

# STUDY OF BIODIESEL PRODUCTION FROM WASTE COOKING OIL BY ETHYL TRANSESTERIFICATION AND ITS PURIFICATION WITH THE USE OF ACTIVATED CARBONS DERIVED FROM OLIVE PITS

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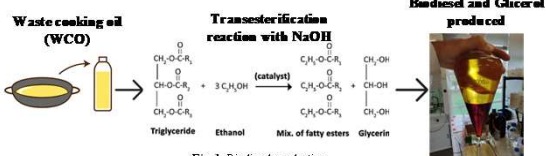
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## INTRODUCTION & MAIN OBJECTIVES

In recent years, a collective effort is made in search of alternative forms of energy through renewable and more friendly to the environment sources, currently, about 80% of the world consumption of energy comes from fossil fuels. The environmental problems associated with the use of these non-renewable fuels include air pollution and global warming. In this scenario, biodiesel presents itself as a renewable fuel, environmentally friendly and with similar characteristics to common diesel.

- The cost of conventional biodiesel production is higher than the production of diesel from petroleum, since it is produced mainly from high quality virgin oils, it is estimated that 70 to 80% of the total cost of biodiesel production is associated with the cost of their raw materials [1].
- Hence, biodiesel production from waste cooking oil (WCO) has become an economic opportunity and an environmental strategy to help address global renewable energy challenges and contribute to a sustainable society [2].



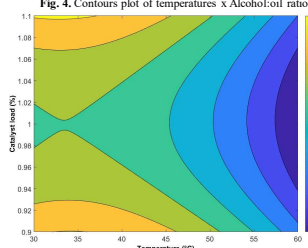
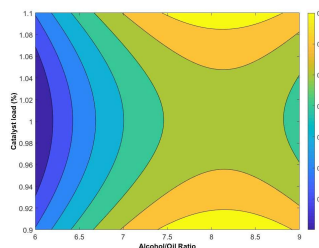
- Transesterification is the most used method to reduce the viscosity of vegetable oils through their conversion into biodiesel. It is a process by which alkyl esters are produced from chemical reactions between an alcohol and vegetable oils in the presence of a catalyst.
- Among the purification processes, the wet wash method, which uses water or acidified water to purify the esters, is the most commonly used [3].
- On average, for each liter of purified biodiesel, the amount of water needed for purification varies from 0.2 to 10 liters [3].
- Dry cleaning offers several advantages over wet cleaning, including ease of integration into an existing plant, shorter purification time, lower water consumption and lower effluent generation [4].
- Some cellulosic and lignocellulosic materials present adsorption potential for the purification of biodiesel [5].



- It is sought the study of ethylic biodiesel production from a WCO sample using a response surface methodology based on a Box-Behnken design with 3 parameters: alcohol/oil molar ratio, reaction temperature and catalyst load, and one response: biodiesel yield.
- The purification of biodiesel produced in optimal conditions is studied using natural adsorbents, based on olive pits, as well as the synthesis of different activated carbons through physical and chemical activation with different compounds.
- These adsorbents will be characterized and its adsorption capacity will be assessed, with the main objective of removing glycerol contaminants from the produced biodiesel, due to the serious problems caused by this substance in combustion engines.

## OPTIMIZATION OF REACTION PARAMETERS

- Temperature of 30°C
- Catalyst Load equal to 1%wt
- Alcohol:oil molar ratio of 7.5



## ACTIVATED CARBON PRODUCTION

- The production of activated carbon followed five different procedures, with carbonization being carried out in a muffle.

Adsorbent	Surface area (m <sup>2</sup> /g)	Micropore area (m <sup>2</sup> /g)
Precursor	1.3798	0.3166
H <sub>3</sub> PO <sub>4</sub> - 500°C	171.7740	153.6220
KOH - 800°C	61.1832	44.3936
Physical - 800°C	374.5070	351.8150
ZnCl <sub>2</sub> - 500°C	936.9390	833.2690
KOK - 750°C	869.7050	754.259
Commercial	295.3310	21.7928

## ADSORPTION STUDIES

- The two best activated carbons in terms of glycerol removal were AC-800°C and AC-ZnCl<sub>2</sub>, both with a removal greater than 70%.
- The  $\Delta H^\circ$  value show an endothermic adsorption and a physisorption process.
- The  $\Delta G^\circ$  value show a spontaneous process.
- Positive  $\Delta S^\circ$  values.

