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Strategies to improve the sustainability of the heterogeneous catalysed biodiesel production from waste cooking oil

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ABSTRACT

This work aims to present the strategies assessment to reduce the environmental impacts of the biodiesel production from waste cooking oil (WCO) catalyzed by a heterogeneous bifunctional catalyst (a mixture of iron and CaO). The assessed strategies were based on varying iron precursor (Fe_2O_3 or $Fe(NO_3)_3{\cdot}9H_2O$), iron content, catalyst loading and alcohol/oil molar ratio. The biodiesel production is cleaner when the iron salt is the catalyst precursor. In this case, the contribution to global warming potential (GWP), photo-oxidation (PO), eutrophication (E) and acidification (A), was 34.69%, 41.90%, 34.7% and 34.71%, respectively. This was established through life cycle assessment (LCA). With any of the catalysts, the most impacted endpoint category was human health, 26.7 mPt when using Fe_2O_3 and 14 mPt when iron salt is the catalyst precursor. The strategy that works the best for any catalyst is to modify its concentration since the GWP and PO can change 20%, 35% the E and A with the $Fe(NO_3)_3{\cdot}9H_2O$ and up to 10% with the Fe_2O_3. It was established, through a sensibility analysis, that by using solar energy instead of energy from fossil fuels, the carbon footprint of the biodiesel production can be reduced ca. 93%: it becomes 48.73 $gCO_2eq\ MJ^{-1}$ when using Fe_2O_3 and 26.48 $gCO_2eq\ MJ^{-1}$ when using the iron salt. With this catalyst precursor, in addition, a ratio of 0.56 $MJ_{in}{\cdot}MJ_{out}^{-1}$ is attained.

1. Introduction

Biodiesel is a promising alternative to diesel fuel because of their similar properties and cleaner burning in compression ignition (CI) engines (Singh et al., 2021). Depending on the feedstock, biodiesel is classified as first, second or third generation. First-generation feedstocks compromise the availability of land and food output. Actually, the current conflict between Russia and Ukraine has raised special concerns and through a careful analysis it has been recommended (Shams Esfandabadi et al., 2022) to switch to higher-generation biofuels by using feedstock like waste cooking oil (WCO) or algae oil. In this sense, there are worldwide generated, per year, approximately 16.5 million tons of waste cooking oil (WCO) (Hosseinzadeh-Bandbafha et al., 2022a) that is typically disposed to drains (66%), soil (8.6%) and garbage (15.8%) (Hartini et al., 2020). Any of these is considered a bad practice from an environmental and economical point of view.

Regarding its hazardous risks to environment, WCO has low solubility, reduces dissolved oxygen content and limits sunlight penetration into water. Under these conditions, acidification and eutrophication are likely to occur and fish are likely to die or not growing (Hosseinzadeh-Bandbafha et al., 2022a), thus negatively affecting the aquatic ecosystem. Regarding the terrestrial ecosystem, the presence of WCO in soil limits germination, plant growth and beneficial organisms like earthworms (Hosseinzadeh-Bandbafha et al., 2022b).The valorization of WCO not only decreases all the aforementioned adverse effects but also reduces the emissions of greenhouse gases (GHG), supports the security energy supply and the technological development. Currently, waste conversion technologies in energy based on WCO are emerging systems

Abbreviations: LCA, Life Cycle Assessment; GWP, Global Warming Potential; WCO, Waste Cooking Oil; GHG, Green House Gases; SDG, Sustainable Development Goals.

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of renewable and sustainable energy, and represent a circular economy model studied as a sustainable measure to ensure economic viability and low carbon (eco-friendly) fuels (Dahiya et al., 2020; Loizidou et al., 2021).

The process to produce biodiesel from WCO includes mainly three stages, pre-treatment, transesterification reaction and separation of methanol (main reagent to conduct the transesterification) and glycerol (transesterification by-product). The process can be either homogeneously or heterogeneously catalyzed. In either of these processes, the pre-treatment usually consists in the addition of sulfuric acid to esterify the free fatty acids (FFA) in the WCO. If this step is not conducted, the yield of transesterification is considerably reduced (Enguilo et al., 2021). The pre-treatment stage can be eliminated, however, by using a bi-functional heterogeneous catalyst with both type of active sites, acid and basic (Alanis et al., 2021; Mandari and Devarai, 2021). This means that the esterification and transesterification reactions are conducted with one catalyst at one stage.

Besides the catalyst, the most relevant process variables to improve the efficiency of the esterification and transesterification reactions are temperature, alcohol/oil ratio, amount of catalyst, and type of WCO. Each of these variables offers a room for improvement in terms of energy and chemicals consumption and therefore also in terms of environmental impact of the process. Actually, the improvement of the sustainability of the biodiesel production remains as a challenge for the scientific community. As aforementioned, one strategy to achieve this purpose is the use of waste cooking oil. Another strategy is the use of bifunctional heterogeneous catalysts that allow to conduct esterification and transesterification reactions of FFA in one stage, due to the presence of both, acid and basic sites onto their surface (Al-Saadi et al., 2020; Elias et al., 2020).

An already successfully proven bifunctional catalyst is the mixed Fe and Ca oxide (Enguilo et al., 2021). In such an investigation, an important variable found to impact the textural, structural and chemical properties of the obtained catalyst was the iron precursor. Through this variable, the attained fatty methyl esters content (FAMEs %) and reaction time were also modified. Although it was demonstrated that using $Fe(NO_3)_3{\cdot}9H_2O$ as iron precursor, leads to a higher FAMEs yield at lower reaction times and with lower amount of methanol than with Fe_2O_3 as precursor, the cost of the salt is ca. six times that of the oxide. Then it is also worth to analyze the environmental implications of using one or the other. Moreover, the identification of the process variable impacting the most to the environment has not been established neither.

Therefore, the main objective of this work was to establish, through life cycle assessment methodology (LCA), the scenario and/or strategy exerting the largest effect on reducing mid-point and end-point environmental impacts of the biodiesel production catalyzed by the bifunctional catalyst (mixed iron-calcium oxide) proposed by (Enguilo et al., 2021). There were assessed two main scenarios and in each of them three strategies were also tested. In Scenario 1, the iron precursor used in the catalyst synthesis was ferric oxide (Fe_2O_3) while in Scenario 2, the iron precursor was an iron salt ($Fe(NO_3)_3{\cdot}9H_2O$). The assessed strategies were three: varying catalyst concentration, iron content and alcohol/oil molar ratio. The response-variables were contribution to mid-point environmental impacts (global warming potential, photo-oxidation, acidification and eutrophication), end-point environment impacts (human health, ecosystems damage and resources) and change in environmental impacts. In addition, a sensibility analysis was conducted to determine the change in carbon footprint when solar energy instead of energy from fossil fuels was used during the WCO transesterification process.

The literature related to biodiesel production with WCO or with oil extracted from a residue like fruit seeds is vast (Yaashikaa et al., 2022); this is not the case; however, when LCA is added to the search. Therefore, this study will contribute to design a more sustainable process to produce biodiesel and it is also expected that the results will help to the decision makers.

2. Materials and methods

This study was conducted according to the ISO 14040 (ISO 14040, 2007) and 14044 (ISO14044, 2006) standards. In concordance, the LCA phases were 1) goal and scope definition, 2) inventory analysis, 3) impact assessment, and 4) interpretation.

2.1. Goal and scope definition

The goal of the LCA was to establish the environmental impacts and benefits of biodiesel production from WCO with heterogeneous catalysts with different iron (III) precursors (Fe_2O_3 and $Fe(NO_3)_3{*}9H_2O$), catalyst concentration (1, 3, 5 and 7 wt%), iron content (III) (1, 2.5, 5 and 10 wt %) over CaO and methanol/WCO molar ratio. The functional unit (FU) for the LCA, in a similar way than in other works (Caldeira et al., 2015; Pasha et al., 2021; Sheinbaum et al., 2013), was 1 MJ of energy from biodiesel produced, based on its calorific value (37.27 MJ L^{-1}). The study was from cradle to gate and included pretreatment, catalyst synthesis, reusability and heterogeneous reaction, leaving outside of the limits of the system the mixing operations, loading and use in vehicles.

2.2. System description

Fig. 1 shows the system of biodiesel production that is defined by the stages: pretreatment of WCO, catalyst synthesis, reusability and heterogeneous reaction. Upstream processes, such as cultivation or oil extraction, were excluded from this analysis. The outputs included waste gas emission carbon dioxide (CO_2) by thermal desorption of the catalyst, wastewater, catalyst waste, methanol emission to air, glycerol and biodiesel production. The gases emitted due to electricity consumption were not explicitly noted in Fig. 1 since the applied model takes them into account based on the consumed kWh.

It is worth pointing out that during the reaction with both catalysts there were not observed emulsification or saponification problems. The boundary of the process was categorized by using a black doted box and the solid line box represents independent subsystems such as pretreatment, catalyst synthesis and the heterogeneous reaction process. WCO was obtained from the local food industry. The fatty acid composition of this oil was lauric (C12:0) (0.03%), myristic (C14:0) (0.16%), palmitic (C16:0) (12.03%), palmitoleic (C16:1) (0.17%), margaric (C17:0) (0.12%), stearic (C18:0) (4.40%), oleic (C18:1) (23.58%), linoleic (C18:2) (52.48%), arachidic (C20:0) (0.33%) and linoleic (C18:3) (6.65%). The WCO was a recycled product with the Cut-off method, so the emissions associated with the recycled product are only those of its collection.

2.2.1. Pretreatment of WCO

The WCO requires a pre-treatment to remove solid particles, soluble salts and moisture. Initially, to eliminate the solid particles, the WCO was filtered. After that, a process with hot water was carried out to remove gums. This process consists of adding water at 80 °C to the previously heated oil, separate and eliminate de excess of moisture. The electricity consumption was 0.098 kWh in this stage, and it is relatively low, compared to the other stages involved in the process. Emissions to water at this stage are discharged for treatment in a wastewater treatment plant.

