

## Experimental evaluation on oxidation stability of biodiesel/diesel blends with alcohol addition by rancimat instrument and FTIR spectroscopy<sup>†</sup>

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(Manuscript Received July 27, 2016; Revised September 6, 2016; Accepted September 16, 2016)

### Abstract

Use of alcohols blended with biodiesel as alternative fuel in diesel engine is an attractive solution for depletion and demand of fossil fuels in transportation and industrial applications. Calophyllum inophyllum is a higher oil yielding species with high heating value and notably non-edible oil. One of the most important criteria used for assessing the quality of biodiesel blended fuel is ‘storage oxidation stability’. Deprived oxidation stability is the important technical obstacle associated with the biodiesel commercialization. This study investigated the oxidation stability of biodiesel blends at 100 % (B100) and 20 % (B20) volume concentrations with diesel through induction time determined by Rancimat instrument. Effects of pentanol addition with B20 biodiesel at 10 % (P10) and 15 % (P15) volume concentrations are also analyzed. FTIR spectroscopy characterizes the oxidation variability of all test fuels. It can be concluded that the biodiesel (B100) shows good oxidation stability (I.P = 8.47 h). Addition of pentanol (10 %) enhances the storage ability by 44.57 % than B20, whereas further addition of pentanol (15 %) declines by 19.48 % when compared to P10. More concentration of pentanol weakens the hydrophilic and hydrophobic clusters formed between pentanol/diesel/biodiesel compounds which have been characterized using infra red spectroscopic analysis.

**Keywords:** Calophyllum inophyllum; Pentanol; Oxidation stability; Rancimat; FTIR

### 1. Introduction

In the year 2014, worldwide fossil fuel exploitation grew by 0.8 million barrels per day. Consumption growth recorded by India is the highest, increased by 7.1 % and Japan recorded declination by -3 %. Whereas, US consumption escalated by 1.2 % than the previous year. This increasing consumption of fossil fuel leads to the search for alternative renewable energy sources and enhances bio-fuel production in the developing and developed countries. In the year 2014, the worldwide biodiesel production augmented by 7.4 %. Present biodiesel production level of US, India, Indonesia, France, China and Spain has been recorded as 5.6 %, 29.1 %, 40.4 %, 2.2 %, 3.3 % and 32.2 % higher than those of previous year 2013 [1]. Since non-edible oils can be environmentally friendly, efficient, economical, by-products gainer and notably eliminates competition for edible products. Calophyllum inophyllum (C.I) belonging to *Clusiaceae* family has been proposed as a biodiesel source [2]. Calophyllum inophyllum possess advantages of better lubrication capability, higher oil yield and high heating value than generally used biodiesels like jatropha,

Table 1. Oil yield and heating value of various feedstocks (Source: Ref. [6]).

Feedstock	Oil yield (kg/ha/year)	Heating value (MJ/kg)
Calophyllum inophyllum	4680	39.25
Jatropha curcas	1900-2500	38.5
Pongamia pinnata	225-2250	34.0
Soybean	200-600	39.623
Rubber	40-50	37.5
Sunflower	500-1500	39.575
Neem	-	33.7

pongamia, rubber seed and neem (Table 1).

C.I methyl ester was investigated at 10 %, 20 %, 30 %, 40 % and 50 % volume blended with diesel and observed that 10 % concentration biodiesel have higher BTE, better fuel economy, lower CO and smoke emission [3]. C.I biodiesel was prepared by two step pretreatment and transesterification process. Blends of 10 % volume produce the superior engine performance and reduced exhaust emissions, apart from NO<sub>x</sub>, compared to neat diesel [4]. C.I biodiesel blends shows higher BTE at 10 % blend and reduced smoke opacity for all biodiesel blends. Peak cylinder pressure and heat release rate

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Table 2. Properties of ethanol, butanol and pentanol (Source: Refs. [42-44]).

Fuel properties	Ethanol	Butanol	Pentanol
Density at 20 °C [kg/m <sup>3</sup> ]	788	810	814
Viscosity at 40 °C [cSt]	1.13	2.22	2.88
Cetane number	8	17	20
Calorific value [MJ/kg]	26.83	33.09	34.65
Flashpoint [°C]	14	35	49

were higher than those of diesel at 20 % volume blend [5]. Atbani et al. reviewed many researches concerning diesel engine overall performance, emission and combustion characteristics powered with Calophyllum inophyllum, they concluded that B10 and B20 blends could be used as substitute for diesel fuel without any additives in biodiesel and also with no modification in engine operating parameters. Meanwhile C.I biodiesel at 20 % volume concentration (B20) with additives can be used in diesel engine without any modification [6].

Various studies revealed that alcohol could be employed in diesel engines as oxygenated fuel additives with diesel, which has the tendency to reduce exhaust emission [7]. First generation biofuel used as blend or pure fuel in transportation was ethanol. Butanol was suggested as alternative to ethanol as it has drawbacks such as high volatility, high hygroscopicity and lower energy density. Uncontrolled autoignition is avoided at lower temperatures due to low reactivity of ethanol and butanol, which makes them suitable for spark ignition engines. Meanwhile autoignition is necessary for diesel engines, for this purpose longer carbon straight-chain alcohol like n-pentanol is suitable as alternative fuel [8]. Pentanol has higher cetane number and energy density comparing with ethanol and butanol (Table 2).

