

BIO-OIL FROM RESIDUAL FRYING OIL: INFLUENCE OF THE 1M HCL RED MUD CATALYST ON PROCESS PERFORMANCE

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Abstract: Residual frying oil is a very abundant waste, which makes it easy and favorable to obtain and desire for industrial reuse. Taking into consideration, the large consumption of oils and diverse uses, a fact that generates inadequate disposal, causing environmental harm. The disposal of waste is generally done improperly and, recognizing these harms, interest is aroused in reuse and safe disposal with the aim of adding value and sustainable functionality.

Aiming at these characteristics, the work aimed to synthesize bio-oil through the reuse of residual frying oil with the use of red mud (LV) as a catalyst (5%, 10%, 15% and 20% m/m) in order to obtaining an increase in yield as well as studying the temperature behavior of the process. This way, the linear behavior of the process temperature over time was observed and the use of LV proved to be effective in breaking down the triglyceride molecules, with a 20% m/mo greater yield of bio-oil (68.73 %).

Keywords: Bio-oil; Residual oil; Catalyst; Red mud.

INTRODUCTION

The development of a biofuel whose central idea is the residual use of a renewable source is very relevant and promising for the technological and social environment, given the current market where taxes and inflation on the prices of products derived from Oil tends to increase as availability becomes low. The decrease in natural resources from non-renewable sources drives us to seek new alternatives, also taking into consideration, the other harms, in addition to future unavailability, there is concern about the ecosystem which, as is generally known, the environmental pollution caused by petroleum products generated during the combustion process are decisive in accelerating the greenhouse effect through the emission of

harmful gases such as carbon monoxide and sulfur compounds (MARZULLO, 2007).

The search for a new alternative to inhibit harmful effects such as the generation of gases is one of the factors that promotes the interest in synthesizing fuels using renewable sources, sources that could be classified as waste that have wide availability and low cost. Mainly those coming from vegetable sources, such as vegetable oil belonging to the chemical class of lipids. A class that is extremely abundant in nature and very easy to find, having in its composition a mixture of different chemical compounds, the most important of which are triacylglycerols, free fatty acids and phosphatides. (SANTOS, 2013).

Environmental pollution caused by the poor disposal of solid and liquid waste around the world is a serious problem that needs to be solved (SANTOS,2020). To recycle oil would not only remove a pollutant from the environment, but would allow the generation of an alternative source of energy as a renewable fuel. In order for the waste to be converted into biofuel, technologies must be applied to the reused raw material. Technological methods such as transesterification and cracking (thermal and thermocatalytic). Cracking presents greater benefits and attractive uses as it allows for a greater variety of fuel types (gasoline, kerosene and diesel) and less generation of by-products. Thermocatalytic cracking forms hydrocarbons similar to those of fossil origin, differentiating their singularities in the fuel generated due to the raw material and catalyst used. (NASCIMENTO,2021; BORGES et al., 2011).

Second National agency for petroleum, natural gas and biofuels – ANP, the production of biofuel synthesized byhydrotreatment of vegetable oil (in natura or residual), establishes the specification of green diesel, with specific quality control obligations to be met by

economic agents and means of mandatory commercialization in the national territory. Thus, the aim is to study the synthesis of a bio-oil from residual frying oils throughofcracking by evaluating product reviews against green diesel legislation. (BRAZIL, 2021).

Therefore, the objective of this study is to investigate the thermocatalytic cracking process of residual frying oil, catalyzed with Red Mud (LV) in order to obtain hydrocarbon mixtures, aiming to increase the yield and temperature behavior of the process.

MATERIALS AND METHODS

Feedstock: The raw material to be used is frying oil from residential kitchens.

Raw material treatment: To use residual frying oil as raw material in the pyrolysis process, it was necessary to filter and dehumidify it in an oven at 110°C, to improve its quality by removing solid residues and sediments in the same present. (Figure 1).

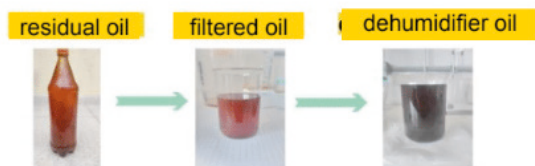


Figure 1 -Raw material treatment process

Pre-characterization of the frying oil: moisture, ash, specific mass, kinematic viscosity and acidity analyzes were carried out.

Humidity determination: (AOAC, 2012): The samples were placed in crucibles in triplicates. Afterwards, approximately 10 g of the sample was weighed. The samples were then taken to the greenhouse and remained there for twenty-four hours. After that, the material was removed from the oven and

taken to the desiccator for 30 minutes to cool and then be weighed.

Ashes:(AOAC, 2012): The analysis was carried out in triplicate, the crucibles were weighed and then approximately 2 g of the sample was weighed. The samples were taken to a preheated muffle furnace at 550° C for 6h. Then, the crucibles were transferred to the desiccator and allowed to cool for about 30 minutes. The material was weighed and the value obtained was noted.

