

## Exergetic analysis of the process of pre-treatment of soybean oil for the production of biodiesel

Análise exergetica do processo de pré-tratamento do óleo de soja para a produção de biodiesel

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### Abstract

*The use of soybean oil for the production of biodiesel has been widely investigated, providing a renewable and biodegradable source to produce biofuels. In this context, exergy analysis is very useful to minimize losses and offer improvements for the efficiency of processes, describing the destroyed exergy and the responsible components for the losses of the system. The present study investigates the exergy efficiency of the soybean oil pretreatment process of a biofuel process production with an installed capacity of 152 million liters/year of biodiesel. Analyses of chemical and physical exergies of the oil refining process flows for biodiesel production were carried out. The operating parameters were used to estimate the exergy efficiency of the process. Results showed that the exergetic efficiency of the soybean oil pretreatment process was 88% and the exergy destroyed was approximately 11%. The efficiency of the chemical reactions of the process was considered satisfactory.*

### Keywords

Exergy analysis. Soybean oil. Biodiesel.

### Resumo

O uso de óleo de soja para a produção de biodiesel tem sido largamente investigada, fornecendo uma renovável e biodegradável fonte de produção de biodiesel. Nesse contexto, a análise exergetica é muito útil para minimizar perdas e oferecer melhorias para a eficiência de processos, descrevendo a energia destruída e os componentes responsáveis pelas perdas do sistema. O presente estudo investiga a eficiência exergetica do processo de pré-tratamento do óleo de soja de um processo de produção de biocombustível com capacidade instalada de 152 milhões de litros por ano de biodiesel. Foram realizadas análises sobre a exergia química e física do processo de refinamento do óleo para produção de biodiesel. Os parâmetros de operação foram usados para estimar a eficiência exergetica do processo. Os resultados mostraram que a eficiência exergetica do processo de pré-tratamento do óleo de soja foi de 88% e a exergia destruída foi de aproximadamente 11%. A eficiência das reações químicas do processo foi considerada satisfatória.

### Palavras-chave

Análise de exergia. Óleo de soja. Biodiesel.

### Como você deve citar?

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## **1 INTRODUCTION**

The use of renewable sources to create biofuels is a potential field of research that allows a reduction of damage to the environment. In this context, biodiesel stands out as a sustainable fuel, being renewable, biodegradable, non-toxic and sulfur-free. This biofuel has been largely used in recent years, showing an alignment with the sustainable concept of the clean production. It can be produced using raw materials like animal tallow, vegetable oil and residual fat [1, 2]. In Brazil, the percentage of pure biodiesel (B100) is added to petro-diesel in proportions according to a national law, reaching 12% in 2020 [3, 10].

The physical and chemical properties of this biofuel have a significant effect to achieve an efficient performance in engines. This effect can be investigated using the first and second law of thermodynamics, quantitatively evaluating the energy in the process (energy analysis using the first law) and verifying the system inefficiencies (exergy analysis using the second law) [4, 11].

The exergy analysis aims to identify where destruction and loss of exergy occur and classify them in order of importance. In addition, the exergy analysis estimates how much exergy is being destroyed and verifies which components of the system are responsible for losses, in order to minimize. Szargut, Morris and Steward [5] define exergy as the maximum amount of work obtained when a mass is brought to a state of thermodynamic equilibrium with the common components of the environment by means of reversible processes involving only interactions with the components of the environment.

Many studies about exergy analysis can be found in the literature in recent years. Karthickeyan [6] studied non-edible oils that were converted into methyl ester of Pumpkin seed oil and Moringa oleifera oil using transesterification process and stated that the first is a promising alternative fuel with 66.51% of exergy efficiency in Toroidal Combustion Chamber engine. On the other hand, Odibi et al. [4] investigated the effect of oxygenated fuels on the energy in a turbo-charged, common-rail six-cylinder diesel engine. The authors used a range of fuel oxygen content based on diesel, waste cooking biodiesel and triacetin. By using the waste cooking biodiesel (B100), a very high exergy destruction (up to 55%) was observed.

