Transesterification of Various Bio-oils: Application and Perspectives in Burkina Faso

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Abstract

The aim of this paper is to study and analyze the possibility of adapting the production of biodiesel in West African countries, in agreement with required standards, using local vegetable oils, for particular use in rural or remote regions. To achieve this study, an original approach based on Komers and Nourreddini theories is proposed, in order to identify the optimal conditions and parameters to produce high quality of biodiesel. Then, a pilot of transesterification is developed. The optimums obtained from theoretical simulations are used to synthesize biodiesels of various vegetable oils. Quantification in order to estimate the transesterification yield and the performance of the pilot is done. Different analytical methods for biodiesel characterization are used to determine main fuel properties including viscosity, density, water content, etc. The obtained values are then compared with international standards. This quality control is completed with gas chromatography for the quantification of tri-, di-, monoglycerides, free and total glycerol, which compose the final mixture of the various biodiesels produced. Good correlation between the results obtained and international standards values are found.

Keywords: Transesterification; Biofuels; Kinetics; Methyl esters; Fatty acid analysis; Chromatography

Introduction

Access to modern energy is unanimously considered as a key factor in the industrial development and in providing basic services for the improvement of life standard, and as a driving force for an economic progress [1,2]. With the increases of oil prices, there is a renewed interest in vegetable oil and their derivatives as alternative fuels for diesel engines [3-5]. The development of renewable technologies and in particular biofuels production in developing countries could provide opportunities for poverty reduction and for energy needs satisfaction in rural and remote region. It could help creating employment and local economic development opportunities. It could contribute to the protection of human health from air pollution, enhancing energy security. Biofuels, as their name implies, are fuels derived from biomass that can be converted through biochemical, physical or thermochemical processes. Vegetable oils can be used as fuel in diesel engines, but the main problem with the use of pure vegetable oils as fuels is related to its high viscosity, resulting problems of vaporization of fuel in the combustion chamber, the difficulties of pumping, clogging of injectors over time and other engine problems [6,7]. Instead, esters derived from vegetable oils show similar features to those of petroleum diesel fuels.

This good potential along with environmental benefits makes biodiesel a prominent perspective for alternative fuels. Biodiesel is a mixture of esters of fatty acids obtained by the transesterification reaction of triglycerides with alcohols (methanol, ethanol, etc.) in the presence of alkali (KOH, NaOH, etc.) as a catalyst [8,9]. While the interest in biofuels is growing worldwide, only few African countries have adopted a program for large-scale production [1-4].

The objective of this paper is to study and analyze the possibility of adapting the production of biodiesel in Burkina Faso, using local vegetable oils. In order to achieve this result, a method has been developed for determining through theoretical simulation, the optimum parameters required for the transesterification. This study is based on an original approach considering a combined model of Komers and Nourreddini [10-12]. The theoretical results was validated through experimental tests, conducted on a transesterification pilot scale with jatropha, palm and soya oils. Then, the main important physico-chemical fuel properties (viscosity, density, water content, …) of biodiesels have analyzed and compared with those of conventional diesel fuels and international standards (EN 14214, ASTM D6751-02) [13]. Chromatographic analysis were then performed in order to quantitatively and qualitatively characterized the different biodiesel synthesized, before drawing some conclusion and perspectives for a possible adaptation of a production unit in Burkina Faso.

Theoretical Approach

The theoretical study of the kinetics of transesterification makes available the parameters that can be used to predict the extent of the reaction at any time under particular conditions, and allows as well determining the optimums without making a high number of experimental tests.

The transition state of vegetable oil to that of alkyl ester of vegetable oil, by transesterification process improves several properties of vegetable oils (reduction of molecular weight, viscosity, density …) for applications as a fuel. As shown in equation (1), transesterification of vegetable oil imply the reaction of one equivalent of triglyceride (TG) with three equivalents of alcohol to give three equivalents of alkyl ester (biodiesel) and one equivalent of glycerol (by-product).

