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Fuel stability of biodiesel from waste cooking oil: A comparative evaluation with various antioxidants using FT-IR and DSC techniques

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ABSTRACT

Valorization of waste for biodiesel production is an important parameter as 75% of biodiesel production cost comes from the feedstock cost itself. Therefore, waste cooking oil appears as one of the best accessible option for biodiesel production globally given its availability and low price. On the other hand, fuel stability is one of the most critical properties related to the commercialization of biodiesel into the global fuel market. Doping of synthetic antioxidants is a convenient method for enhancing the stability of biodiesel. Recent studies investigate the effect of antioxidant addition on fuel stability at different concentrations. In this study, three synthetic antioxidants namely; Pyrogallol (PY), Butylated hydroxytoluene (BHT) and Tert-Butylhydroquinone (TBHQ) were dosed into waste cooking biodiesel at different concentrations ranging from 375, 750, 1000, 1125, 1500 ppm respectively for enhancement of the fuel stability. This was followed by assessing the stability of the samples by means of fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC) instead of conventional Rancimat method. The findings indicated the effectiveness of FT-IR and DSC as reliable methods to assess the oxidation stability and to replace the conventional, time-consuming and costly Rancimat method. TBHQ was found to be the best option to enhance the stability of biodiesel. These findings are in agreement with the existing literature. The current study proved the effectiveness of both FT-IR and DSC methods as cheap, fast and reliable methods and thus can be considered as reliable methods for determination of oxidation stability of biodiesel.

1. Introduction

Industrial growth and development of any country is directly related to their available energy resources. In this context, renewable and fossil fuels play an important role in the transportation sector. However, there have been an increasing interest in alternative fuels due to the decreasing reserves of fossil fuel in addition to their negative impact on the environment. Therefore, biodiesel has been considered as an alternative to petroleum-derived fuels, as it is clean and renewable fuel type, can be used in traditional compression ignition diesel engines with little or no modification along with less harmful emissions such as hydrocarbon (HC) and carbon monoxide (CO) emissions compared to conventional fossil diesel due to the presence of oxygen molecules (García et al., 2017; Ali et al., 2013; Ashok et al., 2017a). Biodiesel is defined as the alkyl esters of fatty acids which are chemically derived from triglycerides found in vegetable, animal fats and waste oils, resulted from the transesterification reaction of low molecular weight alcohols such as methanol and ethanol. This reaction takes place in the presence of readily available catalysts and glycerol is obtained as a by-product of the reaction which adds economical value to the process

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Abbreviations

B100	Waste cooking oil biodiesel
BHA	Butylated hydroxyanisole
BHT	Butylated hydroxytoluene
BSEC	Brake specific energy consumption
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
CFP	Crystal formation peak temperature
CO	Carbon monoxide
CPT	Crystallization peak temperature
CFPP	Cold filter plugging point
D100	Euro diesel
DSC	Differential scanning calorimetry
DU	Degree of unsaturation
FAC	Fatty acids composition
FT-IR	Fourier transform infrared spectroscopy
GC	Gas chromatography
HC	Hydrocarbon
KOH	Potassium hydroxide
LCSF	Long chain saturated factor
MSC_n	1 Monounsaturated carbon
MP_n	Melting point
NaOH	Sodium hydroxide
NO_x	Nitrogen oxides
Na_2SO_4	Sodium sulfate
ppm	Parts per million
PSC_n:2	Polyunsaturated carbon
PSC_n:3	Polyunsaturated carbon
PrG	Propyl gallate
PY	Pyrogallol
R	Alkyl functionals
TBHQ	Tert-Butylhydroquinone
WCO	Waste cooking oil
WCOME	Waste cooking oil methyl ester

(Atabani et al., 2012). Additionally, waste recycling such as waste cooking oil (WCO) could cut down the production cost of biodiesel to a great extent and at the same time could eradicate its disposal issues (Nanthagopal et al., 2019).

Biodiesel has different physico-chemical properties due to the different fatty acids composition (FAC) of the oil sources. These properties include cetane number, calorific value, cloud point, kinematic viscosity, oxidation stability, iodine value, saponification value and acid value (Yaakob et al., 2014). FAC including saturated, monounsaturated and polyunsaturated fatty acids are the main determinants of biodiesel properties. Biodiesel stability can be examined under three categories; oxidation, thermal and storage stabilities. Oxidation stability is the most important one among these parameters as biodiesel has low resistance to oxidation. Oxidation stability is directly related to the degree of unsaturation (DU) and number of double bonds in the polyunsaturated fatty acid chain in the ester molecule which easily reacts with air causing degradation of biodiesel oxidation stability. Consequently, this may lead to further degradation in other important biodiesel properties such as density, calorific value, kinematic viscosity, acid value, cetane number, flash, cloud, pour and cold filter plugging points and peroxide value (Rashed et al., 2015; Rizwanul Fattah et al., 2014a; Yaakob et al., 2014; Buosi et al., 2016). This degradation leads to the formation of hydroperoxide, which, after that decompose to form an array of secondary oxidation products like aldehydes, ketones, carboxylic acids, oligomers, polymers, gum, sediment etc, all of which are undesirable matters in compression ignition engines. For instance, polymers can block fuel lines and pumps. Therefore, keeping the oxidation stability at an acceptable level is always a challenge for biodiesel industry. For the fuel producers, consumers and suppliers, it is very important to avoid these undesirable phenomena and to improve the fuel quality. For this purpose, certain antioxidants (called inhibitors) are doped into biodiesel. Historically, the methodology of determining the oxidative stability known as the Rancimat method was developed by Hadorn and Zürcher to monitor the rancidity of edible oils (Rizwanul Fattah et al., 2014a). Generally, antioxidants are classified into two groups. The first are natural antioxidants, produced from vegetable oils such as tocopherols and the second are synthetic antioxidants produced from petroleum-derived chemicals such as Butylated hydroxytoluene (BHT), Butylated hydroxyanisole (BHA), Tert-Butylhydroquinone (TBHQ), Pyrogallol (PY) and Propyl gallate (PrG) (Rizwanul Fattah et al., 2014a). The hydroxyl functionals (-OH) present in these synthetic antioxidants form stable radicals by providing proton for the oxidized free radicals. Thus, the reaction in the free radical chain is stopped and the start of oxidation is further delayed (Yang et al., 2017). The phases of the autoxidation process, mechanism and stabilizing oils and fats by means of natural and synthetic antioxidants have been well reviewed by (Rizwanul Fattah et al., 2014a).

