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AGRO-FOOD INDUSTRY RESIDUES FOR BIODIESEL PRODUCTION: BIOFFA PROJECT

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Abstract *The aim of the project BIOFFA is to develop processes for the production of biofuels from residual raw-materials with high free fatty acid (FFA). In technological terms, two distinct approaches, leading to different final products, are being assessed: production of fatty acid methyl esters (FAME) – biodiesel, and hydrogenated oil – H-oil. Different residues available in Portugal, including poultry fat, cattle fat, olive pomace oil and used frying oils, were collected and characterised, and the objectives of the project will be considered to be met if it will be possible to produce mixtures of both biofuels (biodiesel + H-oil) similar to the nowadays commercially available formulas (biodiesel + petro-diesel) with the superior advantages of valorising residues and producing the overall mixture from biological materials.*

1. INTRODUCTION

The fossil fuel crisis, due to the diminishing of petroleum reserves, the external dependence and the global environmental heating and climate changes have lead, in the last decade, to an extensive search for alternative fuels. In this context, the European Commission published the Directive 2003/30/EC promoting the substitution of the traditional fuels used in the transportation sector by alternative fuels. This Directive was repealed by the Directive 2009/28/EC that endorse a mandatory 10% minimum target to be achieved by all Member States for the share of biofuels and other renewable fuels in transport sector consumption by 2020 [1].

In Portugal, diesel represents the major share of fuels for the transport sector and so, alternatives to its use are being promoted. Biodiesel is a clean burning fuel that can be used as a substitute or in admixture with diesel, due to similarity in their physical and fuel properties. It provides environmental benefits, since its use leads to a decrease in the harmful emissions of carbon monoxide, hydrocarbons and particulate matter, and to the elimination of SO_x emissions, with a consequent decrease in the greenhouse effect, in line with the Kyoto Protocol agreement [2]. Virgin vegetable oils such as the ones from rapeseed, soybean, sunflower and palm, are the most used raw materials for biodiesel production. However, their price that sometimes approaches that of the fossil diesel fuel and their use as food oils limits the application of these edible-oils as raw materials for biodiesel production [3]. Thus, exploring ways to reduce feedstock cost and testing alternative raw-materials are key points in recent biodiesel research. The use of feedstocks as residues / wastes should help to make biodiesel price competitive due to their availability and low cost, opening a route to recycle / valorise residues. However, the latter are more demanding in technological terms as their high FFA content renders traditional biodiesel production processes less effective due to massic yield losses [4]. That is why the BIOFFA project aims at recycling residues by producing efficiently two different biofuels (FAME – biodiesel, and H-Oil) suitable to substitute diesel in engines without significant changes. H-Oil will be obtained by hydrodeoxygenation (HDO) that is a process involving the catalytic hydrogenation and cracking of raw-materials by the application of hydrogen to the feedstock for obtaining oxygen-free molecules - hydrocarbons. HDO products can be mixed with petro-fuels, fitting existing infrastructure and engines and the major advantages of the application of HDO to glyceridic materials are that it provides a consistent product quality from diverse feedstock and does not generate wastes.

In BIOFFA project, different raw-materials that include animal fats (lard, tallow and poultry), crude olive pomace oil and used frying oils, and different processing techniques were chosen to be assessed and optimised:

- a two-step process of chemical esterification/transesterification production of biodiesel, where an acid esterification pre-treatment will promote the reduction of the FFA allowing to perform a subsequent traditional alkaline catalysis without yield losses;
- a single enzymatic step for biodiesel production;
- a single step conventional catalytic hydrogenation for the production of H-Oil, and
- a single step supercritical catalytic hydrogenation for the production of H-Oil.

In the present paper, the characterization of different animal fats, used frying oils and olive pomace oil, and some results of their use for biodiesel and H-Oil production are reported.

2. MATERIALS AND METHODS

2.1. Materials

Cattle fats and used frying oils were gently provided by SEBOL (Loures, Portugal). Poultry fat and olive pomace oil were kindly provided by AVIBOM (Torres Vedras, Portugal) and UCASUL (Beja, Portugal), respectively.

2.2. Experimental procedures

2.2.1. Esterification / transesterification

In order to reduce the FFA content, two pretreatment processes were considered: (a) Homogeneous catalysis - a catalyst screening using different acids (nitric, phosphoric, hydrochloric and sulphuric) was performed. A factorial design of experiments (four factors each at two levels) was applied to study the influence of the operational conditions on the esterification process of the poultry fat. The organic phase was analysed in terms of FFA. Similar experiments were then performed, at the optimal conditions, using the other raw materials; (b) Heterogeneous catalysis - a catalyst screening using different resins - Amberlyst 15 dry, Amberlyst 36, Amberlyst BD 20, Amberlyst 70 and Dowex 50WX8 – was performed using poultry fat (PF) and cattle fat (CF) as raw material. Esterification reactions were carried out at a methanol:fat molar ratio of 40:1, a catalyst amount of 242 mmol/Kg and a temperature of 55 ºC at 200 rpm. The organic phase was analyzed in terms of FFA and ester content.
The triglycerides conversion (transesterification) of the pretreated fat was carried out using a methanol:fat molar ratio of 6:1, 1 wt% sodium hydroxide as catalyst, a temperature of 55°C and a reaction time of 4 h. The methyl ester layer on the top was separated and washed twice with hot water to remove methanol, catalyst and glycerol residues. The biofuel was then dried under vacuum.

