

# Simulation and life cycle assessment of process design alternatives for biodiesel production from waste vegetable oils

Sérgio Morais<sup>a,b,\*</sup>, Teresa M. Mata<sup>a</sup>, António A. Martins<sup>a</sup>, Gilberto A. Pinto<sup>c</sup>, Carlos A.V. Costa<sup>a</sup>

<sup>a</sup> Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

<sup>b</sup> REQUIMTE/Instituto Superior de Engenharia do Porto (ISEP), Rua Dr. António Bernardino de Almeida, 431 4200-072 Porto, Portugal

<sup>c</sup> Departamento de Engenharia Química, Instituto Superior de Engenharia do Porto (ISEP), Rua Dr. António Bernardino de Almeida, 431 4200-072 Porto, Portugal

## A B S T R A C T

This study uses the process simulator ASPEN Plus<sup>®</sup> and Life Cycle Assessment (LCA) to compare three process design alternatives for biodiesel production from waste vegetable oils that are: the conventional alkali-catalyzed process including a free fatty acids (FFAs) pre-treatment, the acid-catalyzed process, and the supercritical methanol process using propane as co-solvent. Results show that the supercritical methanol process using propane as co-solvent is the most environmentally favorable alternative. Its smaller steam consumption in comparison with the other process design alternatives leads to a lower contribution to the potential environmental impacts (PEI). The acid-catalyzed process generally shows the highest PEIs, in particular due to the high energy requirements associated with methanol recovery operations.

### Keywords:

Biodiesel  
Waste vegetable oil  
Process design  
Process simulation  
Life cycle assessment (LCA)  
Alkali-catalyzed process  
Acid-catalyzed process  
Supercritical methanol process

## 1. Introduction

Some of the biodiesel advantages over petroleum diesel are extensively reported in literature (Heehan et al., 1998; Nas and Berktaç, 2007; Ma and Hanna, 1999; Srivastava and Prasad, 2000; Fukuda et al., 2001; Dorado et al., 2003; Knothe et al., 2003; Beer et al., 2002; Utlu and Kocak, 2008). Among others, it is derived from renewable resources, it is biodegradable and with a higher flash point (423 K) that makes it less volatile and safer during its transportation and handling. Moreover, biodiesel has a more favorable combustion emission profile than diesel, such as lower emissions of carbon monoxide, particulate matter and unburned hydrocarbons.

The high costs and limited availability of biodiesel feedstocks are however critical issues in this industry. The costs of vegetable oils can be up to 75% of the total manufacturing cost, which makes biodiesel production costs approximately 1.5 times higher than

those of diesel (Haas et al., 2002; Phan and Phan, 2008). For this reason, the use of waste vegetable oils can be an effective way of reducing production costs since it is 2-3 times cheaper than virgin vegetable oils (Phan and Phan, 2008). In addition, it helps solving the environmental problems associated with disposal of the waste vegetable oils.

The purpose of this study is to compare the potential environmental impacts of three process design alternatives for biodiesel production from waste vegetable oils, using process simulation and the life cycle assessment (LCA) methodology. The process design alternatives include: (1) the alkali-catalyzed process with free fatty acids (FFAs) pre-treatment, (2) the acid-catalyzed process, and (3) the supercritical methanol process using propane as co-solvent. These process design alternatives are simulated using the process simulator ASPEN Plus<sup>®</sup> in order to estimate the inventory data for the three process typologies, considering the same plant capacity and product purity requirements.

## 2. Biodiesel production from waste vegetable oil

The most common way to produce biodiesel is by transesterification, in which a catalyzed chemical reaction involving

\* Corresponding author. REQUIMTE/Instituto Superior de Engenharia do Porto (ISEP), Rua Dr. António Bernardino de Almeida, 431 4200-072 Porto, Portugal. Tel.: +351 228340500; +351 228321159.

E-mail address: sacm@isep.ipp.pt (S. Morais).

a vegetable oil or fat (mainly composed by triglycerides) and an alcohol, yields fatty acid alkyl esters (or biodiesel) and glycerol. Alcohols such as ethanol, methanol or butanol can be used and the resulting esters are named respectively, methyl, ethyl or butyl esters. Methanol is the alcohol most commonly used industrially due to its low-cost relatively to the other alcohols.

### 2.1. Alkali-catalyzed process

There are several routes to obtain biodiesel from lipidic feedstocks. The most widely used is the transesterification of triglycerides with low molecular weight alcohols in the presence of a homogeneous alkali-catalyst and operated in a batch mode. For this process an excess of methanol must be used in the presence of the alkali-catalyst to shift the reaction to a maximum yield of biodiesel product. Freedman et al. (1984) recommend a methanol to oil molar ratio of 6:1, at reaction temperature of about 333.15 K that is near the methanol boiling point.

The alkali-catalyzed transesterification reaction is very sensitive to the presence of free fatty acids (FFAs) and water in the lipidic feedstocks (Canacki, 2007). When an alkali catalyst is added to these feedstocks, the FFAs react with the catalyst to form soap and water. The soap formation not only consumes catalyst, but also causes emulsions to be formed, which make it difficult to further recover and purify biodiesel. In order to maximize the formation of methyl esters Freedman et al. (1984) recommend to use refined vegetable oils with an FFA content lower than 0.5% (w/w). Additionally, the presence of water may cause ester saponification under alkaline conditions. Ma et al. (1998) reports that the water content of vegetable oils should be kept below 0.06% (w/w).

Impurities such as water and FFAs may hinder an efficient use of waste vegetable oils and other crude oils or fats. Waste vegetable oils typically contain 2–7% of FFAs, while animal fats may contain 5–30% of FFAs (Van Gerpen, 2005). In these cases an acid catalyst such as sulfuric acid can be used to esterify the FFAs to methyl esters. The triglycerides remain essentially unconverted to esters for low methanol to oil molar ratios and short reactor residence times. The acid-catalyzed esterification can be used as a pre-treatment operation to convert FFAs to methyl esters, this way reducing the FFA content of crude oil (Lepper and Friesenhagen, 1986). The pretreated oil can then be transesterified with an alkali-catalyst to convert triglycerides into methyl esters.

