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Simulation and Environmental Assessment of Alternatives for Biodiesel Production Using Residual Microbiota from Colombian Wastewater

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Abstract: Organic load present in wastewater and local environmental conditions, encourage the growth of biomass potentially exploitable in biotechnological processes, microbiota produced in Colombian wastewater treatment plants presents high biomass productivity and high lipid yield compared with other third generation biofuels sources. In this research, three routes of biodiesel production from Wastewater microbiota (WTP) were evaluated by varying the method of lipid extraction: Hexane-Based Extraction (HBE), extraction assisted with High-Speed Homogenization (SHE) and extraction using Ethanol/Hexane mixture (EHE), the evaluation was carried out under a technical approach by process simulation and evaluation of potential environmental impacts. Simulation was performed using Aspen Plus v.8.8, based on real macroscopic composition of the WTP microbiota and real process efficiencies based on experimental information. The environmental assessment was performed using the WAR algorithm taking into account 8 impact categories. Results shows that for a processing capacity of 47 kt/y, SHE pathway presents the highest lipid recovery efficiency in comparison to HBE and EHE pathways, however, the best alternative is not suitable for large-scale processing due to high energy requirements. In the other hand, EHE route presents a lower potential environmental impact generated due to complete transformation of highly harmful substances into other with lower toxicity. In addition, HBE topology presents higher risks associated with toxicity of the solvents used.

Key words: Microbiota, biofuels, yield, environmental evaluation, information, HBE

INTRODUCTION

Globally, the use of fossil fuels has been considered as a great contributor to increasing the CO_2 concentration in the atmosphere which requires the development of clean energy to conserve the environment as well as renewable and non-renewable resources, reducing emissions of greenhouse gases (Singh and Maji, 2012; Munoz *et al*., 2014). In this sense, algae are becoming an attractive alternative that can play the dual function of wastewater bioremediation and biomass generation for the production of biodiesel, bioethanol, fertilizers and other useful products in the cosmetic industry (Frias *et al*., 2015) due to they can grow in different aquatic environments such as freshwater, sea, municipal and industrial wastewater provided with adequate sources of carbon, nitrogen and phosphorus (Razeghifard, 2013; Reyes *et al*., 2017; Husaini, 2017). Drira *et al*. (2016) installed a small scale microalgal biomass culture system using 1 m^3 of domestic wastewater in order to extract and characterize the lipids contained therein. The results showed that the fatty acid profile is comparable to the characterization reported for the Chlorella, Nannochloropsis and Tetraselmis strains which highlights its potential as a biomaterial for the production of bioenergy at relatively low costs compared to the biofuels production from the cultivation of controlled monoclonal algae. In addition, wastewater treatment using microalgae has several advantages over conventional treatments based on activated sludge such as reduced energy demand, reduction of CO_2 footprint and recovery of nutrients in a biomass that can be converted into energy (Mahdy *et al*., 2015) also, the biodiesel generated from microalgae has properties similar to diesel currently used as fuel (Tuccar and Aydyn, 2013). Another benefit of massification of this type of energy alternative is that it allows the actors involved in the biofuels production to establish relationships of collaboration and cooperation

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with the researchers of the region so as to make possible the synergy with the companies in charge of the wastewater disposal, providing value to such effluents and increasing the economic viability of the process (Paredes *et al*., 2015). Regarding biodiesel production this begins with the cultivation of microalgae and the collection of biomass. Then, this last one is dried to prepare it for the cellular disruption required for the removal of lipids. Finally, the esterification and transesterification are carried out, obtaining biodiesel, glycerine and other contaminants that can be separated by unitary operations. The literature has reported that to optimize the obtaining biofuels process and increase their efficiency, the steps and topologies that have higher costs of manufacturing, maintenance, energy consumption and environmental impact potential must be taken into account. In this study, it is presented a comparison of three alternatives for the production of biodiesel from Wastewater Treatment Plants (WWTPs) biomass, focused on the extracting oil step. The processes evaluated correspond to the routes: Hexane Extraction (HBE), high Speed Homogenization (SHE) and extraction using a mixture of Ethanol/Hexane (EHE). The simulation was carried out in Aspen Plus v.8.4 and the environmental impacts were evaluated using the Waste Reduction (WAR) algorithm.

