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Biodiesel From Waste Vegetable Oils

Rodica E. Ceclan*[a], Adrian Pop[a], Mihail Ceclan[a]

[a] Univ. Politehnica of Bucharest, Polizu Str. 1, 011061 Bucharest, Romania;
rceclan@yahoo.com

The valorisation of waste and bio-waste is an important mean of the transition of European Economy to a Green Economy, essential for delivering a sustainable development and a long term growth.

Waste vegetable cooking oils (WVCO) are urban resources, and one of the most environmentally friendly feedstock for biodiesel, with considerable potential for converting a problematic waste into a value-added product. Biodiesel produced from waste grease results in an 86 % reduction in greenhouse gases, compared to petro-diesel, according to EPA's Renewable Fuel Standards Program Regulatory Impact Analysis (February 2010). The WVCO can be valorised as biofuels by a transesterification reaction with a low carbon chain alcohol.

The paper presents an experimental study of the transesterification reaction of WVCO with methanol, leading to biodiesel. The influence of different operational parameters, as WVCO type and quality, chemicals adding way, temperature, mixing conditions, catalyst type and quantity, is presented. The main factors affecting the process are molar ratio methanol/oil, catalyst amount, reaction temperature, and reaction time. A low quality WVCO needs an advanced pretreatment stage, and leads to a decreased yield in biodiesel. The experimental study was conducted using a factorial experimental plan, in order to optimise the quality and the yield of biodiesel.

1. Introduction

Biomass is the only renewable energy resource that can lead to competitive prices for liquid fuels in transport. The main benefits of using this renewable resources are the increased environmental protection, lower emissions, new jobs opportunities, lower level of oil imports (67% of oil is for transportation fuels), increased safety of fuel supply (Demirbas, 2009).

The conversion of renewable biomass in biofuels more and more attractive, and obtaining / using unconventional fuels, such as biodiesel, as alternatives to fossil fuels is an important scientific and technological goal, in a world where pollution has reached more and more alarming levels and oil reserves are becoming more and more limited.

Legislative requirements regarding the restrictions linked with the presence of sources of polluting emissions in fuels, such as sulphur and nitrogen compounds, or aromatic hydrocarbons, are making the technological efforts to remove them from the crude oil fractions difficult and expensive (Demirbas, 2009; Math et al., 2010, Waste Framework Directive, 2006).

Alternative biofuels are produced either from renewable resources, (by higher processing of waste - sawdust, straw), from plants cultivated for this purpose - rapeseed, soybean, castor, etc., or from waste fat materials.

Biodiesel can be obtained from a variety of materials. These materials include vegetable oils obtained from: soybean, cottonseed, palm, peanut, rapeseed, sunflower, coconut and animal fats (tallow) as well as residual oil (e.g. waste vegetable oils, such as used cooking oils). The choice of feedstock depends on geographical location. Depending on the origin and quality of raw materials production process

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changes may be required. The advantage of these types of raw materials is the possibility of their periodic renewal; agriculture and food industry provides thus a full and integrated opportunity of valorizing these cultures (Canakci, 2007; Refaat, 2010).

Biodiesel consists in a mixture of methyl and ethyl esters of fatty acid as lauric, myristic, palmitic, stearic, linoleic, oleic and linolenic. The manufacture of this type of fuel can be achieved by a process of catalytic transesterification of vegetable crude or waste oils (sunflower, soybean, rape, etc. oils) with methanol or ethanol. The resulting esters have physical - chemical characteristics similar to those of fossil diesel, where they are completely soluble (Anh et al., 2008; Pagliaro, 2007).

Biodiesel is the first biofuel produced in the European Union on an industrial scale. The European biodiesel industry is already a well-defined and independent sector (Waste Framework Directive, 2006).

International standards refers to biodiesel as coming only from esterification of vegetable oils or animal fats; the name applies both to esters (B100) and to ester-diesel blends (B20-20% ester, 80% diesel). Biodiesel can be used in normal or modified diesel engines (Demirbas, 2009, Waste Framework Directive, 2006).

The paper presents a study of the transeterification of waste vegetable cooking oils, aiming at obtaining biodiesel.

2. Experimental

2.1 Materials

The transesterification process was realized using three types of waste vegetable cooking oils (WVCO): households, McDonald's fast foods, other fast-food networks from Bucharest, Romania. Methanol was used as transesterification agent, and KOH as alkaline catalyst.

