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# Stability of *Jatropha Curcas* Biodiesel [JCB]

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## ABSTRACT

This article is to review the stability of Jatropha Curcas biodiesel (JCB). Biodiesel stability being a critical quality parameter; JCB is affected adversely by oxidation and improper storage. Addition of antioxidants improved biodiesel quality to meet EN 14112 specification. The oxidation stability and thermal degradation are affected adversely by the container metal; copper has the strongest catalytic effect, whereas, iron has the lowest catalytic effect. Pyrogallol (PY) is the most effective antioxidant for the stability of the JCB.

**Keywords:** Biodiesel, Jatropha Curcas, Oxidation stability, Thermal degradation.

## 1. INTRODUCTION

Nowadays, biodiesel is considered as an important alternative biofuel due to its environmental benefits and simple industrial production from renewable resources. Biodiesel has the added advantage of higher lubricity compared to petro diesel. However, such an ecological friendly liquid fuel has low oxidation stability (Jain and Sharma, 2010a).

At present, approximately 85% of commercially produced vegetable fats and oils are used as edible oil. The rest are used as industrial raw materials (5-6%), and biodiesel fuels (6-7%). It is predicted that the demand for edible fats and oils will increase along with the growing world population (Ichihashi et al., 2011). Utilization of edible oil crops (corn, soy, etc.) for the production of bio-fuels is expected to create a short supply of food consumption; whereas, using non edible oil crops such as *Jatropha Curcas* for the production of biodiesel is potentially attractive (Charlene et al., 2004).

Biodiesels produced from vegetable oils and other feed stocks have been found to be very susceptible to oxidation and thermal degradation. According to European biodiesel standard EN-14214 the minimum requirement of oxidation stability in terms of induction period (IP) is six hours by the Rancimat method (EN-14112). The IP of fresh JCB is 3.27 hours. Also, the thermal stability of J*atropha Curcas* is very poor in terms of activation energy ($E_a$) and frequency factor (f) (for the fresh JCB sample, the activation energy and frequency factor were computed to be 39 kJ/mol and 6501.48 min -1 respectively) (Jain and Sharma, 2011). This work aims to investigate the review of the stability of biodiesel from *Jatropha Curcas* oil.

## 2. PHYSIOCHEMICAL PROPERTIES OF JCB

The physiochemical properties of JCB presented in Table (1) are almost similar to those of ASTM D6751 and IS 15607. The oxidation stability of JCB is satisfying the minimum required value of ASTM D6751 and is lower than IS 15607 requirement (Jain and Sharma, 2012).

The chemical reactivity of fatty oils and their esters is divided into oxidative and thermal stability (Jain and Sharma, 2012). Basically, the key of oxidation stability is the chemical structure. More oleic double bonds in the fatty acid chain of the triglyceride provide better oxidation stability. However, the more conjugated double bonds in the fatty acid chain, the poorer the oxidation stability (Erhan, 2005). On the other hand, highly saturated fats generally have high oxidation stability (Haagenson et al, 2011).

The thermal stability of biodiesel is defined as the resistance of thermal degradation. The effect of thermal degradation and its kinetic behavior through thermo gravimetric analysis (TGA) has not been reported (Jain and Sharma, 2010b). Chand et al. (2009) have found that the TGA is an effective method. Wan Nik et al. (2005) have studied the thermal stability of palm oil as an energy transport media in a hydraulic system, two models were used to evaluate the kinetic parameters of the oil samples as direct Arrhenius plot method and integration method. TGA using the direct Arrhenius plot method has been used by numerous researchers (Chand et al., 2009; Dantas et al., 2007; Freire et al., 2009 and Fritsch et al., 1975). Eq. (1) is used to

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determine the activation energy of oil samples by a direct Arrhenius plot method; the plot ln [1/(1-x). dx/dt] versus (1/T) should give a straight line with slope (($-E_a$ /R) from which the activation energy is calculated.

$$\ln\left[\frac{1}{1-x}\frac{dx}{dt}\right] = \ln\frac{A}{B} - \frac{E_a}{RT} \qquad (1)$$

$$B = \frac{dT}{dt} \qquad (2)$$

Where:

$E_a$: The activation energy.
A: The frequency factor.
R: Ideal gas low constant (8.314 J/mol K).

