# Experimental Investigation of Metals and Antioxidants on Oxidation Stability and Cold Flow Properties of Pongamia Biodiesel and its Blends

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*Received: 01.08.2016 Accepted:09.10.2016*

**Abstract**

Due to fluctuation in fuel prices in recent times the Indian economy is facing a heavy burden on the economic front to meet the energy supply demand. Due to large gap between the supply and demand of petroleum products. The government of India and various other organizations are working on the development of alternative fuel to petro diesel. Pongamia oil (PO) is being identified as second most important source of biodiesel production in India after Jatropha. But the poor stability and cold flow property associated with the Pongamia biodiesel make it difficult for using it as alternative fuel to diesel. The storage of biodiesel is the major issue for its long term utilization. The aim of current work is to investigate the storage impact of various metals on oxidation stability and cold flow property of Pongamia biofuel. The experimental results shows that oxidation stability of various metal varies in order of Iron>Aluminum> Zinc while all these material deteriorate the cloud and pour point of Pongamia biodiesel and make it unsuitable for its long term use. But the use of antioxidant Pyrogallol improves the oxidation stability of Pongamia biodiesel but it has no significant effect on its cold flow properties. The finding also reveals that Pongamia biodiesel can be stored in metal container only when there is addition of antioxidant to meet the standard of biodiesel.

**Keywords-** Pongamia; Biodiesel; Fuel; Oxidation stability; Cloud Point; Pour Point; Cold filter plugging point; Iron; Aluminum; Zinc

## 1. Introduction

Biodiesel is identified as potential alternative source of energy to diesel. For biodiesel production several types of feed stocks are used viz. edible, non-edible and animal fats etc. The edible sources like Sunflower, Soybean, and Coconut etc. are used as food essentials. India is already importing 75% of the edible oils of its requirement and therefore the edible oil cannot be used for biodiesel production. So the nonedible oils are main source for conversion to biodiesel like Jatropha, Pongamia [1]. Biodiesel is the alternate source to diesel that can be used for engine operation [2].But there are two major problems associated with biodiesel is "poor cold flow property of biodiesel" and second one is "poor oxidation stability of biodiesel". The inferior cold flow behaviour of biofuel causes in poor engine performance. The cold flow properties (CFP) such as Cloud point (CP), Pour point (PP) and Cold filter plugging point (CFPP) are responsible for solidification of fuel causes the blockage in fuel lines filters which further leads to fuel starvation in engine operation during starting operation. The proportion of unsaturation in biodiesel is the main reason for its oxidation. The other important parameter for the quality standards of biofuel is 'storage oxidation stability'. Various authors studied the long term storage stability of biodiesel which will result in problem in engine operation [3-9].

Stability and CFP are determined by FFA composition of vegetable oil. Biodiesel consists of long chain fatty acid esters derived from fats or oils like animal fats, vegetable oils, and used cooking oil, etc. which contains saturated and unsaturated fatty acids and usually susceptible to oxygen in air while storage and elevated temperature may result in polymerized compounds as product. Auto oxidation of biodiesel leads into deterioration of properties of fuel by influencing its stability characteristics. The oxidation of fatty acid chain is a complicated activity with various mechanisms process proceeded by a variety of mechanisms. The oxidation of biofuel is mainly because of unsaturated fatty acids which are very readily reactive to oxygen when exposed to atmosphere. The primary oxidation products of double bonds are unstable allylichydroperoxides and result in various secondary oxidation products. This also comprises of rearrangement of product of similar molecular weights resulting in short chain aldehydes, acids compounds and high molecular weight materials [14].

CFPs are affected by the presence of saturated fatty acid present in biodiesel. During cold season with decrease in temperature more solid species are formed and fuel achieves its PP, is the last temperature where flow (pouring) wa s detected after cooling the oil and testing in 3 °C increments. The existence of higher proportion of saturated fatty acids results in rise of CP & PP of biodiesel. Due to high melting point at low temperatures, some components of fuel nucleate to form crystals and block the fuel flow.

Feed stocks with high % saturated fatty acid will have inferior CFPs. On the other hand, higher unsaturated fatty acids will produce fuels having better performance. Higher degree of unsaturation will have significant impact on CFP, with higher unsaturation leading to greatly improved in cold flow properties [4].

