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Distilled technical cashew nut shell liquid (DT-CNSL) as an effective biofuel and additive to stabilize triglyceride biofuels in diesel

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ABSTRACT

We report distilled technical cashew nut shell liquid (DT-CNSL) as a non-transesterified biofuel and also as an additive to convert triglycerides to biofuel, without the need for the formation of methyl esters. DT-CNSL blends of diesel obey physico-chemical parameters of diesel. DT-CNSL offers stability to blends of straight vegetable oil (SVO) and tallow oil in diesel. Fluorescence studies using charge transfer probes show that the blend of DT-CNSL, triglycerides and diesel is a uniform solution, and fluorescence behavior is similar to that of diesel. The economics for the cultivation of cashew (*Anacardium occidentale*), its industrial use and rich carbon sink properties indicate that DT-CNSL could complement or replace traditional biodiesel crops like Jatropha and improve income for farmers.

1. Introduction

Biofuel is a broad term covering any biomass-related product being used for fuel applications [1]. Biodiesel is a form of biofuel obtained by transesterification and it is typically blended with diesel [2]. Biodiesel is reported to have advantages over traditional petroleum fuels with respect to aspects of availability, pollution, and economics [2]. These include reduction in CO emission, higher cetane rating, biodegradability, and being non-toxic [3,4]. Biodiesel is also associated with some drawbacks, which have led some researchers to question the logic of using biodiesel for automotive applications [1,5,6].

There is increasing criticism that some biodiesel is not environmentally friendly and that the high amount of energy needed for the preparation of transesterified biodiesel from triglycerides by using methanol, sodium hydroxide and neutralization of resultant waste products results in high processing costs. Distillation of biodiesel can consume more energy than is obtained from its use [5,6]. Farmers cultivating Jatropha in wastelands of South Asia are increasingly realizing that the yields obtained are significantly lower than those projected by government agencies [7,8]. There are increasing reports that Jatropha leaves and seed husk cannot be used as cattle feed and traces of hydrogen cyanide present in leaves and seeds can be harmful to people associated with processing of seeds and in seed collection [9,10]. In support of this the USA Food and Drug Administration (FDA) has released an advisory in July 2012 asking all food producers to stay away from Jatropha products such as glycerol and protein byproducts [11]. Until now Jatropha producers have relied on food and pharmaceutical applications of rich protein byproducts to offset the costs of supplying Jatropha oil to the biofuel industry, and so the toxic phorbol esters present in Jatropha products are a serious concern for the viability of this crop [12]. In India edible oils such as palm and soybean oils are banned for fuel applications and so alternatives to Jatropha crops need to address the issue of loss of land for use to product food crops.

Abbreviations: DT-CNSLs, distilled technical cashew nut shell liquid; SVO, straight (or waste) vegetable oil; AOT, sodium bis [2-ethylhexyl] sulfosuccinate; PRODANs, N,N-dimethyl-6-propionyl-2-naphthylamine; NILE RED, 9-diethylamino-5-benzo[α]phenoxazinone; TNPP, trinonyl phenyl phosphite; GI cans, galvanized iron cans.

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Finally, the use of land for biodiesel cultivation in places like Asia and Africa, where severe food shortages exist, is coming under increased scrutiny and the logic behind Jatropha cultivation in particular is being seriously questioned [13]. An independent report has suggested that the amount of land currently used for Jatropha cultivation is more than the amount of land used in the USA for corn-based ethanol production. Government agencies should have developed better water conservation techniques in order to grow a variety of crops in arid lands, rather than simply attempting to find a crop which grows with minimal water. Jatropha farmers who relied on research reports about high yields, growing conditions, oil content and prices are now in a crisis.

To overcome some of the difficulties associated with Jatropha farming for biofuel purposes a variety of crops are being assessed for their suitability as biofuel crops. An ideal crop derived biofuel should have the following characteristics: 1) It needs to be from a renewable source that improves food production rather than depleting it; 2) it shouldn't form a gel or cloud at temperatures above −10 °C; 3) it should produce comparable or improved fuel efficiency as compared to standard fuels; 4) it needs to be economically attractive for farmers, biodiesel producers and oil distributors; and 5) byproducts of biodiesel crops should have potential industrial applications. Some non-triglyceride plant oils are used directly as biofuel. Eucalyptol [14] and limonene [15] are reported to result in stable blends with petroleum products. Being terpenes they behave similarly to hydrocarbons and meet physicochemical standards for gasoline [14]. Terpenes usually fall under the essential oil category, are expensive, limited in supply, and the energy needed to produce them is high. These oils are present in 0.1–3% in plant parts and hence the total availability of material is not comparable to that from traditional biodiesel sources, which contain 20–30% in seeds [2]. Therefore, farming to produce these non-triglyceride plant oils for biofuel purposes is not economically feasible.

