Comparative Exergetic Analysis of Two Biodiesel Production Routes

João MARI\(^1\), Marcus MARI\(^1\), Maykon FERREIRA\(^1\), Wagner CONCEIÇÃO\(^1\) and Cid ANDRADE\(^2\,*\)

\(^1\)Mechanical Engineering Department, State University of Maringa, Colombo Avenue 5790, Maringa, Parana, Brazil
\(^2\)Chemical Engineering Department, State University of Maringa, Colombo Avenue 5790, Maringa, Parana, Brazil

*Corresponding author

Keywords: Exergetic analysis, Biodiesel, Transesterification, Supercritical methanol.

Abstract. Biofuels, such as biodiesel has obtained more and more relevance in the national scenario, because of the current concerns related to the burning of fossil fuels, besides of laws in force that determine the increase of biodiesel blend in common diesel each year. Thus, in this study a comparative exergetic analysis was carried out between the biodiesel production from soybean oil via basic homogeneous catalysis, case 1, where sodium hydroxide (NaOH) was used as a catalyst, and by means of supercritical alcohol, case 2, in which methanol was led to critical state. For that, two production plants were simulated in Aspen HYSYS\textsuperscript{®} V9 software accepting the same amount of main feedstock, in this case soybean oil. After the simulations, the exergetic efficiency of each process was calculated through to a global control volume (CV), having as result 94.01 and 93.50 % to the Case 1 and 2, respectively. These results confirm the feasibility of biodiesel production and the little exergetic difference was caused principally by the conditions of temperature and pressure that were imposed in the methanol supercritical case.

Introduction

Fossil fuels have been being the basis of world energy matrix since the industrial revolution to nowadays, however, researchers claim oil reserves have the autonomy to support world consumption for only 51 years [1], thus, European countries, for example, plan to replace 10 % of the fossil fuels by biofuels up to 2020 [2].

In this scenario, an alternative to common diesel could be the biodiesel, due to the excellent molecular similarity, biodiesel can be used in diesel engine without any mechanical modification, besides of to be biodegradable, non-toxic and less polluting than diesel [3].

More than 300 feedstocks are globally identified such as potential crops to produce biodiesel [4], however, feedstock must have low cost and to be available in large scale for a sustainable production, because it represents 75 % of biodiesel production global cost [5]. By the fact of Brazil is the second largest world producer of soybean, producing 95.631 million tons in 2015/2016 harvest [6], there is a big potential of development in the country.

In this context the work aims to use the exergetic analysis to compare two biodiesel production routes, where in the case 1 occurs transesterification via basic homogeneous catalysis, whereas in the case 2 via methanol supercritical.

Description and Simulation of the Processes

Both cases were projected to produce about 8.000 tons/year of biodiesel, the same plant capacity used on [11]. It was also assumed the same quantity of main feedstock (1050 kg/h soybean oil). However, the process steps of case 1 were based on [11], whereas case 2 were based on [10].

Lastly, it was ignored the pressure drop on heat exchangers [11] and the pumps adiabatic efficiency were considered 100 %.
Feedstock Specifications

Information about several components, such as water, methanol, sodium hydroxide and glycerol are available in Aspen HYSYS libraries, on the other hand, by the fact that soybean oil is composed by 22-31 % of oleic acid, 49-53 % of linoleic acid and 2-10 % of myristic, palmitic and linolenic acid [7, 8], triolein was selected to represent soybean oil [8, 9]. Consequently, biodiesel was represented by methyl oleate [9, 10, 11]. For components not available, it was used the tool Hypothetical Manager to insert them.

Thermodynamic Model

The non-random two liquid (NRTL) model was used to estimate properties, due to components of high polarity, such as methanol and glycerol [8, 9, 10, 11, 12]. When not available some binaries iteration parameters, these were estimated using UNIFAC vapour-liquid equilibrium and UNIFAC liquid-liquid equilibrium models [9, 10].

Case 1: Biodiesel Production via Basic Homogeneous Catalysis

The transesterification reaction was carried out with 6:1 molar ratio of methanol to oil, 1 % sodium hydroxide, based on oil, 60 °C and 400 kPa. In the transesterification reactor (R-TRANS), 95 % of oil was assumed to be converted to biodiesel, producing glycerol as a by-product. Fig. 1 shows the flowsheet described.

Case 2: Biodiesel Production via Methanol Supercritical

The transesterification reaction was carried out with 42:1 molar ratio of methanol to oil, 350 °C and 20 MPa, conditions required to lead methanol to supercritical state. It was also assumed 95 % of oil converted to biodiesel. In this process, it is not necessary the utilization of catalyst, thus, some steps such as washing water (WASH-SEP), catalyst separation (SEP-CAT), catalyst removal (CAT-REM) and solid separation (SEP-SOLID) were removed.

In the Fig. 2, the outflow called Met-2 represent a waste of methanol/biodiesel/glycerol mixture, whereas Oil-2 is a waste of soybean oil unreacted.

