Fuel Processing Technology 177 (2018) 336–344

Contents lists available at ScienceDirect

Fuel Processing Technology

journal homepage: www.elsevier.com/locate/fuproc

Research article

Interesterification of rapeseed oil catalysed by a low surface area tin (II) oxide heterogeneous catalyst

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ARTICLE INFO

Keywords:
Biodiesel
Interesterification
Methyl acetate
Tin oxide
Heterogeneous catalysis

ABSTRACT

The interesterification of rapeseed oil was performed in a batch reactor using for the first time low surface area massive tin(II) oxide as heterogeneous catalyst and methyl acetate as acyl acceptor. The effect of reaction temperature, methyl acetate to oil molar ratio and catalyst loading on the performances of the process were investigated.

Yields in fatty acid methyl esters (FAMEs) and triacetin (TA) up to 90% and 70% respectively, were achieved after 4 h of reaction time at 483 K in the presence of 0.69 mol of SnO per mole of rapeseed oil using a methyl acetate to oil molar ratio of 40.

Quite interestingly, the catalyst performances improved when water was added to the reactions system. Moreover the same catalyst sample was used three consecutive times without observing any depletion of the catalytic activity.

Collected results indicate that SnO is a promising heterogeneous catalyst for the interesterification of triglycerides with methyl acetate.

1. Introduction

The main source of energy is actually constituted by fossil fuels whose massive utilization has contributed to increase the CO_2 concentration in the atmosphere to values above 400 ppm [1], with a consequent enhancement of the global warming effect. Owing to the dangerous climate changes that could be induced by this phenomenon, in recent years governments have applied increasingly stringent regulations culminated in the highly challenging COP21 Paris agreement that sets the CO_2 concentration in the atmosphere in 2050 to one third of what planned according to the Kyoto protocol [2]. To match this goal, fossil fuels must be progressively substituted by CO_2 neutral renewable energetic sources. Among the different possible options, biodiesel is considered since many years a viable alternative to fossil diesel, as it is biodegradable, non-toxic and has similar performances [3].

In addition, according to the standards that characterize a fuel, the quality of biodiesel is better in terms of harmful emissions, flash point value and cetane number [3]. To date, the most widely used technology for the production of biodiesel on a large scale is the transesterification of vegetable oils or animal fats also termed alcoholysis [4]. It generally consists of the reaction between one molecule of triglyceride and three molecules of methanol to form three molecules of fatty acid methyl esters (FAME) and glycerol. A molar excess of alcohol with respect to the stoichiometric ratio to triglycerides is adopted to increase the yield of FAME.

Heterogeneous basic and acid catalysts, and even enzymes have been studied to activate the kinetics of the transesterification but in an industrial context homogeneous base catalysts are actually the most used [5]. The main limitation to a widespread diffusion of biodiesel so far has been its high cost of production, which is almost double compared to that of diesel obtained from oil [5].

Several constraints adversely affects the economics of the process: 1) the limited availability of the feedstock, usually constituted by vegetable oils derived from oleaginousness plants [6]; 2) the sensitivity of industrial homogeneous base catalysts to water and free fatty acids in the feed whose concentrations must be reduced to low threshold values [7,8]; 3) the heterogeneous character of the reaction system, initially constituted by a methanol-rich phase dissolving the catalyst that is immiscible with the oil-rich phase [9]; 4) the cost related to the

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https://doi.org/10.1016/j.fuproc.2018.05.017
Received 17 March 2018; Received in revised form 8 May 2018; Accepted 9 May 2018
0378-3820/

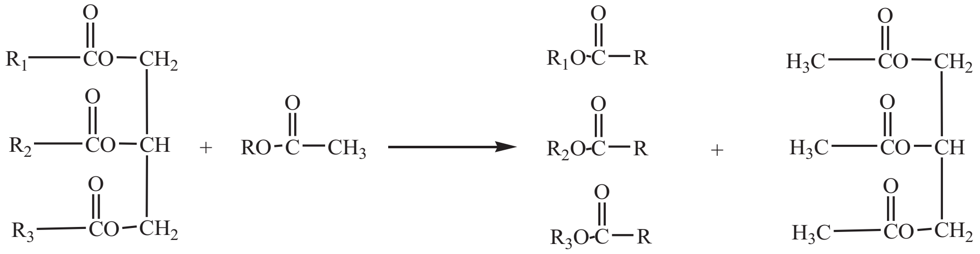

Fig. 1. Interesterification of triglycerides with alkyl acetates for biodiesel production. R = CH_3 or CH_3CH_2.

separation of FAME, unconverted methanol and glycerol coproduced in the reaction [10].

The exploitation of microalgae as a potential source of triglycerides [6] and the development of more efficient technologies for their processing may decrease the cost of biodiesel and make it more competitive with fossil diesel [10]. A possible alternative path to biodiesel that can overcome part of aforementioned drawbacks is the interesterification of tryglicerides with methyl or ethyl acetate. This route is interesting because all reagents are perfectly miscible so that interfacial mass transfer resistances typical of the alcholysis of triglycerides vanish, moreover the coproduction of glycerol is prevented since the utilization of an ester as acyl donor leads to the formation of fatty acids alkyl esters and triacetin (Fig. 1) [11].