### 2.2. Acid-catalyzed process

The pre-treatment operation can be avoided by using the acid catalyst, such as sulfuric acid, for the transesterification reaction, being it less sensitive than the alkali-catalyzed transesterification to the presence of FFAs and providing high conversion rates, although much longer times and higher reaction temperatures are required (Canacki and Van Gerpen, 1999). Moreover, a higher methanol to oil molar ratio is needed to promote high equilibrium conversions of triglycerides to esters. For example Canacki and Van Gerpen (1999) reported a 98.7% conversion in 48 h, at a methanol to oil molar ratio of 30:1, and a reaction temperature of 333.15 K. Zhang et al. (2003a) and Zheng et al. (2006) reported a 97% conversion for a reaction time of 4 h, at a methanol to oil molar ratio of 50:1 and 353.15 K of reaction temperature.

Although the acid-catalyzed transesterification reaction is a one-step process, it relies on a large excess of alcohol for which recover costs may determine the process feasibility. Some authors performed an economic analysis of this process, concluding that the acid-catalyzed transesterification provides higher revenues than the alkali-catalyzed process with an FFA pre-treatment (Zhang et al., 2003a, 2003b).

### 2.3. Supercritical methanol process

The transesterification of triglycerides with supercritical methanol is also receiving much attention (Kusdiana and Saka, 2001a, 2001b; Bunyakiat et al., 2006; Demisbras, 2002; Kiwjaroun et al., 2009) for biodiesel production, since it is a catalyst-free process with high reaction rates, making it possible to perform the reaction in just a few minutes (about 4 min) (Kusdiana and Saka, 2001b). As other advantages this process is insensitive to the presence of impurities in the vegetable oil, such as water and FFAs, and the FFAs can be esterified simultaneously with the transesterification of triglycerides. However as reported by Kusdiana and Saka (2001a) this process requires a very high methanol to oil molar ratio of about 42:1 and a very high reaction temperature and pressure of 623.15 K and 43 MPa respectively, as optimal reaction conditions.

Kiwjaroun et al. (2009) assessed the PEs of the supercritical methanol process in comparison to the conventional alkali-catalyzed process, using process simulation. Results of their study showed that higher PEs are obtained for the supercritical methanol process (in nine of the assessed eleven impact categories) in comparison with the conventional alkali-catalyzed process with an FFA pre-treatment of crude oil. The required higher amount of methanol to perform the supercritical transesterification reaction and subsequently the energy expenditure in methanol recovery are the main reasons for these results.

Alternatively, Cao et al. (2005) proposed the supercritical methanol method, using propane as co-solvent, which decreases the reaction temperature and pressure, as well as the alcohol to oil molar ratio. This is explained since propane decreases the critical point of methanol allowing the supercritical reaction to be carried out under milder conditions than those reported by Kusdiana (Kusdiana and Saka, 2001b). In this case, the optimal reaction conditions are a temperature of 553.15 K, a pressure of 12.8 MPa, an alcohol to oil molar ratio of 24:1 and propane to oil molar ratio of 0.05:1. At these conditions 98% of oils are converted to biodiesel for a reaction time of 10 min. This process was further assessed by Kasteren and Nisworo (2007) who performed an economic analysis, considering an industrial production of biodiesel from waste vegetable oil and claiming that it can compete with the existing alkali and acid-catalyzed processes.

### 2.4. Heterogeneous catalyzed processes

The use of enzymes as a biological catalyst has shown good tolerance for the free fatty acid level of the feedstock (Watanabe et al., 2001), but the research efforts in biocatalysis applied to biodiesel production are largely still at the laboratory stage. The use of zeolites and metal catalysts allow for the use of feedstocks with high FFA content (Kiss et al., 2006), but also scientific and technical barriers persist relatively to its industrial-scale application. Therefore, such processes are out of the scope of this study.

## 3. Study goal and scope definition

This study aims to perform an environmental evaluation of three process design alternatives for biodiesel production from waste vegetable oils, using process simulation and life cycle assessment (LCA).

The process design alternatives considered in this study include: the alkali-catalyzed process with an FFA pre-treatment (AICP), the acid-catalyzed process (AcCP) and the supercritical methanol process using propane as co-solvent (ScMP). These processes were simulated using the process simulator ASPEN Plus® and the potential environmental impacts (PEs) were evaluated using the

LCA methodology as described in EN ISO 14040 (International Standard Organization, 2006) and by Guinée (2002)

The functional unit selected for this study is the production of 1000 kg of biodiesel based on a process plant with a capacity of 3500 tonnes per year.

Some LCA considerations and assumptions for this study are the following:

- Material and energy inputs and outputs associated with biodiesel production processes are estimated based on their simulations using the process simulator ASPEN Plus®.
- Inventory data for energy and materials production, transportation and waste treatment are obtained from the Ecoinvent Database® assuming the European situation.
- Three biodiesel production process alternatives are considered to be placed in the same site or geographical location, allowing for the use of standardized transportation distances.
- The distances considered in this study for materials transportation from its production to consumption and also waste materials transportation from where they are generated to where they are treated, are standard transportation distances for Europe as reported in the Ecoinvent guidelines (Frischknecht et al., 2004).
- Environmental burdens are allocated based on mass flow rates of the valuable products process streams (biodiesel and glycerol).
- The contribution to PEIs concerning the constructing of process equipments and units are not considered in the inventory analysis for this study.
- The PEIs evaluation in this study considers as life cycle impact assessment method the CML 2001 baseline version 2.04 (Guinée, 2002; CML).
- Ten PEI categories are considered for evaluation in this study including: abiotic resources depletion, acidification, eutrophication, global warming, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity, marine aquatic ecotoxicity, terrestrial ecotoxicity and photochemical oxidation.
- The PEI categories are normalized by dividing them by reference values obtained for Western Europe, in 1995, as reported in literature (Huijbregts et al., 2003), whereas the reference values were calculated by applying the same characterization factors of the CML 2001 baseline version 2.04.
- No weighting factors are considered in this study for the normalized PEI categories and therefore results are not aggregated in a single total PEI index.

#### 4. Process design and simulation

In order to gather the process data needed for the inventory analysis, models of the three biodiesel production process alternatives were developed and simulated using ASPEN Plus®. Process plants with production capacities of 3500 tonnes per year for biodiesel production (corresponding to 8500 operating hours per year) were designed to operate in a continuous mode.

Despite the possible differences between results obtained from a process simulator or from a real process operation, the software capabilities of a process simulator allows one to obtain reliable information about the process. Currently available process simulators already incorporate comprehensive thermodynamic packages, vast component libraries and advanced calculation techniques (Canacki and Van Gerpen, 1999; Zheng et al., 2006)

In this study some thermodynamic properties not available in the component library of Aspen Plus® were estimated using this process simulator after providing it with the component molecular structure.