Specific mass:(AOAC, 2012): A 10 ml pycnometer, previously calibrated, is used, then the sample is weighed.

Catalyst: For the production of biofuel, red mud was used, chemically activated with a 1M HCl solution, following the methodology of Oliveira (2019) and Oliveira (2020). Initially, the LV went through the drying process in an oven at 100 °C for 24 hours, comminution for 30 minutes, chemical activation at 1 mol/L with HCl in the mass ratio 2:3 LV:S (red mud, solvent). After 24 hours from the end of chemical activation, the catalysts were subjected to drying again at 100°C for 24 hours and then thermally activated in a muffle furnace at 550° for 2 hours.

THERMOCATALYTIC CRACKING PROCESS

The experimental process was carried out on a bench scale, as described by Santos (2013), Santos (2019) and Nascimento (2021). The tests were carried out in a cylindrical 304 mm stainless steel reactor with a volumetric capacity of 260 ml, heated by an oven with cylindrical ceramic resistances. The heating and temperature rate are controlled through the temperature controller and indicator, connected to a type K thermocouple located inside the reactor. The gases generated from

this reaction were condensed and the liquid Product was collected and stored for later analysis. To study temperature behavior over time, temperature sensors were inserted inside, in the middle and at the top of the reactor, as shown in Figure 2.

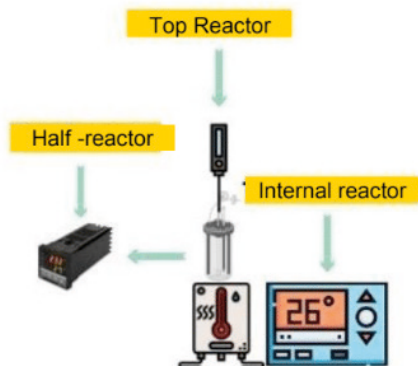


Figure 2 -Temperature indicators in the reactor

Starting from the determination of the sample mass of 70g measured on a semi-analytical balance, with a precision of 0.001 g, as well as the masses of 5%, 10%, 15%, 20% of the catalysts determined for the process. Soon after, the materials are placed in the stainless-steel reactor, the reactor is connected to the condenser, and the assembly is inserted into the cylindrical furnace (heater). Next, the process temperature was set to 400°C on the controller, with a heating rate of 10°C/min. (Figure 3).

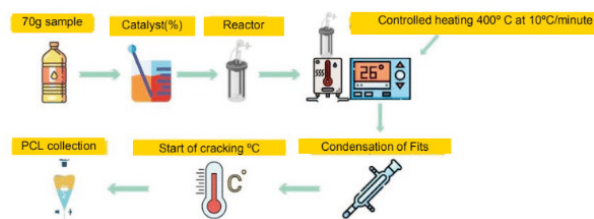


Figure 3 -Thermocatalytic cracking process

To study the variation in temperature Vs time, the temperature inside the reactor (Ti), in the middle of the reactor (Tm) and at the top of the reactor (Tt) was measured at intervals of 5 minutes. the gases being sent to

an exhaust system, and the solid part (coke) retained in the reactor. After carrying out the tests and cooling the system, for the purpose of carrying out the mass balance, the reactor and the collecting flask with the PCL will be subjected to new weighing. The samples will then be stored in vials to be subjected to future analyses. The yields of the cracking process are obtained from equations 1,2 and 3.

$$\times 100\eta_{PCL} = \frac{PCL}{OP} \quad (1)$$

$$\times 100\eta_{coque} = \frac{coque*}{OP} \quad (2)$$

$$\eta_{gás} = 100 - (\eta_{PCL} + \eta_{coque}) \quad (3)$$

PCL = Liquid Cracked Product

OP = Purified oil

Coke = Condensed (solid) constituent of the reaction

η = Yield

RESULTS AND DISCUSSION

PRE-TREATMENT OF RAW MATERIAL

The processing of the raw material, in its search for improvement, was confirmed through analyzes of moisture content, specific mass and ash, carried out in triplicate. The results were compared with the limits established by ANVISA (1999) and ANP No. 842 shown in Table 1.

PARAMETERS	RESULTS
Moisture	0.1701%
Especific mass	0.9083kg/m ³
Ashes	0.6404% (m/m)
Kinematic Viscosity 40°c	26.27 mm ² /s
Acidity	84.93MgKOH/g

Table 1 -Result of moisture, specific mass and ash analyses.

Data presented as mean \pm standard deviation of sample triplicates and duplicates

The moisture content was satisfactory as it presented a negligible percentage of the raw material. Low value which is a positive point, as the presence of water must be low or non-existent for the best use of the oil and thus enabling better performance of the catalyst in fractionation.

