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Production of bio-hydrocarbons by hydrotreating of pomace oil

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HIGHLIGHTS

- 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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ABSTRACT

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: $CoMo/Al_2O_3$, 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.

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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alternatives for these oils valorisation and application, due to the amounts produced annually. About 95% of global production of olive oil is concentrated in the Mediterranean basin, where the producing countries of the European Union (Spain, Italy, Greece, France and Portugal) represent about 76% of world production. Worldwide olive pomace oil production was around 220 thousand tonnes in 2001, being more than 75% from EU countries [6].

Olive pomace oil hydrotreating at moderate temperatures to produce liquid biofuel may be a viable option for its valorisation. Vegetable oils are mostly formed by triglycerides, which are destroyed during hydrotreating and converted into smaller molecules: diglycerides, monoglycerides, carboxylic acids, hydrocarbons, etc. to produce HVO (hydrogenated vegetable oil) to be used as biofuels or biochemicals.

The formation of hydrocarbons requires oxygen removal from the initially formed compounds and different chemical reactions may happen: decarboxylation (1), decarbonylation (2) and hydrodeoxygenation (or dehydration/hydrogenation) (3) [7]. These reactions release H_2O, CO and CO_2. During hydrotreating process, cracking reactions also occur, the small radicals formed are stabilised by hydrogen addition, and thus gaseous molecules are expected to be formed, leading to the increase of gases yield.

$$\text{R-CH}_2\text{-COOH} \leftrightarrow \text{R-CH}_3 + \text{CO}_2 \quad (1)$$

$$\text{R-CH}_2\text{-COOH} + \text{H}_2 \leftrightarrow \text{R-CH}_3 + \text{CO} + \text{H}_2\text{O} \quad (2)$$

$$\text{R-CH}_2\text{-COOH} + 3\text{H2} \leftrightarrow \text{R-CH}_2\text{-CH}_3 + 2\text{H}_2\text{O} \quad (3)$$

Several vegetable oils have been widely hydrogenated mainly with the aim of producing bio-fuels with similar composition to petroleum derived fuels to allow their use in conventional motors without legal restrictions. Several authors have studied rapeseed oil hydrotreating [8–13] and the successful production of bio-fuels has been reported, especially when high hydrogen pressures and specific catalysts are used in the hydrotreating process. Priecel et al. [8] reported that both NiMo–alumina/meso and NiMo–alumina catalysts were suitable for rapeseed oil hydrotreating, though the first catalyst showed better deoxygenation performance, due to its higher specific surface area and total pore volume. At 340 °C, under hydrogen pressure of 7 MPa and in presence of Ni–Mo/alumina hydrorefining catalysts, Šimáček et al. [9] converted rapeseed oil into hydrocarbons with mainly C_{17} and C_{18} n-alkanes. Sotelo-Boyás et al. [13] also reported that the hydrotreating of rapeseed oil in presence of Ni–Mo/γ-Al_2O_3 led to liquid hydrocarbons from C_{15} to C_{18} and with boiling temperature in the range of those of diesel fuels.

Sunflower oil hydrotreating has been studied by several researchers [7,14–16] with the aim of optimising experimental conditions, mainly: reaction temperature and time, hydrogen pressure and catalyst type. The main challenge has been the production of liquid biofuels with properties similar to those of fossil fuels to allow the use in conventional burning devices. CoMo/Al_2O_3 [14], HZSM-5 [15] and NiMo/Al_2O_3 [7] have been the most studied catalysts. Krár et al. [14] results showed that at 380 °C, at 40–60 bar hydrogen pressure and in presence of CoMo/Al_2O_3 catalyst, 100% of triglycerides in sunflower oil were converted into alkanes.

Other vegetable oils have also been hydrogenated. Choudhary and Phillips [17] reviewed the catalytic hydrodeoxygenation of oils with high content of triglycerides and reported the influence of the main parameters: nature of feedstock, operating conditions and catalyst type. Guzman et al. [18] hydrogenated palm oil in presence of NiMo/γ-Al_2O_3 at 40–90 bar of hydrogen and obtained alkanes in the range of those of diesel oils (C_{15}–C_{18}) with good cetane index.