A combination of NRTL (Non-Random Two Liquid) and UNIQUAC (UNiversal QUAsiChemical) thermodynamic/activity models were used to predict the activity coefficients in the process simulations, due to the presence of highly polar components (Zhang et al., 2003a, 2003b; Kiwjaroun et al., 2009)

Some components not directly available in the process simulator were represented by similar components chosen from the available components database. This is the case of triglycerides that are represented by triolein ( $C_{57}H_{104}O_6$ ), FFA's existent in the waste vegetable oil that are represented by oleic acid ( $C_{18}H_{34}O_2$ ) and fatty acid methyl esters (FAME) that are represented by oleic acid methyl ester ( $C_{19}H_{36}O_2$ ). Oleic acid is the major fatty acid present in triglycerides of rapeseed oil, canola oil, palm oil, and peanut oil (Canacki and Van Gerpen, 2003; Harding et al., 2007) and, therefore, it is the major free fatty acid present in waste vegetable oils derived from those vegetable oil feedstocks, although this simplification may not be appropriate for other vegetable oils.

In the three process alternatives, product purities were fixed to be 99.1% (w/w) for biodiesel, higher than the European biodiesel standard (EN 14214) specification for esters content (96.5% w/w), and 91.0% (w/w) for crude glycerol.

Vacuum operation for the methanol recovery and products purification was applied to keep the temperature at suitably low levels because of the FAME and glycerol thermal decomposition temperatures (523 K for FAME and 423.15 K for glycerol). As observed by Zhang et al. (2003a) the use of a flash unit in the AICP and AcCP processes for both FAME and glycerol purification could not achieve the desired high purity requirements as fixed for products, greater than 90% (w/w), therefore it was applied a multi-stage distillation step for both processes.

##### 4.1. Alkali-catalyzed process with FFA pre-treatment

Fig. 1 shows the alkali-catalyzed process model, with FFA pre-treatment, obtained using the process simulator ASPEN Plus®. A waste vegetable oil stream flow rate of 428.50 kg/h (stream 104) is pre-heated in a heat exchanger with the esterification reactor products (stream 106A) and fed to the esterification reactor (R-100) where the FFAs are converted to methyl esters. As proposed by Zhang et al. (2003a) it is assumed a 6% (w/w) of FFA content in the waste vegetable oil.

As reactant to perform esterification, it is used a fresh methanol stream flow rate of 9.50 kg/h (101) mixed together with a stream of recycled methanol (110) and the sulfuric acid catalyst (stream 103).

The esterification reaction is performed at a temperature of 343.15 K, a pressure of 405.3 kPa, a methanol to oil molar ratio of 6:1 and with 5% (w/w) of sulfuric acid catalyst in methanol (Lépper and Friesenhagen, 1986; Zhang et al., 2003a; Harding et al., 2007) For this reaction it is assumed a 95% conversion of FFA in methyl esters (Zhang et al., 2003a).

The esterification products (stream 106A) are cooled to 333.15 K, in a heat exchanger used to simultaneously preheat the oil feed, and then are sent to a glycerol washing column (X-100), where fresh glycerol is used (stream 108) to wash out sulfuric acid and water, through three theoretical washing stages.

The treated vegetable oil that leaves the glycerol washing column (X-100) from the top stream (107) still contains a 0.30% content of non-reacted FFA, which is acceptable to perform then the transesterification reaction.

The remaining components, mainly glycerol, water and acid catalyst leave the glycerol washing column (X-100) in the bottom stream (109) and are then charged into a distillation column (T-100) where most of the non-reacted methanol (stream 110) to be recycled is recovered and fed again to the esterification reactor (R-100).

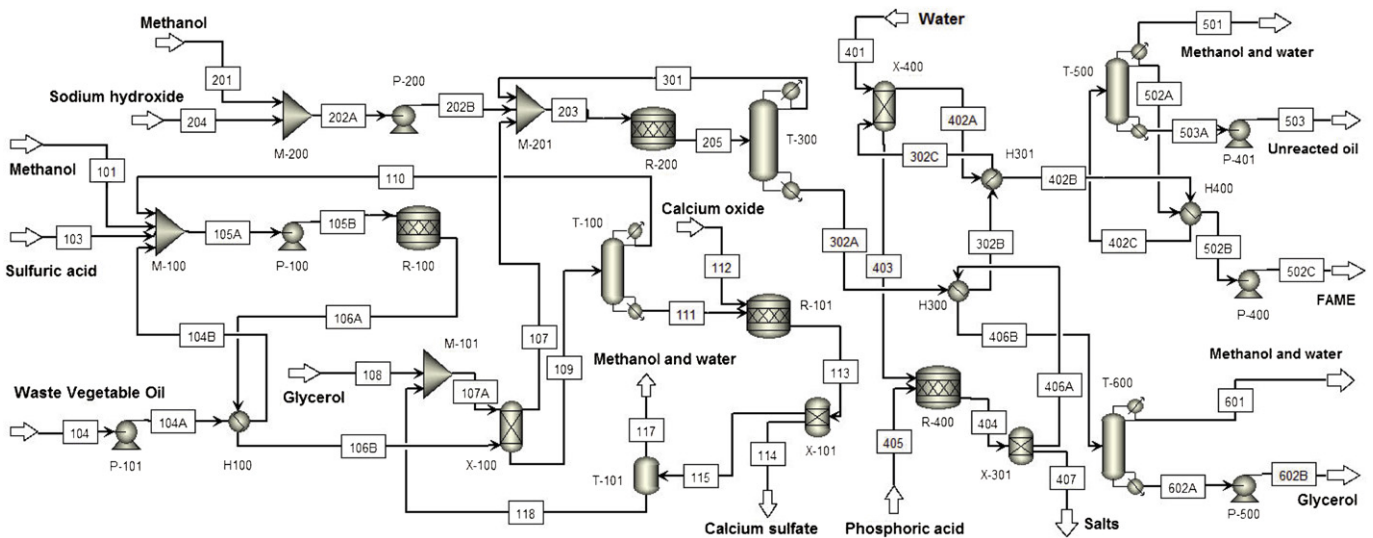


Fig. 1. Alkali-catalyzed process with FFA pre-treatment to produce biodiesel from waste vegetable oils.

