Applied Catalysis A: General 394 (2011) 149–157

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Co-production of butyrate methyl ester and triacetylglycerol from tributyrin and methyl acetate

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ARTICLE INFO

Article history:
Received 15 September 2010
Received in revised form
23 December 2010
Accepted 27 December 2010
Available online 4 January 2011

Keywords:
Interesterification
Ester exchange
Fatty acid methyl esters
Biodiesel
Synthesis of glycerol triacetate

ABSTRACT

The simultaneous synthesis of butyric acid methyl ester, the shortest component of the FAME (fatty acid methyl esters) family, and glycerol triacetate (TAG) from glycerol tributyrate (tributyrin) and methyl acetate was studied as a function of several reaction parameters, such as type of catalyst, temperature and products distribution. The reaction is an interesterification, a multistep consecutive ester interchange catalyzed by either acid or base catalyst. Under optimized conditions, a complete tributyrin conversion and an almost quantitative butyric acid methyl ester accumulation were achieved. The other reaction product, TAG, formed by the complete acetylation of the glycerol moiety, reached almost 70% yield, whereas the mono- and di-acetylated intermediates accumulated in the order of 5–8% and 24–27%, respectively. Similar final conversions and products yields were obtained with either acid or base homogeneous catalysts, suggesting that the final products mixture did not depend on the type of catalysis but might be limited by equilibrium conditions. In spite of similar final yields, base catalysis needed shorter reaction times (minutes instead of hours) and lower temperature (60 °C instead of 130 °C) with respect to the best acid catalyst. On the other hand, unlike heterogeneous basic catalysts, which showed low activity, a heterogeneous acid catalyst almost as active as the homogenous counterpart was found.

1. Introduction

The increase in biodiesel (fatty acids methyl esters, FAME) production as renewable fuel has been accompanied by a concurrent increase in the availability of its main co-product, glycerol. The procedure to reach the high degree of purification needed for most commercial applications is difficult and expensive, thus glycerol exploitation as high grade commodity is an important aspect for improving the production process of biodiesel. A promising possibility is the development of technologies that can transform glycerol into compounds suitable to be mixed with biodiesel to improve low temperature and combustion properties [1,2]. An advantage of using glycerol derivatives in fuels is that, as a bio-component, it could be included in the renewable energy sources category and help to meet EU targets on transportation fossil fuels savings.

Several oxygenated compounds including glycerol carbonates [3], ethers [4] and acetals [5] were proved to successfully enhance fuel properties such as the reduction of viscosity, cloud point and particulate matter emission in diesel and biodiesel blends. A particular class of oxygenated derivatives is that of glycerol esters composed by short chain organic acids such as, for example, acetic acid [2].

In fact, glycerol triacetate (TAG, triacetin) can be added to biodiesel (FAME) without major alteration of the fuel properties [6] and even to gasoline with improvement of the octane parameters [2].

Several routes have been developed to synthesize glycerol organic esters. The direct esterification with organic acids (such as acetic acid) in the presence of acid catalysts (including sulphonic resin and zeolites) is one of the most used methodologies [7,8]. All these approaches are based on the availability of pure glycerol, which has to be independently isolated and purified from the FAME synthesis, a step that, actually, is a common side route of FAME industrial production. In fact, a typical batch or semi-continuous process includes glycerine separation and purification, followed by elimination of the excess methanol used for the initial FAME synthesis. Consequently, FAME and glycerol derivative syntheses are performed in two independent and consecutive steps.

A possible alternative to these conventional processes is the simultaneous co-production of FAME and glycerol oxygenated compounds in the same one-pot reaction, making the glycerin iso-

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doi:10.1016/j.apcata.2010.12.029

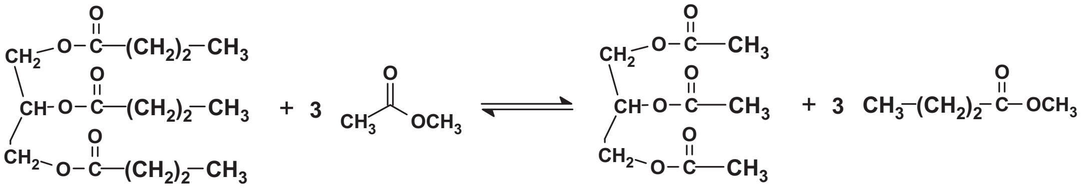

Fig. 1. Overall reaction between tributyrin and methyl acetate to triacetyl glycerol (triacetin) and butyrate methyl ester.

lation and purification steps unnecessary [9]. The simultaneous double synthesis of FAME and glycerol derivatives using vegetable oils as starting material has been carried out by using double group-donor agents, such as methyl or ethyl acetate. These reagents match the concurrent chemical need of an alcohol, necessary for the esterification of the triglyceride fatty acid, and of an acid, necessary for the esterification of glycerol hydroxyl group(s). The reaction, schematically presented in Fig. 1 in the case of tributyrin as starting triglyceride, ideally yields a mixture of FAME and triacetin (59% and 41% (w/w), respectively, if the reaction goes to completion), without co-production of glycerol and intermediates.

