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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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A B S T R A C T

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.

2.3. Physico-chemical analysis

Physico-chemical analysis of DT-CNSL/diesel and DT-CNSL/diesel/triglyceride blended samples were performed as per the IS1460:2005. All the tests were executed based on the standard methods as given in the IS1460:2005 for automotive diesel fuel specification as shown in Table 1.

3. Results and discussion

3.1. Physico-chemical analysis of DT-CNSL fuel blends

IS1460: 2005 is the diesel standard followed in India and is equivalent to international norms for diesel. Considering the tropical climate in India, the norm requires only −3°°C cloud point and the blending of DT-CNSL did not alter this characteristic. A DT-CNSL/diesel blend (0–20%) containing at least 0.01% of anti-polymerizing agent is stable for at least 3 months. Distillation yields were initially low, primarily due to storage in plastic containers and the absence of antipolymerizing agents. Two areas of potential concern were low recovery during distillation and poor cetane number. We found that DT-CNSL is unstable when stored in plastic containers and changes color to 8 (iodine number) within 7 days of storage. When stored in galvanized iron (GI) cans, DT-CNSL is stable for 60 days and if an antipolymerizing agent (TNPP) is present it will take 120 days for significant color change.

We examined the color change of DT-CNSL as per ASTM D 1500. Interestingly, DT-CNSL blended with diesel has no measureable color change over 60 days of storage, probably due to the stabilizers present in diesel. This indicates that the DT-CNSL diesel blends are stable over time, particularly at the anticipated use levels of 5–20% DT-CNSL in diesel. The maximum color allowed for diesel as per IS1460: 2005 is 5 (on the ASTM D 1500 scale) and we tested the color development pattern over time and stabilization with anti-polymerizing agents. When the blends were stored in galvanized iron (GI) cans, the color change of blends was negligible and suggested that the antioxidants in diesel are able to stabilize cardanol. In order to observed color change over time under non-optimised storage conditions we carried out a stability study with freshly prepared blends of DT-CNSL and diesel stored in polyethylene containers, which are known to provide a surface for aerial oxidation. To freshly prepared blends of DT-CNSL and diesel, TNPP was added and the change of color of solutions stored in polyethylene containers was observed over time and data is given in Fig. 1. All samples containing TNPP had a minimum of three months stability. Diesel alone and 0.05% TNPP containing 10% DT-CNSL blend showed 1.5 units of color change over 6 months storage, as measured using the standard test method for ASTM color of petroleum products (ASTM D 1500). 10% DT-CNSL blends having no TNPP was also stable for 60-days, probably because diesel contains some antioxidants, which can also stabilize DT-CNSL.

Diesel norms require that a diesel sample should obey physico-chemical characteristics for a period of at least 90 days during storage and a DT-CNSL/diesel blend containing antipolymerizing agent meets that condition. A slightly higher percentage of anti-polymerizing agent (0.05% TNPP), offers stability of at least 6 months and is comparable to commercial diesel. Cetane number is often mentioned as a practical issue for diesel and biodiesel blends, due to the presence of long chain petroleum components with inadequate calorific values. But the high calorific value of the major DT-CNSL component (cardanol) ensures meeting the practical requirement of efficient burning of fuel and probably eliminates the need of nitro- derivatives in diesel, which act as cetane boosters [28].

The physico-chemical analysis was done for DT-CNSL blended samples containing 5% DT-CNSL in diesel (B5), 10% DT-CNSL in diesel (B10), 15% DT-CNSL in diesel (B15) and 20% DT-CNSL in diesel (B20) and commercial diesel (sample B5, B10, B15 and B20 represent percentage composition of DT-CNSL in diesel). The kinematic viscosity of blends increased with increasing DT-CNSL, but the increase is well below the limit. Carbon residue by Ramsbottom on 10% residue is slightly more than that for diesel, and indicates some black carbon formation. The fuel blend is also observed to have a higher boiling point than traditional diesel, but meets the necessary specifications. The cetane index, sediments, water, sulphur, corrosion, and percentage residue were similar for DT-CNSL blends and diesel. The cetane number for DT-CNSL blends were higher than those for diesel, which could be related to a modification of calorific

Table 1
Physico-chemical characteristics of distilled – technical CNSL (DT-CNSL)/Diesel as per IS:1460:2005.