There have been compatibility issues of pure biodiesels with metals and plastics. It gets degraded and results in formation of more sediments if remains in touch with materials having copper for example bronze and brass or lead, tin etc. Pure biodiesel can also penetrate through plastic in longer run so plastic should be avoided from storing biodiesel [10]. Some metals act as catalysts for the oxidation process, notably tin, brass, copper, zinc, bronze and lead. Steel and aluminium equipment are recommended for the manufacture, processing and storing of biodiesel [11, 12]. Copper exhibited poor oxidation and thermal stability. The catalytic effects of the metals follow the order: Copper >> Iron > Aluminium ≈Zinc. [12]. Jain and Sharma [13] states that the oxidation stability of Jatropha biodiesel (JB) is 3.27 hours and the thermal stability of JB is also inferior in terms of activation energy (Ea) and frequency factor (f). The oxidation and thermal behaviour is also affected adversely by the metal container. It was observed that impact of metals were detrimental to thermal and oxidation stability. The various researchers have found out that Aluminium and Cast iron container are best for storage and transportation of biodiesel while Pyrogallol (PY) is best antioxidant for improving the stability [14-15].

The rate of oxidation for biodiesel increases as these come in contact of carbon steel [3]. Sarin et al. [16] used neat JB and evaluated its oxidation stability (OS) and influence of presence of various transition metals, in the metallurgy of barrels & storage tanks, on OS of biodiesel. It was found that impact of metal concentration was not significant on the OS. Even lesser proportion of metals species have almost same effect on OS as large concentration. The literature review reveals that beyond the metal concentration of 2 ppm there is no effect on OS of biodiesel [15]. Copper exhibited strongest detrimental and catalytic effect. As the percentage of diesel is enhanced in the blend, the OS of biodiesel or diesel blend also happened to improve. It was observed that $B_{100}$ required higher proportion of antioxidants were required to achieve the fuel standards and then followed by lower blends. $B_{70}$ blend of JB was found suitable to meet the standards as it will eventually lower down the cost of fuel significantly and also needs less amount of antioxidant to meet the stability [15].

The problem of storage of biodiesel is major limiting factor to be used it as alternative fuel. Study reveals that biodiesel during storage in various metal containers reacts with it and the quality of biodiesel gets deteriorated with storage of time due to formation of insoluble gum. To avoid the deterioration in the quality of biodiesel the selection of metal container for its storage is various important aspects in the development of alternative fuel. The literature review also reveals that metal containers reacts with biodiesel to decrease its OS to overcome this issue addition of antioxidants is necessary to negate the effect on OS of biodiesel. This study is focuses on to investigate the effect of various metals on OS of Pongamia biodiesel (PB). Various authors [14-17] have studied the effect on OS of biodiesel by using metal and antioxidant but simultaneous study of CFP is not been done. This investigation also focuses on the CFP of biodiesel with the use of metal and antioxidant. As both parameters i.e. OS and CFP should be balanced for the optimum development of alternative fuel.

## 2. Experimental

### *2.1. Biodiesel Production*

PO was procured from Soul Centre Trade Link Pvt Ltd, Bangalore. All chemicals like Potassium hydroxide (KOH), Methanol, PY were of AR grade and 99% pure. Different transition metals, Iron (Fe), Aluminium (Al) and Zinc (Zn) were also purchased from Sigma Aldrich, India and are in fine powdered form. To remove the insoluble materials, PO was filtered followed and then heated at 105 $^0$C for 10 minutes to remove any moisture. The fuel properties of PO after refining were determined as per standard methods. The properties of PO are reported in Table 1.

**Table1.** Physio-Chemical Properties of Pongamia oil

| S.No. | Properties | Pongamia oil |
|---|---|---|
| 1 | Calorific value (MJ/kg) | 29.90 |
| 2 | Flash point ($^0$C) | 206 |
| 3 | Viscosity (cSt, @ 25$^0$C) | 49 |
| 4 | FFA (%) | 0.7 |
| 5 | Density (kg/m$^3$ @ 25$^0$C) | 939 |

The above table shows that a Free Fatty Acid (FFA) content of the oils is as 0.7 %. Due to low FFA content, here we have adopted base catalysed transesterification processes. PB yield of 98.4% was achieved with molar ratio (11.06:1) of methanol to oil using catalyst KOH (1.43 % w/w) in time duration of 81.43 min at the temperature of 56.6ºC.The metal concentration of 0.5- 2 ppm is used for experiment to determine the OS and CFP [1].