This study presents an exergy analysis related to the soybean oil pretreatment process, evidencing the process problems and evaluating the exergetic efficiency in a Brazilian biofuel production process.

## **2 MATERIALS AND METHODS**

### **2.1 The mass balance of the chemical refining process of soybean oil**

The exergetic analysis were performed in a biofuel plant of Minas Gerais (Brazil) with installed capacity of 152 million liters per year. In the process of chemical refining of soybean oil, fatty acids are removed by the neutralization reaction, in which both the acid and base are consumed and new products are formed. The residual gums and soaps are separated by centrifuges and the crude oil is stored in a tank at an initial temperature of 30 °C and heated to a temperature of 75 °C.

Degumming process is the first stage in the refining of soybean oil. At this step, the processing of crude greases, mainly from vegetable source, is used for the elimination, removal or inactivation of phosphatides or related substances, influencing the quality of refined greases to be produced. In this present study, the oil at 75 °C was mixed with the phosphoric acid ( $H_3PO_4$ ) in a stirring reactor for 20 minutes.

The next stage was the neutralization of the oil, with the use of sodium hydroxide (NaOH) and water (H<sub>2</sub>O) at 85 °C. The purpose of crude oil neutralization was the elimination of free fatty acids. A system composed of oil, water, and soap was obtained in this process.

After that, the neutralized oil was separated from the slurry by centrifugation. The neutralization sludge basically consists of water, sodium salts of fatty acids, triglycerides, phospholipids, unsaponifiable matter, oil and soap degradation products [7].

The last step consists of dehumidifying the oil in a drier vessel in order to eliminate moisture from the oil. Finally, the oil was filtered to remove soap scum from the process. Once refined, the oil was stored for later use in the transesterification reaction to produce biodiesel.

In order to perform the mass balance of the soybean oil refining process, all input values were considered: crude soybean oil, phosphoric acid (H<sub>3</sub>PO<sub>4</sub>), sodium hydroxide (NaOH), water (H<sub>2</sub>O), diatomaceous earth and silica, and the output: refined oil, soaps and soap. The mass balance was calculated using the Eq. 1.

$$\sum \dot{m}_i = \sum \dot{m}_o \quad (1)$$

Where  $\dot{m}_i$  is the input mass (kg h<sup>-1</sup>) and  $\dot{m}_o$  is the output mass (kg h<sup>-1</sup>).

## 2.2 Chemical and physical exergies of the system

According to Oliveira [8], chemical exergy is the maximum work when the system changes from the ambient state (T<sub>o</sub>, p<sub>o</sub>) to the dead state (T<sub>o</sub>, p<sub>o</sub>, p<sub>oi</sub>), where T<sub>o</sub> (ambient temperature), p<sub>o</sub> (ambient pressure) and P<sub>oi</sub> (partial pressure of the reference substances present in the environment) interact with the environment.

Szargut, Morris and Steward [5] state that physical exergy is the maximum theoretical useful work as soon as the system goes from the initial state, where the temperature is T and the pressure is P, to the restricted dead state, where the temperature is T<sub>o</sub> and the pressure is P<sub>o</sub>, with heat transfer occurring only with the environment.

The specific exergies of the inputs and outputs of the reactions were calculated according to the Eq. 2 [1].

$$Ex_{ph} = (\Delta h) - T_0(\Delta s) \quad (2)$$

Where  $Ex_{ph}$  is the physical exergy,  $\Delta h$  is the change in enthalpy, T<sub>o</sub> is the reference temperature and  $\Delta s$  is the entropy variation.

The processes found in nature have some degree of irreversibility. The friction generation and the heat transfer occur inherently in the process. The irreversibility for a control system or volume can be quantified using the Eq.3.

$$I = \sum e_i - \sum e_o \quad (3)$$

Where  $I$  is the irreversibility,  $e_i$  is the exergy input and  $e_o$  is the exergy output.

