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Physico-Chemical Characterization of Cotton seed Oil for its Potential use as Biodiesel

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ABSTRACT

The increasing consumption of energy with the depletion of crude oil reserves urges the usage of alternative fuel. Since there is an existing demand for edible vegetable oils, waste vegetable oils and non-edible crude vegetable oils are preferred as potential low priced biodiesel sources. In this study, utilization of Cotton Seed Oil (CSO) was tested for its potential use as biodiesel.The density, viscosity, acid value, saponification number, iodine value, cetane number wereanalyzed and all are found to be within the range specified by the ASTM standards. The Ultrasonic studies gave an idea on the ignition standard, compressibility, relaxation time of the CSO for its use as a biofuel source.The physico- chemical and ultrasonic properties of the blends B10, B20 and 100% CSO B100 were also found to be within the ASTM standards and the blend B20 of the CSO can serve as the potential source for biodiesel
Keywords: Cotton seed oil, biodiesel, physico-chemical parameters, B10, B20 blends.

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INTRODUCTION

Biodiesel has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources [1].The world energy crisis is a result of population growth and increasing consumption of energy in both developed countries and emerging economies [2]. The greater demand for petroleum products as a result of an enormous increase in the number of automobiles serves the growing problem of the developing countries. With crude oil reserves estimated to last only for a few decades, therefore efforts are on way to find out new alternatives to diesel [3]. Depletion of crude oil would cause a major impact on the transportation sector. Of the various alternate fuels under consideration, biodiesel derived from vegetable oils, appears to be the most promising alternative fuel to diesel [4,5]. More than 95% of the world's biodiesel is produced from edible vegetable oils [6], thereby increasing demand throughout the worldwide for vegetable oil production [7].The most commonly used oils for the production of biodiesel are Soybean, Sunflower, Palm, Rapeseed, Canola, Cottonseed [8], and Jatropha. Since the prices of edible vegetable oils are higher than that of diesel fuel, therefore waste vegetable oils and non-edible crude vegetable oils are preferred as potential low priced biodiesel sources.

The contribution of non-edible plant oils as a new sources for biodiesel production have the advantage of not competing with edible oils produced from crop plants [9, 10]. A lot of research work has already been carried out to use vegetable oil both in its pure form and also in modified form. Studies have shown that the usage of vegetable oils in pure form is possible but not preferable [11]. Biodiesel can be used in pure form (100%) or blended with the conventional diesel fuel up to 20% to create a biodiesel blended fuel for its use in the compression ignition engines [12]. It can be used as a standalone fuel or blended with petroleum diesel in diesel engines [13].Biodiesel can be used neat (B100) or at various blend ratios with diesel fuel. A blend of 5% biodiesel (B5) can already be included within existing diesel fuel supplies without identification. Currently, there is resistance from engine manufacturers to warrant engines above 5% biodiesel blends [14].

Biodiesel has attracted considerable interest as a substitute or blend component for conventional petroleum diesel fuel (petro diesel). Biodiesel, defined as simple mono alkyl esters of long chain fatty acids prepared from vegetable oils or animal fats, possesses a number of technical advantages over petro diesel, such as derivation from renewable and domestic feed stocks, displacement of imported petroleum, inherent lubricity, essentially no sulfur content, superior flash point and biodegradability, reduced toxicity, as well as reduction in most regulated exhaust emissions [15].

The Cotton plant is one of the most important raw materials of textile industry for fibers and food industry due to its 17-24% oil and 40-43% protein contents [16]. Turkey has about 760000ha of cotton harvesting area, 882 000tons of cotton fiber production per annum with a yield of 1160 kg/ha of lint cotton and therefore is one of the foremost cotton producing countries of the world [17] . The residue oil cake is also used as a biofertilizer and cattle feed supplement. The fatty acid composition of the CSO is palmitic, stearic, oleic and linoleic acids [18].