*2.2. Methods for the Measurement of Fuel Properties of PB*

The Gas Chromatograph (Netal make) having flame ionization detector and a capillary column to introduce the sample [13]. The GC was used to determine the fatty acid present in the oil.

*2.3. Viscosity*

Viscosity is a measured as per ASTM D-445 method for which Digital rotational viscosity meter (Brook field viscometer) is used.

*2.4. Fatty Acid Calculation*

The FFA content of oils was calculated by using ASTM D5555 – 95. The equation 2 is used in determination of FFA content of oil.

% FFA = (Vol. of alkali (in mL)) ×Normality of Solution × 28.2) / (weight of oil sample) (2)

*2.5. Density*

It is a measure of the compactness of matter within a substance and is defined by the equation:

Density = mass/volume

The standard metric units in use for mass and volume respectively are grams and ml or cm3. Thus, density has the unit gm/ml or gm/ cm$^3$ (g/cc).

*2.6. Calorific Value*

Calorific was measured by Bomb calorimeter is used for the measurement of calorific value of PB.

Calorific value can be calculated using the following Equation 4:

$$CV = \frac{W \times T}{M} \quad (4)$$

Where,
W = Water Equivalent of Calorimeter (2298 Cal/ ˚C)
T = Rising in Temp in C (Temp Difference)
M = Weight of Sample (gm)
CV = Calorific Value (kcal/kg)

*2.7. Oxidation stability measurement*

OS of PB is assessed by the IP which was observed as per the Rancimat method EN14214. Every requirement was done on a Metrohm 873 Biodiesel Rancimat instrument. 3 grams of $B_{100}$ was observed with continuous feeding of air at 10l/h, passing through the fuel and into a vessel containing distilled water. The sample was heated 110 °C. The electrode is connected to a measuring and recording device. Sudden rise in conductivity indicated end of IP. This immediate rise in conductivity is due to the dissociation of volatile carboxylic acids produced when exposed to oxygen and absorbed in the water while conductivity of the sample was observed; curve was plotted from results whose point of inflection gave value of IP [12].

*2.8. Free and total Glycerin*

Free and total glycerin was measured using ASTM D6584

*2.9.Cold flow properties Measurement*

CP and PP were measured according to ASTM D-6751, ASTM D2500, D97 respectively.

*2.10. Flash Point*

The flash point is measured using Pensky-Martens apparatus as per D-93 standard.

The physiochemical properties of PB are shown in table 2.

**Table 2**. Physicochemical properties of Pongamia Biodiesel

| S. No. | Property (unit) | ASTM 6751 | ASTM 6751 limit | IS 15607 | IS 15607 limit | PB |
|---|---|---|---|---|---|---|
| 1 | Flash point (°C) | D-93 | >=130 | IS 1448 | - | 156 |
| 2 | Viscosity at 40 °C (cSt) | D-445 | 1.9-6.0 | IS 1448 | - | 5.76 |
| 3 | Water and sediment (vol%) | D- 2709 | <=0.05 | D- 2709 | <=0.05 | 0.05 |
| 4 | CP (°C) | ASTM D2500 - 11 | - | IS 1448 | - | 20 |
| 5 | PP(°C) | ASTM D97 - 12 | - | IS 1448 | - | 19 |
| 6 | Free glycerin (percentage mass) | D-6584 | <=0.02 | D-6584 | <=0.02 | 0.01 |
| 7 | Total glycerin(% mass) | D-6584 | <=0.24 | D-6584 | <=0.24 | 0.04 |
| 8 | Oxidation stability of FAME, (hours) | | 3 | EN 14214 | >=8 | 1.83 |

The above table shows that PB has poor OS and poor CFP. So for the development of PB as alternative fuel, it is necessary to improve PB in terms of OS and CFP. The figure 1 shows the fatty acid composition of PB.

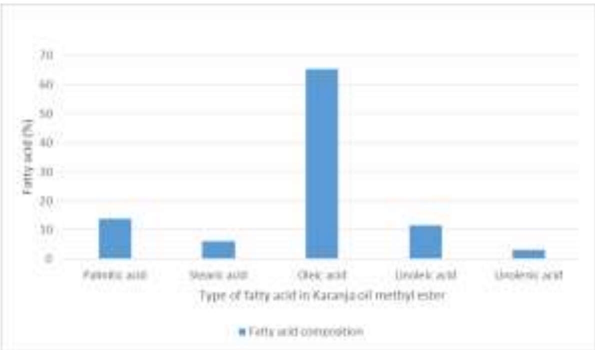


**Figure 1**: Fatty acid composition of PB

The above figure shows that PB contain high amount of unsaturated fatty acid which result in poor physiochemical properties.