An alternative to both seed and plant crops is the use of byproducts from nut production. For example, cashew (*Anacardium occidentale*) is a tropical plant mostly grown in Asia, Africa and South America and is an important nut crop that provides food, employment and hard currency to farmers in developing countries [16]. Though cashew kernel is the most valuable part of cashew, cashew nut shell liquid (CNSL) also has some value. CNSL occurs as a reddish brown viscous liquid in the soft honeycomb structure of the shell of cashew nuts. Based on the mode of extraction, CNSL is classified into two types, natural CNSL and technical CNSL. Natural CNSL is obtained by extraction of cashew nut shell with solvents like hexane, light petroleum (40–60 °C), diethyl ether, or other organic solvents. It mainly contains anacardic acid (78%), cardol (10–15%), and minor quantities of 2-methyl cardol, cardanol, and polymeric material. Technical CNSL contains cardanol (60–65%), cardol (10–12%), methyl cardol (1–2%) and polymeric material (20–23%). All these phenolic compounds exist as mixture of saturated, mono, di, and trienes. Industrial application of cardanol-rich technical CNSL has been thoroughly reviewed previously [17,18].

Piyali das et al. [19] reported that CNSL pyrolysis products have components with characteristics similar to diesel. The major fuel application of CNSL derivatives are based on work by Deepak Kumar et al. [20] that shows that Mannich bases of cardanol have a unique property of allowing blending of ethanol with diesel. It is primarily CNSL derivatives, rather than CNSL itself that are used as biofuels, since CNSL typically contains a percentage of polymeric material, which prevents its use in automobile applications.

Publications on the fuel applications of DT-CNSL are starting to appear in the literature [21–25]. In a recent study [21] DT-CNSL is mentioned as an aid to solubilize ethanol in diesel. Palvannan and Balagurunathan [22] studied DT-CNSL in diesel blends and found them to be compatible with diesel engines. Mallikappa et al. [21] found that all emission and combustion parameters of DT-CNSL blends with diesel are comparable to diesel in single cylinder stationary test beds. The same authors reported [24] that up to 25% DT-CNSL in diesel meets the international diesel fuel specifications, and that both emission and combustion parameters are comparable to diesel. Although Kasundra and Gohil [25] suggested by theoretical calculations that emissions of DT-CNSL blends in diesel could increase unburnt hydrocarbons, NOx, CO, and particulate matter, actual engine emission studies have shown that 5–20% is indeed a viable combination [21–25].

Here, we report distilled technical CNSL (DT-CNSL) as a biofuel for blending up to 20% in diesel. DT-CNSL offers advantages over other biofuels, such as the elimination of transesterification, a low cost of production and the benefit of being a byproduct from a food crop. We discuss the mechanism of triglyceride stabilization in diesel using charge transfer fluorescence probes. DT-CNSL is a useful fuel additive that can stabilize triglycerides of straight vegetable oil (SVO) and Tallow oil in diesel. We also discuss the economics of growing cashew as compared with Jatropha.

2. Materials and methods

CNSL was obtained from a cashew processing facility located in Ankola, Karnataka, with the specification of a minimum of 90% cardanol. We distilled CNSL at 230 °C, at 0.2 mm Hg to obtain DT-CNSL. Plant oils were obtained from exporters based in Bangalore. Tallow oil was obtained from an importer based in India who sourced the material from Australia. Both plant oils & tallow oil have specification of minimum 98% triacylglycerol content and were used after filtration. Tallow oil had a minimum of 70% saturated triglycerides. Diesel fuel was obtained from a Hindustan Petroleum retail outlet located in Bangalore. We performed the physico-chemical analysis of this diesel as per IS1460:2005 [26]. Trinonyl phenyl phosphite (TNPP) was purchased from Aldrich. We used SVO as a common term to define both vegetable oil and waste vegetable oil. Triglycerides term is used when we are referring to both tallow and SVO.

2.1. Fluorescence studies

A stock solution of PRODAN was made in chloroform, so that the final concentration of chloroform in fuel blends was below 0.5% and PRODAN was at 50 μM concentration for each experiment. Fluorescence studies were performed using a Nanodrop fluorimeter (ND3300) and Shimadzu spectrofluorophotometer RF-5301PC.

2.2. Stability studies for DT-CNSL

Cardanol exists in nature as a mixture of monoene, diene and triene. Hence, it has iodine numbers higher than any of the vegetable oils in nature and is theoretically less preferred for fuel applications (iodine number 200–240) [27]. Color is frequently used to standardize on product stability and ASTM D 1500 method [28] determines the grading of oil and petroleum products based on color comparison to standards ranging in value from 0.5 to 8.0. We used TNPP as the anti-polymerizing agent for this study.