During the process, there are three stepwise reactions with...
This method takes into account:
results from a combination of Komers and Noureddini's contributions.
energies does not allow the use of Komers's data for a temperature
encountered in practice, and the non-determination of the activation
of 22.75°C and a molar ratio n=2.03. These conditions are barely
the high number of constant rates (eleven), found for a temperature
aspects of the model proposed by Komers are included in our model
and water [12,17,18]. In order to overcome these simplifications, some
into account side reactions that occur like the effect of saponification
the most common used, but shows some weaknesses: it does not take
process [10,11,14-16]. The model proposed by Noureddini and Zhu is

Several kinetic studies have been published on transesterification
introduction of an efficiency factor of the overall model. It
- The model also foresees, in the calculation method, several
- Introduction of the activation energy: this allows performing
- Effect of water: Komers assumes that the water content
remains constant during the reaction. This is not actually true
for all variables;
- Effect of temperature (activation)
- Introduction of the agitation intensity over the
- The model also foresees, in the calculation method, several
- Introduction of an efficiency factor of the overall model. It
takes into account possible differences between experimental
data and model predictions.

The developed model is constituted by the following system of ten
differential equations:

$$
\frac{dX_{TG}}{dt} = a \cdot \frac{X_{TG}}{X_{H_2O}} \left( -k_1 X_{TG} - k_2 X_{RH} + k_3 X_{DG} \right) + a \cdot \frac{X_{TG}}{X_{H_2O}} K_{OH} X_{OH}
$$

$$
\frac{dX_{DG}}{dt} = a \cdot \frac{X_{DG}}{X_{H_2O}} \left( -k_1 X_{DG} + k_2 X_{RH} + k_3 X_{MG} + k_4 X_{HA} \right) + a \cdot \frac{X_{DG}}{X_{H_2O}} K_{OH} X_{OH}
$$

$$
\frac{dX_{MG}}{dt} = a \cdot \frac{X_{MG}}{X_{H_2O}} \left( -k_1 X_{MG} - k_2 X_{RH} + k_3 X_{DG} + k_4 X_{HA} \right) + a \cdot \frac{X_{MG}}{X_{H_2O}} K_{OH} X_{OH}
$$

$$
\frac{dX_{BD}}{dt} = a \cdot \frac{X_{BD}}{X_{H_2O}} \left( -k_1 X_{BD} + k_2 X_{MG} + k_3 X_{DG} + k_4 X_{HA} \right)
$$

$$
\frac{dX_{ROH}}{dt} = a \cdot \frac{X_{ROH}}{X_{H_2O}} \left( -k_1 X_{ROH} + k_2 X_{H_2O} + k_3 X_{DG} + k_4 X_{MG} \right)
$$

These rates are reaction constants; BD, GL, FFA and SV are respectively:
biodiesel, Glycerol, free fatty acid and soap.

In order to analyze the transesterification reaction and to estimate
the efficiency of the system, some numerical simulations (Mathematica
program), using different values of constructive and operational
parameters of the system are performed.

The purpose of these simulations is to compare the results obtained
by the theoretical model with the experimental observations, in terms
of efficiency.

Experimental Procedures

Materials

Jatropha, palm and soya oils were used as vegetable oils for this study. The alcohol and the catalyst used for the purpose of the experimental tests are methanol and potassium hydroxide. The choice of jatropha and palm as the vegetable oils for biodiesel production in this study is due to their availability in the western Africa region. Soya oil is specifically used in this study in order to compare the results obtained from our approach, with many other ones found in literature. Otherwise, the projects of culture of jatropha are encouraged in Burkina Faso, and some of them are currently in progress.

Although the production of biodiesel from ethanol (ethyl esters)
both allows improvement of energy independence and presents
environmental advantages compared to the methanol industry, in this
study we are presenting the results of transesterification in methanolic
way. This is due to the fact that the production of ethyl esters is limited
by several factors including: water content of bioethanol, the difficult
separation of ethyl esters in reaction environments, etc. that is currently
Experimental design

All our transesterification tests were performed on a pilot developed at our laboratory (LBEB). As it can be seen on Figure 1, the reactor is composed by two tanks equipped with a temperature controller. The small tank is assigned to the pre-mixture of alcohol and catalyst, and the big one to vegetable oils and transesterification reaction. Agitation in each tank was provided by a magnetic stirrer, which was set at a constant speed throughout the experiment. At first, the big tank was filled with vegetable oils and heated to a desired temperature, while in the small tank a known amount of catalyst was dissolved in the required amount of methanol.

The two tanks communicate by a tubing equipped with a floodgate that permits either to isolate or to connect them. Every tank has a floodgate of drench to its basis, that serves to evacuate after decanting, the glycerol and the water of washing, in the case of the big tank.

