fatty acids (acid value < 2). This is important because the competitive reaction that takes place (i.e., soap formation) consumes the catalyst and makes the purification steps complicated. Up to 5% free fatty acids, the reaction can still be carried out under basic conditions but additional catalyst must be added to compensate for the catalyst lost by soap formation. From this point of view, syringa oil is a little over the upper limit for base-catalysed transesterification. Consequently, the amount of catalyst used in the present study was 1%.

The reaction temperature was stated as one of the most important parameters affecting the yield and quality of the product [15]. Other investigators found that a high yield was achieved at a temperature of 25°C for the transesterification of oil with high content of free fatty acids [18].

The reactions conducted under ultrasonic irradiation at 20°C were complete after 3 h but the yield of the isolated product was less than 50%. However, by increasing the reaction temperature at 36°C, the reaction finished faster, and the yield was significantly increased. The results are presented in Table 2.

As basic catalysts, sodium and potassium hydroxides are most commonly used. Usually, the industrial-scale processes have a preference for potassium hydroxide due to its benefits: it is cheaper, can be reused after reaction as fertilizer, and the soap produced in the side reaction is much softer and thus the purification and washing are easier than in the case of sodium hydroxide. With the purpose of testing the most suitable catalyst for the transesterification of syringa oil, a set of experiments, using sodium and potassium hydroxides, was carried out.

As one can see from Table 2, in the case of purified oil, the amount of unreacted intermediates and impurities detected in the final product are almost the same, regardless the type of catalyst used. In the case of crude oil, free glycerol and monoglycerides were present in high amount when KOH was used. The amount of methyl esters and the yield of isolated product was almost the same in all cases.

However, in the presence of NaOH the reactions were completed in 30 min, while the reactions in the presence of KOH were completed after 40 and 60 minutes for 'purified' oil and 'crude' oil, respectively.

The yields of isolated biodiesel are low, compared with other oils. The presence of high amount of free fatty acids determines the formation of soap in a competitive reaction. The soap formation has a dual disadvantage: hinders the transesterification reaction by consuming the catalyst and increasing the solubility of the methyl esters in the glycerol layer [19].

By increasing the amount of catalyst to 1.5% more soap was produced, thus lowering the yield of isolated product to 46% for both types of oil.

Ethanolysis is one important aspect of biodiesel production since ethanol is derived from renewable biomass, making this fuel completely environmentally friendly. Therefore, experiments using ethanol were performed. Usually, the miscibility of oils and ethanol is higher than that of methanol, and thus the reaction is completed faster and with better yields [16, 17]. However, for syringa oil, that was not the case. The yields of isolated ethyl esters were lower than in the case of methanol. Ethanol is a better solvent for both products glycerol and esters. In this case the two layers do not separate, thus a large amount of ester was lost in the purification steps.

In the Table 3 are given the results obtained from the transesterification of syringa oil with ethanol, in the presence of both types of catalysts.
In all cases when ethanol was used for the transesterification the reaction was completed in only 20 minutes. The analysis of the product revealed a higher amount of unreacted intermediates in the case of ethanol.

In the table 4 are given the distributions of methyl and ethyl esters function of unsaturation during the transesterification under ultrasonic irradiation.

As can be seen in the table 4, the distribution of the fatty acids is almost the same in the case of methyl esters, but quite different in the case of ethyl esters, fact that proves that there are some differences in the reactivity between the two alcohols towards lipids and phospholipids. Other oils extracted from seeds were found to contain a high amount of phospholipids [20]. From the results of this study we can assume that the phospholipids are not easily esterified by ethanol, and thus they remain as impurities in the reaction mixture. During the purification and washing steps, they were hydrated, and removed into the water layer. This could be one reason for the low yield of isolated ethyl esters. Another reason could be the presence of FFA that were transformed into soap during transesterification. In the case of methanol, due to the good separation of the phases most of the soap was removed with the glycerol, and only traces remained into esters. In addition, as can be see in table 5, the ethyl ester mixtures have high neutralization numbers, in comparison with methyl esters. This facts lead us to assume that during the neutralization step some of the soap was transformed into salt and FFA. While the salt was dissolved in water, FFA remained in the ester layer, increasing the neutralization number. The low yield of FAEE and the difficult separation of glycerol are the main constrains of the process of ethanolsis, but it could be further improved.