2.2.2. Catalyst synthesis and reusability

Bifunctional catalysts based on iron (III) and CaO were prepared by an ion exchange method. In this method, to prepare Fe/Ca a 10 wt% iron catalyst, 3.6 g of CaO were dispersed in 400 mL of water during 5 min. Two solutions of iron(III) (1.79×10^{-2} M) were prepared, one per each iron precursor, i.e. Fe_2O_3 or $Fe(NO_3)_3{\cdot}9H_2O$. The solution was dropwise added to the CaO slurry and the mixture was stirred for 4 h. The suspension was filtered and the solid was dried overnight at 100 °C. Then the catalyst is calcined at 900 °C in a muffle with a ramp of 2 °C• min^{-1}

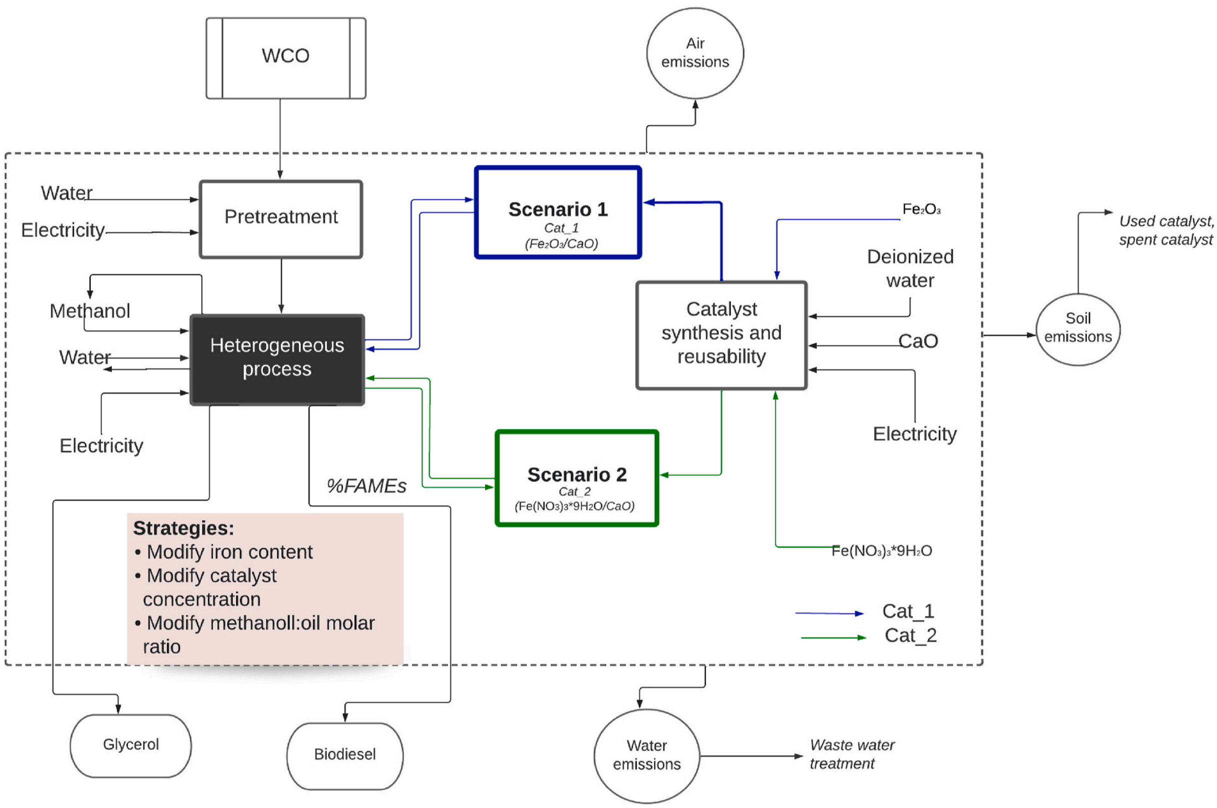

Fig. 1. System boundary for the management of WCO, through a heterogeneous process.

for 8h, to produce the acid and basic sites and to achieve the catalytic stability. This thermal treatment affects both, input and output inventory, especially in the energy consumption and in the emissions items (see Table 1). During this stage, the transformation of $Ca(OH)_2$ (major component of quicklime) to CaO proceeds by means of temperature. This leads to waste gas emission (carbon dioxide) and clean water vapor. The electricity thermal consumption in this stage was 5.837 kWh and, as can be seen in Fig. 3, this is the stage with the highest energy consumption due to the use of a furnace. In order to establish the desorbed carbon dioxide due to the phase transformation of $Ca(OH)_2$ into CaO, a thermogravimetric analysis using the simultaneous TGA/DSC SDT Q600-TA Instruments was conducted.

The stability of the bifunctional catalyst was tested by evaluating its reusability in consecutive transesterification reactions. The catalyst was reused at least three times without sacrificing activity and it was easily recovered. In this step, further energy consumption was not necessary. Nevertheless, when the catalyst deactivates it will represent an emission to soil as depicted in Fig. 1. It is worth pointing out that the limit of reusability of the prepared catalysts has not been determined yet.

2.2.3. *Heterogeneous process*

The biodiesel production was carried out in a glass stirred tank

Table 1
Inventory analysis according to the functional unit (1 MJ) in biodiesel production with a heterogeneous process with different wt% of iron (III) content.

Inventory item	Unit	wt% of iron (III)								Catalyst	Quality data
		1%		2.5%		5%		10%			
		Input	Output	Input	Output	Input	Output	Input	Output		
Methanol	g	6.25	1.38	5.61	0.73	5.48	0.60	5.54	0.67	Cat_1	Experimental
		5.95	1.07	5.74	0.86	5.54	0.67	5.54	0.67	Cat_2	
Biodiesel	MJ		1		1		1		1	Cat_1	Experimental
			1		1		1		1	Cat_2	
% FAME	%		78%		87%		89%		88%	Cat_1	Experimental
			82%		85%		88%		88%	Cat_2	
Electricity consumption	kWh	1.20		1.08		1.06		1.07		Cat_1	Experimental
		0.60		0.58		0.56		0.56		Cat_2	
Pig iron (Fe_2O_3)	g	0.02		0.03		0.07		0.13		Cat_1	Experimental
Vermiculite $Fe(NO_3)_3{*}9H_2O$		0.08		0.18		0.36		0.71		Cat_2	
Lime Hydraulic (CaO)	g	1.02		0.91		0.89		0.90		Cat_1	Experimental
		0.97		0.93		0.90		0.90		Cat_2	
Air emissions (CH_3OH)	g		0.63		0.56		0.55		0.55	Cat_1	Reference (Chung et al., 2019)
			0.59		0.57		0.55		0.55	Cat_2	
Catalyst waste	g		1.03		0.94		0.96		1.03	Cat_1	Experimental
			1.04		1.12		1.26		1.61	Cat_2	
Methanol recovered	g		5.63		5.05		4.93		4.99	Cat_1	Experimental
			5.35		5.16		4.99		4.99	Cat_2	

reactor with baffles, methanol-reflux system and a thermometer to monitor the reaction temperature that was kept constant (T = 60 °C) at all experiments. The stirring (600 rpm) and the heating were conducted through a thermal plate. The reflux system consisted of a condenser that was being constantly cooled by recirculating anti-freeze coolant through the condenser. The electricity consumption at this stage depended on the tested catalyst and considered the following equipment: heating and stirring plate, rotary evaporator, recirculation system, vacuum pump and centrifuge. This was used to conduct the reaction, separate the unreacted methanol via evaporation under vacuum, the catalyst by centrifugation and finally glycerol was recovered by settling.

2.3. Life cycle inventory analysis

The inventory data with experimental quality, were obtained in a 0.25 L stirred tank reactor. The inventory presented in Fig. 2, was calculated according to experimental results previously reported by Enguilo et al. (2021), when the studied variable is the iron precursor and the resulting materials are Cat_1 and Cat_2. Quicklime, source of CaO, was from the lime production hydraulic. Methanol ACS (CH_3OH) 99.9% was supplied by Fermont. Iron (III) nitrate (Fe $(NO_3)_3{\cdot}9H_2O$) 99.0% was bought in MERCK and iron (III) Oxide (Fe_2O_3) 99.0% was obtained from Reasol.

For the purpose of the simulation in SimaPro 9.3.0.3$^{(R)}$, electricity and fuel consumption emissions were modeled with a Mexican database (MX), Ecoinvent v.3 database. The disposal scenarios of solid waste and wastewater were established according to the Ecoinvent v.3 RoW and GLO database. The impact analysis of each process variable was conducted separately. Nevertheless, a general inventory was established (see Fig. 2) and the catalyst synthesis phase was conducted separately in order to observe and evaluate the environmental impacts depending on the iron precursor and the resulting catalyst, Cat_1 and Cat_2. The iron precursor, Fe_2O_3, for Cat_1 was considered from the pig iron market (Flowers et al., 2021) and for Cat_2 (iron precursor: $Fe(NO_3)_3{\cdot}9H_2O$), vermiculite market was elected (Chen et al., 2010). The allocation was made based on energy biodiesel output. The LCA system includes material and energy inputs and environmental emissions (water, air and solid) for each stage.

The emissions of the catalytic synthesis and reusability stage were calculated based on thermogravimetric analysis (TGA) results reported by Enguilo et al. (2021). Each stage in Fig. 3, corresponds to a weight loss observed by TGA and therefore to a chemical transformation that has been indicated in Fig. 3. According to Camacho et al. (2016), Cat_1 in stage 1, between 150 and 200 °C, losses physisorbed water; the second stage at 350–500 °C corresponds to the decomposition of calcium hydroxide ($Ca(OH)_2$) and finally, in the third stage between 550 and 900 °C, the decomposition of calcium carbonate ($CaCO_3$) proceeds and calcium ferrite oxide ($Ca_2Fe_2O_5$) is formed (Enguilo et al., 2021). For Cat_2, four stages can be distinguished: physisorbed water is desorbed between 50 and 100 °C (stage 1), $Fe(NO_3)_3{\cdot}9H_2O$ decomposes between 200 and 250 °C (stage 2); then in the third stage, 350–450 °C, calcium hydroxide becomes calcium oxide, iron oxide (III) is formed and also

