

# Cotton Seed Biodiesel as Alternative Fuel: Production and its Characterization Analysis using Spectroscopic Studies

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*Received: 19.02.2017 Accepted: 01.04.2017*

**Abstract-** Biodiesel production from the cotton seed oil and its characterization is focussed in this experimental investigation. As the FFA content is less than 2.15%, base catalysed transesterification process is adopted with methanol and potassium hydroxide as solvents. The transesterification process is optimized by varying the methanol to oil molar ratio and catalyst concentration with standard operating parameters. By this process, 93.5% of biodiesel is obtained. The biodiesel is subjected to Gas Chromatography Mass Spectrometry analysis which revealed the presence of linoleic acid as the major constituent. Fourier transform Infra-Red and Nuclear Magnetic Resonance spectral studies attributed the GC/MS data confirming the presence of fatty acid methyl esters.

**Keywords** - Cotton seed biodiesel, transesterification, GC/MS, FTIR and NMR.

## 1. Introduction

Significant depletion of fossil fuel in the petroleum reserves and greater environmental contamination through air pollution urged the researchers to identify a substitute to hydrocarbon based fuel source in order to meet the future energy demands. Liquid hydrocarbon extract from vegetable oil seems to be a major alternative to petro-diesel. Usage of straight vegetable oil in compression ignition engine encountered severe technical complications like higher viscosity leading to poor atomization resulting in incomplete combustion due to larger fuel droplets. It also resulted in huge carbon deposition in the combustion chamber walls and valves affecting the performance of the engine with increased emissions. In order to overcome these hurdles, many researchers have experimentally investigated numerous methods to reduce the viscosity of vegetable oil which includes pyrolysis, transesterification, thermal cracking,

heating and many others. Among these methods, transesterification is found to be more suitable in reducing the viscosity of fuel with improved fuel characteristics.

Generally, biodiesel obtained is obtained by single or two stage transesterification process in the presence of primary or secondary alcohol (mainly methanol and ethanol) along with KOH /NaOH as catalyst. Methanol is widely preferred due to its cost effectiveness. Also, the commercial diesel and biodiesel readily mixes with each other with minimal property variation, thereby engine modification cost is removed. Suitable additives can be added to lessen the ignition delay for improving combustion and performance. Many researchers have reported various biodiesel production techniques and characterization methods which encourages the usage of biodiesel and its blends as fuel in compression ignition engine. Onukwuli *et al.* (2016) reported about the experimental investigation for the production of biodiesel

from cotton seed oil and its characterization. Production methods was optimized using RSM and ANOVA methods in which methanol and potassium hydroxide was used. Optimal biodiesel yield of 96% with molar ratio 1:6, 55°C reaction temperature with one hour reaction time was obtained [1]. Suprabhat Seal *et al.* (2015) pyrolysed the cotton seed oil in a batch reactor to obtain fuel like oil. The investigation was carried out between 350-600°C in the absence of oxygen which yielded 58.6% of liquid fraction by weight along with pyro gas and char. GC/MS and FTIR analysis revealed the presence of n-hexadecanoic acid and other high heating value compounds which could be used as transportation fuel [2].

Biodiesel was also produced from used cotton seed oil through transesterification process using calcined egg shell as catalyst. Palmitic acid and linoleic acid was found in prominent quantities. Partially purified biodiesel was found to have favourable flash and fire point with higher calorific value. The engine performance was also improved with reduced CO and HC emissions. Biodiesel production from non-edible vegetable oil through base catalysed transesterification was performed. Molar ratio of 6:1 and 1% catalyst concentration yielded 93% of biodiesel. Soap formation was noticed with the increase in catalyst concentration [4]. Various forms of cotton seed oil was fuelled to CI engine for understanding its suitability as fuel. Straight cotton seed oil, transesterified cotton seed oil, preheated cotton seed oil, orange oil-DEE-diesel blended CSO was used in this study. It was concluded that viscosity reduction through preheating and blending with minimal orange oil-DEE favoured better engine performance. Few other researchers have reported the oil extraction and biodiesel production from non-edible cotton seed and other biodiesel [5-8, 15-19].

