Energy recovery from used cooking oil

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Abstract:

The separate collection of Used Cooking Oil (UCO) is gaining popularity through several countries in Europe. One possibility of recovery the UCO is to feed it to internal combustion engine (ICE) for combined heat and power production (CHP). The collected used cooking oil is generally not suitable for direct use in the ICE, so a pre-treatment process is required based on heating to about 50 °C, in order to decrease the oil viscosity for the further treatments, and consisting of mainly large particles removal by sieving, decanting and sedimentation, in order to remove the smallest particles, and final storage. The possibility of pre-treating the UCO and feed it to ICE was studied in reference to a study case territory where it is estimated to collect about 800 t/year of UCO in the short term. UCO can be also used as s raw material for biodiesel production, which is obtained as a result of chemical processes of trans-esterification and oil separation. In this study, five scenarios, representing different possibilities for UCO re-use are defined and compared. In Scenario 1, used cooking oil is regenerated and employed as a fuel in cogeneration plant. In scenarios 2-5, different options of biodiesel production from UCO focusing on conventional and future technologies are considered.

The aim was to evaluate the environmental impacts generated per unit of UCO, comparing the analysed alterative solutions between themselves. The sensitivity and uncertainty of the impact results in terms of input parameters were was also investigated. For the impact assessment two methods were selected: the Global Warming Potential and Cumulative Exergy Demand. Results showed that the use of UCO in CHP plant has in general lower values of the environmental impact indicators than the use of UCO for biodiesel production.

Keywords:

Used cooking oil, cogeneration, biodiesel production, energy recovery, life cycle assessment, cumulative exergy demand, thermoecological cost.

1. Introduction

Every year in Italy, about 1.400.000 tons of vegetable oils and fats are consumed for edible purposes. The average consumption is about 25 kg per person per year, rising gradually over the next decade.

A significant rate of those oils, about 20%, is disposed of after the cooking process. The properties of the Used Cooking Oils (UCO) are different with respect to the ones of fresh vegetable oils because of the physical and chemical changes (mainly due to oxidative and hydrolytic reactions) that take place during frying [1]. The products of oxidation and decomposition make the UCO unsuitable for edible use and extremely harmful to the environment. Moreover, the increased production of UCO is creating severe disposal problems. In most of the cases, the UCO is drained as a waste, causing water treatment problems.

The UCO, after the necessary process of regeneration, may represents an important renewable energy source. Moreover, providing alternative ways of use for UCO may minimise the negative waste disposal effects. Also, the effective re-use of UCO represents an opportunity to reduce dependency on fossil fuels, reduce carbon emissions (contribute to meeting challenging Kyoto targets) and support local economies.

For these purposes, UCO can be used as s raw material for biodiesel production, which is obtained as a result of chemical processes of trans-esterification and oil separation [2–4]. Nowadays, in Italy as well as other European countries, biodiesel is mainly manufactured from rapeseed oil [5]. However, due to the heavy consumption of oils for edible purpose and to the lower raw material cost, UCO is a promising potential for biodiesel production. It is estimated that biodiesel produced from UCO could replace around 1.5% of the EU27 diesel consumption, helping Member States to reach the 2020 targets [6].

Furthermore, the UCO as regenerated fuel, through physical treatment, may be also used as a fuel for particular CHP diesel engines. Cogeneration, especially if applied locally, leads to additional advantageous effects due to the decrease of energy transformation and distribution losses.

The choice among the possible options of UCO re-use, should be based on the environmental life cycle analysis.

Environmental assessment of biodiesel production, especially involving Life Cycle Assessment (LCA), was implemented in several studies. Escobar et al. [7] and Iglesias et al. [8] compared the biodiesel production from virgin oils and UCO using CML impact assessment. Instead, Kiwjaroun et al. [9] proposed the use of Ecoindicator methodology for evaluating biodiesel synthesis by conventional and supercritical methods. In case of CHP, as an alternative solution of UCO re-use, Ortner et al. [10] proposed GHG balance for environmental assessment.

The environmental assessment of the UCO re-use strongly focuses on classical environmental indicators. Such analysis should be also performed from a natural resources depletion point of view. To address this aim, the exergetic analysis in whole production chain, with the concept of cumulative exergy consumption analysis (CEX) proposed by Szargut [11,12] can be applied to evaluate different quality of energy carriers. Exergy [11] is defined as the maximum ability of an energy carrier to perform work with respect to the common environment or the minimum theoretical work required to obtain the substance with given parameters and composition. The exergetic analysis for biodiesel production from UCO was previously performed in [13–16].

This paper aims to analyse and compare the environmental impacts and the primary resource consumptions due to the different alternative ways of UCO valorization.

In this study, five scenarios, representing different possibilities for UCO re-use are defined and compared. In Scenario 1, used cooking oil is regenerated and employed as a fuel in cogeneration plant. In scenarios 2-5, different options of biodiesel production from UCO focusing on conventional and future technologies are considered.

The impact assessment is carried out adopting: climate change indicator from IPCC (implemented from CML-IA) and analysis of cumulative consumption of non-renewable exergy. Full description of those indicators is presented in [16,17]. Both assessments are carried out using the sequenced method [11]. The impacts are calculated assuming a system expansion and including the avoided effects caused by the substitution of final products of the analysed processes.

The analysis is carried out, reported and described according to the LCA phases (ISO 14040-44, 2009) [19,20]: goal and scope definition and inventory analysis are presented in the materials and methods section, while impact assessment and interpretation will be discussed in the results section.

2. Materials and methods

2.1. Goal and scope definition

Purpose of the present LCA study is to analyse the environmental impacts and resource consumption for different options of UCO re-use. The considered alternative solutions are listed in Table 1.

