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Biodiesel production from Neem seeds (*Azadirachta indica* A. Juss) oil by its base-catalyzed Transesterification and its Blending with Diesel

Diedhiou Djibril[1,2*], Diatta Mamadou Lamine[2], Faye Mamadou[1,2], Vilarem Gerard[1], Sock Oumar[2] and Rigal Luc[1]
[1]Laboratoire de Chimie Agro-Industrielle (LCA), ENSIACET, INP Toulouse, 4 Allée Emile Monso - BP 44362 - 31030 Toulouse Cedex 4, FRANCE
[2]Laboratoire d'Electrochimie et des Procédés Membranaires (LEPM), Université Cheikh Anta Diop de Dakar, BP 5085 Dakar-fann, SENEGAL

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Abstract

Biodiesel, a non-toxic, biodegradable and renewable fuel can be a solution to non-environmentally friendly and exhaustible fossil fuels. The triglycerides transesterification is the most used process in the biodiesel production. However, the blending of the oil with diesel is also used. Neem (Azadirachta indica A. Juss) seeds oil (NSO), a non-edible oil available in large quantities in Senegal may be a second generation feedstock for biofuel production. In this research, the study is focused on its transformation into biodiesel by NaOH catalyzed transesterification and its blending with diesel. The NSO physicochemical properties were determined and compared to those of diesel. The NSO consists of four major fatty acids: oleic acid (C18:1), linoleic acid (C18:2), stearic acid (C18:0) and palmitic acid (C16:0). These fatty acids represent 95.80% of all the fatty acids present in the NSO. The study of the effect of catalyst level, performed at 75°C and for molar ratio alcohol-oil 6:1 has revealed that a rate catalyst of 1% (w/w_{oil}) is more effective. The kinetic study of the reaction confirmed the hight speed of the formation of the ethyl esters (NSOB) with conversion maximum rate achieved after 90 minutes. The physical and thermal properties of neem seeds oil biodiel (NSOB) are close to those of diesel. However, those of the SNO-diesel blend (NSODB) are closer to those of the diesel.

Keywords: *Azadirachta indica*, neem seeds oil, biodiesel, transesterification, blending, diesel.

Introduction

During these last decades, the high price of fossil fuels, concerns about their depletion and the environmental issues justifiy the choice focused on the development of new energy sources. Biodiesel is one of the preferred alternatives of this sector. It is considered as a renewable, biodegradable, non-toxic and affordable fuel[1]. Biodiesel is produced from any source of fatty acids by a transesterification reaction. Vegetable oils, however, are the most used in the biodiesel production. Edible vegetable oils for example rapeseed oil, soybean oil, sunflower oil, palm oil etc., constitute the first generation of feedstocks for biodiesel. However, the use of inedible oils for energy purposes can avoid conflicts between food and energy security. This is why the research is directed towards the use of non-edible oils which form the second generation of biodiesel feedstock[2]. Thus, the neem seeds oil could be an interesting feedstock for biodiesel the production. The neem (*Azadirachta indica* A. Juss) is a plant of the botanical Meliaceae family, which is native to the Indian subcontinent[3]. In Senegal, its population is estimated between 18 and 30 million trees[4]. The neem tree can reach a height of 25-30 m in its home country, and sometimes up to 35 or 40 m in good growth conditions and about 5 to 15 m in Senegal[5,6]. The neem tree normally begins to bear fruits after 3-5 years and become highly productive at 10 years. At maturity, the neem tree can produce up to 50 kg of fruits per year, equivalent to 30 kg of seeds per year[7]. The oil content varies from 30 to 52% for the kernels and from 20 to 32% for the seeds[8,9]. The neem oil has multiple uses, mainly for soaps, pesticides and pharmaceuticals[10].

The aim of this work was to produce biodiesel in the form of fatty acids ethyl esters (FAEE) from neem seeds oil (NSO) by transesterification through NaOH catalysis. It was also to experiment the biodiesel production process by the blending of NSO and diesel (NSODB). Biodiesel properties were compared to those of diesel.

Material and Methods

Plant material: The biological material consisted of some neem oil obtained by solvent extraction from seeds collected in Senegal. These seeds coming from mature fruits, collected in august 2012, were cleaned and dried with sun exposure at open air and then in an oven at 40°C for 7 days.

Solvents and reagents: All the chemical reagents, standards and solvents of analytical grade, were purchased from Sigma-Aldrich, France.