**Table 1:** Physiochemical properties of JCB per different standards

| Property (unit) | ASTM D6751 | ASTM D6751 limits | IS 15607 | IS 15607 limits | JCB |
|---|---|---|---|---|---|
| Flash point (°C) | D-93 | Min 130 | IS 1448 | -* | 172 |
| Viscosity at 40 °C (cSt) | D-445 | 1.9-6.0 | IS 1448 | 0 | 4.38 |
| Water and sediment (vol %) | D-2709 | Max. 0.05 | D-2709 | Max. 0.05 | 0.05 |
| Free glycerin (mass %) | D-6584 | Max. 0.02 | D-6584 | Max. 0.02 | 0.01 |
| Total glycerin (mass %) | D-6584 | Max. 0.24 | D-6584 | Max. 0.24 | 0.03 |
| Oxidation stability of FAME, hrs | EN 14112 | 3 | EN 14112 | Min. 6 | 3.27 |
| Oxidation stability of FAME blends, hrs | 0 | 0 | EN 590 | Min. 20 | 0 |
| Free glycerol | D-6584 | 0.02 (max) | D-6584 | 0.02 (max) | 0.01 |
| Total glycerol | D-6584 | 0.25 (max) | D-6584 | 0.25 (max) | 0.12 |
| Acid value | D664 | 0.5 (max) | D664 | 0.5 (max) | 0.38 |
| Ester content | 0 | 0 | EN 14103 | 96.5 (max) | 98.5 |

(Jain and Sharma, 2012)
* Values not available

## 3. FACTORS AFFECTING THE STABILITY OF JCB

### 3.1. Oxidation

Fatty acid chain of biodiesel with instauration in its fatty acids offers high reactivity with oxygen, especially when it is placed in contact with air and water. As the JCB contains about 75% of unsaturated fatty esters, the oxidation stability is expected to be seriously impacted. Furthermore, the fatty oils with more poly instauration are more prone to oxidation (Madarasz and Kumar, 2011).

### 3.2. Storage

Biodiesel stability is affected by interaction with contaminates, light, and factors causing sediment formation that reduces the clarity of the fuel (Canakci et al., 1999; Mittelbach and Gangle, 2001; Jain and Sharma, 2010b). Long term storage affects biodiesel physical properties, with an increase in viscosity, peroxide value, acid value and density, and a decrease in the heat of combustion (Bondioli et al., 2002; Bondioli et al., 2003; Bondioli et al., 1995; Monyem et al., 2000; Miyata et al., 2004; Ko..k and Acar, 2006).

### 3.3. Metals

Sarin et al. (2009) have reported the influence of metal contaminants on the oxidation stability of JCB. The transition elements like iron, nickel, manganese, cobalt and copper commonly found in metal containers were blended in varying concentrations (ppm) with JCB samples. The presence of metals depressed the oxidation stability of biodiesel, due to acceleration of free radical oxidation and metal-mediated initiation reaction. Relatively, copper has the strongest catalytic effect, while the lowest catalytic effect were obtained by iron. Fig. (1) shows the effect of metal contaminants on IP of JCB, IP decreased with increase in the metal contaminates. IP values became constant at 2ppm metal contamination (Madarasz and Kumar, 2011).