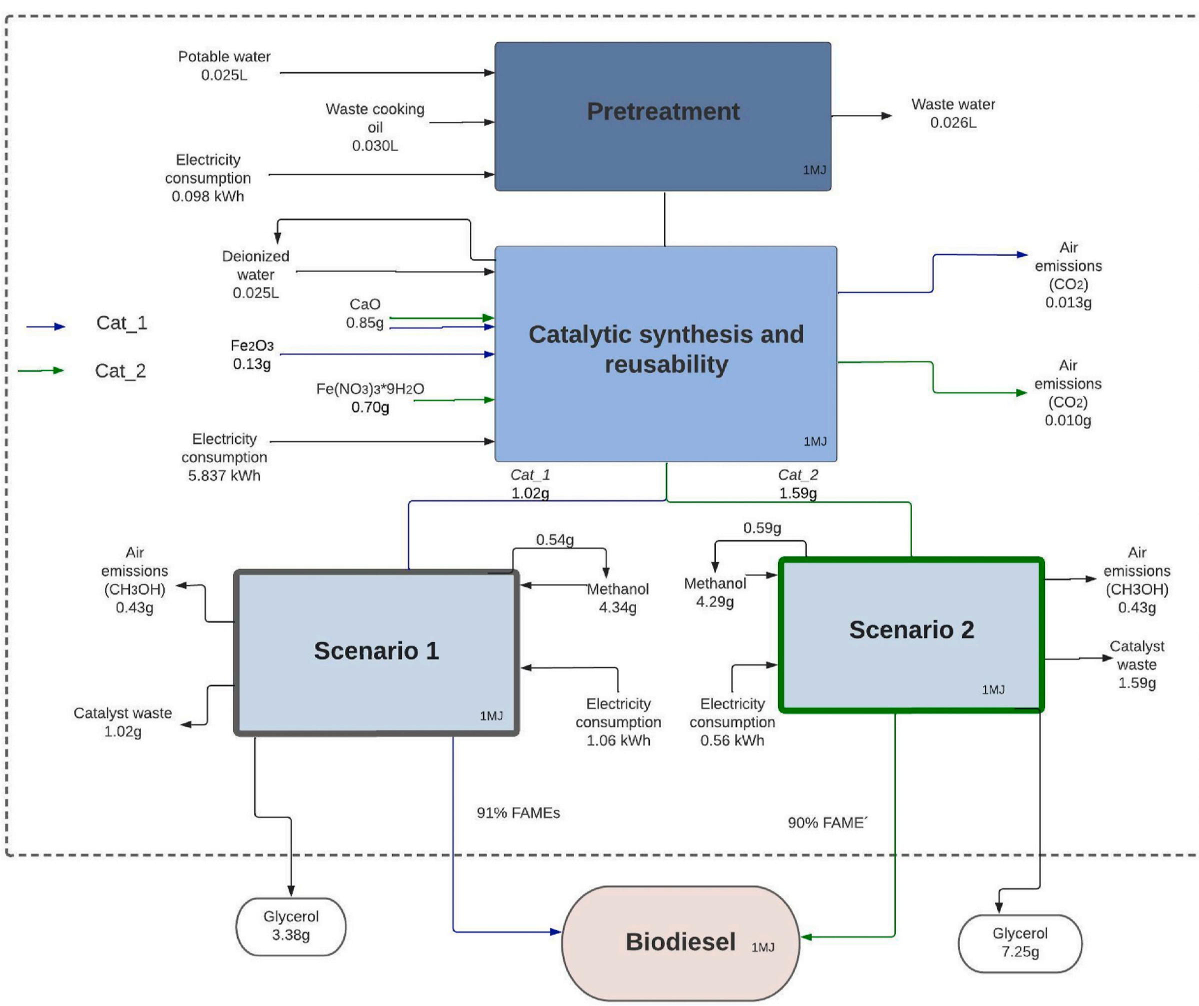

Fig. 2. Inventory analysis data of the heterogeneous production of biodiesel catalyzed by Cat_1 (Iron precursor: Fe_2O_3) (Scenario 1) and by Cat_2 (Iron precursor: Fe $(NO_3)_3{\cdot}9H_2O$) (Scenario 2).

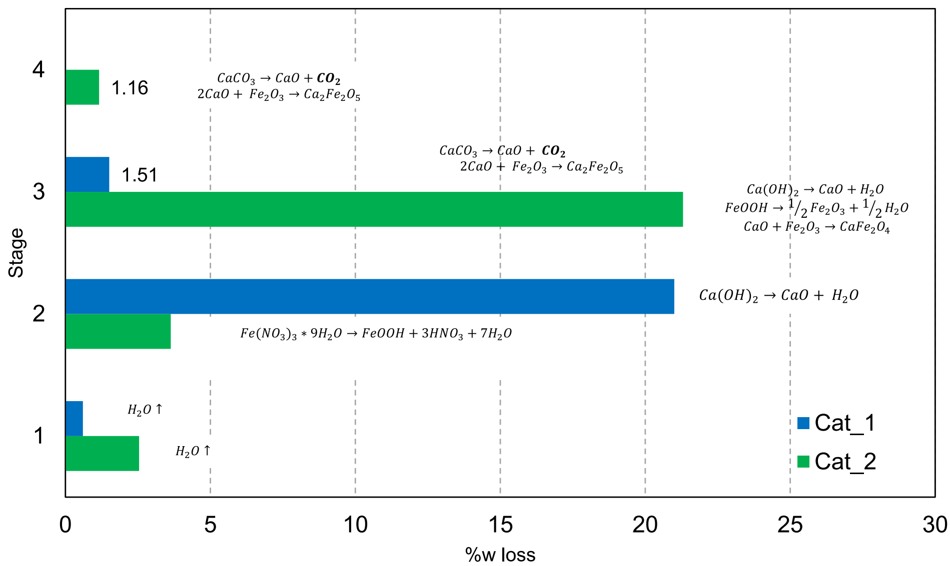

Fig. 3. Weight loss desorption of Cat_1 and Cat_2 in various stages for quantifying emissions of CO_2.

$CaFe_2O_4$ appears. Finally, in stage four, calcium ferrite ($Ca_2Fe_2O_5$) is formed by the interaction of calcium oxide and iron oxide (III). In Figs. 3, 1.51 and 1.16% correspond to the CO_2 desorbed from Cat_1 and Cat_2, respectively (Enguilo et al., 2021).

2.3.1. Strategy 1: modifying the iron content

The conversion of FFA's achieved with a bifunctional catalysts may depend on the equilibrium of acid and basic sites (Atadashi et al., 2013; Maroa and Inambao, 2021), which ensures high catalytic activity. Enguilo et al. (2021), reported that the ratio of acid to basic sites in Cat_2 is almost double than that in Cat_1. This ratio is modified by altering the iron content onto the catalytic surface. To assess the environmental impacts of varying iron content, a new inventory analysis was conducted only in that related to the heterogeneous process since the rest of the stages remain the same. This inventory analysis is presented in Table 1 and the output values were obtained at 2 h of reaction with Cat_1 and after 1 h of reaction with Cat_2. This time is where the highest percentage of FAMEs is achieved according to the results of Enguilo et al. (2021). FAMEs content was determined by gas chromatography and the standard deviation of the analysis was 1%.

As can be seen in Table 1, other than reaction time, there are also variables such as electricity consumption, used and recovered methanol that are affected by the type of employed catalyst. The electricity consumption is practically half with Cat_2 than with Cat_1 since the reaction time, i.e. heating time, to reach the maximum FAMEs% is half than that used by Cat_1. This increase in catalytic activity was ascribed (Enguilo et al., 2021) to the ratio of acid to basic sites, which is higher in Cat_2 than in Cat_1. It can also be observed in Table 1 that the electricity consumption is a function of the iron percentage and this is due to the different catalytic activity exhibited by each of the prepared catalysts that is reflected in the final FAMEs content. It is worth noticing that this consumption is inversely correlated with the FAMEs content.

Table 2
Inventory analysis according to the functional unit (1 MJ) in biodiesel production with a heterogeneous process with different catalyst concentration.

Inventory item	Unit	Catalyst concentration								Catalyst	Quality data
		1%		3%		5%		7%			
		Input	Output	Input	Output	Input	Output	Input	Output		
Methanol	g	6.25	1.38	5.74	0.86	5.48	0.60	8	3.12	Cat_1	Experimental
		7.07	2.19	5.74	0.86	5.54	0.67	8.13	3.25	Cat_2	
Biodiesel	MJ		1		1		1		1	Cat_1	Experimental
			1		1		1		1	Cat_2	
% FAME	%		78%		85%		89%		61%	Cat_1	Experimental
			69%		85%		88%		60%	Cat_2	
Electricity consumption	kWh	1.20		1.10		1.06		1.54		Cat_1	Experimental
		0.72		0.58		0.56		0.82		Cat_2	
Pig iron (Fe_2O_3)	g	0.03		0.08		0.13		0.27		Cat_1	Experimental
Vermiculite $Fe(NO_3)_3*9H_2O$		0.19		0.45		0.71		1.49		Cat_2	
Lime Hydraulic (CaO)	g	0.20		0.55		0.89		1.80		Cat_1	Experimental
		0.23		0.55		0.90		1.82		Cat_2	
Air emissions (CH_3OH)	g		0.63		0.57		0.55		0.80	Cat_1	Reference (Chung et al., 2019)
			0.71		0.57		0.55		0.81	Cat_2	
Catalyst waste	g		0.23		0.64		1.02		2.07	Cat_1	Experimental
			0.41		1.00		1.31		3.32	Cat_2	
Methanol recovered	g		5.63		5.16		4.93		7.20	Cat_1	Experimental
			6.36		5.16		4.99		7.32	Cat_2	

2.3.2. Strategy 2: modifying the catalyst concentration

The second strategy was varying the catalyst concentration (1, 3, 5 and 7%) for Cat_1 and Cat_2. The inventory analysis, Table 2, describes the output values obtained at 2 h of reaction with Cat_1 and after 1 h of reaction with Cat_2. The percentage of FAMEs was studied with reaction time and electricity consumption, used and recovered methanol and catalyst waste. The electricity consumption is also practically half with Cat_2 than with Cat_1 since the reaction time to achieve the maximum FAMEs content was 1 h for Cat_2 and 2 h for Cat_1 (Enguilo et al., 2021). As can be seen in Table 2, the maximum FAMEs % was attained when using 5% iron content.

2.3.3. Strategy 3: modifying the alcohol/oil molar ratio

The inventory analysis modifying the alcohol/oil molar ratio is presented in Table 3. The values for this process variable were 9:1, 12:1, 18:1 and 25:1, the percentage of FAMEs was studied with reaction time and electricity consumption, used and recovered methanol and catalyst waste. The electricity consumption is also practically half with Cat_2 than with Cat_1. The reason for this is that, as in the case of the previous variable, the reaction time with Cat_2 to achieve the maximum FAMEs content was half of that with Cat_1 (Enguilo et al., 2021).

2.4. Life cycle impact assessment

The environmental impact of the whole processes has accuracy, consistency and specification of data collection. The software SimaPro® 9.3.0.3 PhD (Pré Sustainability, Amersfoort, Netherlands) was used to analyze and compare the environmental impact categories. Inventory models for inputs were obtained from the Ecoinvent v.3 database (Ecoinvent, 2019). The method to establish the endpoint LCA damage categories was ReCiPe 2016Endpoint (H) V1.04/World (2010) H/A (ecosystem quality, human health, and resources).

The midpoint assessment of biodiesel production from WCO with heterogeneous catalyst, (Cat_1) and (Cat_2), was conducted using the CML-IA baseline V3.06/EU25 method (CML, 2001) and assessing the impact of variables such as amount of catalyst (with 10% of iron) respect to the mass of oil (1, 3, 5 and 7%), and wt% of iron (III) (1, 2.5, 5 and 10 wt%) over CaO, and the alcohol/oil molar ratio (9:1, 12:1, 18:1 and 25:1). The midpoint categories considered were: Global warming potential (GWP100a) (kg $CO_{2\ eq}$), Photochemical oxidation (PO) (kg C_2H_4 eq), Acidification (A) (kg $SO_{2\ eq}$) and Eutrophication (E) (kg $PO_{4\ eq}$). These environmental impact categories have previously been used by other authors that have performed a LCA (Corral-Bobadilla et al., 2022; Hartini et al., 2021) and were elected because they are related with the consumption of energy by fossil fuels, raw materials and waste that the process generates (Achten et al., 2010).