In this present investigation, in-depth analysis is carried out for the production of biodiesel from cotton seed. Optimization study based on molar ratio, catalyst concentration, reaction time and temperature are analysed to obtain higher biodiesel yield. GC/MS, FTIR and NMR spectroscopic studies are explored to understand the suitability of cotton seed biodiesel as transportation fuel. The physio-chemical properties were also analysed in detail.

## 2. Materials and Methods

Raw cotton seed oil is procured from a local vendor in Padur, Chennai, Tamil Nadu. Anhydrous industrial grade potassium hydroxide and methanol is purchased from scientific chemical supplies, Chennai. Commercial grade diesel is obtained from Shell filling station, Chennai.

### 2.1. Base Catalysed Transesterification

As free fatty acid (FFA) content is found to be less than 2.15% by titration method, single stage transesterification technique is adopted. Methanol, KOH and raw cotton seed oil is used in the base catalysed transesterification. The transesterification is carried in a batch reactor setup. The setup contained multi necked (three) round bottom flask with

magnetic stirrer and heating arrangement. Potassium methoxide solution is prepared by mixing potassium hydroxide and methanol. The agitation speed of 450 rpm at 75°C is maintained for 120 min to dissolve completely. Methanol to oil molar ratio varying between 3 to 14 and catalyst concentration of 0.5 to 3.5% are analysed to obtain optimal yield of biodiesel. Predetermined quantity of raw cotton seed oil is poured in a three necked round bottom flask containing potassium methoxide solution. The reaction temperature of 70°C to 75°C and reaction time of 120 min is maintained throughout the experimentation. After the reaction period, the mixture is allowed to cool during which glycerol-biodiesel layer separation is observed. Separating funnel is used to isolate biodiesel from glycerol followed by washing with distilled water. The biodiesel is heated upto 110°C to remove excess moisture [9].

### 2.2. Biodiesel Characterization

#### Gas Chromatography Mass Spectrometry

Double focussing JEOL GC Mate II GC MS data system with high resolution electron impact is used to analyse cotton seed biodiesel. The instrument has maximum resolution and maximum calibrated mass of 6000 and 1500 Daltons.

#### Fourier Transform Infra-Red Spectrometry

Infra-red spectrum of cotton seed biodiesel originated from Perkin Elmer Spectrum 1 FTIR spectrometer. The instrument consists of mercury vapour and globar lamp as source, interferometer chamber (with KBr and mylar beam splitter), sampler and detector. The spectrum covers the range of 450-4000 $\text{cm}^{-1}$  wave length.

#### Nuclear Magnetic Resonance

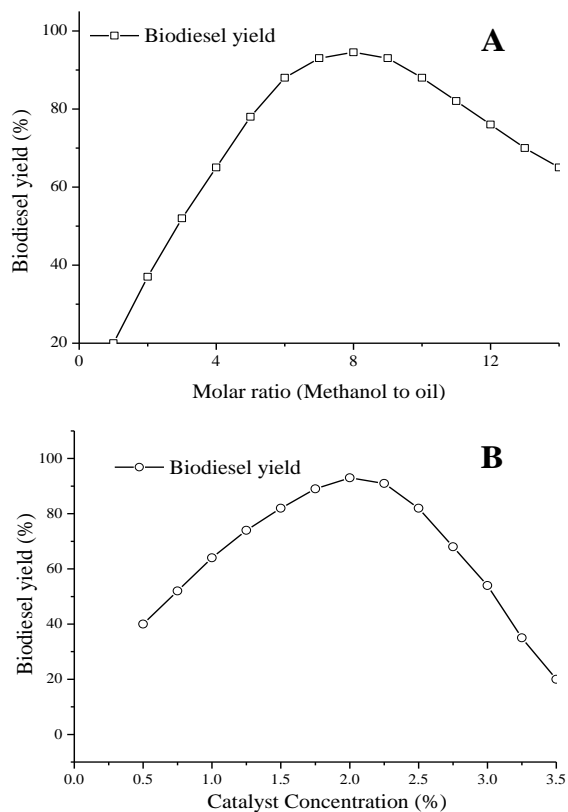
Bruker AVANCE III 500 MHz spectrometer with multi nuclei solution is used to obtain  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR of cotton seed biodiesel. The instrument contains 11.7 Tesla super conducting long hold magnet, cryo shims and 34 channel room temperature shims.