MATERIALS AND METHODS

Modeling of chemical composition biomass: The composition of the biomass obtained from the wastewater was modeled taking into account a real characterization carried out in a Colombian WTP (dry basis) which is composed of carbohydrates (10 %), proteins (55%), ashes (10%) and lipids (25%) where in this last one, the composition of fatty acids and triglycerides were 23.75% and 1.25%, respectively.

The metabolite profiles used in the simulation were selected from two representative strains of the WWTP microbiota. The carbohydrate and protein profiles were taken from the characterization reported for *Chlorella* sp. and the fatty acids profile reported in Table 1 was selected from *Navicula* sp. This profile is advantageous because it contains a high proportion of C_{16}-C_{18} that leads to biodiesel production, since the respective FAMEs reach an appropriate value of cold filter obstruction and a high number of cetane. Ma *et al*. (2016) cultivated *Chlorella vulgaris* in municipal wastewater by adding residual glycerol to increase nutrient uptake and lipid production, in order to assess its potential as a raw material for the biofuel production. The results showed that the fatty acid profile (mainly C_{16}-C_{18}) found in *C. vulgaris* is also found

Table 1: Fatty acid and triglycerides profiles used in simulation

Variables	Name	Composition
Fatty acids	Lauric acid	0.00
	Myristic acid	0.01
	Pentadecanoic acid	0.00
	Palmitic acid	0.00
	Palmitoleic acid	0.03
	Stearic acid	0.00
	Oleic acid	0.00
	Cis arachodic acid	0.01
Tri-glycerides	Glycerin trilaurate	0.15
	Trimyristin	0.11
	1,2,3-Propanetriyl tripentadecanoate	0.15
	Glycerol tripalmitate	0.29
	Glyceryl tripalmitoleate	0.02
	Tristearin	0.01
	Triolein	0.06
	Triarachidonin	0.15

in soybean oil which is used in the United States as the main raw material for biodiesel production. Therefore, the biodiesel obtained from both sources would have similar physical and chemical properties.

In addition, in Table 1 are found the triglycerides composition entered into the simulation in the biomass input stream. It was necessary to introduce some physicochemical properties of the solid compounds such as boiling point, molecular weight and specific heat at constant pressure which were taken from the free database ChemSpider, property of the Royal Society of Chemistry. In addition, a triglyceride structure was added, which was not found in Aspen Plus v.8.4, considering that the three carbon chains are composed for the same fatty acid in order to reduce the possible combinations that would be formed at the time of creation of the molecule (Sanchez *et al*., 2011). This modeling and simulation are more robust and realistic compared to other studies reported in the literature because of the fatty acid, triglyceride, amino acid and complex cellulose profiles were taken into account, resulting in an oil containing six free fatty acids and its triglycerides.

Computer aided simulation: The biodiesel production from wastewater begins with the cultivation of microalgae, the collection of biomass and the cellular rupture. However, in the simulation, the biomass was fed directly to each of lipid extraction routes. The simulation was performed using Aspen Plus v.8.8 with a calculus basis of 47 kt of biodiesel per year (this value represents the 10% of the annual biodiesel production in Colombia) at 1 atm and 298 K.The the rmodynamic models NRTL (Non-Random Two Liquids) and RK-Soave were used, taking into account that these represent properly the polar and non-polar mixtures and a strongly no-ideality in simulation. In addition, to determine the activity coefficients, the UNIFAC (UNIquac Functional group Activity Coefficients) method was used due to allow predicting the Vapor-Liquid Equilibrium based on the molecular interactions, shapes and size of molecules, being the most appropriate to evaluate the behavior of the solutions formed by organic compounds.

As for the lipid extraction pathways these were based on the methodology proposed by Peralta-Ruiz *et al.* (2013) however, the efficiency of the different stages was adjusted to realistic results obtained in laboratory and pilot plant scales. On the other hand, in order to mitigate the environmental impact that solvents can cause as well as to increase the efficiency of the processes, solvents recover and recycled steps were included with a necessary purge because of the load of contaminants present in this recycle stream.

As a first step in the HBE route, hexane was added to the biomass at a rate of 16 L of hexane per kg of dry biomass. Then, the solid and liquid part were separated: the oil-solvent stream was distilled off and the hexane was purged and recycled to the process.

