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Study of an ethylic biodiesel integrated process: Raw-materials, reaction optimization and purification methods

J.M. Dias [a,*], E. Santos [a], F. Santo [a], F. Carvalho [a], M.C.M. Alvim-Ferraz [b], M.F. Almeida [a]

[a] Departamento de Engenharia Metalúrgica e de Materiais, LEPABE, Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal
[b] Departamento de Engenharia Química, LEPABE, Faculdade de Engenharia, Universidade do Porto, R. Dr. Roberto Frias, 4200-465 Porto, Portugal

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ABSTRACT

No studies are reported on ethylic biodiesel integrated processes, considering raw materials, reaction optimization and product purification. The present study aims to: i) select key variables for experimental optimization of ethanolysis using a virgin vegetable oil; ii) perform an optimization study using a waste oil; and iii) evaluate the effectiveness of water free purification methods. Sunflower oil ethanolysis was conducted at different temperatures (30 – 80 °C), catalyst concentrations (0.3 – 2 wt.%), reaction times (0.5 – 4 h) and ethanol: oil molar ratios (2:1 – 12:1). Optimization experiments on waste oil ethanolysis were performed at different temperatures (30 – 50 °C) and ethanol: oil molar ratios (6:1 – 12:1), during 1 h and using 1 wt.% catalyst. Quality parameters were measured according to EN 14214. A cation-exchange resin and a ceramic membrane were evaluated for water-free purification. Regarding sunflower oil ethanolysis, when successful, conversion ranged from 75.2 to 97.7 wt.%. Using both oils under optimized conditions (45 °C, 6:1 ethanol:oil molar ratio), a product with a very high purity (> 98.0 wt.%) was obtained after water washing purification. The 0.1 μm ceramic membrane was more effective than the cation-exchange resin, but it was not possible to obtain a good quality product using both methods.

1. Introduction

Biodiesel is being studied since several years as a renewable and environment-friendly alternative to fossil diesel [1,2]. Chemically, biodiesel is a mono-alkyl ester obtained through a transesterification reaction, by which more complex triglyceride molecules are converted into smaller molecules of fatty acid esters (biodiesel) that present physical and chemical characteristics similar to fossil diesel [3]. Vegetable food oils, such as soybean oil, rapeseed oil, palm oil and sunflower oil are used in more than 95% of biodiesel production plants throughout the world [4]. The transesterification reaction is reversible and involves three steps to convert the initial triglyceride into a mixture of biodiesel and the by-product glycerol (according to stoichiometry, roughly 1 kg of biodiesel and 0.1 kg of glycerol per 1 kg of oil). The technology employed by most industries dedicated to biodiesel production consists of a methanolic route for the reaction, catalysed by a homogeneous alkali reagent (e.g. NaOH, KOH, CH_3ONa, CH_3OK) [3,5].

To contribute for a sustainable biodiesel production, there are two fundamental aspects: raw material diversification and process optimization. These aspects should be studied not only to aim the reduction of costs but also to enable the implementation of "greener" alternatives, with reduced environmental impacts.

Virgin vegetable oils might account for up to 95% of the biodiesel production costs [6]; therefore, raw-material diversification might have significant impact on improving the economic viability of the process. In order to do that, animal fats might be used [7]; in addition, when possible, waste streams, namely from the food processing industry and domestic activities, should be recycled for biodiesel production [7–9]. By using wastes as resources, both the energetic and the waste management problems might be mitigated.

Among the research work which considers the improvement of current production processes, heterogeneous catalysts appear as a very valid contribute, although catalytic activity, leaching and reusability issues still need further developments [10,11].

Another very relevant subject is the alcohol used; the problems associated with the hazardous nature of methanol used in most of the industrial plants, and its non-renewable origin (almost 100% is fossil derived) motivated the research towards the use of an ethanolic route, since ethanol might be easily produced from renewable resources and presents very low toxicity [12], which makes the overall biodiesel production process greener. Although the price of ethanol is higher than that of methanol [12], this alcohol presents much higher solubility in vegetable oils and its extra carbon slightly increases the energy content of the fuel [13]. The higher cost of ethanol results mostly from the fact that it derives from the conversion of biomass, and currently, essentially from food and animal feed crops (e.g. corn and sugarcane) that have great implications on the production cost [14]. The production of bioethanol

* Corresponding author. Tel.: +351 22 5081422; fax: +351 22 5081447.
E-mail address: jmdias@fe.up.pt (J.M. Dias).

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from cellulosic biomass resources has potential to lower the bioethanol production costs [15], although the complexity of cellulosic ethanol production (the difficulties in breaking down such materials, due to the plant cell wall structure) also increases associated costs. Research is still ongoing regarding the production of engineering improved energy feedstocks and other potentially alternative feedstocks for bioethanol production [14]. In the future, biomethanol produced from biomass might also be used [16], but extensive research is still required to make this alternative economically viable. The ethanolic route is in fact more promising; however, the process is much more sensitive and it still needs to be optimized, namely regarding reaction conditions and product separation constraints, to be competitive with the methanolic route [17].

Finally, biodiesel purification is also a major issue even when using heterogeneous catalysts [10,18]. Conventional purification process includes water washing to remove the alcohol (usually used in excess), and residual glycerol, soaps and catalyst [19]. After washing, the remaining water in biodiesel is evaporated, usually using vacuum flash processes. Water washing of biodiesel is generally implemented because it allows the fulfilling of the stringent biodiesel standards such as EN 14214 and ASTM D6751; however, it leads to the production of wastewater that requires further treatment, causing significant economic and environmental impacts [20]. In addition, this process is responsible for high energy and time consumptions and also for low biodiesel yields (there is always product loss during washing stages) [6,16]. No data could be found regarding the quantification of the operational costs of biodiesel purification.