2.2.2. Hydrogenation

The hydrogenation experiments of the different raw materials were carried out in a 1L autoclave from PARR built of Hastelloy C276 (Parr, Inc.) Temperatures between 350ºC and 450ºC, residence time between 30 to 120 minutes and initial hydrogen pressure of 80 and 160 psi were tested. In all the experiments, the following variables were determined: hydrogen consumption, product yield, gas fraction composition and liquid fraction characterization.
The CO_2 supported H_2 has been carried out in 160 mL high pressure reactor (Parr, Inc.). The reactions were carried out at temperatures ranging from 300 to 340 °C, H_2 pressure from 5.5 to 22 bar and total pressure from 120 to 160 bar. The raw material and catalyst were placed in the high pressure reactor and later H_2 was added. After achieving the reaction conditions, CO_2

was added and reaction mixture was rigorously stirred. The reaction was carried out from 2 to 6 hours and after deprussurisation was performed.

2.3. Analytical procedures

All the raw materials were characterized according to national or international standards: fatty acid profile (EN ISO 5508 and 5509), acid value (NP 903), moisture and volatile matter content (ISO 662), iodine value (ISO 3961), saponification value (ISO 3657) and unsaponifiable matter (ISO 3596).
The quality of the final product obtained from the esterification / transesterification reactions was characterized using the methods described in the EN 14214.
Gases produced in the hydrogenation processes were measured and analysed by gas chromatography (GC). Liquid hydrocarbons were distilled and separated in two fractions - the lighter one distilled up to 270°C, whilst the other presented a distillation range higher than 270°C. These fractions were analysed using gas chromatography with a capillary column associated to a mass spectrometry (GC-MS) to identify their main compounds.

3. RESULTS AND DISCUSSION

3.1 Raw materials characterization

The different raw materials were characterized in some physical and chemical parameters (Table 1). All the samples, namely the animal fats, were substantially different regarding the acid value, a parameter that controls the technological process decision. All the cattle fats showed a high level of saturation (≥ 36.1 %) reflected in their solid form at room temperature. The fatty acids saturation is crucial in biodiesel quality because their presence interfere with properties such as CFPP and viscosity.

Parameter	Cattle fat			Poultry fat	Olive pomace oil	Used frying oil
	CF1	CF2	CF3	PF	OPO	UFO
Acid value (mg_{KOH}/g)	0.68	5.7	87.1	15.4	10.5	15.4
Saponification value (mg_{KOH}/g)	206.5	216.2	168.6	181.9	182.8	181.9
Iodine value (g I_2/100g)	60	63	47	80	83	80
Moisture content (%)	n.d.	0.01	2.6	0.34	0.59	0.34
Unsaturated fatty acids (%m/m)	60.7	53.5	49.8	68.2	80.2	82.6

Table 1. Raw-materials characteristics

3.2. Esterification / Transesterification

Among the heterogeneous catalysts tested to reduce the FFA content, Amberlyst 15 (a

sulphonic acid resin) showed to be the most suitable for high acid value levels (15.4 mg KOH/g, PF) and Amberlyst 70 for lower (5.7 mg KOH/g, CF2) (Figure 1). This is probably due to the influence of the water amount generated in the esterification reaction. In what concern the homogeneous catalyst, sulphuric acid allows to obtain the high FFA reduction (data not shown). The main interest for using heterogeneous catalysts lies on their reusage capability.

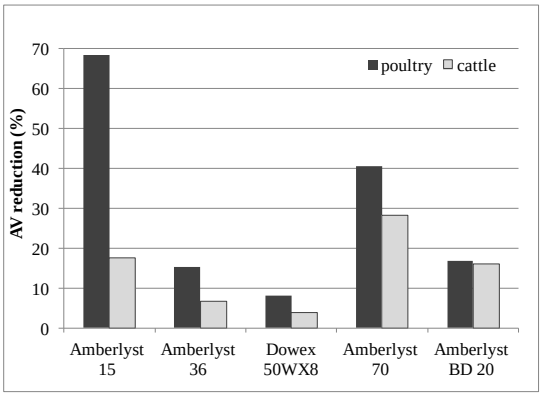

Figure 1 – Screening of acid heterogeneous catalysts for raw-material esterification

Biofuel production by alkaline-catalyzed transesterification was performed using a pretreated sample of poultry fat (by homogeneous catalysis) with a fatty acid content of 0.31% obtained under the optimized conditions (19.4% H2SO4, methanol to FFA molar ratio of 30:1, temperature of 53ºC and reaction time of 94 min). The two-step biodiesel production process provided a fatty acid methyl ester (FAME) content of 96.6%.

