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Exergy Evaluation of Biodiesel Production Process from Euphorbia Lathyris

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At present, studies on the various sources of biodiesel are quite noticeable, due to the reduction of emissions of air pollutants. Research on the advantages and disadvantages of biodiesel establish that higher cetane number, improves the combustion process allowing increasing the compression ratio of the engine. Less sulfur content is safer to store and transport. However, when compared to conventional fuels, it presents costlier production process which also depends on the type of selected raw material.
On this basis, research has been conducted to find the best raw materials and suitable for the production of biodiesel from non-edible sources. In this regard spurge (Euphorbia lathyris) is considered here which is characterized by being a plant of easy culture, can be grown in different environments and is not source human food. Therefore, it is a promising feedstock for biofuels industry, specifically for the production of biodiesel.
The viability of the process was evaluated with exergy analysis, a useful tool to identify the losses energy using the first and second law of the thermodynamics. This tool also evaluates and proposes improvements for emerging technologies. Simulation of biodiesel production process using E. lathyris oil through transesterification with alkaline catalysis in Aspen Plus^{TM} software was performed. Comparing E. lathyris with other raw materials was used for the same purpose. It also have a low free fatty acids (FFA) (0.2 %) content that represents a great benefit in the production of biodiesel because of the esterification process is not necessary. This advantage is reflected in a cost savings due to the reduction of equipment used in the process. The enthalpy, entropy and Gibbs free energy was calculated with help of the software. Finally, for all streams the chemical and physical exergy was calculated and later the efficiency exergetic of the process is estimated. The exergy efficiency of the process (57 %) confirms the potential of this raw material for production of Biodiesel. However more improvements are necessary to increase the energy production of the process.

1. Introduction

Currently, the fuel demand for global transportation has increased significantly leading to a greater global energy demand and consumption. The transport market for vehicles is based on petroleum i.e. diesel and gasoline. The continued use of fossil-derived fuels is recognized as unsustainable due to the exhaustion of supplies and their contribution to environmental pollution. This kind of fuels has to be replaced with clean and renewable energy. In response to this issue, environmental policies worldwide have favored the increase in research, development and the use of biofuels, mainly those that can replace fossil fuels used in transportation. The renewable fuels from biomass, such as biodiesel and bioethanol can replace partial and / or total petroleum fuels in internal combustion engines (Vlysidis et al., 2011). Today the consumption of petroleum fuels is unsustainable, thus the development of renewable fuels for environmental and economic sustainability is unavoidable (Peralta et al., 2013). The use of biodiesel in diesel is a reality in many countries today. In Brazil all diesel must contain five percent biodiesel blend called B5 (França et al., 2011).
Biodiesel is an alternative diesel fuel from vegetable oils; produced by the transesterification reaction with an alcohol of short chain. The main advantages over diesel are that it is biodegradable, low toxicity, produces fewer emissions and is more environmentally friendly. It has a higher flash point (safer to handle and store) and is a

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better lubricant. It has similar properties compared to conventional diesel and can be used in pure form or as a diesel-biodiesel blends. However, it is still more expensive than conventional diesel (Kastritis et al., 2012). The main drawback of the process of biodiesel compared to petroleum diesel is its higher production cost due to the high prices of vegetable oil (Rios et al., 2012).Therefore, a new alternatives are sought to reduce these costs.
In the search for new raw materials for the production of biodiesel, the Tartago (Euphorbia Lathirys) is a promising alternative. It is characterized as an easy to grow plant can also be grown in different environments and is not suitable for human consumption. Productions of biodiesel from Tartago also have advantages such as (Wang et al., 2011) the seeds contain 48 % oil that could be used for industrial purposes (Ayerbe et al., 1984). Wang et al. (2011) reported that biodiesel oil from E. lathyris is considered of good quality and can substitute oil seeds of Jatropha curcas L. Besides, the cakes resulting from the process can be used for production of biofertilizers or thermal energy (Zapata et al., 2012). In this study the biodiesel production from E Euphorbia Lathirys process was modeled and then simulated with the help of specialized software, then the viability of the process was evaluated using exergy analysis

