CHARACTERISATION AND OPTIMISATION OF BIODIESEL'S PRODUCTION FROM WASTE COOKING OIL

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We studied the transesterification of two types of waste cooking oil (WCO), with methanol and ethanol using NaOH. Also the physical characteristics of produced biodiesel were studied and compared with the European standard EN 14214. The WCO used in this study was collected from the Ecole des Mines de Nantes university's restaurant. We used to search the optimum conversion ratio, combining four variables: temperature of reaction, catalyst amount, time of reaction and alcohol to oil molar ratio, the effect of free fatty acid content in the oil and the type of alcohol used in the reaction were also studied.

Keywords: biodiesel, waste cooking oil, transesterification, biodiesel characterization.

1. Introduction

In Europe, 1.5 Million tonnes of waste animal fat (WAF) are produced annually [1]. WAF and WCO are considered as non dangerous wastes [3]. These wastes mustn't be left or burned into the open air, neither poured into the waste water evacuation's networks [4].

The majority of world's energy consumption is based on the fossil fuels resources. Having regard to the rate of actual energy consumption, these resources will be nearly consumed [5]. So the studies are now focused on new energy sources that can replace oil and that can meet emissions standards that are increasingly strict.

During the 1990 biofuel production has started in several European countries and flourished in a meaningful way. In 2003 the European Union (EU) has set a target of the contribution of biofuels to 5.75% of its energy consumption by 2010 and 20% in 2020. France has adopted the EU target and has set more ambitious goals, in 2008 biofuels have represented 5.75% of its energy consumption and it tries to reach 10% in 2015, making an advance of 2 years on European targets [9, 10]. Biodiesel represents 82% of produced biofuels in the EU [9]. It is one of the most available sources of renewable energy, it is non toxic, biodegradable, its heating value is important, it has a low see zero sulfur content and its use in Diesel

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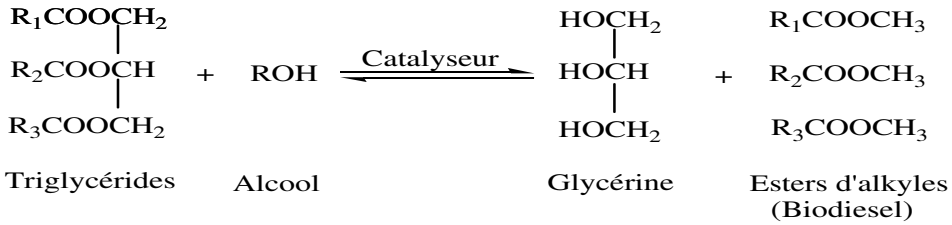
engines reduces soot and unburned emissions [7, 9]. It can be used directly in Diesel engine without introducing any changes to the latter. However, technical problems are related to its flow properties at lower temperatures, the emission of NOx and stability during storage. The most important problem for the moment is its high production's price, raw materials accounts 60-85% of the total price of production [5, 6, 9, 12]. Using fatty wastes as raw material for biodiesel's production may resolve that problem.

Transesterification is a chemical reaction that consists on substituting alcohol groups of an ester by other type of alcohol cf. equation (1). This process is widely used to reduce the viscosity of triglycerides. Transesterification is a reversible reaction, which consists of mixing the reagents, the presence of a catalyst greatly promotes this reaction [5-7, 11-14].

(1)



Several processes have been developed for the production of biodiesel, either by catalysis: acidic, basic, enzymatic or heterogeneous, either by methods that operate without a catalyst at very high temperatures and pressures. The reaction following a basic catalyst is the most widespread in the industrial field, for its low output price and speed of reaction. But the problem of this method is the sensitivity of the response to moisture and the levels of free fatty acids which form soaps in the presence of a strong base [6, 7].

2. Experiments

In a glass Erlenmeyer we mix the waste cooking oil (WCO) with a solution of premixed caustic soda and methanol. This solution is stirred by means of a magnetic stirrer under constant temperature for a while to make sure that the reaction will be accomplished. To ensure the closed systems conditions, we introduced the thermometer through a rubber seal which sealed the neck of the Erlenmeyer. We studied the influence of the following parameters on the reaction: the temperature, alcohol excess or the oil to alcohol ratio, the concentration of the catalyst (caustic soda) and the time of reaction. At the end of each reaction we pour the products on a separatory funnel to separate the glycerol from the biodiesel. After that we wash the biodiesel several times with water, to be sure that all the residual catalyst and methanol will be washed out. Drying of product is enshured using anhydrous calcium chloride, after that the biodiesel is filtered and

weighted. Considering the equation (1) the yield of the reaction is calculated as the percentage of the weighted product from the expected weight from the total reaction. At the end of these operations, we studied the physico-chemical aspects of the produced biodiesel.