Pentanol has been used in some diesel engine investigations. Pentanol blended with diesel at 25 % volume has been proposed as the replacement for 100 % diesel [9]. When diesel-biodiesel-pentanol (40 % diesel-30 % biodiesel-30 % pentanol) blended fuels are investigated, better fuel-air mixture formation, soot reduction, proper ignition characteristics, shorter combustion duration, higher HRR, higher BTE and lower BSFC were recorded [10]. 20 vol % of sunflower oil and 10 vol % of pentanol was blended with diesel and studied for the engine performance and emission characteristics with the addition of 2-ethylhexyl nitrate (EHN). The results obtained are reduction in BSFC, NO<sub>x</sub> about 5.7 % and 2.9 % respectively and increased BTE, HC, CO emissions of about 9.26 %, 23.41 % and 17.7 %, respectively [11]. Pentanol blended with pure waste cooking oil methyl ester at 10 %, 20 % and 30 % by volume (BP10, BP20 and BP30, respectively) resulted in increased BTE for BP10 and lower NO<sub>x</sub> for BP10 and BP20 [12]. Pentanol blended waste cooking oil biodiesel is proposed as an alternative fuel in diesel engines without any engine modification and beneficial cold flow

improver [13].

Calophyllum inophyllum blended with pentanol at 15 vol% and 20 vol% as two proportions blends (Diesel (65 %) + C.I biodiesel (20 %) + Pentanol (15 %) and Diesel (60 %) + C.I biodiesel (20 %) + Pentanol (20 %)) and investigated for engine performance and emission characteristics. Pentanol displayed finer performance and emission. Pentanol treated C.I biodiesel blends show 2.2-10.87 % reduced BSFC, 50-67.7 % diminished HC and 18.4-33.8 % and declined CO emission [14]. From the obtained superior results, Calophyllum inophyllum/pentanol blends could be used in diesel engine as a suitable substitute for diesel fuel. But the commercialization of this fuel blend is mainly dependent on the 'storage oxidation stability'. The aim of this paper is to evaluate the oxidation stability of C.I biodiesel and its blends with pentanol addition by using Rancimat instrument and FTIR spectroscopy.

Rancimat instrument has been used in numerous studies for determining the storage time period of various biodiesel blends. Oxidation stability for rapeseed and used frying oil were investigated at two stages as distilled phase and undistilled phase. The oxidation stability was low for distilled product; meanwhile the undistilled product shows poor oxidation stability while exposed to light and air [15]. Oxidative stability of soybean biodiesel was analyzed by varying storage conditions and observed that addition of antioxidant (TBHQ) increased oxidation stability index [16]. Soh et al. investigated OS of biodiesel derived from used pal oil with the addition of antioxidants like BHA, vitamin E, BHT, TBHQ and PG. They observed the antioxidant effectiveness in the decreasing order as PG > BHA > TBHQ > BHT > vitamin E [17]. Dantas et al. investigated the oxidation stability for soybean and castor biodiesel using Rancimat instrument [18]. Biodiesel extracted from sunflower oil was found to have increased oxidation stability when blended with TBHQ by using Pressure differential scanning calorimetry (P-DSC) and Rancimat [19]. Oxidation stability index was recorded as 0.47 and 0.40 hours for ethylic poultry biodiesel and methylic poultry biodiesel respectively at 110 °C [20]. Effects of antioxidants on oxidation stability of soybean biodiesel were studied using Rancimat instrument [21-23]. Andiroba, jatropha and babassu biodiesel displayed better resistance to oxidation without any additive [24]. Investigation on the effects of antioxidants like A-tocopherol and TBHQ on oxidation stability of biodiesel obtained from peanut oil resulted in higher induction period for TBHQ added biodiesel blend [25]. Fourier transform infrared (FTIR) spectroscopy has been obviously used for monitoring biodiesel production and its purity. FTIR was used in the analysis of purity of soybean and jatropha biodiesel which have been produced using cesium impregnated sodium zirconate acting as a base catalyst [26]. By using FTIR spectra 1437 and 1464 cm<sup>-1</sup>, the transesterification process i.e., the conversion of triglycerides to fatty acid methyl ester was monitored for the quality of conversion analysis [27]. FTIR spectra showing the infrared peak intensities of esters was used to characterize the bio-

Table 3. Determined properties of fuel blends.

Properties/samples	Viscosity @ 40 °C	Density @ 15 °C	Calorific value	Flash point	Pour point	Cloud point	Cetane index	Oxidation stability @ 110 °C
Units	cSt	kg/m <sup>3</sup>	MJ/kg	°C	°C	°C	CCI	h
ASTM D 6751-02	1.9-6	< 890	> 41	< 130	-	-	-	EN14214 > 6 h
Diesel	3.9	833	43.35	63	-3	6.5	54	-
B100	4.78	873	38.33	140	4.3	13.2	55.8	8.47
B20	3.82	842	42.64	73	2.8	8.5	53.2	18.47
Pentanol	2.92	819	34	40	-4	3	23.3	-
P10	3.39	835	42.23	72	-4	3	49.2	23.84
P15	3.41	838	41.49	75	-4	3	47.8	22.81

diesel obtained from frying and fish oils [28]. Moisture content in palm oil biodiesel was investigated and recorded the best wavelength regions 3075-3700  $\text{cm}^{-1}$  and 1500-1700  $\text{cm}^{-1}$  for determining the moisture content in biodiesel blends [29]. FTIR results explained an oxidation-induced breakage of biodiesel (methyl ester) linkages and were used to depict the oxidation stability property of waste cooking oil biodiesel [30].

