

Article

Quality Characteristics of Biodiesel Produced from Used Cooking Oil in Southern Europe

Theocharis Tsoutsos ^{1,*}, Stavroula Tournaki ¹, Zacharias Gkouskos ¹, Orlando Paraíba ², Filippo Giglio ³, Pablo Quero García ⁴, João Braga ⁵, Haris Adrianos ⁶ and Monica Filice ⁷

- ¹ Renewable and Sustainable Energy Lab, Technical University of Crete, 73100 Chania, Greece; s.tournaki@yahoo.gr (S.T.); aris.gkouskos@enveng.tuc.gr (Z.G.)
- ² Energy and Environment Agency of Arrábida, 2910-422 Setúbal, Portugal; orlando.paraiba@ena.com.pt
- ³ Local Energy Agency Province of Cosenza, 87100 Cosenza, Italy; giglio@alessco.it
- ⁴ Energy Management Agency Province of Cádiz, 11–24008 León, Spain; pablo.querogarcia@gmail.com
- ⁵ Regional Energy Agency for Barreiro, Moita, Montijo and Alcochete, 2834-005 Barreiro, Portugal; joao.braga@senergia.pt
- ⁶ ELIN Biofuels S.A., 14564 Athens, Greece; thand@elinbio.gr
- ⁷ Municipality of Castrolibero, 87040 Castrolibero, Italy; monica.filice@gmail.com
- * Correspondence: Theocharis.Tsoutsos@enveng.tuc.gr; Tel.: +30-28210-37825

Received: 27 December 2018; Accepted: 13 February 2019; Published: 16 February 2019



Abstract: The potential of households' used cooking oil (UCO) recycling for biodiesel production is massive. This study aims to promote the shift from UCO inappropriate disposal to sustainable recycling. UCO is classified as municipal waste under the code 20 01 25 (edible oils and fats), according to the European Waste Catalogue. Inappropriate UCO disposal increases the operating cost of wastewater treatment, the risk of groundwater contamination, as well as the greenhouse gas emissions that are associated with its biodegradation. Recycling UCO-to-biodiesel offers a sustainable solution in the exploitation of a problematic waste and its transformation into an energy resource, thus contributing to the reduction of environmental pollution and fossil fuel dependence. This paper includes critical recommendations in order to overcome bottlenecks to successfully promote the UCO-to-biodiesel chain. Quality control of the biodiesel—produced exclusively from UCO—was performed according to the European Standard EN 14214 and the results are presented in the paper. The analysis studies the outcomes from four Southern European countries (Spain, Portugal, Italy, and Greece), which hold the top four places in annual per capita olive oil consumption in the European Union (EU).

Keywords: used cooking oil; biodiesel; quality control; circular economy

1. Introduction

Diesel is considered to be one of the largest contributors to environmental pollution problems worldwide; turning to more environmentally friendly and sustainable fuels has today become a necessity in combating increased Greenhouse Gas (GHG) levels and climate change. Over the past two decades, biofuels have gained continuous interest due to the renewable feedstock and their short life cycle [1]. Biodiesel and its blends with diesel are currently investigated as a viable solution to the problems of fossil fuels depletion and environmental degradation [2,3]. Biodiesel that is produced from Used Cooking Oil (UCO) has lately been tested in diesel engines, providing satisfactory results.

When UCO is improperly disposed, it can cause a significant environmental burden; however, if it is collected and recycled, then it can be proven to be an efficient energy resource. Today, the most commonly met practice of disposing UCO (especially from households) is to throw it in the



sewage system, a practice that leads to several problems. UCO may clog the sewage pipelines, causing malfunctions in the filters and to oil/water separators of wastewater treatment facilities [4,5]. In several cases, the increase of the water treatment cost, due to the oil fraction, has been estimated to be up to 25% [6,7]. Even though the European Union (EU) domestic sector is the main source of UCO, widespread collection systems are still missing. Additional barriers, such as the lack of strong incentives and the limited distribution supply chain networks for UCO based biodiesel were already highlighted in previous studies [8,9]. As a result, more than 60% of households' UCO is improperly disposed [10]. Key success factors for developing a sustainable system have been recorded [11] and they mainly involve the motivation of citizens through setting up a "citizen-friendly" UCO disposal scheme; a strategic focus on citizens' awareness with regular, targeted, multi-channel communication activities; and, active engagement of local administrations, municipal waste management companies and relevant stakeholders.

UCO transformation to biodiesel can have significant energy advantages [12–14], such as the decrease of the energy transport distances, the increase of energy security, and the potential enhancement of the decentralized energy production [15,16].

This process also exhibits important environmental advantages, since UCO is converted to biodiesel, a non-toxic liquid, safer than conventional diesel that biodegrades four times more rapidly than petrodiesel. In addition, biodiesel has the lowest GHG emissions among biofuels, ensuring 88% GHG emission savings [17–19].

Contrary to other biofuel feedstock that is produced by cultivated crops, UCO is not competitive with the food supply, hence maintaining an "ethical advantage". Furthermore, since UCO from households, restaurants, and the food industry is collected and converted to biodiesel, problems that are associated with its inappropriate disposal to the sewage system are tackled. Promoting biofuels can have a positive effect on employment [20,21]; the creation of new green jobs, such as UCO collectors, can enhance the local and circular economy. An additional essential advantage is that, through this approach, dirty UCO can be removed from the food chain.

Biodiesel production is based on the transesterification reaction of vegetable oils, fats, and cooking oils with methanol and catalyst (NaOH and KOCH₃) [22]), where lipids (oils and fats) are converted to biodiesel and glycerol. Biodiesel that is obtained from renewable lipids consists of long-chain fatty acid methyl esters (FAME). Technical difficulties that are associated with biodiesel include low-temperature properties, storage stability, and slightly increased NOx exhaust emissions. However, recent research targets in the optimization of processes that are followed to enhance the characteristics of the biodiesel produced from UCO [7]. Studies especially focus on parameters, such as dosage and type of catalyst [23], humidity, as well as reactions' pressure and temperature, mixing speed, and time [24,25].