Cotton is a sub-shrub which grows well in a wide variety of soils, and thrives best in deep, friable, moisture-holding soils with good humus supply. It is originated from Central America and naturalized in India. In India, cotton is grown in black alluvial and red soils. Cotton is a crop of warm plains, grown commercially from sea level to 1,200 m with some perennial forms at 1,800 m. Cotton plant yields 800-950 kg seeds per hectare and the average oil from the seeds is about 140 kg per hectare. In spite of the multipurpose usage of cottonseed oil in shortening, margarine, protective coverings, salad and cooking oils, it also finds a remarkable application as a Biofuel. The protein rich residue – cotton seed oil cake or meal is mainly used as a supplement for livestock and as a bio fertilizer. The root, bark, leaves, and flowers were known for their medicinal importance. Besides, the cotton plant finds its major application in textile industries and in chemical industries such as rayon, films, shatterproof glass, plastics, lacquers and cellulose explosives [19]. BT cotton production paves a way for the ready availability and cheap source of cotton to meet the raising demands. Since the oil has its use in potential biofuel production**,** the aim of this study is to characterize the CSO along with its blends for its usage as biofuel directly without any further enginemodification.

Cotton is a multi-functional bioenergy crop plantations produce additional environmental benefits [20,21] either dedicated to environmental services such as vegetation filters for waste water, sewage sludge treatment, and shelter belts against soil erosion or generating more general benefits such as soil sequestration, increased soil fertility. It also removes the toxic elements from the soil [22].

However, positive impacts on biodiversity may be realized as a result of ameliorating the rate of change of atmospheric composition and global climate and if bioenergy crops and cropping systems can help to reduce Green House Gases emissions [23]. The development and deployment of dedicated bioenergy crops have been proposed as a strategy to produce energy without impacting food security, or the environment [24, 25]. The dedicated bioenergy crops are mainly perennial herbaceous and woody plant species. Genetic resources for the development of dedicated energy crops with low requirements for biological, chemical or physical pretreatment are more eco-friendly and will contribute more to Global climate change mitigation [26, 27]. Due to the perennial nature of most Second Generation Energy crops, field resistance against diseases and pests should be mutagenic [28].

EXPERIMENTAL METHODS

Blend preparation

The blends were made on a volume basis and stored in glass bottles at room temperature. Biodiesel is used as B100 or in a blend with petroleum diesel. A blend of 20% biodiesel with 80% conventional petroleum diesel, by volume, is termed ''B20" and a blend of 10% biodiesel with 90% conventional petroleum diesel, by volume, is termed ''B10".

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Acid value

Normal titrimetric method was used to measure the acid value. 2gm of the biofuel sample was taken along with 25 ml of isopropyl alcohol and dissolved well. Addition of phenolphthalein with slight warming followed by titration with 0.1N KOH gives faint pink color. Standardization of KOH was carried out with 0.1N oxalic acid.

Saponification number

Five grams of sample along with 25 ml of 0.5N alcoholic KOH taken in a round bottomed flask was refluxed for about an hour and followed by the titration against 0.5N HCl using phenolphthalein as an indicator. The disappearance of pink color was taken as the endpoint. Standardization of HCl was carried out with 0.5N sodium carbonate.

Iodine value

Iodine value was measured using Wij's Iodine method. 2gm of sample was dissolved in 15 ml of chloroform and 25ml of Wij's iodine solution was added. The sample is kept in dark undisturbed for about 30 minutes. 10 cc of 15% KI solution was added and titrated against 0.5N sodium thiosulphate. After the appearance of pale yellow color, 8-10 drops of starch was added and the titration was continued until the blue color was disappeared. Standardization of sodium thiosulphate was carried out with 0.1N potassium dichromate.

Cetane number

The simple empirical determination of cetane number using iodine value and saponification number [42] was as follows

$$CN = 46.3+[(5458/SN)-(0.225*IV)]$$

Average molecular weight

The average molecular weight is calculated by the relationship of the saponification value of pure fatty acids or fatty acid esters.

