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Assessment of commercial resins in the biolubricants production from free fatty acids of castor oil

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ABSTRACT

In this work, different commercial resins (Dowex 50W-X8, Amberlyst-15 and Purolite CT275DR) were characterized by FTIR spectroscopy, N₂ adsorption-desorption isotherms, elemental analysis (CHNS), SEM, XPS data, TG analysis and acid-base titration to determinate the amount of Brønsted acid sites. These resins were tested in the esterification of free fatty acids coming from the castor oil (FACO) with 2-ethylhexanol for production synthetic biolubricants which display higher biodegradability than the traditional mineral lubricants. Under the operating conditions used, all resins were active in the esterification reaction, obtaining better results for macroreticular resins than gel resin. Amberlyst-15 was the most active catalyst, reaching a conversion value close to 90% after 1 h and 100% after 4 h of reaction. The effect of different parameters on catalytic performance was studied, optimizing variables such as: temperature, alcohol-fatty acid molar ratio as well as catalyst loading. The influence of increasing alcohol carbon chain length and branching on esterification rate at 80 °C was also examined using different alcohols. Likewise, reuse experiments indicate that the Amberlyst-15 resin lost activity after the first cycles but it is almost maintained around 60% from the third cycle. The esters synthesized exhibited better physical properties than those shown for its respective free fatty acid.

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1. Introduction

In the last centuries, the growth of the world population together with a greater demand of new resources, mainly due to the evolution of the society, has led to the depletion of the fossil fuel reserves. In addition, the population and particularly the governments are starting to be aware of high pollutant levels of harmful substances coming from fossil fuel sources giving rise to stringent environmental regulations. Consequently, the scientific community is developing alternative resources more environmental friendly.

Biomass is the most sustainable source to obtain energy as well as the unique source together with the fossil fuels that can be used to the synthesis of chemicals [1]. Among them, the synthesis of

basestock oil has focused many efforts to obtain products with good physicochemical properties and low cost. Traditionally, the mineral oils are synthesized from the distillate of petroleum being classified as function of its fraction in alkanes, naphthenic oils and aromatic oils. The mineral oils display many applications in the field of biomedicine, cosmetics or engineering due to the interesting mechanical, thermal or electrical applications [2]. Currently, about a 90% of the world consumption is attributed to mineral oils, although their poor biodegradability make these compounds highly toxic substances even being carcinogenic for humans [2]. The remaining 10% of the world lubricant production is attributed to synthetic esters; however, its high cost limits its implementation at larger scale considering the high demand [2]. Thus, the current challenge is the synthesis of lubricants economically more competitive with appropriate physicochemical properties and higher biodegradability than the traditional mineral oils.

Biolubricants are synthesized from plant oils such as palm, soybean, sunflower, rapeseed, castor and coconut due to faster biodegradability and lower toxicity than mineral oils [3,4]. These

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compounds display high potential due to lubricity, viscosity, and high flash and boiling point which diminishes the friction losses, favors their use in a wide temperature range as well as minimizes the emissions and provides higher safety due to their faster degradation, exhibiting excellent properties in comparison with mineral oils [3,5,6].

Synthetic biolubricants can be prepared by esterification of free fatty acids and transesterification of vegetable oils or biodiesel with alcohols having long alkyl groups (typically $\geq C8$) or complicated hydrocarbon structure with more than one hydroxyl group, as well as linear or branched carbon chain alcohols [7–9]. The combination between long linear chains, branching, double bonds and hydroxyl groups has a large influence on the properties of the final biolubricants, such as viscosity, pour point, oxidative stability and others [8]. However, the great majority feedstock of these biolubricants can compete with the food cycle for land, water and other resources. This fact has led to realize big efforts to develop methods to obtain the same fuels from sources that would not impact the food chain [10]. In this sense, castor oil is one of the most valuable non-edible oils [11]. Castor oil, itself, displays applications in the field of chemical industry such as paints, coatings, inks, lubricants and a variety of products [12]. The high interest of the castor oil is attributed to its high content of ricinoleic acid (ca. 90%) which is an atypical free fatty acid due to the presence of a hydroxyl group in the 12 position that provides a high boiling point and viscosity to this compound due to the formation of hydrogen bonds with adjacent molecules. However, the ricinoleic acid is not the best choice to be directly used as lubricant due to its poor thermo-oxidative stability by the faster oxidation of the unsaturations of the free fatty acids and the peroxide formation and the production of polar oxidation products [13].

The esterification reaction of the free fatty acid is an easy procedure to improve the physicochemical properties of these compounds to be used as biolubricant. Thus, the length of the carbon chain of the fatty acid or the use of linear or branched alcohols can affect to the physicochemical behavior and application of the biolubricants [13,14]. On an industrial scale, the esterification reaction has been carried out in homogeneous phase using mineral acids as H_2SO_4 , HCl, H_3PO_4 or *p*-toluenesulfonic acid. Despite the high conversion values attained in short reaction times, the use of mineral acids as catalysts exhibits several disadvantages as their corrosivity and high water volumes required to remove the acid of the reaction medium. The use of solid acid catalysts has emerged as alternative to the mineral acid catalysts due to the easy recycling and regeneration of the catalysts as well as the easy separation of the catalyst of the reaction medium; however, these catalysts require more severe reaction conditions than the conventional mineral acid catalysts [15–17].

