Eclética Química Journal

Original research publication in all aspects of Chemistry
homepage: http://revista.iq.unesp.br/ojs/index.php/ecletica/
ISSN 1678-4618

| Vol. 41 | 2016 |

Sunflower oil methanolisys and glycerol ketalisation: stepwise production of biofuels and additives with 3-methylimidazolium hydrogensulphate as catalyst

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Resumo: O líquido iônico hidrogenossulfato de 3-metilimidazólio é solúvel na fase glicerol que ele cria, após catalisar a transesterificação do óleo de girassol em ésteres metílicos de ácidos graxos (FAMEs). A separação dessa fase e a adição de acetona permitem a produção do acetal de cinco membros 2,2-dimetil-1,3-dioxolano-4-yl-metanol, no qual o catalisador é insolúvel e é removido por decantação. Após secagem sob vácuo, o líquido iônico pode ser reutilizado para realizar o ciclo de dois estágios sem perda aparente de atividade.

Palavras-chave: óleo de girassol, transesterificação, produção de acetais, glicerol, líquido iônico, aditivo de biodiesel

Abstract: The ionic liquid 3-methylimidazolium hydrogensulfate is soluble within the glycerol phase that it creates, after catalyzing the transesterification of sunflower oil to fatty acids methyl esters with methanol. Separation of this phase and addition of acetone allow the production of the 5-membered ketal 2,2-dimethyl-1,3-dioxylane-4-yl-methanol, in which the catalyst is insoluble and is removed by decantation. After drying under vacuum, the ionic liquid is ready to rerun to the two-stage cycle with no apparent loss of activity.

Keywords: sunflower oil, transesterification, ketal production, glycerol, ionic liquid, biodiesel additive

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Eclética Química Journal, vol. 41, 54-59, 2016.
https://dx.doi.org/10.26850/1678-4618eqj.v41.1.2016.p54-59

INTRODUCTION

The present situation of the research in biofuel production seems to be divided in two different fronts that of the environment friendly preparation of alkyl esters from triglycerides, and the overwhelming concern of what to do with the inevitable byproduct glycerol. The efforts to address the first issue have been nicely put into perspective by Sherstyuk and coworkers[1]. On the other hand, the attempts to transform glycerol into value added chemicals have attracted attention all the way down from the production of C3 chemicals from hydrogenolysis or dehydration[2-5] and glycerol carbonate formation[6], to the more prosaic etherification[7] and reactions with ketones or aldehydes to produce ketals for fuel additives[8-9]. An up to date account of these later efforts have been summarized by Fan et al., who called the attention to the fact that common inorganic acids used as catalysts for the ketalization reactions pose serious erosion of devices and other environmental problems; to circumvent these drawbacks, heterogeneous acidic catalysts such as cation-exchange resins, heteropolyacids, zeolites, solid superacids and supported metal oxides have been developed[10]. However, to the best of our knowledge, there is no account in the literature that describes, at the same time, the production of biodiesel and its ketal additive from a single source, *e.g.*, sunflower oil, with the use of a single catalyst, in our case the ionic liquid 3-methylimidazolium hydrogensulfate.

EXPERIMENTAL PROCEDURES

Refined sunflower oil, anhydrous methyl alcohol (99.3%), acetonitrile, 1-methylimidazole, and glacial sulfuric acid are commercially available and were used without purification.

Preparation of 3-methylimidazolium hydrogensulfate ($[Hmim]^{+}HSO_4^{-}$)

Sulfuric acid (0.98 g, 0.01 mmol) was added dropwise to a stirred solution of 1-methylimidazole (0.82 g, 0.01 mmol) dissolved in 10 mL of acetonitrile at 0 ^{o}C. The mixture was further stirred for 30 min, and the acetonitrile was decanted to afford the ionic liquid in quantitative yield.

General procedure for the biodiesel synthesis

25 mL of sunflower oil, 15 mL of methanol and 10.0 g of ($[Hmim]^{+}HSO_4^{-}$) were added to a 100 cm^3, round-bottomed flask fitted with a reflux condenser. The transesterification was typically allowed to proceed for 24 h with vigorous stirring at the reflux temperature. The alcohol was distilled off in a rotatory evaporator, after which two phases were formed and separated. The upper layer, consisting of biodiesel, was washed with deionized water and dried over anhydrous $MgSO_4$. The lower layer, containing glycerol and catalyst, was dried under vacuum for 4 h and subsequently used for the synthesis of the ketal.

Preparation of ketal 2,2-dimethyl-1,3-dioxolane-4-yl methanol

The ionic liquid and glycerol from the previous preparation was mixed with 15 mL of acetone, and the mixture was heated to the reflux temperature for 12 h. After allowing the mixture to reach the room temperature, the organic layer was separated from the ionic liquid catalyst by decanting, and its composition identified by GC – MS.