Glycerol and sulfuric acid leave the distillation column (T-100) in the bottom stream (111), which is then fed to a neutralization reactor (R-101) where sulfuric acid is removed from glycerol using calcium oxide (stream 112). The precipitated calcium sulfate is then removed in a gravity separator (X-101) and treated as a waste stream (114).

The glycerol stream (115) leaving the gravity separator (X-101) is then further purified in a flash evaporator (T-101) where the remaining methanol and water are removed in the top stream (117) and treated as a waste stream due to its small mass flowrate of 6.97 kg/h. The flash bottom stream (118) is then recycled back to the glycerol washing column (X-100) where it is mixed with a fresh glycerol stream (108).

The pretreated oil stream (107) resulting from the esterification process previously described, is then sent to the transesterification reactor (R-200), where a 6:1 molar ratio of methanol to oil is used with 1% (w/w) of sodium hydroxide to perform the reaction (Freedman et al., 1984; Canacki and Van Gerpen, 1999; Harding et al., 2007). Transesterification takes place at 333.15 K and 405.3 kPa and reaches a 95% conversion of oil to FAME, after 2 h (Zhang et al., 2003a; Kiwjaroun et al., 2009; Mancosky et al., 2007).

Before entering the transesterification reactor (R-200), a fresh methanol stream flowrate of 42.98 kg/h is mixed with anhydrous sodium hydroxide. This last one is in solid state and thus, it takes need to be first dissolved with methanol in a separated mixing unit.

The transesterification reactor products (stream 205) are fed to a vacuum distillation column (T-300), where 94% of methanol is recovered through four theoretical stages with a reflux ratio of 1.5. The column top stream flowrate of 23.04 kg/h of recovered methanol (301) is recycled back to the transesterification reactor, where it is mixed with a fresh methanol stream.

The column bottom stream (302A) mainly containing biodiesel and glycerol, is charged to a washing column (X-400), where water is used to wash biodiesel, providing separation of methanol, soap, glycerol and catalyst from FAME.

The top stream leaving the washing column (402A), mainly containing methyl esters and unconverted oil, is then feed to a vacuum distillation column (T-500), with six theoretical stages and operating at a reflux ratio of 1.5 to separate the remaining methanol and water from FAME and non-reacted oil.

In order to separate FAME from water and methanol, a partial condenser is used in the distillation column (T-500) overhead. FAME is obtained in the bottom stream (502A) of the column

overhead condenser, with a mass flowrate of 411.13 kg/h and 99.10% of purity. Water and methanol is obtained in the same condenser top stream (501) and have a small mass flowrate of 1.77 kg/h that is treated as waste. Unconverted oil is obtained in the column bottom stream (503) with a mass flowrate of 22.44 kg/h. Although it is not considered in this study, this oil stream can be considered for further recycling and conversion within this process.

The bottom stream containing glycerol (403) that leaves the washing column (X-400) is then fed to a neutralization reactor (R-400) in order to remove the catalyst. Hence, phosphoric acid is added in equivalent moles to the NaOH present in the stream. The resulting salts ( $\text{Na}_3\text{PO}_4$ ) are then removed in a gravity separator (X-301) and treated as waste.

Glycerol resulting from the neutralization reactor (R-400) is further purified in distillation column (T-600) with three theoretical stages and operating at a reflux ratio of 1.5. A small water and methanol flowrate of 7.79 kg/h is removed in the column top stream (601) and treated as waste. At the column bottom stream (602A), a glycerol by-product flowrate of 43.73 kg/h is obtained with 91% purity.

#### 4.2. Acid-catalyzed process

The acid-catalyzed process for biodiesel production from waste vegetable oils is presented in Fig. 2.

In this process, a fresh methanol stream (102B) and a recycled methanol stream (201), of respectively 87.00 kg/h and 60.48 kg/h, are mixed with sulfuric acid catalyst (stream 103) and a waste vegetable oil stream flowrate of 420.00 kg/h (101A) and fed to the transesterification reactor (R-100). Reaction takes place at 353.15 K and at a pressure of 405.3 kPa, with waste oil to methanol and to acid molar ratios of 1:50:1.3. At these conditions a 97% conversion of oils to FAME is achieved after 4 h (Zhang et al., 2006).

The transesterification products (stream 106) are then fed to a distillation column (T-200) in order to separate the excess methanol, through four theoretical stages and a reflux ratio of 2. A methanol mass flowrate of 670 kg/h is obtained in the top column stream (201), corresponding to a 94% mass recovery, which is then recycled back to the transesterification reactor.

The bottom column stream (202) containing FAME, glycerol, non-reacted oil and the acid catalyst is fed to a neutralization reactor (R-200), where sulfuric acid is removed with calcium oxide. Equivalent moles of calcium oxide to the sulfuric acid are added,

