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Evaluation of antioxidant action by electrochemical and accelerated oxidation experiments of phenolic compounds derived from cashew nut shell liquid

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ABSTRACT

This paper describes the use of electrochemical methods and accelerated oxidation experiments (EN 14112, Rancimat method) for the determination of antioxidant activity of phenolic compounds (cardanol, cardol and *tert*-butylated cardanol) derived from cashew nut shell liquid (CNSL), a byproduct obtained during the processing of cashew nuts classified as a renewable raw material, natural of low-value. Through the electrochemical study, having as reference the anodic peak potential (Epa) and peak current (Ip), was observed that the cardol had the best performance, followed by *tert*-butylated cardanol and this by cardanol, showing that the presence of electron-donating groups as *tert*-butyl and hydroxyl exerts a positive influence on the antioxidant action of these compounds. These analyzes showed also that unsaturated compounds presented current values superior than saturated ones, indicating that the unsaturated molecules participate in greater number of the electro-oxidation process. The accelerated oxidation experiments were performed through analysis of biodiesel samples additivated with CNSL-based antioxidants at 500 ppm, and the same sequence of activity presented by the electrochemical study was observed, showing that this class of compounds can be applied effectively to inhibit the oxidative process of biofuel.

1. Introduction

Cashew nut shell liquid (CNSL), a byproduct obtained during the industrial processing of cashew nuts from *Anacardium occidentale* L., is a brownish viscous oil composed of phenolic compounds in proportions that vary according to the method of extraction and that present a side chain of fifteen carbon atoms which may present one, two or three unsaturations. In general, the initial composition of natural CNSL (solvent-extracted) is basically a mixture of anacardic acid (70%), cardanol (18%), cardol (10%) and 2-methylcardol (1%) (Fig. 1). Because of the low thermal stability of the carboxylic group of anacardic acid (tendency to get converted to cardanol), the two major components of the technical CNSL (obtained from thermal processing) are the monophenol cardanol and the resorcinol derivative cardol (Amorati et al., 2001, 2011; Attanasi et al., 2012; Balgude and Sabnis, 2014,b; Maia et al., 2012a,b; Oliveira et al., 2011).

Due to their classification as a natural renewable raw material, with low-cost, the CNSL and its components have been used

Abbreviations: ABTS, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid); ANP, Brazilian National Agency of Petroleum; ASTM, American Society for Testing and Materials; BHT, butylated hydroxytoluene; CD-U, unsaturated cardol; CDN-U, unsaturated cardanol; CDN-TU, unsaturated *tert*-butylated cardanol; CNSL, cashew nutshell liquid; DPPH, 2,2-diphenyl-1-picrylhydrazyl; EN, European Standards; E_{pa}, Potential of anodic peak; FAME, fatty acid methyl esters; GC–MS, gas chromatography/mass spectrometry; IT, Induction time; NMR, Nuclear magnetic resonance; SWV, Square wave voltammetry.

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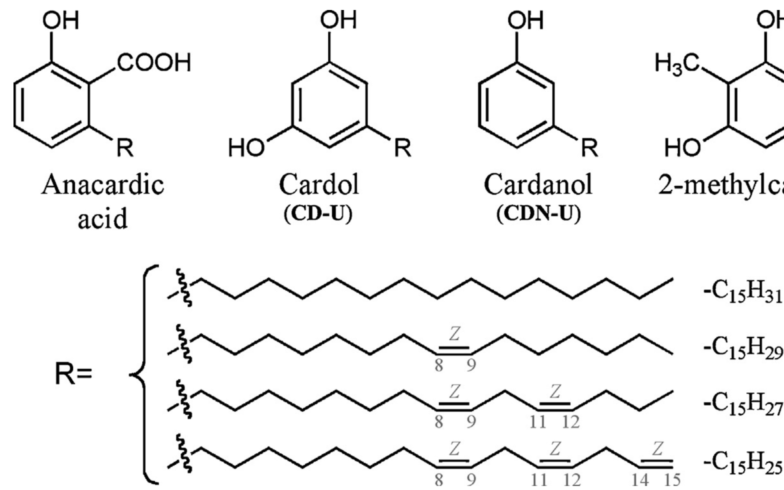

Fig. 1. Molecular structure of Cashew nut shell liquid constituents.

in many studies as a basis for development of eco-friendly products (Balgude and Sabnis, 2014). Among these studies we can highlight the direct application of CNSL components as antioxidants or as start materials for production of new compounds with improved antioxidant action (Amorati et al., 2002, 2011,b; Maia et al., 2012a,b; Rodrigues et al., 2006).