An earlier study conducted by Dunn (2002) reported the positive effect of both TBHQ and α-tocopherol antioxidants on retarding the oxidative degradation of soybean methyl ester (SME). Author emphasized that the availability of unreacted oxygen is an important condition during storage and fuel must kept in very full, sealed storage containers will have longer induction periods. Buosi et al. (2016) conduct a comparative study between the application of natural antioxidants extracted from rosemary, oregano and basil and the synthetic antioxidant TBHQ, BHA and BHT by the Rancimat test at different temperatures of 110, 115, 120 and 125 °C respectively. Results proved the effectiveness of both natural and synthetic antioxidants achieving oxidation stability of more than 6 h at 110 °C. TBHQ was found to be the best performing antioxidants followed by natural antioxidants followed by BHT and BHA.

Ashok et al. (2017b) conducted a comparative engine and emissions performance study on the effects of Ethanox and BHA antioxidants doped with *Calophyllum inophyllum* biodiesel at 200, 500 and 1000 parts per million (ppm) respectively. Results indicated the positive effect of all antioxidants in increasing the brake thermal efficiency (BTE) as, for instance, Ethanox increased it by 5.3% when doped at 1000 ppm with *Calophyllum inophyllum* biodiesel. Doping 500 ppm of BHT and 1000 ppm of Ethanox with *Calophyllum inophyllum* biodiesel reduced the nitrogen oxides (NO_x) emission by 21% and 12.6% respectively compared to neat biodiesel. However; CO, HC and smoke emissions increased with antioxidants. These same phenomena were reported by Rashedul et al. (2015) when doping BHT with *Calophyllum inophyllum* biodiesel. These findings were also similar to those of Rizwanul Fattah et al. (2014b) and Rizwanul Fattah et al. (2014c) where the same trend was observed when doping BHA and BHT with palm oil, Cocos nucifera and Jatropha curcas methyl esters.

Ashok et al. (2017a) conducted a comparative engine and emissions performance study on the effects of BHT and metal oxide nanoparticle TiO_2 doping with *Calophyllum inophyllum* biodiesel at different concentrations. Main findings indicated the positive effect of both BHT and TiO_2 on improving the BTE, brake specific energy consumption (BSEC) and brake specific fuel consumption (BSFC). However, HC and CO emissions increased with BHT and reduced with TiO_2 compared to *Calophyllum inophyllum* biodiesel. Another comparative work done by Ashok et al. (2017c) in which *Calophyllum inophyllum* biodiesel doped with Ethanox and zinc oxides (ZnO) nanoparticle at different concentrations was assessed. At high load conditions, doping of 500 ppm of Ethanox caused a reduction of 17.8% in NO_x emission. In general, antioxidant and nanoparticle reduced NO_x emissions as they act as cetane improver. However, HC and CO emissions increased with Ethanox and reduced with ZnO nanoparticle compared to *Calophyllum inophyllum* biodiesel. Both improved BTE, BSEC and BSFC with ZnO nanoparticle being superior than Ethanox from performance point of view.

Shameer and Ramesh (2017) applied fourier transform infrared spectroscopy (FT-IR) spectroscopy in place of Rancimat method to examine the oxidation variability of biodiesel produced from *Calophyllum inophyllum* doped with TBHQ antioxidant (300–1000 ppm concentration). The findings of this study highlights the effectiveness of FT-IR method as reliable method that can replace conventional Rancimat method. Authors concluded that doping 1000 ppm TBHQ antioxidant with *Calophyllum inophyllum* biodiesel was found to be the best dosage ratio that could enhance the storage period of biodiesel. Botella et al. (2014) applied PetroOXY method as per prEN16091 standard on several biodiesel fuels using 4-allyl-2,6-dimethoxyphenol and catechol with the aim of finding a replacement to Rancimat method with good correlation and matching EN14214 standard. Authors proved the effectiveness of PetroOXY method as faster method.

Based on the presented literature, oxidation stability is a crucial biodiesel parameter that must be kept well within the desired limit to maintain biodiesel quality. Antioxidants can protect the fuel by inhibiting the oxidation reaction. However, the conventional Rancimat method is a time-consuming and costly method. While most of the studies considered Rancimat method to determine the oxidation stability of fuel sample, very few studies tried to adopt some other faster and reliable methods. Therefore, this study aims to examine the influence of three synthetic antioxidants (TBHQ, BHT and PY) on the oxidation stability of biodiesel prepared from WCO using FT-IR and differential scanning calorimetry (DSC) techniques as cheap and fast methods to replace Rancimat method. All antioxidants were doped at 5 different ratios of 375, 750, 1000, 1125 and 1500 ppm respectively. The influence of type and amount of antioxidants and the properties of biodiesel were also considered in this work. This work is believed to promote the application of FT-IR and DSC for future studies.

2. Materials and methods

Herein, the chemicals, materials employed, procedures adopted for the synthesis of biodiesel from WCO along with its purification, selection of antioxidants and addition to waste cooking oil methyl ester (WCOME) and the experimental techniques for the biodiesel characterization used in the study were briefly discussed.

2.1. Materials

All the chemicals and solvents used were of analytical grade and were used as received. They were of best grades of commercially available chemicals from Sigma Aldrich and Fluka Puriss.

