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A Pilot-Scale Study of Waste Vegetable Oil Transesterification with Alkaline and Acidic Catalysts

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Abstract

Biodiesel is a renewable diesel fuel produced from fats and oils. Waste Vegetable Oil (WVO) is an important feedstock for biofuel production. WVOs availability as wastes from restaurants, workplace canteens and residential users and their utilization will reduce environmental pollution. In the present work, WVO has been transesterified in a pilot plant under different conditions. The assessment of the parameters affecting the biodiesel conversion factor has been investigated, namely catalyst type and concentration and alcohol concentration. In order to maximize the yield of the process and to obtain biodiesel with lower specific gravity, an optimization process has been carried out.

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Nomenclature

FAME	Fatty Acid Methyl Ester
FFA	Free Fatty Acid
WCO	Waste Cooking Oil
WVO	Waste Vegetable Oil

1. Introduction

In recent years the use of Renewable Energy Sources (RES) has strongly grown for two main reasons: the need to reduce the pollutants and greenhouse gases emissions and the shortage of fossil fuels reserves [1, 2].

Many countries have focused on RES developing and the European Union enacted some Directives aimed at renewable energy dissemination. In more detail the European Directive 2009/28/EC, also known as “Directive 20-20-20”, set many climate and energy goals to achieve by 2020: greenhouses gases emissions reduction by 20%, 20% of energy production from renewable sources and energy efficiency improvement in order decrease the energy consumption by 20% [3,4].

In this scenario, biomass represents an interesting alternative to fossil fuels in different sectors. It can be transformed into energy through the main known processes: thermo-chemical, bio-chemical and mechanical extraction; indeed they permit to produce solid, liquid or gas form fuels, e.g. biofuel, that can be used for energy generation [5,6]. Biodiesel is a biofuel characterised by significant environmental benefits, such as biodegradability and renewability [7]. According to the IEA (International Energy Agency) study, biomass, biofuel and waste supplied the 10% of the world total primary energy in 2010 [8].

The energy consumption in transport sector has considerably grown in the last decades, as shown in Fig. 1, reaching the 61.5% of the total final consumption of oil in the world [8], 33% of the total final energy consumption in Europe and 34.4% in Italy (according to Eurostat). The latter and the above mentioned reasons have led biofuels (bio-ethanol and bio-diesel) to be increasingly employed in the transport sector (Fig. 2) [9].

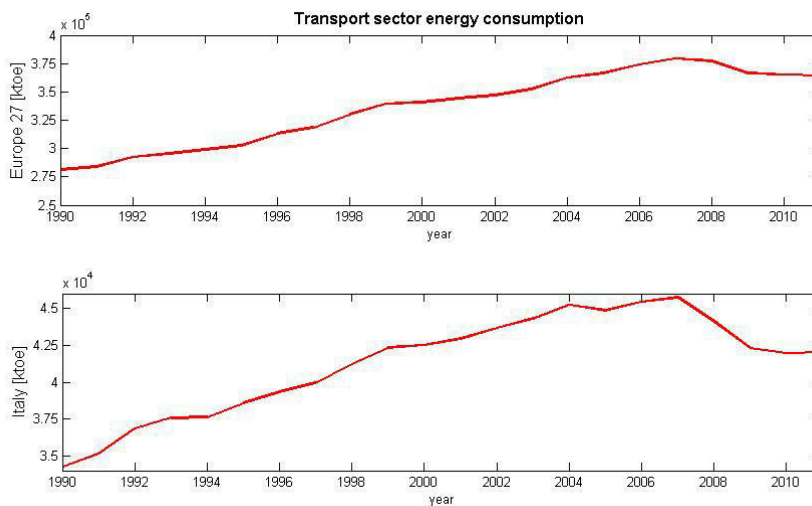


Figure 1. Energy consumption in transport sector in Europe and Italy [ktOE] (according to Eurostat).