As for the CSE route, methanol-chloroform-biomass were mixed in a mass ratio of 6:12:1, homogenized and separated by filtration. The lipid-solvent solution was washed with water in a ratio of 4:1 to eliminate lipids by distillation. The hydroalcoholic solution was also distilled off to recirculate methanol in the process and remove the water thereof.

Finally, in the EHE route, ethanol and biomass were mixed in a mass ratio of 4:1 and separated by a hydrocyclone where the solid part was filtered and re-mixed with alcohol to increase the efficiency of the process. The ethanol-lipid stream was mixed with water to an ethanol concentration of 40% then hexane was added in a 1:1 ratio with the obtained liquor. Then, the mixture entered to a tower where the lipid-hexane stream was removed, the hexane was purged and recycled while the water-ethanol mixture entered a second tower where the water exits the process and ethanol is recycled. In this method, polar and non-polar solvents are used to ensure the complete extraction of both forms of neutral lipids (independent and complex associated with the membrane) (Halim *et al.*, 2012; Ameera *et al.*, 2016). The mass biomass flows calculated in the simulation for the routes HBE, SHE and EHE were 29,420, 21,924 and 50,212 t/h, respectively. Also, the flow of solvents used was 308,227 t/h of hexane for the HBE route, 32,886 t/h of methanol and 65,772 t/h of chloroform in the SHE route, 278,864 t/h of ethanol and 113,454 t/h of hexane for EHE route.

Since the amount of free fatty acids present in the simulated oil is 5%, the biodiesel obtained is acid, therefore esterification is required. Thus, free fatty acids are converted into FAMEs at 4 atm and 70°C using methanol in a 6:1 molar ratio and sulfuric acid equivalent to 1% of the total fatty acid mass and neutralized with NaOH and methanol. After obtaining the FAMEs, the transesterification was carried out using NaOH in a mass ratio of 1% catalyst/oil and methanol in a 6:1 methanol/oil ratio, obtaining biodiesel, glycerin and contaminants which are separated by distillation.

Environmental assessment: The environmental assessment was carried out using the software WAR GUI v.1 which considers eight categories of environmental impact of chemicals and processes: Human Toxicity by Ingestion (HTPI) in Halation or dermal Exposure (HTPE), Ozone Depletion (ODP), Global Warming (GWP), Photochemical Oxidation (PCOP), Acidification (AP), Aquatic Toxicity (ATP) and Terrestrial Toxicity (TTP) potential. The results were analyzed by impact category and as total Potential Environmental Impact (PEI) of the studied processes. The software considers two types of PEI, output and generated where the first refers to how detrimental the process can be in a given site and the second refers to the transformation of the chemical compounds fed into other less polluting.

RESULTS AND DISCUSSION

Simulation of biodiesel production: The simulation of the extraction stage is divided into 3 study that represent the unit operations in each of the routes. These sections are listed and distinguished by frames as follows:

- Mixing and oil extraction section
- Solids separation section
- Solvent recovery and purge section

Figure 1a shows the simulation of the HBE extraction path. In study 1, the hexane and biomass streams are fed into the process and mixed into the B1 equipment. Then, this mixture enters to study 2 where the solid part is separated from the liquid part in a hydrocyclone represented by equipment B2. The free lipid and solvent stream is composed of carbohydrate and protein rich solids. In study 3, the microbiota oil (stream S13) is separated from the solvent (stream S12) before this last one be purged in the equipment B15 and recirculated (stream S19) in the process.

On the other hand, in the simulation of the SHE route (Fig. 1b), it is observed that the streams of chloroform, methanol and biomass are fed to the mixing section. In study 2, the solids are removed from the lipid-solvent solution and the solution is washed with water to enter into study 3 where the lipids are separated from the solvent by distillation which is recycled to the process.