2.2. Method

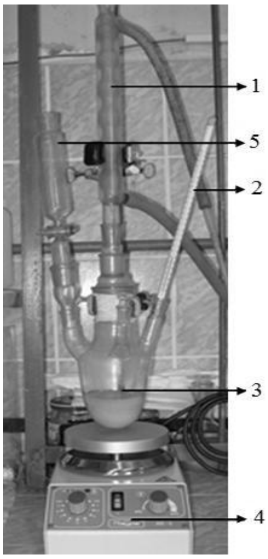

Figure 1: Experimental plant
1-Condenser; 2-Thermometer; 3-KPG flask; 4-magnetic stirrer/ heater; 5-dropping funnel

The experimental setup, presented in figure 1, consists in a 500 ml three necks KPG flask, provided with magnetic stirrer, dropping funnel, thermometer, and reflux condenser. Erlenmeyer flasks with magnetic stirrer were used for preliminary dehydration of WVCO. Separation of the dehydrated oil was realized by vacuum filtration. Separation funnels were used for the separation and purification of the obtained biodiesel. A two level factorial experimental program has been used to study the optimum conditions for the transesterification process.

A pretreatment stage was needed for dehydrating the used cooking oil. The WVCO was dehydrated by using anhydrous calcium chloride, and filtered under vacuum after drying.

Either potassium hydroxide dissolved in methanol (Method 1) was added to vigorously stirred WVCO, or WVCO (Method 2) was added on potassium hydroxide dissolved in methanol under vigorous stirring. Stirring was continued for one hour under certain reaction conditions (temperature, stirring speed). After one hour, stirring is stoped and the mixture is cooled at room temperature. The cooled mixture was transferred to a separatory funnel and the glycerol was allowed to separate for a minimum of 2-3 hours. After draining off the glycerol, the methyl ester was transferred into a clean separatory funnel. It was subjected to repeated washed with water, for removing the methanol, KOH and traces of glycerol. The ester was dehydrated on anhidrous calcium chloride, and filtered after drying.

3. Results and Discussions

Studies on transesterification reaction (TE) conditions showed that the main parameters influencing the reaction are: molar ratio methanol / WVCO, temperature, reaction time, quality of WVCO, order of adding reactants, catalyst quantity, stirring speed. Optimal values for obtaining maximum conversion of triglycerides into methyl esters are depending also on physical-chemical characteristics of WVCOs.

3.1 WVCO quality

A very deteriorated WVCO (source – different Romanian fast-food networks) need a more advanced pretreatment stage (dehydration, filtration), the yield in biodiesel is much lower, and a small density difference makes the separation of phases more difficult. Intermediate results were obtained by using as raw material McDonald's WVCO, and the best results by using the household WVCO.

3.2 Reactants' adding order

Under vigorous stirring, two reactants' adding order possibilities were used: method 1, where potassium hydroxide dissolved in methanol was added to vigorously stirred WVCO, and method 2, were WVCO was added on potassium hydroxide dissolved in methanol.

The permanent excess of catalyst and alcohol ensured by method 2 shifts the reaction equilibrium to higher biodiesel yields.

3.3 Methanol / WVCO molar ratio

Table 1 presents the reaction yields under different methanol/WVCO molar ratios at different moments. Figure 2 shows the influence of the molar ratio of the reactants on the reaction yield. Higher MeOH/WVCO molar ratio and higher reaction time leads to higher biodiesel yields. A 12:1 MeOH/WVCO molar ratio leads to maximum yield in methyl ester.

Table 1:
TE reaction yields versus time and molar ratios

Pos.	*Time [s]*	*Yield [%]*		
		Methanol / WVCO Molar Ratio		
		6:1	*9:1*	*12:1*
1	300	64	65	74
2	600	65	68	76
3	900	67	70	78
4	1200	69	72	82
5	1800	72	75	84
6	2400	74	78	85
7	3000	75	80	86
8	3600	77	82	88

Table 2:
Influence of catalyst amount

Pos.	*Time [s]*	*Yield [%]*			
		% KOH			
		0.25	*0.5*	*0.75*	*1.00*
1	300	32	64	63	68
2	600	40	67	68	71
3	900	44	70	71	73
4	1200	49	72	73	77
5	1800	52	74	74	79
6	2400	53	74	75	81
7	3000	57	74	78	83
8	3600	58	76	79	84

3.4 Catalyst amount

The amount of catalyst was established as a percent of the WVCO.

