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Evaluation of Biodiesel Production Process from Sapium Tree Oil Sebiferum using Exergy Analysis Methodology

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Environmental pollution and declining reserves of fossil fuels has generated the need for new sources of energy that are renewable, is how in the last decade have generated called biofuels, among which are mainly bioethanol and biodiesel. Palm oil, soybean and sunflower at the moment, are the most used raw materials, but some authors claim that the use of these seeds generates competition with human food sources and aggravating the problem of monoculture. Based on these questions the second generation biofuels represent a great advantage since they are characterized by the use of non-edible seeds, taking advantage of the potential that exists in process residues and native seeds are not commercially used.
Besides the use of new energy resources, it is also necessary to be viable. The exergy analysis is a useful tool in the assessment process, which identifies the quantity and quality of energy sources, in addition to being used to design processes and emerging energy-evaluate existing processes.
In this work a biodiesel production process was evaluated from Sapium sebiferum oil, inedible oilseed, through exergy analysis methodology. The process was simulated in the simulation software industry ASPEN PLUS 8.4 and comprises pretreating the oil and subsequent transesterification, washing, solvent recovery and purification and coproduct. All both physical and chemical exergies were determined for each of the process streams including the heating and cooling services. Efficiency and exergy losses for each process unit is determined, the overall exergetic efficiency of the process is finally evaluated.
The results confirm the potential of Sapium sebiferum oil for biodiesel production, presenting a exergy efficiency of 63.79 %, however you must make some technical improvements to the process in order to take the maximum amount of energy.

1. Introduction

During the last decade, biodiesel has emerged as a promising alternative to traditional diesel. It offers many important advantages such as higher cetane number, lower emissions of most regulated species and biodegradability (Plata et al. 2010). Apart from this, the biodiesel is an environmentally friendly fuel and hence it has gained popularity. Despite its importance, more than 95 % of biodiesel is still made from edible oils (Gui et al., 2008), which affects the human food industry Raw materials like oil extracted from Sapium sebiferum, act as a cheaper alternative since they do not require extreme conditions for cultivation. In addition to this, they do not compete with the food industry and are suitable for biodiesel production.
Further, biofuels play a fundamental role in the society, generating large scope in research and providing solutions to world energy problems. Undoubtedly biodiesel has been one of the most important fuels have resolved this issue. The benefits to biodiesel has compared to diesel, environmentally and energetically, have caused optimal biofuel production. This has giving rise to many raw materials for their production. Therefore, our raw material Sapium sebiferum is a crop that can be considered interesting to the energy field of the future when not being used as raw material for the production of food.
The oil is composed of the following free fatty acids: 1.25 % lauric acid, 2.10 % myristic acid, 64.50 % palmitic acid, 4.40 % stearic acid, 27.5 % oleic 0.80 % acid and linolenic acid. The oil has in a high percentage of free

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fatty acids, which justifies the esterification step in the process. To identify the thermodynamic losses and environmental impacts that related, the exergy analysis is the study of the processes that always improvements in them making more efficient the use of resources. Exergy analysis is a thermodynamic analysis technique based on the second law of thermodynamics, which provides an alternative to asses, analyze and compare systems. Exergy analysis yields efficiencies that provide a true measure of how much actual performance approaches the ideal, and existing identifies (Peralta et al., 2010). Exergy, however, makes a distinction between more and less valuable energy. In the exergy calculation, not only the first, but the second law of thermodynamics, are also taken into account. By definition, the Exergy is the maximum useful work as possible during a process that brings the system in thermodynamic equilibrium with a reservoir of heat. The heat sink is usually the environment (Haragovics and Mizsey, 2012).
It is also possible to compare different products and, therefore, different technologies to locate the item with a more efficient use of energy and natural resources. This is a good exergy indicator, since a hight exergy efficiency translates into fewer exergy wasted and, therefore, less environmental damage (Wall and Gong 2006).