## 2. Materials and methodology

### 2.1 Test fuels

Biodiesel yield of about 85 % is obtained by transesterification process. In this process, 25 % (v/vol oil) methanol reacted with raw C.I oil in the presence of 0.9 % (w/vol oil) catalyst sodium hydroxide maintained at 66 °C for 2 hour and 350 rpm stirring speed, resulted in the breakage of molecules of oil into methyl esters and glycerol (by-product). Although this research paper concerns the oxidation stability analysis, the core aim is to discover the best substitute fuel that may reduce the usage of diesel fuel. Hence fuel blends are tested on the basis of reducing the diesel volume concentration. In previous studies, biodiesel at 20 % volume concentration (B20) with additives shows better results in all performance and combustion uniqueness, so B20 blend is kept as constant blend in all mixtures. Meanwhile the volume concentration of Pentanol is varied as 10 % volume (P10) and 15 % volume (P15). The following fuel blends at various proportions were prepared and investigated: (a) Pure biodiesel (B100), (b) 20 % biodiesel + 80 % diesel (B20), (c) 10 % pentanol + 20 % biodiesel + 70 % diesel (P10) and (d) 15 % pentanol + 20 % biodiesel + 65 % diesel (P15). While many researchers concluded that pure biodiesel (B100) has not executed better result in engine performance, it is essential to find its oxidation stability. Only if pure biodiesel shows acceptable induction period of above 6 hours at 110 °C (EN14214), it could be concluded for raw oil storage feasibility at room temperature. The fuel properties were determined using laboratory equipments provided by Centre of Excellence for Environmental Studies (COE-Es), Table 3.

### 2.2 Rancimat instrument

Oxidation stability is measured based on the standard test method EN14214 by using 873 Biodiesel Rancimat instrument manufactured by Metrohm. The accuracy of measurement of induction period with the cell constant of conductivity sensor is at  $1.1 \pm 0.1 \text{ cm}^{-1}$ . The Rancimat test (Fig. 2) involves passing of air at steady rate through a 5 gram sample held in a test tube which is heated to a particular temperature (140 °C-155 °C @ 5 °C interval). The air carrying secondary oxidation products (water soluble carboxylic acids) flows into a measuring vessel containing distilled water, which is continually monitored for conductivity by electrodes. Accumulation of carboxylic acids in water due to sample oxidation is indicated by conductivity rise in cell, depicted by the graph plotted between time (hour) and conductivity ( $\mu\text{S/cm}$ ). This rise in conductivity gradually increases with a steady climb in the curve with respect to time. The curve increases to a maximum value and then it decreases. The point at which the curve starts to drop is termed as “Induction period (IP)”, will be determined by the second derivative conductivity curve (Fig. 1), which is depicted by the automated Rancimat software. Induction period refers to the time at which the sample starts to degrade with respect to specified temperature.

### 2.3 FTIR spectroscopy

FTIR (Fourier transform infra-red spectroscopy) is a receptive method for identifying organic and some inorganic molecular compounds present in the sample. Perkin Elmer spectrum 2 is the instrument used in the present FTIR study. Chemical molecules absorb light in infra red region of electromagnetic spectrum, which corresponds to the bonds in the molecules. FTIR matches the emission spectrum of IR source of the sample with the background emission spectrum of the recorded IR sources. The ratio of the sample emission spectrum to that of the background spectrum is directly proportional to the sample's absorption spectrum. Depending on the absorption frequency range 600 to 4000  $\text{cm}^{-1}$ , the molecular groups present in the sample will be depicted via spectrum

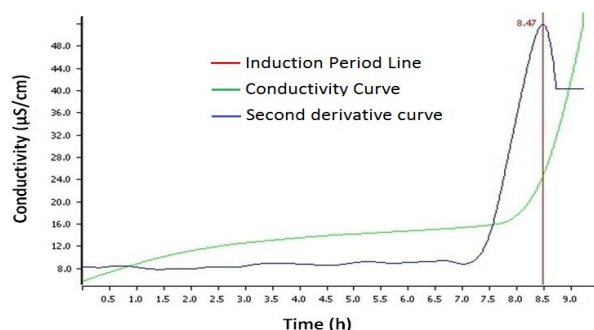


Fig. 1. Induction period of C.I biodiesel (B100) at 110 °C.

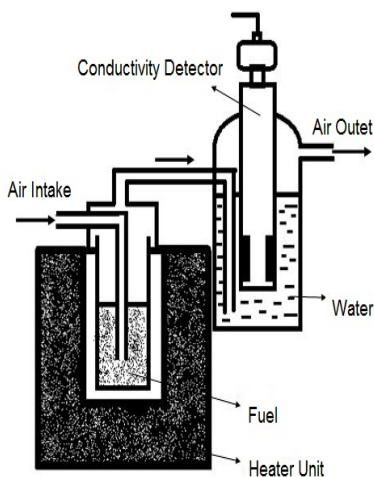


Fig. 2. Rancimat instrument.

data in the automated software.

In this study, the test fuels were analyzed at two stages: (i) Before oxidation stage i.e., before Rancimat measurement (ii) after oxidation stage i.e., after Rancimat measurement. Based on the absorption spectrum frequency ranges of samples, the oxidation characteristics of samples were evaluated by referring the presence and absence of specific molecular groups due to oxidation reaction.

### 3. Results and discussion

#### 3.1 Oxidation stability analysis

The variation of induction periods for pure C.I biodiesel, biodiesel/diesel blends and the effects of pentanol addition were studied by testing the samples at 140 °C, 145 °C, 150 °C and 155 °C (Fig. 3). Then the automated Rancimat software extrapolates the measured IP values and estimates the IP of corresponding fuel blends at 30 °C in terms of hours and years. It shows that B100 blend could be stored for 753.6 hour (or) 0.08 year at normal room temperature of 30 °C without any change in its chemical property. Similarly the storage period of other blends are also extrapolated for identical temperature condition (Table 4).

In the FTIR images, graph plotted between wave number ( $\text{cm}^{-1}$ ) vs. transmittance percentage (%T) shows the regions of

Table 4. Rancimat measurement of fuel blends.