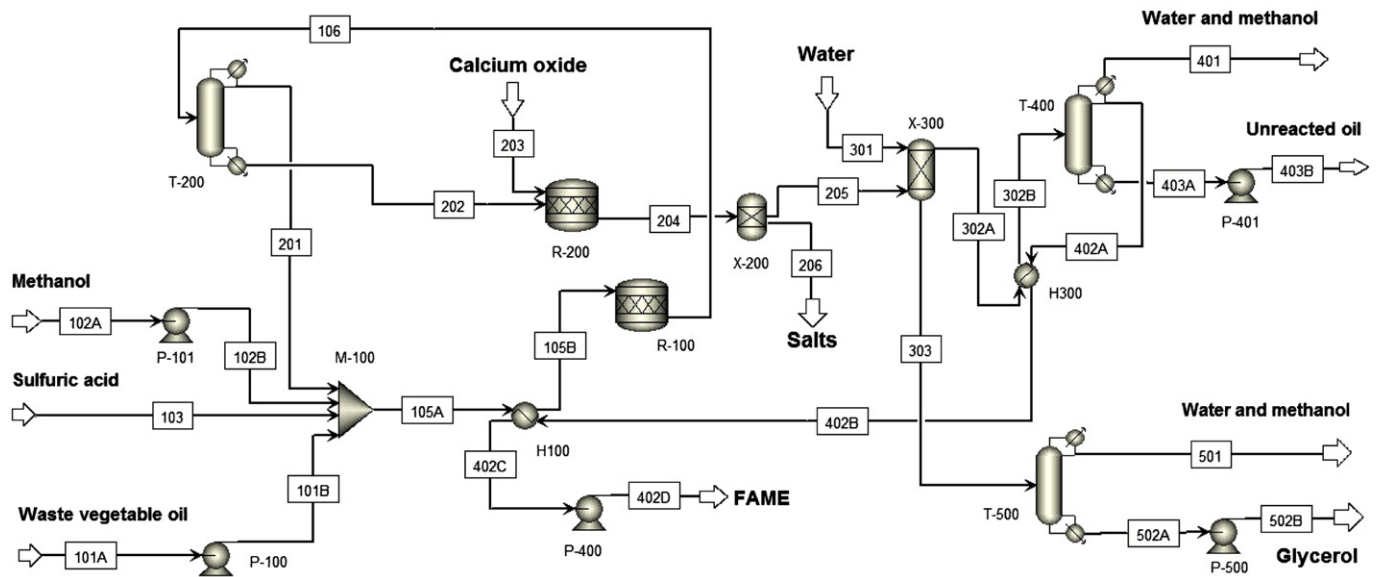


Fig. 2. Acid-catalyzed process for biodiesel production from waste vegetable oils.

producing calcium sulfate and water. Calcium oxide is used due to its low-cost relatively to other alkali substances (Janacki and Van Gerpen, 1999). The salts are then removed in a gravity separator (X-200) and treated as waste.

The remaining water washing column (X-300) and biodiesel and glycerol purification units (T-400 and T-500) are similar to the alkali-catalyzed process in terms of equipment sizing and operating conditions. FAME is obtained in the bottom stream (402A) of the column overhead condenser, having a massflowrate of 408.67 kg/h and 99.14% of purity. The glycerol by-product is obtained in the column T-500 bottom stream with a flowrate of 46.57 kg/h and 91% purity.

#### 4.3. Supercritical methanol process using propane as co-solvent

The supercritical methanol process for biodiesel production from waste vegetable oils is presented in Fig. 3.

In this process, 410 kg/h of waste vegetable oil (stream 101A) is mixed with 45.33 kg/h of fresh methanol (stream 102A), 297.5 kg/h of recycled methanol (stream 202B) and propane (stream 102) and fed to the transesterification reactor (R-100). Reaction takes place at 553.15 K a pressure of 12.7 MPa, an oil to methanol molar ratio of 1:24 and a methanol to propane molar ratio of 1:0.05 (ao et al., 2005).

In order to model the supercritical methanol reaction conditions as accurately as possible, kinetic parameters (heat of reaction, activation energy and the pre-exponential factor from the Arrhenius equation) were used in the simulations. The reaction kinetics are given by Kasteren and Nisworo (2007) and are described in Table 1.

Within this reaction conditions conversion is almost complete after a residence time of 12.6 min, in a plug flow reactor with 10 cm diameter and 7 m length.

The reaction products (stream 105) are fed to flash evaporator (X-200) where pressure is decreased to 506.6 kPa. This pressure drop has as result the transfer of liquid methanol and propane to the gaseous form. The flash gas stream (201) is then recycled back to the reactor, since it contains 92.2% of methanol and 7.5% of propane at a flowrate of 279.93 kg/h. The bottom flash stream 203A is sent to settler unit (X-201) to separate FAME (stream 204A) from the remaining methanol and glycerol (stream 205A).

In order to further purify methyl esters (stream 204A) by removing the remaining methanol and propane flash evaporator

(X-300) is used, where a FAME product (stream 302B) flowrate of 412.69 kg/h is obtained with 99.15% purity.

The glycerol by-product (stream 205A) is also purified in a flash evaporator (X-400) resulting in a glycerol flash bottom stream flowrate of 42.90 kg/h with 91% purity and a methanol and propane flash top stream (401) that is recycled back to the transesterification reactor.

#### 5. Inventory analysis

The data needed for the inventory analysis of this study is obtained after developing the three process flowsheet models and performing their simulations. Table 2 shows the material and energy inputs and outputs per functional unit (i.e. per 1000 kg of biodiesel), for each of the three process alternatives analyzed: alkali-catalyzed process with FFA pre-treatment (AICP), acid-catalyzed process (AcCP) and supercritical methanol process using propane as co-solvent (ScMP).

As shown in Table 2, the higher methanol to oil molar ratio for the acid-catalyzed transesterification reaction, relatively to the other process alternatives, led to a higher methanol flowrate of 670 kg/h in the recycle loop (23 kg/h for AICP and 297.5 kg/h for ScMP). Therefore, a higher consumption of steam is shown in the AcCP and it is particularly due to the intensive steam requirements in the methanol recovery process. Moreover, due to the high catalyst mass flowrate in the acid-catalyzed transesterification reaction and consequently the need for its downstream neutralization and removal, originates a higher amount of solid wastes in comparison to the other alternatives.

The absence of catalyst in the supercritical methanol process greatly simplifies biodiesel purification steps and therefore reduces the generation of wastes.

Although the potential environmental impacts related to equipment construction were not considered in this study scope one may see clear differences among the three process design alternatives. The simulator models for the three process alternatives show for the ScMP 12 main process units, for the AcCP 14 units and for the AICP process 24 units. Moreover, the reactor residence time to perform the transesterification reaction in each of the three process design alternatives is significantly different, leading to different reactor sizes.