In order to ascertain the quality of the biodiesel produced from syringa oil some specific parameters that depend on the type of oil were determined. The characteristics of the biodiesel from syringa oil are close to ASTM specifications for refined rapeseed oil [21].

Among the general parameters, viscosity that controls the characteristics of the injection from the diesel injector is very important. It is essential to keep it within an acceptable level, to avoid negative impacts on the fuel injection system. As one can see in table 5, the FAME derived from syringa oil exhibit a viscosity within the specification range. However, the FAEE have higher viscosities, which may be one drawback in using them in diesel engines.

Cetane index is an indicative of ignition characteristics. Usually biodiesel has a higher cetane index compared to conventional fuel, which results in a higher combustion efficiency. The cetane index of the fatty acid esters derived from syringa oil is in the range of accepted values.

Neutralization number is specified to ensure proper aging properties. It reflects the presence of FFA and also the degradation due to thermal effects. The reason for a high neutralization number in the case of FAEE was already

### Table 4

<table>
<thead>
<tr>
<th>Oil type</th>
<th>Alcohol</th>
<th>Cat</th>
<th>Saturated fatty acids</th>
<th>Mono-unsaturated fatty acids</th>
<th>Poly-unsaturated fatty acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purified</td>
<td>MeOH</td>
<td>NaOH</td>
<td>20.60</td>
<td>20.80</td>
<td>58.61</td>
</tr>
<tr>
<td></td>
<td></td>
<td>KOH</td>
<td>20.62</td>
<td>20.46</td>
<td>58.92</td>
</tr>
<tr>
<td>Crude</td>
<td>MeOH</td>
<td>NaOH</td>
<td>20.78</td>
<td>20.08</td>
<td>59.31</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td></td>
<td>20.49</td>
<td>19.81</td>
<td>59.70</td>
</tr>
<tr>
<td>Purified</td>
<td>EtOH</td>
<td>NaOH</td>
<td>24.88</td>
<td>18.52</td>
<td>56.60</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td></td>
<td>25.84</td>
<td>18.66</td>
<td>55.51</td>
</tr>
<tr>
<td>Crude</td>
<td>EtOH</td>
<td>NaOH</td>
<td>20.22</td>
<td>20.22</td>
<td>59.56</td>
</tr>
<tr>
<td></td>
<td>KOH</td>
<td></td>
<td>22.42</td>
<td>18.75</td>
<td>58.82</td>
</tr>
</tbody>
</table>

### Table 5

<table>
<thead>
<tr>
<th>Property</th>
<th>FAME</th>
<th>FAEE</th>
<th>ASTM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&quot;Purified&quot;</td>
<td>&quot;Crude&quot;</td>
<td>&quot;Purified&quot;</td>
</tr>
<tr>
<td>Neutralization number (mg KOH/g oil)</td>
<td>NaOH</td>
<td>KOH</td>
<td>NaOH</td>
</tr>
<tr>
<td>0.67</td>
<td>0.59</td>
<td>0.50</td>
<td>0.49</td>
</tr>
<tr>
<td>Iodine Value (g I2/100g)</td>
<td>127</td>
<td>130</td>
<td>131</td>
</tr>
<tr>
<td>Peroxide (mnoles)</td>
<td>5.93</td>
<td>5.70</td>
<td>5.72</td>
</tr>
<tr>
<td>Specific gravity (g/ml)</td>
<td>0.894</td>
<td>0.899</td>
<td>0.892</td>
</tr>
<tr>
<td>Kinematic Viscosity (at 40°C, mm²/s)</td>
<td>4.37</td>
<td>4.42</td>
<td>4.32</td>
</tr>
<tr>
<td>Calculated Cetane Index [22]</td>
<td>49</td>
<td>48</td>
<td>48</td>
</tr>
<tr>
<td>Phosphorous (ppm)</td>
<td>21.12</td>
<td>15.13</td>
<td>38.62</td>
</tr>
</tbody>
</table>
explained before, and except these values it is within the required value.