Parameters	Diesel	5% DT-CNSL, 95% diesel	10% DT-CNSL, 90% diesel	20% DT-CNSL, 80% diesel	Specification	Std. method
Appearance	Clear liquid	Clear liquid	Clear liquid	Clear liquid	To report	Observation
Colour	Yellow	Brown	Brown	Light brown	To report	Observation
Acidity inorganic	NIL	NIL	NIL	NIL	NIL	IS 1448, P:2
Acidity total, mg KOH/gm	0.05	0.10	0.07	0.06	To report	IS 1448, P:2
Ash, % by wt.	0.006	0.009	0.007	0.006	0.01 max	IS 1448, P:4/ISO 6245
Carbon residue Ramsbottom on 10% residue, % by wt.	0.19	0.28	0.27	0.24	0.3 max	IS 1448, P:8/ISO 10370
Cetane Index/min	48	49	49	49	48	ASTM D 4737/ISO 4264
Pour point, °C	−12	−18	−18	−18	3 max	IS 1448, P:10/D 59449
Copper strip corrosion for 3 h, at 100 °C	1a	1a	1a	1a	Not worse than 1	IS 1448, P:15/ISO 2160
Distillation recovery, temp °C						
At 85%	304	348	348	348	350 max	IS 1448, P:18/ISO 3405
At 95%	330	364	360	357	370 max	IS 1448, P:18/ISO 3405
Final boiling point, °C	336	374	368	367		IS 1448, P:18/ISO 3405
Residue, % by vol	<1.0	<1.0	<1.0	<1.0		Experimental determination
Flash point, °C (Abel), min	42	44	44	44	35	IS 1448, P:20
Kinematic viscosity at 40 °C, cSt	2.32	3.53	2.78	2.62	2.0–5.0	IS 1448, P:25/ISO 3104
Sediments, % by wt.	<0.05	<0.05	<0.05	<0.05	0.05 max	IS 1448, P:30
Density at 15 °C, g/ml	0.8325	0.8515	0.8425	0.8410	0.82–0.86	IS 1448, P:16 OR P:32/D 4052/ISO 3675
Total sulphur, % by wt.	0.21	0.25	0.20	0.18	0.05 max	IS 1448, P:33
Water content, ppm by wt.	150	172	162	157	500 max	IS 1448 P:40/ISO 12937

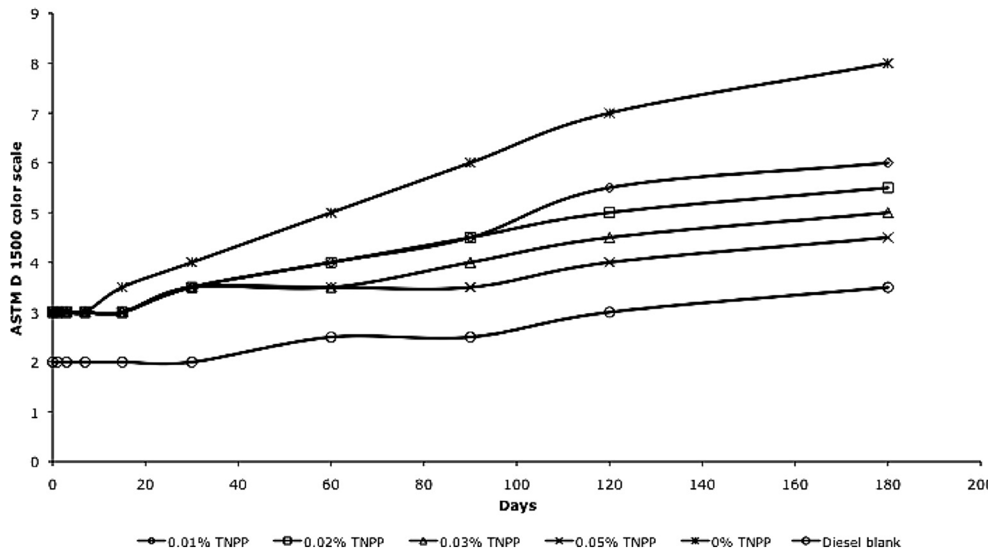

Fig. 1. Trinonyl phenyl phosphite (TNPP) added distilled technical cashew nut shell liquid (DT-CNSL)/diesel blends stability data contains sample 1: 10% DT-CNSL, 0.01% TNPP; sample 2: 10% DT-CNSL, 0.02% TNPP; sample 3: 10% DT-CNSL, 0.03% TNPP; sample 4: 10% DT-CNSL, 0.05% TNPP; sample 5: 10% DT-CNSL/Diesel; sample 6: Diesel control.

