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An economically viable two-step process for biodiesel production from waste cooking oils

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A real sample of waste cooking oil having an acidity of 8 mg_{KOH}/g_{oil} and a water content of 700 ppm was efficiently converted into biodiesel. The process consisted in a two-step reaction: a preliminary treatment with $AlCl_3{\cdot}6H_2O$ to convert free fatty acids into the respective methyl esters, followed by alkaline transesterification using KOH as a catalyst. In detail, pretreatment with $AlCl_3{\cdot}6H_2O$ (345 K, 4 h, weight ratio MeOH:oil:catalyst of 1:3:0.01) allowed to obtain an efficient conversion of starting free fatty acid into the relevant fatty acid methyl esters (yield > 95%). After the reaction a convenient separation of phases was obtained. Two different phases were isolated: an oily phase with a methanol content of 7 % wt, in which methyl esters were dissolved in, with most of glycerides and with a very limited content of water to one side, and a lighter phase, in which most of unreacted methanol and catalyst together with water were solubilized. Such a separation made possible the direct use of the pretreated oily phase with $AlCl_3{\cdot}6H_2O$ in the transesterification without any further treatments, unless to adequate the methanol content. KOH was used to complete the conversion in the second step. Reaction occurred completely in 4 hours and the final biodiesel was conform to EN14214.

Keywords: Biodiesel, waste cooking oils, esterification, transesterification.

INTRODUCTION

Biodiesel is a mixture of fatty acid methyl esters (FAMEs) which have physical and chemical properties that are very similar to petroleum-derived-fuel [1]. Industrially produced by transesterification of refined vegetal oil with methanol in presence of homogeneous alkaline catalysts, namely sodium or potassium hydroxides, carbonates or alkoxides [2], it suffers from being applied on feedstock with high free fatty acid (FFAs) (> 0.5 %wt) and moisture contents [3].

The use of refined oily feedstock generated an economic constraint for the feasibility of the entire production. 80-85% of the total biodiesel cost depended by the feedstock cost. In addition, an inappropriate change of use of land for cultivating oily plants, generated an ethical question land-for-food vs land-for-fuel. For these reason, alternative oily biomasses were investigated, for example waste cooking oils. Waste cooking oils price is 2-3 times cheaper than refined vegetable oils [4]. Besides the economic and environmental benefits, the use of WCO presents some challenges, related to the presence of free fatty acids (FFAs) and high moisture content. A high presence of FFAs (> 1 %) impedes the use of alkaline transesterification, for the concomitant production of soaps. In that case, a two-step process is normally recommended. In this two-step process, a pre-treatment (step 1) is used to reduce the amount of FFAs, through an acid catalyzed direct esterification to obtain FAMEs. Sulfuric acid is typically adopted, but its use need some intermediate processes (washing, neutralization, etc.) among pretreatment and transesterification that results in production of waste and consume of energy [5]. The esterified feedstock is converted in biodiesel through alkali catalyzed transesterification in the second step of the process. In this work, a two-step process was reported in which direct esterification of FFAs is performed under $AlCl_3{\cdot}6H_2O$ catalysis, while the second phase was run in batch through KOH.

MATERIALS AND METHODS

Feedstock and reagents

The waste cooking oil feedstock was provided by GF Energy, S.A. Kiffisias 56, P.C. 15125 Maroussi, Athens, Greece. This oil was characterized in terms of water content (700 ppm), acid value (8.02 mg KOH/g), mono- (0.8 ± 0.1 %wt), di- (3.9 ± 0.3 %wt) and tri-glycerides (90.9 ± 0.3 %wt) and ashes (100 ppm).

Chemical reagents of analytical grade were used directly without further purification or treatment.

All experiments were performed in triplicate, allowing the average value and the standard deviations to be calculated.

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Water content and FFA content determination

Water content was determined according to the ISO 11465 method [6].

Free fatty acids content were determined by dissolving 2 g of sample in 50 mL of diethyl-ether:ethanol solution (1:1 v:v), and 0.1 mL of phenolphthalein indicator were placed into a 250 mL flask. Then, the resultant organic mixture was titrated with 0.1 N KOH solution until a phenolphthalein endpoint (pink coloration persisted for at least 30 s) was reached. The results were expressed as milligrams of KOH required to neutralize 1 g of oil (mg KOH/g) [7].

Identification of the methyl esters

Identification of the different methyl esters were carried out by gas chromatography-mass spectroscopy (GC-MS) using a Perking Elmer Clarus 500 equipped with a Clarus spectrometer.

Quantitative determinations were performed using a Varian 3800 GC-FID: FAMEs were determined using methyl heptadecanoate as internal standard, while mono-, di- and triglycerides were determined respect to 1,2,3-tricaproyilglycerol (tricaprin) after proper derivatization with pyridine and N-methyl-N-trimethylsyliltrifluoroacetamide (MSTFA). Both instruments were configured for cold on-column injections with a HP-5MS capillary column (30 m; Ø 0.32 mm; 0.25 µm film).

