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Oxidation Kinetics of Biodiesel Stabilized with Pyrogallol Using the PetroOXY Method

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The present study investigated the oxidation kinetics of biodiesel stabilized with pyrogallol conducted at 110-150°C using the PetroOXY method. It was demonstrated that the induction period increased with the increasing concentration and decreased with increasing temperature. The natural logarithm of antioxidant concentration varied linearly with respect to induction period, and the consumption of pyrogallol during the induction period followed the pseudo-first-order reaction kinetics over the temperature range studied. An increasing rate of consumption could be observed as temperature increased. Based on the Arrhenius equation, the activation energy for pyrogallol consumption could be calculated, which is different from the apparent activation energy for inhibited oxidation process. The introduction of pyrogallol into biodiesel could possibly lead to a change in the mechanism of oxidation process, due to the possible participation of antioxidant molecules in side reactions other than the main reaction of chain termination.

1. Introduction

Biodiesel has received great acceptance worldwide in the past few decades as a renewable and biodegradable alternative biofuel. However, biodiesel is very sensitive to oxidation because of the high content of unsaturated methyl esters (Dunn, 2008). The resistance of biodiesel against oxidation has always been a concern to suppliers, distributors and potential users. The oxidative deterioration of biodiesel could not only affect the quality of biodiesel, but also bring potential risks to engine operation, such as clogged fuel filters, corroded metal parts, and hardened rubber components. Most of the biodiesels produced do not meet the oxidation stability specifications, and the use of antioxidants to improve the oxidation stability of biodiesel is a widely accepted practice around the world (Fattah et al., 2014, Mittelbach et al., 2003).

Synthetic antioxidants are generally preferred over natural antioxidants because of their high efficiency. The most commonly used synthetic antioxidants are tert-butylhydroquinone, butylated hydroxyanisol, butylated hydroxytoluene, propyl gallate and pyrogallol. These phenolic compounds could interrupt the propagation of the free radical chain by transferring hydrogen atoms from the phenolic hydroxyl groups to intermediate peroxyl radicals. The resulting less-reactive antioxidant radicals do not initiate another free radical due to the stabilization of delocalization of radical electron, and they can also react with free radicals to form stable complex compounds.

Accelerated oxidation test methods are often used to evaluate the antioxidant efficiency on the oxidative stability of biodiesel and biodiesel blends: Rancimat (EN 14112) and PetroOXY (ASTM D7545). Both methods provide elevated temperature and/or high pressure to speed up the reaction and shorten the analysis time. Although either of them truly reflect realistic storage conditions, the study of stability would take too long and be unfeasible without these acceleration methods (Araújo et al., 2009, Dodos et al., 2014, Wierzbicki, 2010).

Rancimat is the most widely accepted and the only standardized method for accessing the oxidative stability of biodiesel treated with antioxidants. The induction period prior to the onset of rapid oxidation is determined by monitoring the continual increase of conductivity, which is caused by the volatile carboxylic acids (secondary oxidation products) formed during the accelerated oxidation process. However, this method has one big disadvantage of test duration being too long, and more time will be needed to finish one single test taking into account the fact that the oxidation stability parameter has increased from the earliest 6h

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(EN14214:2003) to 8h (EN14214:2012). Presently there is a voice of raising the test temperature from 110°C to 130°C to shorten the analysis time. But opposite voice also exists: some antioxidants such as butylated hydroxytoluene can easily volatilize, and high temperature may cause misleading results not truly reflecting its performances (Lapuerta et al., 2012, Karavalakis et al., 2011).

PetroOXY provides a fast, simple and reliable alternative method to measure the oxidation stability of biodiesel and biodiesel blends, and shows good reproducibility and repeatability between different replicates (Machado et al., 2009). This method provides high oxygen pressure in the test chamber, which could reduce the volatilization losses of additives and increase the concentration of reacting oxygen in sample. PetroOXY determines the induction period by monitoring the pressure drop during the oxidation process, and can be used to obtain the oxidation kinetics when the tests are conducted at different temperatures. In this method, the oxidation stability of the fuel sample is directly related to the time needed to achieve a fixed pressure drop (10%). The samples are subjected to more severe test conditions in this method, i.e., maximum pressure of approximately 1000kPa at 140°C, compared to the parameters in the Rancimat method (an air flow of 10 L/h at 110°C).

Considering the potential decomposition and volatilization loss of antioxidants at elevated temperatures, the change of temperature could have tremendous impacts on the antioxidant efficiency and oxidation process. Based on this background, the PetroOXY method was used in this study to investigate the oxidation kinetics of biodiesel stabilized with pyrogallol conducted at various temperatures. Pyrogallol is one of the most effective antioxidants to enhance the oxidation stability of biodiesel. The reaction constant, critical concentration and activation energy for the consumption of pyrogallol could be obtained.