2.2. Synthesis of WCOME and purification

Transesterification process (alcoholysis) is the most common method for production of biodiesel. In this process, triglyceride molecules of WCO have been converted to methyl ester (biodiesel) and glycerol (by-product). WCO was supplied from Faculty of Engineering, Erciyes University, Turkey through personal communication. In this process, 1% (m/m oil) of Potassium hydroxide (KOH) dissolved in 25% (v/v oil) of methanol (CH_3OH) (6:1 M ratio) was added to the pre-heated WCO at 60 °C and 1 h reaction time. The products were then moved to a separation funnel in order to remove methyl ester (biodiesel) from glycerol (by-product of the reaction). Biodiesel was then washed with warm distilled water (60 °C) three times to free it from the glycerol and other entrained impurities. Afterwards, a rotary evaporator was employed to remove the excess water and methanol from biodiesel. Biodiesel was further dried using a chemical dryer namely; sodium sulfate (Na_2SO_4). Finally, a qualitative filter paper (filters Fioroni) was used to obtain high quality final product (Atabani et al., 2015). Methyl ester yield was 97% and the color of the final product was bright yellow. The general equation of biodiesel production with methanol can be expressed in Fig. 1 (Atabani et al., 2012).

2.3. Selection of antioxidants and addition to WCOME

Three types of widely used synthetic antioxidants such as PY, BHT and TBHQ were selected in this study. Each sample was mixed well with an accurate amount of each antioxidant to form different concentrations ranging from 375 to 1500 ppm. For comparison, samples without antioxidant were also considered in this study. Fig. 2 shows the chemical formulae of the synthetic antioxidants while Table 1 shows their properties. Antioxidants were dosed with WCOME at different concentrations as: 375, 750, 1000, 1125 and 1500 ppm. At all concentrations, all antioxidants were completely soluble in WCOME. Table 2 shows the prepared 15 samples besides Euro diesel (D100) and biodiesel (B100) (WCOME).

2.4. Biodiesel characterization

2.4.1. Physico-chemical properties of WCOME

Physico-chemical properties of all samples were determined using the available equipment at Alternative Fuels Research Laboratory (AFRL), Erciyes University, Kayseri, Turkey and shown in Table 3. Density, cloud and pour points, cold filter plugging point and flash point were determined using Krüss DS7800 Density meter (Germany) (accuracy ± 0.0001 g/cm³) (ASTM D1298), Normalab NTE 450 (accuracy ± 0. 1 °C) (ASTM D2500 and D97), Normalab NTL 450 (France) (accuracy ± 0. 1 °C) (ASTM D6371) and Normalab NPM 450 (France) (accuracy ± 0. 1 °C) (ASTM D93) respectively.

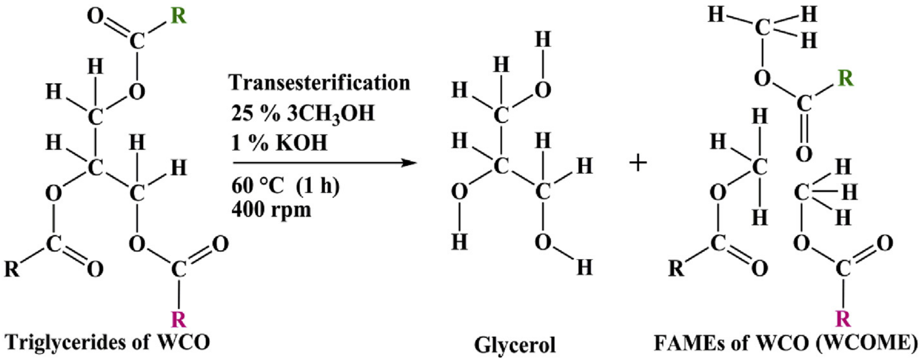


Fig. 1. Transesterification process for biodiesel production from WCO (Atabani et al., 2012).

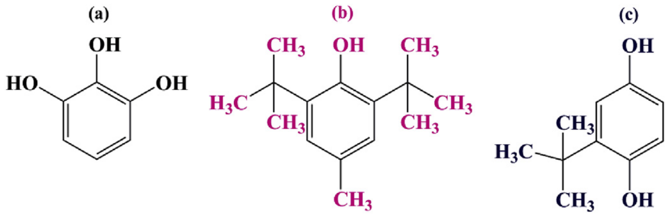


Fig. 2. Structural formulae of synthetic antioxidants (a) PY; (b) BHT; (c) TBHQ (Rizwanul Fattah et al., 2014a).

Table 1
Properties of synthetic antioxidants (Rizwanul Fattah et al., 2014a).

Name	Molecular Weight (g/mol)	Melting Point (°C)	Molecular Formula	Type
PY	126.11	150	$C_6H_6O_3$	Phenolic
BHT	220.35	265	$C_{15}H_{24}O$	Phenolic
TBHQ	166.22	273	$C_{10}H_{14}O_2$	Phenolic

Table 2
Fuel samples details.

Samples	Details
B100	%100 Pure biodiesel
D100	%100 Euro diesel
B100PY1	100% Biodiesel +375 ppm PY
B100PY2	100% Biodiesel +750 ppm PY
B100PY3	100% Biodiesel +1000 ppm PY
B100PY4	100% Biodiesel +1125 ppm PY
B100PY5	100% Biodiesel +1500 ppm PY
B100BHT1	100% Biodiesel +375 ppm BHT
B100BHT2	100% Biodiesel +750 ppm BHT
B100BHT3	100% Biodiesel +1000 ppm BHT
B100BHT4	100% Biodiesel +1125 ppm BHT
B100BHT5	100% Biodiesel +1500 ppm BHT
B100TBHQ1	100% Biodiesel +375 ppm TBHQ
B100TBHQ2	100% Biodiesel +750 ppm TBHQ
B100TBHQ3	100% Biodiesel +1000 ppm TBHQ
B100TBHQ4	100% Biodiesel +1125 ppm TBHQ
B100TBHQ5	100% Biodiesel +1500 ppm TBHQ

Table 3
Physico-chemical properties of WCOME.