1.1 Exergy Analysis

Exergy analysis clearly indicates the locations of energy degradation in a process and can therefore lead to improved operation or technology, also can quantify the quality of heat in a waste stream. A main aim of exergy analysis is to identify meaningful (exergy) efficiencies and the causes and true magnitudes of exergy losses (Jaimes, et al., 2010). Energy and exergy balance for a process flow in a system for a finite time interval can be written as:

$$\text{Exergy input} - \text{exergy output} - \text{exergy consumption} = \text{exergy accumulation} \tag{1}$$

$$\dot{E}x_{mass,in} - \dot{E}x_{mass,out} + \dot{E}x_{heat} - \dot{E}x_{work} = \dot{E}x_{loss} \tag{2}$$

Exergy of a flow may be represented as follows:

$$E = (H - H_0) - T_0(S - S_0) + \sum_i u_{i0}(n_i - n_{io}) \tag{3}$$

The physics exergy related with the temperature, entropy and enthalpy:

$$\dot{E}x_{phy} = (\dot{H} - \dot{H}_0) - T_0(\dot{S} - \dot{S}_0) \tag{4}$$

Where H is the enthalpy, S is the entropy, To is the environmental temperature or in dead state, Ho, and So are the enthalpy and entropy in dead state.
The chemical exergy, related with Free Energy of Gibbs and the elemental chemical exergy of the compound:

$$Ex^0{}_{ch} = \Delta G_f^0 + \Sigma_i n_{elem} * Ex^0{}_{ch,i} \tag{5}$$

When not available, the chemical exergy content of any pure substance, this can be calculated by the approximate Eq(6)

$$B_{ch} = \Delta G_{F0} + \sum_i N_i b_i \tag{6}$$

Where $\Delta G_{F0}$the Gibbs free energy of formation and this is is available for most chemicals. (Kafarov and Ojeda, 2009).
To calculate the lost exergy, the exergy lost for the process and the process efficiency used the following equations.

$$Lost\ Exergy = Total\ exergy\ of\ the\ Inlet\ main\ stream + Total\ exergy\ of\ the\ utilities - Total\ exergy\ of\ the\ outlet\ main\ stream \tag{7}$$

$$Lost\ Exergy\ for\ the\ process = Lost\ Exergy - Total\ Exergy\ of\ the\ Waste\ Stream \tag{8}$$

$$Process\ Efficency = \left(1 - \left(\frac{Lost\ Exergy}{Total\ \ of\ the\ Inlet\ main\ stream + Total\ \ of\ the\ industrial\ services}\right) * 100\right) \tag{9}$$

2. Methodology

2.1 Simulation of biodiesel production process from *Sapium sebiferum.*

The Aspen One software was chosen to be a prestigious software in academia and industry to simulate the biodiesel production process, for which it was necessary to create some hypothetical components do not appear in Aspen One databases especially oil components, their free fatty acids, and alkyl esters formed after transesterification. The thermodynamic package that was applied to the simulation of the process was the NRTL. In the acid esterification, the oil (rich in free fatty acids) was sent to an esterification reactor in which, in presence of a sulfuric acid as acid catalyst react with methanol to produce biodiesel (methyl esters) and water, the process seeks to reduce the content of free fatty acids FFA below a suitable value (less than 2.5%), so the oil can be sent to the basic transesterification stage without causing undesired reactions.
The operating conditions and the stoichiometry of the reaction were found in the scientific literature. Then, in the transesterification stage, the triglycerides present in the oil react with methanol in the presence of a basic catalyst, in this case NaOH, to produce methyl esters (biodiesel) and glycerin. This mixture of biodiesel and glycerin was separated by gravity in a decanter, in which the heavy phase (glycerol) exist the bottom, and the light phase (biodiesel) exits the top (conversion reactor transesterification 97% was assumed based on triglycerides).
The biodiesel stream was sent to distillation steps to recover the alcohol, triglycerides unreacted, and small amount glycerol. The glycerol was sent to acid neutralization (to neutralize the catalyst which could have remained in the stream and recover it) and purification steps.

2.2 Exergy Analysis

Overall mass balance is performed on the main streams of process input and output and thermodynamic properties were obtained necessary to develop the exergy analysis.(Peralta and Sánchez, 2010) The exergy was determined for main streams input and output of the process and. The dead state conditions were made 25 °C and 1 atm.

3. Results

The Figure 1 show the simulation of biodiesel production process obtained in Aspen One V 8.4. The simulation is divided in three parts, pretreatment or esterification of free fatty acids, biodiesel and glycerol production (transesterification) and products and co-products purification.