Table 2 and figure 3 present the influence of the catalyst amount on the process yield. A small catalyst amount leads to an incomplete conversion of triglycerides into methyl esters and to a low biodiesel yield. The maximum biodiesel yield was obtain using a KOH per cent of 1 % of the amount of WVCO. An excessive amount of KOH may facilitate the hydrolysis of the formed methyl esters, so the yield in biodiesel would be decreased.

3.5 Temperature

The reaction was conducted at 37 ^{0}C, 50 ^{0}C, 65 ^{0}C. Table 3 and figure 4 show the influence the reaction temperature has on the yield of biodiesel.

The optimum reaction temperature is 65 ^{0}C. Higher temperature lead to lower biodiesel yields, because the separation of the reaction mass phases is more difficult, involving high biodiesel losses.

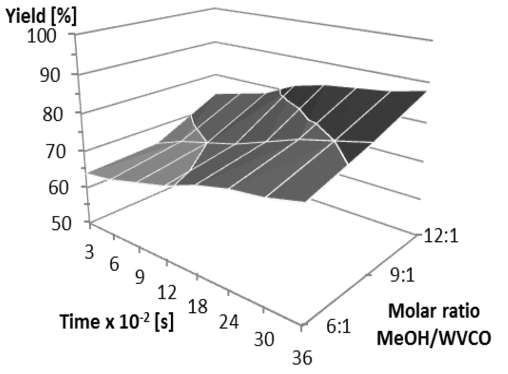

Figure 2: Influence of MeOH/WVCO molar ratio

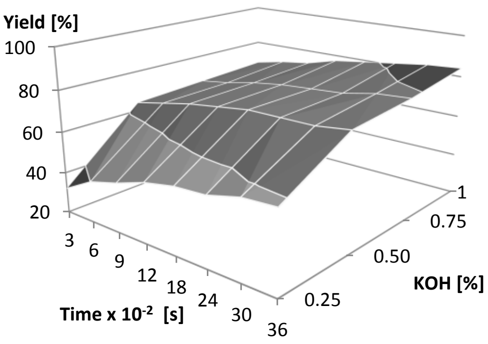

Figure 3: Influence of catalyst amount

Table 3: Influence of temperature

Pos.	Time [s]	Yield [%]		
		Temperature [^{0}C]		
		37	50	65
1	300	51	71	73
2	600	58	75	78
3	900	62	76	79
4	1200	64	77	83
5	1800	67	79	85
6	2400	68	80	87
7	3000	71	82	87
8	3600	73	85	88

Table 4: Influence of stirring speed

Pos.	Time [s]	Yield [%]		
		Stirring speed [rpm]		
		180	300	600
1	300	65,00	72,00	73,00
2	600	67,71	72,50	78,00
3	900	71,14	76,86	79,00
4	1200	73,00	77,50	80,29
5	1800	74,57	82,57	84,86
6	2400	74,57	84,86	86,00
7	3000	75,00	85,50	86,00
8	3600	75,71	86,00	87,00

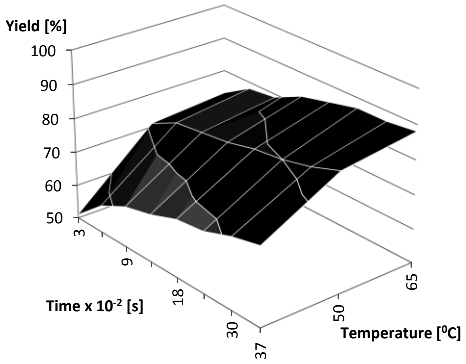

Figure 4: Influence of temperature

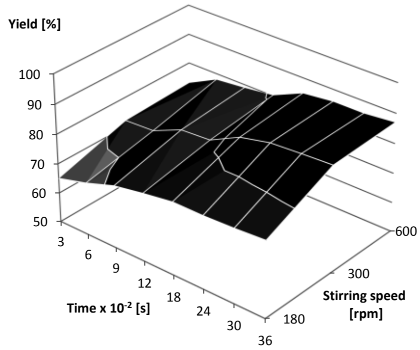

Figure 5: Influence of stirring speed

3.6 Stirring speed

Following stirrer speed were studied: 180 rpm, 360 rpm, and 600 rpm. The best results were obtained at 600. The influence of stirring speed on biodiesel yield is demonstrated in Table 4 and Figure 5. Some physical chemical characteristics of the obtained biodiesel, and the standards followed for their determination are presented in Table 5.

