
REACTIVE DISTILLATION COLUMN TO PRODUCE BIODIESEL FROM RESIDUAL FRYING OIL

Ana Kiese Zelema Geremias, Elson Joel de Melo João, Garcia Cusseiala, Elma Wanete
Gregório da Conceição Mateus, Eder Dias and António André Chivanga Barros

Department of Engineering and Technology (DET), Instituto Superior Politecnico de
Tecnologias e Ciências (ISPTEC), Avenida Luanda Sul, Rua Lateral S10, Talatona, Luanda,
Angola

Abstract

Environment concerns related to the use of fossil fuels is reflected in proposals for new conversion technologies to produce biofuels from biomass. The biofuels produced in this context have the same characteristics as petroleum derivatives, however, with reduced greenhouse gas emissions and with no sulfur in their molecular structures. In this context, a reactive distillation (RD) column was designed, constructed, installed and operated using process intensification principles. It was applied in the production of biodiesel, using residual frying oil as the raw material, by the transesterification reaction, in a continuous regime. The process started with alcohol in excess in the reboiler, located in the bottom of the RD, which was heated through the combustion gas of GLP to produce ethanol vapor, which was recirculated in the column until stabilization. Also, in this stage, the reagents (with masses previously calculated based on stoichiometric relations) were inserted into the respective feed tanks. With the definition of the operation time, the tank valves were opened to give the appropriate flowrate of each reactant. The reaction products were recovered during the experiment from the bottom of the column and they were distilled to obtain two phases, biodiesel (the light phase) and glycerol (the heavy phase). The results obtained from this study show that the use of an RD column based on process intensification principles can produce biodiesel in a continuous regime. Further research is required to improve the yield through optimization of the operation parameters.

Keywords: Reactive Distillation, Transesterification, Biodiesel, Column, Process Intensification

1. Introduction

Interest in fuel production from renewable sources has increased significantly in recent years due to political issues and the economic instability of the oil market. This approach also brings environmental benefits associated with the lower levels of gaseous emissions from the combustion of fuels from non-renewable sources^{[1], [2], [6]}.

Thus, many procedures have been proposed for the production of biofuels, particularly biodiesel, which is a non-petroleum fuel produced by applying transesterification to break down the triglyceride present in fatty acids^{[4], [6]}. In this reaction, the chemical structure of triglycerides in oil is broken down via the exchange of alkyl groups between an ester and alcohol, with the alcohol being used as a reactant.

Biodiesel is a promising alternative to conventional diesel fuel due to its renewable nature and the associated reduction in the emission of particles and greenhouse gases^{[1], [3], [4]}. Homogeneous catalysis can be applied in the transesterification reactions involved in biodiesel production to obtain high yields in a relatively short time. However, since the catalysts cannot be reused and must be neutralized after the reaction, biodiesel does not compete favorably with fossil fuels^[2]. This, together with environmental concerns, has led to the search for solid catalysts, which are eco-friendly and effective^{[2], [3], [4], [5], [6], [7]}.

The use of a solid catalyst in the chemical reaction involved in biodiesel production can also reduce the time and cost of the process. In addition, it could be reused, resulting in a decrease in the level of impurities in the reaction products, and would allow continuous operation in a fixed-bed reactor^{[4], [5]}.

The conversion efficiency is related to the catalytic activity of the solid catalyst used. In general, basic heterogeneous catalysts are more active than acidic heterogeneous catalysts, requiring shorter reaction times and relatively low reaction temperatures. Therefore, there are many advantages to performing the transesterification of triglycerides using a basic heterogeneous catalyst^[2].

The synthesis of biodiesel with a solid catalyst can enhance the production and an economically feasible process can be achieved, mainly due to the lower costs related to the reuse of the catalyst and reduced levels of impurities in the products and byproducts of the reaction^[5].

The methodology developed in this study facilitates a step change in the conceptual design process, offering a tool for the study of reactive distillation (RD) columns, with distillation, extractive distillation, esterification and transesterification being performed in the same equipment, to allow biodiesel production in a continuous process.