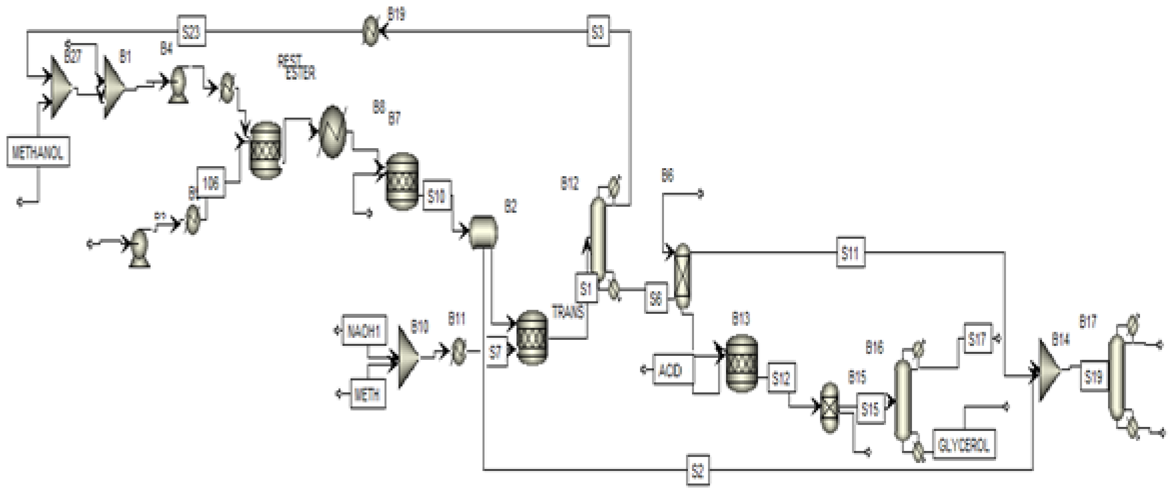

Figure 1: Simulation of biodiesel production process from Sapium sebiferum

The process produces biodiesel as the main product and co-product glycerol. Cleaning and purification of the products was performed with the aid of a washing tower and two distillation towers. The biodiesel produced meets most of the specifications required by the ASTM D7467 standard. The waste streams such as the salts obtained in the neutralization steps were not taken into account as co-products.
The thermodynamic properties of the main currents of the system were determined. After them, the physical and chemical irreversibility were calculated using equations 4, 5 and 6. The total exergy using Eq(1). The results obtained are shown in Table 1.

Table 1: Physical, chemical and total exergy of the main process streams

Streams	Physical Exergy kJ/h	Chemical Exergy kJ/h	Total Exergy kJ/h
H_2SO_4	0	110	110
METHANOL	0	43,727,175	43,727,175
OIL	0	443,398,550	443,398,550
NaOH	0	172,383,695	172,383,695
NaOH1	0	75,131,077	75,131,077
S8	0	21,370	21,371
ÁCID	0	118,305	118,305
S16	0	37,565,556	37,565,556
S17	474	149,916	150,391
GLYCEROL	940	2,058	2,999
S20	3,150	70,029,068	70,032,218
S21	10,234	542,001,949	542,012,184
METH	0	45,512,785	45,512,785

As shown in Table 1, the exergy of biodiesel is greater than the oil which demonstrates the potential of the process. The main streams of input, output and waste according to the figure of the simulation were identified and calculated the total irreversibility of utilities in each heat exchanger. The results are shown in Table 2, 3 and 4

Table 2: Total exergy of the inlet main streams of the process

Inlet Main Streams	Total Exergy (kJ/h)
H_2SO_4	110,696
Methanol	4,327,175
Oil	443,398,550
NaOH	172,383,695
NAOH1	75,131,077
S8	21,371
Acid	118,305
Meth	45,512,785
Total	780,403,656

Table 3: Total exergy of the output main streams of the process

Outlet Main Streams	Total Exergy (kJ/h)
Glycerol	2,999
S21	542,012,184
Solids	37,565,556
Total	579,580,738

Table 4: Total exergy of the waste streams of the process

Waste Streams	Total Exergy (kJ/h)
S20	70,027,609
217	166,746
Total	70,194,355

Where the stream called S21 is the Biodiesel (desired product).
Using the Eq(7), (8) and (9) was calculated the process efficiency, exergy of wastes, exergy of utilities and the total irreversibilities and the results are shown in the Figure 2.

