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Exergy Analysis for Third Generation Biofuel Production from Microalgae Biomass

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In the search for renewable energy, third generation biofuels have become an innovative alternative that offers a wide variety of exceptional benefits. A major advantage of third generation fuels is that the raw materials used as a source does not compete with food sources also have a high percentage of yields per unit area. Nowadays the production of biodiesel from microalgae is an option that has attracted strong interest of the scientific community and should be evaluated to determine the technical, technological, economic and environmental sustainability of the process.
Exergy analysis is a useful tool for measure the quantity and quality of the energy sources and analyze the process sustainability previously mentioned, besides, exergy analysis has been widely used in the design, simulation and the global evaluation and improvement of the processes. The relationship between exergy, energy and environment can recognize that the exergy is closely related to sustainable development. This methodology requires analyzing material and energy flows of each stage of the production process. In this study exergy analysis was applied on two scenarios taking a production capacity of 100,000 t/y of biodiesel from microalgae biomass. *Chlorella vulgaris* (*Chlorella sp)* was used as reference algae. This algae has been widely studied and their characteristics are well known, also one of the algae that have a higher percentage of lipids. In this work a basic process for biodiesel production is showed, comprising the following steps: transesterification, separation and washing the biodiesel. Thermodynamic variables as entropy, enthalpy, Gibbs free energy were determined for all process steps and exergetic losses using the software ASPEN-PLUS®. Finally the exergetic efficiency was calculated for the overall process. The results confirm the potential of third generation biofuels microalgae as an energy source.

1. Introduction

The high cost of oil, the trend to continue increasing or remaining at high levels and the depletion of reserves has affected global energy security. The need for industrialized countries and emerging economies (China, India, etc.) no matter the fuel producers, in addition, concern over the increase in average temperature (global warming) from the planet due to the imbalance of natural processes such as carbon cycle and global warming have caused a great interest in promoting the search for renewable energy

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sources for breaking world energy dependence that exists with fossil fuels. One possible component to the solution of this problem and has taken a lot of strength in recent years is biofuel. The third-generation biofuels are emerging as a promising alternative to using microalgae biomass avoid making use of raw materials that come from food sources.

Exergy analysis is a thermodynamic analysis technique based on the second law of thermodynamics which provides an alternative to asses, analyze and compare systems. Furthermore, exergy analysis yields efficiencies which provide a true measure of how nearly actual performance approaches the ideal, and indentifies existing irreversibilities. Consequently, exergy analysis can assist in improving and optimizing designs as proposed Dincer and Rosen (2007) in their book. In the last few years, authors like Rosen and Horazak (1995), Rosen and Dincer (2003, 2004) have examined exergy analysis methodologies and applied them to industrial system, Dincer and Rosen (2002) and Rosen et al. (2004) for energy system and Crane et al. (1992), Rosen and Dincer (1999) for environmental impact assessment.

1.1.1 Exergy analysis- general relations

For a general steady state, steady-flow process, the four balance equations (mass, energy, entropy and exergy) are applied to find the work and heat interactions, the rate of exergy decrease, the rate of irreversibility, the energy and exergy efficiencies as presented in the work of Dincer et al. (2004) and Balkan et al. (2005) and others.

The total exergy flow of a system Ex can be divided into four components in absence of others forces, namely (i) physical $\dot{E}x^{PH}$, (ii) kinetic exergy $\dot{E}x^{KN}$, (iii) potential exergy $\dot{E}x^{PT}$, and (iv) chemical exergy $\dot{E}x^{CH}$:

$$\dot{E}x_{flow} = \dot{E}x^{PH} + \dot{E}x^{KN} + \dot{E}x^{PT} + \dot{E}x^{CH} \tag{1}$$

The general balance can be written as follows

$$\sum \dot{E}x_{in} - \sum \dot{E}x_{out} = \sum \dot{E}x_{dest} \tag{2}$$

or

$$\dot{E}x_{heat-}\dot{E}x_{work} + \dot{E}x_{mass,in} - \dot{E}x_{mass,out} = \dot{E}x_{dest} \tag{3}$$