Biodiesel preparation

The biodiesel preparation involved a two-hour transesterification reaction, followed by washing and drying. A total molar ratio of methanol to oil of 6:1 (obtained after simulation) is used. A desired quantity of oil was placed in the dry big tank equipped with a magnetic stirrer and thermometer (Figure 1). In the small tank, the methanol was mixed with the catalyst until all of the catalyst dissolved. Then, the mixture was added to the oil. In order to achieve full conversion, the transesterification tests were conducted with some chosen fixed parameters. These ones result from theoretical simulations compared with literature data. So, a temperature of 60°C, with two hours of vigorous agitation (159 prm) are used. At the end of the reaction, sedimentation process is applied to separate the mixture of esters and glycerol obtained. The separated ester was washed several times with distilled water to remove the catalyst and unreacted methanol, until a neutral pH was obtained, then the translucent ester obtained was finally dried.

Results and Discussion

Theoretical results

Several authors have studied the influence of temperature on transesterification reaction with experiments at different temperatures: the rate of reaction increases [14] with temperature [10,19]. With the theoretical approach that we developed, the simulation gives the same conclusions as shown by drawing the yield curve for several values of temperature (Figure 2). It can be noted that the temperature positively influences the final yield, but this influence diminishes beyond 60°C. In fact, the yield will be negatively impacted at a given temperature value because the saponification reaction becomes increasingly significant as it warms up. The model can therefore better reflect the impact of temperature on transesterification and help confirming the current value of 60°C, chosen as optimum temperature.

According to literature, the molar ratio Alcohol/Oil (n) has a positive effect on the yield of the reaction, even if it is not so significant according to some authors [18,20]. Hence the need to analyze the ratio to verify its real influence and find an optimal value, given the costs incurred in the recovery process from alcohol. Figure 3 obtained from our modeling is used to display the influence of the molar ratio Alcohol/Oil on the yield. It can be noticed that it increases with the molar ratio and therefore, the choice of an optimal value of n, remains dependent on the combination of various parameters of transesterification and a trade-off between maximum productivity and cost of production. The values n=6 and n=7 appear to be the best trade-off, which is in the same line with the literature [9,15].

The amount of the catalyst is also a factor that has a positive impact on the reaction rate, while this impact is negative on the yield. Indeed, the more the amount of bases, the greater the saponification is. Figure 4 represents the conversion rate of triglycerides to biodiesel according to time and molar ratio p=catalyst/Oil. We notice that the yield of the reaction increases with the ratio p, up to an optimum approximately around p=0.0785 (i.e. KOH mass=0.3 wt% Oil). After this value, the yield falls down. The decrease is due to the saponification reaction which has more free bases as p increases.

Transesterification tests results

The transesterification tests to validate the theoretical approach were conducted on the pilot plant developed in our laboratory (Figure 1).
The conditions and parameters used for the esters preparation result from theoretical simulations which were compared with data found in the literature, and were the same for all the vegetable oils used in this study.

Many theoretical and practical simulations were carried out, but, the results presented here refer to: a temperature of 60°C, with two hours agitation at 159 rpm; a total molar ratio of methanol to oil of 6:1; a ratio of catalyst to oil of 0.0785 (m_KOH=0.5% by weight of oil). The results obtained for jatropha, palm and soya oil after transesterification tests are summarized in the figures below.

According to literature, the catalysts NaOH and KOH are basic catalysts the most used and the most efficient in homogeneous catalysis. To focus on the choice of catalyst to be used, we conducted several transesterification tests on different vegetable oils, using NaOH and KOH. It appears for all the oils tested, that the catalyst KOH gives better yields (Figure 5). This could be explained not only by the physical and chemical differences of the two components, but also by the fact that potassium dissolves easily in alcohol in the preparation of the catalyst (melting temperature 63°C) than sodium whose melting temperature is 98°C (far from 60°C which is the temperature used for transesterification tests).

The use of potassium hydroxide is also more suitable since, at the end of the reaction, the mixture can be neutralized with phosphoric acid to afford potassium phosphate, which is a fertilizer.