Fuel quality strongly depends on the raw material used. Quality requirements and test methods for biodiesel are defined by the European Standard EN 14214 to make it proper as an automotive fuel. These properties are directly connected to the biodiesel life cycle, from crop to final consumption.

Four Southern European countries (Greece, Spain, Portugal, and Italy) were involved in the RecOil demonstration pilot actions. Pilots were implemented in the following municipalities: Athens, Zakynthos, Rethymno (Greece), Setúbal, Palmela, Sesimbra, Barreiro, Moita, Montijo, Alcochete (Portugal), Cádiz (Spain), Castrolibero, and Castrovillari (Italy), including 1,490,730 citizens and 570,456 households [26]. These four countries were initially selected, since they hold the top four places in annual per capita olive oil consumption among EU countries, according to the latest available data, Greece leads the ranking with 12.8 kg, followed by Spain (11.3 kg), Italy (10.5 kg), and Portugal (7.2 kg) [27]. It was considered that the UCO collected would have similar characteristics and that, due to the large quantities of cooking oil consumed, the approach UCO-to-biodiesel can be proven to be effective and sustainable for these countries.

Currently, the amount of annually recovered UCO in the EU-28 is 3,950 m³. Biodiesel coming from UCO could potentially replace 1.8% of the EU total annual diesel consumption. The biodiesel

consumption for transport in the selected southern Member States during the years 2016–2017 is presented in Table 1.

Countration	Biodiesel Consumption for Transport in Toe					
Country	2017	2016				
Italy	1,027,458	1,008,300				
Greece	151,000	149,000				
Portugal	252,172	256,237				
Spain	1,148,074	980,656				
Total EU 28	12,514,812	11,372,778				

 Table 1. Biodiesel consumption for transport in 2016–2017 [28].

The current work aims to transfer lessons that were learned for the UCO-to-biodiesel chain in these Southern European countries, to provide recommendations for European and national policy, and to present the quality results of the biodiesel that is produced at the local and industrial level.

2. Materials and Methods

The suitability of the UCO based biodiesel as a transportation fuel, as well as its quality characteristics, are initially assessed. UCO is converted to biodiesel through homogeneously catalysed esterification process. The objective is to evaluate the quality characteristics of the produced biodiesel through the analysis of the samples, conducted at ELIN Biofuels Laboratories. Determining the properties of the UCO based biodiesel is essential for the optimal injection and combustion performance of diesel engines [29]. Parameters were compared to the maximum and minimum permitted values, according to the Standard EN 14214: 2012 [30].

2.1. UCO Collection

The initial step was the UCO local collection. Since the quality of UCO affects the quality of biodiesel that is produced, successful UCO collection methods have been investigated within RecOil in order to obtain UCO in large quantities that are as clean as possible. Through an extended survey that covered 900 households and more than 40 UCO collection systems in Europe, the RecOil team concluded that the most typical collection method is by far the establishment of public collection points, in easily accessible public places, like schools, supermarkets, parking lots, municipal buildings, and most visited squares. Nevertheless, within the demonstration projects that were implemented during RecOil action, different collection strategies were investigated: (i) containers in open public areas, (ii) collection points at schools, and (iii) door-to-door collection. In addition, tailor-made communication strategies were put in operation, resulting in the establishment of new UCO collection systems or the expansion of existing ones. The collection. Table 2 provides an overview of status before and after the RecOil campaign in the participating municipalities and regions. The RecOil activities have resulted in a significant increase of collection points and UCO collected volumes. As a result, more than 183,350 L of UCO were collected in a year.

Due to the large scale of the sampling process in different southern Mediterranean sites, a typical experimental design was practically not feasible. Sampling and analysis were based on availability and cost constraints.

	New UCO C	ollection System	Optimized UCO Collection Systems			
Collected (L)	Public Collection Points Door-to-Door Tota		Total	Public Collection Points	ction Door-to-Door	
Number of systems	2	1	3	3	1	4
Number of collection points (or bottles for door-to-door) before RecOil	-	-	-	334	200	-
Number of collection points (or bottles for door-to-door) 2015	177	3500	-	373	2000	-
UCO collected before RecOil/month [L]	-	-	-	10,525	37	10,562
UCO collected 2015/month [L]	6758	805	7563	12,342	852	13,194
UCO collected 2015/month/collection system [L]	3379	805	2521	4,114	852	3299
UCO collected before RecOil /month/collection point (or bottle delivered) [L]	-	-	-	32	0.18	-

3500

3500

38

89

33

124

0.43

2000

|--|

2.2. Samples Selection

UCO collected 2015 /month/collection

point (or bottle delivered) [L] Number of collection points (or bottles

for door-to-door)/system

In order to assess the quality of the UCO based biodiesel, 40 samples, in total, were analysed (Table 3); 24 of the samples were from locally collected UCO, which was later converted to biodiesel by ELIN SA (U-LOCAL). Partners ENA, TUC, MC, and ALESCO produced their own biodiesel from UCO (B-LOCAL) to evaluate the feasibility of local production (16 additional samples). All of the biodiesel samples were then analysed at ELIN laboratories.

Table 3. Overview of UCO and biodiesel samples received and analysed.

Country	Body in Charge ¹	UCO Samples	Biodiesel Samples
Portugal	ENA	5	3
Spain	APEC	4	0
Portugal	SENERGIA	2	0
Greece	TUC	4	3
Italy	MC	2	5
Italy	ALESSCO	2	5
Greece	ELIN	5	0
	Total	24	16

¹ ALESSCO: Local Energy Agency for Renewable Sources and Sustainable Development—Province of Cosenza; APEC: Energy Management Agency Province of Cádiz; ELIN: ELIN Biofuels S.A.; ENA: Energy and Environment Agency of Arrábida; MC: Municipalities of Castrovillari and Castrolibero; SENERGIA: Regional Energy Agency for the municipalities of Barreiro, Moita, Montijo, and Alcochete; TUC: Technical University of Crete.