Table 1: Analysed scenarios

Scenario	Description	Abbreviation
1	CHP plant fed by regenerated UCO	SC1-CHP
2	Alkali-catalytic conventional biodiesel production from UCO using methanol and NaOH	SC2-NaOH
3	Acid-catalytic conventional biodiesel production from UCO using methanol and H_2SO_4	SC3-Acid
4	Alkali-catalytic conventional biodiesel production from UCO using methanol and KOH	SC4-KOH
5	Non catalytic supercritical biodiesel production	SC5-Scrit

The above mentioned options are compared, assuming the functional unit equal to 1 ton of input UCO. Additionally, the impact results are evaluated taking into consideration the avoided effects caused by the substitution of process products and co-products. Moreover, the analysis of the contributions of the different phases of the UCO processing is carried out, highlighting the most impactful ones. Finally, the sensitivity and uncertainty analysis of the results is presented.

The LCA boundaries of the analysed systems include the following processes: containers washing, delivering of UCO to the plants, pre-treatment of UCO, and processing at the plants (respectively CHP or biodiesel production). Collection of UCO was not included in the systems. Collection system and consumption strongly depend on local conditions and arrangements. For this reason, being the collection a preliminary step contributing in the same way to the five compared scenarios, it was not included, for the moment, in the analysis. The UCO is treated as a waste, thus it is assumed as a zero burden input of the system.

The impact assessment is carried out with the use of the following methods of evaluation: CML-IA (for conciseness matter only climate change will be discussed in this paper) and CEX in whole life cycle.

2.2. Life Cycle Inventory Analysis

The inventory analysis is developed according to the ISO 14040 and it includes the required energy and materials (inputs) flows as well as products, co-products, emissions and wastes (outputs) emitted to the environment during all the considered processes.

Data about the pre-treatment of UCO and co-generation were referenced to an Italian study case, while biodiesel processes data were retrieved from literature.

The study is carried out with reference to a study case located in Italy, where it is expected to be able to collect about 800 t of UCO per year [21]. This amount of UCO is considered to feed cogeneration or biodiesel plants.

The UCO collection process, which is assumed to be the same for each the analysed scenarios (and hence not included in the calculation as stated before), starts from the oil collection by means of specific containers with a volume of 3 and 30 litres, respectively, that were previously distributed to the public collection points. The containers arrive in a centralised collection plant where they are emptied and washed in order to be re-distributed to the public. Collected oil is transported to utilisation plants (CHP-based and biodiesel-based). In the present work, the transportation phase is modelled by considering the fuel consumption required for the lorry transport of the UCO to processing plant site. The distance between centralised collection plant and processing plants is assumed to be 200 km. The total fuel consumption during the transportation phase is estimated as 5 000 l. As a matter of fact this distance is rather likely in the case of biodiesel plants, which are not so commonly present on the Italian territory and which require to be not too small to be economically sustainable. On the contrary, CHP plants could be of quite small size and can easily be widespread on the territory, reducing drastically the transportation requirements. However, for the sake of comparison, in this study the same transportation distance was assumed for the CHP and biodiesel scenarios.

The data inventory regarding the sources consumption during the oil container washing and transportation phase is presented in Table 2.

Table 2: Inventory of container washing phase [21]

Inputs/outputs	Total	Data source
Input		
UCO, t	800	Primary
Washing and storage plant		
Input		
Water, l	39 000	Primary
Electricity – containers washing, kWh	5003	Primary
Output		
UCO, t	8 000	Primary
Wastewater, l	39 000	Primary
Transport to plant		
Input		
Diesel, l	5 000	Primary/Ecoinvent database

2.3. The use of UCO in cogeneration plant

The UCO, after being collected, cannot be used directly as fuel in the engine. Thus, several pre-treatment phases are required. The UCO pre-treatment comprises the pre-heating step, which is necessary in order to ensure the correct viscosity for subsequent treatments. After pre-heating, sieving and decantation processes are carried out in a tank that is designed to contain the maximum daily treatable quantity and, therefore, to ensure a residence time which allows the gravity sedimentation of impurities for the first oil clarification. At the end of the sedimentation, the oil is sent to the next process by a lifting pump. Finally, the process of extraction/filtration ensures further separation of the finest particles that have not extracted yet from the previous treatment stages. This process occurs through two tanks at a constant temperature of 50°C and ensures further sedimentation of the particles in the oil; besides it allows the reduction of the volatile fatty acids content because of the heat that is steadily provided. Once the oil is placed inside the tank, it is then sprayed through a sprinkler system with a quantity of water equal to approximately 5% of the oil volume to be treated. This process last about 48 hours and allows the entrainment of suspended particles to the bottom together with the droplets of water, by exploiting the difference of the density of the two fluids. The residual sludge ends up in wastewaters. After this type of pre-treatment, the regenerated oil is suitable to be used within an internal combustion engine. During the regeneration process, it is assumed a mass loss of about 5%, resulting in approximately 768 tons of regenerated UCO available for energy production. The inventory data regarding the sources consumption in the pre-treatment phases are calculated on the basis of consumption of designed devices, using data available in [21], and are presented in Table 3.

Table 3: Inventory of the pre-treatment phase [21]

Inputs/outputs	**Total**	**Data source**
Cogeneration plant - oil regeneration		
Input		
UCO, t	800	Primary
Electricity - pre-heating, kWh	18 754	Primary
Electricity – sieving, decantation and pumping, kWh	177	Primary
Electricity – filtration and extraction, kWh	13 104	Primary
Water, l	40 000	Primary
Output		
Regenerated UCO, t	767	Primary
Wastewater, l	40 000	Primary

In order to evaluate the amount of energy produced in cogeneration plant, the information about chemical composition of the input fuel is needed. The data about the UCO quality were experimentally determined, in previous work [21], using chemical analysis on a representative sample collected from a storage tank, after decanting and after whole of the regeneration processes. Table 4 shows a comparison between the results of that analysis, the limits set by the engine manufacturers and the typical parameters for UCO after the regeneration processes.

