Study of the potential of Neem oil (*Azadirachta Indica A. Juss*) as raw material for the production of methyl esters

Estudo do potencial do óleo de Neem (*Azadirachta Indica A. Juss*) como matéria-prima para a produção de ésteres metílicos

DOI: 10.34117/bjdv6n6-319

Recebimento dos originais: 08/05/2020
Aceitação para publicação: 14/06/2020

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Braz. J. of Develop., Curitiba, v. 6, n. 6, p. 37411-37420 jun. 2020. ISSN 2525-8761
ABSTRACT
More than 80% of the final cost of producing biodiesel in Brazil is due to the raw material. This aspect increases the interest in looking for new sources for this industry. In this scenario, Neem (Azadirachta Indica A. Juss), a high-yield oilseed (1,250 kg / ha.year), becomes an excellent source of raw material. This culture also brings together other attributes of interest to broad segments of Brazilian society, has bactericidal and insecticidal functions, recognized ease of growth in the field, its wood is economically overvalued, has the capacity to withstand extreme conditions of heat and water pollution, improves fertility soil and rehabilitate degraded land. In order to make the commercial use of Neem oil feasible, the present work was developed, whose main objective was to evaluate the potential of this oil as a raw material for the production of biodiesel. For that, we started with crude Neem oil, provided by Laboratório Biológico Farmacêutico SA (LABIOFAM) in the province of Holguín / Cuba, and a technological route was defined that allowed, starting with the inclusion of an oil pre-treatment step raw material prior to conventional transesterification, produce commercial quality biodiesel. Additionally, it was identified that this biodiesel needs an antioxidant additive to reach the quality specification, a behavior similar to soy biodiesel.

Keywords: Neem oil, Neem oil pre-treatment, Biodiesel.

INTRODUCTION
Of the total primary energy consumed in the world today, 81.4% comes from fossil fuels, of which 56% is used in the transport sector. Therefore, it is possible to verify that the transport sector is largely responsible for the use of these fuels, such as: gasoline, jet fuel and diesel. It is also responsible for the emission of a large amount of pollutants to the atmosphere, such as: carbon...
monoxide (CO), hydrocarbons (HC), nitrogen oxides (NOx), sulfur dioxide (SO2), total aldehydes (RCHO) and particulate matter (MP), expressed as carbon dioxide equivalent (CO2eq).\(^1\)

The rampant use of these fossil fuels to supply energy needs is leading to a considerable decrease in world reserves. Even with recent discoveries of reserves such as: those in Venezuela (296.5 billion barrels) and those in Brazil (15.3 billion barrels), there are prognosis of their depletion in the coming decades.\(^2\)

Although the use of biofuels has clear strategic and environmental advantages, there is a need to develop new technologies or ways of obtaining them so that their production is as efficient and sustainable as possible.\(^3\)

Among biofuels, biodiesel residues that can be produced from oils and fats of vegetable or animal origin and prove to be a promoter in reducing soot emissions from engines,\(^4\)\(^-\)\(^9\) and gas residues that promote or affect the economic effect. When using vegetable oils and fats of agricultural origin, there is in many cases, direct competition with food production, mainly in small countries. In that sense, or biodiesel, from non-edible biomass.

The use of biodiesel, produced from non-edible biomass, seems to be an economical solution for deal with soot emissions.\(^10\)\(^-\)\(^11\) The properties of biodiesel are similar to those of diesel,\(^12\) and biodiesel can be produced from various sources including jatropha oil, palm oil, neem oil, soybean oil, rapeseed oil, ground nut oil, and linseed oil.\(^13\)\(^-\)\(^16\)

Its combustion leads to low CO values and unburned hydrocarbon emissions,\(^17\) compared to pure diesel,\(^22\)\(^,\)\(^28\)\(^-\)\(^30\) offers greater combustion efficiency when compared to the cetane number and biodegradability than diesel; does not emit sulfur and aromatics when burned.\(^18\)\(^-\)\(^20\)

Neem oil has become advantageous for small and large producers, has fallen from neem seeds and around 45% oil,\(^21\) suggested for biodiesel production according to the literature,\(^22\)\(^,\)\(^23\)\(^-\)\(^25\) as neem trees can be easily grown in any soil and extreme climates, besides having several functions, acting as a bactericide, insecticide and can also control nematodes, when applied in the form of neem cake, associated with castor cake. It can be reconciled with biological pest control practices, since it does not affect mammals or the environment. Neem is able to withstand extreme conditions of heat and water pollution, improves soil fertility and rehabilitates degraded land.