A blend of oleic acid and tripalmitin (molar ratio 1:3) was used as a model feedstock in hydrodeoxygenation tests at 325 °C with 5 wt% of Pt/γ-Al_2O_3 catalyst for producing renewable diesel oil. At temperatures higher than 325 °C Madsen et al. [19] obtained high conversions of both triglycerides and free fatty acids.

Other types of vegetable oils have also been hydrogenated. Liu et al. [20] hydrotreated jatropha, canola and palm oils. Several catalysts were tested: Ni–Mo/H-Y, Ni–Mo/HZSM-5 and Ni–Mo/SiO_2. The last one led to the best biodiesel composition, as the predominant products from jatropha oil hydrotreating were: n-$C_{18}H_{38}$, n-$C_{17}H_{36}$, n-$C_{16}H_{34}$ and n-$C_{15}H_{32}$. The other two catalysts led to a large amount of gasoline-ranged hydrocarbons. Kwon et al. [21] deoxygenated canola oil at temperatures between 300 and 400 °C, under hydrogen initial pressure in the range of 18.25–85.13 bar in presence of NiMo/γ-Al_2O_3. And found that canola oil was converted mainly into heptadecane and octadecane. Cooking oil hydrotreating has also been studied [22–24]. Though cooking oil was completely converted into hydrocarbons, the presence of Ni based catalysts was more suitable for hydrodeoxygenation reactions than CoMo catalyst, as the formation of olefin was prevented, Toba et al. [22].

The available knowledge about vegetable oils hydrotreating was applied to olive pomace oil with the aim of developing an alternative applications and valorisation to its traditional use. The effect of experimental conditions on oil hydrotreating, namely, reaction temperature and reaction time was studied with the aim of selecting the most favourable conditions to convert olive pomace oil into valuable products. The performance of commercial catalyst like cobalt and molybdenum (CoMo/Al_2O_3), FCC (fluid catalytic cracking) and HZSM 5 was also studied. Krár et al. [15] and Toba et al. [22] have reported that CoMo based catalysts are selective for the production of heavy hydrocarbons with carbon atoms in the range of those of diesel. The other two catalysts were selected due to their huge utilisation in petrochemical industry and also because some authors have also reported the good performance of zeolites in vegetable oils hydrotreating [18,25]. The main objective of this work is the production of renewable valuable liquid hydrocarbons with a wide range of applications, including as biofuels.

2. Experimental part

In Fig. 1 is shown the experimental installation used for hydrotreating tests. The 1L batch reactor was connected to a PID programmable controller for temperature control. After the introduction of the olive pomace oil, the reactor was closed, purged three times with nitrogen and pressurised to a pre-set value with hydrogen. The reaction was carried at the pre-settled reaction temperature during the defined reaction time. After cooling down till room temperature, gaseous and liquid products were collected, measured and analysed.

Gases were analysed by gas chromatography (GC), using a HP 6890 Hewlett–Packard gas chromatograph. The contents of carbon oxides (CO and CO_2), hydrogen (H_2), nitrogen (N_2), oxygen (O_2), methane (CH_4), ethane (C_2H_6), C_3H_8 (propane) and other gaseous hydrocarbons were determined. Gases density was determined by standard IP59-Method C [26].

Liquids were distilled at atmospheric and at reduced pressure conditions. Three fractions were obtained: light fraction, with boiling point below 150 °C, heavy fraction with boiling point between 150 and 340 °C and residual fraction, whose boiling point was higher than 340 °C. Light and heavy fractions were analysed by GC–FID (gas chromatography with flame ionisation detector) to find out triglycerides conversion into hydrocarbons, free fatty acids, monoglycerides and diglycerides. A Thermo Trace GC 2000 gas chromatograph with programmed temperature vaporization injector (PTV) and a flame ionisation detector (FID) of the brand