Table 4: UCO quality comparison [21]

Parameter, unit	**Engine limits**		**UCO after collection**	**UCO after pre-treatment**
	min	**max**		
Density (15°C), kg/m3	900	930	918	916
Flashpoint, °C	220		245	237
Net Calorific Value, MJ/kg	35.00		36.89	37.26
Kinematic viscosity (40°C), mm2/s		38	20	20
Carbon residue, % mass		0.4	<0.1	
Iodine value, g/100g	100	120	114	37
Number of sulfur, mg/kg		20	3.1	3.2
Total contamination, mg/kg		25	8.4	8
Neutralization number, mgKOH/g		2.0	1.5	1.4
Free fatty acids, %		4	0.2	0.1
Oxidation stability, H	5.0		9	10
Phosphorus content, mg/kg		15	3.2	<5
Ash content, % mass		0.01	0.01	0.003
Water content, % mass	0.075	0.065	0.075	0.1

In the present study, referring to [21] a 1 MW diesel cycle engine is considered for electricity and heat production. The operational time for the engine is assumed as 3056 hours per year. The other technical data of the engine are presented in Table 5. The amount of electricity and heat generated in the cogeneration plant are calculated using formula (1) and (2).

$$\text{Gross Electricity Production} = \text{oil flow rate} \cdot \text{NCV} \cdot \text{operating time} \cdot \text{electrical efficiency} \qquad (1)$$

$$\text{Thermal energy} = \text{recoverable thermal power} \cdot \text{operating time} \cdot \text{loss factor} \quad (2)$$

The recoverable thermal power value is extracted from the engine data sheet and it is given by the two contributions from both the engine cooling system and the exhaust heat recovery. The loss factor is assumed equal to 0.85. The inventory data regarding the output streams in the operational phase are presented in Table 6.

The final products – in this case electricity and heat produced by the CHP - may substitute the products which are produced in marginal processes involving fossil fuels. For these streams the appropriate records from Ecoinvent database were considered in the inventory.

Table 5: Engine technical data

Parameter	Value
Mechanical power, kW	1 097
Speed, rpm	1 500
Fuel consumption, kg/h	251
Electric power, kW	999
Thermal Power (LT), kW	440
Thermal Power (HT), kW	440
Hot water production 70-80°C, kg/h	38
Saturated steam production, kg/h	800
Electric efficiency, %	39.9
Thermal efficiency, %	40.2
Total efficiency, %	80.0

Table 6: Inventory of co-generation phase

Inputs/outputs	Total	Data source
Cogeneration plant – operational phase		
Input		
Regenerated UCO, t	767	Primary
Output		
Gross electricity production, kWh	3 167 442	Primary
Heat production, kWh	2 712 670	Primary

2.4. The use of UCO for biodiesel production

Biodiesel is a lower alkyl ester(s) of the long chain fatty acids and it is the product of the transesterification of vegetable oils or by esterification of free fatty acids with lower alcohols in the catalyst presence [22].

Several possibilities for the transesterification of UCO for biodiesel synthesis exist. The environmental effects of the different processes of biodiesel production depend on reaction temperature, molar ratio of alcohol to oil, the type of alcohol used, type of catalyst used and its concentration, reaction time, presence of moisture and free fatty acids (FFA) content on transesterification and different pre-treatment procedures [5].

The catalysts play an important role in the transesterification reaction. Depending on the catalysts, the following types of transesterification are possible: alkali-catalyzed transesterification, acid-catalyzed transesterification, acid- and alkali-catalyzed two-step transesterification, enzymecatalyzed transesterification and non-catalytic conversion technique in terms of use co-solvent or supercritical methanol for transesterification. The comprehensive review of the transesterification methods applied for UCO can be found in [2,5,23,24].

In this work, four different methods of pre-treatment and transesterification of UCO to yield biodiesel are considered. These alternative solutions include three conventional and one supercritical biodiesel production processes.

The inputs and outputs data for each analysed process were collected on the basis of literature review. The detailed process analysis of the inputs and outputs of the transesterification phase are presented in Tables 6-9. The data are implemented according to the literature references [9,14,26]. Thus, for alkali-catalytic conventional biodiesel production from UCO using methanol and NaOH and non catalytic supercritical biodiesel production, the inventory bases on process data presented by Kiwjaroun et.al [9]. For acid-catalytic conventional biodiesel production from UCO using methanol and H_2SO_4 the data proposed by Varanda et al. [26] are employed. Finally, for alkali-catalytic conventional biodiesel production from UCO using methanol and KOH, the analysis is carried out using data presented by Talens et al. [14].

In all of the analysed scenarios, the final products and co-products may substitute the products which are produced in marginal processes involving fossil fuels. In particular in the different biodiesel processes the avoided streams are conventional fossil diesel and glycerol. For these streams the appropriate records from Ecoinvent database were considered in the inventory.

Table 6: Inventory of the alkali-catalytic conventional biodiesel production from UCO using methanol and NaOH

Inputs/outputs	**Total**		**Data source**
	Min	**Max**	
Biodiesel production			
Input			
UCO, t	800		Primary
Methanol, t	97.3	164.0	[9,25,26]
NaOH, t	2.6	8.2	[9,25,26]
KOH, t	-	-	[9,25,26]
H_2SO_4, t	0.0	7.3	[9,25,26]
H_3PO_4, t	0.1	2.1	[9,25,26]
CaO, t	0.0	0.1	[9,25,26]
Propane, t	0.0	0.1	[9,25,26]
Glycerol process, t	0.0	13.9	[9,25,26]
Steam (from natural gas), MJ	1.6E+06	5.7E+0.6	[9,25,26]
Electricity, kWh	6.4E+02	7.7E+03	[9,25,26]
Output			
Biodiesel, t	767.6	799.7	Primary
Glycerol, t	76.8	81.6	Primary
Solid waste (salts), t	1.3	12.3	[9,25,26]
Liquid waste (water, methanol, acids, glycerol), t	29.1	99.3	[9,25,26]