The oil extraction: The oil used for the transesterification and the blending with diesel was extracted with the soxhlet method using cyclohexane as solvent. The soxhlet extractor was equipped at its base with a 250 mL flask in which 200 mL of solvent were introduced. After that, the solvent extract was dry concentrated in a rotary evaporator at 35°C and further dried in an oven at 50°C.

Neem seeds oil, biodiesel physicochemical characterization: The physicochemical properties were determined according to standardized methods : the density (ASTM 4052), the viscosity (ASTM D 445), the flash point (ASTM D 93), the freezing point (ASTM D 97), the pour point (ASTM D 97), the calorific value (ASTM D 4868), the acid value (AFNOR T60-204), the saponification value (AFNOR T60-206), the iodine value (AFNOR T60-203), the peroxide index (AFNOR T60-220), ash content (ASTM D 482), the carbon residue content (ASTM D 189), the sulphur content (ASTM D 4294), the sediment content (ASTM D 4052), the water content (ASTM D 9590). However, the refractive index was measured at 25°C by direct reading with a refractometer ABBE RMT model (EXACTA + OPTECH France 77646 CHELLES, France) while the calorific value for the oil was estimated using the following empirical relationship : Calorific value = 11380 - Iodine value - 9.15 × saponification value[11].

Neem seeds oil fatty acids analysis: The fatty acid profile was performed by analysis of its fatty acids methyl esters (FAME) in gas chromatography (GC) using the French Standard NF ISO 5508. The esterification was carried out in two steps, solubilization of the oil by TBME (Tert-Butyl Methyl Ether) and addition of TMSH (trimethyl sulphonium hydroxide 0.5 M in methanol). The analysis was performed in 3800 type GC equipped with a Varian CP-select column for (Fatty acids Methy Esters) FAME fused silica WCOT (length 50 m, internal diameter 0.25 mm, film thickness 0.25 µm) coupled with a flame-ionization detector (FID) heating the components at 250°C. The carrier gas was helium (flow rate of 1 mL/min). The injection was Split (1:100. 1µL. 250°C for 55 min.). The temperature programming was 185°C for 40 min and then rise from 185°C to 250°C at 15°C/min and finally 250°C for 10.68 min (analysis time 55.01 min). The standard used was the MGFA (SI) and the data was processed with Varian Star software.

Transesterification of the neem seeds oil: Transesterification is a biodiesel production process. This is a reaction between oil and an alcohol, usually methanol or ethanol to have alkyl-esters (often methyl or ethyl) and glycerol. This process reduces the molecular weight of the oil, its viscosity, density and increases the volatility to bring them closer to those of diesel fuel[12]. The reaction is reversible, so an excess of alcohol is used to shift the balance in the direction of the products (esters and glycerol) formation. A molar ratio alcohol-oil 6:1 is often used in the industrial process to achieve higher conversion rate to 98%[13].

Methanol is the most frequently alcohol used. It is cheaper but its higher toxicity makes ethanol a better choice. It leads to a full biofuel[14]. Transesterification is often catalyzed by a base, an acid or enzymes in order to improve the kinetic.

The transesterification was carried out with ethanol in a molar ratio 6:1 and the catalyst (sodium hydroxide) was fixed at 1% of the oil (w/w). The reaction was carried out using a jacketed reactor manufactured by PIGNAT Company (France), equipped with a stirrer EUROSTAR of Ika-Werke type at 75°C. The stirring speed was set at 1200 rpm. At the end of the transesterification, the reaction mixture was neutralized by a solution of citric acid at 6%. The separation of the two phases (glycerol and ester) was carried out using a separatory funnel after 24 hours of decantation.

Neem seeds oil and diesel blending: Blending is a biodiesel production process involving the dilution of vegetable oils with diesel fuel or with a solvent such as ethanol. Much research has focused on it and its effects have also been studied[15-17]. The NSO-diesel blend (NSODB) was made at a ratio 1:5 of the oil-diesel because the ratios of 1:10 to 1:5 were found to be satisfactory[18]. Then, the blending was homogenized by stirring in the reactor at room temperature before being analyzed.

