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Designing Eco-Efficient Biodiesel Production Processes from Waste Vegetable Oils

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Abstract

In this work the conventional alkali-catalyzed transesterification process for biodiesel production from waste vegetable oils is studied considering the two process alternatives normally used industrially: with and without free fatty acids (FFA) pre-treatment. Simulation models of these process alternatives are developed using the chemical process simulator ASPEN Plus® and their potential environmental impacts (PEIs) and economic potentials are determined and compared. Results show that the contribution to total PEIs of the process alternative with the FFA pre-treatment is 25% higher than the alternative without pre-treatment. Concerning the economic potential the process alternative with the FFA pre-treatment is greater showing a net present value of about 1.8 times higher than the alternative without the FFA pre-treatment. The comparison using plant data will be performed as future work.

Keywords: Biodiesel, Waste vegetable oil, Waste Reduction (WAR) algorithm, Alkali-catalyzed process, Free Fatty Acids Pre-treatment.

1. Introduction

Biodiesel is currently the most important alternative diesel fuel in EU, contributing to reduce the external dependence on fossil fuels and simultaneously the environmental impacts of the transportation sector, since it emits substantially lower quantities of most of the regulated pollutants compared to mineral diesel. However, biodiesel industry has some significant difficulties. In particular, feedstock selection can have a profound impact on the production process but also on food prices when food crops such as palm oil are diverted to energy. Additionally, the conversion of forests and other critical habitats for biodiesel feedstocks cultivation have the associated damage on biodiversity, loss of soil quality or land fertility, emissions from carbon stock change and land competition, among others. For these and other reasons the use of waste vegetable oils can be an effective way of minimizing some of the negative impacts associated with biodiesel production and at the same time of using a hard to treat residue.

In which concerns biodiesel production the transesterification reaction is very sensitive to the feedstock purity that directly affect the reaction performance.

Contrarily to refined vegetable oils, waste oils and animal fats usually have a lot of impurities, such as FFA and water that negatively affect the reaction yield, reducing the reaction rate by several orders of magnitude, even in small amounts (Canakci, 2007). For this reason some pre-treatment operations are conducted, such as the esterification of FFA to biodiesel (Aranda *et al*., 2008).

2. Process Design and Simulation

In order to gather the process data needed for the inventory analysis, models of the two biodiesel production process alternatives were developed and simulated using ASPEN Plus®. 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*., 2003ab; Kiwjaroun *et al*., 2009). Some thermodynamic properties not available in the component library of the process simulator were estimated by providing the process simulator with the component molecular structure. Additionally, some components not directly available in the process simulator were represented by similar components chosen from the available components database. The triglycerides are represented by triolein ($C_{57}H_{104}O_6$), the FFA present in the waste vegetable oil are represented by oleic acid ($C_{18}H_{34}O_2$), and FAME are represented by oleic acid methyl ester ($C_{19}H_{36}O_2$). For the two process alternatives, product purities were defined to be 96.5% (w/w) for biodiesel, according to the European biodiesel standard (EN 14214) specification for esters content, and 91.0% (w/w) for crude glycerol. Vacuum operation for methanol recovery and products purification was applied to keep the temperature at suitably low levels because of the FAME and glycerol thermal decomposition temperatures (523K for FAME and 423.15K for glycerol).

Figure 1 shows a model, obtained using the process simulator ASPEN Plus®, of the alkali-catalyzed process for biodiesel production from waste vegetable oils, with and without the FFA pre-treatment. The pre-treatment steps are indicated inside the dashed line. Concerning the biodiesel production with the FFA pre-treatment, a waste vegetable oil stream flowrate of 428.50 kg/h (stream 104) is fed to an esterification reactor (R-100) where the FFA are converted to methyl esters. It is assumed a 6% (w/w) of FFA content in the waste vegetable oil (Zhang *et al*., 2003a). It is used a fresh methanol stream flowrate of 9.50kg/h (stream 101) mixed together with a stream of recycled methanol (110) and the sulfuric acid catalyst (stream 103) as reactants to perform the esterification. The esterification reaction is performed at a temperature of 343.15K, a pressure of 405.3kPa, a methanol to oil molar ratio of 6:1 and with 5% (w/w) of sulfuric acid catalyst in methanol (Lepper and Friesenhagen, 1986; Zhang *et al.*, 2003a; Ma and Hanna, 1999). It is assumed a 95% conversion of FFA's in methyl esters (Zhang *et al*., 2003a).The esterification products are sent to a glycerol washing column (X-100) to wash out sulfuric acid and water.