($[Hmim]^{+}HSO_4^{-}$) was reused for the entire process after removal of water under vacuum, without loss the catalytical activity.

Instrumentation

Gas Chromatograph/Mass Spectrometer GC/MS-QP 2010/AOC-5000 AUTO INJECTOR/Shimadzu, equipped with a split capillary inlet was used. Separation of the different compounds was achieved in an Agilent J&W GC Columns DB-5MS (30^{o}m^{o}x^{o}0.25^{o}mm, 0.25^{o}µm film thickness). Initial oven temperature was set at 100 °C, held for 4 min; ramped at 5 °C min^{-1} up to 200 °C, held for 8 min; ramped at 10 °C min^{-1} up to 260 °C and held for

10 min. The ionization energy used was 70 eV in EI (electron ionization) mode.

A Bruker micrOTOFQ II – Eletrospray Ionisation Time od Flight (ESI-TOF) Mass Spectrometer was used in positive mode detection, with an internal calibration solution of 10 mg/mL NA-TFA (TOF). Analytical conditions: End Plate: 500 V; Capillary: 4500 V; Capillary Exit: 120 V; Skimmer 1: 50 V; Skimmer 2: 22 V; Transfer: 57 µs; Dry Gas Temp 180 ^{o}C; Dry Gas Flow 4 L/min; Neb Gas Pressure of nitrogen gas 0.4 bar.

RESULTS AND DISCUSSION

The most facile and trivial way to perform both transesterification reactions from triglycerides, and the conversion of polyols to ketals, is the use of protic, or Brönsted inorganic acids[8,9]. However, the known environmental hazards derived from the use of those polluting acid residues preclude the large scale implementation of those processes. There is, however, a different kind of Brönsted acids, represented by the cations derived from the direct protonation of suitable tertiary nitrogen molecules, and this field of ionic liquids has been recently reviewed[11]. Some characteristics of these Brönsted acids brought our attention, for instance, their capacity to form hydrogen bonds with suitable Lewis bases[12] suggested that they should easily interact with glycerides and their derivatives. Also, the known ability of imidazol ionic liquids to serve as phase transfer agents[13] should be helpful to keep in contact the hard to mix substances of different polarities. These qualities prompted us to use the easily prepared Brönsted acidic 3-methylimidazolium hydrogensulfate as catalyst for a) the transesterification of sunflower oil, and b) the ketalisation of glycerol with acetone, two reactions which suffer from the poor solubility of triglycerides in methanol, and glycerol in acetone. The known poor catalytic effect of imidazolium cations in etherification reactions[13] indicated that more drastic reaction conditions should be used, if the intended transesterification and ketalisation reactions were to be properly performed. Fortunately, we found that these extreme conditions resumed to methanol or acetone reflux temperatures, with reaction times up to 24 h, two factors that do not imparted the development of the combined processes. On the other hand, the easiness that it was found of the catalyst recovery from either of the chemical reactions now typifies the environmental friendliness of the entire process, which makes it an appropriate candidate for large scale implementation.

In our trial experiments, we determined the optimal conditions for the conversion of sunflower oil into biodiesel, by following the reactions progresses by thin layer chromatography, using a eluting mixture consisting of the addition of two drops of acetic acid to 10 mL of a 5:95 solution of ethyl acetate in hexane, since this mixture allows the separation, and therefore the easy visualization, of the mono and diglycerides produced within the original reaction mixture, with the disappearance of the monoglycerides spots taken as the end point of the experiments. In this way, we found that the conversion of sunflower oil into fatty acid methyl esters (FAME), mediated by the catalyst ($[Hmim]^{+}HSO_4^{-}$) was a slow process, when compared to the traditional methods of using alkaline hydroxides as catalysts[14]. On the other hand, it was very interesting to find that, after stripping off the remaining alcohol from the reacted mixture, the layers of FAME and glycerol separated nicely, as usual, and, more interesting, that the FAME phase was only slightly acidic, requiring few washings to achieve a neutral pH.