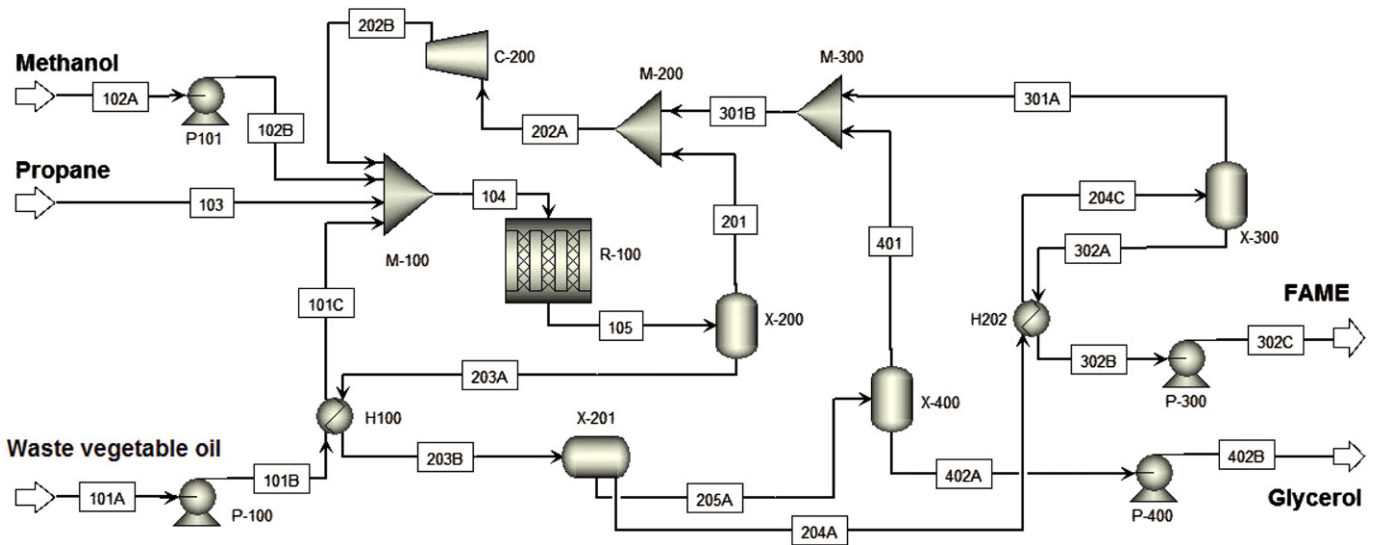


Fig. 3. Supercritical methanol process with propane as co-solvent to produce biodiesel from waste vegetable oils.

## 6. Potential environmental impact assessment

Fig. 4 shows the normalized potential environmental impacts of the conventional alkali-catalyzed process with FFA pre-treatment (AICP). Marine aquatic ecotoxicity is the most significant impact category followed by abiotic resources depletion.

In the AICP process alternative, steam use is the major contributor to almost all the PEI categories. Methanol recovery in both the pre-treatment step and in the downstream transesterification reaction and FAME purification in the multi-stage distillation unit are the most energy intensive process units. Therefore, these are critical aspects to consider from an environmental standpoint.

Fig. 5 shows the normalized PEI categories for AcCP. Similarly to the alkaline catalyzed process, marine aquatic ecotoxicity is the most significant impact category followed by abiotic resources depletion. The use of low pressure steam, mainly in the methanol recovery distillation column, has a significant contribution to all the PEI categories.

Fig. 6 shows the normalized PEIs associated with the ScMP. In this process alternative depletion of abiotic resources is the most significant impact category, mainly due to methanol use. Marine aquatic ecotoxicity is the second largest impact category, mainly due to steam use.

Comparing the three process design alternatives, methanol use has a significant contribution to abiotic resources depletion since it is produced in a refinery based on fossil oil. The remaining resources needed for these processes, along with the waste treatment operations, is of secondary importance in terms of their contribution to the PEIs.

Fig. 7 shows the comparison among the normalized PEI categories of the three process design alternatives. Marine aquatic

**Table 1**  
Kinetic parameters of Arrhenius equation used in the simulations of supercritical methanol reaction.

Kinetic parameter	Unit	Value
Activation energy	kJ/kmol	38 482
Heat of reaction	kJ/s	0.032
Reaction kinetics constant	s <sup>-1</sup>	7 × 10 <sup>-3</sup>

ecotoxicity and abiotic resources depletion are the two most significant PEI categories for the three process alternatives. The PEI categories with a relatively low importance include: eutrophication, ozone layer depletion, human toxicity, fresh water aquatic ecotoxicity and photochemical oxidation.

The AcCP represents, relatively to the AICP, an increase of 62% in abiotic resources depletion, 126% in acidification (mainly due to the use of a large amount of sulfuric acid and a low pressure steam), 67% in global warming and 33% in marine aquatic ecotoxicity.

For the acid-catalyzed transesterification reaction, the use of a higher methanol to oil molar ratio, of 50:1, contributes to the higher energy requirements associated with methanol recovery. This is the main reason for the differences observed between the contributions of the three process alternatives to the PEIs. Also, this aspect of the acid-catalyzed process far outweighs the PEI associated with the FFA pre-treatment in the alkali-catalyzed process alternative.

**Table 2**  
Material and energy inventory data for the three process alternatives.

Inventory	AICP	AcCP	ScMP
<b>Products</b>			
Biodiesel (kg)	1000.00	1000.00	1000.00
Glycerol (kg)	106.37	114.80	105.62
<b>Feed</b>			
Waste vegetable oil (kg)	1042.25	1035.32	995.51
Methanol (kg)	126.80	214.45	110.09
NaOH (kg)	9.80	—	—
H <sub>2</sub> SO <sub>4</sub> (kg)	0.15	149.09	—
H <sub>3</sub> PO <sub>4</sub> (kg)	7.95	—	—
CaO (kg)	0.10	85.24	—
Propane (kg)	—	—	0.02
Glycerol (kg)	0.05	—	—
High pressure steam (300 °C) (kg)	—	—	196.55
Medium pressure steam (250 °C) (kg)	935.30	933.24	239.53
Low pressure steam (100 °C) (kg)	1750.81	3366.96	—
Electricity (kWh)	1.01	0.95	4.01
Water (Process) (kg)	48.65	39.44	—
Water (Cooling) (kg)	3143	5031	510
<b>Waste</b>			
Salts (kg) (to landfill)	16.00	205.71	—
Hazardous liquid waste (kg) (to wastewater treatment)	37.92	172.21	—