The RD process is based on the process intensification concept, taking advantage of the synergy that occurs when combining the catalysis reaction and separation in a single unit, which allows the concurrent production and removal of products. This improves the productivity and selectivity, reduces the energy use, eliminates the need for solvents and leads to highly efficient systems with improved the environmental sustainability^[14].

The use of RD as a reactive separation technology has attracted considerable attention given its high levels of efficiency^[8] and the advantages include energy and capital savings, increased reaction conversion, high selectivity and the use of the reaction heat^[9]. Therefore, RD processes have been previously examined for application in esterification and etherification reactions^{[10], [11], [12], [13]}.

The complexity involved in improving the performance of this process is associated with the

multi-feed positions and selection of the reactants, catalysts and solvents.

In this study, the transesterification reaction was carried out with homogeneous catalysts, in a continuous distillation column reactor, and the operational performance was evaluated in terms of biodiesel production quality. Experiments were also conducted using a reactive distillation column, where the reactant was supplied at the feed position.

The process intensification concept was adopted, using an RD column for the transesterification reaction, to recover the reactant (ethanol) used and to break the azeotrope point between ethanol and water, based on the extractive distillation being performed in the top section of the RD column, as shown in Figure 3.

In this case, a homogeneous catalyst was used in the RD column. The same operational conditions were applied in all cases studied, including the residence time, the mass of reactant and molar mass used in the reaction. The results obtained show good reaction efficiency, which was improved by applying the process intensification principles. This concept can be applied to other synthesis processes carried out in a continuous regime.

2. Experimental

A reactive distillation (RD) column was designed, constructed and installed (Figure 4). It was composed of three modules, which incorporate internally packing to increase the interfacial area for vapor-liquid contact, mass transfer and chemical reaction. The module located in the intermediate part of the column (Figure 1a) receives the limiting reactant (oil) and the excess reactant (ethyl alcohol) with dissolved sulfuric acid, used as a catalyst in the esterification reaction, based on the conversion of free fatty acids into biodiesel. The flow rate of the reagents is associated with the stoichiometric balance. In this module, the mixtures are fed vertically, downward, through the action of gravity, and interact strongly with the ascendant vapor of the alcohol used in excess coming from the reboiler, installed at the base of the equipment.

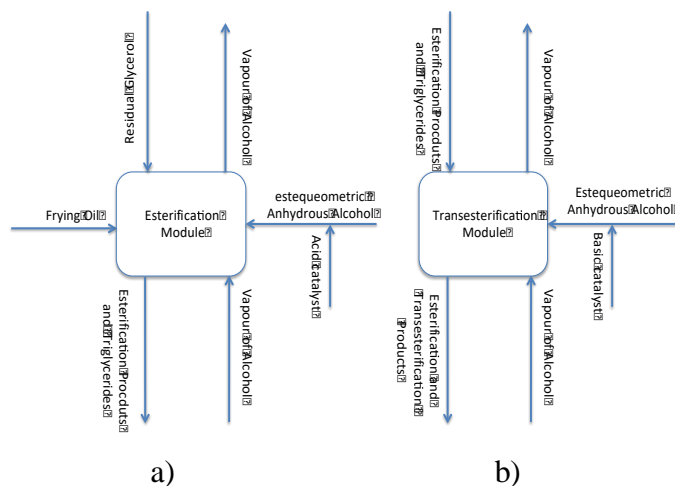


Figure 1. Description of streams associated with chemical reaction modules.

After the esterification reaction, the downward mixture flows to the transesterification module (Figure 1b) where feeding with the basic catalyst occurs. In this case, the feed catalyst must neutralize the acid catalyst from the esterification and the remaining mass acts as a catalyst for the transesterification reaction in the bottom module. As previously mentioned, the transesterification reaction produces biodiesel and glycerol, which are collected in a decanting funnel installed in the bottom of the column. In the decanting funnel, the separation of the products into two phases occurs, that is, a light phase of the crude biodiesel and a heavy phase of crude glycerol.

In the esterification reaction, with dissolution of the catalysts in excess reagent, water is produced. This reduces the level of purity of the alcohol in the vapor phase and thus the capacity of the chemical reaction. For this, a module for extractive distillation is therefore required at the top of column to break the azeotrope point between ethanol and water and to produce the anhydrous ethyl alcohol.