The outcome of the transesterification reaction was also followed by high resolution mass spectrometry. The ESI-MS (positive mode) of the pure oil is shown in Fig. 1, where the tri and diglycerides appear in the regions of *m/z* 880 and 600, respectively. Interestingly, the ESI-MS of the reacting mixture after one hour of reflux, Fig. 2, showed a reduction of the intensities of the peaks around m/z 880, but an increase of the peaks around m/z 960, which probably reflects the complexation of the cation $[Hmim]^{+}$ with the triglycerides. Fig. 2 also shows a remarkable decrease of the peaks around m/z 600, which suggests that the glycerides containing at least one free –OH group may be transesterified first under the Brönsted ionic liquid conditions. This strong R-OH-$[Hmim]^{+}$ interaction may also explain the relative easiness of ketal formation from glycerol and acetone, see below. Figure 3 shows the spectrum of the same reaction mixture after 24 hours of reflux, where the signals around m/z 300 refer to the mixture of methylesters produced. According to the common interpretation of ESI-TOF-MS spectra, the major peaks can be associated to the protonated and sodiated forms of the methyl esters of linoleic ($[M + H]^+$ 293; $[M + Na]^+$ 315), oleic ($[M + H]^+$ 297; $[M + Na]^+$ 319), stearic ($[M + H]^+$ 299; $[M + Na]^+$ 321) and palmitic acids ($[M + H]^+$ 271; $[M + Na]^+$ 393). It is also possible to observe in Fig. 3 the presence of residual diglycerides, however, in quantities well below those accepted by the ASTM D6584 limits for these biodiesel contaminants.

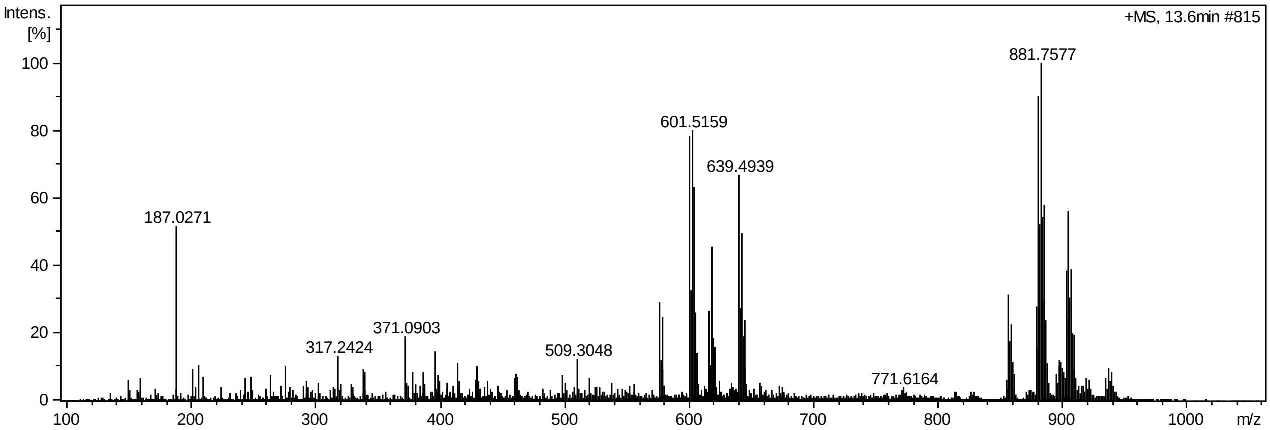

Figure 1. (+)ESI-TOF-MS refined sunflower oil, showing the prevalence of triglycerides around 880 m/z and diglycerides around 620 m/z.

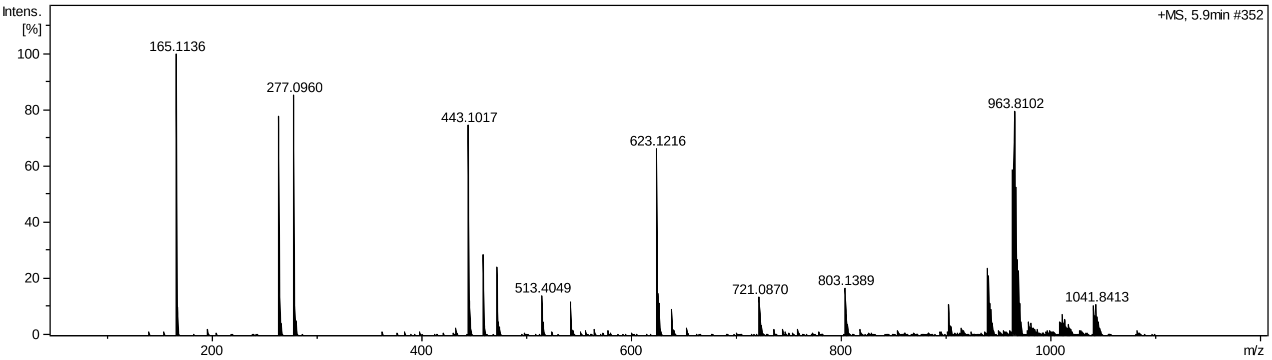

Figure 2. (+)ESI-TOF-MS of the sunflower oil, methanol and catalyst reaction mixture, after 1 hour of reflux. The peaks around m/z 960 are assigned to triglyceride-$[Hmim]^+$ adducts.