Samples	Extrapolated IP at 30 °C	
	(h)	(Year)
B100	753.6	0.08
B20	4480	0.51
P10	8103	0.92
P15	6754	0.77

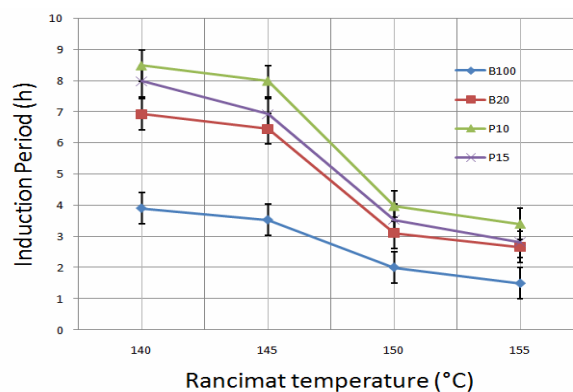


Fig. 3. Oxidation stability for all blends at various temperatures.

spectrum where specific molecular bonds containing in the samples absorb. The wave number and transmittance percentage were marked for O-H ( $3000\text{--}3700\text{ cm}^{-1}$ ), C-H ( $2700\text{--}3000\text{ cm}^{-1}$ ), C = O ( $1500\text{--}1800\text{ cm}^{-1}$ ) and C-O ( $600\text{--}1400\text{ cm}^{-1}$ ) bonds. Oxidation stability is mainly organized by O-H and C-H bonds of samples. C-O and C=O bonds spectrum in FTIR represents the presence of ether or ester molecular groups in a sample. If there is no change in C-O and C=O bonds spectrum after the Rancimat measurement, then the sample contains ether molecular groups. So the significant change in C-O and C=O bonds spectrum in all fuel blend spectrum graphs (Figs. 4-7) characterizes the ester group (Biodiesel), as the CO molecules gets converted into  $\text{CO}_2$  due to oxidation reaction. Each sample is plotted in FTIR spectrum at two conditions; (i) before oxidation (B.O line) - before Rancimat measurement (Marked with stars) (ii) after oxidation (A.O line) - after Rancimat measurement (Marked with triangles). Lower percentage of transmittance in the graph represents higher presence of corresponding molecular bonds in the samples.

#### 3.2 Pure C.I biodiesel blend (B100)

The oxidation stability for biodiesel extracted from C.I oil in its pure form without any mixture concentration of diesel which is denoted as B100 is an important commercialization parameter. As per EN14214 specifications, a pure biodiesel should possess 6 hours of induction period at 110 °C. Calophyllum inophyllum biodiesel (B100) shows 8.47 hours at 110 °C (Table 3), thus fulfilled the basic biodiesel characterization. Due to the presence of higher oxygen molecules, B100 shows lower IP when compared to diesel, but higher oxidation

Table 5. Induction Period of various biodiesel at 110 °C.

Feedstock	IP (h)	Ref
Callophyllum inophyllum	8.47	-
Soybean	4.3	[31]
Soybean	7.8	[32]
Soybean	3.61	[33]
Rapeseed	4.6	[34]
Jatropha	3.23	[35]
Sunflower	5.1	[35]
Cottonseed	4.9	[36]
Cottonseed	6.57	[37]
Karanja	3.17	[38]
Terminalia belerica	3.76	[39]
Linseed	2.2	[40]
Euterpe oleracea	1.5	[40]
Tallow fat oil based	4	[41]

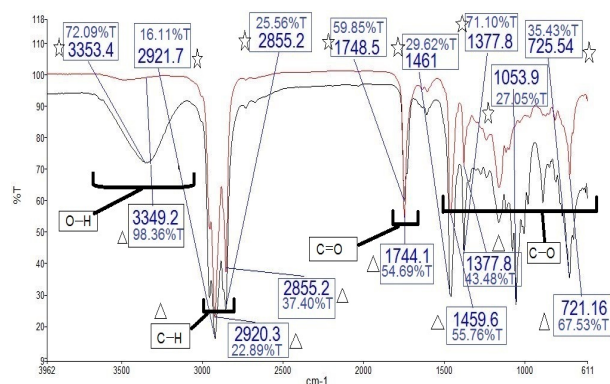


Fig. 4. FTIR spectrum for pure C.I biodiesel (B100).

stability than other biodiesel observed in previous studies (Table 5).

This inferior oxidation stability of biodiesel compared to diesel could be characterized by using FTIR spectrum image (Fig. 4). The presence of broad, strong O-H chain in the wave number of 3353.4  $\text{cm}^{-1}$  (72.09 %T) in B.O line corresponds to prevalence of more oxygen molecules and also linearity of long chain molecules attributed to rapid induction period for B100. Higher oxygen content will always attract other oxygen molecules in the atmosphere, leading to chemical reaction forming free radicals like superoxide, peroxide etc., which will contribute to enhanced oxidation through free radical chain reaction. At room temperature, microorganism prevailing in the ambient consumes the organic molecules in the oil and generates more free radicals that lead to lower storage capability. The induction period of B100 recorded as 0.08 year at room temperature (30 °C). The disappearance of transmission of strong O-H bond in wave number 3349.2  $\text{cm}^{-1}$  (98.36 %T) on A.O line represents the complete oxidation of B100 after being tested in Rancimat instrument.

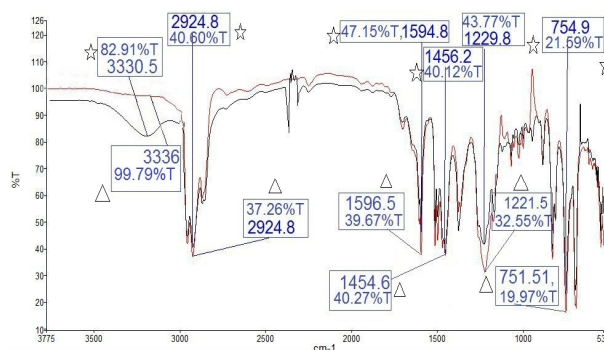


Fig. 5. FTIR spectrum for B20 biodiesel/diesel blend.