Molecular weight of fatty acid esters of monohydric alcohols=56100/SN

Ultrasonic properties

The ultrasonic studies were carried out using Ultrasonic interferometer (Mittal & Co.) with a frequency of about 3 MHz.

Physical properties

Density was measured using specific gravity bottle and viscosity with the help of Ostwald viscometer. The other properties such as pH, conductivity, total dissolved solids, salinity, dissolved oxygen and turbidity were measured using Systronics analyzer.

RESULTS &DISCUSSION

In this present study, the density, viscosity, conductivity, totaled dissolved solids, salinity and dissolved oxygen of the samples were analyzed and given in the Table 1.The novel method for screening the biodiesel is the ultrasonic studies. It is a cheap, quick and best method for screening of vegetable oil both edible and non-edible for its potentiality as biodiesel [36]. The ultrasonic properties like ultrasonic velocity, adiabatic, compressibility, acoustic impedance and relaxation time were found out for CSO and its blends are given in the Table 2 and Figure 1. The acid, Saponification value, iodine value, average molecular weight and cetane number were carried out and listed in Table 3.

Table 1: Physical properties of Cotton seed oil and its blends.

Parameters	B100	B10	B20
Density (g/ml)	0.919±0.00	0.834±0.01	0.847±0.01
Viscosity ($Nm^{-2}s$)	5.91±0.08	3.39±0.11	4.45±0.13
Conductivity (μs)	0.62±0.00	0.61±0.00	0.61±0.00
Total dissolved solids (ppm)	0.26±0.01	0.25±0.01	0.25±0.00
Salinity (ppt)	0.00±0.00	0.00±0.00	0.00±0.00
Dissolved oxygen (ppm)	13.43±0.23	7.73±0.15	9.73±0.15

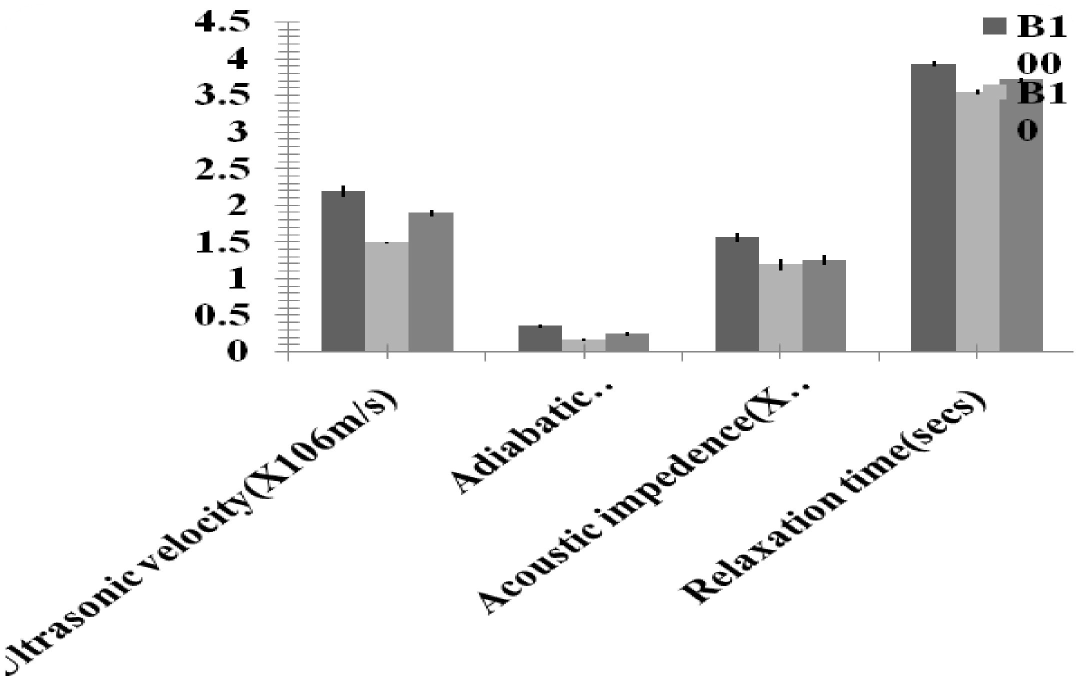
Table 2: Ultrasonic properties of Cotton seed oil and its blends.