Table 5: Biodiesel physical chemical characteristics

Characteristic	Unit	Value	Limits min	Limits max	Standard
Density (15 ^{0}C)	kg/m^3	0.875	860	900	EN ISO 3675
Kinematic viscosity (40 ^{0}C)	mm^2/s	4.6	3.5	5.0	EN ISO 3104
Inflamability	^{0}C	115	120	-	ISO/CD 3679
Water	mg/kg	196	-	500	EN ISO 12937
Methanol	%(w/w)	0.1	-	0.2	Pr EN 14105
Total glycerol	%(w/w)	0.24	-	0.25	Pr EN 14105

3.7 Factorial experiment

In order to study the influence of different process parameters on the process, end their reciprocal influences, a full 2^3 factorial design was applied (Bautista, 2009; VIcente, 2007).

The selected factors were MeOH/WVCO molar ratio, catalyst amount (% by weight of WVCO), and temperature, and the selection was based on the results of the above mentioned experiments. The selected response is biodiesel yield.

All the experiments were carried out at 600 rpm, with four replication experiments in the experimental average conditions. The matrix of the factorial experiment and its results (factorial and centre points) are presented in Table 6.

Table 6: Factorial experiment matrix/results

Pos.	X_{MR}	X_T	X_C	Factor X_{MR} Molar ratio	 X_T Temperature [^{0}C]	 X_C Catalist [%]	Result Yield [% - weight]
1	-1	-1	-1	1:6	50	0.5	64.00
2	+1	-1	-1	1:12	50	0.5	68.00
3	-1	+1	-1	1:6	65	0.5	71.00
4	+1	+1	-1	1:12	65	0.5	73.00
5	-1	-1	+1	1:6	50	1	74.00
6	+1	-1	+1	1:12	50	1	77.00
7	-1	+1	+1	1:6	65	1	81.00
8	+1	+1	+1	1:12	65	1	85.00
9	0	0	0	1:9	58	0.75	80.31
10	0	0	0	1:9	58	0.75	80.25
11	0	0	0	1:9	58	0.75	80.05
12	0	0	0	1:9	58	0.75	80.27

The regression equation characterizing the influence of different considered variables on process yield was obtain:

$$Y = 76.16+1.625\ X_{MR} +3.375\ X_T +5.125\ X_C -0.125X_{MR}X_T +0.125X_{MR}X_C +0.375X_TX_C +0.375X_{MR}X_TX_C$$

The regression equation confirms the big influence of the catalyst amount (X_C), and of the reaction temperature (X_T) on transesterifcation reaction yield. The molar ratio MeOH / WVCO (X_{MR}) has the less important influence. The interactions of factors are not important.

4. Conclusions

The study of transesterification reaction of three types of WVCO showed that the main factors affecting the process are the molar ratio methanol / oil, the catalyst amount, the reaction temperature, and the reaction time.

A low quality WVCO needs an advanced pretreatment stage, and leads to a decreased yield in biodiesel.

The yields in biodiesel are higher for high MeOH/WVCO molar ratio and higher reaction time.

A MeOH / UCO molar ratio of 12:1 leads to a maximum yield in methyl ester. The transesterification reaction was not complete for a molar ratio methanol / oil less than the optimum, leading to a low biodiesel yield.

The maximum biodiesel yield was obtain using a KOH per cent of 1% of the amount of WVCO. An excessive amount of KOH may facilitate the hydrolysis of the formed methyl esters, so the yield in biodiesel would be decreased.

Higher reaction temperature decreases the viscosity of WVCO and has a positive influence on the transesterification rate and on reaction time. The optimum reaction temperature is 65 ^{0}C. Higher temperature lead to lower biodiesel yields, because the separation of the reaction mass phases is more difficult, involving high biodiesel losses.

A regression equation was obtained by analysing the data of a 2^3 factorial experiment. The model confirms the big influence of the catalyst amount, and of the reaction temperature on transesterification reaction yield. The molar ratio MeOH/WVCO has the less important influence. The interactions of factors are not important.

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