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Chemical transformations in technical cashew nut shell liquid and isolated mixture of cardanols, evaluation of the antioxidant activity and thermal stability of the products for use in pure biodiesel

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ABSTRACT

Biodiesel demand is increasing all over the world. The maintenance of oxidative stability is extremely important to biodiesel market, from the point of view of the quality of the fuel as the economic amount involved. In the present work, we synthesized new antioxidant candidates for biodiesel from chemical transformations in alkyl phenols present in technical cashew nut shell liquid (t-CNSL) and, more specifically, in cardanols isolated from t-CNSL. This raw material is viable, easy accessed and low cost. Five chemical transformations were performed in both t-CNSL and cardanols with yields from 50% to 92%. The starting materials and their respective derivatives were characterized by ^{1}H NMR, ^{13}C NMR and IR. Antioxidant activity and thermal stability of the products were evaluated. The induction period for pure biodiesel was 6.35 h and the addition of 0.5% (w/w) of cardanols increased to 7.37 h. Two products presented excellent antioxidant activity, epoxidized cardanols **(4)** and hydrolyzed cardanols **(6)**. They increased the induction period to 15.05 h and 18.62 h, respectively. The oxygenated derivatives also showed better thermal stability than the starting materials.

1. Introduction

Biodiesel has been used pure or blended to diesel in many countries, including Brazil [1]. It is defined as a mixture of alkyl esters of long chain fatty acids, obtained by transesterification or esterification of vegetable or animal fats and oils, with short chain alcohols, like methanol or ethanol [2–7]. Methanol is the most used industrially [8]. It is a renewable, non-carcinogenic, sulfur-free fuel and also reduces emission of polluting gases. The only concerns regarding the use of biodiesel are the increasing in NOx emissions and its low shelf life. The last one has currently being one of the major problems, and this become more evident with the increasing of the concentration of biodiesel in diesel [9,10].

Deposits begin to appear in the tanks during transportation and storage of biodiesel/diesel blends, which leads to clogging of filters, valves and pipes, causing wear on the pumps. The formation of these deposits is due to the chemical and physical differences between biodiesel and diesel. It consists of precipitated compounds due to the polarity difference in the blend, microorganisms that have proliferated due to propitious conditions (biological degradation), and products of the chemical degradation of biodiesel (oxidation and hydrolysis processes) [10]. Biodiesel is highly hygroscopic in comparison to diesel, due to the presence of oxygen atoms in its structure which can form hydrogen bonds with water. The presence of water leads to the growth of bacteria and fungi and its removal is an alternative to prevent the biological degradation, but it is not an easy strategy [11]. Another possibility is the use of biocide additives but the studies on this topic is still few [12–15]. Biodiesel and biodiesel/diesel blends are very susceptible to chemical degradation, mainly due to the composition of the fatty acids of the raw materials used in the production of the biofuel. Soybean oil is widely used as raw material for biodiesel production. It is rich in unsaturated fatty acids, approximately 70% of the fatty acids present in soybean oil has at least one double bond [16]. The presence of unsaturations in the alkyl chain associated with the presence of molecular oxygen in the environment lead to a series of oxidation reactions, which generate free radicals that can recombine and rearrange giving compounds of high molecular mass that deposit in tanks, systems of injection and other parts of the engine. Parts can also be worn and aged by the volatile compounds from the oxidation processes [10]. Absorbed water also degrades biodiesel, increasing its oxidative

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Table 1
Chemical composition of t-CNSL.

Phenolic compounds	t-CNSL (%)
Anacardic acids	1.09–1.75
Cardanols	67.82–94.60
Cardols	3.80–18.86
2-Methylcardols	1.20–4.10
Minority components	3.05–3.98
Polymer material	0.34–21.63

Adapted from [32].

instability which is already quite pronounced by the presence of double bonds in the chain of fatty acids alkyl esters. One way to minimize this problem is the use of additives.

Indeed, antioxidant additives originally applied in the food industry are currently being used for biodiesel. The chemicals used as additives are preferentially oxidized, retarding or even extinguishing the processes of oxidation of the biofuel. BHT (butylated hydroxytoluene), TBHQ (tert-butylhydroxyquinone), PG (propyl gallate), PY (pyrogallol) and BHA (butylated hydroxyanisole) are the most used [17–19]. More recently, these phenolic compounds have also been evaluated as antimicrobial agents in biodiesel [20,21]. Studies involving the use of natural antioxidants as additives for biodiesel have been reported in the literature. Some examples include the evaluation of phenolic acids [22], carboxylic acids [23] and plant extracts [24].

Recent research on antioxidants derived from cardanols has been reported [25–31]. Cardanols are the major constituents of technical cashew nut shell liquid (t-CNSL), by-product obtained from thermo-mechanical method used in the industrial processing of cashew nuts [32]. The chemical composition of t-CNSL can be observed in Table 1 and the chemical structure of CNSL constituents can be seen in Fig. 1.