3.3. Hydrogenation

The conversion of animal fats and UFO into a different biofuel by catalytic and non-catalytic hydrogenation of the fatty acids and triglycerides present in the raw-materials was studied. The results obtained so far showed that the different raw materials can be efficiently converted into a hydrocarbon mixture with similar composition of conventional fuels. The results showed that at the reaction temperature of 380ºC and 30 minutes of reaction time the fatty acids and triglycerides hydrogenation seems to be completed. Also, the increase in reaction temperature favours lighter alkanes (C5 and C6). The increase in reaction time favours alkanes from C5 to C11 and decreases heavier hydrocarbons. In figure 2 is presented a typical GC/MS spectrum of the liquid product obtained in an animal fat hydrogenation experiment. As can be seen in this figure the liquid product is mainly composed by linear alkanes from C5 to C17.

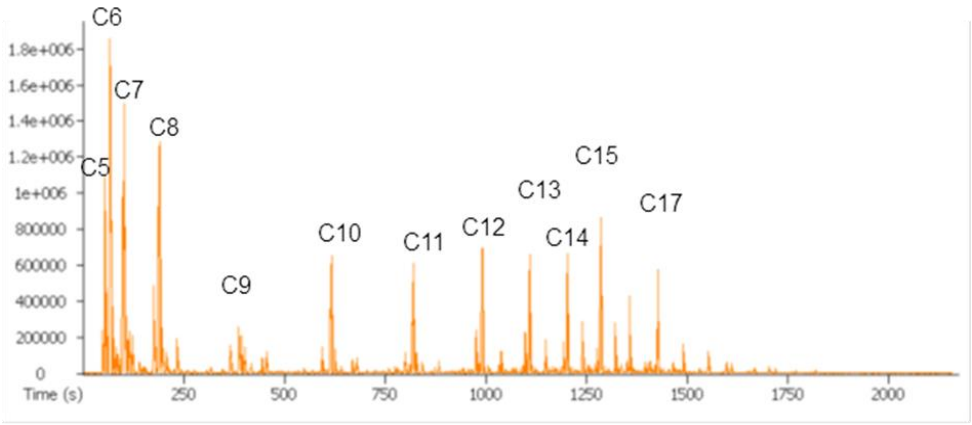

Figure 2. Liquid composition (GC/MS analysis) obtained in animal fat hydrogenation (T=380ºC; reaction time=30 min and initial hydrogen pressure=160 psi)

3.4. Hydrogenation with CO_2

The hydrogenation with CO_2 revealed that CO_2 allows performing reaction at lower temperature compared to the reactions without this solvent. Furthermore, addition of CO_2 allows to obtained different product distribution profile. To compare both processes, reactions with and without CO_2 were carried out and showed that hydrogenation with CO_2 allows to obtain a mixture more rich in C13 to C17 hydrocarbons compared to the reaction without CO_2 (32% vs 67%, respectively). Therefore it can be concluded that CO_2 permit to carry out reaction more selectively leading to the formation of long alkyl chain fatty acids. Figure 3 presents the concentration of mixture composition of uneven saturated carbohydrates.

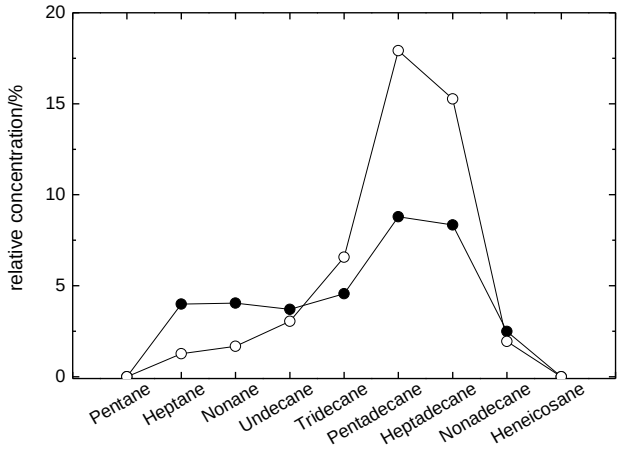

Figure 3. The mixture composition (uneven saturated hydrocarbons) obtained in reactions with (closed symbol) and without CO_2 (open symbol).

4. CONCLUSIONS

The valorisation of residues such as animal fats and used frying oils was one of the objectives of the BIOFFA project. So, the technological approaches studied attempt to define the most efficient and less costly technology to process these raw-materials with high FFA content. The results obtained showed that the same raw materials can be used to produce two different biofuels that seems to be suitable for use in diesel engines – biodiesel and hydrogenated oil. Biodiesel was within EN 14214 specifications, except for cold properties, and hydrogenated oil showed similar composition to petroleum-derived diesel.

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