In general terms, an antioxidant is a molecule capable of inhibiting the oxidation of other molecules. These compounds can be defined as any substance that when present in low concentrations, compared to that of an oxidizable substrate, decreases significantly or inhibits the oxidation of that substrate (Amorati et al., 2002; Ilhami, 2012; Zhang et al., 2014).

Phenolic compounds have been highlighted as an important group of substances with antioxidant action, which can scavenge free radicals formed during the oxidative process (Marquardt et al., 2013). This class of compounds may be divided into two main groups: synthetic, such as butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) *tert*-butylhydroquinone (TBHQ) and propyl gallate (PG) (Ilhami, 2012), and natural, as α-tocopherol (Marquardt et al., 2013), flavonoids (Xi et al., 2014), gallic acid (Hamid and Newair, 2011) and others, which are mostly obtained from vegetable extracts (Gonçalves et al., 2013).

Different methodologies are used to evaluate the antioxidant action of a compound or extract rich in compounds of the same chemical function, for example, scavenging activity toward stable free radicals (DPPH•, ABTS•+) (Taira et al., 2015), peroxyl radical scavenging (Alarcóna and Denicola, 2013) thermochemical methods (Wua et al., 2013), accelerated oxidative studies (Dweck et al., 2013), electrochemical studies (Maia et al., 2012a,b,b; Simić et al., 2007) and others. Among these, the electrochemical methods presents, as main advantage, faster analysis, requires small amounts of sample, presents high sensitivity and effective application in evaluation of antioxidant action of phenolic compounds (Maia et al., 2012a,b,b). That also may provide useful information about the free radical scavenging activity as well as about the mechanism of electrochemical oxidation of phenolic compounds (Hamid et al., 2011). On the other hand, the accelerated oxidation experiments can be classified as the methods frequently used to evaluate the oxidative stability of fats, oils, and biofuels and to determine the performance of different types of antioxidants (Valle et al., 2014). The Rancimat method, for example, is specified by the American Society for Testing and Materials (ASTM) D6751 and European Standards (EN) 14214 as standard for assessing oxidative stability of biodiesel (Dweck et al., 2013).

In a recent work, our group presented a study of the antioxidant activity of phenolic compounds derived of CNSL (cardanol, cardol and *tert*-butylated cardanol, all hydrogenated) showing, through electrochemical analyses, that these derivatives have potential antioxidant activity, even higher than the BHT (one of the most widely used synthetic antioxidant) which has been applied effectively in inhibiting the oxidation process of organic substrates (Maia et al., 2012a,b,b). In this sense, this work has as main objective to continue the study of the antioxidant action of derivatives of CNSL using electrochemical methods and accelerated oxidation experiments, especially in the evaluation of unsaturated (natural) constituents (cardanol and cardol), and *tert*-butylated derivative of cardanol.

Knowing the mechanism of action of phenolic compounds, which is based on donation of hydrogen radical, the electrochemical study developed in this work will be directed primarily on the evaluation of the potential of anodic peak (E_{pa}) of each compound. In general, this parameter allows determining which molecule is most susceptible to suffer an electro-oxidative process that, according with literature is the specie with lowest E_{pa} value and consequently the best antioxidant (Simić et al., 2007).

The Rancimat test, in its turn, determines the time required for intense formation of volatile products of oxidation, defined as induction time (IT), by continuous measuring of electrical conductivity of deionized water when effluent from oxidizing oils is passed through it (Farhoosh et al., 2014). In this sense the induction time was used as a measure of antioxidant activity of phenolic compounds derived from CNSL in buriti (*Mauritia flexuosa*) biodiesel samples additivated with these compounds at 500 ppm and submitted to accelerated oxidation experiments, so that the higher the IT value, the more stable the sample and consequently more efficient is the antioxidant evaluated.

2. Experimental

2.1. Solutions and reagents

Technical CNSL was supplied by Amêndoas do Brasil Ltda. Solvents were supplied by Vetec Química (Brazil). 2-Chloro-2-methylpropane and Zinc chloride ($ZnCl_2$) were purchased from Sigma–Aldrich. Column chromatography was run using silica gel 60, while thin layer chromatography (TLC) was conducted on pre coated silica gel polyester sheets (Kieselgel 60 F254, 0.20 mm, Merck). All reagents used were analytical grade. The 0.04 mol/L Britton–Robinson (BR) buffer solutions, used as the support-