In the case of ricinoleic acid, it has been reported in the literature its esterification using mineral acids such as H_2SO_4 [14] or organo-sulfonic acids doped polyaniline [18–20], although the study has been only limited to the use of methanol as well as enzymatic hydrolysis with the use of lipases [21–23]. The use of cation-exchange resins has shown a high potential in acid catalyzed liquid phase reactions such as esterification of fatty acids due to their high acidity, chemical versatility, mechanical stability and relatively low cost [24–26]. The cation-exchange resins can be classified in gel-type and macro-reticular type as a function of divinylbenzene content leading to different thermal and mechanical stability, ion-exchange capacity and catalytic behavior. Thus, gel-type resins display low divinylbenzene content, with low surface area and low availability of the active sites in the dry state [24]. However, when the resin is in contact with a polar solvent, it suffers a swelling improving the availability of the active sites and hence its catalytic behavior is enhanced. The macro-reticular resins exhibit a rigid matrix with high divinylbenzene content making

them less susceptible to swelling, although it is not necessary due to the presence of interstices in the macroporous structure which leads to higher surface area and favors the mass transfer during the catalytic reaction [25].

The present research evaluates the catalytic behavior of the cation-exchange resins in the esterification of ricinoleic acid with a branched alcohol as 2-ethylhexanol, using one-gel-type resin Dowex 50W-X8 and two macro-reticular resins Amberlyst 15 hydrogen form dry and Purolite CT275DR. In addition, this work studies the influence of different reaction variables such as temperature, the catalyst loading or the reuse of the resins.

2. Material and methods

2.1. Materials

Ion exchange resins used in this research were: Dowex 50W-X8 form wet (16–40 mesh) (BDH Limite Poole), Amberlyst-15 hydrogen form dry (Sigma-Aldrich) and Purolite CT275DR (Purolite®).

The free fatty acid obtained of the castor oil (FACO) was supplied from Miracema-Nuodex (Campinas, Brazil). This acid showed the following composition: ricinoleic acid (C18:1-OH12) 85.37%, linoleic acid (C18:2) 6.61%, oleic acid (C18:1) 5.31%, palmitic acid (C16:0) 1.51% and stearic acid (C18:0) 1.20%. The calculated mean molecular weight of free acid castor oil (FACO) was $295.62 \text{ g mol}^{-1}$. 2-Ethylhexanol (2-EH) with $\geq 99\%$ purity was purchased from Merck. Methanol and 1-butanol was purchased from Vetec with min purity of 99.8 and 99.4%, respectively. Ethanol anhydrous with $\geq 99.8\%$ purity was purchased from J.T. Baker. 1-propanol and 1-octanol was purchased from Acros with ≥ 99 and 98% purity, respectively.

The gases employed were He (Air Liquide 99.99%), H_2 (Air Liquide 99.999%), N_2 (Air Liquide 99.9999%), Ar (Air Liquide 99.99%) and NH_3 (Air Liquide 99.9%).

2.2. Characterization of the catalysts

The textural parameters were evaluated from nitrogen adsorption-desorption isotherms at -196°C as determined by an automatic ASAP 2020 system from Micromeritics. Prior to the measurements, samples were outgassed at 100°C and 10^{-4} mbar overnight to avoid degradation of the resins. Specific surface areas (S_{BET}) were determined by using the Brunauer-Emmett-Teller (BET) equation and a nitrogen molecule cross section of 16.2 \AA^2 [27].

FTIR spectra were collected on a Shimadzu Fourier Transform Infrared Instrument (FTIR8300) between 4000 and 400 cm^{-1} by using wafers of the samples (2 wt%) with KBr. The interferograms consisted of 200 scans, and the spectra were collected using a KBr spectrum as background.

Elemental chemical analysis was performed with a LECO CHNS 932 analyzer (LECO Corporation, St. Joseph, MI, USA) to determine the sulfur content present through the combustion of the samples at 1100°C in pure oxygen to form SO_2 .

The quantification of the acid sites was carried out by titration using 0.1 M NaOH solution for 0.1 g of each resin.

Thermal analysis was performed on a TG-DTG thermobalance (Mettler Toledo, Columbus, OH, USA) with a continuous heating rate of 5°C min^{-1} in air flow 50 mL min^{-1} from 30 to 900°C .

X-ray photoelectron spectra were collected using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Mg $K\alpha$ radiation (300 W, 15 kV, and 1253.6 eV) with a multi-channel detector. Spectra of samples were recorded in the constant pass energy mode at 29.35 eV, using a $720 \mu\text{m}$ diameter analysis area. Charge referencing was measured against adventitious carbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0F software package was used

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