Property	Unit	WCOME
Density at 15 °C	kg/m^3	879.9
Cloud point	°C	13
Pour point	°C	9
Flash point	°C	182
Cold filter plugging point	°C	4

2.4.2. *Gas chromatography (GC) method of WCOME*

FAC of WCOME was determined using GC (PerkinElmer Clarus 680). This device is equipped with a flame ionization detector (FID) and BPX70 capillary column and the test was conducted using the optimized method (Atabani et al., 2015). The carrier gas was hydrogen with column flow rate of 1.00 mL per min. In this test, 1 μL of WCOME was injected into the device to detect the FAC. The detailed operating conditions are presented in Table 4.

As per the results in Table 5, DU (wt%) and long chain saturated factor (LCSF) were calculated from the percentages of saturated, monounsaturated and polyunsaturated fatty acids respectively (Chuah et al., 2016; Al-Samaraae et al., 2017):

$$DU = (monosaturated\ \ C_n{:}1,wt\%) + 2(polyunsaturated\ \ C_n{:}2,wt\%) + 3(polyunsaturated\ C_n{:}3,wt\%) \quad (1)$$

$$LCSF = (0.1 \times C16{:}0) + (0.5 \times C18{:}0) + (1 \times C20{:}0) + (2 \times C24{:}0) \quad (2)$$

Table 5 shows the results of FAC of WCOME. As it can be seen that oleic acid represents the highest fatty acid with 44.96% followed by palmitic acid with 35.99%. it can be also seen that WCOME has balanced level of saturated and monounsaturated fatty acids of 41.68% and 44.96% respectively.

2.5. *FT-IR and DSC assessments of WCOME and antioxidants*

2.5.1. *FT-IR analysis*

FT-IR analysis have been used for identification of the existing functional groups by the appearance of bands in the samples. Spectra of the FT-IR corresponds to various stretching and bending vibrations existing in oils, esters and biodiesel samples. Oils and esters are given strong absorbers in the infrared region of the electromagnetic spectrum (Tariq et al., 2011; O'Donnell et al., 2013; American Laboratory, 2018; Spectro Scientific, 2018). FT-IR analyses of WCOME (B100) and the selected three antioxidants doped in WCOME were done using PerkinElmer device in the range 4000–650 cm^{-1}. The resolution was 4 cm^{-1} and 4 scans. All results were processed with a computer software program spectrum.

2.5.2. *DSC analysis*

DSC method is based on monitoring the energy received or given to the sample in relation to a reference system (inert) whose temperature can be controlled and which is the function of the temperature. The change in temperature causes reactions such as phase rearrangements, dehydration dissociation or decomposition, oxidation or reduction, gelatinization and other chemical processes in the sample. The DSC detects the energy released at the beginning of the reaction (Fonseca et al., 2013).

DSC analyses of WCOME (B100), (D100 and antioxidants doped in WCOME were analyzed by TA Q-2000 DSC. The summary of DSC method is given in Table 6. DSC curves were obtained in a calorimeter model DSC Q20 with RCS90 coupled with a cooling system. Each sample was loaded in an aluminum pan and heat flow was measured differentially by comparing heat flow of an empty reference pan as a reference. The duration of each DSC test was about 17 min. All results were then processed with TA Orchestrator Version V7.2.2.1.

3. Results and discussion

3.1. *Physico-chemical properties of WCOME and antioxidants*

Table 7 shows the properties of biodiesel blends with synthetic antioxidants. It can be seen that no noticeable changes were observed in cloud, pour and cold filter plugging points of all samples when doping with antioxidants with some small differences. However, doping antioxidants slightly increase the density of WCOME at 15 °C. These trends are similar to Rizwanul Fattah et al. (2014b); Rizwanul Fattah et al. (2014c) and Rashedul et al. (2015).

Table 4
GC operating conditions.

Property	Specifications	Unit
Carrier gas	Helium	
Flow rate	1.00 (column flow)	mL/min
Detector temperature	250	°C
Column head pressure	70 (flow control made)	kPa
Column dimension	BPX70	60 m × 0.25μm × 0.3 mm ID
Injector column oven	250	°C
Temperature ramp	60 °C (hold for 2 min)	°C
	10 °C/min 200 °C	°C
	5 °C/min 240 °C (hold for 7 min)	°C

Table 5
FAC, DU and LCSF of WCOME (B100).

Fatty acids	MW	Structure	Name	Formula	B100
Myristic	228	14:00	Tetradecanoic	$C_{14}H_{28}O_2$	0.63
Palmitic	256	16:00	Hexadecanoic	$C_{16}H_{32}O_2$	35.99
Stearic	284	18:00	Octadecanoic	$C_{18}H_{36}O_2$	4.64
Oleic	282	18:01	Cis-9-Octadecenoic	$C_{18}H_{34}O_2$	44.96
Linoleic	280	18:02	Cis-9-cis-12 Octadecadienoic	$C_{18}H_{32}O_2$	13.32
Arachidic	312	20:00	Eicosanoic	$C_{20}H_{40}O_2$	0.46
Saturated					41.68
Monounsaturated					44.96
Polyunsaturated					13.32
Total					100
DU					71.36
LCSF					6.38

Table 6
Summary of DSC method by TA Q-2000 DSC.

Instrument	TA Q-2000 DSC
Sample amount	3 ± 0.5 mg
Gas	Nitrogen
Flow rate	50 ml/min
Temperature range	− 80 °C–20 °C
Ramp rate	10 °C/min

Table 7
The physico-chemical properties of the biodiesel blends with synthetic antioxidants.

