



Hydrogenation of rapeseed oil for production of liquid bio-chemicals

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ABSTRACT

The main objective of rapeseed oil hydrogenation tests was the production of liquid bio-chemicals to be used as renewable raw material for the production of several chemicals and in chemical synthesis to substitute petroleum derived stuff. As, hydrogenation of vegetable oils is already applied for the production of biofuels, the work done focused in producing aromatic compounds, due to their economic value. The effect of experimental conditions on rapeseed oil hydrogenation was studied, namely, reaction temperature and time with the aim of selecting the most favourable conditions to convert rapeseed oil into liquid valuable bio-chemicals. Rapeseed oil was hydrogenated at a hydrogen initial pressure of 1.10 MPa. Reaction temperature varied in the range from 200 °C to 400 °C, while reaction times between 6 and 180 min were tested. The performance of a commercial cobalt and molybdenum catalyst was also studied. The highest hydrocarbons yields were obtained at the highest temperature and reaction times tested. At a temperature of 400 °C and at the reaction time of 120 min hydrocarbons yield was about 92% in catalyst presence, while in the absence of the catalyst this value decreased to 85%. Hydrocarbons yield was even higher when the reaction time of 180 min was used in the presence of catalyst, as the yield of 97% was observed. At these conditions hydrocarbons formed had a high content of aromatic compounds, around 50%. For this reason, the viscosity values of hydrogenated oils were lower than that established by EN590, which together with hydrogenated liquids composition prevented its use as direct liquid fuel to substitute fossil gas oil for transport sector. However, hydrocarbons analysis showed the presence of several valuable compounds that encourages their use as a raw material for the production of several chemicals and in chemical synthesis.

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1. Introduction

Nowadays, modern society relies heavily on energy consumption using mostly solid, liquid or gaseous fuels from fossil sources. Combustion of such fuels has led to increasing CO₂ emissions, this together with the depletion of existing reserves, makes crucial the development of alternatives fuels. European Union wishes to increase the share of renewable sources in energy production, including the production of biofuels for the transportation sector and consequently research and development activities have been encouraged and supported. Fatty acid methyl esters (FAMES), or biodiesel, is produced by transesterification of vegetable oils with methanol. Many fats contain triglycerides, which can be transesterified to produce FAME, however, in Europe are usually used rapeseed oil, soybean oil, sunflower oil and palm oil.

FAME has been used as diesel fuel for many years in Europe, blended with petroleum derived diesel fuel, at amounts lower than 10%, because of FAME different chemical compositions. Some motor manufacturers defend that during combustion some

problems may arise that damage combustion devices or lowers their performance, however, it has been claimed that FAME use as a pure component, without blending, does not affect combustion devices. Hydrogenated Vegetable Oil (HVO) is another option to use vegetable oils as biofuels. HVO is produced by catalytic hydrogenation and its composition is similar to petroleum derived fuels, thus allowing its use in conventional motors without legal limitations. HVO is still a first generation fuel, but it may present several advantages in relation to FAME, namely: superior cold weather properties, higher heating value, higher cetane number, and the process by-product, propane, has better options than glycerol by-product. On the other hand, they may be used in conventional motors without the need of blending with conventional fuels.

Rapeseed oil has been widely studied for the production of bio-fuels via hydrogenation [1–6] with the aim of producing liquid biofuels with the right properties to be used in conventional transportation vehicles. Hydrogenation of rapeseed oil may convert fatty acid triglycerides into hydrocarbons. During triglycerides hydrogenation some chemical bonds are broken down, thus they may be converted into monoglycerides, diglycerides and carboxylic acids, which may be converted into alkanes by three different

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pathways: decarboxylation, decarbonylation and hydrodeoxygenation.

Catalytic hydrogenation improves vegetable oils conversion into suitable biofuels. Ravasio et al. [1] tested different supported copper catalysts to study the effect of catalysts preparation method, the support used and the activation treatment in rapeseed oil hydrogenation and found that 8% Cu/SiO₂ destroyed the trienic component C18:3, reduced considerably the dienic one and the C18:1 compounds content increased till 88% with notable oxidation stability. Priece et al. [2] also studied the influence of catalyst preparation in rapeseed oil deoxygenation by sulfided Ni-Mo-alumina catalysts with different distribution of Ni species and found higher activity in catalysts with higher population of octahedral nickel species than in those with higher population of tetrahedral nickel species. These authors also reported that Ni-alumina catalysts promoted rapeseed oil deoxygenation, through the hydrodecarboxylation pathway and the formation of C₁₇ hydrocarbons, while Mo-alumina catalysts favoured the hydrodeoxygenation pathway and the formation of C₁₈ hydrocarbons [2].