Table 7: Inventory of the acid-catalytic conventional biodiesel production from UCO using methanol and H_2SO_4

Inputs/outputs	**Total** **Min**	 **Max**	**Data source**
Biodiesel production			
Input			
UCO, t	800		Primary
Methanol, t	165.2	173.7	[25,26]
NaOH, t	-	-	[25,26]
KOH, t	-	-	[25,26]
H_2SO_4, t	70.9	115.2	[25,26]
H_3PO_4, t	-	-	[25,26]
CaO, t	40.5	65.9	[25,26]
Propane, t	-	-	[25,26]
Glycerol process, t	-	-	[25,26]
Steam (from natural gas), MJ	6.8E+06	9.2E+06	[25,26]
Electricity, kWh	7.3E+02	6.9E+03	[25,26]
Output			
Biodiesel, t	772.7	811.3	Primary
Glycerol, t	83.3	88.7	Primary
Solid waste (salts), t	124.4	158.95	[25,26]
Liquid waste (water, methanol, acids, glycerol), t	83.7	133.1	[25,26]

Table 8: Inventory of the alkali-catalytic conventional biodiesel production from UCO using methanol and KOH

Inputs/outputs	**Total** **Min**	 **Max**	**Data source**
Biodiesel production			
Input			
UCO, t	800		Primary
Methanol, t	88.9	176.9	[10,14,16]
NaOH, t	-	-	[10,14,16]
KOH, t	0.1	16.6	[10,14,16]
H_2SO_4, t	0.0	10.2	[10,14,16]
H_3PO_4, t	0.0	3.9	[10,14,16]
CaO, t	-	-	[10,14,16]
Propane, t	-	-	[10,14,16]
Glycerol process, t	-	-	[10,14,16]
Steam (from natural gas), MJ	0.0	7.2E+05	[10,14,16]
Electricity, kWh	3.27E+04	1.59E+05	[10,14,16]
Output			
Biodiesel, t	683.8	777.8	Primary
Glycerol, t	67.1	85.0	Primary
Solid waste (salts), t	0.0	15.2	[10,14,16]
Liquid waste (water, methanol, acids, glycerol), t	0.0	106.5	[10,14,16]

Table 9: Inventory of the non-catalytic supercritical biodiesel production

Inputs/outputs	Total		Data source
	Min	Max	
Biodiesel production			
Input			
UCO, t	800		Primary
Methanol, t	88.5	95.4	[9,25]
NaOH, t	-	-	[9,25]
KOH, t	-	-	[9,25]
H_2SO_4, t	-	-	[9,25]
H_3PO_4, t	-	-	[9,25]
CaO, t	-	-	[9,25]
Propane, t	-	-	[9,25]
Glycerol process, t	-	-	[9,25]
Steam (from natural gas), MJ	9.5E+05	6.2E+06	[9,25]
Electricity, kWh	3.2E+03	6.5E+04	[9,25]
Output			
Biodiesel, t	801.2	803.6	Primary
Glycerol, t	84.9	94.2	Primary
Solid waste (salts), t	-	-	[9,25]
Liquid waste (water, methanol, acids, glycerol), t	-	-	[9,25]

3. Results and discussion

In order to evaluate the environmental impacts, the CML impact assessment method is applied. Such method covers the following environmental impact indicators: depletion of abiotic resources (expressed in kg of Sb equivalent or in MJ exergy content), climate change from IPCC methodology (expressed in kg of the CO_2 equivalent integrated over 100 years), stratospheric ozone depletion (expressed in kg of CFC-11 equivalent), photo-oxidant formation (expressed in kg of C_2H_4 equivalent), acidification (expressed in kg of SO_2 equivalent), eutrophication (expressed in kg of PO_4^{3-} equivalent), human toxicity and ecotoxicity: fresh water aquatic eco-toxicity, marine eco-toxicity, terrestrial eco-toxicity (all expressed in kg of 1,4 – DCB equivalent). Full description of the impact indicators is available in [17]. In this paper, only the results for equivalent emissions of CO_2 are presented, for conciseness matter.

The cumulative exergy consumption is calculated using the sequence method proposed by J. Szargut [11,12]. According to those sources, the cumulative exergy demand is defined as a cumulative consumption of non-renewable exergy connected with the manufacturing of a particular product.

3.1. Results of GWP and CEX analysis

A comparison among the analyzed systems is presented in the following Table 10, only considering the effective consumptions and emissions from the UCO valorization processes, i.e. excluding the avoided effects described before.

Table 10: Exergy and environmental impact of the 1 ton of UCO re-use

Scenario	Cumulative Exergy Demand, GJ_{ex}	Global Warming Potential, t CO_{2eq}
SC1-CHP	0.517	0.039
SC2-NaOH	6.501	0.224
SC3-Acid	17.332	0.813
SC4-KOH	8.702	0.233
SC5-Scrit	13.190	0.683

Impact effects range, in terms of CEX, from a minimum value of 0.517 GJ_{ex} per 1 ton of UCO for the Scenario 1 (cogeneration plant) to a maximum of 17.332 GJ_{ex} per 1 ton of UCO corresponding to the Scenario 3 (acid-catalyzed biodiesel production), while for the GWP indicator the values vary between 0.039 t CO_{2eq} and 0.813 t CO_{2eq} for the same options. As expected, such results prove that the use of UCO in cogeneration plant is more environmentally efficient with respect to the re-use for biodiesel production. This is due to the different complexity of the processes involved in the analysed scenarios.

When comparing the obtained impacts, concerning the biodiesel production, the alkali-catalyzed processes involving NaOH and KOH as a catalyst are the best solution from CEX and GWP point of view.

The resulting impacts are higher for the acid catalysed and supercritical biodiesel production, mainly because of the higher energy requirements. In particular, it is possible to notice that the impact, in terms of both CEX and GWP, of 1 ton of UCO employed in acid-catalyzed process is from 2 to 2.7 times greater than the ones in the alkali-catalyzed process in terms of CEX and from 3.5 to 3.6 times greater in terms of GWP.