According to ANVISA (1999), the specific mass for clean soybean oil is 0.916 to 0.922 g/cm³. The specific mass of residual frying oil, 0.908 g/cm³, is outside the limits for refined oil, which can be explained by the fact that the storage time led to degradation, and also by the impurities acquired due to the frequency of use, which leads to the breakdown of fatty acids and also the absorption of moisture, factors that must be determining due to the slight difference to the standards of refined oils.

In the analysis for ash, the value of 0.6404 was obtained. According to ANP No. 842, the speculated limit is 0.01% (m/m). Thus, this result presents a theoretically large amount for biofuels, since this value results in a high amount of minerals, which is a negative point as a high concentration can reduce the calorific value and even cause engine corrosion.

Kinetic viscosity is one of the main properties evaluated in fluid products. The obtained value of 26.27 mm²/s is outside the limits accepted in ANP no. 842, which is speculated to be 4.5 mm²/s. The sudden difference in the evaluation of this parameter may have been caused by the degradation of the residual oil, due to excessive use and exposure to high temperatures. According to MARZULLO, (2007) these possible changes in these physicochemical properties can impact the resistance offered to flow.

This physical-chemical parameter is one of those that undergo the greatest changes as a result of the heating process due to the amount of free fatty acids present in oils. The value found (84.93MgKOH/g) was much higher

than the values found in the literature and even with the current standard (0.3MgKOH/g). This result suggests, therefore, that this oil presents a high level of degradation, and for the production of biodiesel, an improved treatment prior to synthesis is necessary to reduce the high acidity and not compromise the quality of the product formed ROSSI et al, (2018).

THERMOCATALYTIC CRACKING

The study of temperature over time is clearly represented in fractionation graphs. (Figure 3 to 7).