Šimáček et al. [3] hydrogenated rapeseed oil over a temperature range from 260 to 340 °C and under a pressure of 7 MPa in presence of three Ni–Mo/alumina hydrorefining catalysts in a laboratory flow reactor. Reaction products were affected by reaction conditions, as at temperatures lower than 310 °C, the final organic liquid product contained fatty acids and triglycerides, but at higher reaction temperatures only hydrocarbons were detected, mainly C₁₇ and C₁₈ n-alkanes and about 40 wt.% of i-alkanes C₁₆–C₁₈. In a more recent publication [4] the same authors blended the organic liquid product obtained at 360 °C and 7 MPa in concentrations from 5 to 30 wt.% with mineral diesel fuel. Most of the standard parameters of these blends were similar to or even better than those of pure mineral fuels, meeting the European diesel fuel specification EN 590. But the low-temperature properties were worse (pour point higher than +20 °C), which prevented the use of the organic liquid product obtained by hydrogenation in the pure form. The hydrogenation of 5 wt.% of rapeseed oil mixed with pure petroleum vacuum distillate at 420 °C, under a hydrogen pressure of 18 MPa and in presence of a commercial Ni–Mo catalyst led to a final product with acceptable low-temperature properties (cloud point: 23 °C, CFPP: 24 °C) and similar to those obtained from pure petroleum raw material [5]. Šimáček et al. [5] reported that the rise of hydrogenation temperature from 400 to 420 °C allowed decreasing the content of n-heptadecane and n-octadecane in the final product by increasing the formation of i-alkanes, which improved the low-temperature properties of the co-processed product. According to these authors the hydrogenation of petroleum raw material blended with vegetable oil may be a potential alternative to produce green diesel using refinery technologies already known.

Rapeseed oil cracking studied in the presence of different catalysts and at temperatures from 350 to 440 °C under atmospheric pressure were reported by Buzetzi et al. [6]. The yield of the liquid reaction products changed between 85 and 90 wt.% and presented paraffins, olefins and fatty acids. Due to the presence of oxygenated compounds, viscosity and density values were higher than those permitted by EN 590 standard. However, mixtures of 3–7 vol.% of these organic products with fossil diesel fuels allowed to meet the requirements of EN 590 standard.

Sotelo-Boyás et al. [7] studied the effect of three different catalysts (Pt/H-Y, Pt/H-ZSM-5, and sulfided NiMo/γ-Al₂O₃) in hydrocracking of rapeseed oil at a temperature range from 300 to 400 °C, initial hydrogen pressures from 5 to 11 MPa and reaction time limited to 3 h. the conversion of triglycerides and fatty acids into hydrocarbons was reported to be highly affected by pressure and temperature. Pt-zeolite catalysts had a strong catalytic effect in cracking and hydrogenation reactions, producing more iso-

n-paraffins in the range of C₅–C₂₂. On the other hand, the highest yield of liquid hydrocarbons with the boiling temperature in the range of those of diesel fraction, with compounds from C₁₅ to C₁₈, was obtained in presence of Ni–Mo/γ-Al₂O₃.

A basic thermodynamic model was proposed to evaluate vegetable oil conversion into hydrocarbons by Smejkal et al. [8], who reported good agreement with experimental data. According to this model, the main reaction products were C₁₈ hydrocarbons, whose formation depended on reaction temperature and pressure and were limited by hydrogen transfer.

Neste Oil [9] and UOP/Eni Ecofining [10] are commercial processes for HVO production. Plant-derived oils are mixed with recycle hydrogen to saturate and completely deoxygenate the oil by catalytic reaction, producing a paraffin-rich product, compatible with petroleum diesel and with environmental benefits. Thus, large-scale industrial production may have an important role in fulfilling world's growing need for clean diesel fuel.

Most of research works about hydrogenation of vegetable oils have been done with the goal of producing fuels similar to those obtained from petroleum. However, other utilisation should also be considered and investigated, due to the depletion of existing petroleum reserves. Nowadays mankind depends on petroleum to produce many valuable raw materials and it is urgent to find a bio-product that could substitute petroleum, hydrogenation of vegetable oils may be a possibility to attain this goal.

The main aim of the rapeseed oil hydrogenation experimental work presented in this paper was the production of renewable valuable liquid hydrocarbons with different applications either than as liquid biofuels. Thus, the production of valuable bio-hydrocarbons, like aromatic were the target compounds. The effect of experimental conditions on rapeseed oil hydrogenation was studied, with the aim of decreasing temperature and pressure conditions by the presence of an active cobalt and molybdenum catalyst.

The innovations aspects of this work were the use of different experimental conditions, namely a catalyst commonly used in petrochemical industry, lower temperature and lower hydrogen pressures with the objective of decreasing operational costs and increasing the viability of hydrogenation process to produce biochemicals.

2. Experimental part

Hydrogenation tests were carried out in a discontinuous reactor with a capacity of 1 L inside a furnace, as shown in Fig. 1. The reactor was connected to a PID programmable controller for temperature control and with agitation speed and pressure sensors. The reactor was loaded with rapeseed oil, closed, purged and pressurised to a pre-set value with hydrogen. After the pre-settled reaction temperature was reached, the reaction was carried during the defined reaction time. Afterwards, the autoclave was cooled down till room temperature and gaseous and liquid products were collected, measured and analysed. Both gases and liquids yields were calculated by common procedures, using the rates between each product formed and the initial amount of rapeseed oil.

Rapeseed oil elemental analysis is presented in Table 1 and some of its physicochemical properties are shown in Table 2. Density was measured at 20 °C according to ISO 12185:1996 and viscosity was determined at 40 °C by EN ISO 3104. HHV was determined by CEN/TS 14918 standard and LHV was calculated from HHV, considering water content. The same standards and procedures were also used for the determination of physicochemical properties of hydrogenated oils obtained at different experimental conditions.

Rapeseed oil was hydrogenated at different experimental conditions. The following range of experimental parameters was

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