The data presented in Figure 6 summarize the results obtained after transesterification of 5 liters of oil (soya, palm, jatropha), taking into account the experimental conditions and parameters mentioned above. It appears from these results that the proportions of biodiesel obtained with different samples of vegetable oils are: 93.4% for soya, 94.2% to 96.4% for palm and jatropha (Figure 6). As the conditions and parameters used for the transesterification are the same for all the vegetable oils considered in this study, the explanation on why some oils are yielding slightly better conversion can be found in the physico-chemical properties of the initial vegetable oils and also in the specific parameters of theses ones, like viscosity, saponification and values of fatty acids of oils [6]. These results are satisfactory and encouraging and can stimulate the establishment of small decentralized production units, with the clear advantage of good quality biodiesel production, with local resources and for local use.

The good yield presented by the jatropha oil transesterification (96.4%) is particularly interesting, as it is non-edible oil. Therefore the production of this vegetable oil is not competitive with those of foodstuffs and the high resistance of this plant in arid climate, confer to jatropha a considerable energy potential to be explored. Countries such as Burkina Faso, facing lack of access to energy, land-locked, with more or less arid climate, should explore the possibility of producing these crops and develop strategies to popularize them as alternative or complementary energy sources, particularly for rural use. Several programs of jatropha are in progress in Burkina Faso.

**Biodiesel analysis**

The primary criterion for biodiesel quality is that it matches appropriate standards that are EN 14214 for Europe and ASTM D6751-02 for USA. These standards present the property values required for a mixture of methyl esters to be considered biodiesel. When these limits are met, the biodiesel can be used raw or blended with gasoil in most modern engines without modification, while maintaining the engine’s durability and reliability.

Table 1 shows the viscosity, density, acidity and water content of three methyl ester biodiesels obtained by transesterification process of soya, palm, and jatropha oils. The viscosity is one of the most important parameters of biofuels, since it affects the operation of fuel injection equipment, particularly at low temperatures, when the increase in viscosity affects the fluidity of fuels. Transesterification process allows to considerably decrease the viscosity values of the original vegetable oils. The viscosity of the three vegetable oils used in this study ranged from 24.1 mm²/s to 61 mm²/s. After transesterification, the viscosity (at 40°C) of the esters obtained was reduced to 4.06 for palm, 4.79 for jatropha, and 5.53 mm²/s for soya. These are in concordance with the

<table>
<thead>
<tr>
<th></th>
<th>Density (25°C)</th>
<th>Viscosity (40°C)</th>
<th>Acidity (%)</th>
<th>Water content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jatropha</td>
<td>0.876</td>
<td>4.79</td>
<td>0.11</td>
<td>0.08</td>
</tr>
<tr>
<td>Soya</td>
<td>0.882</td>
<td>5.53</td>
<td>0.09</td>
<td>0.07</td>
</tr>
<tr>
<td>Palm</td>
<td>0.870</td>
<td>4.06</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td>Commercial gazol</td>
<td>0.856</td>
<td>3.37</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

Table 1: Properties of the synthesized biodiesels and comparison with a conventional diesel.
specification of biodiesel according to EN 14214 and ASTM D6751 standards. These standards generally limit the viscosity of biodiesel around 3.5 to 5 mm²/s [13,21].

The densities of the three vegetable oils and their biodiesel esters had also been analyzed. The densities of the esters obtained were significantly lower than that of source oils and varied from 0.870 for palm to 0.882 g/ml for soya. These results are also consistent with EN significantly lower than that of source oils and varied from 0.870 for palm to 0.882 g/ml for soya. These results are also consistent with EN standards, which limit the viscosity of biodiesel to 3.5 to 5 mm²/s.

As it can be seen in Table 1, acceptable values of acidity and water content were also obtained after transesterification of the vegetable oils used (soya, palm, jatropha).

Esters characterization–chromatography results

The quality control of biodiesel is very important for the success of its commercialization. Determining fuel quality involves the characterization and the quantification of by-products or reagents which can still be present in the final product. Chromatography and spectroscopy are usually the analytical methods the most used for biodiesel characterization, but according to Mittelbach [22], only GC meets all requirements for the determination of low contents of mono-, di-, and triglycerides in biodiesel.

During biodiesel production, the triglycerides are first converted into diglycerides, which in turn are converted into monoglycerides, and then into glycerol. The ASTM specification requires a total glycerol content above 0.24% in the final biodiesel, it is measured using a gas chromatographic method.