Free Fatty Acid (FFA) and H₂O content of the collected UCO were initially measured (Table 4). To determine the FFAs, the EN 10105 standard was followed, whereas water content measurements were applied according to the DIN EN ISO 8534 [31,32].

Table 4. Average Free Fatty Acid (FFA) and H₂O content of the collected UCO samples.

Partners that Locally Collected UCO	FFA (%)	H ₂ O (%)
ENA-U-LOCAL	0.34	0.17
ALESSCO-U-LOCAL	1.23	0.18
APEC-U-LOCAL	2.58	0.26
ELIN-U-LOCAL	2.66	0.33
SENERGIA-U-LOCAL	0.52	0.15
TUC-U-LOCAL	0.81	0.16
MC-U-LOCAL	0.17	0.08
Average	1.19	0.19

2.3. Biodiesel Production

The method that was adopted for the UCO-to-biodiesel transformation was the homogeneously catalyzed esterification, which is the most common in the biodiesel industry. The aim of the transesterification process was the production of biofuel that was to be used in transportation. 24 samples were sent to ELIN laboratories for esterification/transesterification and analysis according to EN 14214. The steps followed included: washing, neutralizing, drying, and filtering. No actual problems were recorded during the samples' production process. The parameters of the biodiesel produced from UCO (U-LOCAL) are presented in Table 5, which shows the average values of the produced biodiesel per area, thus the 24 samples are categorized into seven groups.

Regarding the biodiesel produced, the water content was identified according to EN ISO 12937 and the acid value (KOH/g) according to EN14104. The physical properties were measured according to various standards: density at 15 °C (EN ISO 12185); viscosity at 40 °C (EN ISO 3104); flash point (EN ISO 3679); cold filter plugging point (CFPP) (EN 116); and, cloud point (EN23015).

Table 6 shows the relevant results of the quality check of the locally produced biodiesel by ENA, APEC, TUC, and MC.

Parameter	Unit	Min	Max	Specification EN 14214: 2012	1	2	3	4	5	6	7
Density at 15 °C	kg/m ³	860	900	EN ISO 12185	891	882	885	529	887	881	883
Viscosity at 40 °C	mm^2/s	3.5	5.0	EN ISO 3104	5.6	4.5	4.6	4.4	4.5	4.6	4.3
Flash Point	°C	101	-	EN ISO 3679		173	>170	171.8	173.5	>195	174
Sulphur Content	mg/kg	-	10.0	EN ISO 20846	3.3	9.6	44.9	9.2	6.2	20.3	18.4
Cetane Number	-	51.0	-	EN ISO 5165	53.3	56.7	56.0	53.1	53.7	59.2	54.8
Sulphated Ash	% m/m	-	0.02	ISO 3987	0	0	0	0	0	0	0
Water Content	mg/kg	-	500	EN ISO 12937	1,439	683	464	369	600	601	564
Total Contamination	mg/kg	-	24	EN 12662	24	7	73	20	13	14	16
Copper Strip Corrosion	rating	Class 1	Class 1	EN ISO 2160	1	1	1	1	1	1	1
CFPP	°Č	-	13	EN 116	-5	$^{-1}$	-3	$^{-1}$	-4	0	0
Cloud Point	°C	-	16	EN23015	-3	2	1	2	2	2	7
Ester Content	% m/m	96.5	-	EN 14103	-	96.8	94.3	95.6	93.8	95.7	>99
Linolenic Acid Methylester	% m/m	-	12	EN 14103	-	0.9	0.9	1.5	0.4	0.4	0.1
Polyunsaturated Methyl Esters (\geq 4 double bonds)	% m/m	-	1	EN 15779	-	<0.6	< 0.6	< 0.5	<0.6	< 0.6	<0.6
Oxidation Stability at 110 °C	h	8	-	EN 14112	4.40	3.70	4.14	4.46	2.10	2.05	3.79
Acid Value	mg KOH/g	-	0.50	EN 14104	0.48	0.19	0.34	0.23	0.21	0.28	0.16
Iodine Value	g iodine/100g	-	120	EN 14111	-	97	100	109	114	84	118
Monoglyceride Content	% m/m	-	0.700	EN 14105	-	0.537	0.462	0.330	0.449	0.490	0.414
Diglyceride Content	% m/m	-	0.200	EN 14105	-	0.084	0.088	0.097	0.084	0.066	0.066
Triglyceride Content	% m/m	-	0.200	EN 14105	-	0.002	0.009	< 0.015	< 0.006	0.009	0.002
Free Glycerol	% m/m	-	0.020	EN 14106	-	0.008	0.005	0.004	0.006	0.003	0.005
Total Glycerol	% m/m	-	0.250	EN 14105	-	0.157	0.136	0.106	0.133	0.139	0.121
Phosphorous Content	mg/kg	-	4.0	EN 14107	-	< 0.5	<2.3	<4	< 0.5	< 0.5	< 0.5
Metals I (Na/K)	mg/kg	-	5.0	EN 14108	0	0	0	0	0	0	0
Metals II (Ca/Mg)	mg/kg	-	5.0	EN 14538	-	<1	<1	<1	<1	<1	<1
Methanol Content	% m/m	-	0.20	EN 14110	0	0	0	0	0	0	0

Table 5. Comparison of biodiesel produced at ELIN ELIN Biofuels S.A. lab from UCO collected from seven different areas.

1: ENA-U-LOCAL; 2: ALESSCO-U-LOCAL, 3: APEC-U-LOCAL4; ELIN-U-LOCAL, 5: SENERGIA-U-LOCAL; 6: TUC-U-LOCAL; 7: MC-U-LOCAL.