2.5. Interpretation

To complete the life cycle impact assessment, a sensitivity analysis was carried out to evaluate each scenario based on allocation energy. Such an analysis is presented to identify the environmental impact of GWP affecting the biodiesel production viability, to contrast with sustainability criteria already established by the Renewable Energy Directive (RED). These criteria are based on the evaluation of CO_2 emissions, saving targets and comparison to fossil fuels, reported in LCA studies (Caldeira et al., 2015; Hosseinzadeh-Bandbafha et al., 2022b). The modified variable was energy source, i.e. fossil fuels or solar.

3. Results and discussion

3.1. Midpoint impact assessment of scenario 1 and scenario 2

Under the best conditions of biodiesel production (5 wt% amount of catalyst and 10 wt% of iron (III) over CaO) (Enguilo et al., 2021), the midpoint assessment of Cat 1 and Cat_2 summarized in Fig. 4, shows the biodiesel production catalyzed with Cat_1 has the greatest environmental contributions in next categories: 65.31% GWP, 58.10% PO, 65.30% A and 65.29% E. The principal contributor to the environmental impact is the use of electricity, mainly produced from fossil fuels in Mexico (Santoyo-Castelazo et al., 2014).

3.1.1. Global warming potential (GWP 100a)

The GWP 100a, was evaluated for a time horizon of 100 years, and for this stage was 0.60 $kgCO_2$ $eq\bullet MJ^{-1}$ for Cat_1 and 0.32 $kgCO_2$ $eq\bullet MJ^{-1}$ for Cat_2, due to the effect of electricity consumption and methanol inputs in the heterogeneous reaction. This concurs with that reported by other research groups, regarding the heterogeneous process exerting the highest damage level, since it contributes to a large electricity consumption and to the energy expenditure in methanol recovery (Chung et al., 2019).

3.1.2. Photochemical oxidation (PO)

Photochemical oxidation recorded in kg non-methane volatile

Table 3
Inventory analysis according to the functional unit (1 MJ) in biodiesel production with a heterogeneous process with different alcohol/oil molar ratio.

Inventory item	Unit	Alcohol/oil molar ratio								Catalyst	Quality data
		9:1		12:1		18:1		25:1			
		Input	Output	Input	Output	Input	Output	Input	Output		
Methanol	g	4.82	1.16	5.42	0.54	7.78	0.47	11.54	1.38	Cat_1	Experimental
		4.21	0.55	5.54	0.67	8.31	1	11.54	1.38	Cat_2	
Biodiesel	MJ		1		1		1		1	Cat_1	Experimental
			1		1		1		1	Cat_2	
% FAMEs	%		76%		90%		94%		88%	Cat_1	Experimental
			87%		88%		88%		88%	Cat_2	
Electricity consumption	kWh	1.24		1.04		1		1.07		Cat_1	Experimental
		0.57		0.56		0.56		0.56		Cat_2	
Pig iron (Fe_2O_3)	g	0.16		0.13		0.13		0.13		Cat_1	Experimental
Vermiculite $Fe(NO_3)_3{\cdot}9H_2O$		0.72		0.71		0.71		0.71		Cat_2	
Lime Hydraulic (CaO)	g	1.04		0.88		0.84		0.90		Cat_1	Experimental
		0.91		0.90		0.90		0.90		Cat_2	
Air emissions (CH_3OH)	g		0.48		0.54		0.78		1.15	Cat_1	Reference (Chung et al., 2019)
			0.42		0.55		0.83		1.15	Cat_2	
Catalyst waste	g		1.20		1.01		0.97		1.03	Cat_1	Experimental
			1.63		1.61		1.61		1.61	Cat_2	
Methanol recovered	g		5.49		5.42		7.47		11.27	Cat_1	Experimental
			4.33		5.65		8.48		11.77	Cat_2	

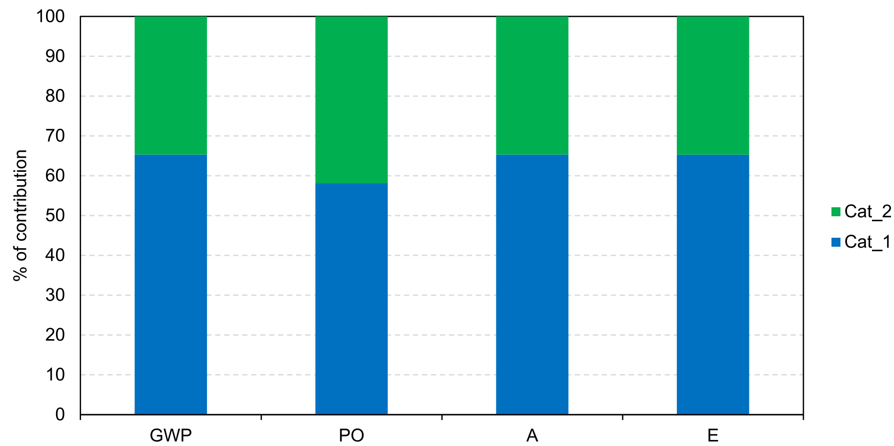

Fig. 4. Comparative results of life cycle environmental impacts for 1 MJ of biodiesel production from waste cooking oil with Cat 1 (Fe_2O_3) and Cat_2 ($Fe(NO_3)_3$*$9H_2O$), using CML-IA baseline V3.06 midpoint indicators.

organic compounds equivalent refers to emissions of reactive substances injurious to human health and ecosystems. In this impact category, the production of methanol contributes 1.69E-04 kg C_2H_4eq when using Cat_1 and 1.22E-04 kg C_2H_4eq when using Cat_2. Nevertheless, it is plausible that this impact category is affected by the catalyst synthesis stage (because of the raw materials) and therefore the catalyst dosing will also affect this indicator (Al-Muhtaseb et al., 2021).

3.1.3. Acidification (A) and eutrophication (E)

Acidification measured in kg SO_2 equivalent is caused by the emission of acidifying substances that decrease the pH of rainwater released into the environment. This impact category derives from acidifying pollutants, such as NH_3, NO_2, NOx, SO_2 and SOx reaching the atmosphere and reacting with water vapor to form acids. The transesterification stage contributes (2.48 E−03 kg SO_2eq) with Cat_1 and (1.32E-03 kg SO_2eq) with Cat_2, respectively. This could be due to the use of methanol and electrical energy from fossil fuels, which has been related to the emission of acidifying substances (Al-Muhtaseb et al., 2021). Also, a contribution to this impact category might be given by the extraction of pig iron, vermiculite and calcium oxide. It is also worth noting, that based on previous LCA studies on biofuels, biodiesel from WCO has lower acidification and eutrophication than fossil diesel (Pasha et al., 2021).

Eutrophication consists of the effect of releasing an excessive amount of nutrients reported as kg PO_4 equivalent. The eutrophication impact comes from the waste liquid effluents that are released into water bodies, increasing eutrophication levels produced during transesterification, for Cat_1 (2.33 E−04 kg PO_4eq) and Cat_2 (1.24E-04 kg PO_4eq), respectively. The LCA of electricity generation in Mexico reports that eutrophication potential from the operation of coal, heavy fuel oil and gas power plants contributes 27%, 24% and 30% (Santoyo-Castelazo et al., 2011), respectively.

3.2. Endpoint impact assessment of scenario 1 and scenario 2

According to the endpoint analysis presented in Fig. 5, Cat_1 contributed a total of 26.7 mPt and Cat_2, 14 mPt. The highest damage category was human health and this has been documented to be impacted by toxicological effects and climate change (Finnveden et al., 2009). Thus, this category includes Global warming, Human toxicity and Ozone layer depletion. The relative high single score of this category can be ascribed to the required heating and time to conduct the biodiesel production (Kumar et al., 2022), and it is also impacted by the use of methanol that has been associated to the damage of human health (Hosseinzadeh-Bandbafha et al., 2022b). Cat_1 contributed with 25.20

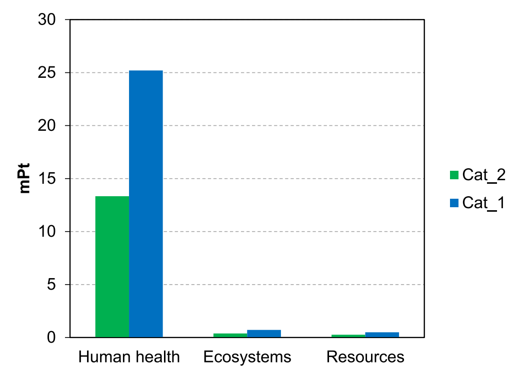

Fig. 5. ReCiPe's endpoint impact categories for the production of 1 MJ of biodiesel from waste cooking oil with Cat 1 (Fe_2O_3) and Cat_2 ($Fe(NO_3)_3$*$9H_2O$).

mPt and Cat_2 with 13.34mPt to the category of Human Health. This is related to the impacts of environmental degradation that results in an increase of and duration of loss-of-life-years due to ill health, disability or early death.

These results demonstrate that the process of biodiesel production with Cat_2, not only implies the valorization of WCO but also provides environmental improvements in the use and production of alternative renewable energies instead of fossil fuels. Nevertheless, the cost of raw materials to produce Cat_2 is about six-fold than that of Cat_1 (Enguilo et al., 2021). Therefore, it is worth to analyze if by any of the assessed strategies in this work, the environmental impacts of Cat_1 can get near to those of Cat_2 with the purpose of utilizing Cat_1 instead of Cat_2 since the cost of the former is lower than the latter.

3.3. Strategy I: modifying iron (III) content

From a chemical point of view, the variation of the iron (III) content implies a change in acid sites concentration on the catalytic surface, available to conduct the esterification reaction of free fatty acids. From an economical perspective, this variable implies a cost change of the catalyst preparation, i.e. higher iron (III) content implies a higher catalyst cost. So far, the environmental implication of this variable has not been determined and this is the objective of this section. For this purpose, Fig. 6 was generated for scenario 1 and 2. It can be observed that the changes in impacts are a function of catalyst. Nevertheless, the changes in impacts per category and per catalyst overlapped.