Sample	Cloud point (°C)	Pour point (°C)	Density at 15 °C (kg/m^3)	CFPP (°C)
B100	13.0	9.0	879.9	4
B100PY1	9.1	11.0	880.2	4
B100PY2	9.0	11.0	880.3	3
B100PY3	10.0	10.0	880.2	5
B100PY4	13.0	13.0	880.7	4
B100PY5	11.0	7.0	880.9	5
B100BHT1	10.0	10.0	880.1	3
B100BHT2	10.0	11.0	879.9	3
B100BHT3	10.0	11.0	880.2	4
B100BHT4	10.0	11.0	880.2	4
B100BHT5	10.0	11.0	880.3	5
B100TBHQ1	11.0	11.0	880.7	5
B100TBHQ2	10.0	11.0	881.1	5
B100TBHQ3	10.0	11.0	881.1	5
B100TBHQ4	10.0	11.0	881.2	4
B100TBHQ5	10.0	11.0	881.7	4

3.2. DSC assessment of WCOME and antioxidants

As mentioned earlier, oxidation stability of biodiesel is directly related to the number of double bonds present in the polyunsaturated fatty acids. FAMEs are mixtures of long chain fatty acid esters that has different carbon chain length and the degree of saturation and unsaturation. Crystallization temperature of each ester depends on the carbon chain length and interactions between the molecules. Compared to unsaturated fatty acids, saturated fatty acids have higher melting points and therefore they crystallize at a higher temperature. DSC method is an effective tool to detect the crystallization onset temperature of biodiesel and can be plotted graphically against heat flow. It also determines formation of the crystals and these crystals begin with nucleation process which continue to form aggregates and clusters. These aggregates need to reach a size and a determinable size in order to achieve standard growth. During the growth of crystals; the solute molecule is adsorbed onto the crystal surface, and this process concerns the solid phase transition of the material from the liquid phase. This stage can control further growth of the crystals. Additional ingredients such as biodiesel antioxidants are added to prevent or delay crystal formation and growth (Fonseca et al., 2013; Borugadda and Goud, 2014; Mohanan et al., 2015). The significant effects of three synthetic antioxidants as PY, BHT and TBHQ on the crystallization onset temperature of FAME were shown in Fig. 3(a)-3(c) and Table 8

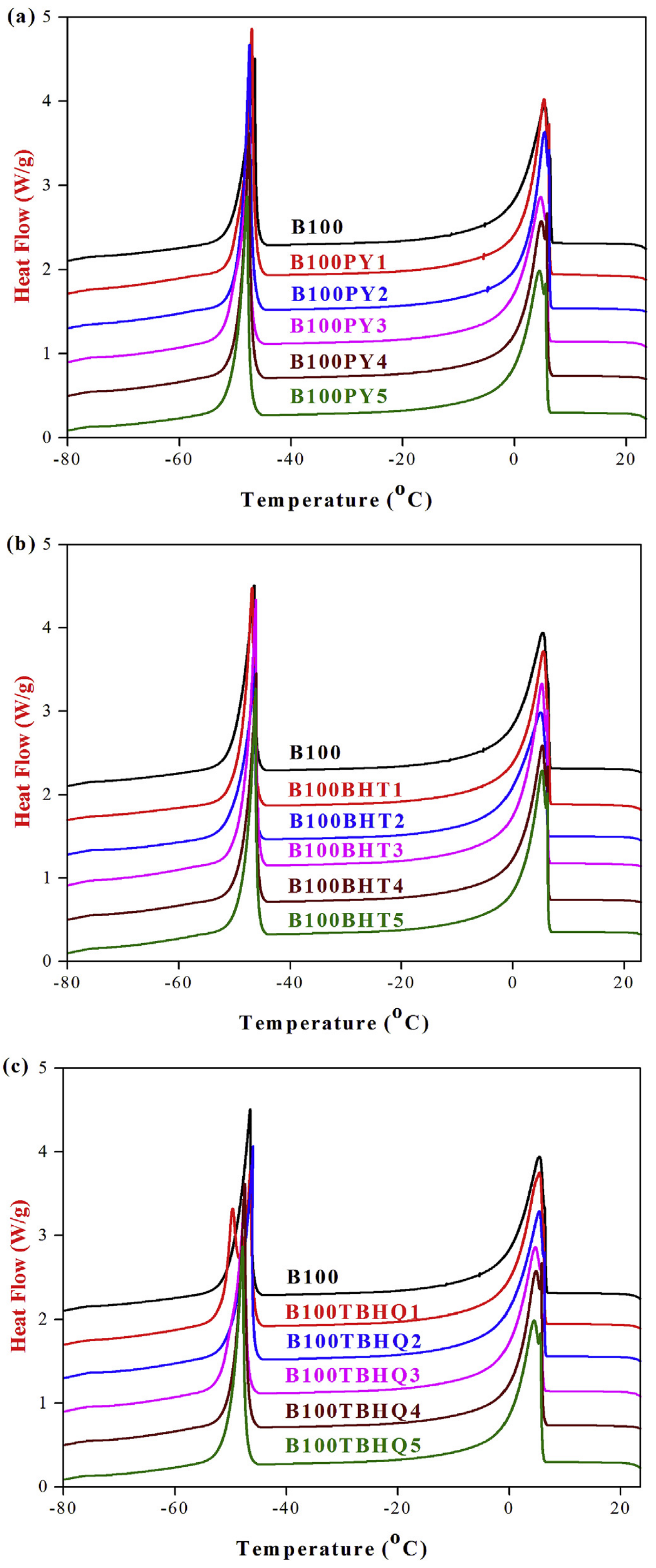


Fig. 3. DSC of WCOME with **(a)** PY antioxidant; **(b)** BHT antioxidant; **(c)** TBHQ antioxidant at different concentrations.

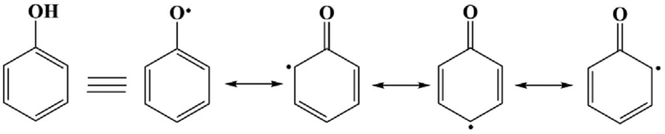
Table 8
Summary DSC phase change of WCOME blends with different antioxidants.