Iodine number gives an indication of storage stability. Biodiesel tends to deteriorate due to hydrolytic and oxidative reactions. A high degree of unsaturation makes biodiesel susceptible to thermal and/or oxidative polymerisation that may lead to formation of insoluble products that cause problems in the injection pumps.

Peroxide value indicates also the storage stability. Biodiesel oxidation leads to the formation of hydroxyperoxides, which can further polymerise to form insoluble gums and cause plugging in fuel system and filters.

The characteristics are not completely fulfilled mainly due to the inadequate purification procedure. Also the lost in the yield of the isolated product was due to washing with water, which may not be practical in the cases of oils with high content of free fatty acids.

With the aim to have a complete knowledge about syringa oil composition the methyl and ethyl esters obtained via ultrasonic technique were determined by GC-MS analysis and the results are given in table 6.

The fatty acid composition of syringa oil is very similar with the common edible oils. Some differences between methyl esters and ethyl esters were found.

From the fatty acids distribution in syringa oil the average molecular mass was calculated to be 874.54.

If the decision to use syringa oil as source for making biodiesel will be made, then a most accurate determination of the optimum amount of catalyst, as well as more technological research should be done. Better method to obtain good quality syringa oil should also be developed. In this study only the potential of syringa oil for biodiesel was taken in consideration and proved to be realistic.

Conclusions

The oil extracted from syringa berries was characterized for its basic properties, fatty acids content and its molecular mass calculated for the first time. It was tested as a potential feedstock for the production of biodiesel under ultrasonic irradiation.

The yield of the transesterification reaction is not very high compared with other oils, especially due to the higher content of free fatty acids (acid value around 5.8). When present in the oil, the free fatty acids are transformed into soap, thus consuming the catalyst. In order to reach the completeness of the reaction a higher amount of catalyst than in other cases is required. The optimum parameters for the transesterification of syringa oil were 1% catalyst and 36°C.

Potassium hydroxide had higher yields than the reactions performed in the presence of sodium hydroxide. The main drawback of ethanolyis is the miscibility of the layers, which results in low yield of an impure isolated product.

Even if the distribution of the fatty acids in the syringa oil is similar with those of other oils usually employed as starting materials for biodiesel production, the ASTM biodiesel specifications were not fulfilled. One reason is the presence of too much unreacted intermediates. Other reason could be the different distribution of the fatty acids in the constituent triglyceride of syringa oil compared with other oils that may play an important role in the transesterification mechanism.

Further studies on syringa oils, obtained from different parts of the tree, (syringa wood is rich in triglycerides) are under investigation and will be the matter of a further publication.

Acknowledgements: The authors express their gratitude to dr. Feridoun Salak Asghari, Osaka Prefecture University, for his helpful advice and valuable suggestions during the experimental work for this paper.

References

6. KANEDA, M., ARIMA, K., YONEZAWA, H., UCHIKOBA, T., Purification and properties of a protease from the sarcocarp of bead tree fruit, Phytochemistry, 35, 1994, p. 1395
8. **Biodiesel Report, National Biodiesel Board, 1996; Jefferson City, MO.**
17. STAVARACHE, C., VINATORU, M., NISHIMURA, R., MAEDA, Y., Fatty Acids Methyl Esters from Vegetable Oils by Means of Ultrasonic Energy, Ultrasonics Sonochemistry, 12, 2006, p. 367
20. ZLATANOV, M., IVANOV, S., AITZETMÜLLER, K., Phospholipid and fatty acid composition of Bulgarian nut oils, Lipid-Fett., 101, 1999, p. 437

Manuscript received: 10.10.2007