value by CNSL [19,29]. Overall, the physico-chemical characteristics of the DT-CNSL blends obey diesel fuel norms and so these blends should perform similar to diesel in engines. Physico-chemical characteristics of DT-CNSL fuel blends as per IS:1460:2005 is shown in Table 1. The physico-chemical characteristics of blends of diesel/triglycerides/CNSL are shown in Table 2.

In Table 2, samples of tallow oil show some “Carbon Residue”. We observed a similar trend with vegetable oils, although to lesser extent. Whenever we used unrefined triglycerides obtained from commercial sources, the “Carbon Residue” was higher than the recommended level of less than 0.3%. However, with distilled triglycerides the “Carbon Residue” was below the recommended level [30]. The crude oils provided an opportunity to study stabilization by DT-CNSL and our results in Table 1 indicate that DT-CNSL does not contribute to an increase in “Carbon residue”. The second parameter that was of concern was the acidity of tallow oil. We observed that the tallow oil acidity increased significantly, which was not observed for the vegetable oil containing samples. We conclude from these results that refinement of triglycerides before blending is required. In general, addition of tallow in diesel causes precipitation and non-uniformity of fuel. Addition of CNSL produced solution uniformity and surprisingly all the fuel blends obey IS1460:2005. To better understand how CNSL as an additive to diesel/triglyceride mixtures created solution uniformity we explored the stability of these blends.

3.2. Stabilization of blends of triglycerides and diesel by DT CNSL

A major aim of this study was to find an alternative to transesterification of SVO, which also maintains the benefits of a renewable fuel, such as reduction in emissions and decreased pollution [1]. We showed that DT-CNSL can be used as an additive to stabilize mixtures of diesel and SVO triglycerides, thereby avoiding the expensive and environmentally unfriendly process of converting SVO to the methyl ester form normally required for blending with diesel.

In the absence of DT-CNSL additive we observed that SVO and tallow oil were partially insoluble in diesel and separated into two

Table 2
Physico-chemical characteristics of straight vegetable oil (SVO) and distilled technical CNSL (DT-CNSL) blends in diesel: Compositions of blends used for studies were Sample 1: 10% DT-CNSL, 90% diesel, Sample 2: 10% Jatropha oil, 90% diesel, Sample 3: 5% DT-CNSL, 5% Jatropha oil, 90% diesel, Sample 4: 5% DT-CNSL, 10% Jatropha oil, 85% diesel, Sample 5: 5% Jatropha oil, 95% diesel, Sample 6: 5% DT-CNSL, 5% tallow oil, 90% diesel, Sample 7: 5% DT-CNSL, 10% tallow oil, 85% diesel, Sample 8: 5% tallow oil, 95% diesel, Sample 9: 10% tallow oil, 90% diesel.

Parameters	Diesel	1	2	3	4	5	6	7	8	9
Acidity inorganic	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil
Total acidity, mg KOH/g	0.020	0.14	0.01	0.07	0.08	0.01	0.86	1.64	0.75	1.5
Ash, % by wt.	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Carbon residue Ramsbottom, on 10% residue by wt.	0.12	0.74	1.44	1.73	1.68	0.54	1.36	1.80	0.86	1.52
Cetane index	54	55	55	56	52	57	52	49	53	52
Pour point °C	−15	−15	−15	−12	−12	−12	−18	−18	−18	−21
Copper strip corrosion for 3 h @ 100 °C	1a	1a	1a	1a	1a	1a	1a	1a	1a	1a
Distillation recovery, temp Uc										
at 350 °C	93	85	90	85	85	86	92	87	92	95
at 370 °C	97	96	97	96	95	97	98	98	98	98
Flash point, (Abel), °C	42	50	50	52	50	50	42	42	44	44
Kinematic viscosity @ 40 °C, cSt	2.50	3.00	3.12	3.10	3.49	2.84	2.17	3.58	2.04	3.17
Sediments, by wt.	0.010	0.029	0.025	0.026	0.026	0.026	0.013	0.012	0.012	0.017
Density @ 15 °C, g/ml	0.8254	0.8329	0.8314	0.8319	0.8374	0.8264	0.8367	0.8422	0.8308	0.8368
Total sulphur, % by wt.	0.18	0.16	0.17	0.16	0.13	0.14	0.14	0.13	0:13	0.23
Water content, ppm by wt.	237	133	153	167	126	179	244	327	254	235.