Sample	CFP (°C)	CPT (°C)
B100	5.38	−46.21
B100PY1	5.49	−47.69
B100PY2	5.46	−47.53
B100PY3	4.50	−47.56
B100PY4	4.78	−47.59
B100PY5	4.70	−47.61
B100BHT1	5.33	−46.42
B100BHT2	5.30	−45.82
B100BHT3	5.12	−46.32
B100BHT4	5.40	−46.03
B100BHT5	5.22	−46.06
B100TBHQ1	5.33	−46.26
B100TBHQ2	4.84	−45.98
B100TBHQ3	4.97	−46.47
B100TBHQ4	5.40	−46.81
B100TBHQ5	4.91	−46.99

respectively. All the curves have two state transitions. The first state is liquid-liquid crystal formation. In this transition, unsaturated compounds are solidified and in the second state unsaturated compounds are frozen. First signals at temperature of about −1.1 °C is due a crystallization of saturated esters, second signal of about −45 °C is caused by crystallization of unsaturated esters of the samples (Fonseca et al., 2013).

The crystallization onset temperature analysis using DSC was carried out for the biodiesel samples. It was based on the parameters *viz* B100 with and without antioxidant. The onset temperature for B100 and D100 are 5.38 °C and −10.41 °C respectively and accordingly pure biodiesel crystallizes faster than the pure diesel. Fig. 3(a)-3(c) and Table 8 show that the crystallization onset temperature of B100 with 375 ppm antioxidant additives were observed in the range of 5.49, 5.33 and 5.33 respectively as crystal formation peak temperature (CFP) in °C and −47.69, −46.42 and −46.26 as crystallization peak temperature (CPT) in °C for B100PY1, B100BHT1 and B100TBHQ1 biodiesel samples. Similarly, B100 with 750 ppm additives were 5.46, 5.30 and 4.84 respectively as CFP in °C and −47.53, −45.82 and −45.98 as CPT in °C for B100PY2, B100BHT2 and B100TBHQ2 samples. Furthermore, the values observed for B100PY3–B100PY5, B100BHT3–B100BHT5 and B100TBHQ3–B100TBHQ5 biodiesel samples were depicted and shown in Fig. 3(a)-3(c) and Table 8. The values below B100 signifies that addition of antioxidant additives reduces both the crystallization temperatures in terms of CFP and CPT for the biodiesel samples. Moreover, the results reveal that the observed reductions of more than 5 °C for all the representative temperatures confirm the addition of antioxidant to biodiesel samples. The area of the peaks of Fig. 3(a)-3(c) represents the existence of waxy crystals in the samples and it reveals that there is a decrease in crystallization with increasing the concentration of antioxidant additives in the biodiesel samples. Thus, the crystallization onset temperature of biodiesel can be lowered by the addition of PY, BHT and TBHQ antioxidants. The greater the antioxidants concentration in biodiesel samples, the lower is the waxy crystal formation. The addition of 1500 ppm of TBHQ antioxidant resulted in the maximal reduction in the onset temperatures of B100 blended samples, which lowered the onset temperature by 0.47 CFP in °C and 0.78 CPT in °C. Furthermore, the addition of antioxidants decreases the concentration of saturated methyl esters present in the saturated fatty acids of the samples which leads to a reduction in the crystallization onset. The presence of antioxidant additives not only reduce the temperature at which the crystals melt but also leads to a tremendous reduction in the heat flow, associated with this process. This reduction is more vital for the low-temperature freezing crystals of unsaturated components of the biodiesel samples. This phenomenon reinforces the existence of potential interactions between antioxidants and the unsaturated fatty acid methyl esters at very low temperatures. A low melting point values could also define lower gel formation temperatures (Garcia-Perez et al., 2010).

Thus, from the results, the ranking of antioxidant additives amongst the blended biodiesel samples was as follows: TBHQ > PY > BHT. It is owing to the effect of the antioxidant additives on the oxidative stability of the biodiesel samples which mainly depend on the number of hydroxyl (-OH) groups attached to the aromatic ring (Rashed et al., 2015). In the case of BHT, it has only one hydroxyl group in the aromatic ring and a methyl group at the *para*-position thereby, it possesses less effect on the blended biodiesel stability. Though, the stability of the phenoxy radical (C6H5 − O−$^{\bullet}$) is increased by the bulky *tert*-butyl groups at the *ortho*-position due to their + *I* effect. In the meantime, PY and TBHQ are strongly effective as they have the ability to produce the canonical forms *via* delocalization (resonance) and are more dynamic towards the formation of an intermediate between the free radical of the antioxidants and methyl ester of the biodiesel (Wang et al., 2014). The general canonical forms of all the three antioxidants are shown below.



It is also due to the substitution by alkyl functionals in *ortho*- and *para* position to develop the electron density around the –OH group by inductive effect (-*I*). Thus, based on the above said facts based on their electro negativities along with the phenolic antioxidants can be positioned in terms of their antioxidant activity as BHT < TBHQ < PY (Rashed et al., 2015).

3.3. FT-IR assessment of WCOME and antioxidants

The FT-IR spectral data for all the degraded biodiesel samples represent certain characteristic absorption bands, appearing for the functionals present in the samples, the FT-IR spectra of the biodiesel samples were affected highly during their degradation followed by oxidation as the formation of hydroperoxides, acids, aldehydes, alcohols, and ketones and it occurs on the of unsaturated aliphatic carbons chain double bonds of the lipids in the biodiesel samples. In general, the characteristic absorption bands responsible for methyl and methylene asymmetric ν(C − H) & methyl and methylene symmetric ν(C − H) bonds of the biodiesel samples are easily prone to the oxidation process. Further, such an evaluation for the biodiesel stability depends on monitoring the bands which are attributed to carboxylic and carbonyl ν(C=O) bands and the less stable nature of the biodiesel samples are confirmed by the existence of more aldehyde and ketone carbonyl functionals (Arisoy, 2008).