### 3. Result and Discussion

*3.1.Impact of metal species on the oxidation stability of biodiesel/diesel blends*

For evaluating the impact of metal species on the OS of PB, various metals (Fe, Al and Zn) with concentration range of between 0.5 and 2 ppm are introduced to biodiesel and their impact of these on OS is shown in Fig. 2.

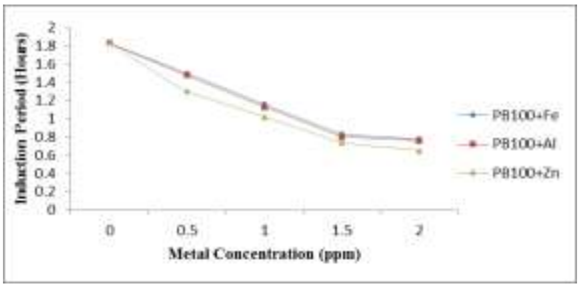


**Figure 2** Effect of Metal Species on the oxidation stability of fresh PB

It is clear from figure that as the % concentration of metals increases from 0.5 to 2 ppm the OS decreases but after 2 ppm concentration OS of PB become constant. This can be attributed to the catalytic effect of metals on OS [15, 17]. The figure 2 also show that the OS of PB with various metals varies in order of Fe>AL>Zn. But the stability deteriorates for all the metals. As per EN14214 standard the stability requirement for biodiesel fuel is minimum of 8 hours. But PB with all these metals deteriorates the stability as well as fuel quality. To improve the stability characteristics of PB it is added with PY antioxidant in various proportions from 100 to 550 ppm and to evaluate the impact of various metal species (concentration 2 ppm) was also added to PB. The metal concentration of 2 ppm is taken for all metal species beyond the concentration of 2 ppm there is no change in the fuel quality and similar study on JB is done by Jain and Sharma [15]. So for further evaluation for all the blends of PB from figure 3-7 the metal concentration of 2 ppm is taken. The result of stability investigation for PB with metals and antioxidants is shown in figure 3.

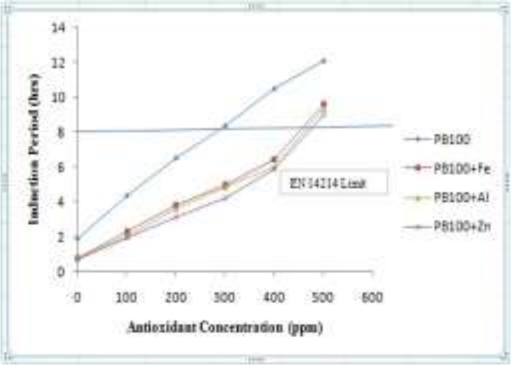


**Figure 3.** Effect of Antioxidant and Metal species (Concentration 2ppm) on the oxidation stability of fresh $PB_{100}$

Fe is observed to have minimal catalytic effect on OS followed by Al and Zn. This statement is in agreement with the previous study on JB [15]. The figure 3 show that $PB_{100}$ with various metal species (Concentration of 2ppm) and antioxidants varies in order of Fe>Al>Zn.The $PB_{100}$ with various metals require 550 ppm of PY to maintain the OS standard as per EN14214.

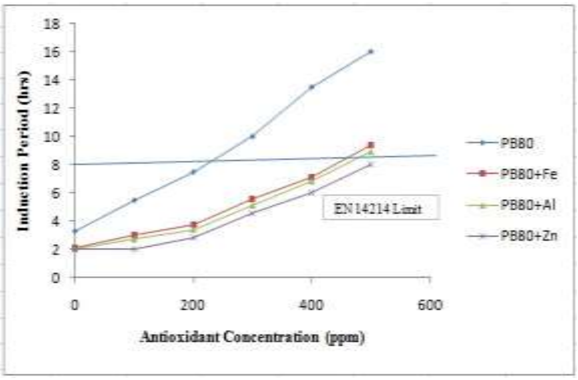


**Figure 4.** Effect of Antioxidant and Metal species (Concentration 2ppm) on the oxidation stability of fresh $PB_{80}$

The figure 4 shows the effect of Antioxidant and Metal Species (Concentration of 2ppm) on the OS of fresh $PB_{80}$. The result of investigation shows that the stability of $PB_{80}$ with PY and various metals varies in order of Fe>Al>Zn. While PY concentration of 520 ppm is required to maintain the stability for various blends as per EN14214 standard.