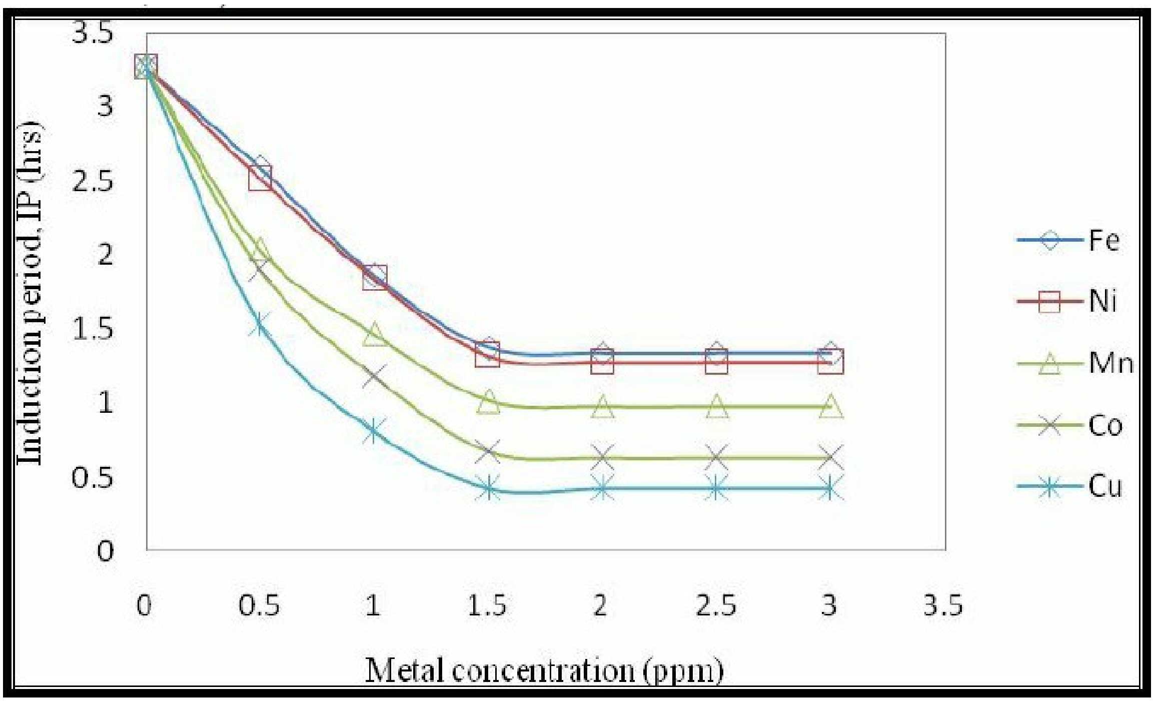


**Fig. 1:** The effect of metal contaminants on IP of JCB; (Jain and Sharma, 2012).

## 4. ANTIOXIDANTS

### 4.1. Natural Antioxidants

Tocopherols are naturally occurring antioxidants in vegetable oils (alpha, beta, gamma and delta). Alpha tocopherols provide protection to the oil against photooxidation (oxidation under visible light). Beta tocopherols are found at very low concentrations in oils and their functions are not fully known. Gamma and delta tocopherols protect oils against auto oxidation (Gupta, 2008). However, processing of biodiesel deactivates tocopherols that were originally present in the vegetable oil feed.

Liang et al. (2006) have reported the effect of natural and synthetic antioxidants on the oxidative stability of palm biodiesel. Crude palm oil methyl ester contains about 600 ppm of vitamin E, which exhibit oxidative stability for more than six hours that conform to the specification of the European standard of biodiesel EN 14214. Sarin et al. (2007) have investigated blending JCB with palm biodiesel. Since JCB has poor oxidation stability, while palm biodiesel has good oxidation stability, the combination of JCB and palm biodiesel is expected to improve the blended biodiesel properties.

### 4.2. Synthetic Antioxidants

Synthetic antioxidants were added to enhance biodiesel stability (Madarasz and Kumar, 2011), without affecting the properties of biodiesel such as viscosity, density, carbon residue and sulfated ash (Mittelbach and Schober, 2003; Schober. and Mittelbach, 2004). A number of research groups investigated substances that inhibit oxidation process (Jain and Sharma, 2010b; Jain and Sharma, 2010c). Fritsch et al. (1975) have studied the effect of antioxidants on palm oil biodiesel; TBHQ (tetra- butyl hydroquinone) is more effective than BHT (butylated hydroxytoluene) and BHA (butylated hydroxyanisol).

Fig. (2) shows the effect of antioxidants on the oxidation stability of JCB. The oxidation stability of JCB is increased with increase in dosage of antioxidant, Pyrogallol (PY) is the most effective antioxidant; 100 ppm of PY is the minimum concentration required to meet EN14112 specification (Jain and Sharma, 2011). The effect of thermal stability of JCB is shown in Fig. (3) and Fig. (4). Activation energy of fresh JCB (39 kJ/mol) increased up to 80.99 kJ/mol by addition of 600 ppm of PY. Therefore, PY is the best additives used. The frequency factor has behavior similar to that of activation energy; which increased from 6501.8 min-1 for fresh JCB to 100391198.1 min-1 with 600 ppm PY.