The impact of adding different antioxidants to biodiesel samples at different concentrations in accordance with the above information are shown in Fig. 4(a)-4(c). The spectra of the degraded biodiesel samples confirm that all the samples *viz* B100PY1–B100PY5, B100BHT1-B100BHT5 and B100TBHQ1-B100TBHQ5 exhibit ν(OH) rocking and wagging mode of vibrations by a broad band in between the region of $\nu_{(\mathrm{OH})}$:3700 − 3000 cm^{-1}, indicate the presence of moisture content (residual water) and its availability is around 1.95% which makes less possibility to degradative oxidation for the biodiesel samples. The main reason for this is the presence of the oxygen molecule with a transmittance of nearly 95% at a wavenumber of about 3006 cm^{-1}, clearly visible with the FT-IR spectrum. Since oxygen is more electronegative than the carbon element, it can easily form a bond with the hydrogen present in the biodiesel structure (Shameer and Ramesh, 2017). It is evident from Fig. 4 that no alcoholic functional ν(O − H) bonds were found in the biodiesel samples.

Moreover, the IR spectra of all the biodiesel samples indicate a decrease in the intensity of the bands at $\nu_{(\mathrm{C-H})}$: 3000 − 2700 cm^{-1}

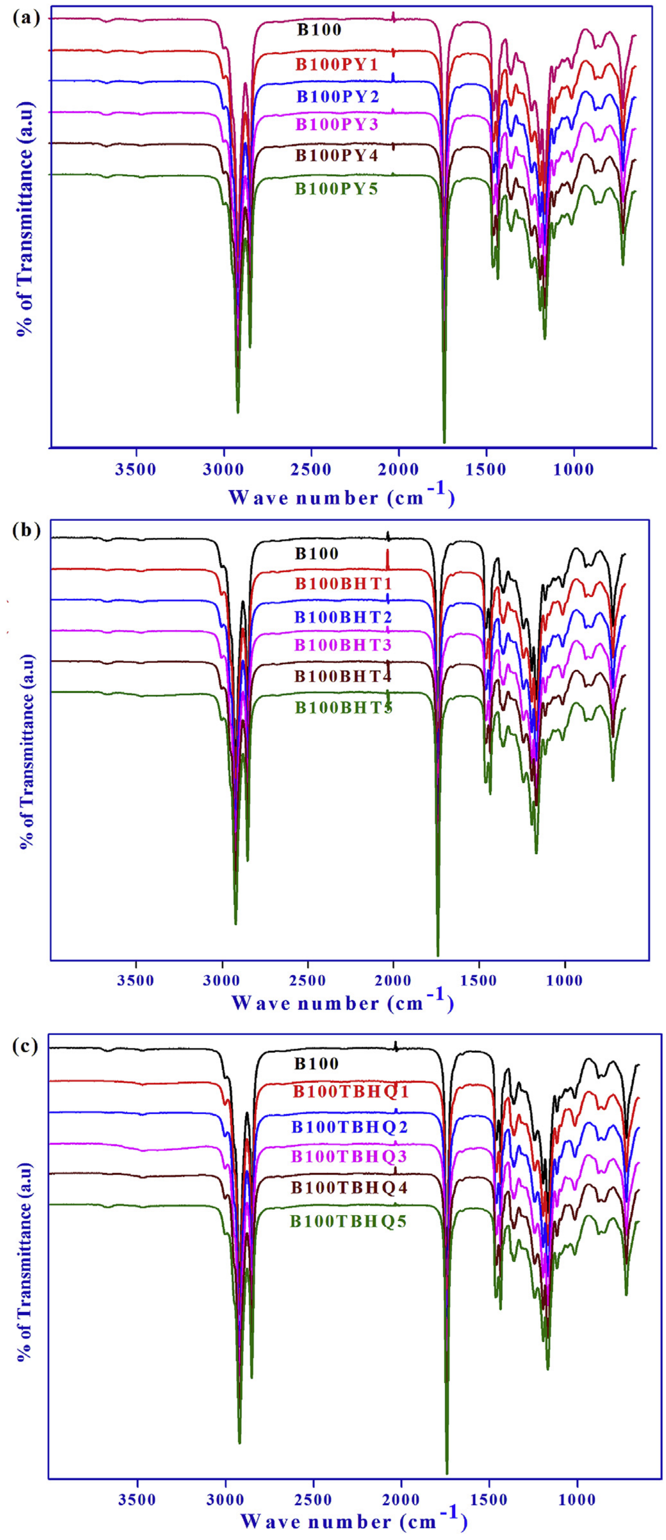


Fig. 4. Impact of addition of **(a)** PY; (**b**) BHT; (**c**) TBHQ antioxidants to B100 in FT-IR spectra.

which are responsible for ν(C − H) bonds and its availability falls in the range between 1.66 and 1.75% because of increase in unsaturation represents that there is a lack of possibility in favor of oxidative polymerization reaction (Garcia-Perez et al., 2010). The general spectrum exhibits strong characteristic absorption bands for the essential ester carbonyl functionals $\nu_{(\text{–O–C}=\text{O–})}$ at > 1741 cm^{-1} and the absence of another band adjacent to this, confirms the non-existence of carboxylic acids. From the results, these biodiesel samples have a storage and oxidation stability due to the rate of oxidation is very low with almost all the samples.

3.4. *Mechanism for anti-peroxidation path*

The phenolic antioxidants (PH) provide the resistivity towards the oxidative stress by means of scavenging free radicals and thereby inhibiting peroxidation of the lipid molecules exist in the biodiesel samples. A possible multi-step peroxidation chain mechanism of the biodiesel samples mainly involves double bonds of the olefinic polyunsaturated aliphatic carbon fatty acid chains in their lipid moieties as they have potential activity towards the degradative oxidation. This reaction leads to the formation of primary products *viz* conjugated diene hydroperoxides which undergoes degradation and form several secondary oxo-products like acids, aldehydes, alcohols, ketones *etc*., by means of their self-interaction. The degradative oxidation path of the biodiesel involves four stages. In the first stage, abstraction of a –H atom from the allyl group of the ester content occurs. The second stage involves attack of oxygen at either end of the radical center to produce peroxy radicals as reaction intermediates. In the third stage, there is a formation of a monohydroperoxide free radical and which is followed by formation of the oxo-products and water by means of its partial degradation, as a fourth stage (Fig. 5).

