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Supercritical ethanolysis for biodiesel production from edible oil waste using ionic liquid $[HMim][HSO_4]$ as catalyst

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ABSTRACT

Catalytic ethanolysis of waste cooking soybean oil using the ionic liquid $[HMim][HSO_4]$, as catalyst, to yield ethyl esters has been investigated. The ionic liquid, labeled as IL, showed stability under high conditions of temperature and pressure. Transesterification temperature was monitored and was maintained constant. The contents of ethyl esters in all samples were determined through GC (by normalization method) and ^1H NMR techniques. Highest yield (97.6 %) was obtained after 45 min of reaction, at 528 K under 9.62 MPa in the presence of 0.35 mL of IL. The transesterification did not occur with high yielding using the same conditions but in absence of the catalyst. The presence of water in reaction medium, in the range of 1.0–3.0% (v/v) due to ethanol impurity, does not affect the ethyl esters yield. The method proposed in this paper is advantageous over others reported in the literature due to the lower reaction time required and the higher biodiesel yield. The results showed that the biodiesel production by transesterification through supercritical ethanolysis is environmental-friendly and presented promising perspectives.

1. Introduction

Diesel is a fuel of complex composition and largely used in transport vehicles, farming, industrial and commercial sectors, to generate potency and mechanic energy. This oil has, as main components, paraffinic, olefinic and aromatic hydrocarbons and by-components (impurities) substances having sulfur, nitrogen and metallic atoms [1,2]. Biodiesel is an alternative fuel to diesel engines. Furthermore, it is renewable, biodegradable and nontoxic. Fatty acids alkyl esters of long chains are produced through transesterification reaction between alcohol and animal fat or vegetal oils [3,4]. Biodiesel is considered more environmental friendly than diesel because it presents reduced emissions of sulfur compounds (SO_x) and particulates based on phosphorus (P) compounds. The combustion reactions for diesel and biodiesel are shown in Scheme 1 [5].

Reaction-catalyzed systems developments are being constantly reported and there is a requirement about the products (that should be easily purified) and the catalysts (that should be recovered) [6]. Replacement of acidic liquid catalysts for nontoxic, non-corrosive, easy-to-handle and environmental friendly compounds is a pursuit in the field of catalysis. In this direction, ionic liquids, IL, are profitable from both economic and practical points of view [7].

The Belgian patent of 1937 (n. 422,877), entitled 'Procedé de transformation d'huiles végétales em vue de leur utilization comme carburants' [granted to Brussels University's researcher Charles George Chavanne] showed the first reporting of what nowadays we call biodiesel [8]. In such study, ethylic esters were obtained from palm oil by transesterification in acidic medium. However, the term biodiesel was published for the first time lastly, in 1988, in a Chinese work entitled 'Development of biodiesel fuel' [9–11]. Nowadays, vegetal oil biodiesel can be produced by several methods such as microemulsions, pyrolysis, catalytic cracking and transesterification, being the last the most promising and used method [12,13].

Transesterification reaction can be performed under homogeneous medium using acid or basic catalysts. In the basic catalysis,

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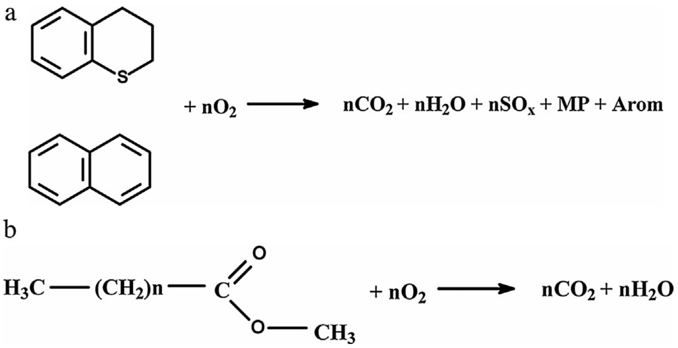

Scheme 1. Combustion reactions of (a) Diesel and (b) Biodiesel. MP means microparticulates. Arom means not or partially reacted aromatic compounds. Based on J.V. Visentainer and O.d.O.S. Júnior's book [5].

the saponification reaction results in products with difficulties in purification. This problem is not remarkable in the acidic reaction, but the reaction occurs in lower speed [14]. Transesterification at room temperature and ambient pressure is relatively low due to two-phase formation between oil and alcohol. However, biodiesel production can be accelerated using, or not, catalyst when the alcohol is under supercritical conditions [15,16].

Products obtained from the oil transesterification reaction under supercritical ethanol (scEtOH) are primarily monoalkyl esters of long chain fatty acids (biodiesel), glycerol as by-product and, depending on the used stoichiometry, either monoglycerides, diglycerides as reaction intermediates [17]. The general transesterification reaction of oil (triglyceride) by an alcohol is shown in Scheme 2.