Esterification of the WCO

The direct esterification reaction was carried out in a 500 mL Pyrex reactor using $AlCl_3{\cdot}6H_2O$ as a catalyst. 1.00 g $AlCl_3{\cdot}6H_2O$ was dissolved into 100 g of methanol, then 300 g WCO was added in order to have a final weight ratio (R_w) of oil to methanol equal to 3:1. The reactor was closed and placed into a thermostatic bath at 343 K for 4 h under agitation using a magnetic stirrer. At the end of the reaction, the system was cooled and a bi-phasic system composed by an upper methanolic phase and a lower oily phase was observed. The two phases were separated, weighed, and analysed for methanol (gas-chromatographically determined), water (loss of weight at 378 K for 24 h), ash, metals, residual acidity, FAMEs, mono-, di- and tri-glycerides content. The oily phase recovered from such a pretreatment was analysed and then directly used in the transesterification.

Transesterification of pretreated WCO with methanol using KOH as a catalyst

10.0 g oily phase obtained from pretreatment of WCO with $AlCl_3{\cdot}6H_2O$ was directly weighted into a 20 mL glass reactor equipped with a silicone septum, which allowed sampling throughout the reaction without interruption, agitation and heating the system. 5 g of methanol was then added.

The reactor was closed, introduced into a thermostatic oil bath (343 K) and magnetically stirred (400 rpm). Reaction time started when a previously prepared 0.84 KOH in 1.82 g MeOH solution was introduced via syringe into the reactor. Samples (0.5 mL) were up-taken after 1, 2.5, 5, 10, 15, 30, 60, 120, 240 and 480 minutes, and transferred into vials, in which 0.05 g glacial acetic acid was previously weighted to immediately quench the transesterification. Then, methanol was evaporated and residual oil was analysed.

ANALYSIS OF RESULTS

$AlCl_3{\cdot}6H_2O$ was used as a catalyst for pretreating WCO containing 8 mgKOH/g oil.

After 4 h at 345 K, residual acidity become 0.85 mgKOH/g oil: about 90 % of initial FFAs were converted into FAMEs.

$AlCl_3{\cdot}6H_2O$ not only promoted the reaction, but induced at the end, a separation of phases with a very convenient distribution of final products. Catalyst was completely dissolved in the alcoholic phase, together with most of water, whereas the resulting methyl esters were dissolved into the oily phase. This composition made the pretreated oil a suitable feedstock to be transesterified through conventional basic catalysts without further treatments and without generating salty waste. In fact, the direct use of KOH as a catalyst was tested. Concentration of FAMEs, mono-, di- and triglycerides were monitored along the time. Results are reported in Fig. 1.

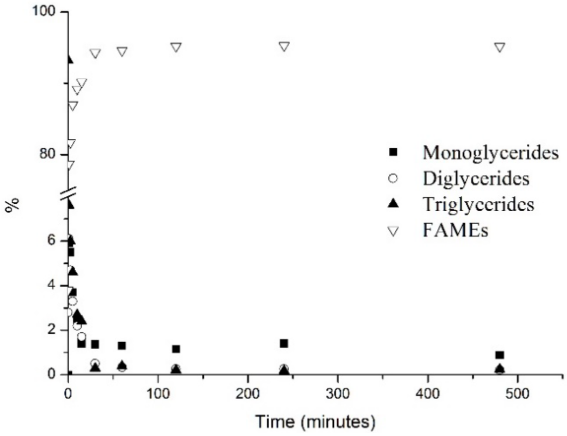

Fig. 1: Time course of FAMEs, mono-, di- and triglycerides

Transesterification occurred really fast: in about 30 minutes, FAMEs content was 95 % approximately and an almost complete conversion of glycerides were obtained.

The results obtained open the possibility to develop a two-step process based on two batches in series with the following benefits:

1. a sustainable route to produce biodiesel from low-cost feedstocks
2. an esterification process based on hydrated salts that allow the recovery of the catalyst and remove the washing steps used with traditional acid catalysts
3. a directly usable esterified oily phase to be treated with KOH for the transesterification step
4. a reduced number of equipment to develop the whole process
5. the possibility to decrease the capital and operative costs connected to the biodiesel production

CONCLUSIONS

This work describes a very efficient chemical two-step process for the conversion of waste cooking oil into biodiesel. Cheap and safe $AlCl_3 \cdot 6H_2O$ efficiently promoted direct esterification of FFAs into methyl esters. The direct esterification reaction took place in the methanolic phase, in which the catalyst was completely soluble (homogeneous catalysis). At the end of the pre-treatment, it was totally recovered from the methanol phase. Besides the conversion of FFAs, a concomitant reduction of the starting water content in the reacted oily phase made the pre-treated oily phase a suitable feedstock to be directly used in the next step for obtaining biodiesel. Alkaline transesterification using KOH without any further treatment was used for the second step. At the end, biodiesel compliant with EN14214 specifications was isolated.

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