2.4. Biodiesel Analysis

Biodiesel analysis results were compared to the minimum and maximum values that were determined in EN 14214: 2012. Measurements were performed according to the tests/methods presented in Tables 5 and 6 (column 5). Similar to the previous parameters' presentation (Table 5), the samples were grouped into four clusters that were based on the origin/production area.

Parameter	Unit	Min	Max	Specification EN 14214: 2012	1	2	3	4
Density at 15°C	kg/m ³	860	900	EN ISO 12185	885	889	887	877
Viscosity at 40°C	mm ² /s	3.5	5.0	EN ISO 3104	4.3	7.3	5.4	3.9
Flash Point	°C	101	-	EN ISO 3679	177.2	124.5	111	90
Sulphur Content	mg/kg	-	10.0	EN ISO 20846	12.0	1.2	17.7	~5.0
Cetane Number	-	51,0	-	EN ISO 5165	54.5	55	58.2	53.2
Sulphated Ash	% m/m	-	0.02	ISO 3987	0	0.01	0	0.08
Water Content	mg/kg	-	500	EN ISO 12937	537	467	2,047	688
Total Contamination	mg/kg	-	24	EN 12662	82	65	26	71
Copper Strip Corrosion	rating	Class 1	Class 1	EN ISO 2160	1	1	1	1
CFPP	°C	-	13 (*)	EN 116	-3	-	$^{-1}$	1
Cloud Point	°C	-	16 (*)	EN23015	1	-	1	
Ester Content	% m/m	96.5	-	EN 14103	-	94.0	84.9	91.9
Linolenic Acid Methylester	% m/m	-	12	EN 14103	1.6	0.4	0.9	0.3
Polyunsaturated Methyl Esters (> 4 double bonds)	% m/m	-	1	EN 15779	-	-	<0.6	<0.6
Oxidation Stability at 110 °C	h	8	-	EN 14112	3.2	1.1	1.7	2.1
Acid Value	mg KOH/g	-	0.50	EN 14104	0.23	0.38	0.51	0.04
Iodine Value	g iodine/100g	-	120	EN 14111	119	90	91	118
Monoglyceride Content	% m/m	-	0.700*	EN 14105	0.413	0.64	0.944	0.73
Diglyceride Content	% m/m	-	0.200	EN 14105	0.062	1	1.802	1.01
Triglyceride Content	% m/m	-	0.200	EN 14105	-	0.110	5.416	0.275
Free Glycerol	% m/m	-	0.020	EN 14106	0.003	0.006	0.013	0.380
Total Glycerol	% m/m	-	0.250	EN 14105	0.116	0.264	1.075	0.61
Phosphorous Content	mg/kg	-	4.0	EN 14107	-	0.1	< 0.5	0.3
Metals I (Na/K)	mg/kg	-	5.0	EN 14108	0	0.297	0	3.03
Metals II (Ca/Mg)	mg/kg	-	5.0	EN 14538	-	5.9	<1.	3.5
Methanol Content	% m/m	-	0.20	EN 14110	0	0.74	0	1.09

Table 6. Comparison of biodiesel produced locally from ENA, APEC, TUC, and MC.

1: ENA-B-LOCAL; 2: APEC-B-LOCAL; 3: TUC-B-LOCAL; 4: MC-B-LOCAL. (*) "Maximum values. Acceptable combinations are defined on National Annexes based on tables 3a and 3b of EN14214."

3. Results and Discussion

3.1. UCO Samples Converted at ELIN Laboratories

All 24 UCO samples met the specifications of EN 14214: 2012 regarding density, viscosity, flash point, cetane number, copper strip corrosion, CFPP, cloud point, linolenic acid methyl ester, polyunsaturated methyl esters, acid value, glycerides content, glycerol content, phosphorus content, and metals Ca/Mg content.

Sulphur content was out of specifications for 13 of the samples that were analysed. The most probable reason for the observed increased values of sulphur content is the various foods that cooking oil comes in contact with. Sulphur though can be removed from the final product (biodiesel) via vacuum distillation. High sulphur levels in the diesel may give rise to the production of H_2SO_4 and sulphates compounds in the engine. H_2SO_4 causes corrosion in the engine, while sulphates lead to increased particulate matter emissions.

Water content was out of specifications in 10 of the samples. Values for these samples ranged from 520 to 1068 ppm (upper limit: 500 ppm), which was probably attributable to insufficient drying or inappropriate storage. When stored, biodiesel can absorb more humidity than conventional diesel, since FAMEs are hygroscopic compounds. Even though relevant high values (>1000 ppm) have been recorded, for biodiesel, different techniques are available to absorb humidity [33]. The high water content in biodiesel may lead to the corrosion of some engine parts resulting to engine failure. Moreover, the increased water content may lead to microbial contamination of the fuel that can cause filter plugging problems.

Total contamination values exceeded the 24 mg/kg limit in six of the samples. High values of total contamination may lead to filter plugging or particle deposition in the fuel injection system.

In 15 of the samples, ester content was out of specifications. This was expected since oils when heated during cooking/frying are oxidized and polymerized. The products of these reactions are soluble in biodiesel and they result in low ester content of the final product. The only way to remove these polymerized compounds is by vacuum distillation of biodiesel. Low ester content fuels may result in operational problems of the engine due to depositions in its parts. In relevant published studies, low values have been recorded for ester content varying from 91.3% to 95.0% where biodiesel was produced from palm oil, olein oil, and stearin oil [34].

All 24 samples that were analysed were out of specifications in terms of oxidation stability. This was expected, since most of the biodiesel, as produced from vegetable oils, has less than 8h of oxidation stability, which is the limit; thus, antioxidant additives must be added before use. As the unsaturation degree increases, oxidation stability of biodiesel decreases, thus biodiesel is less oxidation that is resistant to conventional diesel due to the presence of unsaturation in its ester chains. Low values are also commonly met in biodiesel derived from other feedstock (e.g. soybean and corn; less than 5.1 h) [35]. In addition, the cooking/frying process has a negative impact on the oxidation stability of the final product. Low oxidation stability results in fast oxidation of the fuel, which produces compounds that may cause fouling and deposits in the fuel injection system of the engine. In addition, fuels' oxidation process produces acid compounds.

