Exergetic Analysis of Biodiesel Production Routes

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Abstract. Biodiesel is a possible successor to conventional diesel. Several methods, with the most varied raw materials and different routes, are available in the literature, directed to the production of biodiesel. In this way, the objective of this work was to evaluate the energetic conversion process from two routes: via basic homogeneous catalysis and via heterogeneous acid catalysis. The purpose of the study was to verify which of the two routes spends (or destroys, from the exergetic point of view) less energy. Since the route that destroys less energy becomes more energetically viable than the other. Due to the particularity of each method, the operational parameters were different, but for a concise analysis, the same raw materials were used for both cases.

Introduction

Biodiesel is a biofuel that has emerged as the successor to conventional diesel (of fossil origin). The conventional route, used in the production of biodiesel in large scale, uses the homogeneous basic catalysis [1]. This route guarantees high conversions in short time intervals. However, homogeneous alkaline catalysis requires raw materials with low concentrations of fatty acids, since alkaline catalysts NaOH or KOH in contact with fatty acids react to form soaps, causing numerous inconveniences in the operational process [2]. Therefore, studies have been carried out with the aim of finding routes that present the same advantages of homogeneous alkaline catalysis, but without these same drawbacks [3, 4, 5].

According to studies, one of the main advantages of the use of heterogeneous acid catalysts in the production process is that it does not require a pretreatment of the raw material that has high concentrations of fatty acid. The heterogeneous acid catalysts have active sites capable of performing both esterification and transesterification reactions. These catalysts can also be recovered and reused. According to some authors, the use of these catalysts provides the obtaining of purer products [6, 7, 8, 9]. A comparative study is necessary to evaluate the efficiency of each process [10].

Thus, the first stage of this work consisted in carrying out a bibliographical review, in order to select in the available literature, articles related to the biodiesel production process through alkaline homogeneous catalysis (conventional) and via heterogeneous acid catalysis. In the second stage of this work, an exergetic analysis of these two processes was carried out, aiming to verify, through mathematical/computational tools, which of the two processes requires less energy (destroys less exergy) for the conversion of raw materials into biodiesel and its by-product, glycerol. Therefore, from the energy point of view it, was shown which of the two processes is most feasible, according to our hypotheses.

Materials and Methods

Exergetic analyzes were performed for reactions of biodiesel production via: homogeneous alkaline catalysis and heterogeneous acid catalysis. For the homogeneous alkaline catalysis, was used the work done by (Freedman, et al., 1984) [11]. Moreover, for heterogeneous acid catalysis, the work developed by (Abreu, et al., 2005) [12] was used. Due to the particularity of each catalytic process, the
operating parameters were different. However, for a concise analysis, work was using the same raw materials: refined soybean oil and anhydrous methanol.

For the development of the work the following considerations were made for both processes:

- Was realized the energy balance in the reactors.
- Was disregarded Shaft work performed by the agitator in the reactor.
- Were inconsiderate the kinetic and potential energies in the system.
- Considered constant pressure in the reactors.
- Considered constant the specific heats of the reactants and products.
- Considered 500 mL of soybean oil as the calculation basis.
- Considered a free fatty acid concentration of 1% in soybean oil.

Mass balance in the system:

\[
m_{\text{accumulation}} = \sum m_e - \sum m_s
\]

Energy balance in the system:

\[
\Delta E = \sum m_e c_p T_e - \sum m_s c_p T_s + Q
\]

where:

- \( m_{\text{accumulation}} \) = mass accumulation in the system
- \( m_e \) = mass of the component entering the system
- \( m_s \) = mass of the component exiting the system
- \( \Delta E \) = destroyed energy
- \( c_p \) = specific heat of the component
- \( T_e \) = temperature that the component enters the system
- \( T_s \) = temperature that the component leaves the system
- \( Q \) = heat added to the system

Homogeneous Alkaline Catalysis

For the development of this work considered the homogeneous alkaline catalyst sodium hydroxide (NaOH). Moreover, the following parameters proposed by (Freedman, et al., 1984) [11].

a. Reaction temperature of 60 °C.
b. Molar ratio methyl alcohol/oil of 6:1.
c. Mass concentration of 1% catalyst, relative to oil mass.
d. Reaction time of 1 hour and yield of 98%.

Heterogeneous Acid Catalysis

For the development of this stage of work, the work developed by (Abreu, et al., 2005) [12] was used. Considering the SnO catalyst. Moreover, the following parameters:

a. Reaction temperature of 60 °C.
b. Molar ratio methyl alcohol/oil of 4.5:1.
c. Mass concentration of 1% catalyst, relative to oil mass.
d. Reaction time of 1 hour and yield of 92.6%.

Results and Discussion

It should be noted that the energy balance was calculated taking into account the actual masses of biodiesel and glycerin produced, since the yield values of the reactions were given in both studies. Energy balances performed in this way provide close (or even identical) values. Since in both
balances (exegetic or energetic using actual data) they provide energy/exergy destroyed during the conversion processes of the reagents into products.