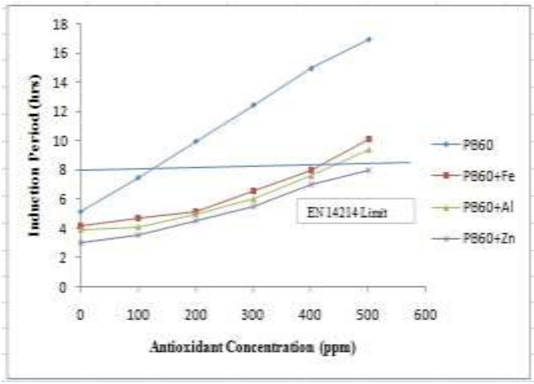


**Figure 5.** Effects of Antioxidant and Metal species (Concentration 2ppm) on the oxidation stability of fresh $PB_{60}$

The figure 5 shows the effect of Antioxidant and Metal Species (Concentration of 2ppm) on the OS of fresh $PB_{60}$. The result of investigation shows that the stability of $PB_{60}$ with PY and various metals varies in order of Fe>Al>Zn. While PY concentration of 510 ppm is required to maintain the stability for various blends as per EN14214.

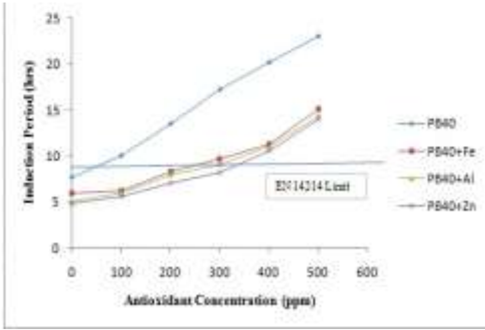


**Figure 6.** Effects of Antioxidant and Metal species (Concentration 2ppm) on the oxidation stability of fresh $PB_{40}$

The figure 6 shows the effect of Antioxidant and Metal Species (Concentration of 2ppm) on the OS of fresh $PB_{40}$. The result of investigation shows that the stability of $PB_{40}$ with PY and various metals varies in order of Fe>Al>Zn. While PY concentration of 320 ppm is required to maintain the stability for various blends as per EN14214 standard.

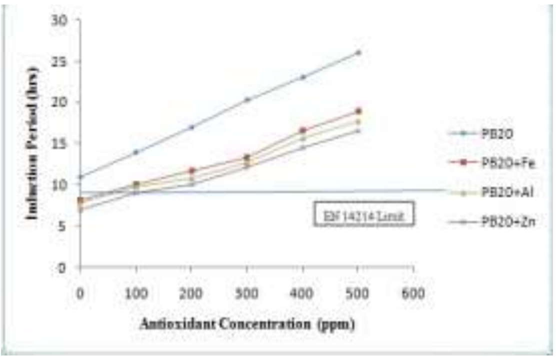


**Figure 7.** Effects of Antioxidant and Metal species (Concentration 2ppm) on the oxidation stability of fresh $PB_{20}$

The figure 7 shows the effect of Antioxidant and Metal Species (Concentration of 2ppm) on the OS of fresh $PB_{20}$. The result of investigation shows that the stability of $PB_{20}$ with PY and various metals varies in order of Fe>Al>Zn. While PY concentration of amount of 180ppm is required to maintain the stability for various blends as per EN14214 standard.

The result of investigation in Figures 3-7 shows that very few blend of PB with metal species meet the specification of OS as per EN14214 standard. This problem is rises due to oxidation of PB and its blends on reacting with various metal species. The maximum reaction occurs with Zinc so the PB with Zinc metal species shows poor CFP as compared to PB and its blends on reacting with Iron and Aluminum. But for storage purpose this problem is resolved by the addition of antioxidant PY which improves the stability characteristics of all the blends so they meet the necessary standard.