In this process, the residual glycerol recovered at the bottom of reactive distillation column is used as a solvent in the extractive distillation, being fed at the top of this equipment and flowing down ward through the action of gravity. Along its path the solvent interacts with the ethanol vapor and the interaction between the flows modifies the thermodynamic characteristics of the ethanol, breaking the azeotrope point and increasing the purity of this compound (Figure 2a). The top products are condensed and flow downward to the reboiler where they are heated to produce the vapor needed for the RD column (Figure 2b).

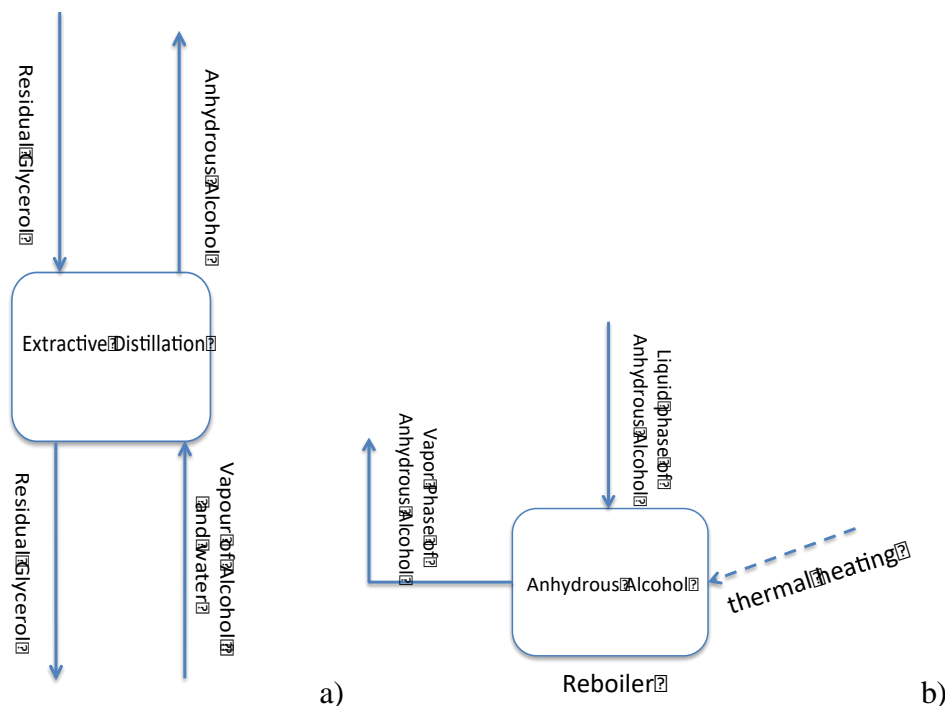


Figure 2. Description of streams associated with chemical reaction modules.

Based on this principle, the alcohol vapor in excess operates in the recirculation circuit, being involved in the esterification and transesterification reactions and the extractive distillation, and in the last step the crude glycerol is used as a solvent. On the other hand, the steady-state characteristic of this process guarantees continuous feeding and removal of the products at the bottom of this equipment, with the recirculation of ethanol, used in this study as the reactant in excess.

Figures 1 and 2 are compressed into Figure 3, which represents the reactive distillation (RD) column, with the three modules described herein. There are four feed flows in the RD column. The operations involved in this process occur in the top condenser, the bottom decanting funnel and the reboiler, used to produce the vapor flow, and vapor is used to allow effective chemical reactions to produce biodiesel and glycerol.