layers within a few days of storage. Pictures of the DT-CNSL tallow samples are shown in Fig. 2. Double refined vegetable oil, which contains more than 99% triglycerides, stayed in diesel for up to 14 days, after which droplets of oil were observed forming on the walls of the storage tubes, indicating partial separation of oil and diesel. We tested the solubility of SVO from nine different sources of vegetable oil and found that all the oils have similar behavior. The SVO's tested included Pongamia, Jatropha, palm, neem, soybean, sunflower, coconut, ground nut and rapeseed oil. All 9 oils partially separated from diesel in a few days. Hence, we conclude that SVO is partially insoluble in diesel and these non-uniform fuels can possibly cause problems if used in engines, such as increasing NOx, improper spraying and burning of fuel, and increase in smoke and pollutant production. In general, waste vegetable oil and tallow oil partially separate within a day from diesel in the absence of DT CNSL. However, a 1:1 blend of SVO and DT-CNSL in diesel has physico-chemical characteristics comparable to diesel. This kind of stabilization of SVO in diesel is reported with isobutanol [31], but isobutanol's flash point of 28 °C makes it unsuitable for use in diesel engines. SVO used in diesel in the form of emulsions using water and water-soluble alcohols has been attempted but never made it to the market due to a variety of undesirable properties [32].

Here we report the successful use of SVO in combination with diesel without the need for transesterification, using DT-CNSL as an additive. SVO and tallow oil are primarily triacylglycerols and have reasonable solubility in diesel. However, these oils are not stable over time, particularly due to the formation of free fatty acids and other more minor components such as polymers [33]. We show that DT-CNSL can stabilize tallow oil in diesel without the need for transesterification for about 18 months. For example, a DT-CNSL/Tallow oil/Diesel blend (1:1:8) was stable for more than 18 months without forming any gum or greasy layer (Fig. 2). Millions of gallons of tallow oil is produced in Australia and around the world. The thermal pyrolysis-based conversion of tallow oil to smaller hydrocarbons is not economical and currently tallow oil is primarily an industrial waste product. Even after undergoing expensive transesterification to form methyl esters, tallow oil is not suitable for many biodiesel applications because of its high saturated fatty ester content and its tendency to solidify at room temperature. However, DT-CNSL addition enables the formation of a uniform liquid between tallow oil and diesel enabling the use of natural waste triglycerides directly as biofuel.

3.3. Mechanism of stabilization of triglycerides in diesel by DT-CNSL

A mechanism for stabilization of SVO in diesel was not been reported in previous studies using alternative stabilization methods [30,32]. Here we use charge transfer probes PRODAN and Nile red to investigate the phase uniformity of the components in solution. The application of charge transfer probes to understand reverse micellar systems is well known. PRODAN identifies four different regions in AOT (sodium bis [2-ethylhexyl] sulfosuccinate)/n-heptane reverse micelles [34]. Similar applications are reported with Nile red in diverse solution systems [35]. Charge transfer probe exists in polar and non-polar forms depending on polarity of the medium, with each form having different fluorescent spectra. Depending on the polarity of the medium, its fluorescence emission shifts and if more than one region of different polarity is present in solution, the charge transfer probe localizes in each region and gives fluorescence spectra corresponding to that region's polarity, as shown in Fig. 3.

