



Production of bio-hydrocarbons by hydrotreating of pomace oil



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H I G H L I G H T S

- Production of renewable liquid hydrocarbons through pomace oil hydrotreatment.
- Hydrogenation at lower hydrogen pressure with catalysts commonly used in petrochemical industry.
- Analysis of pyrolysis pre-treatment of pomace oil on the overall hydrotreatment process.
- Comparison of the two-step process (pyrolysis + hydrotreatment) with single pyrolysis or hydrogenation.
- Analysis of hydrogenated products applications as bio-chemicals.

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Olive pomace oil is a by-product from the olive oil industry that is still being used in the food industry as a low value vegetable oil. Crude olive pomace oil needs to be refined and is blended with virgin olive oils before being used as edible oil. The detection of toxic compounds led to more restricted legislation and to the search of alternative valorisation processes, such as hydrotreating to obtain bio-hydrocarbons. Hydrotreating of olive pomace oil at moderate temperatures (from 300 to 430 °C) and in presence of initial hydrogen pressure of 1.1 MPa led to triglycerides destruction and to their conversion into a large range of organic compounds with predominance to hydrocarbons. Even without any catalyst, conversions into hydrocarbons were always higher than 90% (v/v). Catalyst presence, such as: CoMo/Al₂O₃, FCC (fluid catalytic cracking) or HZSM-5 changed hydrogenated liquids composition. The highest content of alkanes was obtained with CoMo catalyst, while FCC and HZSM-5 led to the highest contents of aromatic compounds. The results obtained showed that olive pomace oil can be efficiently converted into bio-hydrocarbons with a wide range of applications. It was also studied the effect of pyrolysing olive pomace oil prior to its hydrotreating. Pyrolysis pre-treatment seems to have favoured hydrotreating process by promoting initial cracking reactions. Thus, it was possible to increase the production of liquid compounds with a higher content of light molecules. However, the advantages of using a more complex two steps process still need to be proven.

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1. Introduction

Biofuels for transport sector has become a political priority of the European Union (EU) in recent years. The use of endogenous resources such as wastes, residues, non-food cellulosic material and wood-cellulosic material for biofuels production will help to reach EU targets without the use of agricultural areas for energy production. Olive pomace oil is the oil obtained by treating olive pomace with solvents or other physical treatments to obtain crude olive pomace oil, which is not suitable to be used as edible oil. After this crude oil refining, a refined olive pomace oil is obtained, whose free acidity, expressed as oleic acid, has to be not more than 0.3 g

per 100 g and other characteristics has to correspond to those defined in EU Regulations [1]. Refined olive pomace oil is blended with virgin olive oils. The free acidity of the blend has to be not more than 1 g per 100 g, according to EU Regulations [1].

In the extraction process used for crude olive pomace oil are commonly used high temperatures that may lead to the formation of toxic compounds [2], such as polycyclic aromatic hydrocarbons (PAHs). High PAH levels have been recently found in pomace oil [3], some of those already detected are considered potentially carcinogenic, either alkylated or unalkylated [4]. Thus, the International Olive Oil Council has recommended olive oil producers to adopt a maximum limit of 2 µg/kg for benzo(a)pyrene content, determined according to ISO standard 15302 [5]. Though, these measures were taken to restore consumer confidence in olive pomace oil, the used of olive pomace oil for food purposes, may be compromised in the future. Therefore, it is important to find

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