Various UCO samples and oils from different crops were used in other studies [36] (sunflower, olive, maize, soybean, palm) to produce biodiesel; the iodine values varied from 72 to 121 g iodine/100 g, depending on the samples' feedstock. In our case, only two samples were out of specifications regarding iodine value (>120 g iodine/100 g); however, the vast majority of the values received where within the max value that was set by the relevant standard. Iodine value limitations are imposed in order to record the natural tendency of the fuel to oxidize. Higher iodine values result in increased oxidation.

Specifications can be further enhanced when biodiesel is blended with diesel. Blends studied in the literature [37–39] can offer optimized properties.

3.2. UCO Samples Converted to Biodiesel Locally

16 biodiesel samples were locally produced by four different partners of the consortium and then analysed at ELIN laboratories. However, none of the samples from small-scale labs attained all EN 14214 specifications.

Viscosity exceeded the limit of 5 mm²/s in four samples, indicating incomplete reaction (UCO remnants in biodiesel). High viscosity levels can cause engine operational problems due to reduced fuel flow.

Flashpoint was lower than the minimum value of 101 °C in two samples. This is caused by methanol, which was probably not adequately removed from the final product. Flashpoint is a property mostly used to classify fuels according to safety standards for handling, storage, and transport; on the other hand, flashpoint limitation in biodiesel is imposed to ensure that no methanol is left in the fuel. Low flashpoint can cause engine ignition problems. For conventional diesel, the flashpoint value is close to 65 °C, whereas in UCO, values usually range above 100 °C [40].

Water content was off specifications in all 16 biodiesel samples, with values up to 2600 ppm (limit 500 ppm), due to insufficient drying. Two biodiesel samples exceeded the 24 mg/kg upper limit regarding total contamination, thus affecting fuel performance.

Acid value exceeded the 0.5 mg KOH/g limit in three samples, which is probably because of either the presence of free fatty acids in the final product due to incomplete reaction or because of the insufficient washing/separation in the neutralization phase of the catalyst.

Ester content was out of specifications in all 16 samples. This may be the reason for either incomplete reaction or due to the nature of the collected UCO.

Glycerides and total glycerol exceeded specifications in all 16 samples. Glycerides are the main components of vegetable oils and their presence indicates an incomplete reaction. High levels may cause problems to the viscosity of the fuels and thus to the flow behaviour, as well as the filter plugging problems.

The results of the analysis indicated that local transesterification processes were not successful. On the contrary, ELIN laboratories achieved the production of biodiesel that, in most cases, met EN 14214 standards, indicating that industrial level laboratories can produce biodiesel fuel, from 100% UCO, of satisfactory quality.

4. Policy Recommendations

Recycling UCO-to-biodiesel can offer a sustainable alternative for transportation fuel. Biodiesel from UCO is by far the most sustainable biofuel from the viewpoint of the conservation of fossil resources [11]. Benefits that are gained from the UCO-to-biodiesel chain should be widely spread to the relevant stakeholders and policymakers in order to encourage and facilitate the procedures that were followed within this chain.

Appropriate policies and supporting measures can lead to the efficient implementation of the UCO-to-biodiesel chain and they can facilitate the expansion and replication of such initiatives. Due to the economy of scale, this will decrease the unit cost of biodiesel [41].

Awareness raising campaigns should be the first step for the promotion of UCO-to-biodiesel production. The current UCO recovery is very limited due to collection and processing barriers, which mainly include insufficient collection systems, limited feasibility studies on local biodiesel production, unfavourable or underdeveloped regulatory framework, and low-level biodiesel blends.

EU policy could stimulate the regional/municipal administrations to establish new UCO collection systems. Since local authorities are usually the main development planners at the local level, policy changes should also initially be promoted by them. EU Directives could work in parallel with the Covenant of Mayors in order to boost the dissemination of best practices and UCO recycling targets, within the context of local Sustainable Energy Action Plans (SEAPs).

Administrations should develop plans, including UCO collection and recycling, as well as UCO-based biodiesel usage in public transportation. Information campaigns should also focus on how to implement the double counting system, with clear and homogeneous custody rules, procedures, and documents. Different policy instruments can be locally implemented for the promotion of cleaner fuels and vehicles in cities: tax exemptions for biofuels; reduction of parking fee for cars using biodiesel; funding of relevant innovative projects; and, funding for new infrastructures (UCO collection systems and small-scale biodiesel units).

Directives for alternative fuels [42–44] do not provide clear directions for biodiesel. A potential amendment to the EU Water Framework Directive could be a great opportunity to raise awareness on UCO recycling benefits. The recent adoption by EU Council of Ministers of the new Renewable Energy Directive, which sets a target of at least 14% of energy from renewable sources in transport, could intensify the deployment of sustainable bioenergy, as a critical tool to mitigate climate change [45].

Member States can have a critical role in the support of UCO-based biodiesel. Within the context of the Alternative Fuels Infrastructure Directive [42], national governments will have to design and establish national frameworks for the development of alternative fuels, like advanced biofuels. Thus, governments could define ambitious goals and incentives to further encourage the promotion of UCO-based biodiesel. These incentives should conform to the Directive and relevant competition rules.

Consumption could also be stimulated by setting higher mandatory biofuels blending targets. This measure could greatly assist the market uptake, but it requires strong collaboration with automobile manufacturers, so that the engines can be compatible with greater blends of biofuels. The definition of an ambitious, mandatory, and clear target for the post-2020 period with penalties that are high enough to prevent buyouts could greatly support the market of UCO-based biofuels. UCO is

a waste that needs to be treated in a viable way. EU members need to encourage the separate collection and the treatment of bio-waste in a way that fulfils a high level of environmental protection.