The triacetin is perfectly miscible with FAME and in concentration up to 10% by mass in the mixture, it does not change the quality of fuel that continues to meet applicable quality standards [12]. Moreover pure triacetin is a high added value chemical that can be used as green plasticiser for polymers and as additive in the cosmetic and pharmaceutical industry [13]. Interesterification of vegetable oils was performed in the absence of any catalyst at temperature higher than 573 K in supercritical condition with methyl acetate [7], [14–17] or ethyl acetate in microreactors [18]. The process was carried out also at room temperature using base homogeneous catalysts such as potassium or sodium hydroxide and/or methoxide [19–23]. The alkaline compounds are only partially soluble in the reaction mixture and to enhance the kinetics of the reaction it was necessary to dissolve them in methanol or to use low molecular weight poly(ethyleneglycol) as complexing agent. Homogeneous base catalysts were also used to study the effect of the nature of the alkyl ester [23] and of ultrasound activation [24] on the performances of the process. Also in interesterification, the use of heterogeneous catalysts would avoid the step of catalyst neutralization that results in the production of unwanted liquid wastes to be disposed.

Heterogeneously catalysed interesterification processes have been much less investigated with respect to the heterogeneously catalysed transesterification.

Most of the research in this field has been addressed to study the utilization of immobilized enzymes as heterogeneous catalysts for the interesterification [25–29] even using magnetic nanoparticle support [30], fluidized bed bioreactors [31,32] or ultrasound assisted processes [33,34]. These catalysts are active at mild temperature but long reaction times are necessary to reach high biodiesel yields. Nafion SAC-15 and Amberlyst-15, sulphated and tungstate zirconia, zeolite β, alkaline form of ETS-10 TiO_2 based catalyst, high porosity sodium aluminate spherical absorbent and several Mg-Al mixed oxide have been tested as catalysts in the interesterification of tributyrin with methyl acetate to obtain triacetin and butyrate methyl ester [35]. Base catalysts allowed faster reaction rate at lower temperature i.e. 60–80 °C. Phenyl-sulfonic acid-functionalized SBA-15 catalysts were also tested for the preparation of biodiesel through the interesterification of extra virgin olive oil with ethyl acetate (molar ratio acyl donor/oil 20) leading to triglyceride conversion of 48% after 6 h at 130 °C using catalyst loading of 30% w/w referred to the oil quantity [36]. In another study the catalytic performances of high specific area niobium phosphate, niobium oxide, γ-alumina and zeolite HY have been studied in interesterification reaction of macaw oil with methyl acetate at 250 °C. Total yield of 52.5 wt% and 49.8 wt% were reached for γ-alumina and niobium phosphate, respectively, after one hour of reaction time [37]. We have recently studied the interesterification of rapeseed oil using tin (II) octanoate as homogeneous catalyst. This complex was found to be completely soluble in the reaction system at investigated concentrations and allowed the operator to reach FAME yields close to 90% and TA yield of about 60% after 20 h of batch reaction at 210 °C with initial methyl acetate to oil molar ratio of 40 [38]. The recovery of tin (II) octanoate is a serious challenge for the practical use of this catalyst and for this reason, we performed several attempts to heterogenize it on suitable supports. Unfortunately in all cases in which we achieved effective bonding of the active ion on the support we observed a marked depletion of the catalytic performances (the results of these researches were not published anywhere).

In the attempt of finding a tin(II) based unsoluble heterogeneous catalyst we decided to test commercial tin (II) oxide (SnO) powder in the reaction of interesterification of rapeseed oil with methyl acetate as acyl donor. Quite interestingly, we have found that this catalyst exhibits performances similar to that of the homogeneous tin (II) octanoate without any detectable leaching of the active ion in spite of its low specific surface. Aim of this research was to study the effect of selected operative parameters on the performances of SnO in the interesterification of rapeseed oil.

2. Experimental

2.1. Materials

Refined rapeseed oil used in this study was purchased from a local supermarket. Its fatty acid composition was determined as reported after and it is summarized in Table 1. Methyl acetate (MA) (HPLC grade > 99,8%) from Carlo Erba Reagents was used as acyl donor. Tin (II) oxide (99.9%) was purchased from Alfa Aesar. The native catalyst powder was ground with a laboratory mortar under inert environment in a glove box and stored in sealed vial each loaded with 200 ± 10 mg of SnO.

Sodium methoxide (98%) from Alfa Aesar and methanol (99.8%) from Sigma-Aldrich were used as homogeneous catalyst and alcohol respectively for the quantitative transesterification performed to characterize the rapeseed oil. Citric acid (99%) Sigma-Aldrich was used to neutralize the alkaline mixture obtained at the end of the transesterification reaction.

Methyl palmitate (C 16:0, ≥99%), methyl stearate (C 18:0, ~99%), methyl oleate (C 18:1, 99%), methyl linoleate (C 18:2, ≥99%), methyl linolenate (C 18:3, ≥99%), and triacetin (TA) (99%) were purchased

Table 1
Fatty acid composition of the vegetable oil used in this study.

Fatty acid (C-length: no. = bonds)	16:0	18:0	18:1	18:2	18:3
% w/w	4.5	1.5	65.1	16.5	10.8