Results and Discussion

Physicochemical properties of the neem seeds oil: Several physicochemical properties of the NSO were determined (table-1). The small amount of free fatty acids resulted in a low acidity index (9.10 $mg.g^{-1}$). This slight acidity will require little basic solution to neutralize the free fatty acids, which will not limit the performance of the transesterfication reaction[18-20]. Its high saponification index (200.54 $mg.g^{-1}$) revealed its high proportion of saponifiable. In this case, a high proportion of water or an insufficient amount of alcohol may cause soap formation during the reaction of transesterification. Its low water content (<0.05%) did not promote the saponification during the transesterification and subsequent operations of separation and washing after the transesterification. The ash (0.02%), lower thant the maximum value (0.1%), won't to affect the injection pump and the cylinder when in use in engines. The sulfur content (0.11%) is lower than the maximum limit required for use as a fuel. However, the carbon residue content sufficiently high (1.45%), which is higher than the maximum recommended limit for diesel (0.2%) may result in deposits after combustion[21]. The relatively high gross calorific value (39.53 $MJ.kg^{-1}$) can give the NSO a good criterion for biodiesel production. The high flash point (227°C) confirms the absence of risk of fire during handling or storage. The freezing point (10°C) and the pour point (12°C), well below those of diesel confirm the difficulty for use as fuel in the low-temperature conditions. The viscosity of the NSO which is 49.79 $mm^2.s^{-1}$ is considerably higher than that of diesel and, for fuel application, shall be reduced by conversion of the triglycerides into fatty acids esters or by dilution with diesel.

Neem seeds oil fatty acids composition: The four main fatty acids (Table-2) are oleic acid (41.91±0.69%), linoleic acid (19.59±0.44%), stearic acid (18.71±0.46%) and palmitic acid (15.59±0.27%). This high linoleic and oleic acid proportion is noted in Jatropha oil and *Pongamia Pinnata* (Karanja)[22,23]. These fatty acids represent 95.80% of the total fatty acids of the neem seed oil. The fatty acid profile is similar to those presented in the literature[24]. Indeed, the ratio unsaturated/saturated fatty acids, being at about 60%, confirm the unsaturated behavour of the oil.

Table-1
Physicochemical properties of NSO

Characteristics	Value	Methods
Acid value ($mg.g^{-1}$)	9.10	AFNOR T60-204
Saponification value ($mg.g^{-1}$)	200.54	AFNOR T60-206
Iodine value ($g.100g^{-1}$)	74.82	AFNOR T60-203
INS	126	-
Peroxyde value (meq $O_2.kg^{-1}$)	1.49	AFNOR T60-220
Density at 25°C	0.912	ASTM D 4052
Refraction index at 25°C	1.465	Direct reading
Viscosity at 37.8°C ($mm^2.s^{-1}$)	49.79	ASTM D 445
Calorific value ($MJ.kg^{-1}$)	39.53	-
Flash point (°C)	227°C	ASTM D 93
Freezing point (°C)	10°C	ASTM D 97
Pour point (°C)	12°C	ASTM D 97
Ash (wt%)	0.02	ASTM D 482
Carbon residue (wt%)	1.45	ASTM D 189
	0.11	ASTM D 4294
Sediments (wt%)	0.01	ASTM D 4052
Water content (%v)	< 0.05	ASTM D 9590

Effect of Catalyst concentration on ester yield: The analysis of the effects of the catalyst concentration, at 0.5%, 1%, 1.5% of the oil (w/w), performed at 75°C for 4 hours (figure-1) shows that the catalyst is most effective when it is about 1%. Indeed, this concentration gives the best ester yield (about 98%). Higher levels led to the formation of soap. This causes a significant decrease in the formation of esters. The soap formation during the transesterification makes the separation and purification of the biodiesel harder. Similar results were obtained for *Brassica carinata* oil with KOH catalyst, on the Thumba oil with KOH-NaOH and on the rice bran oil with NaOH catalyst[15-17].

Table-2
Fatty acids composition of neem seeds oil

Composition	%
C16:0 Palmitic acid	15.59±0.27
C16:1 Palmitoleic acid	0.12±0.00
C18:0 Stearic acid	18.71±0.46
C18:1 Oleic acid	41.91±0.69
C18:2 Linoleic acid	19.59±0.44
C20:0 Arachidic acid	1.33±0.01
C18:3 Linolenic acid	0.44±0.01
C20:1 Gadoleic acid	0.08±0.00
C22:0 Behenic acid	0.86±0.38
Saturated fatty acids	37.00
Unsaturated fatty acids	63.00

Effect of reaction time on ester yiel: The effect of reaction time on the formation of the ethyl esters is analyzed at 75°C with 1% (w/w_{oil}) of catalyst and a molar ratio 6:1. The analysis carried out after 30 min, 60 min, 90 min, 120 min, 150 min 180 min, 210 min and 240 min (Figure-2) reveals that the formation of esters is quick. After 30 minutes, the ethyl esters yield is at 58% and after 60 minutes at 92%. However, the maximun rate conversion (93-95%) is reached after 90 minutes of reaction. These results are comparable to those of some other authors such as on *Jatropha* oil with KOH catalysis, on the oil Thumba with NaOH and KOH catalysis and on the palm oil in alkalic catalysis[16,25,26].

