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Sustainable biodiesel production from alternative oils

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Introduction

Biodiesel, besides bioethanol, is the only renewable energy source in liquid form that can be actually produced on a large scale at the moment. The main barriers still limiting the widespread use of this fuel are twofold: the ethical issues posed by the competition of the raw materials used for its production with the food requirements and the relatively high manufacturing costs of biodiesel production, making it not competitive with normal diesel. Waste oils or oils extracted from specifically selected vegetable cultures represent potential substitutes to edible oils. The main drawback of these raw materials is their high content of free fatty acids (FFA), which cause saponification problems during the transesterification [1,2]. Moreover, FFA concentrations lower than 0.5% per weight are required by the European standard for biodiesel EN 14214.

In the present work the deacidification of different kinds of alternative oils is investigated. The proposed method consists in the esterification of FFA with methanol and in presence of an acid catalyst so to obtain methyl esters already at this stage, as represented in the following scheme: RCOOH + MeOH → RCOOMe + H_2O. Acid ion exchange resin Amberlyst®46 (A46, Dow Advanced Materials) was selected by the authors after some preliminary studies carried out to assess its performance and durability in the reaction environment [3]. The use of oils extracted from *Brassica juncea*, *Cartamus tinctorius*, i.e. crops not addressed to the food market, and waste cooking oil (WCO), is studied. In the case of WCO a study on the lifetime of the catalyst was also carried out recycling it through multiple runs. The potential of the adopted feedstock was investigated taking into account EN 14214 standard.

Experimental

The performed deacidification experiments are listed in Table 1. All the esterification tests have been carried out in slurry modality adopting A46 as catalyst. A46 is a sulphonic ion exchange acid resin which has the peculiarity of being sulphonated only on its surface [3].

Table 1: Esterification experiments.

Oil (common name)	**Initial acidity (FFA wt %)**	**Experiment(s)**	**Conditions**
B. juncea (indian mustard)	0.74	biphasic	65 °C MeOH:oil=16:100
		monophasic	80 °C MeOH:oil=5:100
C. tinctorius (safflower)	1.75	Biphasic	65 °C MeOH:oil=16:100
		monophasic	80 °C MeOH:oil=5:100
Waste Cooking Oil (WCO)	2.30	biphasic, recycle of the catalyst	65 °C MeOH:oil=16:100
WCO:rapeseed oil 1:1	2.20	Biphasic	65 °C MeOH:oil=16:100
WCO:rapeseed oil 3:1	2.20	Biphasic	65 °C MeOH:oil=16:100

The experiments in monophasic conditions were arranged by mixing the oil with the necessary amount of methanol to obtain a single liquid phase at 80°C. The purpose of these tests was to investigate if a maximized contact between methanol and FFA could be beneficial.

Each test has been carried out for six hour, withdrawing samples from the reactor at pre-established times to analyze their acidity content through acid-base titrations [4]. Biodiesel was produced from the oilseeds following the well known procedure described in literature [5]. Product composition was analyzed through gaschromatography. Iodine value (gI_2/100 g oil), density, viscosity of the tested oils were measured by standard methods in order to verify the compliance with the EN 14214 requirements.

Results and Discussion

The main characteristics of the tested oils, as per EN 14214 standard, are listed in Table 2.

Table 2: Values of some properties of the selected oils

Oil (common name)	**Iodine value (gI_2/100g oil)**	**Viscosity (mm^2/s 40 °C)**	**Density (kg/m^3 15° C)**
B. juncea	111	32.6	914
C. tinctorius	109	n.d.	n.d.
WCO	54	82.2	918
WCO:rapeseed oil 1:1	85	52.8	914
WCO:rapeseed oil 3:1	100	40.5	926
Rapeseed	115	n.d.	n.d.
Biodiesel standard EN 14214	<120	3.5-5	860-900

All the tested samples are characterized by an iodine value satisfying the required limit. Iodine values exceeding the imposed limit may in fact be responsible of fuel's instability to the oxidation, making it unsuitable for diesel engines. On the other hand, oils with too low iodine values and high viscosities, such as WCO, cannot be used as well, as they may plug equipment filters [7]. Regarding viscosity it has to be however considered that the original value will be reduced of 1/10-1/15 after the transesterification process [6]. It is possible to adjust properties like iodine value and viscosity, so as the fall within the required limits, by blending the feedstock with oils characterized by opposite properties. This is shown in Table 2 by the values obtained in the case of the mixtures of WCO and rapeseed oil.
The results of the deacidification tests performed on the selected feedstock are shown in Figure 1.

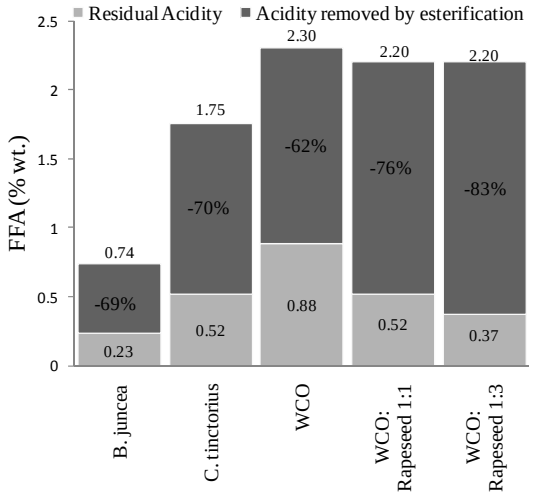

Figure 1: Deacidification of different oils with A46, slurry reactor, wt ratio catalyst: oil=10: 100, wt ratio MeOH: oil=16:100, 65° C, 6 hours.

As can be seen the use of the catalyst A46 allows, in most of cases, to lower acidity below 0.5% within 6 hours . In the case of WCO the acidity removed by esterification is not enough to enable a potential application on a larger scale. This is probably due to the high viscosity of this medium which prevents an optimal contact between the reagents and the catalyst. A possible solution might be to blend the feedstock with other raw oils characterized by lower viscosity, so as to reach the required acidity limit within 6 hours of reaction. The effectiveness of this approach is evidenced in the graph by the residual acidities obtained when WCO is mixed with rapeseed oil, achieving the plateau of conversion within the six hours of reaction.
Experiments at 80 °C, using the methanol amount vs. oil required at this temperature to obtain a single liquid phase, were also carried out in the case of *B. juncea* and *C. tinctorius* oilseeds. The outcome of this study evidenced how the quantity of methanol adversely affects FFA conversion within 6 hours, notwithstanding the higher operating temperatures and the better contact between reagents. Therefore, when operating in slurry modality, biphasic esterification is to be preferred to the process in monophasic conditions.
In the case of WCO, the same batch of the catalyst A46 was recycled for 5 runs, showing no significant decrease in its catalytic activity.
Biodiesel of 98.5% of purity was obtained from *B. juncea* oilseed.

Conclusions

The esterification reaction of FFA contained in raw oils with the use of Amberlyst®46 as a catalyst is an effective and efficient method of deacidification.
Brassica juncea and *Cartamus tinctorius* represent two valuable choices for what concerns the selection of the substrates to be used for biodiesel production. However, it is possible to improve the properties of the raw materials by mixing different oils, as demonstrated by the blends of waste cooking oil (characterized by low iodine value and high viscosity) with rapeseed oil.

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