The avoided effects for the production of electricity, heat, biodiesel and glycerol were then included. Table 11 shows the avoided effects associated with the generation of each unit of products and co-products in the analysed process. Table 12 shows the overall values of CEX and GWP when avoided effects are included in the five scenarios.

Table 11: Avoided effects of the products and co-products generation

Scenario	Product/Co-product	Substituted product	Avoided CEX	Avoided GWP
SC1-CHP	**Electricity**	Electricity from Italian electricity mix	-5.00 MJ_{ex}/kWh	-0.518 $kgCO_{2eq}$/kWh
SC1-CHP	**Heat**	Heat from natural gas	-1.1 MJ_{ex}/kWh	-0.072 $kgCO_{2eq}$/kWh
SC2-NaOH	**Biodiesel**	Diesel, petroleum product	-51.08 MJ_{ex}/kg	-2.68 $kgCO_{2eq}$/kg
SC2-NaOH	**Glycerol**	Glycerol, from epichlorohydrin	-47.15 MJ_{ex}/kg	-2.26 $kgCO_{2eq}$/kg
SC3-Acid	**Biodiesel**	Diesel, petroleum product	-42.40 MJ_{ex}/kg	-2.20 $kgCO_{2eq}$/kg
SC3-Acid	**Glycerol**	Glycerol, from epichlorohydrin	-46.23 MJ_{ex}/kg	-2.21 $kgCO_{2eq}$/kg
SC4-KOH	**Biodiesel**	Diesel, petroleum product	-48.04 MJ_{ex}/kg	-2.64 $kgCO_{2eq}$/kg
SC4-KOH	**Glycerol**	Glycerol, from epichlorohydrin	-46.84 MJ_{ex}/kg	-2.25 $kgCO_{2eq}$/kg
SC5-Scrit	**Biodiesel**	Diesel, petroleum product	-45.95 MJ_{ex}/kg	-2.32 $kgCO_{2eq}$/kg
SC5-Scrit	**Glycerol**	Glycerol, from epichlorohydrin	-46.43 MJ_{ex}/kg	-2.21 $kgCO_{2eq}$/kg

Table 12: Avoided effects of the 1 ton of UCO re-use

Scenario	Cumulative Exergy Demand, GJ_{ex}	Global Warming Potential, t CO_{2eq}
SC1-CHP	-23.28	-2.27
SC2-NaOH	-54.55	-2.86
SC3-Acid	-44.88	-2.33
SC4-KOH	-43,57	-2.40
SC5-Scrit	-49.00	-2.45

The values of the obtained avoided effects are negative for all of the studied cases. This means that by substituting the products from marginal processes, saving in terms of both CEX and GWP can be achieved. With focus on the product generation, the computed values seem to indicate that the most eco-sustainable solution is the employment of UCO for alkali-NAOH catalyzed process, for both glycerol and biodiesel production. Despite the re-use of UCO as a fuel in cogeneration plant is characterized by the lowest environmental impacts, as shown in Table 10, the savings obtained by the substitution of products and co-products are significantly higher in biodiesel production process. In particular, by using the UCO in the NaOH-catalyzed biodiesel production process instead of CHP solution, the savings are 2.3 and 1.3 times greater for CEX and GWP, respectively.

Next step of the evaluation consists of the contribution analysis. Figures 1 and 2 show the contribution of each sub-process (excluding the avoided effects for products and by-products generation), including oil container washing phase, transportation of the collected UCO to the plant site, final processing stage and waste management phase.

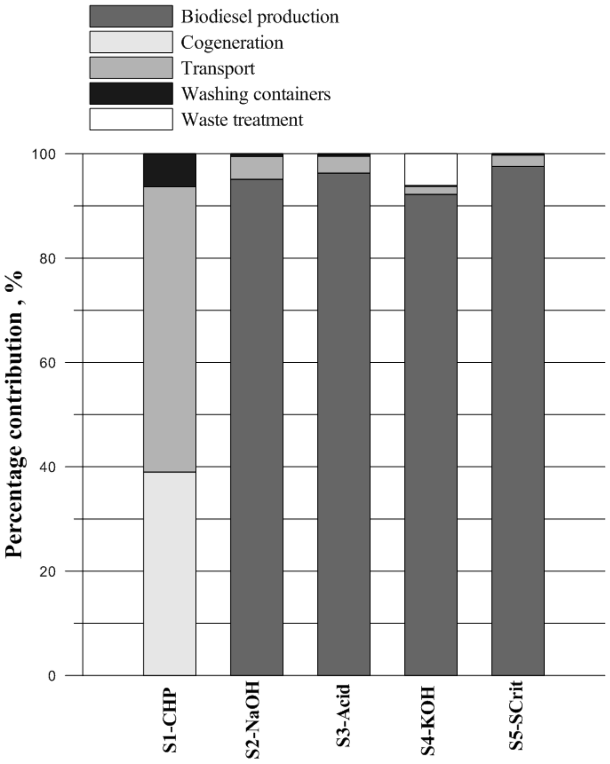

Fig. 1 Life cycle phase's contributions to the total values of CEX for analysed scenarios.