## 3. Results and Discussion

### 3.1. Effect of Molar ratio and catalyst concentration on biodiesel yield

Figure 1A depicts the variation in the yield of cotton seed biodiesel with methanol to oil molar ratio. The molar ratio is varied between 3:1 and 14:1 with potassium hydroxide as catalyst. The transesterification reaction is maintained at agitation speed of 425-450 rpm, 70-75°C reaction temperature and 120 min reaction time. Deviating from operating parameters resulted in negligible or negative improvement in the yield of biodiesel. From Figure 1, it can be noticed that, yield of biodiesel is maximum upto 93.5% at molar ratio 8:1 which was also retriated by Thomas *et al.* [10]. The biodiesel yield is found to be lowered at 78.7% at molar ratio 6:1 which is further going down with the

reduction in methanol concentration. On the other hand, increase in methanol to oil (molar ratio) also exhibited a decline in the biodiesel yield significantly. At a molar ratio of 10:1, the biodiesel yield is noticed to be less than 84% which is further deteriorating. This may be due to unbalanced chemical equilibrium and excessive methanol concentration during transesterification reaction.



**Fig. 1.** Effect of molar ratio (A) and Catalyst concentration (B) on biodiesel yield.

Figure 1B depicts the effect of catalyst concentration on the yield of cotton seed biodiesel. The transesterification process is conducted with optimal operating parameters as detailed. The quantity of KOH catalyst in the form of potassium methoxide is incremented by 0.25 wt% from 0.5 wt% to 3.5 wt% as shown. It can be observed that increase in KOH concentration encouraged the triglyceride-ester conversion rate and resulted in higher yield of biodiesel upto 1.65 wt.%. Maximum yield of biodiesel was noticed at 1.8 wt% at optimal operating parameters. Further increase in KOH concentration upto 3.5 wt% showed a negative improvement shifting the equilibrium reaction in the reverse direction. Higher catalyst concentration than optimal range influenced more soapy formation thereby reducing the transesterification efficiency [11-13].

### 3.2. Gas chromatography Mass Spectrometry

GC/MS mass spectrum of cotton seed biodiesel is shown in Figure 2. The Mass spectrum discloses the presence of unsaturated and saturated fatty acids in the biodiesel. It can be noticed that, there are 10 different short chain and long chain hydrocarbon esters present at various retention time.

NIST-MS1 library (National Institute of Standards and Technology) is used to identify the various fatty acid methyl esters on comparison with the fragmentation pattern of cotton seed biodiesel. The GC/MS spectrum exhibited the base peak at RT 24.35. McLafferty rearrangement process at  $m/z$  74.25 is also observed validating the base peak. At RT 24.35, linoleic acid is found to be the major compound along with Capric acid, Lauric acid, Myristic acid, Palmitic acid, Arachidic acid, Heneicosanoic acid, Behenic acid, Tricosanoic acid and Lignoceric acid in prominent quantities. The detailed FAME's present in the CSB is given in Table 1 [14].