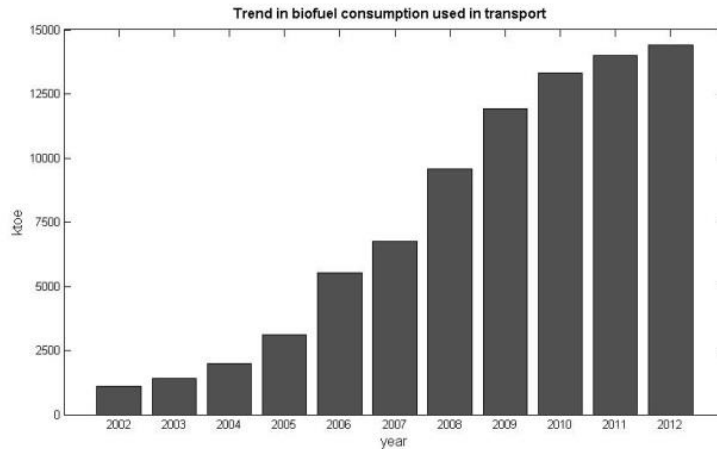


Figure 2. Trend of biofuel consumption in Europe [ktce] [7].

The main biofuel consumptions encompass primarily biodiesel and bio-ethanol. Biofuels have been classified in four categories depending on the developed products, the raw materials used and the technology progress, as reported in Table 1 [10].

Table 1. Biofuels classification [10]

Biofuels	Periods	Raw materials	Products	Possible uses
First generation	2000-2010	Agricultural products and residues	Biodiesel, bio-ethanol, ethanol involution	Standard internal combustion motors
Second generation	2010-2030	Lignin-cellulosic raw materials, materials not including food, agricultural and forest residues	Vegetable oil, biodiesel, bio-ethanol, recycling from biomass or liquid fuel technology products	Flex-fuel motors Thermo-electric (heat-electricity) stations
Third generation	Post 2030	Fluid, gas and solid biofuels using new raw materials not including food and algae	Biofuels produced using genetically modified new plans with high-level oil or cellulose	Integrated biorefinery
Fourth generation	Post 2030	Genetically modified raw materials	No permission to emit exhausts gases to atmosphere after using biofuels	Integrated biorefinery

The European biodiesel consumptions in 2011 are reported in Table 2[9].

Table 2. Biodiesel consumption in Europe - 2011 [9]

Country	Bio-diesel [toe]	Country	Bio-diesel [toe]	Country	Bio-diesel [toe]
Germany	2 143 929	Portugal	310 253	Lithuania	35 372
France	2 034 500	Czech Republic	240 566	Slovenia	31 433
Spain	1 474 331	Finland	102 465	Latvia	14 644
Italy	1 286 450	Romania	138 746	Bulgaria	16 791
United Kingdom	729 077	Hungary	110 003	Cyprus	15 899
Poland	859 604	Denmark	82 502	Estonia	0
Sweden	226 953	Slovakia	97 747	Malta	0
Austria	411 822	Greece	103 396	TOTAL EU	11 018 915
Belgium	273 308	Ireland	67 704	Croatia	2 651
Netherlands	172 327	Luxemburg	39 092		

Biodiesel production typically involves the transesterification of a triglyceride feedstock with methanol or other short-chain alcohols. Vegetable oil contains saturated hydrocarbons (triglycerides) which consist of glycerol and esters of fatty acids. In more detail, when a vegetable oil chemically reacts with an alcohol, it can produce Fatty Acid Methyl Ester (FAME), a biofuel which can be used in diesel engines [11].

All fatty acids sources, such as animal fats or plant lipids, can be employed for biodiesel production. Nevertheless these sources are important food chain materials and their use is not recommended [12]; indeed it has received harsh criticism from several non-governmental organisations (NGOs) worldwide [13] due to the resulting increase in vegetable-edible oil demand. Therefore, the biodiesel research has focused on non-edible oils or waste vegetable oils, in particular Waste Cooking Oil (WCO) represents an excellent feedstock for biodiesel production.