2.1. Raw materials

WCO: the WCO was collected from the university's restaurant of the Ecole des Mines de Nantes (EMN). Its composition was described on the products wrapping. And it was as follows: 45% palm oil, 45% sunflower oil of which 35% are enriched with oleic acid, and 10% of rapeseed oil. We had two kinds of WCO: WCO1 which was used to make French fries and WCO2 which was used to cook meat and fishes. The characteristics of these WCOs are described in table 1.

Table1

Characteristics of WCOs

Acid value (mg KOH/g)		Moisture	Viscosities @40°C	HHV	Melting point	density
WCO1	0,8-1,4	<0,05%	μ = 32,9 mPa.s ν = 37,8 mm²/s	40 MJ/kg	30°C	0,87 kg/l
WCO2	6,5					

μ = dynamic viscosity, ν = cinematic viscosity.

The following materials where purchased from sigma Aldrich laboratory:
Methanol: 99% of purity, Ethanol: 99% of purity, Caustic soda: 99% of purity and Calcium chloride: 99% of purity

2.2. Transesterification of WCO1

2.2.1. Methyl esters:

We studied the effect of: temperature (30, 40, 45, 50 and 60°C), oil to alcohol ratio (1:6, 1:9 and 1:12), and catalyst amounts were varied also (0.5, 0.6, 0.8 and 1% of total oil weight) and the time of reaction (30, 45 and 60 minutes).
We started with the following combination: 40°C, with 1:6 oil to alcohol ratio (based on literature [6, 7, 13, 14]), with 1% of catalyst amount for 60 minutes, and we had a reaction yield of 79.2%. Then we tried to minimize the catalyst amount to reduce the cost of production. But we had a lower yield of biodiesel (cf. figure 1), so we kept the value of 1:6 as optimal value.
Then we studied the effect of oil to alcohol ratio, at 40°C with 1% of catalyst amount for 60 minutes by varying the oil to alcohol ratio, we obtained the following results: 79.2% with 1:6, 80% 1:9 and 82% with 1:12 so we kept the 1:6

value, because we had a small increase of yield by increasing largely the amount of alcohol.
The temperature's effect was studied keeping the optimal values of oil to alcohol ratio and the catalysts amount for 60 minutes under stirring. At 60°C (the temperature recommended by literature because it is near to methanol's ebullition point [6, 13, 14]) and 50°C we had a gel and soap formation without any phase separation. At 45°C and 40°C we had conversion ratios of 75% and 79.2% respectively. And at 30°C we did not notice any phase separation, which means that we had a small conversion ratio. So we adopted the temperature of 40°C as optimal value.
We tried to minimize the time of reaction, so we used to lead the reaction for 45 minutes and for 30 minutes. We had almost the same conversion ratio, but we had a problem of reproducing the reaction at 30 minutes so we took the value of 45 minutes as a compromise between cost and quality of product. Figure 1 represents the effects of studied parameters on the reaction.
At the end of our work, we received a WCO with low acid number (WCOLA) it has a value of 0.8 mg KOH/g. With this acid, at the mentioned optimal conditions we had a yield of 97%.

2.2.2. Ethyl esters

The same approach was used with WCO1 and WCOLA in substituting the methanol with ethanol. The optimal values of temperature and catalyst amount have remained the same, although, the oil to ethanol ratio changed. For a ratio of 1:6 the reaction did not take place, for a ratio of 1:9 we had a yield of 75.9% and with 1:12 the yield decreased to 69%. And the reaction time required was 60 minutes. With WCOLA with these new conditions we had a yield of 95%.