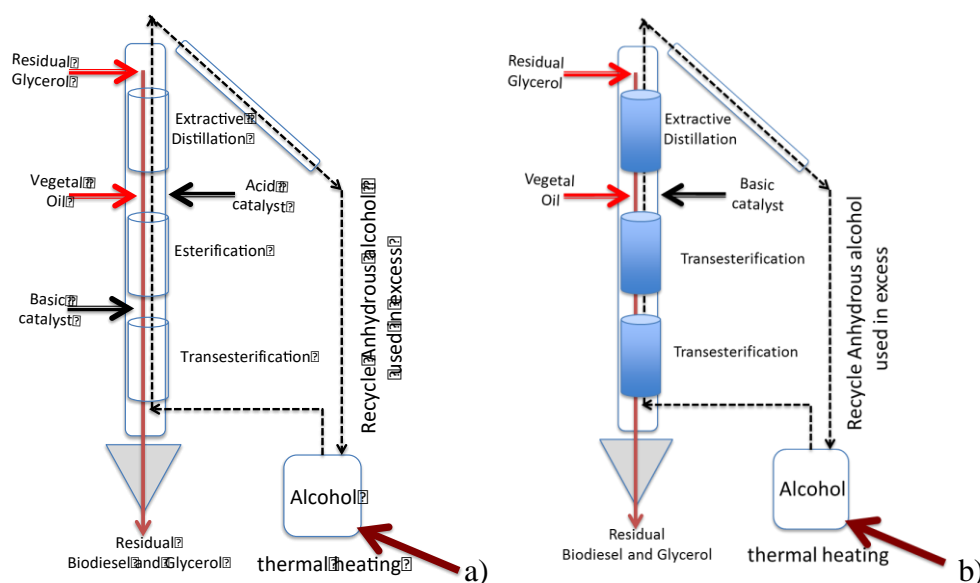


Figure3. Reactive distillation column proposed herein where: a) processing of raw material with high acid index and b) processing of raw material with a reduced acid index.

2.1. Experimental procedures

2.1.1. Reactive distillation column operation

To carry out the biodiesel production experiments in the reactive distillation (RD) column, the procedures involved the following steps:

- The limiting reactant was characterized to determine the acidity index. Under these conditions, the operational sequence can be defined with or without the esterification reaction. If the acidity index is lower than that established in the literature, only the transesterification reaction is used (Figure 3b);

- b) After establishing the quality of the raw material, the stoichiometric equation is used to determine the masses of reagents needed for the chemical reaction. The calculated mass is then converted into flowrates;
- c) The appropriate masses of limiting and excess reactants and the catalyst are weighed out. In this case, the catalyst mass was determined from a previous transesterification reaction study performed in a laboratory batch-scale reactor. Under the study conditions, 1.2% catalyst mass in relation to the oil mass was defined;
- d) In the next step, the mass of limiting reactant was heated to the reaction temperature, in this case until reaching the boiling point of ethanol. The mass of alcohol in excess was heated and used to dissolve of catalyst mass;
- e) The previously heated masses were inserted into the respective feed tanks. The use of heated mass minimizes the thermal barrier due to the temperature difference between the ascendent vapor and the feed flow;
- f) The anhydrous alcohol, previously held in the reboiler tank, produces the vapor that flows into the reactive distillation column, based on the recirculation process described above. Thus, the valve of the reactant tank is open, and the flow rate is based on the values established in the stoichiometric balance. Since the acidity index value was below that established in the literature, esterification and transesterification modules were used in the transesterification reaction, as described in Figure 3b; and
- g) The feed flowrates and the operation temperature were adequately controlled and the products were removed progressively until the end of the reaction.

2.1.2. Measuring the process performance

When the reaction was concluded, the products were purified using a batch distillation column to recover of the alcohol in excess. For this, phase separation into a light phase containing biodiesel and a heavy phase of glycerol occurred. The biodiesel recovered was used to determine the yield, in term of biodiesel mass-produced in relation to the frying oil mass initially used in the process. The biodiesel was then neutralized and dried by evaporation to ensure appropriate quality for use in internal combustion to produce electricity.

2.1.3. Batch biodiesel production

Before the experiments were performed in the reactive distillation column, tests were performed in a batch reactor using the reagents under the same operational conditions, with following methodology:

- a) The acidity index of the frying oil was determined. As this parameter is below the limit established in the literature, only the transesterification reaction was carried out;
- b) The stoichiometric balance was determined and the masses of reactants for the transesterification reaction were weighed out. For the excess reactant an amount 6 times more than the stoichiometric mass was used;
- c) The reagent masses previously weighed out were heated until the reaction temperature and the basic catalyst was dissolved in the heated alcohol;

- d) The mass of alcohol with the catalyst was inserted in the reactor with the previously heated oil, starting the transesterification reaction, which proceeded for 1 h;
- e) At the end of the reaction, the mixture was placed into a distillation flask to recover the alcohol in excess. The remaining mass was then placed in the decanting funnel for the phase separation into biodiesel (light phase) and glycerol (heavy phase).

