

STUDY OF BIODIESEL PRODUCTION FROM WASTE COOKING OIL BY ETHYL TRANSESTERIFICATION AND ITS PURIFICATION WITH THE USE OF NATURAL ADSORBENTS

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INTRODUCTION

In recent years, a collective effort is being done in search of alternative forms of energy through renewable and more friendly to the environment sources. Thus, currently, about 80% of the world consumption of energy comes from fossil fuels. Some of the most severe environmental problems associated with the use of non-renewable fuels include air pollution and global warming. In this scenario, biodiesel presents itself as a renewable fuel, environmentally friendly and with similar physicochemical 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, moreover 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].

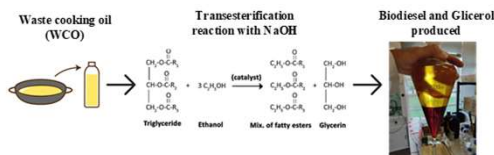


Fig. 1. Biodiesel production.

- 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 used method [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 volume generation [4].
- Some cellulosic and lignocellulosic materials present adsorption potential for the purification of biodiesel [5].



Fig. 2. Activated carbon production and adsorption.

OBJECTIVES

- This work presents the optimization of the 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.
- Six different types of activated carbons are prepared from olive pits using physical and chemical activation methods. Then, all the prepared adsorbent carbon-based materials are characterized using several analytical techniques.
- Finally, the removal of glycerol contaminants from the produced biodiesel is evaluated using the most promising adsorbent materials. In this task, the kinetics of adsorption, the adsorption equilibrium, and multiple adsorption steps with combination of wet and dry washing strategies will be studied.

OPTIMIZATION OF REACTION PARAMETERS

Optimal conditions

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

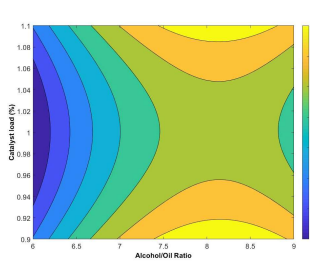


Fig. 3. Contours plot of alcohol:oil ratio x catalyst load (%).

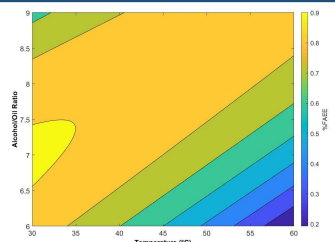


Fig. 4. Contours plot of temperatures x alcohol:oil ratio.

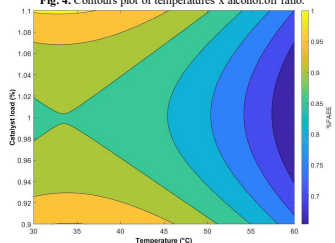


Fig. 5. Contours plot of temperatures x catalyst load (%).

ACTIVATED CARBON PRODUCTION

Table 1. Textural properties of the six prepared adsorbent materials and an extra commercial studied material.

Adsorbent	Surface area (m ² /g)	Micropore area (m ² /g)	Global Yield
Precursor	1.38	0.32	-
H ₂ PO ₄ - 500°C	171.77	153.62	35.96%
KOH - 800°C	61.18	44.39	22.58%
Physical - 800°C	374.51	351.81	25.85%
ZnCl ₂ - 500°C	936.94	833.27	49.37%
KOH - 750°C	869.70	754.26	21.23%
Commercial	295.33	21.79	-

ADSORPTION STUDIES

- The two best activated carbons in terms of glycerol removal were AC-800°C and AC-ZnCl₂, both with a removal greater than 70%.

- The models that best fit the experimental points were the Pseudo-second-order for the kinetics and Sips for the isotherm points (See Table 2).

- For these two adsorbents (See Table 3):
 - Positive ΔH° values show endothermic adsorption and a physisorption process.
 - Negative ΔG° values show a spontaneous process.
 - ΔS° values are positive.

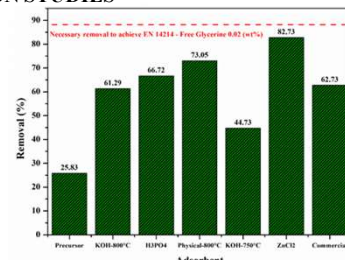


Fig. 6. Preliminary results of purification.

KINETIC AND ISOTHERM STUDIES

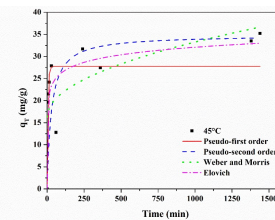


Fig. 7. Kinetic plot of adsorption of glycerol in AC- 800°C - T= 45°C.

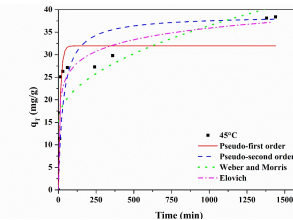


Fig. 8. Kinetic plot of adsorption of glycerol in AC- ZnCl₂ - T= 45°C.

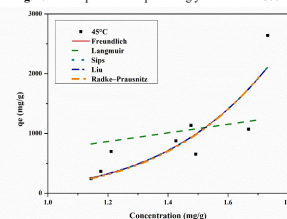


Fig. 9. Isotherm plot of adsorption of glycerol in AC- 800°C - T= 45°C.

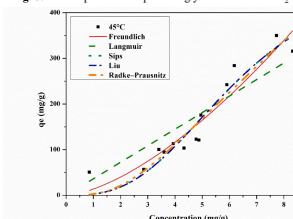


Fig. 10. Isotherm plot of adsorption of glycerol in AC- ZnCl₂ - T= 45°C.

Table 2. Values of R² of kinetics and isotherms for different temperatures.

Models	T (°C)	AC- 800°C		AC- ZnCl ₂	
		Pseudo-second order	Sips	Pseudo-second order	Sips
Pseudo-second order	25	0.9998	0.9856	0.9942	0.9983
	35	0.9985	0.9954	0.9985	0.9954
Sips	25	0.9164	0.2740	0.9164	0.2740
	45	0.6304	0.8968	0.6304	0.8968

Table 3. Results of the thermodynamic analysis.

AC	T (°C)	ΔG° (kJ. mol ⁻¹)	ΔH° (kJ. mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)	R ²
800°C	25	-5.17	10.89	53.89	0.9984
	35	-5.71			
ZnCl ₂	25	-6.25	12.25	58.20	0.9878
	35	-5.10			
	25	-5.68			
	45	-6.26			

ADSORPTION PROCEDURES

- Multiple adsorption steps and combination of dry washing and wet washing analytical techniques.
- Both selected adsorbents achieve the glycerol contents maximum of 0.02%wt required by ASTM D6751/EN 14214.

Table 4. Experimental glycerol content after the biodiesel purification using different adsorbents and washing techniques.

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 ₂ 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 ₂ 5%)	0.016 ± 0.001	0.015 ± 0

CONCLUSIONS

- Best conditions found by the optimization of the transesterification reaction: 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 m²/g for AC-ZnCl₂ and 374.51 m²/g for AC-800°C, provides good affinity for free glycerol adsorption, even in comparison to commercial adsorbents.
- The best adjustments found were the pseudo-second order for the kinetics and Sips for the Isotherm points, showing good fits for all temperatures of the study.
- Endothermic adsorption with physisorption as the main mechanism; positive value of ΔS° 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 ΔG° , 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.
- With the aim of further reducing water consumption, the best methodology for purifying biodiesel was found using AC-ZnCl₂ 5% and two adsorption steps.

ACKNOWLEDGMENTS

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