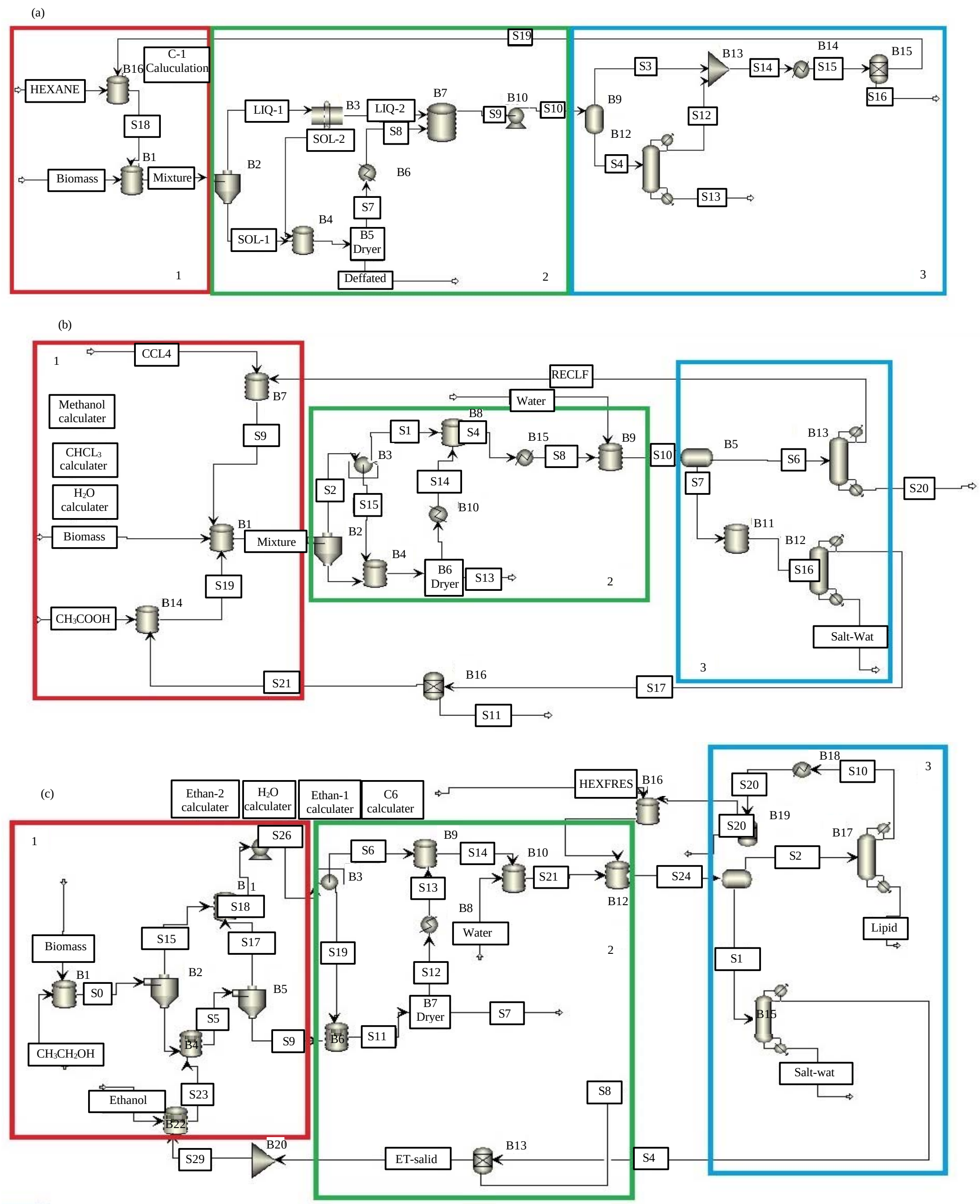

Fig. 1: Simulation of: a) HBE; b) SHE and c) EHE routes for oil extraction towards biodiesel production from wastewater biomass

Stream S16 is a hydroalcoholic solution which is also distilled off, to recirculate a portion of methanol (Stream S17) and a SALT-WAT stream. In this study, the Stream S17 is also purged and recirculated to the process.

Figure 1c shows the simulation of the EHE path where the biomass and ethanol streams are mixed in equipment B1 in study 1 then this mixture enters to a hydrocyclone where the solids are removed. However, to improve the process efficiency, a new ethanol stream was required which is fed to the solid rich stream S3 and once again is separated through a hydrocyclone represented by the B5 equipment. The lipid-solvent-free solids exit in stream S7. The S14 stream containing ethanol-lipids is mixed with water and hexane before entering study 3. In