We hypothesized that DT-CNSL could be increasing the solubility of SVO in diesel making the solution more uniform. When different blends of SVO in diesel stabilized with DT-CNSL were studied using PRODAN as a probe, the fluorescence emission spectra are similar to diesel, as shown in Fig. 4. The same fluorescence study repeated for a tallow oil blended sample, using PRODAN as a probe, is shown in Fig. 5. As the percentage of SVO increased in the sample the diesel-like property is maintained in the blend by DT-CNSL and so the blends (SVO, diesel, DT-CNSL) are stable for months without any precipitation. A fluorescence study on the same sample was also done using Nile red as a probe, as shown in Fig. 6. We compared these results with those from an alcoholic solvent, which clearly shows multiple regions in diesel, including AOT reverse micelle regions observed with PRODAN. This indicates that the mechanism of DT-CNSL in stabilizing SVO/diesel blends is through increasing solubility and the resulting blend is similar to diesel in polarity. We could not study SVO in diesel alone as a control because SVO and diesel were not fully soluble.

The chemical structure of the main DT-CNSL component (cardanol) indicates that it may act as a surfactant similar to AOT. But a major structural difference between AOT and cardanol is that AOT is negatively charged. The chemical structures of AOT and cardanol are shown in Fig. 7 and have several structural differences. AOT can

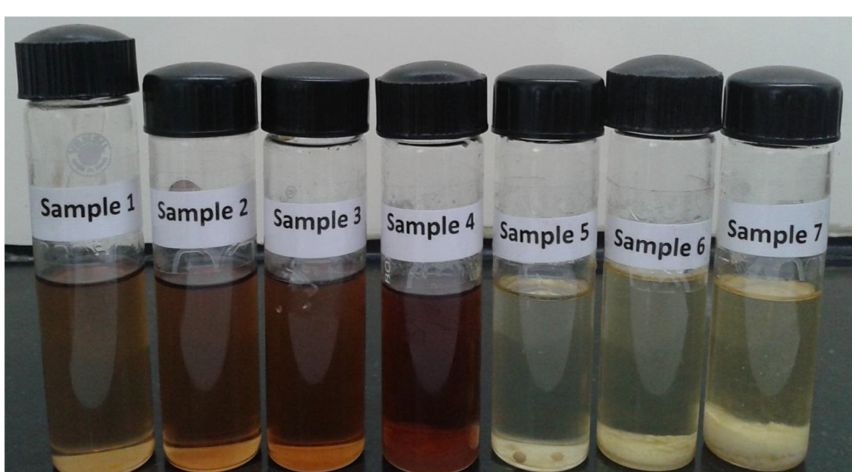

Fig. 2. The samples are distilled technical cashew nut shell liquid (DT-CNSL) and tallow oil blended with diesel. 1) 2.5% Tallow oil, 2.5% DT-CNSL, 95% diesel; 2) 5% DT-CNSL, 5% Tallow oil, 90% diesel; 3) 10% DT-CNSL, 10% Tallow oil, 80% diesel; 4) 20% DT-CNSL, 20% Tallow oil, 60% diesel; 5) 5% Tallow oil, 95% diesel; 6) 10% Tallow oil, 90% diesel; and 7) 20% tallow oil, 80% diesel. Samples 1–3 are clear solutions (16 month stability), while control samples 5, 6 and 7 have precipitates. Sample 4 with 20% tallow also has some precipitate.

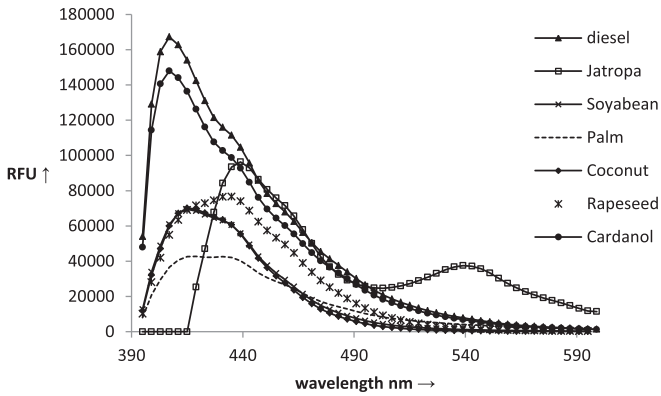

Fig. 3. Polarities of different straight vegetable oil (SVO) in comparison to diesel and cardanol, determined using charge transfer probe PRODAN. The difference in polarity of diesel versus SVO causes the precipitation of SVO. Cardanol has both polar and non-polar functional groups and its presence helps SVO to behave like diesel. 50 μM PRODAN is used & excited with UV light.