The quantification of formed esters can be made through many techniques, such as ^{1}H NMR spectroscopy [18–20], gaseous chromatography (GC) [21–23], among others. In addition, this can be done using different ways, through a calibration curve, standard addition and normalization, as examples. For instance, studying impurity components of amphetamine, Pikkrainen showed that normalized results of GC were accurate; data processing studies for further pattern recognition studies indicated superiority of data normalization over quantitation [24]; also Bicchi et al. reported accuracy data by characterizing components of peppermint oil, where ultrafast module-GC and conventional GC normalized areas percentage were perfectly comparable [25].

Supercritical fluids are largely used in research. Related studies started in 1879 and a model describing the solubility in this condition was proposed in 1907 [26,27]. Solvents possess advantages in supercritical conditions, due to changes in solvent density and solvation power [28,29]. Conversion of oils to methyl esters using supercritical conditions started in the beginning of 2000's in Japan using basic catalyst [30].

Brazil is one of the most important ethanol producer. Ethanol is renewable and non toxic, thus can be used as alternative to methanol in the fatty acids transesterification process.

To overcome some difficulties related to transesterification reaction speed at ordinaries temperature and pressure conditions, new methodologies using alcohols in supercritical conditions has been proposed [31,32]. Procedures using IL as catalysts and/or solvents have been developed [33]. ILs are considered "green solvents" that attract great interest due to its distinctive characteristics: such as possibility for compound optimizing through a good selection of cations and anions, thermal and electrochemical stability, non volatility, low inflammability [34,35]. In this way, ILs have been largely used in the extraction, catalysis [36,37], electrochemistry [38] and organic synthesis [39,40]. ILs have melting points frequently smaller than 373 K, possess low viscosity and vapor pressure and usually are derivative from 1,3-dialkylimidazolium with counter ions that can be PF_6^-, BF_4^-, $CF_3SO_3^-$ etc. Furthermore, to be used as catalysts, IL should be soluble in the ionic phase and not in organic solvents. Then an organic solvent can be used to extract the formed organic products [41] allowing separation of catalyst.

In this study the IL 1-hydrogen-3-methylimidazolium hydrogen sulfate ([HMim][HSO_4]) was used as catalyst for the transesterification reaction of soybean waste oil under supercritical ethanol (scEtOH). The aim of this work was to determine the influences of reaction time and amount of water on yield of the biodiesel produced through the reaction catalyzed by [HMim][HSO_4]. The recovering of used catalyst was also evaluated.

2. Experimental

2.1. Synthesis of [HMim][HSO_4]

The [HMim][HSO_4] was synthetized according to the method described by Hajipour et al. [42]. For this, a 1-methylimidazol solution (1.59 mL, 20 mmol) was prepared in acetonitrile (5 mL) and maintained at close to 273 K, under stirring. Over this solution concentrated sulfuric acid (1.03 mL, 20 mmol) was added, drop-to-drop. The reaction was maintained under stirring for further 3 h (1 h at 273 K and 2 h at room temperature). In the end of the reaction time, the obtained IL was washed repeatedly with ethylic ether (3 × 5 mL), to remove any non ionic residues and, then, dried under reduced pressure (0.4 kPa) at room temperature for 24 h. The 1-hydrogen-3-methylimidazolium hydrogen sulfate was obtained like colorless and viscous oil, with high purity (as will show after).

2.2. Ionic liquid stability in scEtOH

The IL [HMim][HSO_4] was exposed to ethanol at room temperature (ca. 298 K) and ambient pressure conditions (ambEtOH) and also to ethanol under supercritical conditions (scEtOH), both during 45 min. To evaporate the excess of ethanol and remove ethanol/water residues, vacuum oven (Marconi, MA 030/12, Piracicaba, SP, Brazil), set at 313 K and reduced pressure of 20 kPa; and lyophilizer (Martin Christ, Alpha 1-2 LDs Plus, Germany) set at 233 K and reduced pressure of 0.4 kPa were used, respectively.

FTIR spectra (Perkin Elmer model Frontier, São Paulo, Brazil) in the range of 4000–400 cm^{-1}; ^{1}H NMR spectra (Varian model Mercury Plus, Palo Alto, CA, USA) operating at 300 MHz (DMSO-d_6, Cambridge Isotope Laboratories Inc, Andover, MA, USA); and Mass spectra (Micromass, model Quattro micro API, Beverly, Massachussets, USA) were acquired and analyzed in order to confirm the stability of IL.

2.3. Acquirement and samples preparation of soybean waste oil

Soybean oil was purchased in a local supermarket (Maringá, PR, Brazil); waste sample of this soybean oil was generated by submit a given amount of oil to six cycles (10 min, 453 K). Soybean oil and soybean waste oil samples were used in the transesterification reactions. Before the reaction, the sample was previously heated up to 373 K for 20 min to remove the moisture. Therefore, it was filtered with paper filter in simple funnel to remove any solid impurity.

2.4. Transesterification of soybean waste oil under scEtOH catalyzed by [HMim][HSO_4]

Transesterification process was performed according to the methodology described by Nunes et al. [43] for PET depolymerization and using the same apparatus. Reaction was carried out in a 0.1 L home-made batch-type reactor made of 316® stainless steel,