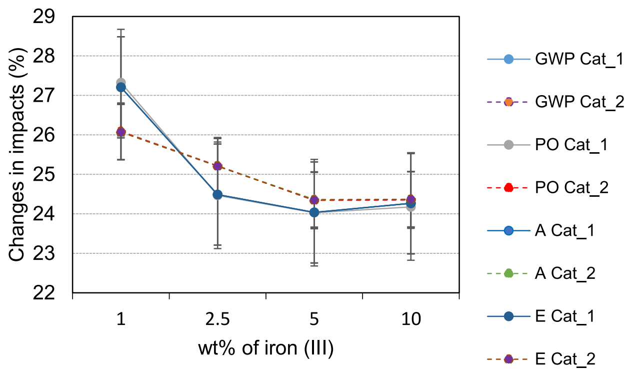

Fig. 6. Effect of iron content on the changes of midpoint environmental impacts using Cat_1 and Cat_2.

When Fe_2O_3 is used as catalyst precursor, this is Cat_1, all the four assessed categories, i.e. GWP, PO, A and E, are similarly affected with the iron content. Actually, it can be seen in Fig. 6, that the impact on the four categories is decreased when the iron content is increased from 1% to 5%, the change in impact is from ca. 27%–24%. A similar behavior was observed with Cat_2. In this case, however, the change in impacts was lower than that for Cat_1 since it changed from 26 to ca. 24%. In both cases, this behavior can be ascribed to an increase in FAMEs content (see Table 1) that leads to a decrease in energy consumption to produce 1 MJ. It is worth noticing in Fig. 6, that an increase in iron content beyond 5% does not imply a further change in impacts.

Summarized in Table 4 are the input and output energy values for each wt% of iron (III). The input energy refers to the fossil energy consumption and the output energy refers to the functional unit that is 1 MJ of biodiesel. Therefore, the ratio means the used energy from fossil fuels required to produce 1 MJ of energy from biodiesel. This ratio has been reported to be a function of the type of produced biofuel (Jeswani et al., 2020). This ratio, for instance, is 0.35 for the average studies related to second generation bioethanol. In the context of biodiesel, the average ratio is 0.5 although there are studies in the 3rd quartile that report values up to 0.58 (Jeswani et al., 2020). From now onwards, this ratio will be referred as fossil energy use and is expected to be as low as possible with the objective of reducing the dependence of fossil fuels and contribute to goal 13 for climate change mitigation and consequently to meet national strategies, policies and planning.

For Cat_2, the ratio was between 0.6 and 0.56 $MJ_{input}\bullet MJ_{output}^{-1}$ and for Cat_1 varies between 1.20 and 1.07 $MJ_{input}\bullet MJ_{output}^{-1}$ (see Table 4). The difference is due to the longer time required for Cat_1 to achieve a maximum compared to Cat_2 and to the high energy requirements for heating and stirring plate, rotary evaporator, recirculation system, vacuum pump and centrifuge. This is reflected in the global warming potential (see Table 5), that is about twice when using Cat_1 than when using Cat_2.

Table 4
Effect of the iron content on the fossil energy use ($MJ\bullet MJ^{-1}$).

Inventory item	Unit	wt% of iron (III)				Catalyst
		1%	2.5%	5%	10%	
Output energy	MJ	1	1	1	1	Cat_1
		1	1	1	1	Cat_2
Input energy	MJ	1.20	1.08	1.06	1.07	Cat_1
		0.60	0.58	0.56	0.56	Cat_2
Ratio		1.2	1.08	1.06	1.07	Cat_1
		0.6	0.58	0.56	0.56	Cat_2

Table 5
Environmental impact due to biodiesel production process (1 MJ) and effect of the iron content, using CML-IA baseline V3.06.

Impact Category	Unit	wt% of iron (III)				Catalyst
		1%	2.5%	5%	10%	
Global warming (GWP100a)	kg CO_2 eq	0.76	0.68	0.67	0.68	Cat_1
		0.36	0.37	0.36	0.38	Cat_2

3.4. Strategy 2: modifying the catalyst concentration (W_{cat})

This variable implies a higher number of acid and basic sites available to conduct both reactions, esterification and transesterification. It also implies an increased cost of the process due to a higher catalyst concentration per batch. In a multiphase reaction, like the one in this study, when the process is free of mass transport resistances, then an increase in this variable will lead to an increase in reaction rate (Peña et al., 2009). Thus, it is important to establish if such an improvement is worthy in terms of environmental impacts.

Regarding Cat_1, Fig. 7, the effect of catalyst concentration in the range of 1–5% is not considered significant for the contribution to environmental impacts, since all impacts are changed only between (24-22%), the change becomes significant when using a 7% of catalyst loading. In the case of Cat_2, all impacts of midpoint analysis exhibit an important change when changing catalyst concentration: GWP (25–36%), PO (24–37%), A (19–47%) and E (19-48%).

For the purpose of improving the environmental contribution by varying the amount of catalyst, Cat_2 has significant percentage changes in all the impacts categories studied, compared to Cat_1. The environmental impacts that presented higher changes were: A and E. This might be due to increase inputs such as catalyst concentration (vermiculite and lime hydraulic) and electricity consumption, and outputs (catalyst waste). Therefore, this strategy can be concluded to exert an important effect on the changes in impacts when using Cat_2. With this catalyst, the catalyst concentration with the minimum impacts was 5%. With this concentration, the environmental impact of GWP for Cat_1 was 0.67 kg CO_2 eq and Cat_2 was 0.36 kg CO_2 eq, see Table 5. It is worth noting that with the same catalyst concentration, the carbon footprint is reduced ca. by half when using Cat_2 instead of Cat_1.

3.5. Strategy 3: varying the alcohol/oil molar ratio

According to the stoichiometry of the triglycerides transesterification reaction, 3 mol of methanol are required to produce 3 mol of methyl esters (biodiesel) by means of reaction 1 (Galván Muciño et al., 2016),

$$T + 3CH_3 - OH \rightarrow G + 3ME \quad (1)$$

this reaction, however, is reversible and to promote the direct reaction instead of the reverse one, a typical action is the use of a higher alcohol/oil molar ratio than the stoichiometric one (Camacho et al., 2018; Muciño et al., 2014). Therefore, although reported that the reaction rate increases directly with the alcohol/molar ratio, it is important to establish whether or not such an improvement justifies the increase in methanol consumption and the changes in environmental impacts.

Fig. 8 shows the effect of varying the alcohol/oil molar ratio on changes in impacts, when using Cat_1 and Cat_2. In this case, PO was identified as the impact category with the most significant change, for Cat_1 this impact changes between 23-31% and 19–36% with Cat_2. This category is the most affected because of the increased use of a volatile compound, methanol. The other impacts for Cat_1, i.e. GWP, A and E, overlap and vary from 28 to 23% when increasing the alcohol/oil molar ratio from 9 to 18. This reduction is due to the increase in reaction rate that implies a change in the inventory, specifically in energy consumption (see Table 3). According to the inventory, the energy consumption decreases from 1.24 to 1 kWh and then increases again to 1.07 with the

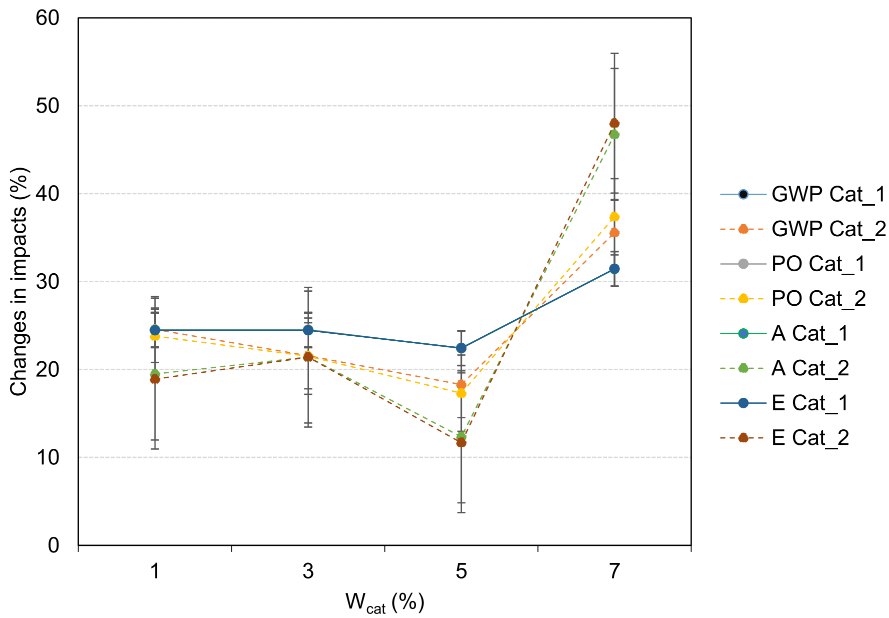

Fig. 7. Effect of catalyst concentration on the change of environmental impacts with Cat_1 and Cat_2.

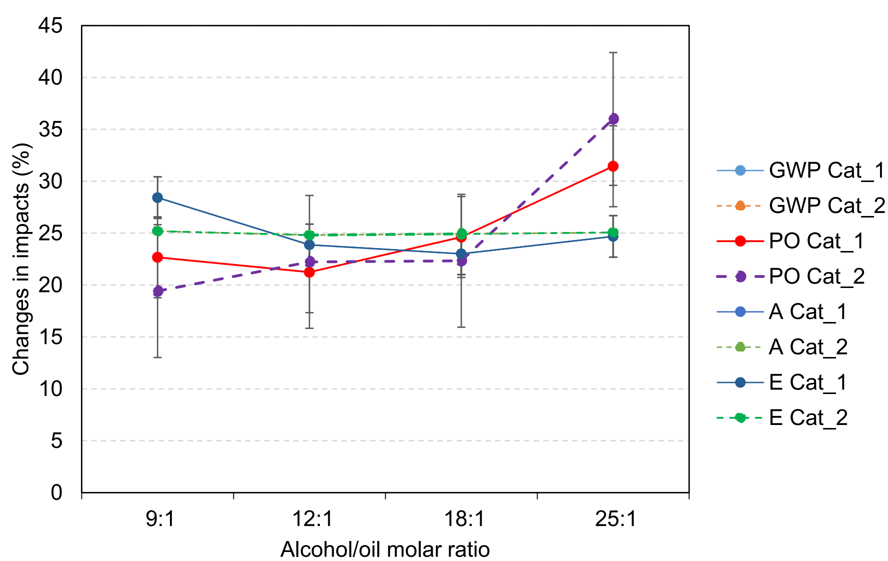

Fig. 8. Effect of alcohol/oil molar ratio on the change of environmental impacts when using Cat_1 and Cat_2.

highest assessed alcohol/oil molar ratio (25:1). This also explains why the change in impacts also slightly increases (see Fig. 8).