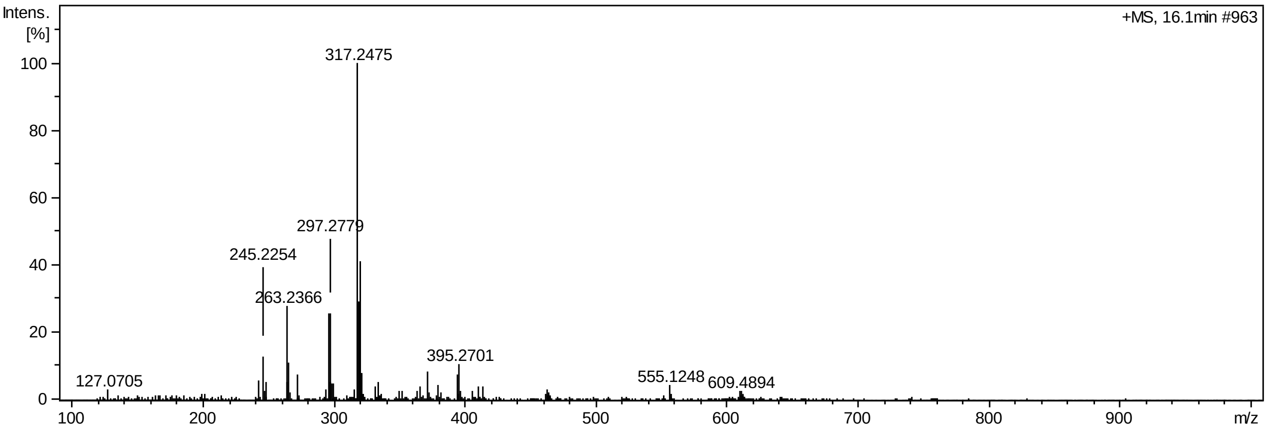

Figure 3. (+)ESI-TOF-MS of the reaction mixture after 24 hours reflux, showing the total consumption of triglycerides.

After the completion and cooling to room temperature of the transesterification reaction, the FAME phase was decanted, and the phase containing both glycerol and catalyst was mixed with the desired amount of acetone, and this mixture was heated to its reflux temperature for 12 h. After cooling down of the system to room temperature, it was found that the addition of a small portion of diethyl ether was beneficial, but not indispensable, for the rapid separation of the organic components from the ionic liquid. The ether being removed, the fragmentation pattern of the GC-MS spectrum of the organic phase revealed it to be consisted of 93% of the five membered ring ketal 2,2-dimethyl-1,3-dioxolan-4-yl methanol **1**, its six membered ring isomer being absent; the ether 1,4-dioxane-2,6-diyl dimethanol, **2** could be identified among the other 7% of the mixture; it is important to emphasize that these highly oxygenated compounds are themselves serious candidates for biodiesel fuels.

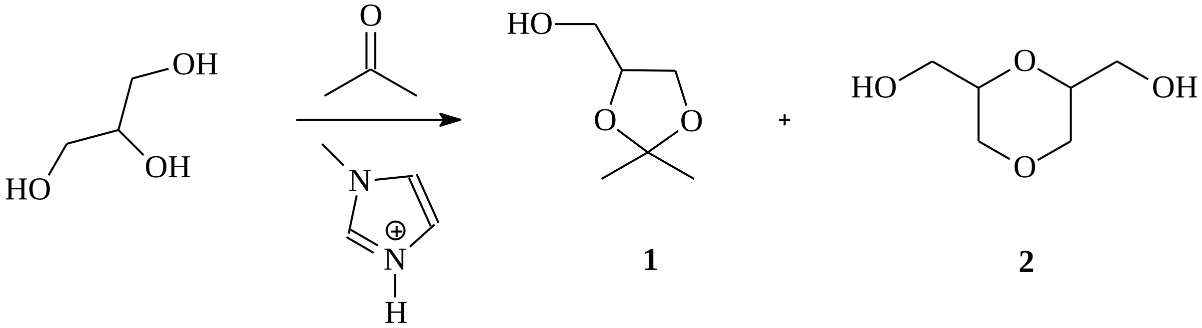

Figure 4. Major byproducts of the ketalisation of glycerol with acetone with $[Hmin]^+(HSO_4)^-$.

CONCLUSION

FAMEs biodiesel can be conveniently produced by the transesterification of sunflower oil with methanol, catalyzed by the easily prepared ionic liquid 3-methylimidazolium hydrogensulfate. The resulting solution of the catalyst and the glycerol byproduct can be sequentially used in a ketalisation process with acetone, affording quantitative amounts of biodiesel additives, 93% of which consisted of 2,2-dimethyl-1,3-dioxolan-4-yl methanol. The catalyst can be easily recovered.

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