The exergy flow physic can be a calculate as follows

$$\dot{E}x_{PH,flow} = (H - H_0) - T_0(S - S_0) \tag{4}$$

And the exergy flow chemical:

$$\dot{E}x_{CH} = \sum_i (\mu_{io} - \mu_{ioo}) N_i \tag{5}$$

or

$$\dot{E}x_{CH} = \Delta G_f + \sum_i N_i \, ex_i \tag{6}$$

Where ΔG_f signifies the standard Gibbs free energy of formation of the substance [J/kg]; ex_i; chemical exergy of the ith pure element of the substance [J/kg]; N_i, molar fraction of the i^{th} pure element of the compound; and μ_i, chemical potential of substance i for the system. Kafarov et.al (2009).

2. Methodology

2.1 Application for biodiesel production

The process was simulated by software Aspen Plus in comprising the following step: transesterification, methanol recovery, water washing and fame purification. Based on the data reported by Petkov and García (2007) for *Chlorella sp*. algae composition was selected and normalized to include those four fatty acids with the highest compositions. In this way, triglycerides 16:0, 16:2, 18:2, and 18:3 were used. In this work it was assumed that oil free fatty acid (FFA) content is negligible. Thus, a basic catalyst transesterification is selected because it performs faster and has less corrosion issues that the acid catalyzed alternative. NaOH have been selected as the basic catalyst. A small amount, i.e. 1% catalyst/oil mass ratio was used. Short chain alcohols (C_1-C_5) have been studied for the transesterification reaction. Despite of its safety issues, methanol is preferred on industrial scale because of its high reactivity and its low cost. According to the stoichiometry, a mole of triglyceride (MAO) reacts with 3 moles of alcohol (methanol) to produce 3 moles of fatty acid methyl esters (BD) and a mole of glycerol. To favor the reaction towards the formation of products, an excess of methanol is used. In this way, a 6:1 methanol/oil mol ratio was used.

First, the methanol and the NaOH were pumped and mixed inside a tank to dissolve the catalyst. Then, the mixture was pre-heated until 60 °C in order to avoid formation of methanol vapors. In order to obtain biodiesel (BD) from microalgae oil (MAO) a transesterification reaction was performed in a continuous stirred tank reactor. In this reactor, 97.7 % of the triglycerides which enters were transformed into BD and glycerol. A small amount of unreacted oil, catalyst, and alcohol was present in the BD and glycerol products. In order to remove the glycerol rich phase a decanter was used. Both BD rich phase and glycerol rich phase contains basic catalyst that must be neutralized with an acid (H_2SO_4 in stoichiometric proportion) to avoid the formation of soaps and emulsion (Zhang et al., 2003; Van Gerpen et al., 2004). Glycerol phase then was sent to a flash separator where most of the methanol was removed and a 77.5 % (mass basis) stream of glycerol was obtained. The BD received after neutralization was sent to a distillation tower in order to remove methanol. A ten ideal stage with total condenser, kettle reboiler, and a 2.5 reflux ratio were used to remove approximately 90% of the methanol in the BD stream. After glycerol and methanol removal the BD stream was sent to washing stage in order to remove impurities. A decanter was used to separate water from BD. Waste water was sent to water treatment in order to reduce environmental impacts and for further reuse in the process. Finally, BD stream is sent to a distillation tower in order to remove excess water. Three ideal stages with total condenser, kettle reboiler, and a 1.5 reflux ratio were used to obtain a BD stream according to ASTM standards. However, since the initial composition of the microalgae oil has a high proportion of TG 18:3 (linolenic acid), the BD obtained also possesses a high percentage of this component. According to the European standard pr EN 14103d a maximum of 12% of linolenic acid methyl ester must be produced. In this case a content of 25.40% for this fatty acid methyl esters was obtained. Despite this drawback, the BD obtained from the microalgae satisfies most of the ASTM specifications. Finally, 91,252 tonnes per year of BD were obtained from 90,807 tonnes per year of MAO and 20,800 tonnes per year of methanol.