In 2009, Rodrigues et al. investigated the antioxidant activity of hydrogenated cardanol by pressure differential scanning calorimetry (PDSC) and UV/Vis spectrophotometer techniques. Hydrogenated cardanol has improved cotton biodiesel oxidative stability, even after heating process [25]. As far as we know it was the first study that evaluated t-CNSL, more specifically cardanols, as antioxidant for biodiesel. In 2012, Lomonaco et al reported the synthesis of phosphorylated compounds by functionalization of the phenolic hydroxyl of cardanol; and the evaluation of the products as antioxidants for biodiesel using thermogravimetric analysis [26]. The results showed an increase in the thermal stability of biodiesel, making it more resistant to thermo-oxidative process. In 2013, the addition of hydrogenated cardanol and tert-butylated hydrogenated cardanol in soybean biodiesel influenced the biofuel stability with an increase of at least 70%, determined by Rancimat method [27]. Maia et al (2015) evaluated the antioxidant activity of buriti biodiesel added with both unsaturated and saturated cardanol, cardol and tert-butylated cardanol. The Rancimat method was used and it was also observed an increase in the value of induction period (IP) for all phenolic compounds. The values of IP obtained from analysis of unsaturated compounds were superior to that obtained for the saturated compounds [28]. In the same year, the electrochemical modification of t-CNSL led to the formation of a product that increased the oxidative stability of soybean biodiesel. The authors suggest that the electrolysis process produces dimers or oligomers by reaction between phenols present in t-CNSL [29]. The first and only antioxidant test involving a derivative from an effective chemical transformation in the alkyl chain of cardanols was reported by Liu et al. [30]. Until that moment, only the hydrogenation of the double bonds had been mentioned for this purpose. Epoxidized cardanol was synthesized and its effect on the oxidative stability of methyl oleate and methyl linoleate was tested using Rancimat method. It was observed an improvement in the oxidative stability of both methyl esters with the addition of epoxidized cardanol. In 2017, Bastos and Tubino evaluated the antioxidant activity of t-CNSL in biodiesels prepared from soybean oil, corn oil, canola oil and sunflower oil using Rancimat method [9]. In the same year, Kleinberg et al. verified the influence of the addition of natural CNSL and t-CNSL on the stability oxidation of beef tallow [31]. Following, the authors determined the induction period for the biodiesel produced from the additive raw material. By both methods, the addition of CNSL shows an increase in the oxidative stability of biodiesel.

Efforts to solve the low oxidative stability are an important step to ensure the quality of biodiesel. Cardanols and other alkyl phenols present in t-CNSL are characterized as chain breakers type antioxidants as well as the commercially used phenolic antioxidants. The present work reports the synthesis and evaluation of new t-CNSL and cardanols derivatives as antioxidants for biodiesel. The strategy was to preserve the phenolic structure and functionalize the double bonds of the alkyl

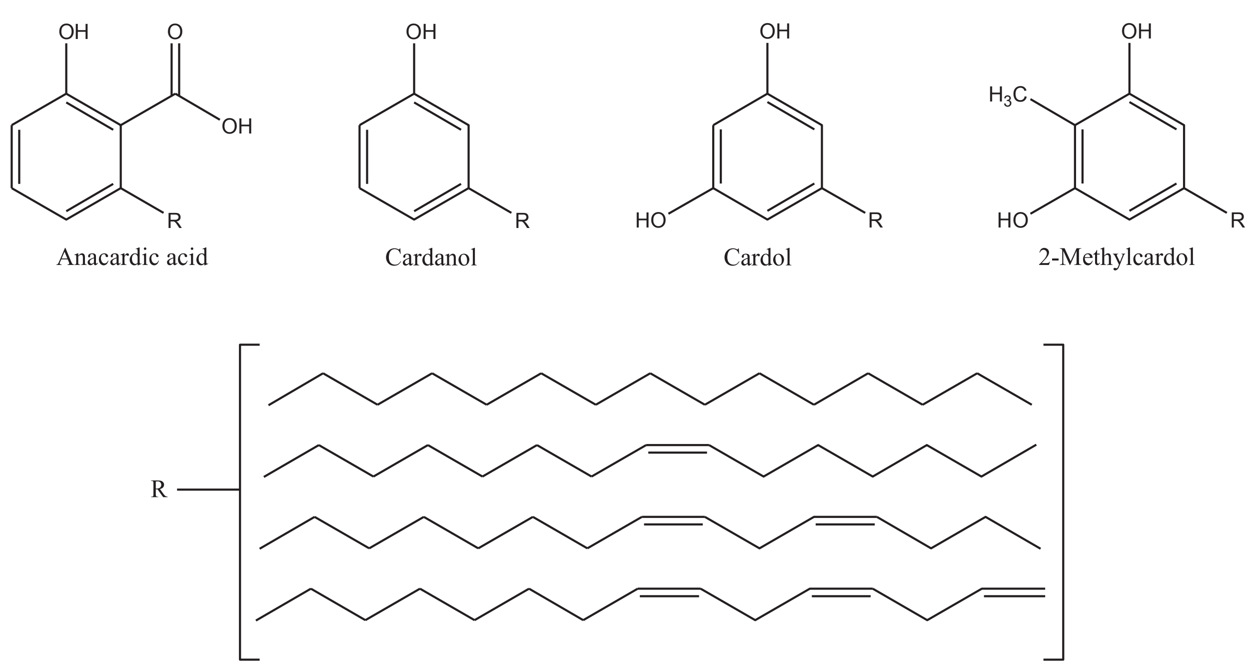

Fig. 1. Chemical structure of CNSL constituents.