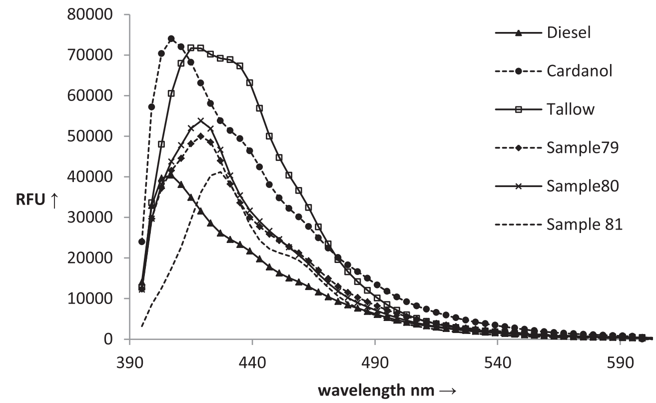

Fig. 5. Uniformity of Tallow oil Blends with cardanol and diesel characterized by PRODAN fluorescence. Sample 79, 80 & 81 are 5, 10 and 20% respectively of tallow oil and cardanol in diesel. 50 μM PRODAN was used and excited with UV light.

form reverse micelles in non-polar solvents due to presence of a sulphonate group. These surfactants can form a spherical structure with the polar head groups pointed towards the center and the non-polar tail distributed towards the non-polar medium.

DT-CNSL has cardanol as the major constituent and can be viewed as a surfactant. The polar head is a phenolic group and a long C-15 aliphatic chain provides a hydrophobic tail. The behavior of DT-CNSL is expected to be similar to that of a non-ionic detergent. Non-ionic detergents such as Triton X-100 contribute to solubility and can stabilize protein structures. Similarly we hypothesized that DT-CNSL will help solubilize triglycerides in diesel. Triglycerides alone in diesel form droplets in the diesel on walls of the container during storage. Depending on the specific triglycerides this can take between two days and two weeks, and this phase separation increases with time. Our samples stabilized