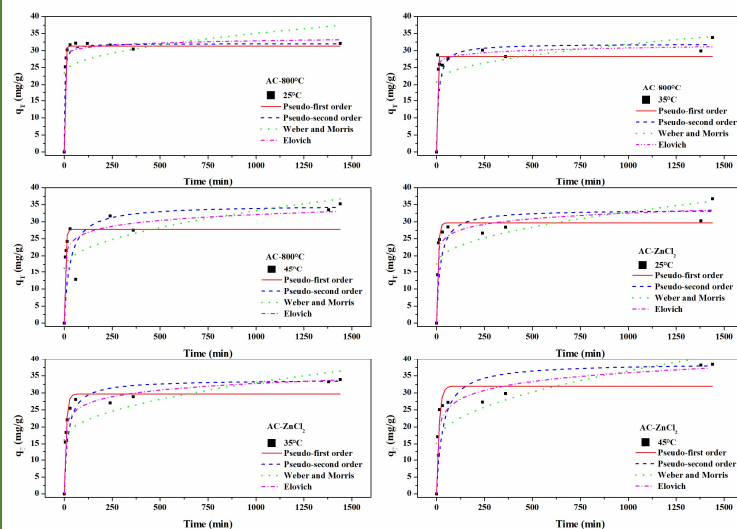
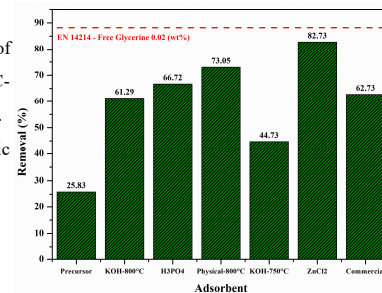


Table 2. Results of the thermodynamic analysis.

	T (°C)	$\Delta G^\circ$ (kJ/mol)	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol.K)	R <sup>2</sup>
800°C	25	-5.17			
	35	-5.71	10.89	53.89	0.9984
	45	-6.25			
ZnCl <sub>2</sub>	25	-5.10			
	35	-5.68	12.25	58.20	0.9878
	45	-6.26			

## ADSORPTION PROCEDURES

- Multiple adsorption steps and combination of dry washing and wet washing methodologies.
- Both coals studied provide the glycerol contents required by legislation.

Table 3. Results of the biodiesel purification.

Biodiesel Sample	Free Glycerol (wt%)	
	A	B
Initial Concentration	0.955 ± 0.023	0.238 ± 0.029
Fifth Wash	0.013 ± 0.001	0.013 ± 0.004
2 Adsorptions (AC - 800°C 5%)	0.035 ± 0.019	0.012 ± 0.002
2 Adsorptions (AC - ZnCl <sub>2</sub> 5%)	0.019 ± 0	0.02 ± 0.002
1 Wash + 1 Ads (AC - 800°C 5%)	0.021 ± 0.002	0.016 ± 0.005
1 Wash + 1 Ads (AC - ZnCl <sub>2</sub> 5%)	0.016 ± 0.001	0.015 ± 0

## CONCLUSIONS

- Best conditions found by the optimization of the transesterification reaction were: reaction temperature, 30°C, catalyst load, 1%wt, and alcohol:oil molar ratio, 7.5.
- Increasing the superficial area of the precursor (olive pits) reaching 936.94 m<sup>2</sup>/g for AC-ZnCl<sub>2</sub> and 374.51 m<sup>2</sup>/g for AC-800°C, provides good affinity for free glycerol adsorption, even in comparison to commercial adsorbents.
- Endothermic adsorption with physisorption as the main mechanism; positive value of  $\Delta S^\circ$  representing an increase in the disorder of the system, which may suggest a competition of the active sites of the adsorbent by the different impurities and solvent used; and negative  $\Delta G^\circ$ , representing a spontaneous process that is favored by increasing the temperature.
- Adsorption process can be a substitute for the conventional wet washing process, achieving the same degree of purity in biodiesel purified by both the methodologies (dry washing and wet washing) and reaching the free glycerol content determined by ASTM D6751/EN 14214 standards.

## ACKNOWLEDGMENTS

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