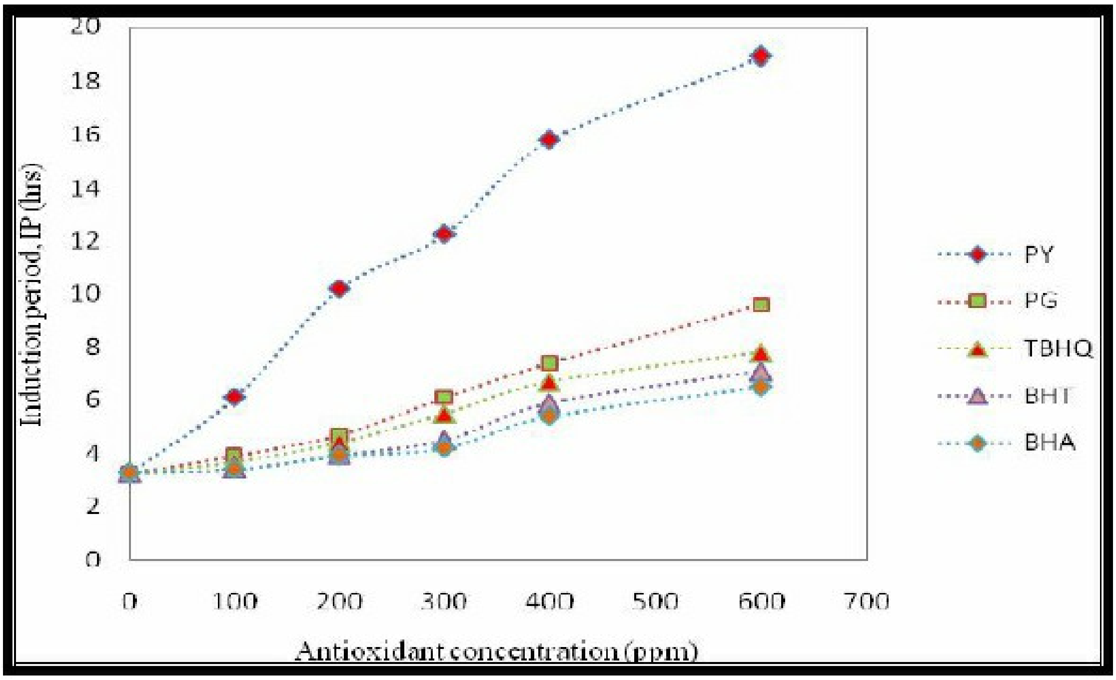


**Fig. 2:** Effect of antioxidants on the oxidation stability of JCB.

PY: Pyrogallol; PG: Propyl Gallate; TBHQ: tetra-butyl hydroquinone; BHT: butylated hydroxytoluene; BHA: butylated hydroxyanisol; (Jain and Sharma, 2011).