2. Material and methods

The biodiesel used in this study was derived from waste cooking oil, which was one of the representative feedstocks for biodiesel production in China. This biodiesel was obtained from Chengdu Hengrun Hi-tech Co., Ltd, and known not to contain any antioxidant additives. The physiochemical properties of the biodiesel meet all requirements of the EN 14214 standard, with the exception of the oxidation stability. Pyrogallol was purchased from Aladdin Industrial Corporation (analytical grade), and treated at the concentration of 100, 250, 500, 750 and 1000 ppm (by weight) to the neat biodiesel, and kept in darkness to protect the samples from uncontrolled autoxidation.

The PetroOXY test was carried out as per ASTM D7545 using a PetroOXY device from Anton Paar, Dahlewitz, Germany. A 5 ml volume of sample was placed in the small hermetically sealed test chamber. After pressurized with pure oxygen to 700 kPa (approximately 7 bar), the reaction vessel was heated quickly to a specified temperature (110-150°C). The oxygen in the chamber was slowly consumed and the subsequent pressure drop was recorded every second with a data acquisition system. The time elapsed from the start of test to the breakpoint, which was defined as a 10% pressure drop below the maximum pressure developed in the system, was the induction period at the test temperature. The data acquisition did not stop at the breakpoint, but continued to get a full picture of the pressure drop curves.

3. Results and discussion

Figure 1 shows the evolution of the pressure drop curves for biodiesel stabilized with pyrogallol during the PetroOXY test, which exhibit distinct macroscopic kinetic stages of induction and acceleration. The oxidation stability is usually characterized by the length of induction stage, also known as induction period. The longer the induction period, the better the oxidation stability. As can be seen, the presence of pyrogallol could effectively improve the oxidative stability of biodiesel by extending the induction period. Biodiesel displays 29.83min of induction period at 110°C according to the PetroOXY method, which could be greatly enhanced to 296.45, 429.70, 546.28, 600.82, 614.30min with the treatment of 100, 250, 500, 750, 1000 ppm pyrogallol, respectively. The great antioxidant efficiency could be explained by the antioxidant structure. Pyrogallol possesses three hydroxyl groups (OH) in its aromatic rings, and the hydrogen atom abstracted from OH can be donated to the oxidized free radicals to interrupt the chain propagation and inhibit the rate of oxidation in methyl esters. The resulting antioxidant radical is stable, and can react with other fatty acid free radicals to further contribute to oxidation inhibition (Litwinienko et al., 1998).

Figure 2 shows the influence of antioxidant concentration on the oxidation stability of biodiesel conducted at the temperature range of 110-150°C. The induction period values of the neat biodiesel at 140 and 150°C could not be obtained because of the extremely low oxidation stability. As can be seen, the influence of reaction temperature on the induction period is pronounced. The higher the temperature, the shorter the induction period, which is approximately halved by a 10°C increase in temperature. In addition, the higher the pyrogallol concentration, the longer the induction period. The effect of pyrogallol concentration on the

induction period could be illustrated by the slope of the curve, which is more evident when the antioxidant concentration is less than 100 ppm. When the concentration gets larger, the slope becomes smaller.

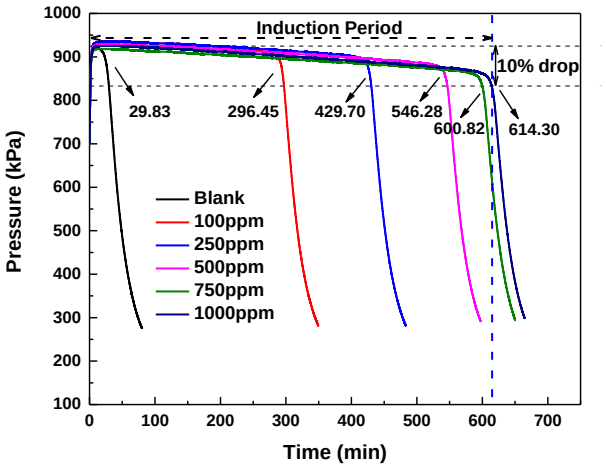

Figure 1: PetroOXY pressure drop curves vs. time for biodiesel stabilized with pyrogallol conducted at 110°C.