Finally, investment support by the EU should be enhanced at the national and regional level for research and production in non-commercial environmental resources. According to this study, good biodiesel quality can be achieved on a large scale, but additional effort is needed to optimize procedures at the local level (small scale).

EU policymakers and local authorities are highly encouraged to take measures in favour of local biodiesel production. The decentralized energy (self) production will encourage the creation of the necessary quality assurance infrastructure.

In brief, these final critical recommendations are depicted in Table 7.

Level	Recommendations
Global	It is urgent that UCO, as a waste, to be treated in a viable full-chain way in favour of the environment and the society.
EU/States	Further support of efficient systems to collect and treat UCO produced in households; The bottled UCO collection is preferred versus the bulk one; EU policymakers should take measures in favour of decentralised local biodiesel (self)production, which will change the local collection culture, as well as the production infrastructure; Capacity building efforts will improve the awareness of the policymakers.
Industries	Although industrially produced biodiesel from 100% UCO is close to the specifications set in the EN 14214 Standard, still, blending with non-UCO biodiesel is considered necessary to enhance properties.
Local authorities/communities	Conversion procedures should be upgraded locally to meet the biodiesel standards of EN 14214. There is a need for transferring processing plant technology and know-how, from industrial scale to small-scale viable biodiesel plants.

Table 7. Critical recommendations to improve the UCO-to-biodiesel chain.

5. Conclusions

The increasing production of UCO from households and other sources (restaurants, industries, etc.) is a growing problem in cities globally. UCO is a residue that is regularly disposed in the drain, potentially contaminating groundwater supplies or causing problems to wastewater treatment plants resulting in reduced treatment efficiency and increased cost. In other cases, UCO may be led back into the food chain through animal feeding, which likely causes human health problems. Even though authorized service providers often collect UCO that is generated in restaurants, most countries lack efficient systems to collect and treat UCO produced in households. The technical and scientific team of this work investigated the best practices of the UCO collection from households, concluding that the most typical and efficient collection method is the establishment of public collection points in open public places. In addition, it was recorded that the bottled UCO collection as compared to the bulk collection is preferred, as it can minimize the risk of contamination with other fluids or waste, as well as the aesthetic degradation of the UCO bin and its surroundings.

The results from the top four EU countries in per capita olive oil consumption are presented in this study; it was seen that the specifications of the industrially produced biodiesel from 100% UCO are not far from those in the EN 14214 Standard; however, blending with non-UCO biodiesel is considered to be necessary to enhance its properties. The results presented are similar to other studies on the quality of biodiesel from UCO [46] and are close to the values that were recorded for biofuels from other feedstock [47]:

• Hight sulphur content, which is due to the various foods that cooking oil comes in contact with, which might cause corrosion in the engine and increased particulate matter emissions.

- High water content, since FAMEs are hygroscopic compounds, which might lead to the corrosion
 of engine parts and microbial contamination.
- Low ester content since oils when heated during cooking/frying are oxidized and polymerized, which might result in operational problems of the engine due to depositions in its parts.
- Low oxidation stability, requiring antioxidant additives, which produces compounds that may cause fouling and deposits in the fuel injection system of the engine.

Analysis of the 16 locally produced biodiesel samples indicates that the final product does not fulfil the specifications set. Water content, ester content, glycerides, and total glycerol were off specifications for all of the samples. Unfortunately, local laboratories do not possess appropriate infrastructure and an advanced level of expertise to produce an output of high quality, like industrial laboratories. Conversion procedures should be upgraded at the local level in order to meet the biodiesel standards of EN 14214. In several cases when biodiesel was produced locally, efforts were made to achieve properties' optimization by experimenting with different catalysts (type and quantity) at different temperatures and residence time. Biodiesel samples that were sent to ELIN labs to be tested were mostly the output of experimental methods rather than the result of a standardized approach.

It becomes apparent that there is a need for transferring processing plant technology and know-how, from industrial scale to small-scale viable biodiesel plants. The decentralized production of biodiesel and biofuels could become key for future sustainable schemes. The concept of small-scale fully autonomous certified commercial biodiesel units can be proven to be an efficient solution for small producers (e.g. municipalities) that can later act as best practice examples to locally promote UCO recycling.

Author Contributions: Conceptualization, T.T., S.T. and O.P.; methodology, T.T., S.T. and O.P.; validation, T.T., O.P., F.G., P.Q.G., H.A. and M.F.; investigation, T.T., O.P., F.G., P.Q.G., H.A. and M.F.; writing—original draft preparation, T.T., S.T. and O.P.; writing—review and editing, T.T. and Z.G.; supervision, T.T. and O.P.; project administration, O.P. and S.T.

Funding: This publication was supported by the European Commission under the Intelligent Energy - Europe Programme, within the framework of the project RecOil—Promotion of used cooking oil recycling for sustainable biodiesel production, Contract number: IEE/11/091/ SI2.616369; the INTERREG MED programme, within the framework of the project "COMPOSE - Rural communities engaged with positive energy" co-funded by the European Regional Development Fund (Project No: 1001/MED 2014-2020). The sole responsibility for the content of this paper lies with the authors. The European Commission is not responsible for any use that may be made of the information contained therein.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Chen, R.; Qin, Z.; Han, J.; Wang, M.; Taheripour, F.; Tyner, W.; O'Connor, D.; Duffield, J. Life cycle energy and greenhouse gas emission effects of biodiesel in the United States with induced land use change impacts. *Bioresour. Technol.* **2018**, 251, 249–258. [CrossRef] [PubMed]
- 2. Abed, K.A.; El Morsi, A.K.; Sayed, M.M.; El Shaib, A.A.; Gad, M.S. Effect of waste cooking-oil biodiesel on performance and exhaust emissions of a diesel engine. *Egypt. J. Pet.* **2018**, in press. [CrossRef]
- 3. Mohd Noor, C.W.; Noora, M.M.; Mamata, R. Biodiesel as alternative fuel for marine diesel engine applications: A review. *Renew. Sustain. Energy Rev.* **2018**, *94*, 127–142. [CrossRef]
- 4. Mandolesi de Araujo, C.D.; Andrade, C.C.; de Souza e Silva, E.; Dupas, F.A. Biodiesel production from used cooking oil: A review. *Renew. Sustain. Energy Rev.* **2013**, *27*, 445–452. [CrossRef]
- 5. Phan, A.N.; Phan, T.M. Biodiesel production from waste cooking oils. Fuel 2008, 87, 3490–3496. [CrossRef]
- 6. Jiang, Y.; Zhang, Y. Supply chain optimization of biodiesel produced from waste cooking oil. *Transp. Res. Procedia* **2016**, *12*, 938–949. [CrossRef]
- Aboelazayem, O.; Gadalla, M.; Saha, B. Valorisation of high acid value waste cooking oil into biodiesel using supercritical methanolysis: Experimental assessment and statistical optimisation on typical Egyptian feedstock. *Energy* 2018, 162, 408–420. [CrossRef]