### 3.3. Fourier Transform Infra-Red spectrometry

The mid region infra-red spectrum of the FTIR presenting the various functional group of cotton seed biodiesel is shown in Figure (3). The spectrum comprises of major and minor peaks which are formed due to stretching and bending vibrations. At wavelength  $3469\text{ cm}^{-1}$ , stretching peak due to methylene proton is observed. Similar stretching vibrations is also noticed between  $2679\text{ cm}^{-1}$  and  $2036\text{ cm}^{-1}$  may be due to methoxy proton rearrangement. Fatty acid methyl ester formation is noticed between  $1459\text{ cm}^{-1}$  and  $1017\text{ cm}^{-1}$  with stretching and bending vibrations along with OH group disappearance. Minor peak at  $722\text{ cm}^{-1}$  and  $877\text{ cm}^{-1}$  confirms the presence of C=C (alkene group). Continuous stretching vibrations is observed at  $1017\text{ cm}^{-1}$ ,  $1118\text{ cm}^{-1}$ ,  $1117\text{ cm}^{-1}$  and  $1196\text{ cm}^{-1}$  which also indicated the presence of carboxylic group along with minimal unsaturated esters.

### 3.4. Nuclear Magnetic Resonance

The characterization of cotton seed biodiesel is carried out with Nuclear Magnetic Resonance studies. Both  $^{13}\text{C}$  NMR and  $^1\text{H}$  NMR are conducted using methanol D4 as solvent having boiling and melting point of  $64.6^\circ\text{C}$  and  $-97.8^\circ\text{C}$  respectively.  $^{13}\text{C}$  NMR characteristic spectrum is presented in the Figure (4). The chemical shifts in  $^{13}\text{C}$  NMR spectrum of cotton seed biodiesel are interpreted between 0-200 ppm. Weaker signal at 22.364 ppm, 26.737 ppm and 33.431 ppm indicate the presence of methyl group in the injected sample. Few strong signals were seen at 47 ppm confirms the existence of carbonyl group in CSB which may be due to chemical rearrangement during transesterification reaction. Less significant peak are also observed at 129 ppm and 174 ppm which are due to aromatic substitutes.

$^1\text{H}$  NMR characteristic spectrum is presented in Figure (5). It can be seen that few strong signals of singlet and triplet peaks were present in the spectra indicates the presence of fatty acid methyl esters in CSB. At 3.670 ppm, a strong singlet signal of methoxy proton and at 1.33 ppm, a strong triplet signal of  $\alpha\text{-CH}_2$  proton confirms the presence of carboxylic group. Several singlet are also observed at 3.370 ppm and 4.871 ppm which showed the presence of methoxy group in CSB. These singlet and triplet peaks showed a greater affinity towards blending cotton seed biodiesel with diesel to a large extent. Furthermore, absence of peak and signal beyond 5.4 ppm revealed the absence of oleic and

aliphatic hydrogen atoms which deteriorate the conversion efficiency of triglycerides into fatty acid methyl esters.