Given these advantages offered, this crop has been used around soybean and other oilseed plantations used in the production of biodiesel such as sunflower and jatropha, in order to protect it from pest attacks.\(^26\)
Aiming at the production of biodiesel from cheaper raw materials, reduction of the environmental impact and positive social impacts, this work has as general objective the use of Neem oil, as raw material for the production of biodiesel.

2 MATERIALS AND METHODS

The raw material used in this work was neem oil, provided by Laboratório Biológico Farmacêutico S.A. (LABIOFAM) in the province of Holguín, Cuba.

Pre-treatment of Neem crude oil: For crude oil, the need to include a pre-treatment step, prior to the production of biodiesel, was identified.

Drying: The collected neem oil was dried at a temperature of 80°C, using a heating plate with stirring for one hour. For this, 200mL of sample was transferred to a 350mL beaker that was placed on a heating plate.

Chemical refining: the dry crude oil has undergone a chemical refining process in order to reduce acidity and remove possible phosphatides (gums). The reaction was carried out in a 350 mL beaker centered on a heating plate and constant stirring. The reaction system was kept under stirring for 30 min after the temperature reached 65 °C. After 15 minutes of reaction, 30% w / w sodium hydroxide solution (NaOH).

Centrifugation: After the reaction, the product was transferred to 50ml FALCON tubes that were centrifuged for 15 minutes at 3500 rpm in order to separate the polar phase, rich in glycerin.

Washing: the biodiesel-rich phase was subjected to several washing steps until ph = 7 was obtained. In the first washing step, a 60 °C hot water solution with 0.05% v / v phosphoric acid was used to
neutralize the catalyst and remove unreacted alcohol. In the following steps, only distilled water was used at a temperature of 60ºC.

Drying: The collected neem biodiesel was dried at 80ºC, using a heating plate with stirring for one hour.

**Biodiesel production and characterization.** This step was subdivided into a few steps that will be described below: 1) Biodiesel was produced by alkaline transesterification of the pre-treated oil (MM = 883.54 g / mol), using methanol and a homogeneous sodium hydroxide catalyst (NaOH).

The reaction system was kept under constant agitation for 60 minutes at temperature of 40ºC (Figure 2). The condition chosen for transesterification was 1: 9 (oil: methanol). 27

**Physical-chemical characterization of biodiesel.** The biodiesel sample was characterized, following the physical-chemical indices established in ANP Resolution No. 45 of 08/25/2014.

**3 RESULTS AND DISCUSSION**

The physicochemical characterization of the crude oil of Neem was essential to define if necessary the inclusion of a pre-treatment stage of the oil, prior to the production of biodiesel. The results of this characterization are shown in Table 1.

| Feature                  | Unity     | Methodology   | Results      |
|--------------------------|-----------|---------------|--------------|
| Aspect                   | -         | NBR 16048     | Brown Liquid |
| Specific gravity at 20ºC | Kg/m²     | ASTM D 1298   | 927.40       |
| Viscosity at 40ºC        | mm²/s     | ASTM D45      | 48.92        |
| Acidity level            | mgKOH/g   | AOCS Cd3d-63  | 3.89         |
| Water content            | %         | EN 6304       | 1.18         |
| Iodine index             | gI₂/100g  | AOCS Cd 1-25  | 64.00        |

Source: author
Analyzing the results of the characterization, shown in Table 1, it is possible to verify that it has an acidity index and a high water content, when compared with a refined oil (acidity index <0.7 mg KOH / g and humidity <0.1%). Thus, it is recommended to carry out a pre-treatment step in order to improve the quality of the raw material and guarantee its processing, through the transesterification route, present in all biodiesel plants in Brazil.