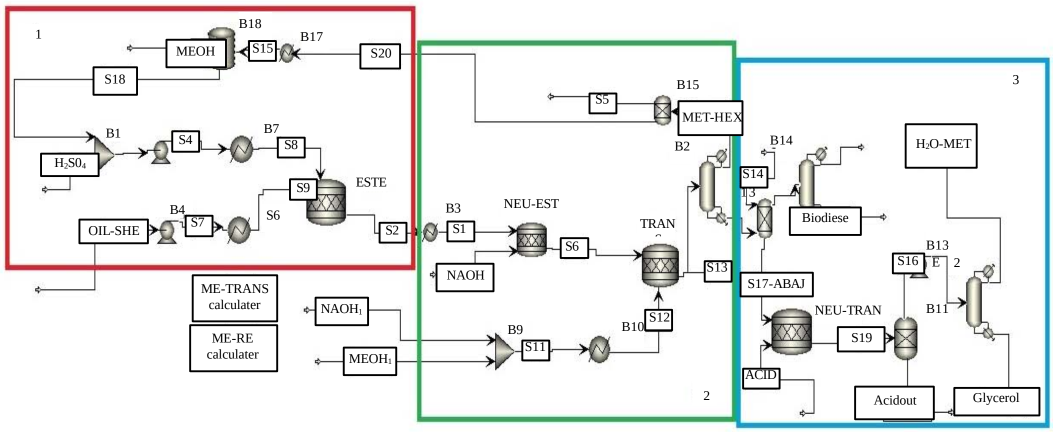

Fig. 2: Simulation of esterification and transesterification steps for biodiesel production from wastewater biomass

this study, the stream S2 is separated in hexane and lipids in the distillation tower B17, the lipids are contained in the stream Lipid and hexane is purged and recirculated in the process. In addition water and ethanol are also separated in a second distillation tower (B16) where the water exits in the Salt-Wat stream and the ethanol is purged in B13 and recirculated in the process.

Finally, a simulation of the esterification and transesterification steps was carried out. Similarly this stage is divided into sections that are listed and distinguished by frames in the simulation as follows:

- Esterification section
- Transesterification section
- Biodiesel purification

Figure 2 shows that the lipid stream from the respective distillation tower in each extraction route enters to study 1 where it reacts with methanol and sulfuric acid as the catalyst in the ESTE reactor under the optimal reaction conditions. In this reactor, the esterification takes place then the sulfuric acid present in the outlet stream is neutralized with NaOH in the NEU-EST reactor. The neutralized stream enters to the TRANS reactor in study 2 where the basic transesterification reaction is carried out. The biodiesel obtained enters to study 3 where the water formed as a by-product in the esterification reaction and the glycerine formed as a by-product in the transesterification reaction are eliminated.

Potential environmental impacts

Terrestrial (TTP), Aquatic (ATP) and Human Tosxicity Potential by Ingestion (HTPI) and Inhalation or Dermal Exposure (HTPE): Figure 3a shows that under TTP impact category, the EHE route has a higher PEI output (14,200 PEI/h) which means that the biodiesel production in case of being commercially implemented should be carried out in a place that has a high ecological resistance and little contact with flora and fauna. Respect to PEI generated, EHE route (-11,900 PEI/h) presents in its products, less toxic chemical compounds that entered in the feeding currents respect to other evaluated routes.

Regarding the ATP impact category, Fig. 3b shows that the EHE route has the highest PEI (28,400 PEI/h) which indicates that if it is run on a commercial scale it should be located in a remote area of any aquatic ecosystem. For the generated PEI, the EHE route obtained the highest PEI which means that this process has in its products more substances toxic for aquatic ecosystems than the chemicals fed to it. In turn, the negative PEI route HBE (-24.5 PEI/h) indicates that the substances present in their outflows have been transformed into substances less toxic than the compounds fed to the system.

The third impact category is HTPI, under which the EHE route has the highest PEI output (14,200 PEI/h), followed by HBE and CSE as it is observed in Fig. 3c. The results obtained for PEI generated indicate that the EHE routes (-11,900 PEI/h) and CSE (-150 PEI/h) have a significant transformation of their chemical components into substances with high lethal dose while the HBE route presents the highest PEI generated (1,980 PEI/h) because of the outflows present substances with lower lethal dose than the incoming currents.