2.1.4. Characterization of reaction products

The characterization of the biodiesel was carried out through the analysis of the ester content, kinematic viscosity, acid index and specific mass. The kinematic viscosity was obtained using an Ostwald viscometer based on the ABNT NBR 10441 methodology and, to determine the acidity index, titration with potassium hydroxide was carried out based on the ABNT NBR 14448 method. The specific mass was determined at room temperature (20 ± 2 °C) using a 25 mL pycnometer calibrated with distilled water. These procedures were also used in a study by Barros et. al. ^[1], who conducted the experiment using a batch reactor.

3. Results and Discussion

3.1. Batch experiments

The experiments in the reactive distillation column were carried out based on reference data obtained in a batch reactor, mainly related to the following parameters: a) reaction time; b) reagents and catalyst mass; c) agitation degree; and d) mass ratio. The transesterification data from the batch reactor were used to close the mass balances and to determine the conversion rates in terms of the biodiesel mass produced. In this study, frying oil (92.352 g), anhydrous ethanol (88.9 g) and KOH catalyst (1.108 g) were used. The equivalent catalyst mass was 1.2% of the frying oil mass. The crude biodiesel produced was characterized to determine the quality of the biofuel and the results were as follows: density 0.8785 g/ml; kinematic viscosity 1.920 mm²/s and acidity index 3.1668 mgOH/g. These parameters deviated from the specifications established by the ANP ^[16], but the biofuel needs to be purified prior to the final evaluation.

The operational parameters of the batch reactor were used to carry out the experiments in the RD distillation column, with the configuration shown in Figure 3b. Only two modules were used for the transesterification and the purification of the ascending and recycled alcohol vapor by extractive distillation (performed in the top module). The separation of the products from the RD column in the decanting funnel is shown in Figure 4, where the biodiesel is the light phase and glycerol is the heavy phase.



Figure 4. Crude biodiesel obtained using batch reaction.

3.2. Reactive Distillation Column Operation

The experiments were performed in a reactive distillation column with the transesterification reaction carried out using two modules. Extractive distillation was conducted in the top module of the unit. During the experiments the performance efficiency was monitored, with the ethanol vapor flowing into the column and passing through each module until stabilization (the steady-state) was reached. When the reagents are inside the valves of the feed tank open, allowing the interaction between liquid and vapor phases, ensuring the turbulence necessary for effective mass and heat transfer and the chemical reaction to occur. The feed flow was previously heated to minimize the thermal barriers in the column, characterized by the condensation of the vapor flow, due to interaction between the phases. If this phenomenon occurs, there will be a decrease in the vapor flow rate toward the top of the equipment, which can limit the operational quality of the process. During the operation of the RD column, the bottom products are progressively recovery and after distillation they are placed in the decanter tank where two phases are formed: a light phase (biodiesel) and a heavy phase (glycerol).

To obtain the results 1240.00 g of frying oil, 208.79 g of anhydrous ethanol (99.9%) and 14.888 g of catalyst (equivalent to 1.2% of the frying oil) were used. Based on the performance of the experiments over 1 h the following feed flowrates were defined: a) frying oil 20.67 g/min and b) anhydrous ethanol with dissolved catalyst 3.728 g/min. Using these operational conditions, with the RD column in the steady-state, the measured flow rate of the ethanol vapor in excess was 16.42 g/min, corresponding to 4.4 times less than the stoichiometric flowrate.

During the experiments, the products were collected from the bottom of the reactive distillation column, as shown in Figure 5.



Figure 5. Biodiesel from reactive distillation column.