*3.2. Effect of Metal and Antioxidant on CP and PP of PB and its blends*

Crystal formation of the saturated fatty acids in lower temperature regions result in fuel clogging and operational problems as solidi material blocks the fuel lines and filters. With dropping temperature, formation of solids increase & fuel achieves the PP. It is noted that the more proportion of saturated fatty acids improves the CP & PP of biodiesel, introduction of additives that enhance the impact of crystal morphology; and blending with a fuels such as kerosene result in lowering the freezing point. Best method has not been identified to assess colder region performance of fuel. On the other hand, it is the responsibility of fuel provider to give colder region operating conditions of fuel by examining its CP. Various laboratory tests are also used to identify low temperature properties of biodiesel. Inferior CFP are mainly due to the presence of longer chain saturated FA esters in biodiesel. The figure 8-12 shows the CP and PP for PB with metal and antioxidant.

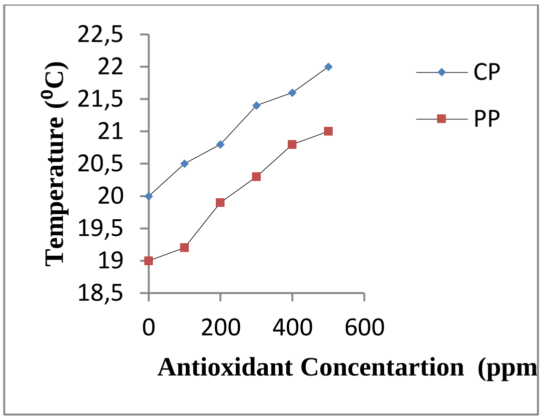


**Figure 8 (a):** Variation of CP and PP for PB

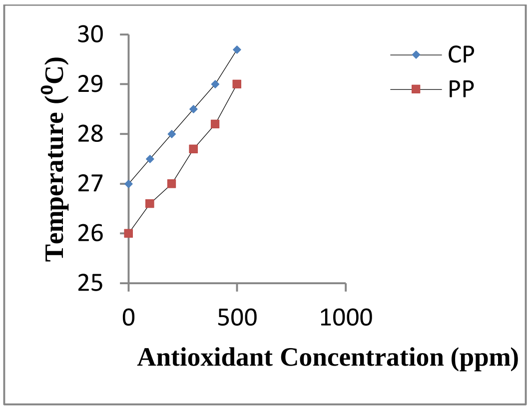


**Figure 8 (b):** Variation of CP and PP for PB with Fe as metal species (Concentration 2ppm)

The Figure 8 (a-b) shows that as the percentage of antioxidants increases for PB with or without metal species. There is increase in Cloud and Pour point. The increase in CP and PP is due to formation of small solid crystals are formed in sample due to presence of antioxidant and metal species. As the percentage of Antioxidant PY increases in the sample the CFP getting deteriorated and biodiesel cannot be used for engine operation.