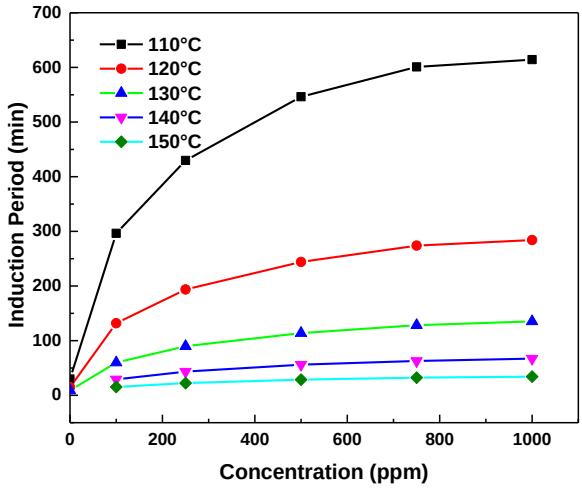

Figure 2: PetroOXY induction period vs. antioxidant concentration conducted at 110-150°C.

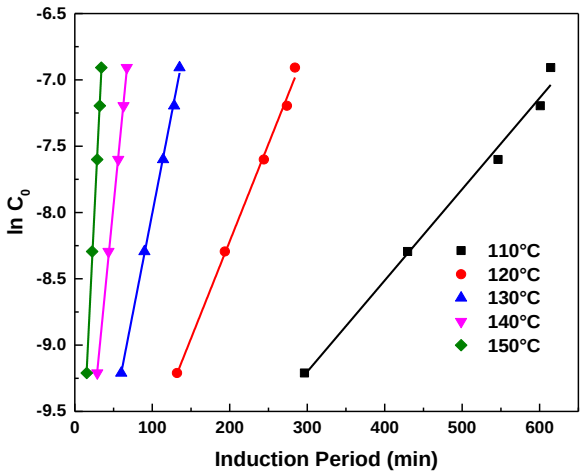

Figure 3: Natural logarithm of antioxidant concentration (ln C) vs. induction period conducted at 110-150°C.

The curves of induction period vs. antioxidant concentration in Figure 2 appear to be exponential function, and the first order reaction kinetics may be used to describe the mechanism of antioxidant consumption: $dc/dt=-k \cdot c$, where t is the time, c is the concentration of pyrogallol, and k is the reaction constant of pyrogallol consumption. During the induction stage, the antioxidant gradually decreases from initial concentration C_0 to critical concentration C_{cr} at the end of induction period, below which value the antioxidant is no longer effective to retard the oxidation of biodiesel. According to this assumption, the natural logarithm of antioxidant concentration (ln C) plotted against induction period should follow a straight line, which could be clearly seen from Figure 3. The straight line implies that the consumption of antioxidant during the induction stage possibly follow the same mechanism over the temperature studied. From the slope and intercept of the straight line, the reaction constant k, critical concentration C_{cr} could be calculated as shown in Table 1.

Table 1: Reaction constant k, critical concentration C_{cr} and correlation coefficient (R^2) for consumption of pyrogallol

Temperature, °C	k, min^{-1}	C_{cr}, ppm	R^2
110	0.00688	14.32	0.9881
120	0.01467	17.37	0.9959
130	0.03005	21.28	0.9987
140	0.05968	–	0.9988
150	0.11947	–	0.9978

Temperature change has an exponential influence on the reaction constant of the pyrogallol consumption. The natural logarithm of the reaction constant (ln k) plotted against reciprocal of temperature (1000/T, K^{-1}) results in a straight line as shown in Figure 4, which follows the Arrhenius equation: $\ln k=-Ea/RT+B$, where Ea is activation energy, R is ideal gas law constant (8.314 J/mol K). The activation energy calculated for pyrogallol consumption is Ea= 95.87 kJ/mol, consistent with the findings of Xin (2009).

Activation energy is equal to the energy barrier that must be exceeded for the consumption of antioxidant to occur. It must be borne in mind that the consumption of antioxidant may involve side reactions of antioxidant molecule and its radicals formed in the inhibition process. Although the consumption of pyrogallol during the induction stage could possibly follow the same mechanism over the temperature studied, the pseudo first order reaction kinetics does not have universal validity.

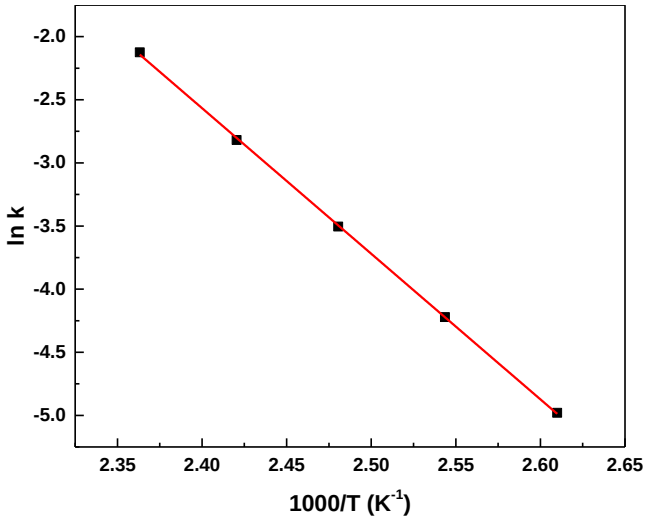

Figure 4: Temperature dependence of the reaction constant k of the pyrogallol consumption.