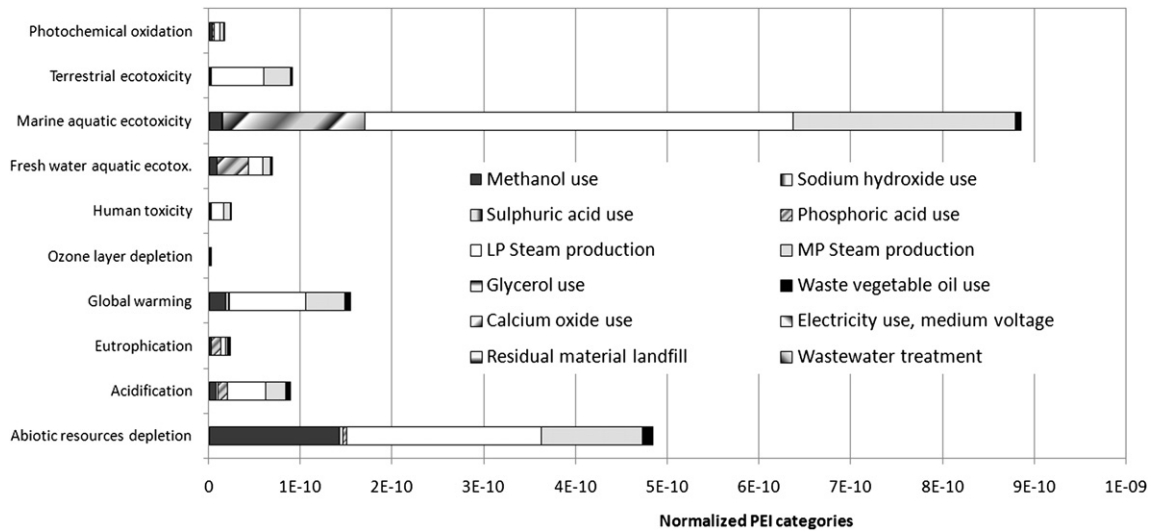


Fig. 4. Contribution of resources use and waste treatment to the normalized PEI categories of the alkali-catalyzed process with FFA pre-treatment.

The ScMP is the one with the least contribution to the PEI which makes it the most environmentally favorable process design alternative for biodiesel production. In comparison with the AICP, the ScMP reduces abiotic resources depletion by 313%, acidification by 754%, global warming by 496% and marine aquatic ecotoxicity by 793%. It should be noted that the intended conclusions can be drawn without the need of a total PEI index, avoiding the inherent subjectivity of a weighting procedure.

The overall decrease in steam consumption associated with the ScMP in comparison with AICP and AcCP, is of fundamental importance to the observed differences. Also, the downstream operations associated with the supercritical methanol process are simpler than for the other process alternatives. This is explained because no catalyst is used, methanol is recovered just by decreasing pressure in a flash evaporator and glycerol is separated from FAME and further purified in simple flash evaporators for both product streams with substantial energy savings. Noteworthy is the

comparison of these results with the outcome of the study undertaken by [Kiwjaroun et al. \(2009\)](#) in which the supercritical methanol process showed higher PEI than the conventional alkali-catalyzed process with an FFA pre-treatment, due to the required higher amount of methanol to perform the supercritical transesterification reaction and subsequently the energy expenditure in methanol recovery. The use of a co-solvent in the ScMP still have the advantage of avoiding waste production, but at lower temperature and methanol to oil molar ratios reaction conditions, enabling a better environmental performance relatively to the conventional AICP. Additionally, [Kiwjaroun et al. \(2009\)](#) used an energy intensive multi-stage distillation process to separate glycerol from biodiesel in the supercritical methanol process (instead for example of using a simpler flash unit or a settler unit), which can be explained since it may be the only way of obtaining the desired high purity requirement for FAME (99.54%), although a lower purity was obtained in the alkali-catalyzed process (99.10%).

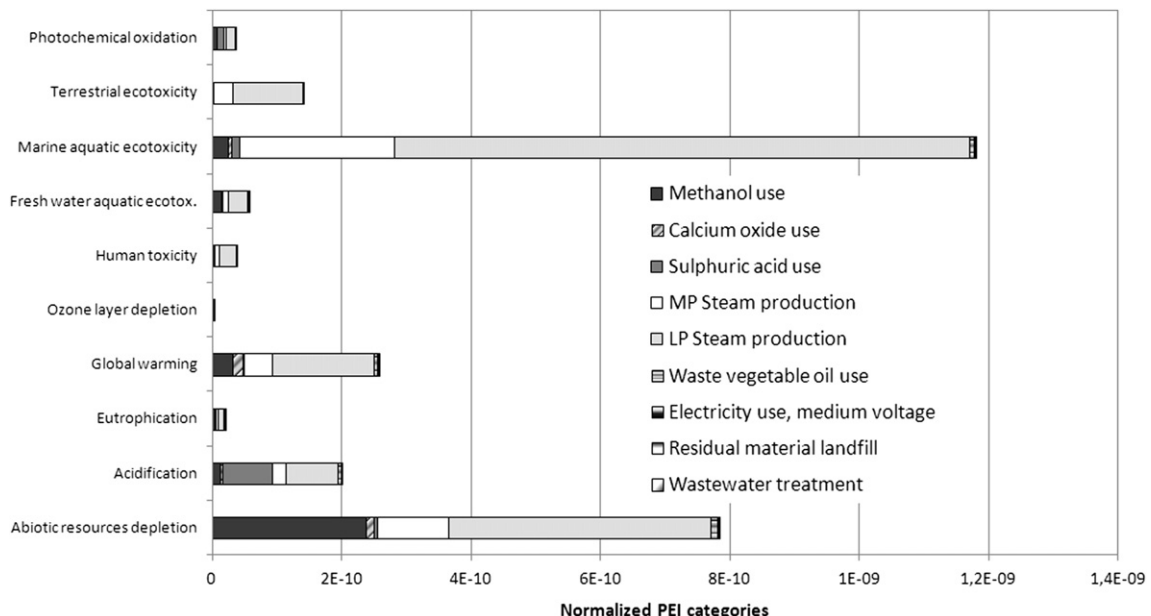


Fig. 5. Contribution of resources use and waste treatment to the normalized PEI categories of the acid-catalyzed process.