- Avinash, A.; Sasikumar, P.; Murugesan, A. Understanding the interaction among the barriers of biodiesel production from waste cooking oil in India—An interpretive structural modeling approach. *Renew. Energy* 2018, 127, 678–684. [CrossRef]
- Sahar; Sadaf, S.; Iqbala, J.; Ullah, I.; Nawaz Bhatti, H.; Nouren, S.; Rehman, H.; Nisar, J.; Iqbalh, M. Biodiesel production from waste cooking oil: An efficient technique to convert waste into biodiesel. *Sustain. Cities Soc.* 2018, 41, 220–226. [CrossRef]
- Paraíba, O.; Tsoutsos, T.; Tournaki, S.; Antunes, D. Strategies for optimization of the domestic used cooking oil to biodiesel chain—The European project RecOil. In Proceedings of the Energy for Sustainability. Sustainable Cities: Designing for People and the Planet, Coimbra, Portugal, 8–10 September 2013.
- Tsoutsos, T.D.; Tournaki, S.; Paraíba, O.; Kaminaris, S.D. The Used Cooking Oil-to-biodiesel chain in Europe assessment of best practices and environmental performance. *Renew. Sustain. Energy Rev.* 2016, 54, 74–83. [CrossRef]
- 12. El Libro. The Handbook for Local Initiatives for Biodiesel from Recycled Oil, Biodienet. Available online: www.sec.bg/userfiles/file/BioDieNet/EL%20LIBRO.pdf (accessed on 8 November 2018).
- Sheinbaum-Pardo, C.; Calderón-Irazoque, A.; Ramírez-Suárez, M. Potential of biodiesel from waste cooking oil in Mexico. *Biomass Bioenergy* 2013, 56, 230–238. [CrossRef]
- 14. Fernando Bautista, L.F.; Vicente, G.; Rodríguez, R.; Pacheco, M. Optimisation of FAME production from waste cooking oil for biodiesel use. *Biomass Bioenergy* **2009**, *33*, 862–872. [CrossRef]
- 15. Renewable Energy Directive 2009/28/EC. Available online: https://eur-lex.europa.eu/legal-content/EN/ ALL/?uri=celex%3A32009L0028 (accessed on 8 November 2018).
- 16. Fuel Quality Directive 2009/30/EC. Available online: https://eur-lex.europa.eu/legal-content/EN/TXT/ ?uri=celex%3A32009L0030 (accessed on 8 November 2018).
- Talens Peiro, L.; Lombardi, L.; Villalba Méndez, G.; Gabarrell i Durany, X. Life cycle assessment (LCA) and exergetic life cycle assessment (ELCA) of the production of biodiesel from used cooking oil (UCO). *Energy* 2010, 35, 889–893. [CrossRef]
- Sarantopoulos, I.; Franklin, C.; Tsoutsos, T.; Bakirtzoglou, V.; Azangue, W.; Donatien, B.; Mulluh Ndipen, F. An evaluation of a small-scale biodiesel production technology: Case study: Mango'o Village, Center Province, Cameroon. *Phys. Chem. Earth* 2009, 34, 55–58. [CrossRef]
- 19. Tsoutsos, T.; Kouloumpis, V.; Zafiris, T.; Foteinis, S. Life Cycle Assessment for biodiesel production under Greek climate conditions. *J. Clean. Prod.* **2010**, *18*, 328–335. [CrossRef]
- 20. Gardy, J.; Demirbas, A.; Rashid, U.; Budzianowski, W.M.; Pant, D.; Nizamia, A.S. Waste to biodiesel: A preliminary assessment for Saudi Arabia. *Bioresour. Technol.* **2018**, 250, 17–25. [CrossRef]
- 21. Gardy, J.; Hassanpour, A.; Lai, X.; Rehan, M. The influence of blending process on the quality of rapeseed oil-used cooking oil biodiesels. In Proceedings of the International Conference on Environment and Renewable Energy, Paris, France, 7–8 May 2014.
- 22. Silalertruksa, T.; Gheewala, S.H.; Hünecke, K.; Fritsche, U.R. Biofuels and employment effects: Implications for socio-economic development in Thailand. *Biomass Bioenergy* **2012**, *46*, 409–418. [CrossRef]
- 23. Corral Bobadilla, M.; Lostado Lorza, R.; Escribano García, E.; Somovilla Gómez, F.; Vergara González, E.P. An improvement in biodiesel production from waste cooking oil by applying thought multi-response surface methodology using desirability functions. *Energies* **2017**, *10*, 130. [CrossRef]
- 24. Hsiao, M.C.; Hou, S.S.; Kuo, J.Y.; Hsieh, P.H. Optimized Conversion of Waste Cooking Oil to Biodiesel Using Calcium Methoxide as Catalyst under Homogenizer System Conditions. *Energies* **2018**, *11*, 2622. [CrossRef]
- 25. Xuan NguyenThi, T.; Bazile, J.P.; Bessières, D. Density Measurements of Waste Cooking Oil Biodiesel and Diesel Blends Over Extended Pressure and Temperature Ranges. *Energies* **2018**, *11*, 1212. [CrossRef]
- 26. Paraíba, O.; Tsoutsos, T.D.; Tournaki, S.; Antunes, D.; Magnolfi, V.; Cocchi, M. Full chain analysis of the domestic used cooking oil to biodiesel chain—The European Initiative RecOil. In Proceedings of the 22th European Biomass Conference & Exhibition, Hamburg, Germany, 23–26 June 2014.
- 27. International Olive Council. Trends in World Olive Oil Consumption, Market Newsletter. 2016. Available online: www.oliveoilmarket.eu/wp-content/uploads/2016/03/NEWSLETTER_FEBRUARY-2016_ENGLISH.pdf (accessed on 6 December 2018).
- 28. EurObserv'ER, Biofuels Barometer. Available online: https://www.eurobserv-er.org/biofuels-barometer-2018 (accessed on 8 November 2018).