The analysis method is based on gas chromatography (GC), and uses the European standard EN-14105 to determine the free glycerol and residual mono-, di-, and triglycerides in the fatty acid methyl esters obtained from our transesterification pilot.

According to Knothe [23] and Mittelbach [22] the amount of glycerol and glycerides is a major factor in determining fuel quality. Glycerol can cause damage to the engine as well as hazardous emissions. As a consequence, the quality control of this compound is essential. According to ANP legislation, and EN standard, 0.02% of free glycerol is the maximum quantity permitted [13]. The following results presented for soya, jatropha and palm esters, in Tables 2 to 4 are less than 0.005, so in agreement with required standards [13]. The proportion of total glycerol obtained in each case of the synthetized methyl esters (Tables 2 to 4) are also in concordance with EN 14214 whose limit is 0.25 and with ASTM D6751-02 whose specification is 0.24.

The quantification of mono-, di-, and triglycerides of the palm and jatropha esters provides values which are all included in EN standards (Tables 2 to 4), and so, gives indications on the quality of the production process.

<table>
<thead>
<tr>
<th>Type</th>
<th>Results</th>
<th>EN 14214 standard</th>
<th>ASTM D 6751 standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoglycerides</td>
<td>0.66</td>
<td>0.80</td>
<td>_</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>0.136</td>
<td>0.20</td>
<td>_</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>0.31</td>
<td>0.20</td>
<td>_</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>&lt;0.005</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Total Glycerol</td>
<td>0.24</td>
<td>0.25</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 2: Glyceric composition of soya ester.

<table>
<thead>
<tr>
<th>Type</th>
<th>Results</th>
<th>EN 14214 standard</th>
<th>ASTM D 6751 standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoglycerides</td>
<td>0.99</td>
<td>0.80</td>
<td>_</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>0.18</td>
<td>0.20</td>
<td>_</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>0.15</td>
<td>0.20</td>
<td>_</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>&lt;0.005</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Total Glycerol</td>
<td>0.19</td>
<td>0.25</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 3: Glyceric composition of jatropha ester.

<table>
<thead>
<tr>
<th>Type</th>
<th>Results</th>
<th>EN 14214 standard</th>
<th>ASTM D 6751 standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monoglycerides</td>
<td>0.56</td>
<td>0.80</td>
<td>_</td>
</tr>
<tr>
<td>Diglycerides</td>
<td>0.16</td>
<td>0.20</td>
<td>_</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>0.14</td>
<td>0.20</td>
<td>_</td>
</tr>
<tr>
<td>Free glycerol</td>
<td>&lt;0.005</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Total Glycerol</td>
<td>0.19</td>
<td>0.25</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Table 4: Glyceric composition of palm ester.

Figure 7 shows chromatograms of the transesterification products obtained by GC instruments. These chromatograms gave details of the peaks of the esters compounds and revealed that the composition of the methyl esters analyzed closely approximated the general characteristics seen in the standard transesterified mixtures [9,14,24,25].

The results obtained within this study correlated with several physical properties limited by EN 14214 and ASTM D6751 standards, so, ensured our biodiesels quality and the performance of the transesterification pilot developed. Meeting a quality standard is essential for proper performance of the fuel in the engine and will be necessary for a widespread use of biodiesel.

As technological application of biodiesel production and characterization is adaptable in West African countries such as Burkina Faso, a trade-off between the economic justification of biodiesel usage and its real opportunities must be found. To summarize a comprehensive assessment of the potential of biofuels in developing countries, three editions of ‘International Conferences on Biofuels in Africa’ were organized by our Institution in partnership with CIRAD.
(International Center for Agricultural Research for Development) and the government of Burkina Faso [3,4]. The aim of these conferences is to examine a variety factors such as the technical, economic, social, environmental and political aspects of biofuels; availability of acreage and potential competition with existing land-use patterns; expected cost differences between bio and fossil fuels; etc.

**Conclusion**

From the transesterification tests performed for various oils, it appears that the optimums parameters resulting from theoretical simulations, lead to biodiesels of good yields and good quality, which otherwise, point out the efficiency of the developed pilot.

The quantification of tri-, di-, monoglycerides, free and total glycerol and the characterization of the biodiesel samples in regards to their viscosity, density, etc. give values which meet the requirements of biodiesel standards. These results show that, it is possible to make biofuel programs which might present opportunities for African countries.

**References**