Parameters	B100	B10	B20
Ultrasonic velocity($X10^6 m/s$)	2.180±0.08	1.48±0.01	1.89±0.05
Adiabatic compressibility($kg^{-1}ms^{-2}$)	0.35±0.03	0.16±0.02	0.24±0.03
Acoustic impedence($X\ 10^6 kgm^{-2}s^{-1}$)	1.55±0.06	1.19±0.08	1.25±0.07
Relaxation time(secs)	3.93±0.03	3.54±0.04	3.71±0.03

Table 3: Chemical properties of Cotton seed oil and its blends.

Parameters	B100	B10	B20
Acid value(mg KOH/g)	0.96±0.02	0.67±0.05	0.83±0.03
Saponification number	217.51±2.02	210.06±0.66	213.23±0.68
Iodine value	87.79±1.12	73.69±1.19	79.29±1.27
Average molecular wt	257.51±3.05	267.07±7.54	263.09±2.25
Cetane number	51.64±0.63	55.70±1.05	54.06±0.43

Figure 1: Ultrasonic properties of Cotton seed oil and its blends.



Many authors compared the blends with different content biodiesel. The authors believed that, with increasing the content of biodiesel, engine fuel consumption will increase [29, 30, 31]. Carraretto et al [32] found that the increase of biodiesel percentage in the blends resulted in a slight decrease of both power and torque over the entire speed range for different blends (B20, B30, B50, B70, B80, B100) of biodiesel and diesel on a 6-cylinder DI diesel engine.

Aydin et al [33] reported that the torque was decreased with the increase in CSOME (cottonseed oil methyl ester) in the blends (B5 B20 B50 B75 B100) due to higher viscosity and lower heating value of CSOME. The high viscosity of vegetable oils and their low volatility affects the atomization and spray pattern of the fuel, leading to incomplete combustion and severe carbon deposits, injector choking and piston ring sticking. The methods used to reduce viscosity are pyrolysis, blending with diesel, transesterification, and emulsification [3]. Generally, the viscosity and density of the vegetable oil will be several times higher than that of diesel. By mixing the vegetable oil with conventional diesel at B10&B20, the density and viscosity were found to be similar to that of diesel. Hence the viscosity of vegetable oils can be reduced by several methods which include blending of oils, microemulsification, pyrolysis and transesterification [34]. Fuels with poor lubricity can cause failure of diesel engine parts that rely on lubrication from fuels, such as fuel pumps and injectors [35].

Ultrasonic velocity of blended cotton seed oil is found to coincide with those predictions of Gladwell (1985) [37].Acoustic impedance is almost reciprocal of adiabatic compressibility. Compressibility decreases with the increase of concentration, whereas the acoustic impedance increases [38].Compressibility is inversely proportional to the velocity. It is primarily the compressibility that changes with structure. This leads to a change in ultrasonic velocity. The greater the attractive forces among the molecules of a liquid, the smaller will be compressibility. It shows the reverse effect as that of impedance which produces the peaks which again confirms the formation of complex molecule which is due to the ion-solvent interactions [38]. The ultrasonic values obtained in this study coincide with the results of Meena Devi etal (2009).

The authors found that the torque and power reduced by 3–6% for pure cotton seeds biodiesel compared to diesel, and they claimed that the heating value of biodiesel was less 5% than that of diesel. But they contributed to the difficulties in fuel atomization instead of the loss of heating value. It was reported that there was no significant difference in engine power between pure biodiesel and diesel [39, 40, 41].

