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Kinetics of biofuel generation from deodorizer distillates derived from the physical refining of olive oil and squalene recovery

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ABSTRACT

The recovery of squalene from deodorizer distillate derived from the physical refining of olive oil was evaluated by combining pressurized acidic esterification in a closed system with vacuum distillation. Esterification was carried out at 341, 359, 366, 391 and 395 K. The reaction at 395 K was found to be satisfactory as it decreased the acid value by 99.21% and generated a FAME concentration of 67.53% within 1 h. In order to demonstrate that the generation of FAME from deodorizer distillate was mainly due to the transformation of FFA, the reaction extent, which characterizes the reaction and simplifies calculations, was evaluated for FFA removal and the generation of FAME. Subsequent vacuum distillation allowed the separation of one fraction rich in FAME (94%), which can be used as a biofuel and accounted for 85% of the initial mass, and another fraction that was rich in squalene (78%) and may be used for manufacturing pharmaceutical products. The global squalene yield was 117 g kg^{-1} initial deodorizer distillate.

1. Introduction

During the physical refining of olive oil a residual oily fraction is obtained. This fraction, which is called deodorizer distillate, is a very complex mixture containing free fatty acids (FFA), phytosterols, tocopherols, sterol esters, hydrocarbons and breakdown products of fatty acids, aldehydes, ketones and acylglycerols. Moreover, deodorizer distillate contains squalene, which is a hydrocarbon and a triterpene, and is a natural and vital part of the synthesis of cholesterol, steroid hormones, and vitamin D in the human body, playing a crucial role in structural and specific metabolic functions. Squalene has wide applications as a textile lubricant and it is used in cosmetics, and more recently as an immunologic adjuvant in vaccines [1,2]. Squalene may be obtained from shark liver oil, but behalf of protecting marine ecosystems, there is a need to develop a systematic technology that permits recovering of vegetal-squalene in high purity and in short time. Olive oil contains around 98%–99% triglyceride and 1%–2% of minority compounds including squalene, FFA, wax and vitamins; specifically, olive oil contains 0.2%–0.7% squalene [3].

Olive oil is frequently refined or distilled in order to obtain a high purity final product and a residual stream containing squalene. Vacuum distillation is commonly used for this purpose, but the technical procedure is questionable as squalene is thermolabile [4]. Moreover, this direct physical refining generates high amounts of degradation products and

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results in the loss of n-alkanes. On the other hand, the saponification of FFA is one of the most frequent methods employed to obtain squalene from deodorizer distillate derived from the physical refining of olive oil [5]. Nevertheless, the main disadvantage of saponification is that a high percentage of squalene is retained in the soapy phase, which is a non-valuable liquid stream. Given that physical refining deodorizer distillates contain high concentration of FFA and small amounts of mono, di and triglycerides, they are an interesting substrate for producing fatty acid methyl esters (FAME) that may be used as a renewable fuel [6]. Additionally, the esterification enables squalene to be concentrated by a subsequent vacuum distillation of the methyl ester rich phase.

Numerous studies have shown the suitability of the esterification reaction applied to different raw materials. Khan et al. [7] reported a 95% reduction in FFA in raw palm oil by carrying out the esterification reaction for 3 h at 338 K with a methanol:oil molar ratio of 15:1 and a mass fraction of 0.5% sulfuric acid as an acidic catalyst. This reaction can be carried out at atmospheric pressure [8] or in a closed system [9]. On the other hand, Akgün [10] studied the esterification of olive oil deodorizer distillate with supercritical methanol followed by an extraction of squalene using supercritical CO_2. The optimal results were obtained at a temperature of 325 K, pressure of 10.48 MPa and extraction time of 10,800 s. Although refining with carbon dioxide under supercritical conditions seems to be more advantageous than conventional distillation techniques, the main drawback is that the economic investment and energy requirements could make the process uncompetitive from an economic standpoint [11]. In contrast, vacuum distillation after the esterification process allows the FAME to be separated in the distillation heads at a lower temperature than if raw olive oil is directly distilled, while leaving squalene in the distillation tail [12,13]. This is advantageous given that squalene is a thermolabile compound.

This study derives from the need to develop sustainable industrial processes, while increasing the competitiveness of the final product. The main purpose of this study was to evaluate the valorization of deodorizer distillate derived from the physical refining of olive oil by carrying out an esterification step to obtain FAME followed by a vacuum distillation post-treatment to recover the remaining squalene. Moreover, a kinetic model to predict the behavior and time required for the esterification has been formulated and assessed. The model describes the variation in FFA and FAME concentrations with time (reaction extent) under different operational conditions.

2. Materials and methods

2.1. Substrate

The raw material utilized in this work was olive oil deodorizer distillate collected by the Pradomudo, S.L. company (Spain). Deodorizer distillates derived from the physical refining of olive oil produced from olives harvested in the provinces of Córdoba, Jaén and Seville. These provinces are located in the region of Andalusia (south of Spain), which is one of the main production areas of olive oil in the world. The olives were harvested from olive trees belonging to the specie *Olea europaea*, during the period 2009–2010. Once the olive oil was extracted and refined by the company Pradomudo S.L., the deodorizer distillates were stored hermetically under isothermal conditions at 277 K. The experiments were carried out during the subsequent weeks to avoid possible modifications in the deodorizer distillates composition due to rancidity. The deodorizer distillates composition did not show significant variation among different harvesting periods; just little variations (<5%) could be observed in its acidity content, which would modify slightly the final biofuel production yield. The deodorizer distillate had an acid value of 133 g kg^{-1}, expressed as KOH content. Additional characteristics of this deodorizer distillate are shown in Table 1.

2.2. Experimental set-up

FFA removal and the generation of FAME depend on the well-known esterification reaction:

$$R_1{-}COOH + R_2{-}OH \leftrightarrow R_1{-}COOH{-}R_2 + H_2O$$

which is catalyzed by acids. In this work, R_1 was a linear chain of 14–22 carbon atoms containing a variable number of unsaturations depending on the particular origin of the raw material, and R_2 was a methyl radical. This reaction is homogeneous since methanol is soluble in deodorizer distillate as is its main components (FFA and squalene). However, this requires stirring in order to correctly mix the fluidized deodorizer distillates and prevent mass transfer control [14].

Table 1 – Chemical analysis of olive oil deodorizer distillate and fatty acid profile (free and linked acids).

Variable	Mass fraction (%)	Variable	Mass fraction (%)
FFA (oleic acid)	66.67	Squalene	13.00
Monoglyceride content	0.02	Aliphatic wax (C40 + C42 + C44 + C46)	1.02
Diglyceride content	0.05	Sterol and triterpene wax	0.96
Triglyceride content	0.80	Others (vitamins, phenol compounds, degradation products from olive oil purification, etc.)	17.48
Fatty acid profile	**Mass fraction (%)**	**Fatty acid profile**	**Mass fraction (%)**
C14:0 Tetradecanoic (myristic)	0.16	C18:3 Octadecatrienoic (linolenic)	2.14
C16:0 Hexadecanoic (palmitic)	16.32	C20:0 Eicosanoic (arachidic)	0.93
C18:0 Octadecanoic (estearic)	3.19	C20:1 Eicosenoic (gadoleic)	1.19
C18:1 Octadecenoic (oleic)	59.22	C22:0 Docosanoic (behenic)	0.17
C18:2 Octadecadienoic (linoleic)	10.47	C22:1 Docosenoic (erucic)	6.22