Further, the anti-peroxidation path involves reaction of the formed peroxy radicals with antioxidants as free radical terminators and then converts them to alcohols. This path involves the following three steps. In the initiation step, there is formation of a carbon centered lipid radical as a result of the abstraction of a methylene − H atom from polyunsaturated fatty acids (RH) by free radicals(OH$^{\bullet}$).

$$R - H + \mathrm{OH}^{\bullet} \rightarrow R^{\bullet} + H_2O\ (Initiation)$$

The propagation involves the formation of peroxyl radical(ROO$^{\bullet}$)by the reaction of this radical(R$^{\bullet}$)with environmental O$_2$ molecule; consequently the polyunsaturation of the biodiesel lipids has been isomerized to a conjugatediene (radical intermediate). Then the phenolic antioxidants (PH: free radical terminators) provide a highly labile − Hatom to the peroxyl radical(ROO$^{\bullet}$)thereby the formation of a hydroperoxide (ROOH). The phenolic antioxidant (PH) thus reduces the peroxyl radical(ROO$^{\bullet}$)to a hydroperoxide (ROOH) at the same time as transforming itself into a stable radical (P$^{\bullet}$).

$$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$$
$$ROO^{\cdot} + PH \rightarrow ROOH + P^{\cdot}\ (\mathrm{Pr}opagation)$$

Termination take places by the reaction between peroxyl radical(ROO$^{\bullet}$)and the antioxidant (PH) derived stable radical(P$^{\bullet}$)to yield the non-radical products. Moreover, these reactions are exothermic and if the bond dissociation energy of RH and PH increases, the activation energy of these reactions also increases and strength of the P–H bond decreases, the efficiency of the phenolic antioxidants increases (Yang et al., 2013; Rizwanul Fattah et al., 2014a).

$$ROO^{\cdot} + P^{\cdot} \rightarrow ROOP\ (Ter\min ation)$$

4. Conclusions and recommendations

The usage of biodiesel remarkably contributes to reduce the world's dependence on fossil fuels besides its well-known positive environmental impact. As biodiesel can be obtained from different sources, physico-chemical properties and chemical composition depend on the fatty acid composition and the quality of the feedstock. Waste cooking oil has been proved to be one of the best options for biodiesel production as it can be easily collected besides it does not create any land issue and food versus energy conflict. However, oxidation stability of biodiesel is a major issue that faces this vital industry. Fast degradation of biodiesel creates some undesirable products such Aldehydes,

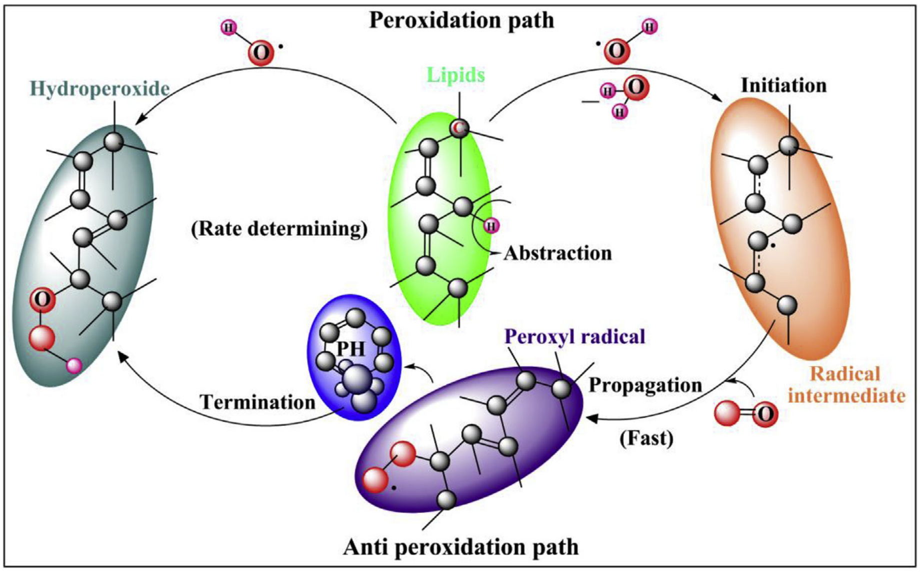


Fig. 5. Anti-peroxidation path of biodiesel lipids with phenolic antioxidants (PH).

ketones, acids, peroxides and polymers. These products are responsible for the properties degradation of biodiesel and thus negatively affect engine and combustion performance in CI engines. Oxidation stability can be tested using the conventional Rancimat method. However, this method is costly and time-consuming one. Therefore, looking for other methods such as fourier transform infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC) have attracted the attention both to researchers and industries as they are reliable, cheap and fast. This paper examines different dosages effect of three synthetic antioxidants namely; butylated hydroxytoluene (BHT), Tert-Butylhydroquinone (TBHQ) and Pyrogallol (PY) by means of FT-IR and DSC techniques. Results, revealed the effectiveness of these methods to detect the oxidation stability of biodiesel as substitutes to conventional Rancimat method and confirmed that dosing TBHQ antioxidant was found to be the best option to enhance the oxidation stability of biodiesel from waste cooking oil among BHT and PY antioxidants. In conclusion, this work supports that oxidation stability of biodiesel can be well characterized by FT-IR and DSC methods. Therefore, doping other types of natural and synthetic antioxidants at different concentrations with biodiesel may be further examined by these techniques in future studies.

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