1.1 Exergy Analysis

Energy analysis includes balances based on the first law of thermodynamics, and calculation of energy efficiencies for the steps studied. However, an energy balance neither offers information related with the energy degradation nor quantifies the usefulness or quality of the mass and energy streams of the system evaluated. Exergy analysis is presented as an alternative which overcomes the limitations of the first law of thermodynamics. Exergy analysis can be used as a useful tool for evaluating the power or the available work. The energy of a process is not destroyed, it transformed in other forms become less suitable for feeding and driving processes. Therefore, the energy must be evaluated in quantity and quality. The concept of exergy investigates the ability to perform useful work in a natural setting. Technically, the exergy is defined using the principles of thermodynamics as the maximum amount of work that can be produced by a system or a flow of matter or energy, as reaches equilibrium with reference environment. The exergy consumed or destroyed is due to the irreversibility for any processes (Raei, 2011). Regular use of exergy analysis starts in the second half of this century. For this reason, the exergy analysis is a useful tool to identify the type, location and quantity of material thermal losses and chemical and thermal processes (Modarresi et al., 2011).
In the last decade, the biodiesel production research has focused on the optimization of the operating conditions and the choice of the most appropriate raw material. At present, improving the energy efficiency of the process and the reduced energy inefficiencies of different components captures the interest of researchers. The Exergy Analysis combines the second with first law of thermodynamics to quantify the thermodynamic inefficiencies in the process, through an analysis of exergy losses and destruction of useful work that takes place during the process. Exergy analysis reveals two aspects: the irreversibility in a system component and exergetic efficiency, which in turn shows how effectively we have used the exergy resources provided to a component (Blanco-Marigorta et al., 2013).
Exergy is defined as the maximum amount of work that can be obtained as a process is changed reversibly from the given state to a state of equilibrium with the environment, or the maximum work that can be obtained from any amount of energy. However, there are really only irreversible processes. For practical reasons, reference environment defined for the environment. Exergy analysis shows the sites of energy degradation in a process and can help to improve a unitary operation, a technology or a process. The exergy calculation is based on the determination of two thermodynamic state functions, enthalpy and entropy (Tarighaleslami et al., 2011).
The Total exergy of a system mainly consists of four types exergy such as: physical $\dot{Ex}^{PH}$; potential $\dot{Ex}^{PT}$; kinetic $\dot{Ex}^{KN}$ and chemical exergy $\dot{Ex}^{CH}$ and can be calculated using equation 1.

$$\dot{\mathrm{Ex}}_{\mathrm{flow}} = \dot{\mathrm{Ex}}^{\mathrm{PH}} + \dot{\mathrm{Ex}}^{\mathrm{PT}} + \dot{\mathrm{Ex}}^{\mathrm{KN}} + \dot{\mathrm{Ex}}^{\mathrm{CH}} \tag{1}$$

The physical exergy flow can be calculated as follows

$$\dot{\mathrm{Ex}}^{\mathrm{PH}}_{\mathrm{flow}} = (\mathrm{H} - \mathrm{H_O}) - \mathrm{T_O}(\mathrm{S} - \mathrm{S_O}) \tag{2}$$

The first term on the right side of Eq (2) represents the total enthalpy of the system, the second term on the right side represents the total entropy of the system and the term is TO room temperature. Chemical exergy can be determined in two different ways, which are shown in Eq (3) and (4).

$$\dot{\mathrm{Ex}}^{\mathrm{CH}}_{\mathrm{flow}} = \sum\nolimits_{\mathrm{i}} (\mu_{\mathrm{io}} - \mu_{\mathrm{oo}})\mathrm{N_i} \tag{3}$$

$$\dot{Ex}_{flow}^{CH} = \Delta G_f + \sum_i ex_i\, N_i \quad (4)$$

Where ΔG_f signifies the standard Gibbs free energy of formation of the substance; ex_i is the chemical exergy of the ith pure element of the substance; N_i molar fraction of the ith pure element of the compound; and μ_i chemical potential of substance i for the system (Peralta et al., 2010).

2. Methodology

2.1 Feedstock

The development of process simulation mainly involve selecting chemical components used in the process, choosing an appropriate thermodynamic model, determining plant capacity, using suitable operating units and setting up input conditions such as flow rate, temperature, pressure, among others (Technology, 2006).. The composition of free fatty acids (FFA) Tártago are Palmitic acid (C16: 0), Oleic acid (C18: 1), Linoleic acid (C18:2) and Linolenic acid (C18: 3). By comparing the E. lathyris with other raw materials used for the same purpose, it is found that the biodiesel produced from it is characterized by high monounsaturation (82.66 % mass), a low poly-unsaturated (6.49 % mass). It has the appropriate proportion of saturated components (8.78 % mass) and the low percentage of Free Fatty acids (FFA) (0.2 %) (Wang et al., 2011). Therefore, it presents a great promise in the production of biodiesel, i.e., the esterification process is not needed to carry out.