Figure 1. Case 1.

where the outflows called MET-WAT and Oil-2 represent waste of a methanol/water mixture and soybean oil unreacted, respectively.
Global Exergetic Analysis

To realize an exergetic analysis a control volume was defined surrounding each process, allowing only global inputs and outputs as thermal energy, work and matter. Thus, intermediate flows were not considered. From this, it is possible to apply the exergy balance by means of Eq. 1 [13].

\[
\frac{dE_x}{dt} = \sum (1 - \frac{T_0}{T_b}) \dot{Q} - \sum (\dot{W} - \dot{P} \frac{dv}{dt}) + \sum (\dot{m} e_x)_e - \sum (\dot{m} e_x)_s - T_0 \dot{\sigma}
\]

where, \(E_x\), \(t\), \(T\), \(\dot{Q}\), \(\dot{W}\), \(P\), \(v\), \(\dot{m}\), \(e_x\) and \(\dot{\sigma}\) represent the total exergy, time, temperature, thermal energy flow, mechanical power, pressure, volume, mass flow, total specific exergy and entropy generation, respectively. Whereas the subscripts \(o\), \(b\), \(e\) and \(s\) refer to dead state, boundary conditions, input and output, respectively. On the other hand, the total specific exergy is defined by Eq. 2 [14].

\[
e_x = e^{KN} + e^{PT} + e^{PH} + e^{CH}
\]

where, \(e^{KN}\), \(e^{PT}\), \(e^{PH}\) and \(e^{CH}\) refer to specific kinetic exergy, potential, physics and chemical, respectively. In this work, the potential and kinetic exergies can be ignored, reducing the Eq. 2 to Eq. 3.

\[
e_x = h - h_0 - T_0 (s - s_0) + e^{CH}
\]

where, \(h\) and \(s\) represent the specific enthalpy and entropy, respectively. On the other hand, the specific chemical exergy of some solid and liquid industrial fuels can be calculated by Eq. 4 [15].

\[
\varphi = \frac{e^{CH}}{NCV}
\]

where, \(NCV\) is the net calorific value. For some biomass substances such as biodiesel and glycerol, \(\varphi\) can be defined by Eq. 5 [15].

\[
\varphi = 1.0374 + 0.0159 \frac{h'}{c'} + 0.0567 \frac{o'}{c'}
\]

where, \(h'\), \(c'\) and \(o'\) are the mass fractions of hydrogen, carbon and oxygen, respectively.
Exegetic Efficiency

Once determined the exergy of all input and output flows of control volume, it is possible to calculate the global exegetic efficiency by means of Eq. 6 [16].

\[
\mathcal{E} = \frac{\sum E_{\text{products}}}{\sum E_{\text{inputs}}}
\]

(6)

In this work, it was considered only the useful products, biodiesel and glycerol, as seen in [16].

Results and Discussion

After simulated both cases, Table 1 and Table 2 show some properties of streams available in Fig. 1 and 2, respectively.

Table 1. Streams of case 1.

<table>
<thead>
<tr>
<th>Stream name</th>
<th>Methanol</th>
<th>NaOH</th>
<th>Oil</th>
<th>Water</th>
<th>Na₃PO₄</th>
<th>BIODIESEL</th>
<th>Oil-2</th>
<th>GLYCEROL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>25.00</td>
<td>195.30</td>
<td>523.10</td>
<td>190.50</td>
</tr>
<tr>
<td>Pressure (kPa)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>10</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Molar flow (kgmole/h)</td>
<td>3.6580</td>
<td>0.2500</td>
<td>1.1880</td>
<td>0.6106</td>
<td>0.1531</td>
<td>3.3760</td>
<td>0.0591</td>
<td>1.2070</td>
</tr>
<tr>
<td>Mass flow (kg/h)</td>
<td>117.20</td>
<td>10.00</td>
<td>1050.00</td>
<td>11.00</td>
<td>20.50</td>
<td>997.30</td>
<td>52.26</td>
<td>104.40</td>
</tr>
<tr>
<td>Component mass fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Using those data and also the Eq. 1 to 6, previously established the boundary conditions as 25 °C and 100 kPa, it was determined the exergetic efficiency of each process, resulting in 94.01 and 93.50 % to Case 1 and 2, respectively.

Conclusion

Exergetic analysis is a powerful tool that has been extensively used to evaluate the performance of thermal systems, hence, it was utilized to compare two different processes: biodiesel production via basic homogeneous catalysis and via methanol supercritical.

For this, both processes were simulated in Aspen HYSYS, obtaining biodiesel and glycerol with purities more than the standards established by ASTM.
Lastly, despite the case 2 has produced 6.7 kg/h of biodiesel more than the case 1, it was concluded that looking at exergetic point of view, the biodiesel production via basic homogeneous catalysis is more feasible than via methanol supercritical.

This fact can be explained by the high molar ratio methanol to oil used in case 2, however, the main factor is associated with the critical conditions of temperature and pressure imposed on transesterification reactor.

Acknowledgement
This work has been realized with support of Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES)–Brazil.

References