The pretreated oil stream (107) resulting from the esterification process is 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 (Canacki, 2007; Freedman *et al*., 1984, Ma and Hanna, 1999).

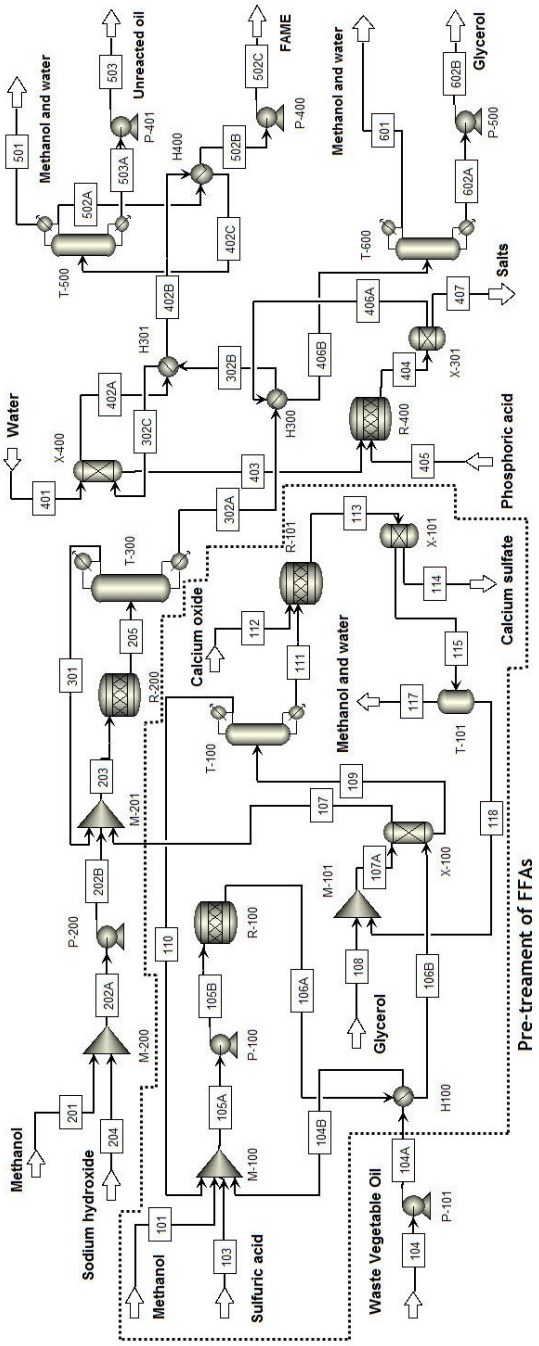

Figure 1 - Alkali-catalyzed process with and without FFA pre-treatment steps, indicated by the dashed line

A fresh methanol stream flowrate of 42.98 kg/h is mixed with anhydrous sodium hydroxide as catalyst and fed to the reactor. Transesterification takes place at 333.15K and 405.3kPa and reaches a 95% conversion of oil to FAME, after 2h (Zhang *et al*., 2003a; Kiwjaroun *et al*., 2009). The transesterification reactor products are fed to a vacuum distillation column (T-300), where 94% of methanol is recovered through four theoretical stages. 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) in order to separate FAME from water and methanol. FAME is obtained in the bottom stream (502A) of the column overhead condenser, with a mass flowrate of 411.13kg/h. The washing column bottom stream containing glycerol (403) is then fed to a neutralization reactor (R-400) in order to remove the catalyst using phosphoric acid. The resulting salts (Na_3PO_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 at a flowrate of 43.73kg/h.

Concerning the biodiesel production without the FFA pre-treatment that is represented outside the dashed line in Figure 1, the waste vegetable oil stream (104) is mixed with the unreacted oil stream (503), obtained from the bottom stream of distillation column T-500, at a flowrate of 428.5kg/h and is sent to the transesterification reactor. A 6:1 molar ratio of methanol to oil is used with 1% (w/w) of sodium hydroxide. It is also assumed a 6% (w/w) of FFA content in the waste vegetable oil. The transesterification reaction occurs at 333.15K and 405.3kPa and reaches a 78% conversion of oil to FAME, after 2 h, due to the presence of FFA's (Yan *et al*., 2008). The next steps of the process are quite similar to the process alternative with the FFA pre-treatment. In the vacuum distillation column T-500, the FAME is obtained in the bottom stream (502A) of the column overhead condenser, with a mass flowrate of 330.22kg/h.

