Fuel 144 (2015) 415–422

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

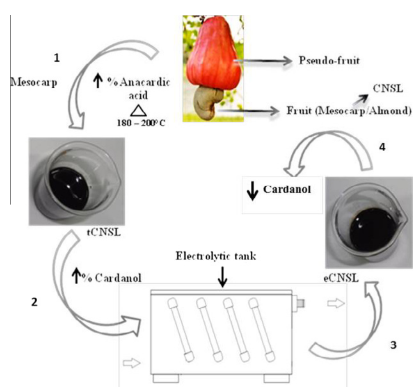
Development of an electrolytic method to obtain antioxidant for biodiesel from cashew nut shell liquid

Raimunda Cardoso dos Santos [a], Adriany das Graças Nascimento Amorim [a], Sérgio Scherrer Thomasi [f], Francisco Cardoso Figueiredo [b], Clécia Silva Carneiro [d], Paulo Robério Pinho da Silva [c], Wilson Rosas de Vasconcelos Neto [e], Antônio Gilberto Ferreira [f], José Ribeiro dos Santos Junior [b], José Roberto de Souza de Almeida Leite [a,*]

[a] *Center for Biodiversity Research and Biotechnology, Federal University of Piauí, Av Sãn Sebastião, 2819, Reis Veloso, 64202-020 Parnaíba, PI, Brazil*
[b] *Bioelectrochemistry Group, Federal University of Piauí, Campus Minister Petronio Portela, 64049-550 Teresina, PI, Brazil*
[c] *Anhydrous Extractions of Brazil S.A, Rua Pilocarpina, 1000, Igaraçu, 64216-815 Parnaíba, PI, Brazil*
[d] *National Service of Industrial Learning, Av. Industrial Gil Martins, 1810, 9°andar, Ed. Albano Franco, Redenção, 64017-650 Teresina, PI, Brazil*
[e] *Federal Institute of Piauí, BR 402, Km 3, 64.215-000 Parnaíba, PI, Brazil*
[f] *Laboratory of Nuclear Magnetic Resonance, Federal University of São Carlos, Rodovia Washington Luiz, Km 235, PO Box – 676, São Carlos, SP, Brazil*

GRAPHICAL ABSTRACT

Illustration of the CNSL (Cashew Nut Shell Liquid) decarboxylation process during extraction by heating to tCNSL obtention (Stage 1). Then, tCNSL with high percentage of cardanol (Stage 2) was electrolyzed in an electrolytic tank (Stage 3) in order to obtain eCNSL with low percentage of cardanol (Stage 4).



ARTICLE INFO

Article history:
Received 1 September 2014
Received in revised form 20 November 2014
Accepted 25 November 2014
Available online 23 December 2014

Keywords:
Anacardium occidentale
CNSL
Antioxidant

ABSTRACT

An electrochemical method was applied in order to obtain a new antioxidant for soy biodiesel conservation, from the technical CNSL (tCNSL). The electrochemical modification occurred in an electrolytic tank under controlled conditions, including the voltage, electrical current and tCNSL flow. Physico-chemical analysis and Fourier Transform Infrared (FTIR) were carried out on tCNSL and eCNSL, while Gas Chromatography coupled to Mass Spectrometry (CG–MS) and Nuclear Magnetic Resonance (NMR) was carried out only on eCNSL to characterize the occured transformations after the electrolysis process. The Rancimat results showed that when eCNSL was added to the soy biodiesel, it was able to increased it is oxidative stability and the Induction Period (IP = 7.31 ± 0.20) values were higher than that required by ANP (Agency of Petroleum, Natural Gas and Biofuels). The electrolytic tests results combined with GC–MS displayed a significant decrease in the cardanol percentage which can promote the formation of dimers or oligomers that may be

* Corresponding author. Tel.: +55 86 8854 9286; fax: +55 86 3323 5841.
E-mail addresses: raimundaphb@gmail.com (R.C. dos Santos), adriany1210@gmail.com (A. das G.N. Amorim), secherrer@yahoo.com.br (S.S. Thomasi), fcfigueiredo19@hotmail.com (F.C. Figueiredo), cscarneiro@hotmail.com (C.S. Carneiro), wilson.rosas@gmail.com (W.R. de Vasconcelos Neto), giba_04@yahoo.com.br (A.G. Ferreira), jribeiro@ufpi.edu.br (J.R. dos Santos Junior), jrleite@pq.cnpq.br (J.R.de.S.de A. Leite).

http://dx.doi.org/10.1016/j.fuel.2014.11.082

Biofuel
Electrolysis

responsible for the increased antioxidant activity of the eCNSL. Therefore, the electrolysis process resulted in an effective biofuel antioxidant that presents interesting commercial advantages.

1. Introduction

The cashew tree (*Anacardium occidentale* Linn), a member of the Anacardiaceae family, is a species cultivated and distributed in all tropical regions of the world [1,2]. The main product of the cashew tree is the cashew, whose kernel is world renowned and one of the most important exportations products. The worldwide production of cashew nut in 2009 was around 3,300,000 tonnes, and 25% of the total weight of the cashew nut is CNSL, in this period Brazil was one of main nut producers [3,4].