When triglycerides containing long chain fatty acids are used, the final mixture could be used directly as component in diesel and biodiesel blends, without further treatment. This can be clearly concluded from the data presented in Table 1, where the fuel properties of diesel/FAME and diesel/FAME–TAG blends are compared with the pure base diesel. As it can be seen, the addition of 10 vol% FAME to a standard base diesel improved somewhat the fuel properties of the base diesel by increasing slightly cetane parameters and flash point. The mixture FAME/TAG at 10% level did not further induce any major change with respect to FAME alone. In particular, distillation-95% temperature and viscosity were slightly lowered and closer to the base diesel values.

Transesterification with methyl acetate has been studied to some extent by using enzymes as catalysts [10,11]. It was found that vegetable oils from different sources can be converted almost quantitatively to the corresponding FAME (yields >90%) in the presence of methyl acetate. Suitable enzyme catalysts are lipases, mainly bacterial, which are able to function in organic media and, after immobilization, to withstand recycling without significant loss of activity. Although the yield of FAME is almost quantitative, no detailed analysis was carried on the compositions of the final products mixture, nor on the yield of triacetin, the end product of the multi-acylation step. The enzyme catalyzed reactions have the advantages of the mild reaction conditions (temperature as high as 40–60 °C, no catalyst purification, and possible catalyst recycling). However, they suffer from some important drawbacks such as long reaction times (40–60 h), sensitivity to hydration and reactivity dependent on the length of the triglyceride fatty acid. In order to overcome these problems, it would be important to find out a catalyst, either homogenous or heterogeneous, able to overcome these disadvantages, still affording high triglyceride conversion and triacetin yield.

The simultaneous production of FAME and TAG from vegetable oils has been successfully accomplished in supercritical conditions without catalyst [6,12]. Since the reactivity of triglycerides and methyl acetate is not very high without a catalyst, extreme (supercritical) reaction conditions are required to obtain high products yields [6], thus imposing a significant challenge on the actual scalability of the process. Good yields of the FAME–TAG mixtures were obtained at rather high temperatures (350 °C) and pressures (20 kPa) even after reaction parameters optimization by statistical methods [13]. Although FAME production was nearly quantitative, the final yield of the FAME/TAG mixture was lower (about 80%) than the theoretical value.

In this work, the simultaneous synthesis of both FAME and glycerol oxygenated derivative, i.e. glycerol esters, from tributyrin in the presence of methyl acetate has been studied in detail. Tributyrin, a butter component, which is the shortest naturally occurring triglyceride besides triacetin, has been chosen as the representative model compound of the triglyceride series which includes the vegetable oils used for biodiesel production. A screening of different catalysts, acids and bases, either homogeneous or heterogeneous, were assayed in order to optimize the reaction time and products yields.

2. Experimental

2.1. Materials

Reagent grade methyl-acetate, methyl butyrate, tributyrin, triacetin and tetradecane were from Acros Organics (Italy). 1,8-Diazo-bicyclo-[5.4.0]undec-7-ene (DBU) and 1,5,7-Triaza-bicyclo [4.4.0]dec-5-ene (TBD) were from Fluka (Switzerland). Potassium-*tert*butoxide, acetic acid, sulphuric acid, trifluoromethanesulphonic acid, methanesulphonic acid and acetic anhydride were from Sigma–Aldrich (Italy). Sodium methoxide was freshly prepared for each reaction, by carefully weighting the appropriate amount of sodium metallic, according to the procedure described in the literature [14]. In order to obtain full solubility in methyl acetate, dry powder of sodium methoxide was prepared from sodium (0.041 g, 1.8 mmol) and methanol (1.58 g, 49.3 mmol). After 3 h under vigorous stirring, methanol was evaporated with nitrogen, until a dry fine powder was obtained.

Nafion Sac-13 was from Sigma–Aldrich (Italy). Amberlyst 15 was a generous gift of Rohm and Haas (Italy). Both were washed with methanol and dried under vacuum overnight at 90 °C before use. According to the producers, Nafion SAC 13 and Amberlyst 15 have 0.14 and 4.7 mmol equiv$_{\mathrm{H}}{}^{+}$/g, respectively (Table 2).

Zirconia sulphate (XZO1249, containing 7 wt% SO_3) and zirconia tungstate (XZO1251, containing 16 wt% WO_3) were a gift from MEL Chemicals (UK). The powders, separated on a 600 μm sieve, were calcined at 550 °C for 5 h and transferred to the reaction vessel under dry nitrogen atmosphere. Zeolite β (CP814E) was purchased from Zeolyst International (The Netherlands). It was calcined at 460 °C for 5 h and stored under dry nitrogen atmosphere. The SiO_2/Al_2O_3 mole ratio was 20 and the Al content was 1.6 mmol/g. Acid sites (Table 2) were measured by IR analysis of pyridine absorption at 250 °C according to the procedure described in the literature [15].

The alkaline form of ETS-10 sample was supplied by Engelhard (Iselin, NJ, USA). Elemental analysis gave TiO_2 18.5%, Na_2O 12.0% and K_2O 3.9%. ETS-10 is a microporous crystalline material having 12- and 7-membered ring channels. Its structure is topologically similar to that of zeolite β. Katalco 59-3, a high porosity sodium aluminate spherical absorbent, was from JM Group (UK). Pural Mg 70, from Sasol Germany GmbH (DE) is a commercial hydrotalcite-like anionic clays MgO = 71% Al_2O_3 = 29.2%. All these materials were thermally activated for 3 h as shown in Table 2.

Mixed oxides samples Mg:Al 3:1 and Mg:Al 3:1 + 10% Fe were prepared from layered double hydroxides (LDH) hydrotalcites and