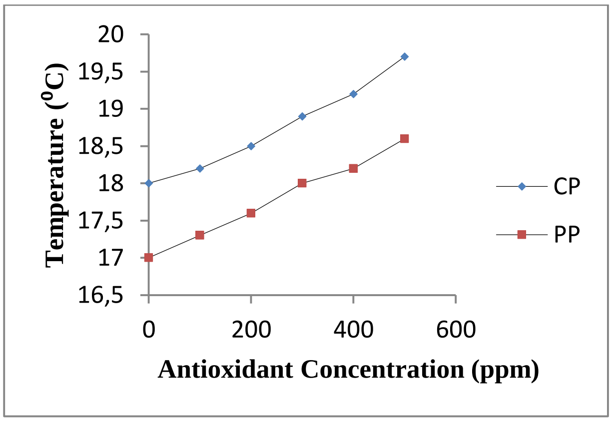


**Figure 9.** Variation of CP and PP for $PB_{80}$

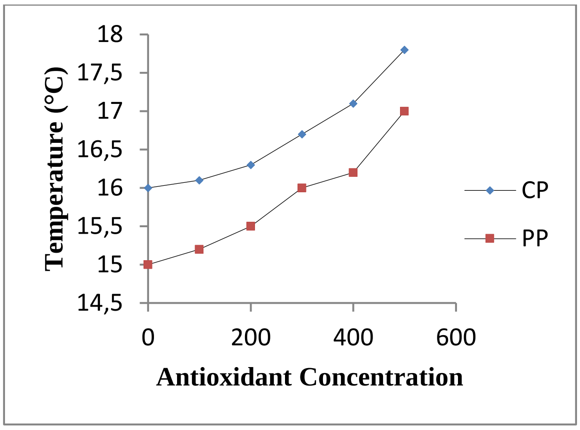


**Figure 10.** Variation of CP and PP for $PB_{60}$

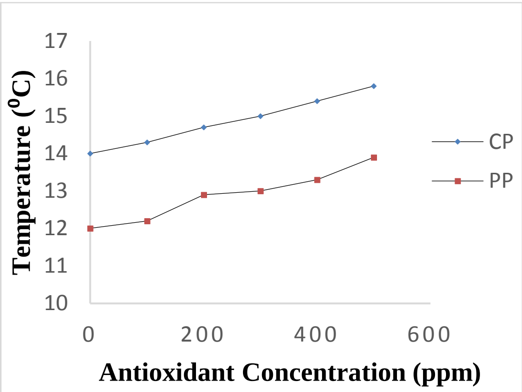


**Figure 11.** Variation of CP and PP for $PB_{40}$

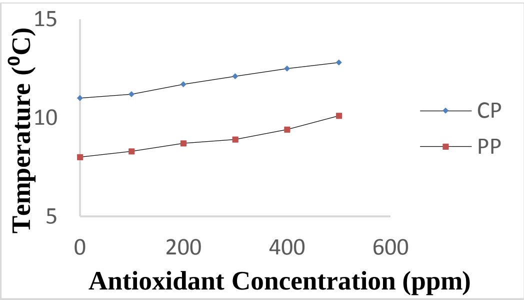


**Figure 12.** Variation of CP and PP for $PB_{20}$

The above figures 8-12 shows the variation of CP and PP for PB with Zn as metal species (Concentration 2ppm). The figure 8-12 shows that as the percentage of antioxidants increases for PB with or without metal species. There is increase in Cloud and Pour point. The increase in CP & PP is due to formation of small solid crystals are formed in sample due to presence of antioxidant and metal species. As the percentage of Antioxidant PY increases in the sample the CFP getting deteriorated and biodiesel cannot be used for engine operation.

The result of the investigation in figure 9-12 shows that for all blends of PB i.e. $PB_{80}$, $PB_{60}$, $PB_{40}$, and $PB_{20}$ the addition of all metal species Fe, Al and Zn and antioxidant PY result in poor CFP and make the all blends unsuitable for use in engine operation. High degree of saturation causes high melting points and temperatures of crystallization and in colder regions these will crystallize before the mono-unsaturated and poly-unsaturated fatty acids. Due to the high temperature of crystallization exhibited by the saturated fatty acids, biodiesel with high composition of saturated fatty acid esters exhibits worse cold flow and has higher CP indicating the crystallization of the esters of these saturated fatty acids. On achieving CP, longer chain hydrocarbons start forming small wax crystals & on substantial formation of wax crystals of diameter more than 0.5 mm, fuel seems to have cloudy appearance. On lowering the temperatures further down, crystals keep on growing until these become large enough to block filters of fuel system. In addition to it, the fuel can gel up itself also & becomes unable to be poured even though much of the fuel has not frozen. Due to high CP and PP value fuel is difficult to flow and engine will not operate. The result of experimental investigation shows that addition of metal deteriorates the OS and CFP of biodiesel while addition of antioxidant improves the stability characteristics of biodiesel. In previous study it was found out that CP and PP of diesel is respectively 6°C and 5 °C in Indian condition [4] which is comparable to CP and PP of $PB_{20}$ as reported in figure 12. $PB_{20}$ can be recommended as alternative fuel to diesel in cold climatic condition

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## 4. Conclusion

The result of investigation shows that PB have poor OS and poor CFP and it is due to presence of various fatty acid (saturated and unsaturated) in biodiesel. The OS of PB will improved by addition of antioxidant PY while the metal species deteriorates the OS and CFP. The result of investigation shows that Iron, Aluminum and Zinc metal deteriorates the quality of PB. The effect on OS is minimum in case of Iron and maximum in case of Zinc while all these metal deteriorates the CFP. The study recommend that PB cannot be stored in these metal container unless the addition of PY. The addition of PY 520 ppm in PB makes it suitable to be stored in metal container. The CFP of PB can be improved by using cold flow improver to be used it for operation in cold climatic condition. $PB_{20}$ with metal species require very less amount of antioxidant i.e. 180 ppm of PY required to maintain the storage stability and CFP.

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