### 3.3 C.I biodiesel/diesel blend (B20)

When biodiesel blended with diesel at 20 % volume concentration (B20), obviously the oxidation stability of the blend escalated by 84.31 % compared to B100 with an induction period of 0.51 year at 30 °C. Oxygen is more electronegative than carbon, so if there is a presence of hydrogen group in the oil it will be seized by oxygen molecules which contributes to lower OS of B100. The reason behind the superior result of B20 is addition of more aromatic closed chain compounds (diesel), the ring structure of the blend resists oxidation for longer time than linear chain of biodiesel. Lower oxygen content in B20 hinders the formation of free radical chain reaction, hence the concentration of free radical is reduced and so the fewer free radicals has less impact on oxidation reaction. It can be viewed via strong, sharp C-H bond in wave number of 2924.8  $\text{cm}^{-1}$  (40.60 %T) and comparatively lower O-H bond (82.91 %T) in B.O line than those of B100 (Fig. 5). Higher C-H molecules consume oxygen for formation of Carbon dioxide, which leads to longer duration for degradation of sample. The conversion of medium O-H bond (3336  $\text{cm}^{-1}$ ) from B.O into weak O-H bond at 3330.5  $\text{cm}^{-1}$  in A.O line characterizes the termination of oxidation reaction of B20 after being employed in Rancimat instrument.

### 3.4 C.I biodiesel/diesel/pentanol blend (P10)

Pentanol addition of 10 % volume with 20 % biodiesel blend resulted in higher induction period of almost 1 year at room temperature, which is 44.57 % higher than that of B20. As pentanol is a longer chain alcohol with 5-carbon straight chain, the formation of strong hydrogen bonds as clusters between diesel and pentanol resulted in greater oxidation stability. Cluster compounds are very complicated to oxidize than linear compounds. Hydrophobic entities (C-H group) formed by diesel-alcohol molecules are surrounded by hydrophilic entities (O-H group) formed between alcohol-biodiesel, this cluster contributed to delay the induction period of P10. As the hydrophobic entities do not contain oxygen molecules, the site for free radical attack is reduced. Hence more free radicals are required for breaking the cluster, which may take long duration. This stretched period for breaking cluster re-

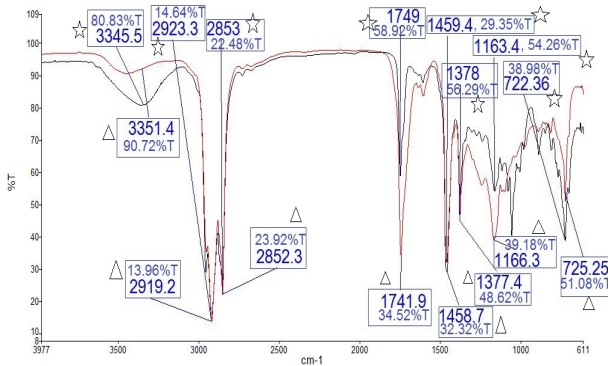


Fig. 6. FTIR spectrum for P10 blend (10 % vol pentanol).

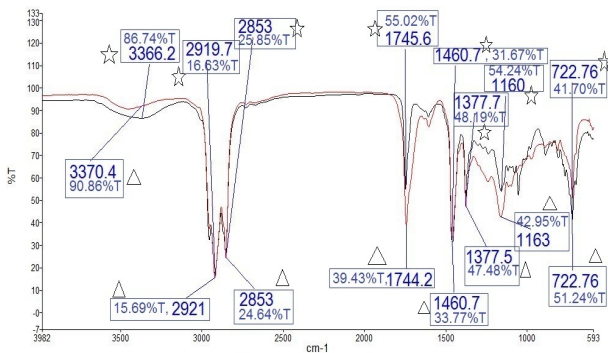


Fig. 7. FTIR spectrum for P15 blend (15 % vol pentanol).

sulted in longer induction period. It could be characterized through FTIR spectrum image Fig. 6, by higher prevalence of C-H molecular bonds in wave number 2923.3  $\text{cm}^{-1}$  with 14.64 % transmittance percentage which is lower than that of B20 (40.60 %T). As stated previously, lower transmittance percentage corresponds to higher molecular bonds prevalence. Hence P10 blend with 10 % volume of pentanol shows better oxidation stability. Degradation of O-H molecules in the sample after oxidation reaction could be viewed in A.O line with higher transmittance of 90.72 % in the range of 3350  $\text{cm}^{-1}$ .

### 3.5 C.I biodiesel/diesel/pentanol blend (P15)

In previous section, the addition of pentanol (10 %) shows increment in oxidation stability of fuel blend. Meanwhile increase in pentanol addition concentration (15 % volume) resulted in lower induction period of 0.77 year, which is 19.48 % lower than P10 and 33.77 % higher than B20. Further addition of pentanol causes destabilization of formed hydrophilic and hydrophobic clusters between alcohol-diesel-biodiesel compounds by reversing the cluster orientation, exposing hydrophilic group to oxygen. Hence this caused exposure of more biodiesel molecules to oxygen, leading to rapid oxidation reaction of P15 when compared to P10. At wave number 2919.7  $\text{cm}^{-1}$ , P15 possess 16.63 %T of C-H bonds which is higher than P10 (14.64 %T) resulted in lower C-H molecular chain than that of P10, Fig. 7. This character attrib-

uted to comparatively lower induction period. In A.O line, the O-H bonds degradation in wave number 3366–3372  $\text{cm}^{-1}$  represents the oxidation reaction of P15 blend occurred in Rancimat instrument.