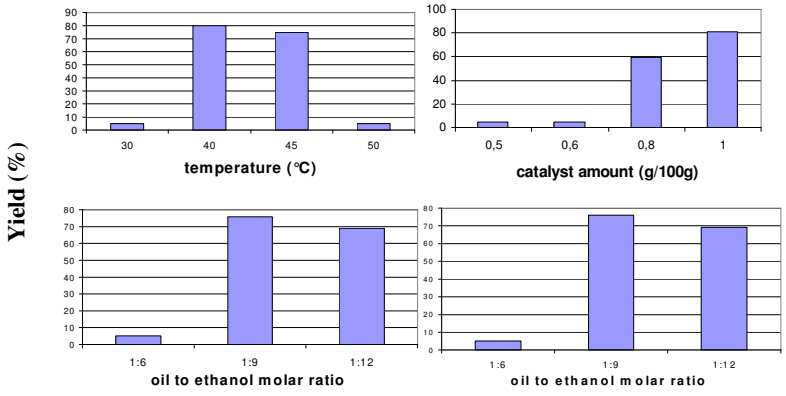


Figure 1. Effect of variables on biodiesel's yield from WCO1

2.3. Transesterification of WCO2

2.3.1. Methyl esters

This time we used the same approach as for WCO1. Starting from the optimal conditions reached above, the reaction hasn't occurred, so we started by varying the catalyst amount, because we knew that the high acid content reacted with the catalyst to make soap so, it neutralized its effect [7]. By increasing the amount of catalyst, we will overcome this problem. So we tried the amounts of (1.25, 1.5 and 2%) of catalyst. Between 1.25 and 1.5 we had the better yields without noticing a big difference between them. But with 2% we had soap and gel formation. So we fixed the value of 1.25 as optimal value.
In order to optimize the oil to alcohol ratio, we tried the following values: 1:6.5, 1:7.5 and 1:9. The maximum yield was of 72.5% for 1:6.5, with values above 1:6.5 we had lower yields caused by the tendency of esters to make emulsions with glycerol at higher amounts of alcohol [7].
The effect of temperature was also studied and we had the best yield at 45°C.
The required time of reaction remained 45 minutes.

2.3.2. Ethyl esters

The transesterification reaction of WCO2 using ethanol failed after several experiments, we had always gels and soaps without any phase separation observed. So we conclude that the production of ethyl esters is more sensitive to acid content than that of methyl esters. We will discuss that later in the conclusion of this paper.

2.4. Physico-chemical characteristics of produced biodiesel

The produced biodiesel was subject of several tests to determine its characteristics:
Viscosity: using a vibro-viscosimeter SV-10 made by AND, we measured the dynamic viscosities of ethyl and methyl esters between 25 and 60°C. The results are gathered in table 2 and the curves of dynamic viscosities are plot in figure 2.
Acid value: using the volumetric titrimetry we measured the values of acidity of the produced biodiesel, we had values lower than 0.1 mg KOH/g
Water content was determined using distillation with Xylene method, and we did not notice any presence of water in our samples of produced biodiesel.
Elemental analysis was conducted using the device « CHNS-O ANALYSER FLASH 1112 series EA », we had the following composition:

76% C, 12.8% H, 0% S, 0% N and 11.2% O. So we concluded the empirical formula of the product: $C_9H_{18}O$.
The higher heating value (HHV) = 40MJ/kg. it was measured with the isoperibolic calorimeter « PARR 6200CLEF ». Basing on the empirical formula of the biodiesel we concluded the lower heating value (LHV). LHV = 37 MJ/kg.
Flash point = 160°C, it was measured by the « PENSKY MARTENS NPM440 ».

3. Conclusions

In this work we succeeded to elaborate biodiesel from waste cooking oil by base catalyzed transesterification reaction, using two types of alcohol, methanol and ethanol. Also we determined the optimal conditions for these reactions, depending on WCO and alcohol types. We studied the effects of: temperature, catalyst amount, alcohol's type and excess, time of reaction and the acidity of WCO. This study conducted to the following conclusions:

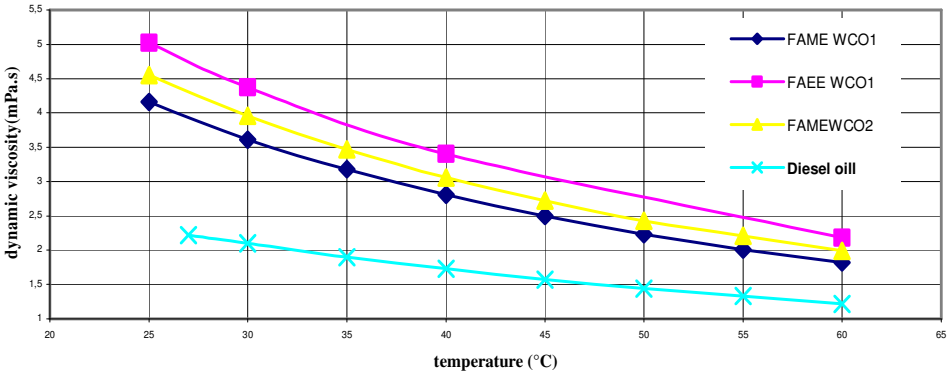


Figure 2. Dynamic viscosities of biodiesel compared to diesel oil

The temperature has an essential effect on the speed of reaction and the yield of biodiesel. Increasing temperature accelerates the reaction and increases biodiesel's yield [6, 7, 13, and 14] but in the other hand, it promotes the parallel reaction, the saponification which could stop the transesterification [6, 7]. From the literature we noted that the optimum temperature depends on oil's type, but in general it is recommended to be near to the alcohol's boiling point [6, 13, and 14]. But *Dreger* [7] recommends the temperature of 40°C to avoid saponification. In our study, the results were congruent with *Dreger*'s notes. That comes probably from the fact that the WCO is acid, contains impurities and it was subject of thermal treatment which maybe affected its structure.
The catalyst amount is very important in the reaction. Without catalyst, the reaction does not occur unless if used the supercritical alcohol method which requires high temperatures and pressures. For the case of using a base catalyst,

increasing the catalyst's amount accelerates the reaction but beyond a certain value saponification reaction occurs [7, 11, 13, 14].
Transesterification reaction, as mentioned above, is a reversible reaction between 1 mole of triglycerides and 3 moles of alcohol. The excess of alcohol pushes the equilibrium in the direction of forming biodiesel and accelerates reaction [5-8, 14]. *Arrowsmith, Trent and Percy* [7] noticed that increasing the excess of alcohol could decrease the required amount of catalyst, but it enhances the formation of emulsions of biodiesel in glycerol phase which decreases the recovered fuel. They also noticed that this problem is worst with ethanol, and that explains the lower yields of ethyl esters and the decrease in recovered biodiesel when we increased the excess of ethanol. *Trent* also noticed that the esters produced using ethanol or longer chain alcohols have more tendencies to form gels in presence of formed soap. *Percy* also noticed that are good emulsifiers that can make emulsions of alcohol, oil and esters which stops the reaction [7]. Considering the notes of *Trent* and *Percy* in our case, could explain the decreasing of yield while the acid value of oil increases and the tendency of ethanol to have lower yield with WCO1 and the formation of gel and soaps with WCO2.
The acid content of oil has a negative effect on the whole process. First of all, the free fatty acids forms soap with the catalyst, which neutralizes its effect. That increases the required amount of catalyst. Secondly the formation of soap during reaction makes emulsions which capture the alcohol and reduce the amount that enters in reaction. Finally, during the separation and washing phases, emulsions induce the esters to the glycerin and water phases respectively, causing a loss in recovered biodiesel.
The established optimum conditions for the reaction are listed in table 2.

Table 2

Optimal conditions for biodiesel's yield

Oil	Alcohol's Type	Acidity mgKOH/g	Molar ratio	Temperature (°C)	Catalyst amount	Time	Yield
WCO1	Methanol	1,4	1 :6	40	1%	45 min	81%
WCOLA	Methanol	0,8	1 :6	40	1%	45 min	97%
WCO1	Ethanol	1,4	1 :9	40	1%	60 min	72,5 %
WCOLA	Ethanol	0,8	1 :9	40	1%	60 min	95%
WCO2	Methanol	6,5	1 :12	45	1,25%	45 min	79%

The methanol is better to be used in transesterification when we have high acid content in the raw material, because we saw how the acidity affects dramatically the yield in biodiesel when we used ethanol.
The physical and chemical properties of produced biodiesel were almost the same and independent of the acidity of raw materials. We had a slight difference

between ethyl esters and methyl esters and it was going on with literature [9]. Biodiesel's characteristics undergo with European norm EN 14214 (cf. table 4)
The LHV of the biodiesel is a little bit lower than that of diesel oil. This will induct higher fuel consumption on the engine.

Table 3

Characteristics of biodiesel compared to European norm EN 14214

	unit	min	max	produced Biodiesel
cinematic Viscosity	mm²/s	3,5	5	3,5 - 4
Flash point	°C	110	-	160
Water content	mg/kg	-	500	0
Acid value	mg KOH/g	-	0,5	<0,1
Sulfur content	mg/kg	-	10	0

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