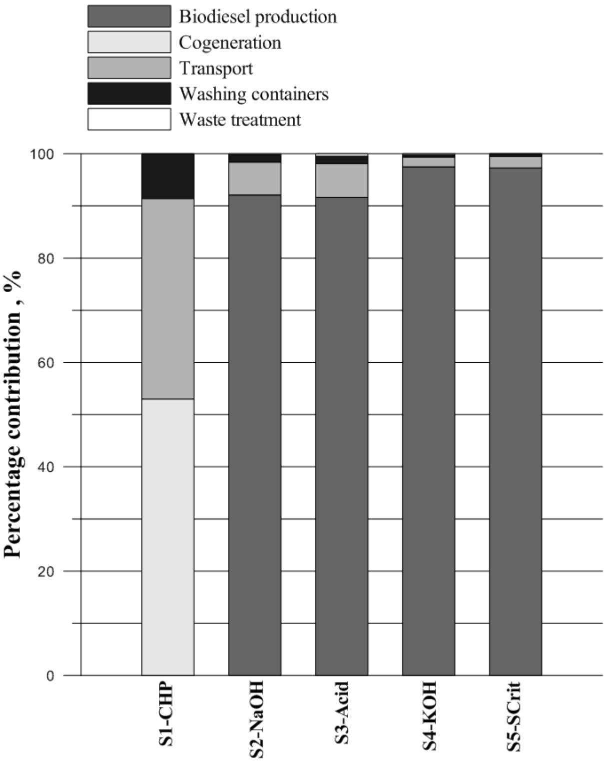

Fig. 2 Life cycle phase's contributions to the total values of GWP for analysed scenarios.

As can be observed, the final processing stage is the highest contributor for biodiesel production scenarios. The contribution of this phase in terms of CEX and GWP varies from 92% to 97% for both impacts.

As far as CHP concerns, the share of this phase is 39% and 52% for CEX and GWP, respectively.

Specifically, in all of the analysed scenarios, high primary energy consumption has been observed during the pre-treatment in cogeneration plant as well as in the esterification process. In the analysis, it has been assumed that the electricity delivered to the site plant comes from the Italian electricity mix, while process steam is generated from natural gas combustion process.

However, in case of CHP, the transportation phase plays a significant role with a contribution of 55% and 39% for CEX and GWP, respectively. In contrast, for biodiesel production the contribution of this phase varies from 1.5% to 4.0 % for CEX and 2% to 6% for GWP. Increasing the distance from the centralised collection plant to the considered CHP plant, the obtained effects may significantly increase, resulting in a higher primary energy consumption. For this reason, CHP plant should be applied locally, in order to minimize the transport distance from the collection point to the CHP plant.

Concerning the washing containers phase, the maximal contribution of 6% and 8% for CEX and GWP, respectively, is observed for scenario with cogeneration plant. For biodiesel production scenarios, this phase contributes from 0.2 to 0.5% in CEX and from 0.5 to 1.4% in total GWP.

The waste treatment stage seems to be an important phase only for the biodiesel production scenario with acid-catalyst (6%). For others cases this phase is negligible with a contribution lower than 0.5%.

To sum up, the most influent parameters are heat, electricity and fuel consumption for the transport. The sensitivity analysis for these parameters is conducted in the next section.

3.2. Sensitivity and uncertainty analyses

A conventional perturbation analysis is performed to find out the sensitivity of the results reported in Table 10 for the most influential parameters, which are: electricity, diesel for the transport and heat consumption. In this analysis one parameter is changed (±10%) at time and the influence on the result is studied. In Figures 3-8 the results are presented.