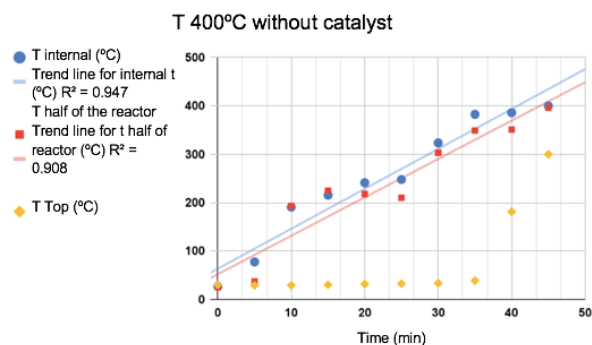


Figure 3- Cracking Without catalyst

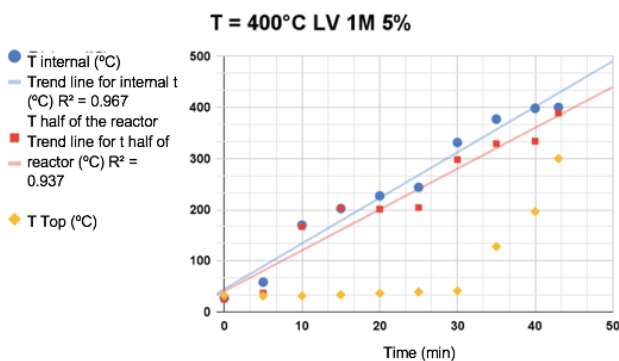


Figure 4- Cracking with 1 molar 5% LV catalyst

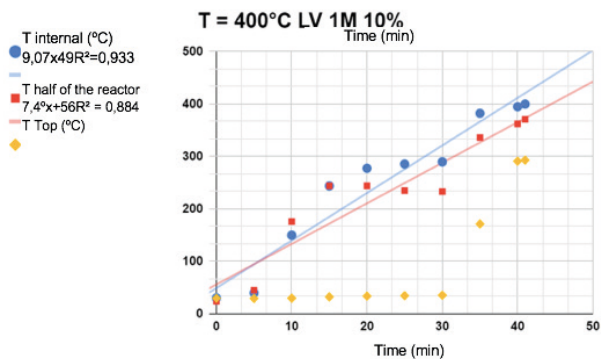


Figure 5- Cracking with 1 molar 10% LV catalyst

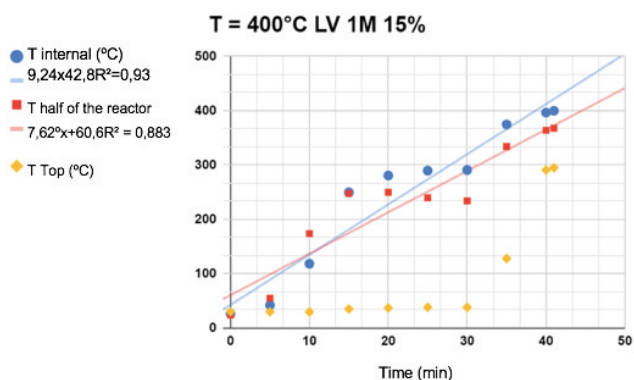


Figure 6- Cracking with LV catalyst 15%

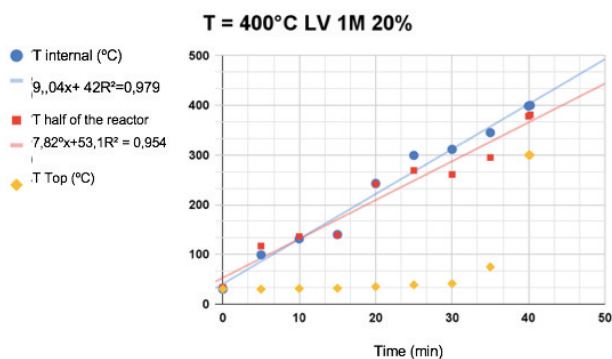


Figure 7- Cracking with LV 20% catalyst

From the graphs, it is possible to observe similarities in the cracking processes even with the variation in catalyst percentages, similarities that may be linked to the internal reaction of the red mud with the oil, as is the fact of temperature stabilization ($230^{\circ}C \sim 240^{\circ}C$), observed in the intervals between 10 min and 30 min of reaction. This temperature stability over time is caused by small explosions

of the catalyst due to the transition of the catalyst's crystalline phase, causing the release of energy through endothermic reactions NASCIMENTO, (2021). It was also found that increasing the catalyst percentage, LV 1M HCl, reduces the initial cracking temperature and consequently reduces the activation energy. In line with this, it appears that measuring the top temperature can be useful in determining the beginning of the molecular breakdown of triglycerides, verified by the sudden change in the angular coefficient.

The results of the influence of the amount of catalyst on the yields of the process phases were then shown in table 2.

	*Ti (°C)	PCL (%)	Coke (%)	Gas (%)
No LV	381.2	57.24	32.50	10.26
5% LV1M	377.2	63.39	22.34	14.27
10% LV1M	376.7	52.43	35.79	11.78
15% LV1M	376.0	54.29	32.94	12.77
20% LV1M	337.0	68.73	16.83	14.44

Table 2 -Income from PCL, Coke and Gas.

* Ti - Initial cracking temperature

Observing Ti, it is possible to state that the use of the catalyst led to a reduction in the initial cracking temperature, indicating a reduction in activation energy, probably due to the increase in the added catalyst, which can be seen in the process without LV, the temperature was ($381.2^{\circ}C$) and Ti with 20% LV 1 M was ($337.0^{\circ}C$) which presented a reduction of $44.2^{\circ}C$, that is, the activation energy decreases and is in line with what PEREIRA, (2017), The results show that, increasing the percentage of catalyst caused the initial cracking temperature for 30 minutes to decrease from 69 to $66^{\circ}C$.

The yield of the phases showed variations consistent with the increase in the percentage of catalyst. The highest yields of the liquid and gaseous phases were observed for the process with 20% LV, indicating that this percentage of catalyst achieved the highest conversion

of residual frying oil into bio-oil. In general, the use of red mud as a catalyst proved to be efficient in converting this waste into biofuel. This behavior is in accordance with Santos, (2013), Ferreira, (2023) and Oliveira, (2020).

It is notable that in the process yields, high rates of PCL formation were obtained both when carried out without catalyst (57.24%) and with 20% LV (68.39%). The opposite behavior (decrease in yield with an increase in the percentage of catalyst) was obtained by Bernar et al (2022) who carried out the pyrolysis of fats with activated carbon as a catalyst. While Mota et al (2014) obtained a yield of 65.86% for the liquid fraction when pyrolysis ($T = 450^{\circ}\text{C}$) of palm oil with 20% (m/m) of Na_2CO_3 as a catalyst.

It was also observed that the percentage of coke generated in the process was high in all tests, ranging from 16.83% to 35.79%, indicating the possibility of increasing PCL yield if part of this coke was broken, probably by the increase in temperature. Veloso (2012) and Santos (2019) observed in their cracking

experiments with sunflower oil, soybean oil and waste tire, respectively, that greater yields of liquid products were obtained as the temperature increased.

CONCLUSION

It can be concluded that the processing of the raw material and the use of red mud as a catalyst added to the better efficiency of the pyrolysis process and bio-oil productivity. It was also noted that the increase in the rate of breakdown of carbon chains was caused by the increase in catalytic concentrations (5%, 10%, 15% and 20%). It was observed from the graphs that the temperature inside and in the middle of the reactor was linear over time. The top temperature proved to be an important parameter to identify the beginning of cracking through the sudden increase in the angular coefficient. The yield of the phases obtained variations consistent with the increase in the percentage of catalyst and significant amounts regarding the liquid and gaseous part in the 20% LV fraction.

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