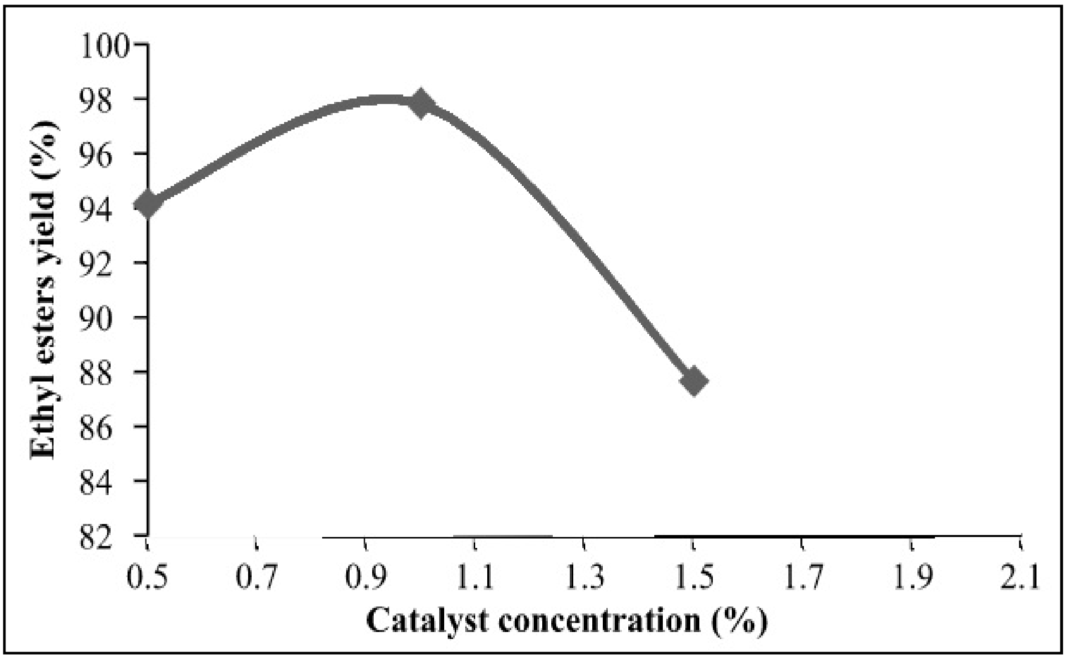

Figure-1
Effect of catalyst concentration on ethyl ester yield at 75°C, molar ratio 6:1

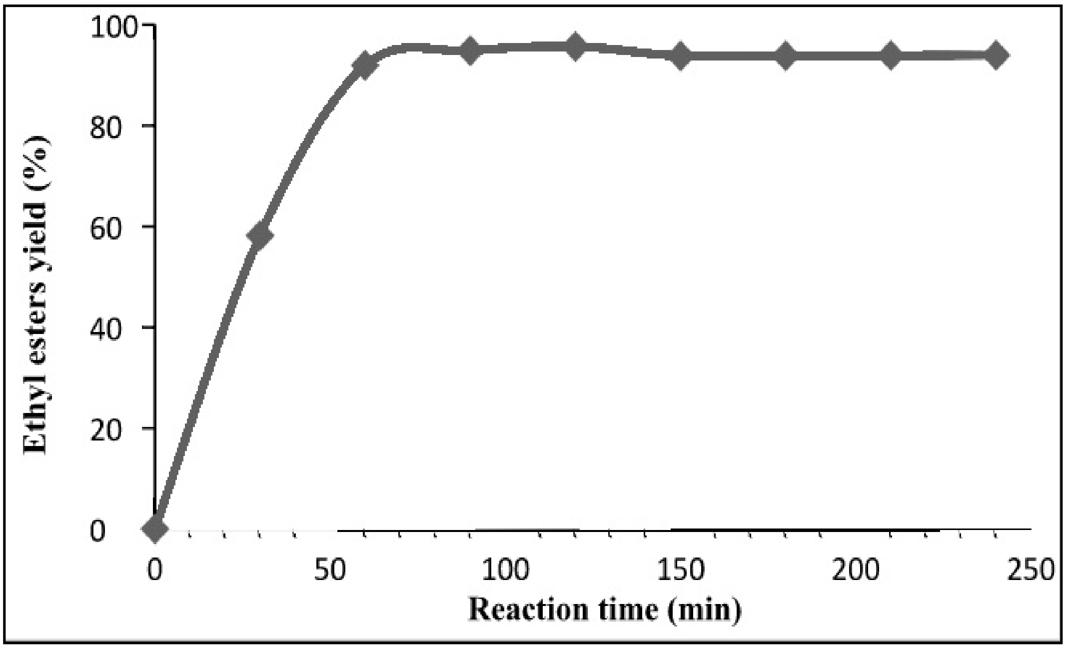

Figure-2
Effect of reaction time on ethyl ester yield at 75°C, molar ratio 6:1 and catalyst 1% (w/w)