- 29. Hassan, U.; Al-Zubaidi, I.; Ibrahim, H. The Effect of Off-Spec Canola Biodiesel Blending on Fuel Properties for Cold Weather Applications. *ChemEngineering* **2018**, *2*, 30. [CrossRef]
- 30. Liquid Petroleum Products—Fatty Acid Methyl Esters (FAME) for Use in Diesel Engines and Heating Applications—Requirements and Test Methods; EN 14214; BSI Group: London, UK, 2012.
- 31. Fat and Oil Derivatives. Fatty Acid Methyl Esters (FAME). Determination of Free and Total Glycerol and Mono-, Di-, Triglyceride Contents; BS EN 14105; BSI Group: London, UK, 2011.
- 32. Animal and Vegetable Fats and Oils—Determination of Water Content—Karl Fischer Method (Pyridine Free); DIN EN ISO 8534; German Institute for Standardization: Berlin, Germany, 2017.
- 33. Fregolente, B.; Wolf Maciel, M.; Oliveira, L. Removal of water content from biodiesel and diesel fuel using hydrogel adsorbents. *Braz. J. Chem. Eng.* 2015, *32*, 895–901. [CrossRef]
- 34. Cardoso, C.; Celante, V.; Ribeiro de Castro, E.; Duarte Pasa, V. Comparison of the properties of special biofuels from palm oil and its fractions synthesized with various alcohols. *Fuel* **2014**, *135*, 406–412. [CrossRef]
- 35. Viegas, I.; Barradas Filho, A.; Marques, E.; Pereira, C.; Marques, A. Oxidative stability of biodiesel by mixture design and a four-component diagram. *Fuel* **2018**, *219*, 389–398. [CrossRef]
- Cordero-Ravelo, V.; Schallenberg-Rodriguez, J. Biodiesel production as a solution to waste cooking oil (WCO) disposal. Will any type of WCO do for a transesterification process? A quality assessment. *J. Environ. Manag.* 2018, 15, 117–129. [CrossRef] [PubMed]
- 37. Zahos-Siagos, I.; Karonis, D. Exhaust Emissions and Physicochemical Properties of Hydrotreated Used Cooking Oils in Blends with Diesel Fuel. *Int. J. Chem. Eng.* **2018**, 2018, 4308178. [CrossRef]
- Hafizil Mat Yasin, M.; Mamat, R.; Majeed Ali, O.; Fitri Yusop, A.; Adnin Hamidi, M.; Yusri Ismail, M.; Rasu, M. Study of diesel-biodiesel fuel properties and wavelet analysis on cyclic variations in a diesel engine. *Energy Procedia* 2017, 110, 498–503. [CrossRef]
- 39. Benjumea, P.; Agudelo, J.; Agudelo, A. Basic properties of palm oil biodiesel-diesel blends. *Fuel* **2008**, *87*, 2069–2075. [CrossRef]
- 40. Zahos-Siagos, I.; Karathanassis, V.; Karonis, D. Exhaust emissions and physicochemical properties of n-nutanol/Diesel blends with 2-ethylhexyl nitrate (EHN) or hydrotreated Used Cooking Oil (HUCO) as cetane Improvers. *Energies* **2018**, *11*, 3413. [CrossRef]
- 41. van Kasteren, J.M.N.; Nisworo, A.P. A process model to estimate the cost of industrial scale biodiesel production from waste cooking oil by supercritical transesterification. *Resour. Conserv. Recycl.* 2007, 50, 442–458. [CrossRef]
- 42. Directive 2014/94/EU on the Deployment of Alternative Fuels Infrastructure. Available online: https://eur-lex. europa.eu/legal-content/en/TXT/?uri=CELEX%3A32014L0094 (accessed on 8 November 2018).
- 43. Waste Framework Directive 2008/98/EC. Available online: http://ec.europa.eu/environment/waste/ framework/ (accessed on 8 November 2018).
- 44. Amending Directive on waste 2018/851. Available online: https://eur-lex.europa.eu/eli/dir/2018/851/oj (accessed on 8 November 2018).
- 45. Renewable Energy Directive II. Available online: https://ec.europa.eu/energy/sites/ener/files/documents/ directive_renewable_factsheet.pdf (accessed on 12 December 2018).
- 46. Agarwal, M.; Chauhan, G.; Chaurasia, S.P.; Singh, K. Study of catalytic behavior of KOH as homogeneous and heterogeneous catalyst for biodiesel production. *J. Taiwan Inst. Chem. Eng.* **2012**, *43*, 89–94. [CrossRef]
- 47. Suthisripok, T.; Semsamran, P. The impact of biodiesel B100 on a small agricultural diesel engine. *Tribol. Int.* **2018**, *128*, 397–409. [CrossRef]



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).