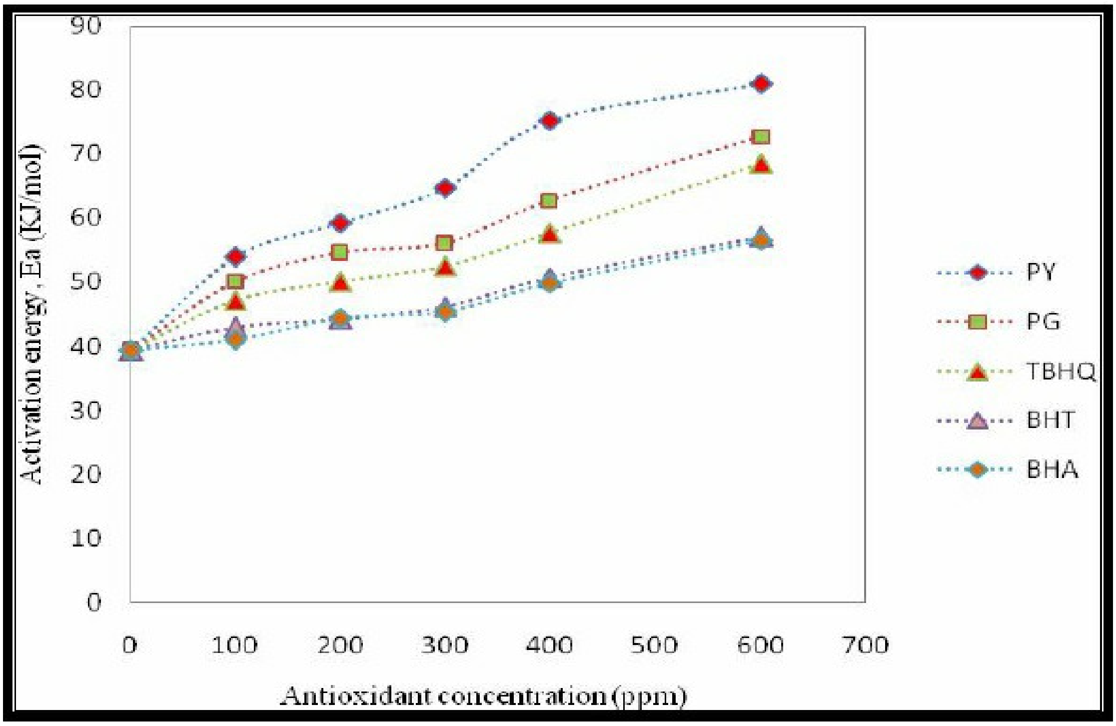


**Fig. 3:** Effect of antioxidants on the activation energy of thermal degradation.

PY: Pyrogallol; PG: Propyl Gallate; TBHQ: tetra-butyl hydroquinone; BHT: butylated hydroxytoluene; BHA: butylated hydroxyanisol; (Jain and Sharma, 2011).

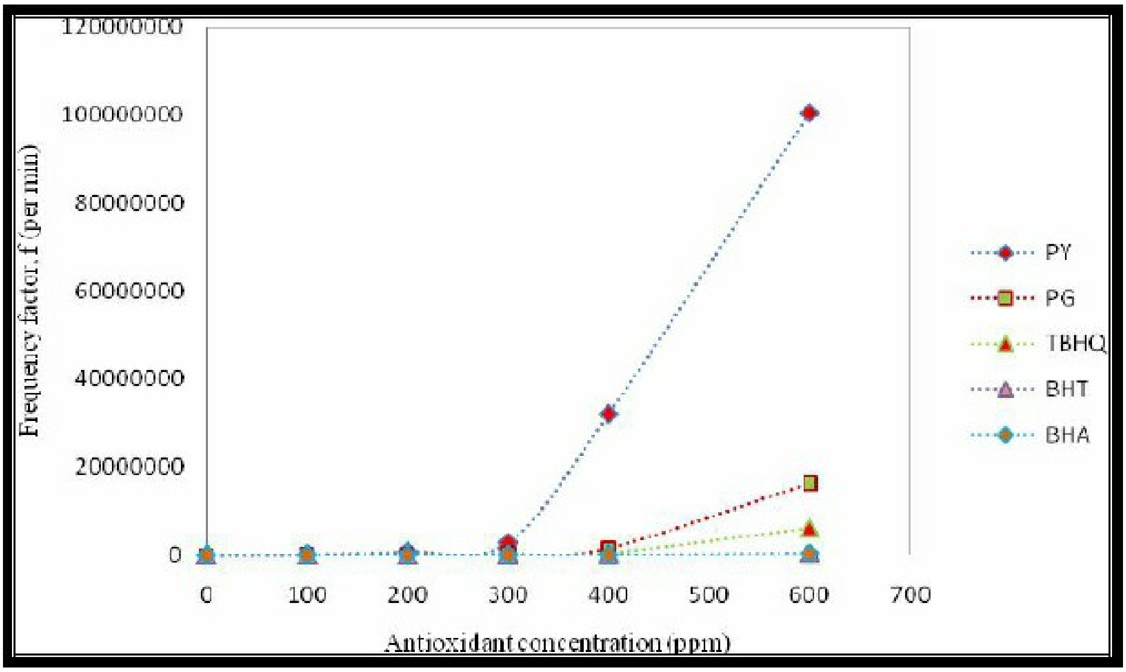


**Fig. 4:** Effect of antioxidants on the frequency factor

PY: Pyrogallol; PG: Propyl Gallate; TBHQ: tetra-butyl hydroquinone; BHT: butylated hydroxytoluene; BHA: butylated hydroxyanisol; (Jain and Sharma, 2011).