According to the iodine index obtained (64gI₂ / 100g), it can be seen that the raw material is a more saturated oil than soybean oil (approx. 125 gI₂ / 100g), the main raw material used in production biodiesel in Brazil. It is important to highlight that due to the high degree of unsaturation of the fatty acids (Figure 3) that make up the triglycerides of soybean oil, all biodiesel produced from the oil of this oilseed needs an antioxidant additive.

**Figure 3.** Fatty acid profile present in neem oil.

![Fatty acid profile present in neem oil](image)

The fact that Neem is a more saturated oil is a positive aspect that could minimize the use of antioxidant additives in biodiesel. On the other hand, it is more unsaturated than beef tallow which has an iodine index of approx. 50 gI₂ / 100g, which is a positive aspect when analyzing the freezing point.

**Biodiesel production and characterization.** Biodiesel was produced by alkaline transesterification. In this stage, a yield of 90% was obtained in relation to the pre-treated oil, used as raw material.

In Figure 4 shows the procedure followed in the transesterification of pre-treated neem oil.
The characterization of the biodiesel produced is shown in Table 2.

Table 2. Physico-chemical characterization of NEEM biodiesel.

| Feature Aspect                  | Unity        | Methodology | Results                                      |
|---------------------------------|--------------|-------------|----------------------------------------------|
| Specific gravity at 20°C        | Kg/m³        | ASTM D 1298 | 878.9                                        |
| Viscosity at 40°C              | mm²/s        | ASTM D45    | 4.93                                         |
| Water content                  | mg/kg        | EN12937     | 272.2                                        |
| Flash point                    | °C           | ASTM D93    | >130                                         |
| Ester content                  | % massa      | EM 14103    | 97.05                                        |
| Corrosivity to copper, 3h at 50°C | -           | ASTM D130  | 1A                                           |
| Cold clogging point            | °C           | ASTM D6371  | 12                                           |
| Acidity level                  | mg KOH/g     | ASTM D664   | 0.48                                         |
| Free glycerol                  | % massa      | ASTM D6584  | 0.003                                        |
| Total glycerol                 | % massa      | ASTM D6584  | 0.4                                          |
| Monoacylglycerol               | % massa      | ASTM D6584  | 0.10                                         |
| Diacylglycerol                 | % massa      | ASTM D6584  | 0.08                                         |
| Triacylglycerol                | % massa      | ASTM D6584  | 0.001                                        |
| Methanol                       | % massa      | EN 1410     | 0.004                                        |
| Oxidation stability at 110°C   | h            | EN 14112    | 1.2                                          |

According to the results obtained in the characterization of biodiesel produced from pre-treated neem oil, it is possible to verify that the product complies with the quality specification. Only the water content, specified at a maximum of 200 mg / kg, was slightly above the limit. This problem can be solved with a more intensive drying step.

Oxidation stability was also below specification (8 h). Indicating the need for mandatory addition of antioxidant additive. However, this is not uncommon in the biodiesel industry, as currently all biodiesel produced from soybean oil is added with an antioxidant. One aspect that may also have had a negative influence on this index was the oil storage time, approximately 14 months.
4 CONCLUSIONS

The crude oil of Neem, used as raw material in this work, presented a high acidity index (3.89 mg KOH / g) and a high water content (1.18%).

In order to guarantee the production of a neem biodiesel specified by means of transesterification technology, existing in all biodiesel plants in Brazil, it was necessary to include a pre-treatment stage of crude neem oil. With the proposed pretreatment it was possible to reduce the acidity index to 0.315 mg KOH / kg, below 0.7 mg KOH / kg, and the water content to 0.024%, well below the maximum allowable limit for processing by transesterification (0.1%).

From the transesterification of pre-treated neem oil, it was possible to produce biodiesel with an ester content greater than 96.5%, showing that it is a potential raw material to be used in the production of biodiesel.

Neem oil proved to be a potential raw material to be used in the production of biodiesel.

ACKNOWLEDGMENT

We thank the National Council for Scientific and Technological Development (CNPq) for the financial support and the GREENTEC Laboratory (UFRJ) for their support in the research.

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