2.2 Biodiesel production process

The production of Biodiesel from tártago (Euphorbia lathyris) was simulated in Aspen ONE^{TM} V 8.4. Which has been widely used for studies related to simulation of existing and emerging technologies for biofuels and co-products production in large scale using several feedstocks (Silva et al., 2011) (Morales et al., 2010) (Santori., 2012). This simulation includes the following steps: transesterification, methanol recovery, washing with water and purification of biodiesel. The thermodynamic package which was used to carry out this simulation was NRTL this model was chosen because of its good representativeness of polar-non polar mixtures. Binary interaction coefficients were calculated by the UNIFAC method. The oil-alcohol ratio was 1: 6 on molar basis.

Streams in the process reactor inlet (B6) were pre-heated to 70° C to prevent the formation of methanol vapors. The transesterification reaction is carried out properly in this stage. Oil reacted with methanol in the presence of basic catalyst (NaOH) to produce methyl esters (biodiesel) and glycerol. This stream was taken to a distillation tower for recovery the methanol which is recycled in the process. The biodiesel stream is contaminated, therefore washed with water to remove the salts of the glycerol of the biodiesel. Then the biodiesel goes to a distillation tower to remove impurities. The glycerol stream obtained in the washing step was sent to a neutralization step. Sulphuric acid (H_2SO_4) is used to neutralize the catalyst. This stream is sent to a separator where the salt formed was separated. Then the glycerol was purified.

3. Results and Discussion

Figure 2 illustrates the simulation of the process described above. The process are divided in three stages, transesterification, washing of the biodiesel and purification of the biodiesel and glycerol. The overall mass balance of the process was performed and the thermodynamic properties were obtained to develop the exergy balance. The exergy was determined for each compound, mixtures and utilities. In some streams the entropy and enthalpy of dead state conditions (25° C and 1 atm.) were calculated, in order to find the exergy required. In Table 1 shows physical, chemical and the total exergy for the main inlet and outlet streams the process. Table 2 presents the results of exergy for utilities of the process. The process has a high amount of utilities because of heating and cooling needs current, in addition to the needs of the distillation towers used for the purification of biodiesel and glycerol.

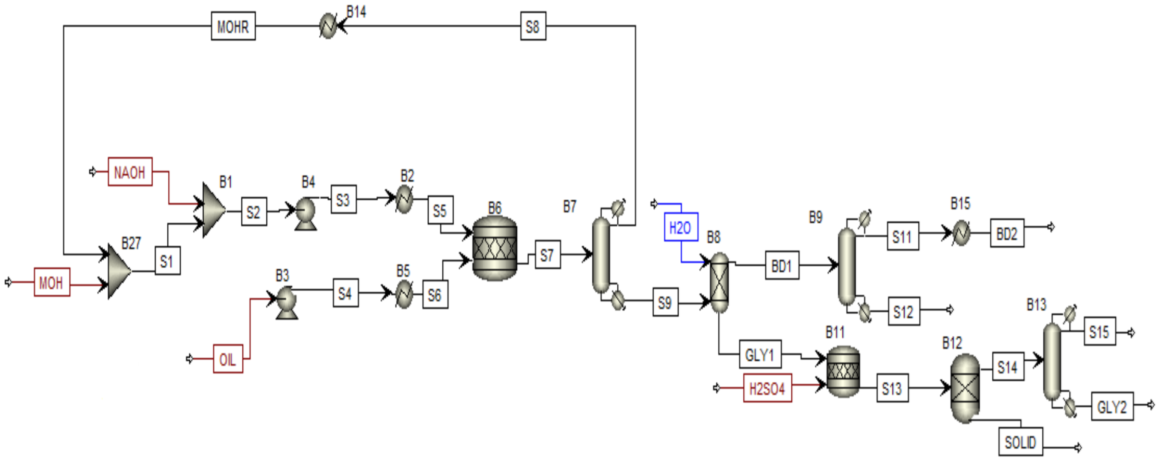

Figure 2: Biodiesel Production Process from Euphorbia Lathyris.

Table 1: Physical and chemical exergy of streams

Streams	Chemical Exergy kJ/h	Physical Exergy kJ/h	Total Exergy kJ/h	Total Exergy MJ/h
MOH	24,551,910	0	24,551,910	24,551
OIL	558,937,952	0	558,937,952	558,937
NAOH	86,191,864	0	86,191,864	86,191
H2O	21,370	0	21,370	21
H_2SO_4	135,722	0	135,722	135
BD2	391,724,204	0	391,724,204	391,724
GLY2	2,911	142,432	145,343	145
SOLID	43,095,915	0	43,095,915	43,095
S12	16,428,458	122,583	16,551,042	16,551
S15	335,357	15,639	350,996	350

Table 2: Physical and chemical exergy of the utilities.