## 4. Conclusion

The following conclusions are obtained from this research on the effect of pentanol concentration on biodiesel derived from *Calophyllum inophyllum* feedstock. All samples meet EN14214 requirement on oxidation stability (> 6h @ 110 °C). C.I biodiesel (B100) shows 8.47 hours at 110 °C. Biodiesel at 20 % volume blend with diesel was dosed with pentanol at 10 % and 15 % volume concentration. Induction period at room temperature was extrapolated from Rancimat measurements at 140 °C, 145 °C, 150 °C and 155 °C. FTIR spectroscopy was used to study the oxidation characterization of four blends (B100, B20, P10 and P15) before and after Rancimat measurement. Based on the results it was found that biodiesel/diesel blend shows higher oxidation stability than pure biodiesel due to the addition of aromatic closed chain compounds of diesel. When pentanol was added upto 10 % volume with B20, the oxidation stability is superior, 44.57 % higher stability than B20 blend due to higher C-H bond chains in its composition which restricts the blend to get oxidized rapidly. Meanwhile 15 % volume of pentanol addition leads to degradation in oxidation stability by 19.48 % when compared to 10 % pentanol addition, which is due to destabilization of formed hydrophilic and hydrophobic clusters between alcohol/diesel/biodiesel compounds. Hence it could be concluded that pentanol addition only upto 10 % volume to fuel blend increases the oxidation stability, above which it declines the storage stability. Further studies should be performed to ensure the optimum range for the addition of pentanol to *calophyllum inophyllum* biodiesel for obtaining the superior induction period.

## Acknowledgement

The authors would like to acknowledge Dr. Meenambal, Principal Advisor, TEQIP II - Centre of Excellence for Environmental Studies (COE-Es), Government College of Technology, Coimbatore- 641013, Tamil Nadu state, India, for their support to conduct this series of experiments.

## Nomenclature

<i>C.I</i>	: <i>Calophyllum inophyllum</i>
<i>BTE</i>	: Brake thermal efficiency
<i>BSFC</i>	: Brake specific fuel consumption
<i>BSEC</i>	: Brake specific energy consumption
<i>HRR</i>	: Heat release rate
<i>PG</i>	: n-propyl gallate
<i>BHA</i>	: 3-tert-butyl-4- hydroxyanisole
<i>TBHQ</i>	: A-tocopherol and 2-tert butyl hydroquinone

BHT : 2,6-di-tert-butyl-4-methyl-phenol  
 OS : Oxidation stability  
 IP : Induction period  
 B.O : Before oxidation  
 A.O : After oxidation