Finally, Fig. 3d shows that for the HTPE impact category, the HBE route represents the topology with the highest impact potential (165 PEI/h) followed by EHE and CSE, indicating that the HBE route is the one that expels a greater flow of mass directly to the atmosphere. For the generated PEI, the EHE route has the lowest impact potential (-32.10 PEI/h) indicating that its chemical components in the product have been transformed into substances that have Tolerance Values Limits (TVL) lower

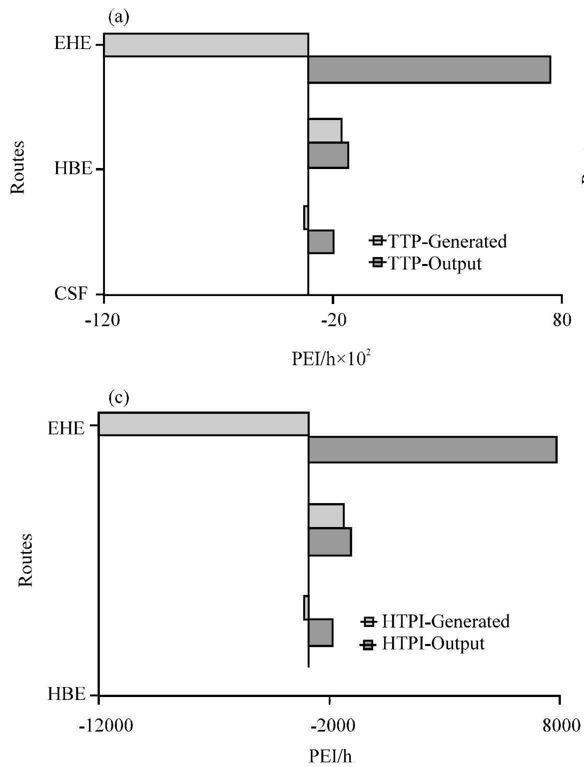

Fig. 3: Comparison of PEI output and generated for the biodiesel obtained based on the three routes evaluated under the impact categories: a) TTP; b) ATP; c) HTPI and d) HTPE

than those fed into the process. In contrast, the HBE route contains the highest PEI being 10 times higher than CSE (19.70 PEI/h), indicating that the HBE route contains quantities of substances in its product that exceeds the TVL.

Ozone Depletion (ODP), Global Warming (GWP), Acidification (AP) and Photochemical Oxidation (PCOP) potential: Figure 4a shows that results for the generated and output PEI were: 1.31×10^{-3}, 6.04×10^{-4} and 1.73×10^{-4} PEI/h for EHE, CSE and HBE routes, respectively such low values indicate that biodiesel production from wastewater does not produce ozone depletion compared to Chlorofluorocarbon Compounds (CFC). Figure 4b shows that the EHE route has the largest PEI output for the GWP category, indicating that this process emits chemicals that persist longer in the environment due to their low oxidation, followed by CSE and HBE. For all processes, the values of PEI generated and output are very similar, since from all the routes are produced chemical products with less capacity to degrade in the environment.

Figure 4c show that under the AP impact category, the PEI output and generated for each process were the same. The EHE route had the greatest impact (3,580 PEI/h), followed by CSE (1,650 PEI/h) and HBE (473 PEI/h). Finally, Fig. 4d shows the high discrepancy between the evaluated routes. The results showed that for the PEI output, the EHE route was the highest (196,000 PEI/h), followed by HBE (11,800 PEI/h) and CSE (4,800 PEI/h).

Total potential environmental impact; output and generated: Regarding the total PEI, the EHE route has the highest output (257,200 PEI/h), followed by HBE and CSE, indicating that the CSE route might be commercially developed in an environment more sensitive than the other two routes evaluated. Figure 5 indicates that for the PEI generated, the components present in the output streams of the EHE route are less polluting than the substances present in the feed stream whereas results for the HBE and CSE routes indicate that the output streams have a higher environmental impact potential than input ones. This agrees with results reported by Pardo-Cardenas *et al.* (2013) who explain that the PEI output as an energy requirement is high, mainly due to solvent recovery performed in the oil extraction stage in order to increase efficiency. As for the differences between the three biodiesel production topologies evaluated, the EHE route presents a better environmental