The WCO is mentioned in the European Waste Catalogue with the code 200125; the disposing of WCO on the ground or in landfill could cause water and soil pollution and disturb the aquatic ecosystem in addition to being a human health concern. The growing concern for the environment is mainly due to the increasing WCO production by private consumers and restaurants.

In Italy about 1 400 000 t/year of vegetable oil are released for consumption, 20% of whom remains as residue. Every year about 280 000 t of WCO are returned to the environment as frying residue oil, full of pollutants [14].

CONOE - the Italian National Consortium for mandatory collection and processing of waste vegetable and animal Oils and fats - organises the collection of WCO produced by restaurants, pubs, school canteens and industrial activities. WCO collected is sent to treatment unit and is used to prepare soaps, additive for lubricating oil and to produce biodiesel.

The WCO produced by private consumers is not collected by CONOE, the waste is usually poured down the sink drain, leading to rise the wastewater treatment costs.

Many municipalities have organised a collection service of the WCO coming from private consumers in order to use it to produce biodiesel to employ, for instance, in public transport.

WCO is obtained using edible vegetable oil [15], such as corn, sunflower, palm, olive, soybean, rape and peanuts oils, and animal-based lipid (e.g. butter) for cooking.

The chemical and physical properties of WCO are different from those of fresh oil since some changes, due to chemical reactions - such as hydrolysis, oxidation, polymerization, and material transfer between food and vegetable oil - occur during the frying process [16].

The typical chemical and physical characteristics of WCO are shown in Table 3 [17, 18].

Table 3. Main properties of WCO [17, 18]

Property	Units	Value
Density	g /cm ³	0.91÷0.924
Kinematic viscosity (40°C)	mm ² /s	36.4÷42
Saponification value	mgKOH/g	188.2÷207
Acid value	mgKOH/g	1.32÷3.6
Iodine number	gI ₂ /100g	83÷141.5

The properties of WCO can change depending on the frying conditions, such as temperature and cooking time. Indeed a vegetable oil subjected to thermal stress, such as during frying, completely varies its chemical and physical original characteristics. The amount of heat and water in the frying increases the hydrolysis of triglycerides, therefore it causes a growth of the Free Fatty Acids (FFAs) percentage in the WCO [19]. Moreover oxidation and polymerization reactions produce an increase of the viscosity and of the saponification number in the WCO if compared with the original oil [20]. Furthermore the transport of matter and heat between the frying food and the vegetable oil occurs and causes a higher content of water in the WCO if compared with the original oil [21].

During the transesterification reaction, the presence of water in the WCO samples often leads to hydrolysis, whereas high FFA content and saponification number lead to saponification reactions. Both hydrolysis and saponification reactions cause low biodiesel yield and catalyst consumption [21].

The aim of the present paper is to investigate the optimal conditions for the transesterification reaction in a 100 l

pilot plant using WCO from domestic dwellings. Various tests have been carried out to study the type and the optimal concentration of alcohol and catalyst. The process parameters have been defined in order to ensure high biodiesel yield.

2. Materials and Methods

Samples of WCO have been collected from domestic dwelling. The most used vegetable oils for frying purposes are generally olive, sunflower and peanut ones. As for these oils, the fatty acid composition is dominated by oleic and linoleic fatty acids in addition to smaller quantities of stearic and palmitic acids [22].

The transesterification reaction depends on several parameters, namely, reaction temperature, type and quantity of alcohol used, agitation rate, catalyst type, and original oil characteristics.

In the present work an experimental study has been carried out, using WCO samples, in order to investigate the optimal operating conditions of a pilot plant for biodiesel production.

The pilot plant is composed as shown in figure 3-4. R1 is the stainless steel reactor jacketed of 100 litres capacity. The WCO samples are filtered, through filter F1, before being automatically loaded in the reactor. Catalyst and reagent are placed into two tanks, D1-D2, and automatically moved to the reactor depending on the volume and the FFA percentage.

The produced biodiesel is passed through a ionic resins filter, F2, in order to remove the residues of waste material. As for the wastes resulting from the reaction, they can be removed from the bottom of the reactor.