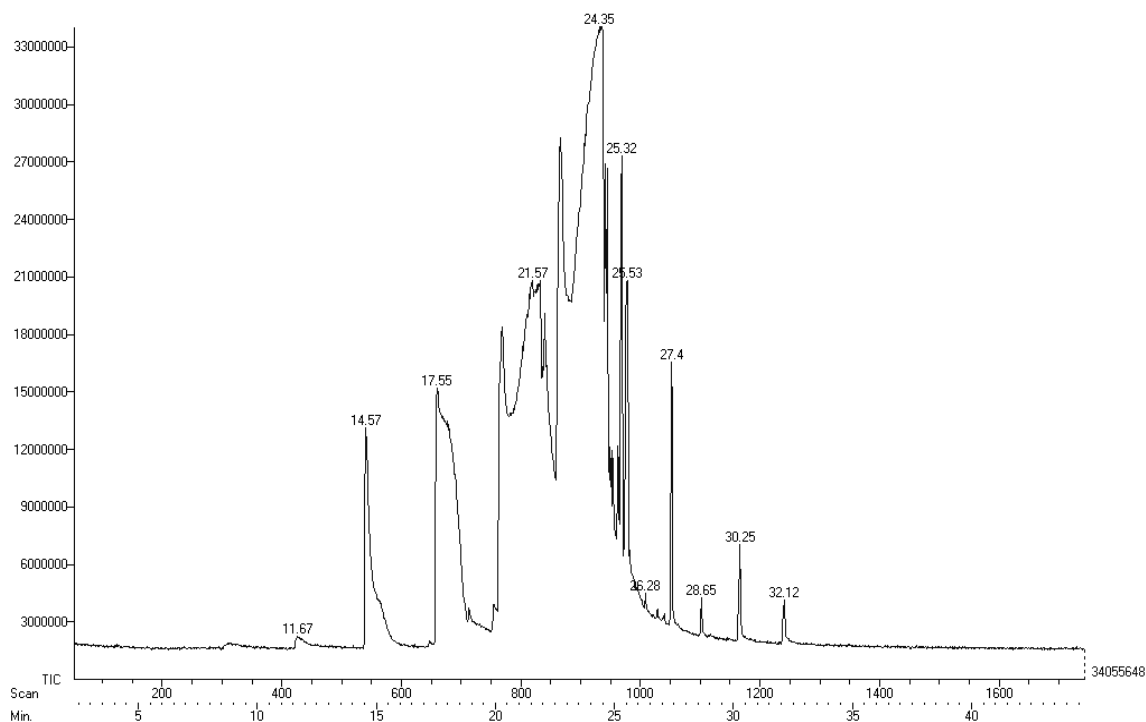


Fig. 2. GC-MS Spectrum of Cotton Seed biodiesel.

Table 1. Fatty acid methyl esters of Cotton seed biodiesel

Name of the ester	Fatty acids	Scan	Ions	RT	Molecular structure
Decanoic acid methyl ester	Capric acid	426	1280	11.67	
Dodecanoic acid methyl ester	Lauric acid	541	1105	14.57	
Methyl tetradecanoate	Myristic acid	660	1095	17.55	
Pentadecanoic acid 14 methyl-methyl ester	Palmitic acid	820	1075	21.57	
11-octadecanoic acid methyl ester	Linoleic acid	931	920	24.35	
Eicosanoic acid methyl ester	Arachidic acid	978	968	25.53	
Heneicosanoic acid methyl ester	Heneicosanoic acid	1008	1119	26.28	
Docosanoic acid methyl ester	Behenic acid	1052	986	27.4	
Tricosanoic acid methyl ester	Tricosanoic acid	1102	1230	28.65	
Tetracosanoic acid methyl ester	Lignoceric acid	1166	1116	30.25	

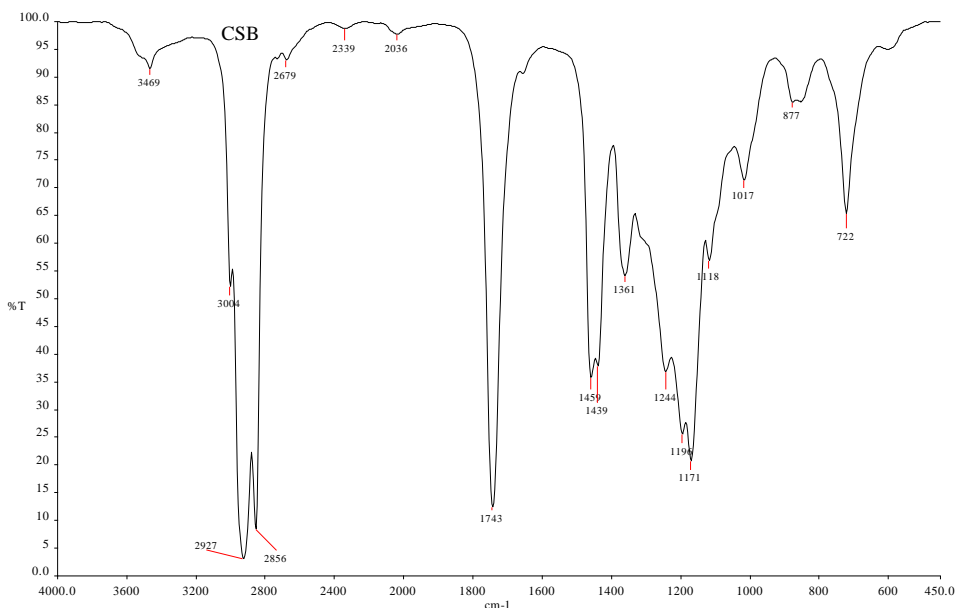


Fig. 3. FTIR Spectrum of Cotton Seed Biodiesel.