Considering the exergy of all flows that enter and leave the system, the exergy balance can be obtained according to the Eq. 4.

$$\sum e_i = \sum e_o + I \quad (4)$$

### 2.3 Obtainment of calorific power of the fuel

The calorific power is an important characteristic of a fuel, being an indication of the amount of heat released during the complete combustion of the fuel. This indicator can be obtained by experimental and analytical studies, when the chemical composition of the substance is known [7].

The lower calorific power and the higher calorific power of liquid fuels can be found as proposed by Velásquez-Arredondo [9], by calculating the lower calorific power assuming that the water formed from the hydrogen forming part of composition of the fuel is in the vapor phase, as showed in Eq. 5.

$$LCP = HCP - 0.0894 * 2442.3 * H \quad (5)$$

Where the  $LCP$  is the lower calorific power ( $\text{kJ kg}^{-1}$ ),  $HCP$  is the higher calorific power ( $\text{kJ kg}^{-1}$ ) and  $H$  is the Hydrogen percentage in mass.

The value of  $2442.3 \text{ kJ kg}^{-1}$  corresponds to the enthalpy of vaporization of water at a pressure of 1 bar and the calculation of the HCP is performed according to the Eq. 6:

$$HCP = 349.1C + 1178.3H + 100.5S - 103.4O - 15.1N - 21.1A \quad (6)$$

Where C, H, S, O, N and A are respectively the percentages in mass of carbon, hydrogen, sulfur, oxygen, nitrogen, and ashes in the fuel.

### 2.4 Exergetic efficiency in the pre-treatment of soybean oil

Pre-treatment process of soybean oil was investigated using the Eq. 7, to evaluate the efficiency exergetic of the biodiesel system ( $\eta_{E,B}$ ):

$$\eta = \frac{\sum e_o}{\sum e_i} \quad (7)$$

Where  $\eta$  is the exergetic efficiency,  $\sum e_o$  is the output exergy and  $\sum e_i$  is the input exergy.

### 3 RESULTS AND DISCUSSION

Table 1 shows the mass balance ( $\text{kg h}^{-1}$ ) of the analyzed system. Crude oil is the main component of mass used in the process input, with 98.45% (electricity wasn't considered in this index). On the other hand, refined oil is the higher component of the process output, representing 97.46% of output mass.

**Table 1** - Mass balance of the system

| Inputs                  |                           | Outputs     |      |
|-------------------------|---------------------------|-------------|------|
| Crude oil               | 7000                      | Refined oil | 6930 |
| $\text{H}_3\text{PO}_4$ | 4.1                       | Dreg        | 155  |
| NaOH                    | 2.1                       | Soap        | 25   |
| $\text{SiO}_2$          | 7.2                       | -           | -    |
| $\text{H}_2\text{O}$    | 92.4                      | -           | -    |
| Diatomaceous Earth      | 4.2                       | -           | -    |
| Electricity             | 50 ( $\text{kW h}^{-1}$ ) | -           | -    |

Source: Authors

In the case of the sludge, the formation was 69% of water, 29.5% of soap and 1.5 of pure oil [7]. Thus, to calculate the chemical exergy, it was considered as formation the exergy of the water, the exergy of the soap that was calculated by means of the elemental composition and the exergy of the oil. These values can be observed in Table 2. The physical and chemical exergy are represented, respectively, by  $\dot{e}^{\text{ph}}$  and  $\dot{e}^{\text{ch}}$ , and the sum of the exergies is represented by  $\dot{e}^{\text{utter}}$ . The physical exergy values for each flow are smaller when compared to the chemical exergy values. The chemical exergy share associated with each chain has a greater weight in the total exergy value, due to the chemical processes associated with the system.