3.3. Characterization of products

The physico-chemical characteristics of the residual biodiesel from the batch reactor and from the RD column, produced based on process intensification principles, were determined and the results compared with international standards. The values obtained for the density, acidity index, refractive index and kinematic viscosity can be seen in Table 1.

Table 1. Physico-chemical parameters for biodiesel obtained in this study.

Reference	Processed mass (g)	Density 20°C (kg/m ³)	Refraction Index at 20°C	Acidity Index (mgKOH/g)	Kinematic Viscosity at 40°C (mm ² /s)	Yield (%)
Batch Reactor	92.352	878.5	1.453	3.1668	1.920	92.306
RD Column	1 240.0	876.7	1.454	2.0255	1.812	15.441
International Standard	----	850.0 – 900.0	1.45	≤ 0.5	3.0 – 6.0	-----

The international standard values for the biodiesel parameters were extracted from the Brazilian standards NBR 7148 and NBR 14065 for density at 20°C, NBR 14448 for the acidity index and NBR 10441 for kinematic viscosity at 40°C. A comparison between the data shows significant deviations, mainly for the acidity index and kinematic viscosity. In this study, purification of the product is required for the biodiesel to meet the international standards. In general, the purification process is based on extraction with an acid solution followed by evaporation to dry the biodiesel ^[15].

In this context, for better qualification of the crude biodiesel, liquid-liquid extraction was carried out with an acid water solution, and the masses used were previously defined based on a titration procedure. An acid water solution was employed in association with the basic catalyst used in the transesterification reaction. In this procedure, the acid mass required for the titration was determined, the acid solution was prepared, heated up to 60°C and then mixed with biodiesel under agitation. After this step, the mixture was transferred to a decanting funnel and left to stabilize for approximately 40 min. The phases were separated and the biodiesel phase was transferred to a distillation flask to eliminate traces of water by drying.

When the purification step was finished, the biodiesel was characterized using the procedures described in methodology section of this paper, and the results are given in Table 2.

Table 2. Physico-chemical data for purified biodiesel.

Reference	Processed mass (g)	Density 20°C (kg/m ³)	Refraction Index at 20°C	Acidity Index (mgKOH/g)	Kinematic Viscosity at 40°C (mm ² /s)	Yield (%)
Batch Reactor	92.352	876.387	1.456	1.1077	1.885	92.306
RD Column	1 240.0	880.682	1.455	0.5027	1.651	15.441
International Standard	----	850.0 – 900.0	1.450	≤ 0.5	3.0 – 6.0	-----

Table 2 shows the characteristics of the biodiesel samples obtained from the reactive distillation (RD) column and batch reactor. The acidity index for the former adheres to the established international standard, but this is not the case for the biodiesel from the batch reactor. For both cases studied, the kinematic viscosity was below the value given in the standard, probably due to the quality of the raw material used in this study. However, the refraction index and density of both samples lie within the ranges set by the international standard.

The results obtained in this study are similar to those reported by Colombo et al.^{[2],[4],[5]} and Barros et al.^[1], who investigated biodiesel production by esterification and transesterification, in recirculation reactors and in a batch reactor, using a raw material with a reduced acidity index.

A limitation of this study is related to the rate of conversion of the raw material into biodiesel (approximately 15.441%). This could be due to the reduced residence time in the reactive distillation column and/or the turbulence resulting from the interaction between the two phases involved in the process. Thus, further studies need to be conducted to determine the optimum feed reactant flowrate to maximize the residence time and increase the degree of conversion. Alternatively, the length or number of modules in the reactive distillation column could be increased in order to increase the reaction rate.

However, the turbulence phenomenon involves strong interaction between the liquid and vapor phases and this should be further investigated to better understand the relevance in term of conversion rates. In addition, the use of other types of internal packing may improve the yield or the degree of conversion of the raw material to biodiesel.

4. Conclusions

The results reported herein can be used to conclude that:

- The reactive distillation column developed and used in this study is an apparatus with high operational flexibility to carry out esterification, transesterification, conventional and extractive distillation, under different conditions and evaluate the parameters which affect the conversion rate;

- b) The batch reactor can be used to support continuous processes, characterized by the use of reactive distillation columns, with high operational flexibility;
- c) The reduced residence time in reactive distillation columns limits the application of this technology process, which requires optimization to increase the conversion rate and obtain products with high purity;
- d) The reactive distillation column can be characterized as innovative, mainly when the reactant in excess is used as a circulating vapor, which is purified in the top module by extractive distillation and recycled to the bottom tank; and
- e) The reactive distillation column promotes a continuous process with potential to increase the production flow rate to meet industrial demand.