## References

- [1] Shameer P. M. and Ramesh K., Experimental evaluation on performance, combustion behavior and influence of in-cylinder temperature on NOx emission in a D.I diesel engine using thermal imager for various alternate fuel blends, *Energy* (2016) <http://dx.doi.org/10.1016/j.energy.2016.11.017>.
- [2] Mohamed Shameer P., Ramesh K., Sakthivel R. and Purnachandran R., Effects of fuel injection parameters on emission characteristics of diesel engines operating on various biodiesel: A review, *Renewable and Sustainable Energy Reviews*, 67 (2017) 1267-1281 ISSN: 1364-0321. DOI: <http://dx.doi.org/10.1016/j.rser.2016.09.117>.
- [3] H. C. Ong, H. H. Masjuki, T. M. I. Mahlia, A. S. Silitonga, W. T. Chong and K. Y. Leong, Optimization of biodiesel production and engine performance from high free fatty acid Calophyllum inophyllum oil in CI diesel engine, *Energy Convers Manage*, 81 (2014) 30-40, <http://dx.doi.org/10.1016/j.enconman.2014.01.065>.
- [4] H. C. Ong, H. H. Masjuki, T. M. I. Mahlia, A. S. Silitonga, W. T. Chong and T. Yusaf, Engine performance and emissions using Jatropha curcas, Ceiba pentandra and Calophyllum inophyllum biodiesel in a CI diesel engine, *Energy*, 69 (2014) 427-445, <http://dx.doi.org/10.1016/j.energy.2014.03.035>.
- [5] I. M. Monirul, H. H. Masjuki, M. A. Kalam, M. H. Mosarof, N. W. M. Zulkifli, Y. H. Teoh and H. G. How, Assessment of performance, emission and combustion characteristics of palm, jatropha and Calophyllum inophyllum biodiesel blends, *Fuel*, 181 (2016) 985-995, <http://dx.doi.org/10.1016/j.fuel.2016.05.010>.
- [6] A. E. Atabani and A. da Silva Cesar, Calophyllum inophyllum L. - A prospective non-edible biodiesel feedstock. Study of biodiesel production, properties, fatty acid composition, blending and engine performance, *Renew Sust. Energ. Rev.*, 37 (2014) 644-655, <http://dx.doi.org/10.1016/j.rser.2014.05.037>.
- [7] A. K. Agarwal, Biofuels (alcohols and biodiesel) applications as fuels for internal combustion engines, *Energy Combustion*, 33 (2007) 233-271, DOI: 10.1016/j.pecc.2006.08.003.
- [8] K. A. Heufer, J. Bugler and H. J. Curran, A comparison of longer alkane and alcohol ignition including new experimental results for n-pentanol and n-hexanol, *Proceedings of the Combustion Institute*, 34 (2013) 511-518, <http://dx.doi.org/10.1016/j.proci.2012.05.103>.
- [9] C.-F. Javier, J. M. Arnal, J. Gomez and M. P. Dorado, A comparison of performance of higher alcohols/diesel fuel blends in a diesel engine, *Appl. Energ.*, 95 (2012) 267-275, DOI:10.1016/j.apenergy.2012.02.051.
- [10] L. Li, W. Jianxin, W. Zhi and X. Jianhua, Combustion and emission characteristics of diesel engine fueled with diesel/biodiesel/pentanol fuel blends, *Fuel*, 156 (2015) 211-218, <http://dx.doi.org/10.1016/j.fuel.2015.04.048>.
- [11] E. Ileri, Experimental study of 2-ethylhexyl nitrate effects on engine performance and exhaust emissions of a diesel engine fueled with n-butanol or 1-pentanol diesel-sunflower oil blends, *Energy Convers Manage*, 118 (2016) 320-330, <http://dx.doi.org/10.1016/j.enconman.2016.04.015>.
- [12] L. Zhu, Y. Xiao, C. S. Cheung, C. Guan and Z. Huang, Combustion, gaseous and particulate emission of a diesel engine fueled with n-pentanol (C5 alcohol) blended with waste cooking oil biodiesel, *Appl. Therm. Eng.*, 102 (2016) 73-79, <http://dx.doi.org/10.1016/j.applthermaleng.2016.03.145>.
- [13] A. Atmanli, Comparative analyses of diesel-waste oil biodiesel and propanol, n-butanol or 1-pentanol blends in a diesel engine, *Fuel*, 176 (2016) 209-215, <http://dx.doi.org/10.1016/j.fuel.2016.02.076>.
- [14] H. K. Imdadul, H. H. Masjuki, M. A. Kalam, N. W. M. Zulkifli, A. Alabdulkarem, M. Kamruzzaman and M. M. Rashed, A comparative study of C4 and C5 alcohol treated diesel-biodiesel blends in terms of diesel engine performance and exhaust emission, *Fuel*, 179 (2016) 281-288, <http://dx.doi.org/10.1016/j.fuel.2016.04.003>.
- [15] M. Mittelbach and S. Gangl, Long storage stability of biodiesel made from rapeseed and used frying oil, *J. Am Oil Chem. Soc.*, 78 (2001) 573-577, DOI: 10.1007/s11746-001-0306-z.
- [16] R. O. Dunn, Oxidative stability of soybean oil fatty acid methyl esters by oil stability index (OSI), *J. Am Oil Chem. Soc.*, 82 (2005) 381-387, DOI: 10.1007/s11746-005-1081-6.
- [17] S.-K. Loh, S.-M. Chew and Y.-M. Choo, Oxidative stability and storage behavior of fatty acid methyl esters derived from used palm oil, *J. Am Oil Chem. Soc.*, 83 (2006) 947-952, DOI: 10.1007/s11746-006-5051-9.
- [18] M. B. Dantas, A. R. Albuquerque, L. E. B. Soledade, N. Queiroz, A. S. Maia, M. G. Santos, A. L. Souza, E. H. S. Cavalcanti, A. K. D. Barro and A. G. Souza, Biodiesel from soybean oil, castor oil and their blends, Oxidative stability by PDSC and rancimat, *J. Therm Anal Calorim*, 106 (2011) 607-611, DOI: 10.1007/s10973-011-1410-3.
- [19] M. L. A. Tavares, N. Queiroz, I. M. G. Santos, A. L. Souza, E. H. S. Cavalcanti, A. K. D. Barro, R. Rosenhaim, L. E. B. Soledade and A. G. Souza, Sunflower biodiesel, Use of P-DSC in the evaluation of antioxidant efficiency, *J. Therm Anal. Calorim.*, 106 (2011) 575-579, DOI: 10.1007/s10973-011-1357-4.
- [20] E. F. S. M. Ramalho, A. R. Albuquerque, A. L. Souza, A. K. Barro, A. S. Maia, I. M. G. Santos and A. G. Souza, Use of different techniques in the evaluation of the oxidative stability of poultry fat biodiesel, *J. Therm. Anal. Calorim.*, 106 (2011) 787-791, DOI: 10.1007/s10973-011-1545-2.
- [21] J. Dweck, R. S. Leonardo and M. L. M. Valle, Evaluating antioxidants efficiency during storage of ethylic and methylic biodiesel by low pressurized DSC and Rancimat