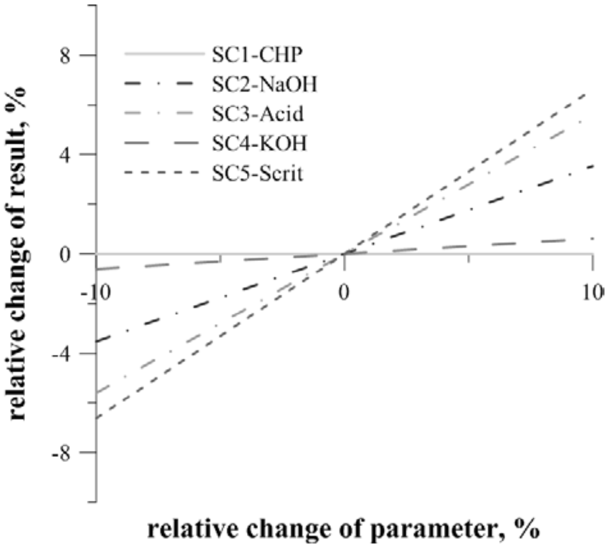

Fig. 3 Sensitivity of CEX on heat consumption

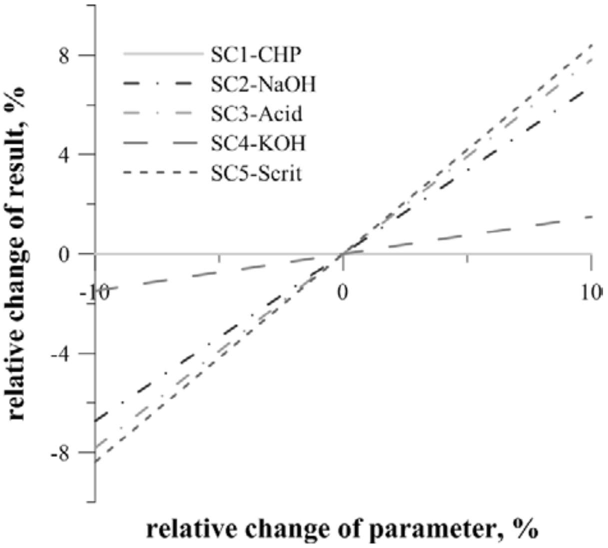

Fig. 4 Sensitivity of GWP on heat consumption

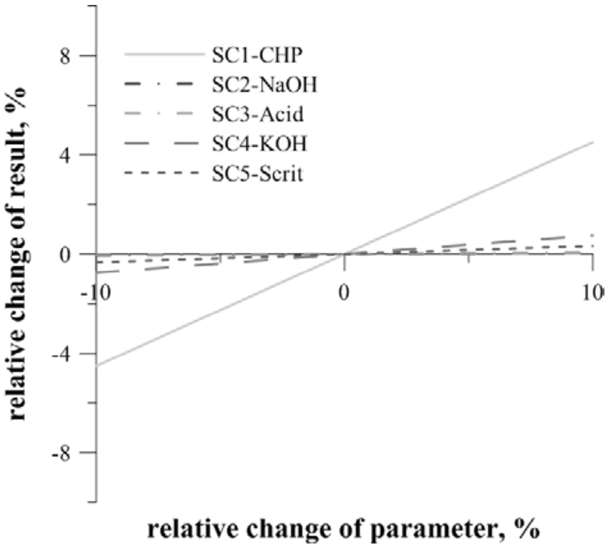

Fig. 5 Sensitivity of CEX on electricity consumption

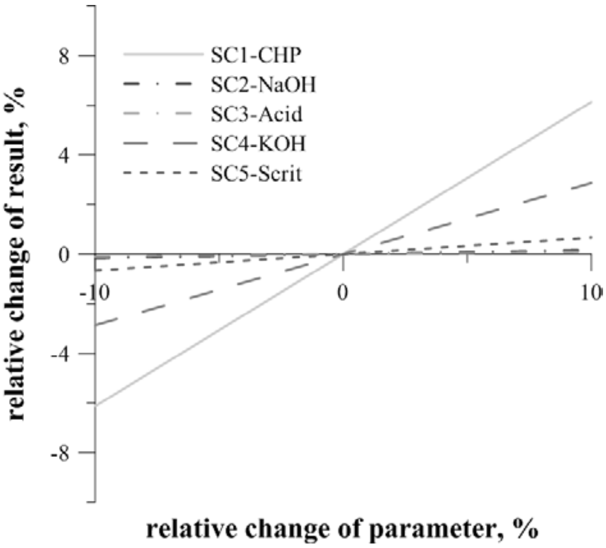

Fig. 6 Sensitivity of GWP on electricity consumption

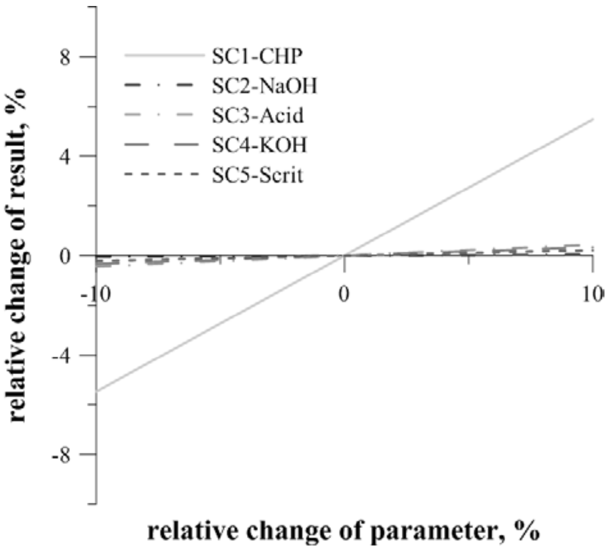

Fig. 7 Sensitivity of CEX on fuel consumption for transport

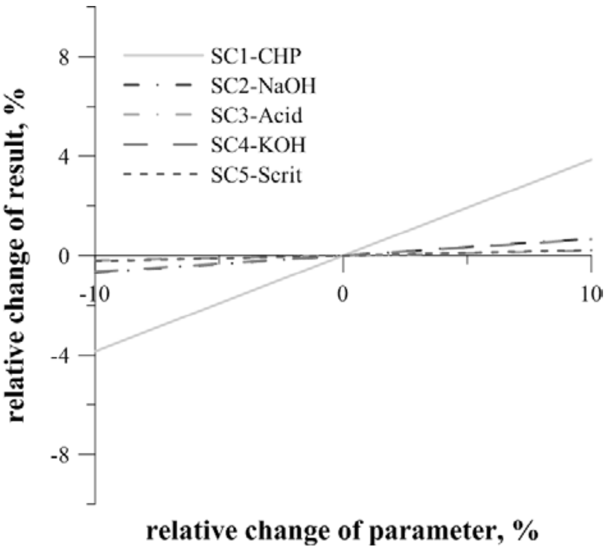

Fig. 8 Sensitivity of GWP on fuel consumption for transport

Concerning the heat consumption, the SC5-Scrit indicators are subjected to the most significant variations that are ± 6.6 % for the CEX and ±8.4% for the GWP. In contrast, the analysed indicators for the SC4-KOH seem to be not affected by a variation of the heat consumption in a sensitive way.

As far as the electricity consumption parameter concerns, both indicators, for all the cases of study results very low influenced, with the exception of the SC1-CHP which values varies of ±4.5% and ±6.3% for the CEX and GWP, respectively.

Similar behaviour is observed for the diesel consumption related to the transport. Also in this case, for the SC1-CHP indicators the greatest variations are registered (±5.5% and ±3.8% for CEX and GWP, respectively), while they are not influenced by variations of the considered factor for all the other cases under analysis.

Because of the high variability of data available in literature, an uncertainty analysis is required. In fact, as it possible to notice observing Tables 6-9, the collected data regarding the particular process inventory differ from each other substantially. For example, Ortner et al. [10] assumed both heat and electricity consumption on the pre-treatment stage, while primary calculations conducted in the present study does not consider heat consumption. Moreover, in [10] the unitary water and electricity consumption in the collection and pre-treatment phases are extremely higher than the ones reported in this study. The water consumption from the mentioned source is 2 000 l/tUCO, while it is 50 l/tUCO in this study. In case of electricity consumption, in [10] it was assumed as 70 kWh/tUCO, while in the present study is taken as 6 kWh/tUCO. Moreover, as mentioned before, the heat consumption in this analysis is not considered, while in [10] the unit amount of heat necessary for pre-treatment processing is equal to 272 kWh/tUCO.

Similar situation can be observed for biodiesel production scenarios. The process data, especially energy consumption, vary from each other, as it is shown in Tables 6-9.

Such variability of the input parameters, especially energy carriers consumptions, which are the most impactful contribution among the analysed effects, may have influence on the final results.