Cashew Nut Shell Liquid (CNSL), extracted from the kernel mesocarp is emerging as the main byproduct of the cashew production, thus, this important byproduct has commercial value for the kernel processing industry and is also receiving attention in the petrochemical industry as an additive for biofuels [5].

According to the extraction mode, CNSL can be classified as natural CNSL (nCNSL) or technical CNSL (tCNSL). They contain a mixture of meta alkylphenols with different insaturations degrees and presents the following major compounds: cardanol, cardol, anacardic acid and traces of methylcardol [6–8]. If a temperature range of 180–200 °C is applied to the nCNSL extraction process it occurs a decarboxylation of anacardic acid, obtaining cardanol in a concentration of 60% to 70% [3,9,10].

The industrial applications of CNSL based products are numerous. Recently, studies have documented that the CNSL phenolic compounds can act as antioxidants in lubricants, greases and gasoline stabilizers [3,11,12]. In addition, phenolic compounds, such as cardanol when used as biofuel additives, present antioxidant activity due to their ability of inhibiting oxidation and delaying the decomposition of organic matter [8].

Research conducted with CNSL showed that cardanol hydrogens are able to neutralize the action of free radicals with similar antioxidant potential as synthetic antioxidants, when present in organic matter [6]. Biodiesel, for example, is an organic matter that has received worldwide prominence due to it is features: nontoxic, originated from are renewable resource, biodegradable, and alternative fuel able to replace (partial or total) diesel derived from petroleum considered more polluting [13–15]. However, the oxidative stability of biodiesel is lower than that of petroleum originated diesel and this fact has stimulated studies with emphasis on the investigation of compounds with antioxidant action for biofuels industry [16,17].

Some studies reported that in order to improve the potential antioxidant activity of CNSL it needs changes in its chemical structure, mainly by addition of phosphorus groups with stabilizing action, responsible for decomposing hydroperoxides and oxyradicals [3]. However, the combination of a significant number of chemical reagents needed during this process makes this technological alternative expensive and impractical for industrial scale production.

Based on the potential advantages of an antioxidant obtained from CNSL, representing a renewable raw material, biodegradable and abundant in Brazilian Northeast, this work has as main objective the modification of the tCNSL chemical composition by an inexpensive electrochemical method, in order to increase its antioxidant activity when added to biodiesel. This work also aims to assign more value to the CNSL production chain, improving the use of this industrial waste in the biofuel industry.

2. Experimental

2.1. Materials

Commercial vegetable soybean oil, sodium hydroxide (NaOH, 99%), and methanol (99.8%) were from VETEC used for biodiesel production by transesterification.

Cashew nut shell was obtained from EUROALIMENTOS (Teresina – PI, Brasil), industrial methanol (99.95%), shaped electrodes plates (stainless steel 304), and electrolytic tank for the electrolysis process.

For physico-chemical parameters pyridine (VETEC), methanol (99% JT Baker), Potassium chloride (KCl 99%, VETEC) were used.

Helium gas, BSTFA (Bis-Trimethylsilyl trifluoroacetamide – SUPELCO) silylating agent, and ethyl acetate (99.5%, VETEC) for GC–MS analysis.

Chloroform ($CDCl_3$, 99.8%) for Nuclear Magnetic Resonance (NMR) ^{1}H. All reagents used were analytical grade.

2.2. Electrolyzed CNSL preparation

The tCNSL sample was mixed with methanol in an industrial reactor (1:3) and transferred to the electrolytic tank. The inflow of the mixture, the voltage and electric current tub were controlled parameters and temperature used was 25 °C as describe in Vasconcelos Neto et al. [39]. The process was completed with the evaporation of methanol on a rotary evaporator BUCHI R-215 with controlled temperature and vacuum.

2.3. Biodiesel preparing (B100)

Biodiesel production by transesterification was carried out in the laboratory of ANIDRO, Parnaíba, Brasil. The soybean oil was pretreated using Sodium hydroxide (NaOH) 0.625 M, as catalyst in anhydrous methanol, to convert some of the fatty acids into esters by alkaline transesterification. Methanol was chosen as reagent because of it is low cost and fast reaction time. The processor was programmed to stirr at a temperature of 50 °C for 20 min, after that the mixture was poured into a decanter, and was separated in two layers: biodiesel (B100) and glycerol which was the denser phase. The glycerol was drained off by gravity and the excess of methanol in the biodiesel was removed in a flash evaporator hot plate. To further remove impurities, the B100 was washed in ultrapure water at 60 °C, of volume ratio 1–4 to remove the catalyst. Finally, the clean biodiesel was dried by heat at 50 °C for 15 min., and traces of water were removed by heating [18].

2.4. Physicochemical parameters of tCNSL and eCNSL

Viscosity assessment was carried out using Rotational Viscometer Microprocessor QUIMIS (Q860M21). A beaker containing 200 mL of the sample was put into the viscometer device. The viscosity was obtained at constant temperatures (25 ± 0.1 °C) and values were recorded as cP.

To determine the moisture content a Volumetric Karl Fischer, model AF8 from ORION was used. For titration, Karl Fischer pyridine (VETEC) and methanol (J.T. Baker) were employed.