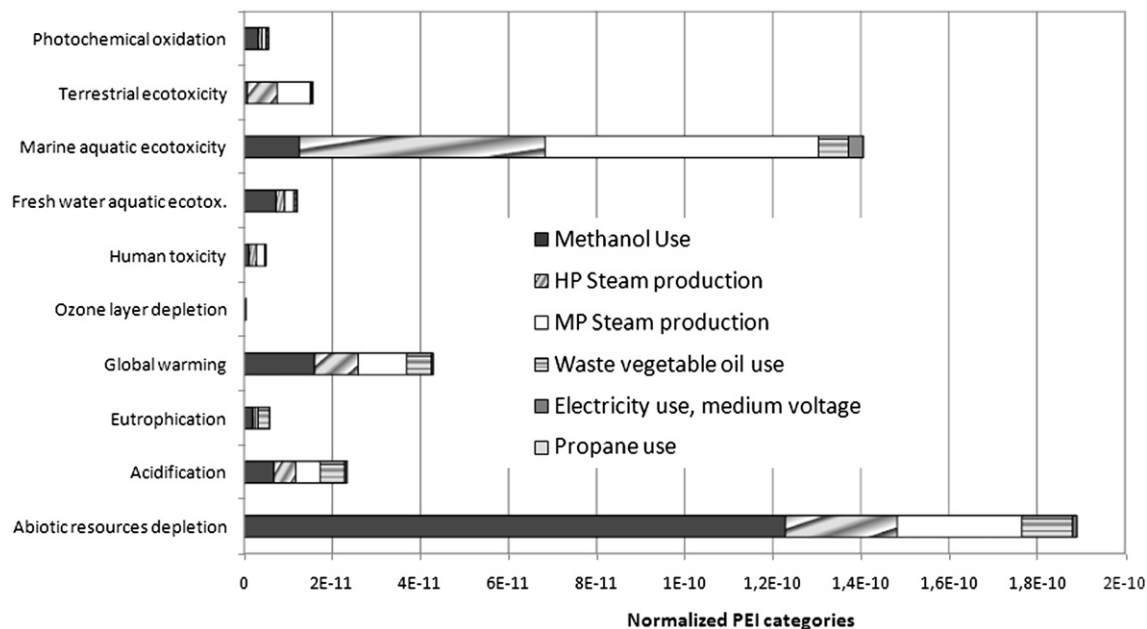


Fig. 6. Contribution of resources use to the normalized PEI categories of the supercritical methanol process using propane as co-solvent.

A larger scale production may make economically viable the further recovery and purification of methanol and unconverted oil waste streams in both the alkali and acid-catalyzed processes. However in this study the impacts associated with waste management and treatment operations are of secondary importance. Also, any possible savings of methanol and unconverted oil from these waste streams are not expected to produce any significant change in the comparison results of the three process alternatives.

In the present study it is assumed that steam is produced using fossil fuels (natural gas and heavy fuel oil). Since steam use has a major contribution to the PEI of the three process design alternatives, it would be interesting to evaluate as a future work the potential environmental benefits of using by-product glycerol as fuel, at least in order to reduce depletion of abiotic resources. This assessment is especially relevant because of the expected increase of the worldwide production of biodiesel, which should contribute

to an oversupply of glycerol which will decrease its market value or even becoming a waste product.

Other process alternatives may be environmentally and economically interesting, such as the application of a hydrodynamic cavitation reactor in the alkali-catalyzed process in order to minimize mass transfer resistance during the transesterification reaction. It is claimed that this alternative, with a much lower reaction time, can lead to less saponification or emulsification, allowing the use a variety of feedstocks with broader range of free fatty acid concentrations, avoiding the FFA pre-treatment (Mancosky et al., 2007). Moreover, the use of a co-solvent in the alkali-catalyzed process, such as tetrahydrofuran or methyl tertiary butyl ether, also minimizes the reaction mass transfer resistance decreasing the reaction time to 7 min and enabling the conversion of FFA into methyl ester (Boocock et al., 1998). As future work, these process alternatives should be further assessed and compared with the results of the present study.

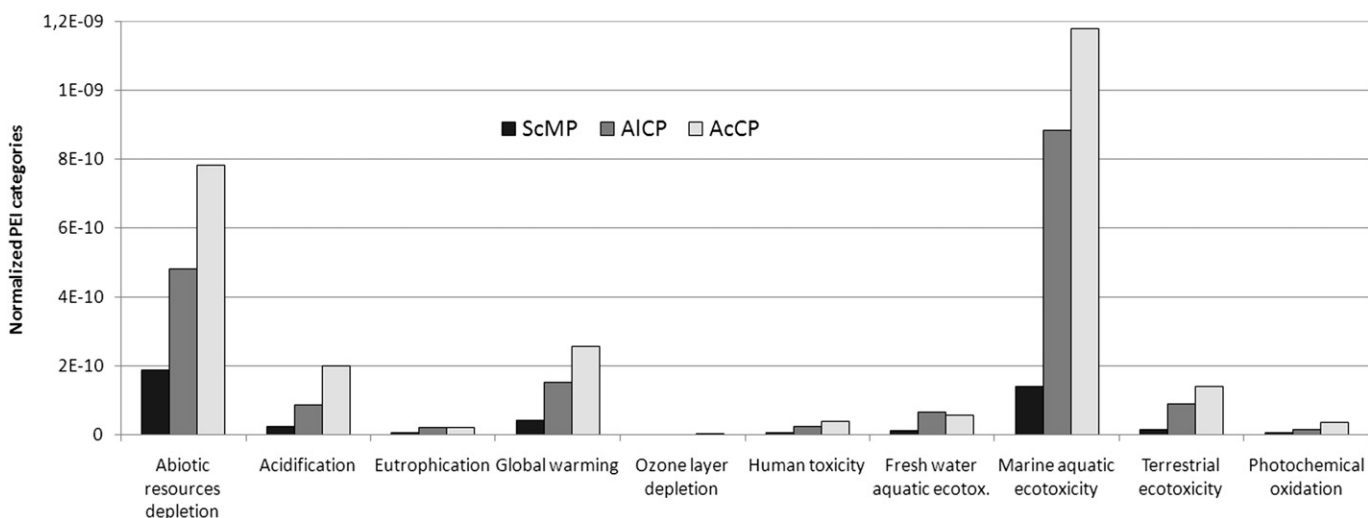


Fig. 7. Comparison of normalized PEI categories for the three process design alternatives: supercritical methanol process using propane as co-solvent (ScMP), alkali-catalyzed process with FFA pre-treatment (AICP) and acid-catalyzed process (AcCP).



## 7. Conclusions

For the three process alternatives analyzed, marine aquatic ecotoxicity and depletion of abiotic resources are the most relevant PEI categories. Results show generally higher PEI for the acid-catalyzed process, which is particularly pollutant due to the high energy requirements of its methanol recovery unit.

The supercritical methanol process, using propane as co-solvent, is among the three process alternatives the most environmentally favorable, even though methanol and steam usage has an important contribution to its PEI. Although the supercritical methanol process is highly energy intensive, the downstream operations of methanol recovery and products purification are much simpler, enabling a decrease in the overall energy consumption by comparison to the other process alternatives.

Steam production is also one of the major contributors to the PEI's of both the alkali and acid-catalyzed processes. Therefore, any effort to reduce the steam requirements of the three process alternatives is seen as a good opportunity for their improvement, in particular to decrease their environmental burdens.

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