Thus, in order to evaluate the uncertainty of the resulting impacts, a Monte Carlo simulation is conducted. The random values from the assumed probability distribution are selected in 10 000 runs and the forecast distribution, for both CEX and GWP indicators, is obtained between 10th and 90th percentile. The Monte Carlo simulation is performed assuming uniform distribution of all the input data. For the biodiesel production scenarios, the parameters of the probability distribution, namely minimum and maximum values, are assumed on the basis of literature data, presented in Tables 6-9.

The variability of the fuel consumption for transportation is assumed to be arbitrary, from 0 to 5 000 l per year. In case of scenario with cogeneration plant, the variability of the input parameter, namely electricity, water and heat consumption, is assumed comparing the primary data with the data presented by Ortner et al. [10]. Thus, for the uncertainty estimation related to the CHP scenario results, the following data variability is assumed: 50-200 l/tUCO for water consumption, 6-70kWh/tUCO for electricity consumption and 0-272 kWh/tUCO for heat consumption. The results of the uncertainty analysis are presented in Tables 13 and 14.

Table 13: Uncertainty analysis of the CEX impact

Scenario	**Mean, GJ_{ex}/tUCO**	**Median, GJ_{ex}/tUCO**	**SD, GJ_{ex}/tUCO**	**CV, %**	**10th**	**90th**
SC1-CHP	0.357	0.356	0.107	30.0	0.111	0.600
SC2-NaOH	10.707	10.690	1.855	17.3	6.904	14.589
SC3-Acid	7.045	7.052	1.070	15.2	4.822	9.276
SC4-KOH	18.942	18.957	0.964	5.1	17.154	20.726
SC5-Scrit	9.169	9.131	2.138	23.3	5.400	12.969

Table 14: Uncertainty analysis of the GWP impact

Scenario	**Mean, $kgCO_{2eq}$/tUCO**	**Median, $kgCO_{2eq}$/tUCO**	**SD, $kgCO_{2eq}$/tUCO**	**CV, %**	**10th**	**90th**
SC1-CHP	0.029	0.029	0.008	28.6	0.010	0.049
SC2-NaOH	0.444	0.446	0.111	25.0	0.239	0.646
SC3-Acid	0.221	0.221	0.035	15.7	0.139	0.304
SC4-KOH	0.943	0.943	0.063	6.7	0.823	1.065
SC5-Scrit	0.427	0.425	0.140	32.8	0.177	0.679

The Coefficient of Variation (CV) shows the variability of the resulting impacts caused by risk parameters. For the first scenario, the CV was obtained at 30% and 28.6% for CEX and GWP respectively. The highest uncertainty (32.9%) is observed for the GWP factor in the scenario of biodiesel production with supercritical methanol.

In this case the uncertainty is caused mainly due to high variability of heat and electricity consumption reported in literature.

On the contrary, the lowest variation of both analysed impacts (5.1% for CEX and 6.7% for GWP) is observed for biodiesel production scenario with KOH as a catalyst. In this case, the data were confirmed to be delivered by real producers.

4. Conclusions

The purpose of this Life Cycle Assessment study was to analyse and compare the environmental impacts and the primary resource consumptions due to the different alternative ways of UCO valorization.

Five scenarios, representing different possibilities for UCO re-use were defined and compared. In Scenario 1, used cooking oil is regenerated and employed as a fuel in cogeneration plant. In scenarios 2-5, different options of biodiesel production from UCO focusing on conventional and future technologies are considered.

The impact assessment was carried out adopting: climate change indicator from IPCC (implemented from CML-IA) and analysis of cumulative consumption of non-renewable exergy. The impacts were calculated including the avoided effects caused by the substitution of final products in marginal production processes. .

Results showed, as expected, that the option with cogeneration plant has in general lower values of the environmental impact indicators per unit of processed UCO. This is mainly due to the less complex process of UCO re-use. Concerning the biodiesel production, the alkali-catalyzed processes involving NaOH and KOH as a catalyst are the best solution from CEX and GWP point of view. The resulting impacts were higher for the acid catalysed and supercritical biodiesel production, mainly because of the higher energy requirements.

It was also reported that by substituting the products from marginal processes, saving in terms of both CEX and GWP can be achieved. With focus on the product generation, the computed values seem to indicate that the most eco-sustainable solution is the employment of UCO for alkali-NAOH catalyzed process, for both glycerol and biodiesel production. The savings obtained by the substitution of products in biodiesel production processes are significantly higher than in CHP solution. In particular, by using the UCO in the NaOH-catalyzed biodiesel production process instead of CHP solution, the savings are 2.4 and 1.3 times greater for CEX and GWP, respectively.

It was investigated that the final processing stage is the highest contributor for biodiesel production scenarios. The contribution of this phase in terms of CEX and GWP varies from 92% to 97% for both impacts. In case of CHP option, the share of this phase was 39% and 52% for CEX and GWP, respectively. It was also noted that for CHP, the transportation phase plays a significant role with a contribution of 55% and 39% for CEX and GWP, respectively.

Concerning the sensitivity analysis, the heat consumption, was the parameter which caused the most significant variations that are ± 6.6 % for the CEX and ±8.4% for the GWP.

The highest Coefficient of Variation (32.9%) was observed for the GWP factor in the scenario of biodiesel production with supercritical methanol. On the contrary, the lowest variation of both analysed impacts (5.1% for CEX and 6.7% for GWP) was reported for biodiesel production scenario with KOH as a catalyst.

To sum up, the UCO can be effectively transformed into energy, both as a biodiesel burned in vehicle engines as well as fuel in cogeneration plant. Even if, the CHP solution is a simpler process, the highest savings in the biodiesel production state that this is most efficient from environmental point of view, additionally the biodiesel option is more preferable also from political point of view. To include these different aspects, the further analysis should be carried out by implementing multicriteria analysis. The environmental criterion can be merged and described as a thermoecological cost which in contrast to other methods of ecological assessment, can bring all environmental impacts into one measure which is the exergy of the consumed natural, non-renewable resources.

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