It is known that an effective biodiesel separation and purification is crucial, because impurities resulting from ineffective processes can cause operational problems during engine functioning, such as filter plugging, injector coking, additional carbon deposits and remarkable engine wear [16]. Therefore, purification technologies to be developed must be effective and without risks of causing the mentioned problems.

Alternative water-free purification processes have been developed, employing the use of different materials such as absorbents (e.g. ®magnesol), adsorbents (e.g. activated carbon), solvents (e.g. ether), resins (e.g. Purolite®) and membranes (organic or inorganic) [16]. From the existing processes, dedicated ion exchange resins are being highly promoted for biodiesel purification. For instances, Purolite® (PD206) is a commercial cation-exchange resin, manufactured to purify biodiesel with the purpose of removing residual catalyst, water and other impurities, being known for acting mostly as an adsorbent [18,20]. The use of membranes on the treatment of organic solutions is emerging. Taking into account biodiesel purification, inorganic, ceramic membranes have high potential due to their very high chemical and thermal stability [19,21].

The literature review shows that there are no studies concerning integrated processes for ethylic biodiesel production, focusing on raw materials (including wastes), reaction optimization and product purification (using water-free methods). It is therefore a novel approach towards this field of study, because it considers simultaneously the raw material diversification and the process optimization, focusing on greener alternatives (by reducing environmental impacts associated with the use of methanol, the management of wastes and the wastewater treatment) and the reduction of costs (especially by replacing raw-materials but also by avoiding wastewater treatment).

In agreement with what was previously stated, the present study aims to: i) select key variables for experimental optimization of ethanolysis reaction using a virgin vegetable oil; ii) perform an optimization study on ethanolysis, by varying reaction conditions, using a waste oil as raw material; and, iii) evaluate the effectiveness of currently proposed water free methods for biodiesel purification, obtained from waste oil or refined oil.

2. Materials and methods

2.1. Materials

The sunflower oil (SFO) was obtained commercially and used without any treatment. The waste frying oil (WFO) was obtained from a voluntary collection system (different domestic sources) implemented at *Faculdade de Engenharia, Universidade do Porto*. Before being used, WFO was pre-treated with anhydrous sodium sulphate (25 wt.% relative to oil mass) followed by vacuum filtration, to remove solid impurities and residual water.

The resin used was commercial Purolite®PD206. A housing G1-1/6-Swageloc and a monochannel ceramic membrane with a pore diameter of 0.1 μm were supplied by Atech Innovations Gmbh. The ceramic membrane tube presented an outside diameter of 10 mm and a length of 250 mm, providing a filtration area of approximately 0.0048 m^2 for the entire membrane.

The most relevant reagents used during synthesis, purification and quality evaluation procedures were: ethanol absolute (P.A., Panreac), sodium hydroxide powder 98% (Sigma-Aldrich, Reagent Grade), heptane (analytical grade, Merck), ethyl pentadecanoate (Aldrich), sodium standard for AAS (TraceCERT®, 1000 mg/L Na in nitric acid, FLUKA) and CombiCoulomat frit Karl Fischer reagent for the coulometric water determination for cells with diaphragm (Merck).

2.2. Methods

2.2.1. Biodiesel production procedures

To start the transesterification reaction, the necessary amount of oil (around 50 g for preliminary experiments and 120 g for optimization experiments and around 250 g in each batch for water-free purification studies) was added to a three-necked batch reactor, immersed in a temperature controlled water bath, set according to the reaction temperature (30–80 °C), and equipped with a water-cooled condenser. After reaching the desired oil temperature, an ethanolic solution containing the NaOH catalyst (0.3–2.0 wt.%, with respect to oil) and the ethanol (2:1–12:1 ethanol:oil molar ratio) was added to the reactor. The transesterification reaction was carried out under atmospheric pressure, with vigorous magnetic stirring (stirring plate regulated to 600 rpm), for the desired time (0.5–4 h). Biodiesel and glycerol phases were separated by gravitational settling and, following, the excess ethanol was removed from both phases in a rotary evaporator at reduced pressure.

When conducting a two-step process, the reaction was stopped after the first established period, the products were left to settle and then the glycerol phase was removed. After, the excess ethanol was recovered from the biodiesel phase that was either submitted directly to the second step or purified by washing and then used in the second step. When water washing was performed, it was conducted as described by Dias et al. [4].

2.2.2. Dry purification processes

The dry purification methods were applied after excess ethanol removal. When the cation-exchange resin was used, biodiesel was treated with 2–40 wt.% (in respect to biodiesel mass) of resin, under magnetic stirring (magnetic stirring plate regulated to 500 rpm), during 1 h, at room temperature. After, the resin was filtered and the biodiesel was analysed according to Section 2.2.3.

Regarding the ceramic membrane separation system, 250 mL of crude biodiesel was poured into a feed vessel and cross-filtered once by the membrane ceramic tube, using a peristaltic pump at 6.25 L h^{-1} (Aspen, Standard model).

2.2.3. Evaluation of raw materials and biodiesel quality

The following key quality parameters were determined in the raw materials: (i) acid value, by volumetric titration according to NP