Therefore, it can be concluded that when using Cat_1 the strategy of increasing the alcohol/oil molar ratio up to 12:1 reduces GWP, PO, A and E; a further increase not only will not significantly improve these categories but will negatively affect PO. Regarding Cat_2, the only affected impact category is PO and this is, once again, due to the increased use of methanol. The other impact categories overlap and are not affected since the energy consumption to obtain 1 MJ was very similar with any of the assessed alcohol/oil molar ratios, ca. 0.56 kWh.

The environmental impact of GWP with 12:1 alcohol/oil molar ratio for Cat_1 was 0.66 kg CO_2 eq and Cat_2 was 0.36 kg CO_2 eq. Thus, the carbon footprint is reduced by about half when the iron nitrate is used as precursor of the catalyst. The photochemical oxidation is also considerably reduced, about 40%, when changing iron precursors (see Fig. 9). This is because with the same amount of alcohol, a higher FAMEs% is obtained after 1 h of reaction with Cat_2 than with Cat_1.

3.6. Sensitivity analysis

The impact categories GWP and PO could be minimized by substituting the electricity mix from carbon to other energy sources with lower carbon and Sulfur content. A possible way of reducing such dependency is to increase the electricity production and chemicals from renewables, as for example the production of electricity with solar panels. There is presented in Fig. 10, the sensitivity analysis when electricity consumption was solar energy. In such a case, the GWP decreases approximately 93%, for both catalysts, Cat_1(48.73 $gCO_2eq{\bullet}MJ^{-1}$) and Cat_2 (26.48 $gCO_2eq{\bullet}MJ^{-1}$), when conducting the process with a catalyst loading of 5%, an iron content of 10% and a 12:1

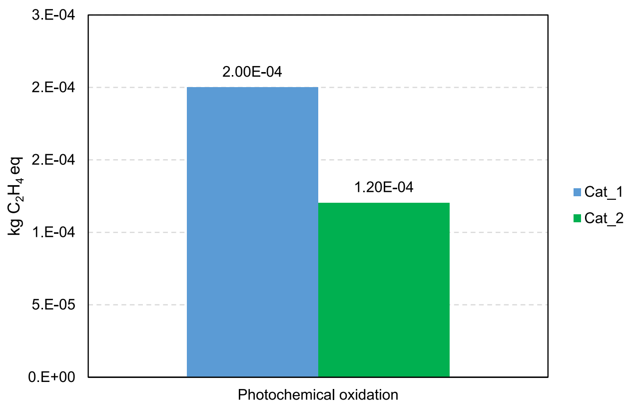

Fig. 9. Photochemical oxidation impact category of biodiesel production on Cat_1 and Cat_2 with 9:1 alcohol/oil molar.

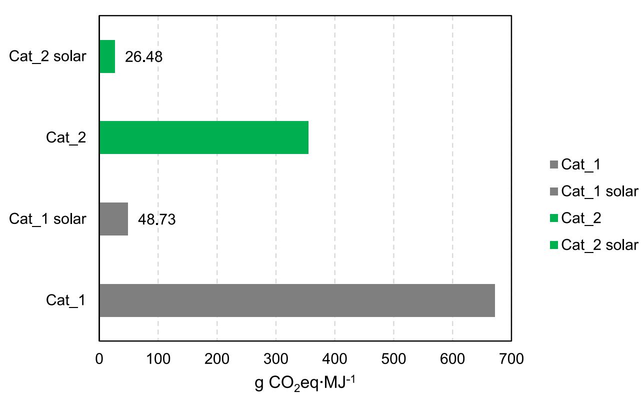

Fig. 10. Sensitivity analysis of electricity consumption by fossil fuels and solar energy, measure in GWP (g CO_2eq•MJ^{-1}).

alcohol/oil molar ratio.

The energy allocation indicates the importance of clearly identifying, describing and motivating the choice of energy use indicator (Arvidsson et al., 2012), as per the RED approach leads to GHG emissions of 15–20 gCO_2eq MJ-1 (Shonnard et al., 2015). The RED has established a typical greenhouse gas emission for biofuels systems using allocation energy content (European Parliament, 2018; Malça y Freire, 2012), this measure in the EU has motivated the use of biofuels instead of fossil fuels. The recently established goal is that at least 32% of the total EU energy needs are met with renewables by 2030 (EPF, 2018).

Biofuels regulations, such as those established by the RED, use the energy content of biofuels (MJ) as the functional unit (Caldeira et al., 2015; Jeswani et al., 2020). Mexico has committed to an unconditionally goal of reducing 22% of GHG emissions by 2030 with respect to a business as usual baseline (SEMARNAT, 2018). Therefore, under the framework of this energy reform, the state must introduce a clean energy certificate market that forces power generators to include clean energy sources such as wind, photovoltaic, and biomass. In this sense, the results shown in Fig. 10 demonstrate that biodiesel from WCO importantly contributes to this goal.

3.7. Implications

There are in Table 6 summarized the works and the results obtained when applying LCA to establish midpoint category impacts and endpoint damage impact on human health. The works included in this table are merely those that have assessed the biodiesel production from some type of waste, catalyzed by heterogeneous catalysts. Because the FU of this work (1 MJ) is different to that of the references shown in Table 6 (1000 kg), a direct comparison is not straightforward. Nevertheless, by contrasting the reaction conditions some practical implications of this work can be established. These being providing by the first time the global warming potential of biodiesel production with the prepared bifunctional catalyst and the damage to human health. In addition, if the calorific value of biodiesel, 43.28 MJ/kg (Al-Muhtaseb et al., 2021), is taken into account, then the minimum GWP per 1000 kg of biodiesel of the assessed process in this work is 1125.3 kg CO_2 eq when using solar energy and Cat_2 (see last row in Table 6). This value is higher than those reported in the literature and this might be due to the fact that the values from literature correspond to only one stage of the process (the one contributing the most to GWP) while the value reported from this work includes the separation of glycerol and catalyst by centrifugation and the recovery of methanol by evaporation-condensation in a rotatory evaporator. In addition, the relative high GWP values of the processes conducted with energy from fossil fuels, might be due to the before-mentioned unit operations being conducted at lab-scale and then the input data in the inventory correspond to the same scale; which would not be really practical to purify 1000 kg of biodiesel. An important indicator, however, of the viability of using the herein proposed catalyst is the 0.56 energy ratio ($MJ_{in}\cdot MJ_{out}^{-1}$) obtained with Cat_2. In addition, this research contributes to United Nations Sustainable Development Goals (SDG) by providing a pathway to clean energy options (SDG 7) and is aligned to SDG 13 (Climate Action) and SDG 12 (Responsible Consumption and Production). Going forward, it is crucial that the innovations applying circular economy approaches not only entail production and chemical processes but also assess life cycle environmental impacts (H. Al-Muhtaseb et al., 2022).

3.8. Challenges and future directions

There were shown in this work, some scenarios and strategies to face an important challenge in the biodiesel production, i.e. decrease the associated environmental impacts. An important result was the ratio of energy input and energy output being lower than 1. Nevertheless, it is challenging to further decrease such a ratio since this is intrinsically associated with the mid-point and end-point category impacts, because of the electricity consumption from fossil sources. For this, reaction time and temperature should be reduced.

The above mentioned can be achieved by optimizing the catalyst synthesis, especially in the precursor and in the calcination temperature aspects. The challenge here is to produce a highly active catalyst at low temperatures, with both type of sites, acid and basic, that could be synthesized from waste like clam shells (Cerón-Ferrusca et al., 2021) and egg shells (H Al-Muhtaseb et al., 2022) and which synthesis implies the minimum of resources, i.e. electricity, water and chemicals. Actually, the high calcination temperature and lengthy calcination to prepare the catalysts for this study can be considered as one of the drawbacks that might limit their use. A relevant review on different biowastes utilized as catalyst of the biodiesel production has been given by (Hosseinzadeh-Bandbafha et al., 2022a). At this point, hybrid systems, i.e. biological and inorganic might become important. In addition, there is also other type of catalyst synthesis that might result in lower energy consumption, such as molten salt (Sikalidis, 2011).

The type of reactor also plays an important role since its design will intensify mass transfer and that might reduce reaction time. This has also been pointed out by (Hosseinzadeh-Bandbafha et al., 2022b). Other challenges to increase the sustainability of biodiesel production is the actual re-utilization of methanol and valorization of glycerol. In this sense, a sustainable production of methanol might also help to reduce the environmental impacts observed in this work. Actually, Brandão et al. (2022) have recently pointed out the importance of incorporating the uncertainty associated to feedstocks and LCA modelling approach.

Table 6
LCA of biodiesel production from waste and with heterogeneous catalysts.

Reaction conditions	Assessed environmental impact categories	Stage or process variable that contributes the most to environmental impacts	Midpoint category impact (GWP) (kg CO_2 eq)	Endpoint damage impact (Human health) Points (Pt)	Reference
Catalyst: H_2SO_4 and Waste Chicken Eggshell derived CaO T: 65 °C Reactor type: Batch Raw materials: methanol, WCO Reaction time: 2h % FAMEs: 80%	ISO 14044 FU: 1000 kg de biodiesel Software: SimaPro 7 Database: Ecoinvent Method: Eco-indicator 99 midpoint (11 impact categories) and endpoint (3 damage categories)	Transesterification of WCO	27.2	0.138	(Chung et al., 2019)
Catalyst: CaO/CeO_2 T: 70 °C Reactor type: Batch Raw materials: loquat seed oil and methanol Reaction time: 1.5h % FAMEs: 90.14%	ISO 14044 FU: 1000 kg de biodiesel Software: SimaPro 8.0 Database: Ecoinvent Method: midpoint CML-IA baseline V3.06 (11 impact categories), endpoint ReCiPe 2016 (3 damage categories).	Catalyst preparation and a regeneration	402.28	119.19	(Al-Muhtaseb et al., 2021)
Catalyst: SrO–La_2O_3 T: 65 °C Reactor type: Batch Raw materials: prunus Armeniaca seeds oil and methanol Reaction time: 1.25h % FAMEs: 97.28%	ISO 14044 FU: 1000 kg de biodiesel Software: SimaPro v9 Database: Ecoinvent Method: CML-IA baseline V3.06 (4 impact categories) Sensitivity analysis	Transesterification of WCO	445.59	NR	(Al-Muhtaseb et al., 2022)
Catalyst: Fe_3O_4 T: 55 °C Reactor type: Batch Raw materials: waste date seed oil and methanol Reaction time: 47 min % FAMEs: 90%	ISO 14044 FU 1000 kg biodiesel Software: SimaPro v9 Database: Ecoinvent Method: midpoint CML-IA baseline V3.06 (11 impact categories) and endpoint ReCiPe 2016 (3 damage categories).	Catalyst preparation and reuse	726.80	199.81	(Al-Mawali et al., 2021)
Catalyst: Cat_1 (Fe_2O_3) and Cat_2 (Fe $(NO_3)_3{\cdot}9H_2O$) T: 60 °C Reactor type: Batch Raw materials: WCO and methanol. Reaction time: Cat 1 (2 h) and Cat_2 (1 h) % FAMEs: Cat_1 (88%) and Cat_2 (88%)	ISO 14044 FU: 1 MJ biodiesel Software: SimaPro 9.3.0.3 Database: Ecoinvent Method: midpoint CML-IA baseline V3.06 (4 impact categories) and endpoint ReCiPe 2016 (3 damage categories).	Transesterification of WCO	Cat_1 (Fe_2O_3) 0.67 Cat_2 Fe $(NO_3)_3{\cdot}9H_2O$ 0.36 Solar: Cat_1 (Fe_2O_3) 0.048 Cat_2 Fe $(NO_3)_3{\cdot}9H_2O$ 0.026	Cat_1 (Fe_2O_3) 0.0252 Cat_2 Fe $(NO_3)_3{\cdot}9H_2O$ 0.0133	This work

This work may be limited in this sense and further analysis is necessary to include all relevant types of uncertainty and variability related to LCA study. This will require the development of consensus methodologies for quantifying model and scenario uncertainties.