Table 1. Mass balance results for homogeneous alkaline catalysis.

| Input currents       | Output currents     |
|----------------------|---------------------|
| Mass of oil          | 461.00 g            |
| Mass of alcohol      | 101.47 g            |
| Mass of catalyst     | 4.61 g              |
| Total                | 567.08 g            |
| Mass of biodiesel    | 449.27 g            |
| Mass of glycerin     | 47.17 g             |
| Accumulation         | 70.64 g             |
| Total                | 567.08 g            |

Table 2. Results of the energy balance for homogeneous alkaline catalysis.

| Input currents       | Output currents     |
|----------------------|---------------------|
| Oil                  | 22589.00 J          |
| Alcohol              | 6418.18 J           |
| Catalyst             | 452.93 J            |
| Heat supplied to the reactor | 41244.16 J       |
| Biodiesel            | 51756.46 J          |
| Glycerin             | 6254.20 J           |
| Destroyed energy     | 12693.61 J          |

Another value the mass balance carried out for homogeneous alkaline catalysis, where considered as destroyed energy, in the mass and energy balance the input or output currents of the heterogeneous catalysts were not considered. Hypothesized that heterogeneous catalysts are recovered and reused in the process.

Table 3. Mass balance results for heterogeneous acid catalysis.

| Input currents        | Output currents     |
|----------------------|---------------------|
| Mass of oil          | 461.00 g            |
| Mass of alcohol      | 76.10 g             |
| Total                | 537.10 g            |
| Mass of biodiesel    | 428.81 g            |
| Mass of glycerin     | 45.02 g             |
| Mass accumulation    | 63.28 g             |
| Total                | 537.10 g            |

Table 4. Results of the energy balance for heterogeneous acid catalysis.

| Input currents        | Output currents     |
|----------------------|---------------------|
| Oil                  | 22589.00 J          |
| Alcohol              | 4813.64 J           |
| Heat supplied to the reactor | 38363.69 J       |
| Biodiesel            | 49398.56 J          |
| Glycerin             | 5969.28 J           |
| Destroyed energy     | 10398.49 J          |

Comparing the results in the energy balances, presented in Tables 2 and 4, it is possible to conclude, second our hypotheses, that the acid catalysis destroys less energy, when compared with the alkaline catalysis. The homogeneous alkaline catalysis demanded a greater excess of alcohol and the catalyst is not recovered, causing more destruction of energy. However, if we take into account the decay of the catalytic activity of the heterogeneous acid catalyst and the energy destroyed in the recovery process of these catalysts, the energy destroyed in the process through heterogeneous acid catalysis may present a higher value than the one presented in this work. It is important to note that alkaline catalysis, despite destroying more energy, requires a lower reaction time (or residence time) than acid catalysis, which is three times lower.

**Conclusion**

It is possible to conclude that, according to our hypotheses, heterogeneous acid catalysis destroys less energy when compared to basic homogeneous catalysis. One of the factors that may contribute to these results is not to have considered the decay of the catalytic activity as destruction of exergy. Unlike the basic catalysis, where the energy destroyed from the catalyst was considered.
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References

[1] M.E. Borges and L. Díaz. Recent developments on heterogeneous catalysts for biodiesel production by oil esterification and transesterification reactions: A review. Renewable and Sustainable Energy Reviews. Vol. 16. pp. 2839-2849 (2012).

[2] A. Abbaszaadeh [et al.] Current biodiesel production technologies: A comparative review Energy Conversion and Management. Vol. 63. pp. 138–148 (2012).

[3] A.A. Apostolakou [et al.] Techno-economic analysis of a biodiesel production process from vegetable oils. Fuel Processing Technology,. Vol. 90. pp. 1023-1031 (2009).

[4] M.E. Cunha [et al.] Beef tallow biodiesel produced in a pilot scale. Fuel Processing Technology. Vol. 90. pp. 1949-1954 (2009).

[5] T.P Quessada [et al.] Biodiesel obtention from soybean and corn oil using basic catalysts and acid catalyst. Enciclopédia Bioesfera. Vol. 6. pp. 1-25 (2010).

[6] J. Alcañiz-Monge, Trautwein and J. Marco-Lozar. Biodiesel production by acid catalysis with heteropolyacids supported on activated carbon fibers. Applied Catalysis A, General. Vol. 468. pp. 432-441 (2013).

[7] Z. Helwani [et al.] Solid heterogeneous catalysts for transesterification of triglycerides with methanol: A review. Applied Catalysis A: General. Vol. 363. pp. 1-10 (2009).

[8] D.Y. Leung, X. Wu and M. Leung. A review on biodiesel production using catalyzed [Periódico] // Appl. Energy. - 2010. - Vol. 87. - pp. 1083–1095.

[9] S. Semwal [et al.] Biodiesel production using heterogeneous catalysts. Bioresource Technology. Vol. 102. pp. 2151-216 (2011).

[10]E.A. Abdelaziz R. Saidur and S. Mekhilef A review on energy saving strategies in industrial sector Renewable and Sustainable Energy Reviews. Vol. 15. pp. 150–168 (2011).

[11]F.R. Abreu [et al.] New multi-phase catalytic systems based on tin compounds active for vegetable oil transesterification reaction. Journal of molecular catalysis. A, Chemical. Vol. 227 . pp. 263 -267 (2005).

[12]B. Freedman, E. Pryde and T. Mounts Variables Affecting the Yields of Fatty Esters from Transesterified Vegetable Oils. Journal of the American Oil Chemists Society. Vol. 6. pp. 1638-1643 (1984).