- methods, *J. Therm. Anal. Calorim.*, 113 (2013) 1317-1325, DOI: 10.1007/s10973-013-3028-0.
- [22] A. S. R. Maria, F. P. S. Francisco, J. N. M. Francisco and E. M. Selma, Evaluation of antioxidants on the thermo-oxidative stability of soybean biodiesel, *J. Therm. Anal. Calorim.*, 112 (2013) 921-927, DOI 10.1007/s10973-012-2650-6.
- [23] M. L. Murta Valle, R. S. Leonardo and J. Dweck, Comparative study of biodiesel oxidation stability using Rancimat, PetroOXY and low P-DSC, *J. Therm. Anal. Calorim.*, 116 (2014) 113-118, DOI: 10.1007/s10973-014-3706-6.
- [24] M. A. M. F. Melo, M. A. R. Melo, A. S. G. C. Pontes, A. F. F. Farias, M. B. Dantas, C. D. Calixto, A. G. Souza and J. R. C. Filho, Non-conventional oils for biodiesel production: a study of thermal and oxidative stability, *J. Therm. Anal. Calorim.*, 117 (2014) 845-849, DOI: 10.1007/s10973-014-3825-0.
- [25] L. M. Pinto, A. L. de Souza, A. G. Souza, I. M. G. Santos and N. Queiroz, Comparative evaluation of the effect of antioxidants added into peanut (*arachis hypogae* l.) oil biodiesel by P-DSC and rancimat, *J. Therm. Anal. Calorim.*, 120 (2015) 277-282, DOI 10.1007/s10973-014-4181-9.
- [26] A. T.-R. Daniela, C. R.-I. Issis, I. A. Ibarra and H. Pfeiffer, Biodiesel production from soybean and *Jatropha* oils using cesium impregnated sodium zirconate as a heterogeneous base catalyst, *Renew Energ.*, 93 (2016) 323-331, <http://dx.doi.org/10.1016/j.renene.2016.02.061>.
- [27] D. Reyman, A. S. Bermejo, I. R. Uceda and M. R. Gamero, A new FTIR method to monitor transesterification in biodiesel production by ultrasonication, *Environ. Chem. Lett.*, 12 (2014) 235-240, DOI 10.1007/s10311-013-0440-4.
- [28] C. G. Mothe, B. C. S. de Castro and M. G. Mothe, Characterization by TG/DTG/DSC and FTIR of frying and fish oil residues to obtain biodiesel, *J. Therm. Anal. Calorim.*, 106 (2011) 811-817, DOI 10.1007/s10973-011-1795-z.
- [29] M. E. S. Mirghani, N. A. Kabbashi, Md. Z. Alam, I. Y. Qudsieh and M. F. R. Alkatib, Rapid method for the determination of moisture content in biodiesel using FTIR spectroscopy, *J. Am. Oil Chem. Soc.*, 88 (2011) 1897-1904, DOI: 10.1007/s11746-011-1866-0.
- [30] P. Y. Furlan, P. Wetzel, S. Johnson, J. Wedin and A. Och, Investigating the oxidation of biodiesel from used vegetable oil by FTIR spectroscopy: Used vegetable oil biodiesel oxidation study by FTIR, *Spectros Lett.*, 43 (2010) 580-585, <http://dx.doi.org/10.1080/00387010.2010.510708>.
- [31] S. S. Damasceno, N. A. Santos, I. M. G. Santos, A. L. Souza, A. G. Souza and N. Queiroz, Caffeic and ferulic acids: An investigation of the effect of antioxidants on the stability of soybean biodiesel during storage, *Fuel*, 107 (2013) 641-646, <http://dx.doi.org/10.1016/j.fuel.2012.11.045>.
- [32] D. M. Fernandes et al., Storage stability and corrosive character of stabilised biodiesel exposed to carbon and galvanised steels, *Fuel*, 107 (2013) 609-614, <http://dx.doi.org/10.1016/j.fuel.2012.11.010>.
- [33] M. Lapuerta, J. Rodríguez-Fernández, Á. Ramos and B. Álvarez, Effect of the test temperature and anti-oxidant addition on the oxidation stability of commercial biodiesel fuels, *Fuel*, 93 (2012) 391-396, <http://dx.doi.org/10.1016/j.fuel.2011.09.011>.
- [34] M. Serrano, A. Bouaid, M. Martínez and J. Aracil, Oxidation stability of biodiesel from different feedstocks: Influence of commercial additives and purification step, *Fuel*, 113 (2013) 50-58, <http://dx.doi.org/10.1016/j.fuel.2013.05.078>.
- [35] R. Sarin, M. Sharma, S. Sinharay and R. K. Malhotra, *Jatropha-Palm* biodiesel blends: An optimum mix for Asia, *Fuel*, 86 (2007) 1365-1371, <http://dx.doi.org/10.1016/j.fuel.2006.11.040>.
- [36] D. M. Fernandes, D. S. Serqueira, F. M. Portela, R. M. N. Assunção, R. A. A. Munoz and M. G. H. Terrones, Preparation and characterization of methyl and ethyl biodiesel from cottonseed oil and effect of tert-butylhydroquinone on its oxidative stability, *Fuel*, 97 (2012) 658-661, <http://dx.doi.org/10.1016/j.fuel.2012.01.067>.
- [37] H. Tang, A. Wang, S. Salley and K. Y. S. Ng, The effect of natural and synthetic antioxidants on the oxidative stability of biodiesel, *Journal of American Oil Chemist's Society*, 85 (2008) 373-382, doi:10.1007/s11746-008-1208-z.
- [38] A. Obadiah, R. Kannan, A. Ramasubbu and S. V. Kumar, Studies on the effect of antioxidants on the long-term storage and oxidation stability of *Pongamia pinnata* (L.) Pierre biodiesel, *Fuel Processing Technology*, 99 (2012) 56-63, <http://dx.doi.org/10.1016/j.fuproc.2012.01.032>.
- [39] M. Chakraborty and D. C. Baruah, Investigation of oxidation stability of Terminalia bellerica biodiesel and its blends with petrodiesel, *Fuel Processing Technology*, 98 (2012) 51-58, <http://dx.doi.org/10.1016/j.fuproc.2012.01.029>.
- [40] S. S. Pantoja, L. R. V. da Conceição, C. E. F. da Costa, J. R. Zamian and F. G. N. da Rocha, Oxidative stability of biodiesels produced from vegetable oils having different degrees of unsaturation, *Energy Conversion Management*, 74 (2013) 293-298, DOI: 10.1016/j.enconman.2013.05.025.
- [41] Z. Yang, B. P. Hollebone, Z. Wang, C. Yang and M. Landriault, Factors affecting oxidation stability of commercially available biodiesel products, *Fuel Processing Technology*, 106 (2013) 366-375, <http://dx.doi.org/10.1016/j.fuproc.2012.09.001>.
- [42] M. Lapuerta, R. Garcia-Contreras, J. Campos-Fernandez and M. P. Dorado, Stability, lubricity, viscosity, and cold-flow properties of alcohol-diesel blends, *Energy Fuels*, 24 (2010) 4497-4502, DOI: 10.1021/ef100498u.
- [43] H. Abou-Rachid, K. E. Marrouni and S. Kaliaguine, DFT studies of the hydrogen abstraction from primary alcohols by O<sub>2</sub> in relation with cetane number data, *Journal of Molecular Structure: THEOCHEM.*, 631 (2003) 241-250, [http://dx.doi.org/10.1016/S0166-1280\(03\)00257-4](http://dx.doi.org/10.1016/S0166-1280(03)00257-4).
- [44] M. Gautam and D. W. Martin, Combustion characteristics of higher-alcohol /gasoline blends, *Proceedings of the Institution of Mechanical Engineers, Part A: Journal of Power and Energy*, 214 (2000) 5497-5511, doi: 10.1243/0957650001538047.





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