Acknowledgment

The author wishes to thank Prof. Dr. A. A. Chivanga Barros for your dedication to develop of this project, mainly for spend particular money to finance this study.

Conflict of interest

The author declares that there is no conflict of interest regarding the publication of this manuscript.

References

- Barros, A.A.C., Wust, E., Meier, H.F., Study of the technical-scientific feasibility of biodiesel production from fatty residues. *Eng. Sanit. Ambient* 13 (3), 255–262, 2008.
- Colombo, K.; Ender, L.; Santos, M.M.; Barros, A.A.C.; Production of Biodiesel from Soybean Oil and Methanol, Catalyzed by Calcium Oxide in a Recycle Reactor; *South African Journal of Chemical Engineering* 28, 19-25, 2019.
- Colombo, K., Biodiesel production via transesterification with heterogeneous catalysis using CaO as a catalyst. Master's thesis. Blumenau Regional University, 2013.
- Colombo, K.; Ender, L.; Barros, A.A.C.; The study of biodiesel production using CaO as a heterogeneous catalytic reaction. *Egypt. J. Petrol.* 26 (2), 341–349, 2017.
- Fernando D. Pitt, Anabela M. Domingos, A.A. Chivanga Barros; Purification of Residual Glycerol Recovered from Biodiesel Production, *South African Journal of Chemical Engineering*, Volume 29, 42-51, 2019.
- Luana Chiarello, Tuane Porto, A. A. Chivanga Barros, Edésio Simionatto, Vanderleia Botton, Vinicyus Wiggers; Bosting an Oil Refinery into a Biorefinery; *Angolan Mineral, Oil & Gas Journal*, Volume 1, 1-5, 2020.
- Semwal S., Arora A.K., Badoni R.P., Tulli D.K., Biodiesel production using heterogeneous catalysts., *Bioresour. Technol.* 102, 2151–2161, 2011.
- Stankiewicz, A.I.; Moulijn, J.A. Process intensification: Transforming chemical engineering. *Chem. Eng. Prog.* 96, 22–34, 2000.

- Cárdenas-Guerra, J.C.; López-Arenas, T.; Lobo-Oehmichen, R.; Pérez-Cisneros, E.S.A. Reactive distillation process for deep hydrodesulfurization of diesel: Multiplicity and operation aspects. *Comput. Chem. Eng.* 34, 196–209, 2010.
- Subawalla, H.; Fair, J.R. Design guidelines for solid-catalyzed reactive distillation systems. *Ind. Eng. Chem. Res.* 38, 3696–3709, 1999.
- Taylor, R.; Krishna, R. Modeling reactive distillation. *Chem. Eng. Sci.* 55, 5183–5229, 2000.
- Huss, R.S.; Chen, M.; Malone, M.F.; Doherty, M.F. Reactive distillation for methyl acetate production. *Comput. Chem. Eng.* 27, 1855–1866, 2003.
- Huang, K.; Wang, S.J. Design and control of a methyl tertiary butyl ether (MTBE) decomposition reactive distillation column. *Ind. Chem. Eng. Res.*, 46, 2508–2519, 2007.
- Kiss, A.A.; Novel Catalytic Reactive Distillation Processes for a Sustainable Chemical Industry. *Top Catal.* 62, 1132–1148 (2019). <https://doi.org/10.1007/s11244-018-1052-9>.
- Dib, F. H. Production of Biodiesel from Recycled Waste Oil; Master's thesis, Ilha Solteira (SP), 2010.
- Agência Nacional do Petróleo, Gás Natural e Biocombustíveis (ANP). Biodiesel [Internet]. Brazil [cited 2020 May 18]. Available from: <http://www.anp.gov.br/biocombustiveis/biodiesel>, 2020.