Table 2. Physio-chemical properties of Cotton seed biodiesel

Properties	Units	Cotton seed oil	Cotton seed biodiesel	Testing Methods
Density @ 15°C	kg/m <sup>3</sup>	910	865	IS:1448 P:16
Cetane Index	-	-	55	IS:1448 P:9
Kinematic viscosity, @ 40°C	Cst	27.12	4.87	IS:1448 P:25
Gross Calorific value	MJ/kg	40.87	35.82	IS:1448 P:6
Acid value	Mg/KOHg	0.25	0.19	-
Flash point	°C	254	145	IS:1448 P:20
Fire point	°C	289	154	IS:1448 P:20

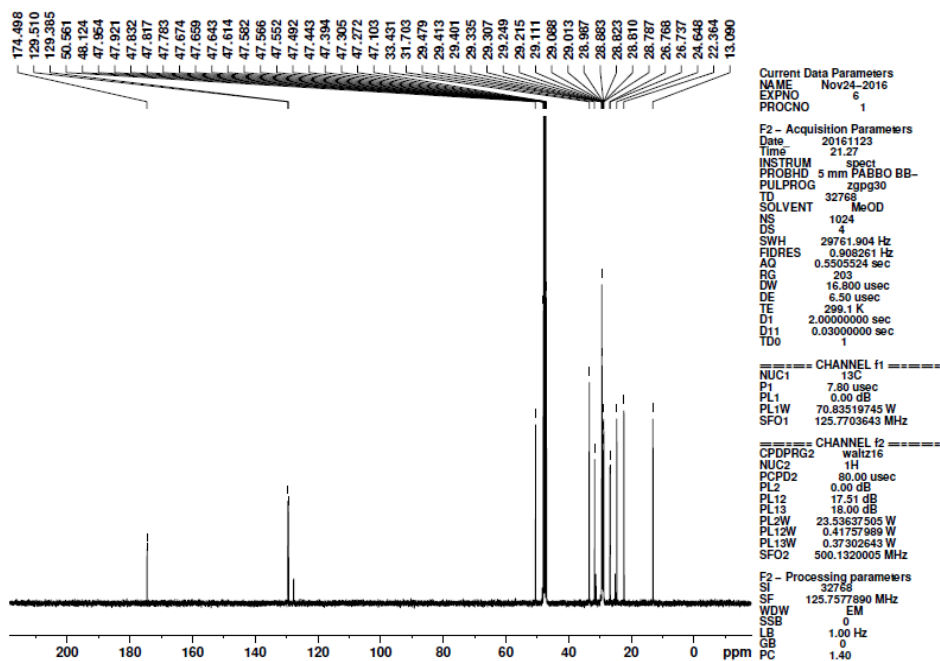


Fig. 4. NMR Spectrum (<sup>13</sup>C) of Cotton Seed Biodiesel

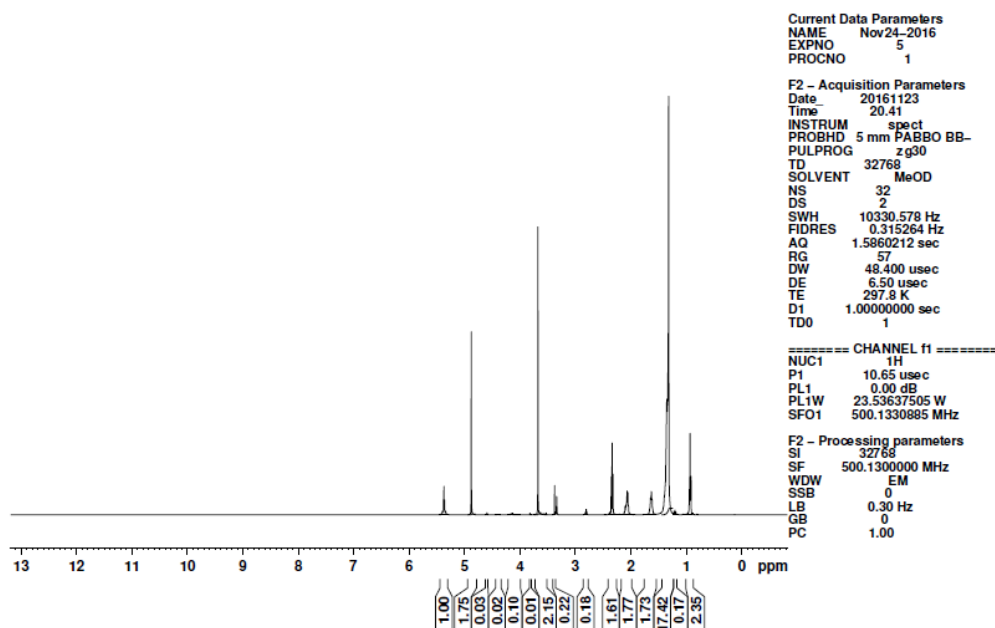


Fig. 5. NMR Spectrum (<sup>1</sup>H) of Cotton Seed Biodiesel.

### 3.5. Physio-chemical properties of cotton seed biodiesel

Table (2) illustrates the comparison of physio-chemical properties of cotton seed oil and its biodiesel. Due to transesterification process, the density of CSB is brought to 865 kg/m<sup>3</sup> from 910 kg/m<sup>3</sup>. The cetane number of cotton seed biodiesel is found to be 55 favouring to be blended with diesel for its usage as transportation fuel. It can be noticed that the kinematic viscosity is drastically reduced to 4.87 cSt from 27.12 cSt thereby improving its atomization property. The gross calorific value of cotton seed oil and cotton seed biodiesel is found to be 40.87 MJ/kg and 35.82 MJ/kg respectively. The flash and fire point of biodiesel and crude cotton seed oil was found to be 145 & 154 and 254 & 289 respectively. It was also noticed that these values lie close to each other and was significantly lower than cotton seed oil with minimal reduction in acid value [9].