Physicochemical properties of neem seeds oil biodiesel (NSOB) and neem seeds oil blended with Diesel (NSODB): The results show that the transesterification of the NSO leads to a significant change in its physical and thermal properties. The comparison of the NSOB properties with those of the oil reveals a decrease of the viscosity (49.79 to 35.80 $mm^2.s^{-1}$), of the flash point (227 to 64.3°C), of the freezing point (10 to 8°C), of the pour point (12 to 11°C) and an increase the of the gross calorific value (39.53 to 41.97 $MJ.kg^{-1}$). These tendencies are also observed on *B. aegyptiaca* oil and its biodiesel, on *Jatropha* oil and its biodiesel and on *Simarouba glauca*[27-29]. However, concerning the composition, we can note an increase in levels of some compounds such as ash carbon residue and sediments in the NSOB versus NSO. We remind that these compounds have adverse effects on the engines. The NSOB properties are compared with those of Jatropha, desert date, rapeseed and cotton methyl esters (table-3).

The transesterification of the NSO provides the NSOB, whose properties are close to those of the diesel (table-4). Its use in engines can thus be envisaged. The NSODB provides physical and thermal properties more similar to those of diesel. They confirm that *Jatropha* oil blend with diesel for a ratio 1:1 can be used in diesel engines without any major problems[14].

Conclusion

The results of this work show that neem seeds oil (NSO) can be developed as a renewable fuel. Its development as a biodiesel requires the transesterification of its triglycerides. The physical and thermal properties of the ethyl esters (NSOB) obtained by transesterification NSO with NaOH catalysis are close to those of diesel. The SNO-diesel blend (NSODB) provides even closer properties. Thus, the use of the NSOB and the NSODB as biofuel in the diesel engines can be envisaged.

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Table-3
Physicochemical properties of NSOB compared to those of Jatropha, desert date and rapessed methyl esters

Properties	NSOB	Jatropha[13]	Desert date[27]	Rapessed[30]
Cetane number	41.63	-	-	-
Density at 15°C (kg.m^{-3})	907.0	886	880	880
Viscosity at 37.8°C (mm^2.s^{-1})	35.80	38.60 (at 40°C)	4.8	7 (at 20°C)
Calorific value (MJ.kg^{-1})	41.97	39.84	39.23	41
Flash point (°C)	64.3	230	135	183
Freezing point (°C)	8	-	-	-
Pour point (°C)	11	-3.5	2	-12
Ash (wt%)	0.12	0.03	0.012	-
Carbon residue (wt%)	1.50	3.0	0.20	-
Sulfur (wt%)	0.11	0.11	-	-
Sediments (wt%)	0.83	-	-	-
Water content (%v)	< 0.05	1.4	0.0125	-

Table-4
Properties of NSOB and NSODB compared to the Diesel

Properties	NSOB	NSODB	Diesel[31]	Methods
Cetane number	41.63	43.42	> 40	ASTM D 4737
Density at 15°C ($kg.m^{-3}$)	907.0	887.9	835 - 930	ASTM D 4052
Viscosity at 37.8°C ($mm^2.s^{-1}$)	35.80	7.24	< 15	ASTM D 445
Calorific value ($MJ.kg^{-1}$)	41.97	42.21	43.8	ASTM D 4868
Flash point (°C)	64.3	78.8	> 61	ASTM D 93
Freezing point (°C)	8	3	-	ASTM D 97
Pour point (°C)	11	0	< 15	ASTM D 97
Ash (wt%)	0.12	-	< 0.1	ASTM D 482
Carbon residue (wt%)	1.50	-	< 0.2	ASTM D 189
Sulfur (wt%)	0.11	-	< 1,0	ASTM D 4294
Sediments (wt%)	0.83	-	< 0.01	ASTM D 4052
Water content (%v)	< 0.05	-	< 0.05	ASTM D 9590

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