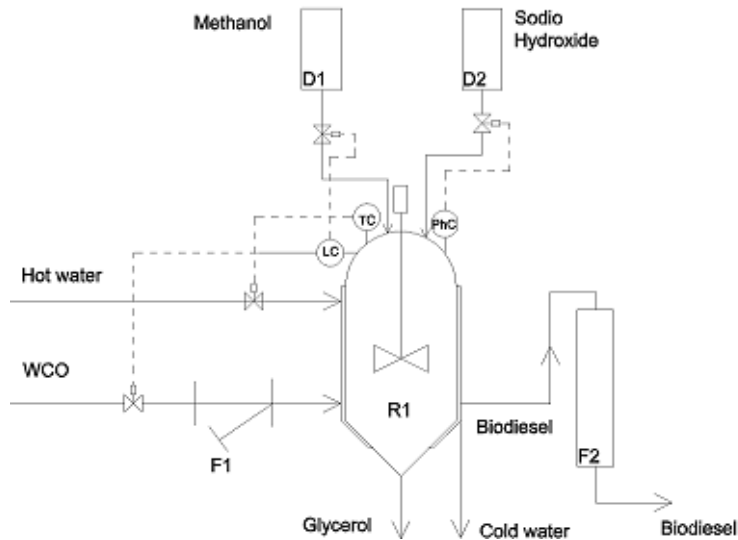


Figure 3. Plant layout

All parameters have been monitored by a computerised system with a touch screen interface.



Figure 4. Pilot plant for biodiesel production.

The first phase of the study concerned the analysis of the oil sample. The main chemical and physical characteristics of the WCO used in the transesterification tests are reported in table 4.

Table 4. Main properties of the analysed WCO

Property	Units	Value
Density	g /cm ³	0.913÷0.918
Kinematic viscosity (40°C)	mm ² /s	35.7÷41.3
Saponification value	mgKOH/g	186.3÷189.8
Acid value	mgKOH/g	1.54÷2.7
Iodine number	gI ₂ /100g	82.8÷96.8

In the studied case the average value of the acidity has been 2.12 mgKOH/g, namely the weight percent of FFA has been equal to 3%, and the average saponification value has been 188.05 mgKOH/g. Considering this data the experimental plant has been developed.

The methods used for biodiesel production from WCO are very similar to the conventional transesterification process.

The FFA content has allowed to perform transesterification tests both with basic catalyst (NaOH) and with acid catalyst (H₂SO₄). Furthermore, the influence of the type and the quantity of alcohol has been investigated.

Methyl and ethyl alcohol are generally used as reagents in transesterification reactions. Methanol is widely available, has low cost and high reactivity if compared with ethanol and permits to decrease the reaction time [20]. The major advantage of the ethanol 95% (commercial ethanol, with 95% of ethanol and 5% of water) is that it comes from renewable agricultural sources.

The experimental plan involved three levels of the NaOH (0.5, 0.75, 1.0 %w/w_{WCO}) and H₂SO₄ (1.0, 1.5, 2.25 M); moreover two different molar ratios alcohol/oil have been considered (3:1 and 6:1).

Depending on the type of catalysis, different operating conditions have been studied:

- base catalysis, reaction temperature equal to 60°C and reaction time of 60 minutes;
- acid catalysis, reaction temperature equal to 95°C and reaction time of 180 minutes.

During the acid and base catalysis tests, some problems have been encountered using ethanol. The separation between biodiesel and residues of the reaction has not occurred, in other words soapy paste has been produced during the reaction but it has not to be separated from the reaction products. Various tests have been carried out

using different concentrations of catalyst and ethyl alcohol, but the same results have been obtained. The purity of the alcohol could be the reason of the above-mentioned results, indeed the tests have been conducted using ethyl alcohol pure at 95%, thus the presence of water at 5% could be the cause of the inseparable soapy paste formation.