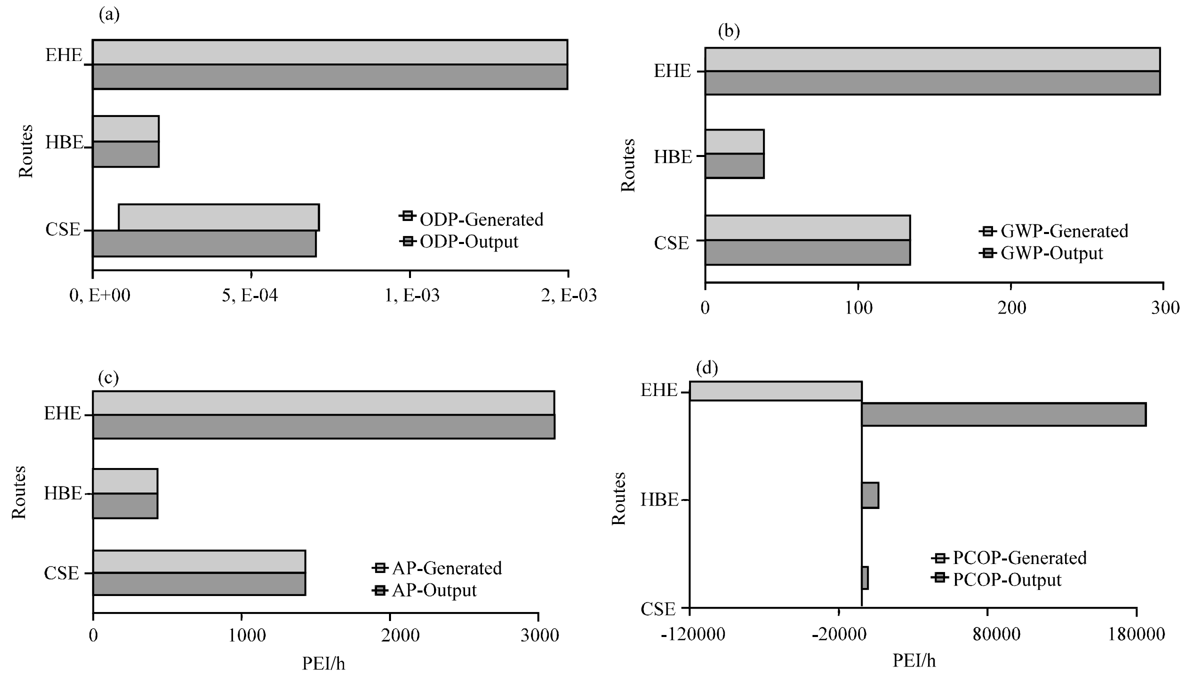

Fig. 4: Comparison of PEI output and generated for the biodiese obtained based on the three routes evaluated under the impact categories of: a) ODP; b) GWP; c) AP and d) PCOP

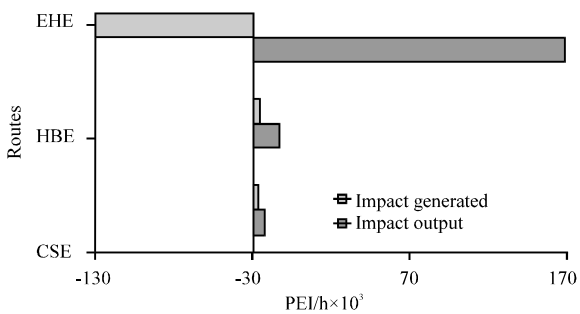

Fig. 5: Comparison of potential enviromental impact output and generated for the three biodiesel obtaining routes evaluated

performance in all the categories analyzed with the exception of Ozone Depletion (ODP) and Global Warming (GWP).

CONCLUSION

Three routes for oil extraction from wastewater biomass for biodiesel production were simulated under Colombian conditions, based on real efficiencies obtained experimentally in order to make the simulation more robust and realistic compared with studies found in literature where this value is assumed as 100%. The SHE route had a yield of 100% due to less biomass is required at the entrance for the biodiesel production, resulting in themost adequate route from the technical point of view. The EHE was the less efficient (45.66%) and the one with the highest energy costs since it processes a greater amount of biomass (50.2 kt/h) compared to the other two routes (29.4 and 21.9 kt/h for HBE and CSE, respectively) which leads to require a larger amount of reagents during esterification and transesterification. The type and quantity of these substances such as sulfuric acid, cause a greater environmental impact and influence on the total PEI output. However, the EHE route shows a smaller PEI generated due to complete transformation of highly noxious substances into less environmentally toxic ones. Based on the results obtained, HBE route is the most energy-efficient alternative for a production of 47 kt of biodiesel per year. Finally, the categories that less contribute to the total PEI are ODP, HTPE, GWP and those that contribute the most are TTP, ATP and PCOP.

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