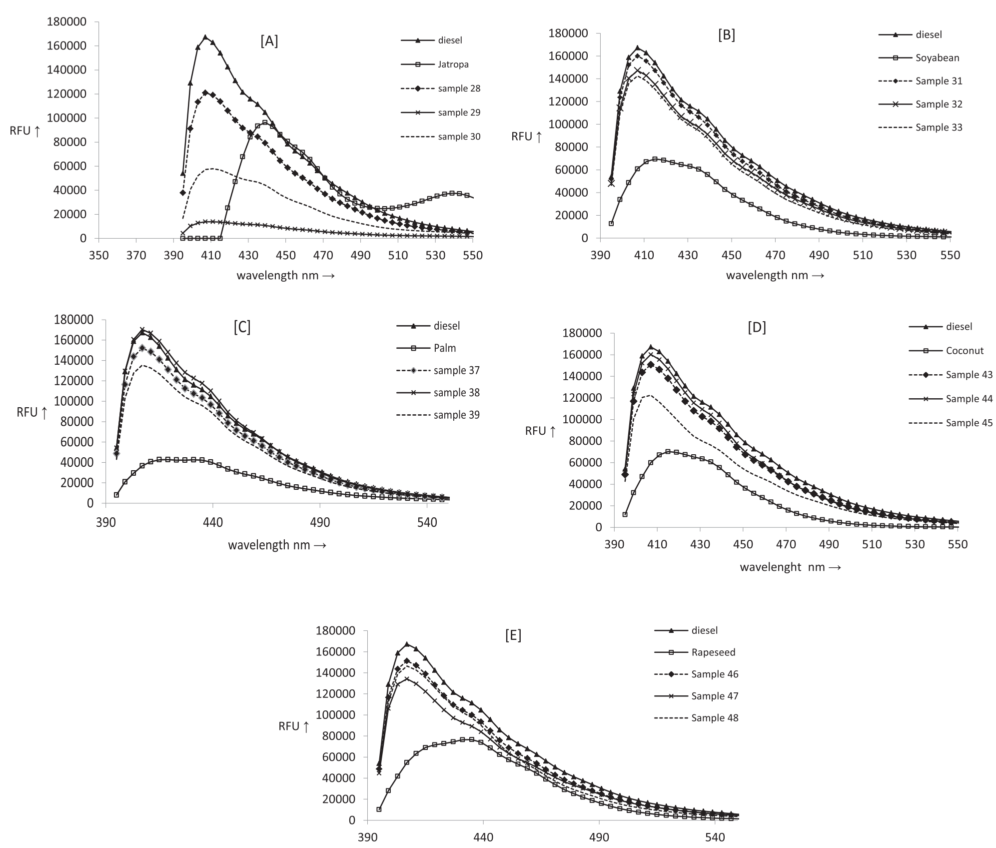

Fig. 4. Uniformity of straight vegetable oil (SVO) Blends with cardanol and diesel characterized by PRODAN fluorescence. As the percentage of SVO increased in the sample due to presence of cardanol, the diesel-like property is maintained in the blend and this is the reason why the blends (SVO, Diesel, Cardanol) are stable for months without any precipitation. A) Sample 28, 29 & 30 are 5, 10 and 20% respectively of Jatropha oil and cardanol in diesel. B) Sample 31, 32 & 33 are 5, 10 and 20% respectively of soybean oil and cardanol in diesel. C) Sample 37, 38 & 39 are 5, 10 and 20% respectively of palm oil and cardanol in diesel. D) Sample 43, 44 & 45 are 5, 10 and 20% respectively of coconut oil and cardanol in diesel. E) Sample 46, 47 & 48 are 5, 10 and 20% respectively of Rapeseed oil and cardanol in diesel. 50 uM PRODAN was used and excited with UV light.

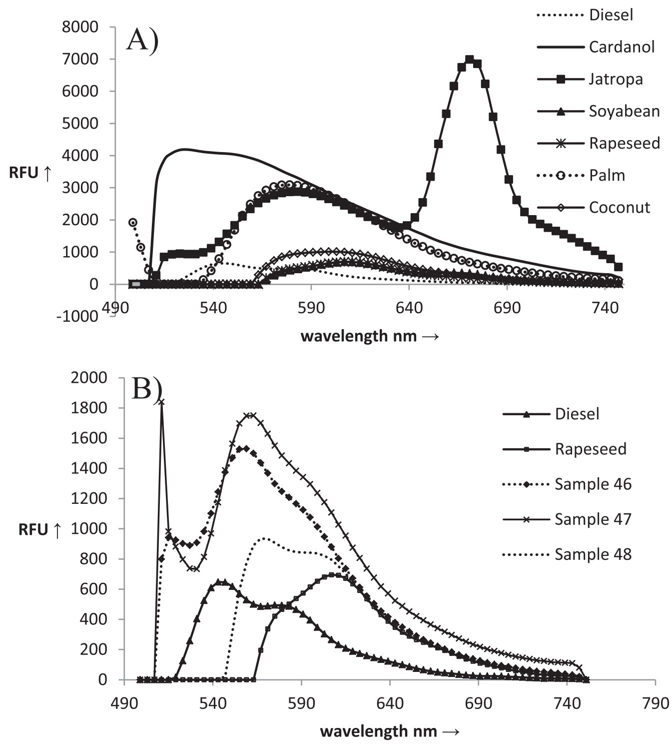

Fig. 6. A) Nile red spectra of different straight vegetable oil (SVO) in comparison with diesel & cardanol. The wide distribution of fluorescence spectra clearly demonstrates the polarity difference in SVOs. B) Sample 46, 47 & 48 are 5, 10 and 20% respectively of Rapeseed oil and cardanol in diesel. 50 μM Nile red is used and excited with blue light.

with DT-CNSL were stable for more than four years without any observable droplets formation. The fluorescence study also shows that the addition of DT-CNSL causes triglycerides/diesel mixtures to behave similarly to diesel alone.