Acid value of the oil indicates the amount of fatty acid present in the sample. The acid value of the CSO is nearer to the ASTM standard value. The biodiesel standard ASTM specifies the acid value of biodiesel as 0.8mg KOH/g.

Saponification value indicates the non-fatty impurity and the amount of alkali that would be required by the fat for its conversion to soap. The saponification value is given in table 3 and it is found to be nearer to the acceptable range of biodiesel standards in the samples B100, B10 & B20.

Average molecular weight determined by the acidimetric constant should be low to avoid the combustion problems during its usage as biodiesel. The oil with a less viscosity will have a low molecular weight. When compared with the other petro crops, the average molecular weight of CSO is found to be normal.

The number of double bonds in a vegetable oil is calculated by treating it with iodine. The higher the iodine number, higher will be the amount of iodine needed to break the double bonds and also higher is the efficiency of that oil as a biodiesel. The normal value does not exceed 120. From the results, iodine value is found to be within the range of ASTM standard value for biodiesel (Table 1). The Iodine Value, a measure of unsaturation, was used in a cetane number correlation by Krisnangkura (1986) [42]. Krisnangkura's equation indicates that each unit of Iodine Value increase lowers the cetane number by 0.225.

CN of B100, B10 & B20 lies within the normal range in this study (Table 1). Cetane number is a measure of ignition delay time. A higher CN, desirable property in diesel engine, indicates shorter time between the ignition and the initiation of fuel injection into the combustion chamber. The higher CN is correlated with the reduction of nitrogen oxides and unburnt hydrocarbon exhaust emissions which is important for alleviating air pollution [43]. Biodiesel standards of USA (ASTM D6751), Germany (DIN 51606) and European organization (EN14214) have set this CN value as 47, 49 and 51 respectively [44, 45, 46, 47].

The physical properties such as pH, conductivity, total dissolved solids, salinity and dissolved oxygen were also found to normal. All these were found to increase with the increase in oil percentage. Tests carried out on differing blends of biodiesel with and without a conductivity showed that above B20, the additive was not required due to the increased conductivity of the biodiesel itself [14].

CONCLUSION

The increasing demand for fuels along with the depletion of fossil fuel reserves raises the need for an alternative source of fuel. Biodiesel can act as a best substitute for petroleum diesel fuel thereby strengthening the economy of the country mainly in rural areas. Naturally, biodiesel is made from the treatment of vegetable oil (edible and non-edible) and animal fats with alcohol in the presence of NaOH/KOH as a catalyst. The use of edible oils for biofuel production is limited by the growing population in India. Hence, there comes the essentiality of using non-edible oils in biodiesel production with a hope to solve the problem of insufficient diesel fuel supply, price escalation, and safer green environment. As a progressive step in the direction of alternate fuel, there is a need to identify suitable non-edible oil yielding plants.

A wider study on energy security, trends, scenarios and policies, including fuels production and supply, their use and emissions was prepared by the IEA, in its 2006 World energy Outlook. The main conclusions of this study are related to the unsustainable energy future that is being created. It emphasizes that if this is continued as before and we are trying to meet the needs of the world's economy over the next 25 years, the energy supply is very vulnerable. Biofuel production from bioenergy crops has a variety of positive effects on local and regional environments, and may help to relax some of these constraints.

The use of such bioenergy crops for biodiesel adds environmental benefit such as emission of low smoke and particulate matters, thereby developing an eco-green environment. Also cultivation of bioenergy crops results in the utilization of waste lands, preventing soil erosion.

This study evaluates the properties of CSO for its usage as potential biofuel and succeeds thereby protecting the environment from further pollution. Accordingly an increasing order of results was found in the values of B10, B20 and B100 biodiesel of CSO.

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