3. Potential Environmental Impacts

The Waste Reduction algorithm (WAR) developed by U.S. EPA algorithm was applied in order to evaluate the potential environmental impacts (PEIs) of the two process alternatives. It enables the assessment of the streams' PEIs crossing the system boundaries and uses a database for more than 1600 chemicals PEIs (Smith *et al*., 2004). The mass flowrate of each component in the process streams is multiplied by its chemical potency to determine its contribution to the PEIs.

The WAR algorithm database values include local impact categories such as human toxicity by dermal/inhalation and ingestion routes (HTTPi and HTTPe), terrestrial toxicity and aquatic toxicity (TTP and ATP). Regional impact categories include photo-chemical oxidation and acidification (PCOP and AP), while global categories include ozone depletion and global warming (ODP and

GWP). Each of these categories has scores that have been normalized within the category, while weighting factors are applied between categories. In this work all of the weighting factors are set to 1.0 (equal to each other) and it is assumed that the impacts from the various categories are additive.
Figure 2 shows the PEIs of the alkali-catalyzed process of biodiesel production from waste vegetable oils comparing both process alternatives with and without the FFA pre-treatment. As shown in Figure 2, the process alternative without the FFA pre-treatment has a lower contribution to the PEIs in all the impact categories. Also, the total PEI of this process alternative is 20% lower PEI than the alkali-catalyzed process with FFA pre-treatment.

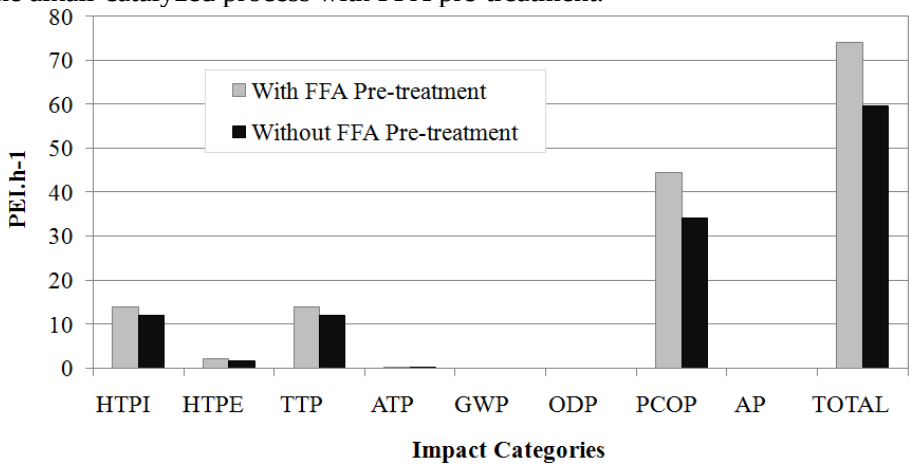

Figure 2 – PEIs of the alkali-catalyzed process of biodiesel production from waste vegetable oils with and without the FFA pre-treatment

4. Economic Analysis

The economic evaluation of both process alternatives is also performed to provide an opportunity to identify the potential relationships between economic potentials and PEIs (Mata *et al.*, 2003). Table 1 shows the economic evaluation of both alkali-catalyzed process alternatives for biodiesel production from waste vegetable oils, with and without the FFA pre-treatment, where the economic indicators determined are the net present value (NPV), the internal rate of return (IRR) and the payback period, calculated for a window of three years.

Table 1. Initial investment, Net present value (NPV), internal rate of return (IRR) and payback period comparing both process alternatives, with and without the FFA pre-treatment

Economic indicators	**With FFA pre-treatment**	**Without FFA pre-treatment**
Investment (EUR)	410.366	274.768
NPV (EUR)	906.460	489.556
IRR (%)	102,9	84,2
Payback period (years)	1,15	1,32

As shown in Table 1 the process alternative with the FFA pre-treatment is more advantageous economically. Although its higher investment it has a greater

NPV and IRR and a shorter payback period by comparison with the alternative without the FFA pretreatment. This is because the FFA pre-treatment improves the conversion of triglycerides and fatty acids to biodiesel.

5. Conclusions

This work compares the two alternatives normally used industrially for the alkali-catalyzed transesterification process: with and without a pre-treatment step of FFA. Models of these process alternatives are developed using the process simulator ASPEN Plus® and their PEIs are evaluated WAR algorithm. The economic potential of both process alternatives are also evaluated showing that there are environmental and economic trade-offs between the two designs. The process alternative with the FFA pre-treatment has a higher contribution to the PEIs but is more advantageous economically than the process alternative without the FFA pre-treatment. The comparison using plant data will also be performed as future developments of this work.

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