2.2 ExergyAnalysis to biodiesel production

The global mass balance of all currents of the process was performed, and the thermodynamic properties needed to develop the exergy balance were obtained. Each unit operation was made independently balance. Exergy was determined for each compound, mixture and utilities. As dead state conditions temperature 25 °C and pressure 1 atm were taken. The chemical exergy of the heating steam flows was taken as 528 kJ / kg (Szargut et al., 1988) and the chemical availability of biodiesel, oil, glycerol and methanol of the work Ozilgen and Sorguven (2010).

3. Results and Discussion

In Figure 1 shows the simulation developed in the Aspen Plus ® software for the process described above.

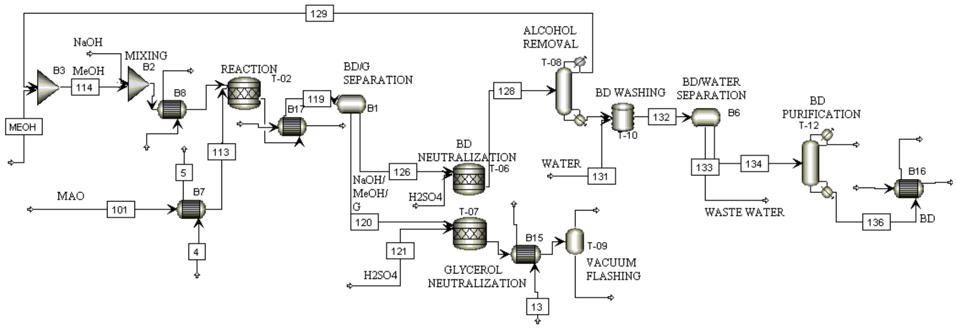

Figure 1: Biodiesel production for microalgae biomass

Physical and chemical exergy of each stream of the process were calculated with the help of the thermodynamic properties calculated by Aspen Plus®. Figure 2 shows a simplified mass and exergy flow diagram for the process.

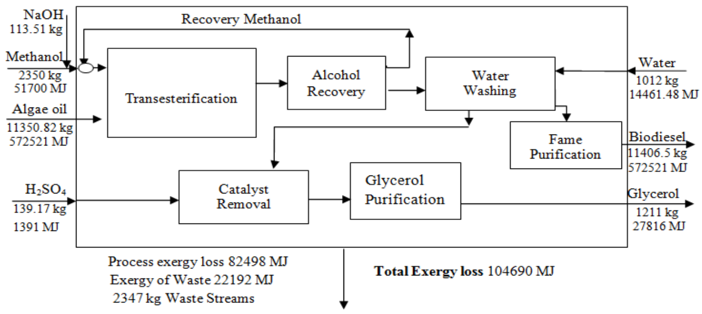

Figure 2: Simplified mass and exergy flow diagram

The global mass and exergy balance of biodiesel production process shows that the major exergy inputs are the microalgae oil and methanol, and the major exergy outputs are biodiesel. It present output waste streams of 2,347 kg with an exergy of 22,192 MJ. The amount of exergy input is not converted into useful exergy in the process was called "exergy loss." The exergy losses can be calculated with an exergy balance environmental conditions, where it was only necessary to know the composition of inflows and the main products as proposed by Ayres et al. (1998). In the process presents an exergy loss of 82 498 MJ which along with the exergy of waste streams in a total of 104,690 MJ of exergy losses.

From exergy viewpoints, a gauge of how effectively the input is converted to the product is the ratio of product to input. That is, the exergy efficiency can be written as one minus the ratio between the exergy loss of a process and the total exergy input to accomplish that process as proposed by Dincer and Rosen (2007). The exergetic efficiency calculated is 79 %. The exergy losses can be reduced increasing the number of recycles in the process. In this plant only the methanol stream is recycled, besides, some waste streams that present composition can be used as fertilizer, which would provide other value-added product decreasing exergy losses for waste streams. In addition energy integration can reduce the amount of exergy of the utilities of the process.

4. Conclusions

It was shown that exergy analysis is a powerful tool for efficiency evaluation of third generation biofuels production from microalgae biomass.

The results show an exergy efficiency of 79 %, therefore is necessary increase the number of recycles for the process. Additionally, it is possible to extract value-added products such as fertilizers from the process waste streams; it may be helpful to improve the exergy efficiency.

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