Streams	Chemical Exergy kJ/h	Physical Exergy kJ/h	Total Exergy kJ/h	Total Exergy MJ/h
M1 (VAP)	162,748	62,424	22,5172	225
M2 (LIQ)	1,955	317,365	319,321	319
M3 (VAP)	325,576	124,879	450,455	450
M4 (LIQ)	8,030	1,303,106	1,311,136	1,311
M5 (VAP)	5,000,260	1,917,928	6,918,188	6,918
M6 (LIQ)	2,527	410,132	412,659	412
M7 (VAP)	2,805,130	1,075,950	3,881,080	3,881
M8 (LIQ)	29,351	4,762,868	4,792,219	4,792
M9 (LIQ)	3,426	556,046	559,473	559
M10 (VAP)	345,567	2,095,261	2,440,828	2,440

The utilities, wastes exergy was calculated, also the total of irreversibilities and the exergetic efficiency, the results was showed in Figure 3.

The main process exergy losses were found in streams of wastes (6 MJ/kg of biodiesel), consumption of utilities (2 MJ/kg of biodiesel). The loss for irreversibilities internal of the process is high with a value of 30 MJ/kg of biodiesel. The overall exergetic efficiency of the process was 57 % and is acceptable value compared to a process highly developed and worked during the last decades such as the production of biodiesel from palm oil which has an exergetic efficiency of 72% (Jaimes et al., 2009). The above this indicates that the biodiesel production process with Euphorbia Lathyris should be improved, as shown by the results of exergy analysis. A good starting point is the use of the largest possible number of waste streams and the decrease the internal irreversibilities with changes technological of the process.

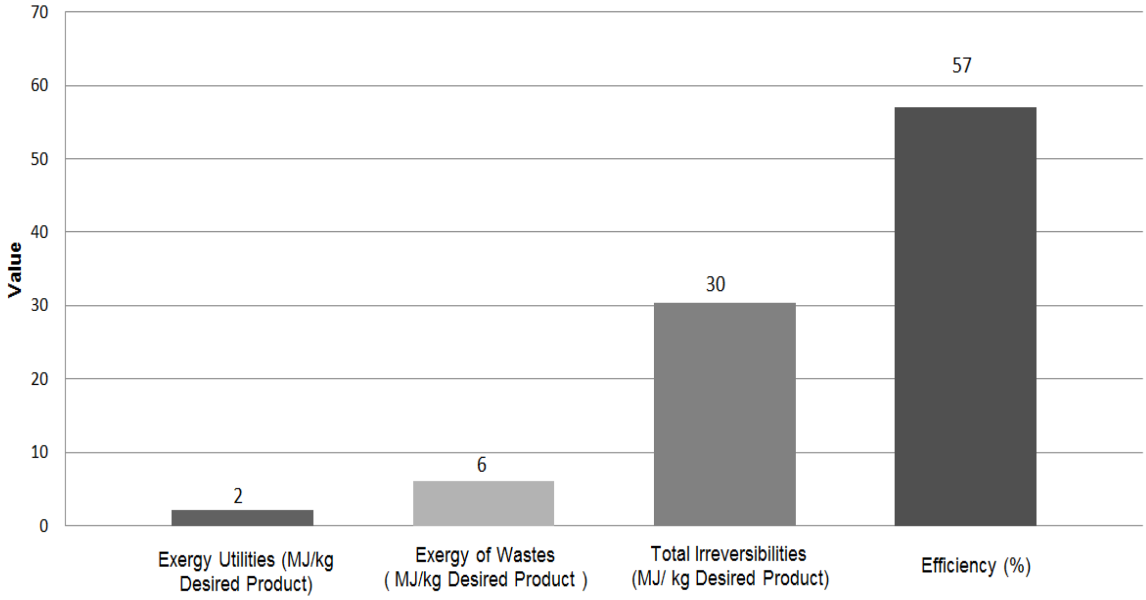

Figure 3: Exergy Analysis of Process

Taking advantage the process waste streams and having in its composition high salts as the output currents neutralization reactor can be to obtain a co-product valuable to be used as fertilizer in agricultural product industry.

4. Conclusions

Application of exergy analysis for the evaluation of the use of novel materials and routes for biomass processing for biofuels production constitutes a useful tool for generating, screening and designing alternatives towards sustainable development.
From the results obtained with the exergy analysis, it was found that this is an excellent tool for evaluating the efficiency and to identify the main irreversibility of the process of producing biodiesel from Euphorbia Lathyris. The results of the exergetic efficiency indicate that the process is promising, but compared with others process with different feedstocks as the palm it is still low and shows the need to increase the exergetic efficiency and to decrease the many causes of irreversibilities of the process as the exergy loss of the wastes.
It should review the application of the mass integration and the use of the streams wastes with sodium sulfate as feedstock for fertilizers production. Also, it should reduce and optimize the use of industrial services with the use of energy integration of the process.

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