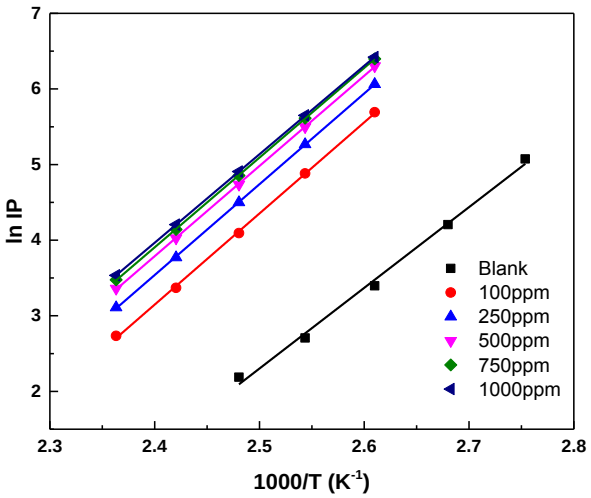

Figure 5: Natural logarithm of induction period vs. reciprocal of temperature for biodiesel stabilized with 100-1000 ppm pyrogallol.

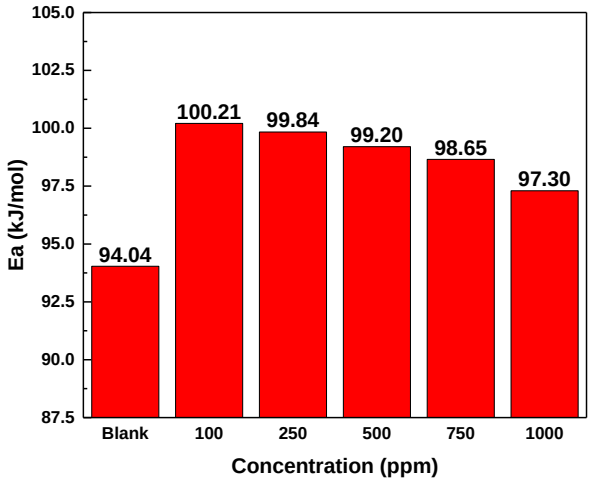

Figure 6: The apparent activation energy vs. antioxidant concentration calculated from the slope (Ea/R) of the regression line.

As observed in Figure 1, the exponential dependence, not linear dependence, of the induction period on increasing concentration indicates the participation of the antioxidant molecules in side reactions ($AH+O_2 \rightarrow A\cdot+HOO\cdot$) other than the main reaction of chain termination ($ROO\cdot+AH \rightarrow ROOH+A\cdot$) (Marinova et al 2003). In other words, the introduction of pyrogallol into biodiesel leads to a change in the mechanism of oxidation process, which could be reflected in the change of apparent activation energy obtained by the following empirical equation: ln IP= Ea/RT+B, where IP is the induction period, Ea is apparent activation energy, and R is ideal gas law constant (8.314 J/mol K) (Dinkov et al., 2015).

As seen in Figure 5, the plot of ln IP versus 1/T gives a straight line with high coefficient of determination (R^2>0.999). The slope (Ea/R) of the straight line gives the apparent activation energy Ea as seen in Figure 6, which indicates the degree of temperature sensitivity. The apparent activation energy of the biodiesel used in this work is measured as 94.04 kJ/mol, which could be further increased to 100.21, 99.84, 99.20, 98.65, 97.30 kJ/mol with the treatment of 100, 250, 500, 750, 1000 ppm pyrogallol, respectively. A decrease of Ea is observed with increasing concentration of pyrogallol, which could be ascribed to the possibility of antioxidant participatation in other side reactions that change the course of inhibiting oxidaiton, consistent with the above assumptions that high levels of antioxidants is not always beneficial. Clearly different from the activation energy for the consumption of antioxidant (calculated from Figure 4), the apparent activation energy obtained (seen in Figure 6) could be seen as the energy barrier that must be exceeded for the process of biodiesel

degradation to occur, which should be used with caution to represent the antioxidant efficiency due to possible participation of side reactions.

4. Conclusions

The PetroOXY method shows great potential for evaluating the antioxidant efficiency. Pyrogallol displays excellent antioxidant efficiency over the temperature range studied. Temperature change exerts an exponential influence on the induction period. The efficiency of pyrogallol decreases with increasing temperature with respect to induction period. However, the consumption of pyrogallol following first order reaction kinetics does not have universal validity. High concentrations of antioxidants may involve the participation of side reactions other than main reaction, which could be reflected in the change of apparent activation energy.

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