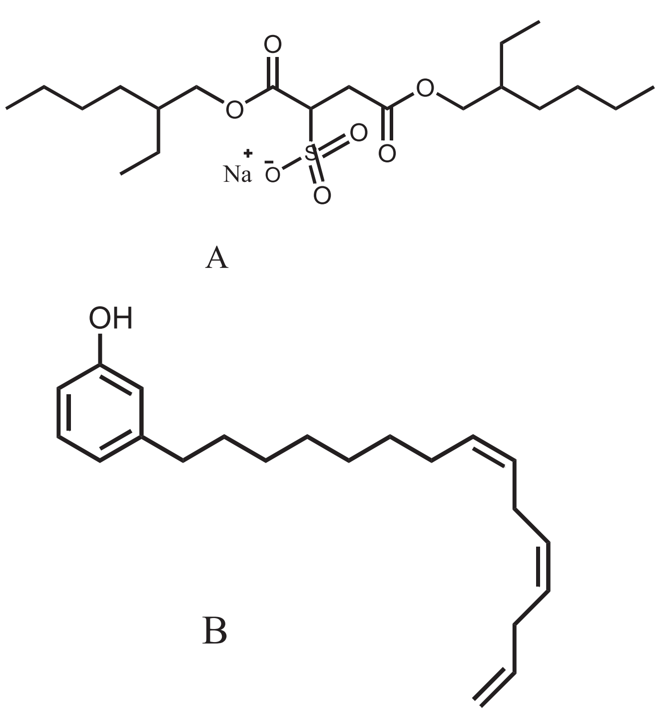

Fig. 7. The chemical structures of AOT (A) and Cardanol (B).

Table 3
Comparison of Jatropha, Pongamia & cashew in relation to farming and biofuel.

Property	Jatropha	Pongamia	Cashew
Toxicity	Yes	Yes	No
% oil present in seed	20–30%	20–30%	20–25%
Seeds/nuts per hectare (kg)	1000–3000	1000–3000	1500–3000
Price per kg seed/nut	US$0.1–0.2	US$0.1–0.2	US$1.0–1.2
Average income to farmer per hectare per year (before overheads)[a]	US$250	US$250	US$1850
Improvement in mileage with 10% blend in diesel	No report	No report	About 5–10% from initial studies
Ability to grow in most parts of world	Yes	Yes	Yes
Is it a food source	No	No	Byproduct is food
Biofuel yield per hectare (kg)[b]	200–500	200–500	150–300

[a] Income to farmer per hectare is calculated based on the published literature and information from local farmers.
[b] Biofuel is after complete processing (seeds to transesterified liquid).

3.4. Economic benefits

Jatropha is a non-food crop that grows on most types of land and gives about US$200–300 gross revenue per hectare per year to the farmer (Table 3). Almost every Asian country has a dedicated program for growing Jatropha plants. Jatropha oil is the only useful product from the plant, while the leaves and Jatropha cake (after extracting oils from seeds) are useless for human or animal use due to presence of hydrogen cyanide [10,36]. Though toxicity and deaths due to consumption of Jatropha seeds was reported in the literature [36], and the FDA has recommended banning Jatropha byproducts for human and animal consumption, governments worldwide made a decision to go ahead with this plant for biofuel purposes. Now there are increasing reports that farmers with semi-arid lands are also approaching oil companies for cultivating Jatropha due to low income from food crops. This unregulated increase in Jatropha plant growth will contribute to the world food shortage. Cashew is a food crop and the DT-CNSL produced is a non-food byproduct, and so has farming and societal advantages over the cultivation of Jatropha, as illustrated in Table 3.

Economic calculations indicate an advantage of using DT-CNSL as an additive to enable the use of SVO directly with diesel, compared with transesterified biodiesel. Essentially, the use of the DT-CNSL eliminates the cost of transesterification. Additional potential benefits include reduction in pollution, better employment creation, proper utilization of land for both food and biofuel production, and improved income for farmer. It may also be possible to use cashew fruit for alcohol production, suggesting that there is scope for increased biofuel production from cashew.

4. Conclusion

DT-CNSL offers an alternative to traditional transesterified biofuel. Although DT-CNSL cannot be technically called biodiesel, the ability to substitute traditional biodiesel makes it a biofuel of interest. DT-CNSL stabilized triglycerides in diesel by increasing their solubility and this probably occurs through DT-CNSL acting as non-ionic detergent. Stability and fluorescence studies indicate that upon addition of DT-CNSL, the three component mixture of diesel, triglycerides and DT-CNSL becomes a uniform liquid. Growing cashew as a good and biofuel crop could improve farmer income compared with growing Jatropha as a non-food biofuel crop. Considering that the future of Jatropha is in doubt as biofuel crop, cashew offers a unique alternative that could provide improved income to farmers, while providing both food and biofuel in a single crop.

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