## 4. Conclusion

In the present experimental investigation, cotton seed biodiesel production and its characterization was successfully carried out. The following conclusions are drawn based on the investigation results.

- Base catalysed transesterification process proved to be an effective technique on the production of cotton seed biodiesel.
- Maximum biodiesel production is noticed by optimizing the methanol to oil molar ratio and catalyst concentration. The optimal parameters is found to be 8:1 molar ratio, 1.8 wt.% catalyst concentration, 450 rpm agitation speed, 75°C reaction temperature and 120 minutes reaction time.
- GC/MS mass spectrum revealed the presence of ten prominent fatty acid methyl esters. At RT 24.35, linoleic acid is found to be the major constituent.

- FTIR mid region spectrum confirmed the presence of FAME's by indicating stretching-bending vibrations between 2679 cm<sup>-1</sup> and 2036 cm<sup>-1</sup>.
- NMR studies also attributed the GC/MS and FTIR results. <sup>13</sup>C NMR showed strong signal at 47 ppm indicated the existence of carbonyl group. <sup>1</sup>H NMR revealed strong singlet and triplet signals at 3.67 ppm and 1.33 ppm showing the presence of carboxylic group
- The density and kinematic viscosity of CSB is found to be 868 kg/m<sup>3</sup> and 4.87 cSt respectively. The cetane number of CSB is noticed to be 55. The gross calorific value of CSB is found to be lower than cotton seed oil.

## Acknowledgements

The authors are grateful to Sophisticated Analytical Instrumentation Facility (SAIF), Indian Institute of Technology Madras, Chennai, India for providing the facilities to carry out spectroscopic analysis.

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