Jain and Sharma (2011) have studied the effect of PY metal contaminants on JCB in terms of IP (see Fig. 5). Optimum antioxidant dose is obtained by 2 ppm metal impurities concentration. IP improved with increase of antioxidant concentration at constant level of metal contaminants. Furthermore, Jain and Sharma (2012) estimated the optimum concentration of PY (see Table 2) for 2 ppm metal contaminated biodiesel for IP of six hours using response surface methodology (RSM). Oxidation stability of JCB is not affected when the metal concentration is more than 2 ppm.

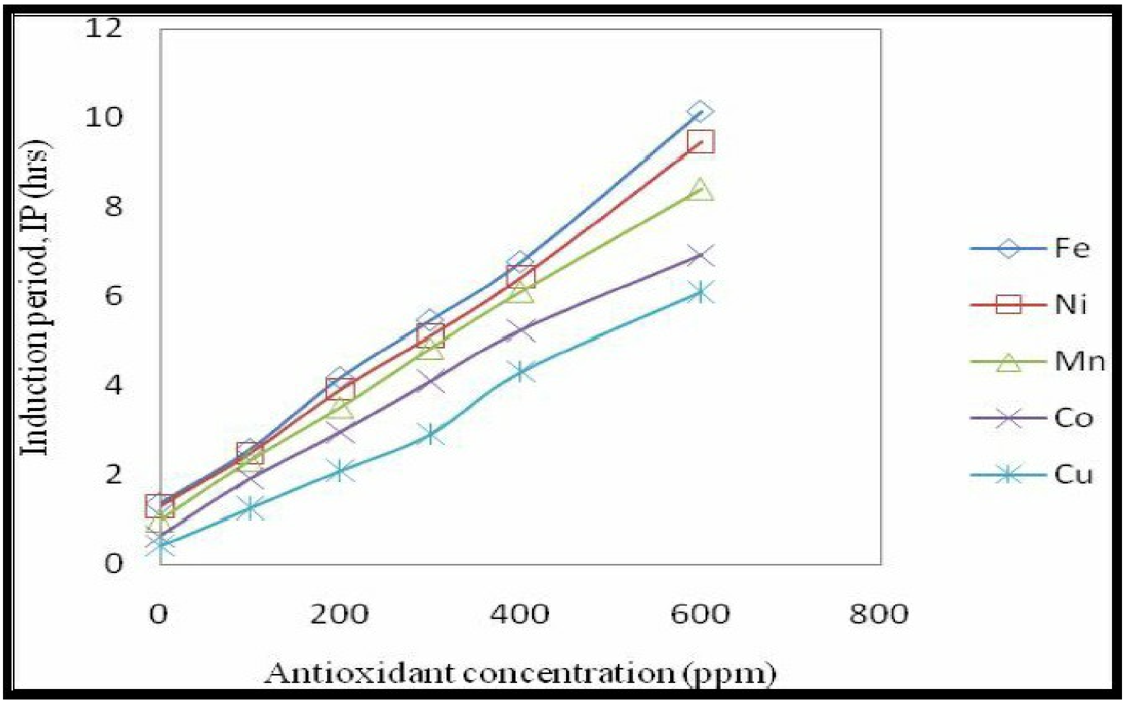


Fig. (5): Effect of PY antioxidant on metal contaminated biodiesel in term of IP (Jain and Sharma, 2012).

**Table 2:** Optimum amount of antioxidant for six hours IP

| Metal | Antioxidant concentration (ppm) |
|---|---|
| Fe | 326.96 |
| Ni | 361.64 |
| Mn | 386.15 |
| Co | 471.24 |
| Cu | 600 |

(Jain and Sharma, 2012).

## 5. CONCLUSION

Biodiesel stability being a critical quality parameter; and it was found to be affected adversely by oxygen, storage and the containers metals. Also the thermal and oxidation stabilities of the biodiesel were found to be very critical parameters. The addition of some antioxidants to the *Jatropha Curcas* biodiesel (JCB) are required to meet EN 14112 specifications. Pyrogallol (PY) was found to be the most effective antioxidant for oxidation and thermal stability of the *Jatropha Curcas* biodiesel (JCB). Natural antioxidants e.g. Tocopherols occurring in vegetable oils as well as synthetic antioxidants were added to enhance biodiesel stability; and they were found to be very effective in enhancing the stability of the JCB. Also more investigation is required for clear understanding of the JCB stability; since the demand for using this renewable source of energy became a world demand.

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