Finally, it can be said that because of all the involved variables in the biodiesel production it is recommended the use of machine learning technology in order to optimize quality of biodiesel and input resources like human labor, energy, water and chemicals (Aghbashlo et al., 2021).

4. Conclusions

Biodiesel production with waste cooking oil as feedstock is cleaner when $Fe(NO_3)_3{\cdot}9H_2O$ (Cat_2) is used to prepare the catalyst instead of Fe_2O_3 (Cat_1). The former contributes the lowest (ca. 35%) to midpoint environmental impact categories such as global warming potential, photochemical oxidation, acidification and eutrophication. Regarding the endpoint environmental impact categories, the human health damage is the most affected indicator. In this case also, Cat_2 is 52.89% lower than that with Cat_1.

For both catalysts, varying the catalyst loading (W_{cat}) in the reaction system is the strategy that decreases the most the environmental impact categories of E, A, GWP and PO. For Cat_2, beyond $W_{cat} = 5\%$, the environmental impacts increase. The methanol/oil molar ratio should be kept at a minimum to decrease PO. It was concluded that the global warming potential decreases about 93%, for Cat_1(48.73 $gCO_2eq\ MJ^{-1}$) and Cat_2 (26.48 $gCO_2eq\ MJ^{-1}$) when conducting the biodiesel production with solar energy instead of energy from fossil fuels. A ratio of 0.56 $MJ_{in}{\cdot}MJ_{out}^{-1}$ is attained with Cat_2 and this about half than that obtained with Cat_1.

Further analysis is necessary to include all relevant types of uncertainty and variability related to LCA study. This will require the development of consensus methodologies for quantifying model and scenario uncertainties.

CRediT authorship contribution statement

Claudia Alanis: Investigation, Data curation, Methodology, Writing – review & editing, Software, SimaPro. **Liliana Ivette Ávila Córdoba:** Supervision, Software, SimaPro, Writing – review & editing, Resources. **Gustavo Álvarez-Arteaga:** Supervision, Methodology, Resources, All authors have read and agreed to the published version of the manuscript. **Rubi Romero:** Investigation, Methodology, Validation. **Alejandro Padilla-Rivera:** Conceptualization, Formal analysis, Writing – review & editing. **Reyna Natividad:** Supervision, Conceptualization, Formal analysis, Writing – review & editing, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Abbreviations

LCA	Life cycle assessment
WCO	Waste cooking oil
FFA	Free Fatty Acids
GHG	Greenhouse gases
FAMEs	Fatty methyl esters
FU	Functional unit
TGA	Thermogravimetric analysis
GWP100a	Global warming potential
PO	Photochemical oxidation
A	Acidification
E	Eutrophication
RED	Renewable Energy Directive
SDG	Sustainable Development Goals
mPt	milipoints
CONACYT	Consejo Nacional de Ciencia y Tecnología
GISRO	Integral and sustainable organic waste management

Nomenclature

Cat_1	Catalyst prepared using Fe_2O_3 as iron precursor
Cat_2	Catalyst prepared using $Fe(NO_3)_3{\cdot}9H_2O$ as iron precursor
CaO	Calcium oxide Lime hydraulic
Cat_1_solar	Biodiesel production conducted with Cat_1 and solar energy instead of energy from fossil fuels
Cat_2_solar	Biodiesel production conducted with Cat_2 and solar energy instead of energy from fossil fuels
$Fe(NO_3)_3{\cdot}9H_2O$	Nonahydrated iron nitrate Vermiculite
Fe_2O_3	Iron (III) oxide Pig Iron
$Ca_2Fe_2O_5$	Calcium ferrite
$Ca(OH)_2$	Calcium hidroxide
$CaCO_3$	Calcium carbonate
$CaFe_2O_4$	Calcium iron oxide
CH_3OH	Methanol Air emissions
CO_2	Carbon dioxide
C12:0	Lauric acid
C14:0	Myristic acid
C16:0	Palmitic acid
C16:1	Palmitoleic acid
C17:0	Margaric acid
C18:0	Stearic acid
C18:1	Oleic acid
C18:2	Linoleic acid
C20:0	Arachidic acid
kg $CO_{2\ eq}$	Equivalent kilograms of carbon dioxide
kg C_2H_4 eq	Equivalent kilograms of ethylene
kg $SO_{2\ eq}$	Equivalent kilograms of sulfur dioxide
kg $PO_{4\ eq}$	Equivalent kilograms of phosphate
NH_3	Ammonia
NO_2	Nitrite
NOx	Nitrogen oxides
SO_2	Sulfur dioxide
SOx	Sulfur oxides
T	Triglycerides

ME Methyl Esters
G Glycerol
MJ_{in}/MJ_{out} Ratio of the input energy from fossil fuels to the output energy from the produced biodiesel

Symbols
kWh Kilowatt-hour
MJ Mega joules
kg Kilograms
h Hour
°C Celsius
min Minutes
rpm Revolutions per minute
L Liters
MX Mexican database
RoW Rest of the world
GLO Global
wt% Percentage weight
W_{cat} catalyst loading
CML-IA Faculty of Science of Leiden University method
ISO International Organization for Standardization

References

Achten, W.M.J., Vandenbempt, P., Almeida, J., Mathijs, E., Muys, B., 2010. Life cycle assessment of a palm oil system with simultaneous production of biodiesel and cooking oil in Cameroon. Environ. Sci. Technol. 44, 4809–4815. https://doi.org/10.1021/es100067p.

Aghbashlo, M., Peng, W., Tabatabaei, M., Kalogirou, S.A., Soltanian, S., Hosseinzadeh-Bandbafha, H., Mahian, O., Lam, S.S., 2021. Machine learning technology in biodiesel research: a review. Prog. Energy Combust. Sci. 85, 100904 https://doi.org/10.1016/J.PECS.2021.100904.

Al-Mawali, K.S., Osman, A.I., Al-Muhtaseb, A.H., Mehta, N., Jamil, F., Mjalli, F., Vakili-Nezhaad, G.R., Rooney, D.W., 2021. Life cycle assessment of biodiesel production utilising waste date seed oil and a novel magnetic catalyst: a circular bioeconomy approach. Renew. Energy. https://doi.org/10.1016/j.renene.2021.02.027.

Al-Muhtaseb, Ala'a, H., Jamil, F., Osman, A.I., Tay Zar Myint, M., Htet Kyaw, H., Al-Hajri, R., Hussain, M., Ahmad, M.N., Naushad, M., 2022. State-of-the-art novel catalyst synthesised from waste glassware and eggshells for cleaner fuel production. Fuel 330, 125526. https://doi.org/10.1016/J.FUEL.2022.125526.

Al-Muhtaseb, Ala'a, H., Osman, A.I., Jamil, F., Mehta, N., Al-Haj, L., Coulon, F., Al-Maawali, S., Al Nabhani, A., Kyaw, H.H., Zar Myint, M.T., Rooney, D.W., 2022. Integrating life cycle assessment and characterisation techniques: a case study of biodiesel production utilising waste Prunus Armeniaca seeds (PAS) and a novel catalyst. J. Environ. Manag. 304, 114319 https://doi.org/10.1016/J.JENVMAN.2021.114319.

Al-Muhtaseb, A.H., Osman, A.I., Murphin Kumar, P.S., Jamil, F., Al-Haj, L., Al Nabhani, A., Kyaw, H.H., Myint, M.T.Z., Mehta, N., Rooney, D.W., 2021. Circular economy approach of enhanced bifunctional catalytic system of CaO/CeO2 for biodiesel production from waste loquat seed oil with life cycle assessment study. Energy Convers. Manag. 236, 114040 https://doi.org/10.1016/j.enconman.2021.114040.

Al-Saadi, A., Mathan, B., He, Y., 2020. Biodiesel production via simultaneous transesterification and esterification reactions over SrO-ZnO/Al2O3 as a bifunctional catalyst using high acidic waste cooking oil. Chem. Eng. Res. Des. 162, 238–248. https://doi.org/10.1016/J.CHERD.2020.08.018.

Alanis, C., Ávila, L., Romero, R., Natividad, R., 2021. Biodiesel production as an alternative to reduce the environmental impact of University food courts, en: Women in Science Engineering and Technology, pp. 31–50. https://doi.org/10.35429/H.2021.6.37.50.

Arvidsson, R., Fransson, K., Fröling, M., Svanström, M., Molander, S., 2012. Energy use indicators in energy and life cycle assessments of biofuels: review and recommendations. J. Clean. Prod. 31, 54–61. https://doi.org/10.1016/j.jclepro.2012.03.001.

Atadashi, I.M., Aroua, M.K., Abdul Aziz, A.R., Sulaiman, N.M.N., 2013. The effects of catalysts in biodiesel production: a review. J. Ind. Eng. Chem. 19, 14–26. https://doi.org/10.1016/j.jiec.2012.07.009.

Brandão, M., Heijungs, R., Cowie, A.L., 2022. On quantifying sources of uncertainty in the carbon footprint of biofuels: crop/feedstock, LCA modelling approach, land-use change, and GHG metrics. Biofuel Res. J. 9, 1608–1616. https://doi.org/10.18331/BRJ2022.9.2.2.

Caldeira, C., Queirós, J., Freire, F., 2015. Biodiesel from waste cooking oils in Portugal: alternative collection systems. Waste Biomass. Valorization. 6, 771–779. https://doi.org/10.1007/s12649-015-9386-z.