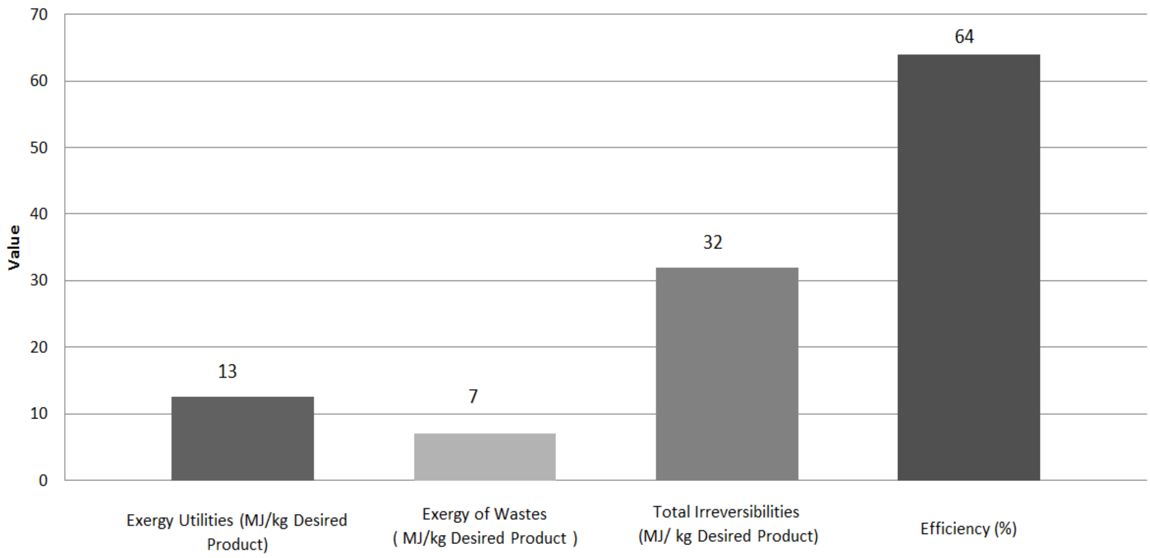

Figure 2: Results exergy analysis biodiesel production of process

Exergetic efficiency of the process was 64%, a value that corresponds to the potential that had identified with respect to exergies input versus output process. The exergy utilities were high, and are due to energy consumption having heat exchangers for heating and cooling flows into the process, besides the necessary purification processes in distillation towers.

4. Conclusions

The simulation process proposed for the production of biodiesel from Sapium sebiferum was realized through Aspen One software. The results were obtained satisfactorily and produced the data required for analysis; the process was compared and validated with other studies of oil transesterification from non-edible feedstock.
Methodology exergy analysis was applied, and the exergy efficiency was 64 %, due to the exergetic losses from utilities and the contribution of the waste losses. The process is efficient since the stages do not cause major irreversibility. Therefore it is recommended to implement a heat integration to reduce exergetic losses from utilities, and then apply the exergy analysis again to check decreased irreversibility and a finally mass integration to reduce the use of raw materials and thus reduce the irreversibility obtained by waste. The composition of waste streams shows a high potential to be used as fertilizers because they have a high percentage of sodium sulfate.
Likewise, it is recommended to apply exergy analysis in each stage to identify where the exergy losses and to recommend improvements.

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References

Gong, M. & Wall, G., 2001. On exergy and sustainable development—Part 2: Indicators and methods. Energy, 1(4), pp. 217-233.
GUI, M., 2008. Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. Energy, 33(11), pp. 1646-1653.

Haragovics, M. & Mizsey, P., 2012. Exergy analysis of multicomponent distillation systems for efficiency ranking. Chemical Engineering Transactions, Volumen 29, pp. 343-348.
Jaimes, W., Acevedo, P. & Kafarov, V., 2010. Exergy analysis of palm oil biodiesel production. Chemical Engineering Transactions, Volumen 21, pp. 1345-1350.
Ojeda, K. & Kafarov, V., 2009. Exergy analysis of enzymatic hydrolysis reactors for transformation of lignocellulosic biomass to bioethanol. Chemical Engineering Journal, 154(1-3), pp. 390-395.
Peralta, Y., Sánchez, E. & Kafarov, V., 2010. Exergy Analysis for Third Generation Biofuel Production. Chemical Engineering Transactions, Volumen 21, pp. 1363-1368
Plata, V., Kafarov, V. & Moreno, N., 2010. Optimization of Third Generation Biofuels Production: Biodiesel from Microalgae Oil by Homogeneus Transesterification. Chemical Engineering Transactions, Volumen 21, pp. 1201-1206.