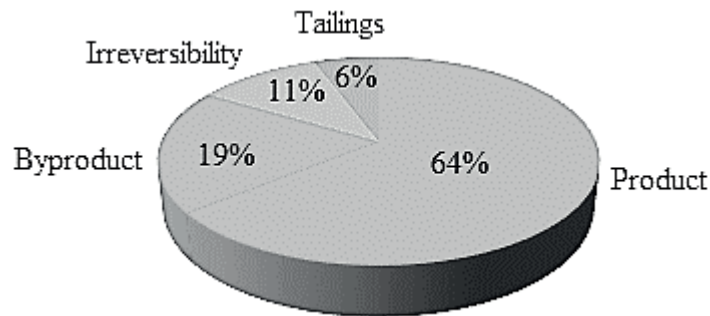
**Table 2** - Exergetic values of the analyzed flows

| Flows                   | $\dot{m}$ (kg) | $C_p$<br>( $\text{J kg}\cdot\text{K}^{-1}$ ) | $T_0$<br>(K) | $T_1$<br>(K) | $h$<br>( $\text{kJ kg}^{-1}$ ) | $s$<br>( $\text{kJ kg}\cdot\text{K}^{-1}$ ) | $\dot{e}^{\text{ph}}$<br>( $\text{kJ kg}^{-1}$ ) | $\dot{e}^{\text{ch}}$<br>( $\text{kJ kg}^{-1}$ ) | $\dot{e}^{\text{utter}}$<br>( $\text{kJ kg}^{-1}$ ) |
|-------------------------|----------------|--|--------------|--------------|--------------------------------|---|--|--|---|
| Crude oil               | 7000           | 2468   | 303          | 348          | 111.06                         | 0.34  | 7.51   | 39439  | 39446.51  |
| NaOH                    | 2.1            | 4063   | 348          | 358          | 40.63                          | 0.11  | 0.57   | 2112.25  | 2112.82   |
| $\text{H}_2\text{O}$    | 92.4           | 4184   | 348          | 358          | 41.84                          | 0.12  | 0.59   | 733.30   | 733.89  |
| $\text{H}_3\text{PO}_4$ | 4.1            | 1480   | 348          | 358          | 14.80                          | 0.04  | 0.21   | 2112.25  | 2112.46   |
| $\text{SiO}_2$          | 7.2            | 0.740  | 358          | 365          | 5.18                           | 0.01  | 0.05   | 1900   | 1900.05   |
| Diatomaceous earth      | 4.2            | 0.740  | 358          | 365          | 5.18                           | 0.01  | 0.05   | 1900   | 1900.05   |
| Refined oil             | 6930           | 2468   | 365          | 303          | -153.02                        | -0.45                                       | 14.68  | 39439  | 39453.68  |
| Dreg                    | 155            | 2898   | 348          | 358          | 28.98                          | 0.08  | 0.41   | 11887  | 11887.41  |
| Soap                    | 25             | 2343   | 348          | 358          | 23.43                          | 0.07  | 0.33   | 3506.66  | 3506.99   |

Source: Authors

The distribution of exergy in percentage is shown in Figure 1. The useful exergy was bigger (64%) and if the utilization of the byproduct is considered, the exergy of the system increases to 83%. The irreversibility or destroyed exergy can be considered a high value of energy or work that was not somehow used in the process. Considering the use of tailings, the result of the exergetic efficiency was approximately 88%.

**Figure 1** – Exergy distribution of the system (in percentage)



Source: Authors

#### 4 CONCLUSIONS

The exergy analysis of the soybean oil pretreatment process included the determination of the physical, chemical and total exergy of the plant, as well as irreversibilities and exergetic efficiency. The efficiency of the chemical process reactions was considered satisfactory. It was observed based on the high values of exergetic efficiency of the process. The exergetic efficiency of the soybean oil pretreatment process was 88% and the exergy destroyed was approximately 11%. It is important to improve the efficiency of the process to reuse the byproduct, avoiding to increase the destroyed exergy.

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