Each sample of WCO (100 litres) has been previously filtered in order to remove any food residues, furthermore each specific mixture of WCO with reagent and catalyst has been prepared according to the experimental plan. Each mixture has been heated for a specific period, cooled and left to stand in order to separate it into two layer: the upper one is the biodiesel, whereas glycerol is accumulated in the bottom.

After each test the reaction yield and the biodiesel density have been calculated.

3. Results

In figure 5 the main results of this study are reported. Fig. 5a and 5b refer to base catalysis tests, whereas Fig. 5c and 5d refer to acid catalysis tests.

Fig. 5a and Fig. 5b show the influence of the catalyst amount on the biodiesel specific gravity and the reaction yield considering two methanol concentrations (3:1 and 6:1). When the catalyst concentration grows, the biodiesel specific gravity and the reaction yield decrease. It is important to highlight that the growth of the catalyst content leads to a rise of the reaction residues, furthermore, starting from the NaOH concentration of 0.75% w/w_{oil}, soapy paste has formed causing a reaction yields reduction.

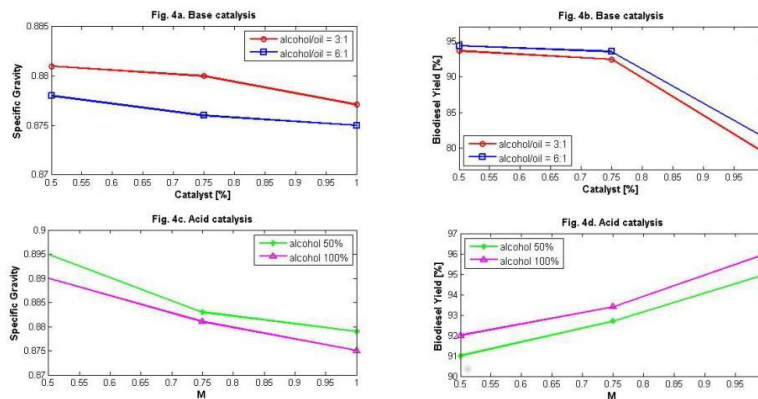


Figure 5. Reaction yield and biodiesel specific gravity.

The amounts of residues and soapy paste depending on the NaOH concentration are reported in Table 5 for the case of molar ratio (methanol to oil) equal to 3:1.

The transesterification tests with base catalysis, in surplus of methanol conditions (6:1 molar ratio), have shown a yield increase and a better biodiesel quality. In Fig. 5c and Fig. 5d the results of the acid catalysis tests can be observed. According to the experimental plan, the tests have been performed considering different concentrations of H₂SO₄ and two levels of methanol surplus: 50% and 100% (corresponding to 4.5:1 and 6:1 molar ratio). The results obtained have shown a maximum yield of 96% with a biodiesel density of 0.873 g/cm³.

The results obtained from base catalysis and acid catalysis tests have been compared: in both cases the reaction yields have been higher than 94% and the biodiesel density have been around 0.875 g/cm³, although the operating conditions have been different.

The acid catalysis reaction is slower than the base one and temperatures higher than 90°C are needed; moreover H₂SO₄ can produce a large number of salt interaction, which is a cause of corrosion.

The tests carried out on WCO samples coming from domestic dwelling and characterised by a FFA content equal to 3%, have shown that NaOH concentration of 0.5% w/w_{oil} and 100% of methanol surplus represent the best operating conditions, indeed they permit to obtain a reaction yield of 94.3% and a biodiesel density of 0.875 g/cm³.

Table 5. Residues and soapy paste quantities.

Amount of catalyst (%)	Amount of residues (g)	Amount of soapy paste (g)
0.5	59.1	/
0.75	70.2	2.2
1	114.5	3.1

3.1. Conclusions

The aim of the present work has been to investigate the operating conditions that maximize the biodiesel production from WCO. The conversion of waste cooking oil from domestic dwelling by transesterification reaction is useful in order to obtain a biodiesel.

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In the future the physico-chemical properties of the biodiesel will be analysed according to the European Standard EN 14214.

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