Camacho, J.N., Natividad, R., Galvan Muciño, G.E., García-Orozco, I., Baeza, R., Romero, R., 2016. Comparative study of quick lime and CaO as catalysts of safflower oil transesterification. Int. J. Chem. React. Eng. 14, 909–917. https://doi.org/10.1515/ijcre-2015-0144.

Camacho, J.N., Romero, R., Galvan, G., Natividad, R., Martínez, S., Pérez, C., 2018. Kinetic modeling of canola oil transesterification catalyzed by quiklime. J. Appl. Res. Technol. 6, 446–454.

Cerón-Ferrusca, M., Romero-Romero, R., Natividad, R., Martínez-Vargas, S.L., 2021. Bifunctional catalysts applied to produce biodiesel from waste cooking oil, en: CIERMMI Women in Science Engineering and Technology TXV, pp. 20–36. https://doi.org/10.35429/h.2021.6.20.36.

Chen, Q., Wu, P., Dang, Z., Zhu, N., Li, P., Wu, J., Wang, X., 2010. Iron pillared vermiculite as a heterogeneous photo-Fenton catalyst for photocatalytic degradation of azo dye reactive brilliant orange X-GN. Separ. Purif. Technol. 71, 315–323. https://doi.org/10.1016/J.SEPPUR.2009.12.017.

Chung, Z.L., Tan, Y.H., Chan, Y.S., Kansedo, J., Mubarak, N.M., Ghasemi, M., Abdullah, M.O., 2019. Life cycle assessment of waste cooking oil for biodiesel production using waste chicken eggshell derived CaO as catalyst via transesterification. Biocatal. Agric. Biotechnol. 21, 101317 https://doi.org/10.1016/j.bcab.2019.101317.

CML, 2001. Life Cycle Assessment: an Operational Guide to the ISO Standards. CML. https://doi.org/10.7312/zhan14058-004.

Corral-Bobadilla, M., Lostado-Lorza, R., Somovilla-Gómez, F., Íñiguez-Macedo, S., 2022. Life cycle assessment multi-objective optimization for eco-efficient biodiesel production using waste cooking oil. J. Clean. Prod. 359, 132113 https://doi.org/10.1016/J.JCLEPRO.2022.132113.

Dahiya, S., Katakojwala, R., Ramakrishna, S., Mohan, S.V., 2020. Biobased products and life cycle assessment in the context of circular economy and sustainability. Mater. Circ. Econ. 2, 7. https://doi.org/10.1007/s42824-020-00007-x.

Ecoinvent, 2019. System Models in ecoinvent 3 [WWW Document]. Ecoinvent. URL. https://www.ecoinvent.org/database/system-models-in-ecoinvent-3/system-models-in-ecoinvent-3.html.

Elias, S., Rabiu, A.M., Okeleye, B.I., Okudoh, V., Oyekola, O., 2020. Bifunctional heterogeneous catalyst for biodiesel production from waste vegetable oil. Appl. Sci. 10 https://doi.org/10.3390/app10093153.

Enguilo, V., Romero, R., Gómez-Espinosa, R.M., Romero, A., Martínez, S.L., Natividad, R., 2021. Biodiesel production from waste cooking oil catalyzed by a bifunctional catalyst. ACS Omega. https://doi.org/10.1021/acsomega.1c03586.

Epf, 2018. Renewable energy directive recast (RED II) [WWW Document]. Renew. ENERGY Dir. URL. https://europanels.org/european-policy-developments/climate-energy/renewable-energy-directive-recast-red-ii/.

European Parliament, 2018. Directive (EU) 2018/2001 of the European Parliament and of the Council on the Promotion of the Use of Energy from Renewable Sources. Off. J. Eur. Union.

Finnveden, G., Hauschild, M.Z., Ekvall, T., Guinée, J., Heijungs, R., Hellweg, S., Koehler, A., Pennington, D., Suh, S., 2009. Recent developments in life cycle assessment. J. Environ. Manag. https://doi.org/10.1016/j.jenvman.2009.06.018.

Flowers, P., Theopold, K., Langley, R., Clark, J., 2021. Metallurgy of Iron and Steel.

Galván Muciño, G.E., Romero, R., Ramírez, A., Ramos, M.J., Baeza-Jiménez, R., Natividad, R., 2016. Kinetics of transesterification of safflower oil to obtain biodiesel using heterogeneous catalysis. Int. J. Chem. React. Eng. 14, 929–938. https://doi.org/10.1515/ijcre-2015-0108.

Hartini, S., Puspitasari, D., Roudhatul Aisy, N., Widharto, Y., 2020. Eco-efficiency level of production process of waste cooking oil to be biodiesel with life cycle assessment. E3S Web Conf 202, 10004. https://doi.org/10.1051/e3sconf/202020210004.

Hartini, S., Widharto, Y., Indarto, S.R., Murdikaningrum, G., 2021. Eco-efficiency analysis of waste cooking oil recycling into liquid dish soap using life cycle assessment. IOP Conf. Ser. Earth Environ. Sci. 896, 012066 https://doi.org/10.1088/1755-1315/896/1/012066.

Hosseinzadeh-Bandbafha, H., Li, C., Chen, X., Peng, W., Aghbashlo, M., Lam, S.S., Tabatabaei, M., 2022a. Managing the hazardous waste cooking oil by conversion into bioenergy through the application of waste-derived green catalysts: a review. J. Hazard Mater. 424, 127636 https://doi.org/10.1016/J.JHAZMAT.2021.127636.

Hosseinzadeh-Bandbafha, H., Nizami, A.-S., Kalogirou, S.A., Gupta, V.K., Park, Y.-K., Fallahi, A., Sulaiman, A., Ranjbari, M., Rahnama, H., Aghbashlo, M., Peng, W., Tabatabaei, M., 2022b. Environmental life cycle assessment of biodiesel production from waste cooking oil: a systematic review. Renew. Sustain. Energy Rev. 161, 112411 https://doi.org/10.1016/J.RSER.2022.112411.

2006 ISO 14040, 2007. Gestión ambiental. Ánálisis de ciclo de vida. Principios y marco de referencia (México).

ISO14044, 2006. Environmental Management. Life Cycle Assessment. Requirements and Guidelines [WWW Document]. NTC-ISO 14044. URL. http://tienda.icontec.org/brief/NTC-ISO14044.pdf.

Jeswani, H.K., Chilvers, A., Azapagic, A., 2020. Environmental sustainability of biofuels: a review: environmental sustainability of biofuels. Rural Sociol. 476, 1–37. https://doi.org/10.1098/rspa.2020.0351.

Kumar, A., Singh, J., Trivedi, J., Atray, N., 2022. Bioresource Technology Reports Comparative LCA studies of biodiesel produced from used cooking oil using conventional and novel room temperature processes. Bioresour. Technol. Reports 18, 101072. https://doi.org/10.1016/j.biteb.2022.101072.

Loizidou, M., Moustakas, K., Rehan, M., Nizami, A.-S., Tabatabaei, M., 2021. New developments in sustainable waste-to-energy systems. Renew. Sustain. Energy Rev. 151, 111581 https://doi.org/10.1016/J.RSER.2021.111581.

Mandari, V., Devarai, S.K., 2021. Biodiesel production using homogeneous, heterogeneous, and enzyme catalysts via transesterification and esterification reactions: a critical review. BioEnergy Res. https://doi.org/10.1007/s12155-021-10333-w.

Maroa, S., Inambao, F., 2021. A Review of Sustainable Biodiesel Production Using Biomass Derived Heterogeneous Catalysts 1-35. https://doi.org/10.1002/elsc.202100025.

Muciño, G.G., Romero, R., Ramírez, A., Martínez, S.L., Baeza-Jiménez, R., Natividad, R., 2014. Biodiesel production from used cooking oil and sea sand as heterogeneous catalyst. Fuel 138, 143–148. https://doi.org/10.1016/J.FUEL.2014.07.053.

Pasha, M.K., Dai, L., Liu, D., Guo, M., Du, W., 2021. An overview to process design, simulation and sustainability evaluation of biodiesel production. Biotechnol. Biofuels 14, 1–23. https://doi.org/10.1186/s13068-021-01977-z.

Peña, R., Romero, R., Martínez, S.L., Ramos, M.J., Martínez, A., Natividad, R., 2009. Transesterification of Castor oil: effect of catalyst and Co-solvent. Ind. Eng. Chem. Res. 48, 1186–1189. https://doi.org/10.1021/ie8005929.

Santoyo-Castelazo, E., Gujba, H., Azapagic, A., 2011. Life cycle assessment of electricity generation in Mexico. Energy 36, 1488–1499. https://doi.org/10.1016/j.energy.2011.01.018.

Santoyo-Castelazo, E., Stamford, L., Azapagic, A., 2014. Environmental implications of decarbonising electricity supply in large economies: the case of Mexico. Energy Convers. Manag. 85, 272–291. https://doi.org/10.1016/j.enconman.2014.05.051.

SEMARNAT, & INECC., 2018. Sexta Comunicación Nacional y Segundo Informe Bienal de Actualización ante la Convención Marco de las Naciones Unidas sobre el Cambio Climático. PNUD.

Shams Esfandabadi, Z., Ranjbari, M., Scagnelli, S.D., 2022. The imbalance of food and biofuel markets amid Ukraine-Russia crisis: a systems thinking perspective. Biofuel Res. J. 9, 1640–1647. https://doi.org/10.18331/BRJ2022.9.2.5.

Sheinbaum, C., Caldero, A., Ramı, M., 2013. Potential of biodiesel from waste cooking oil in Mexico. Biomass Bioenergy 6. https://doi.org/10.1016/j.biombioe.2013.05.008.

Shonnard, D.R., Klemetsrud, B., Sacramento-Rivero, J., Navarro-Pineda, F., Hilbert, J., Handler, R., Suppen, N., Donovan, R.P., 2015. A review of environmental life cycle assessments of liquid transportation biofuels in the Pan American region. Environ. Manag. 56, 1356–1376. https://doi.org/10.1007/s00267-015-0543-8.

Sikalidis, T.K.E.-C., 2011. Molten Salt Synthesis of Ceramic Powders. IntechOpen, Rijeka. https://doi.org/10.5772/20472. Ch. 4.

Singh, D., Sharma, D., Soni, S.L., Inda, C.S., Sharma, S., Sharma, P.K., Jhalani, A., 2021. A comprehensive review of biodiesel production from waste cooking oil and its use as fuel in compression ignition engines: 3rd generation cleaner feedstock. J. Clean. Prod. 307, 127299 https://doi.org/10.1016/j.jclepro.2021.127299.

Yaashikaa, P.R., Kumar, P.S., Karishma, S., 2022. Bio-derived catalysts for production of biodiesel: a review on feedstock, oil extraction methodologies, reactors and lifecycle assessment of biodiesel. Fuel 316, 123379. https://doi.org/10.1016/J.FUEL.2022.123379.