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Weighing Oxidation Stability Tests for Biodiesel

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Biodiesel is an alterative fuel derived primarily from vegetable oil or animal fat. It consists of mono-alkyl esters of saturated or unsaturated long-chain fatty acid, depending on the feedstock. Unsaturated fatty acid alkyl ester-like linoleic and linolenic acid esters are more susceptible to oxidation than saturated fatty acid ester. As a result, biodiesel can become oxidized by the oxygen in the air during storage. The oxidation rate can be influenced by many factors such as temperature and chemical composition. Oxidative degradation is harmful and can deteriorate many physical properties of the biodiesel including viscosity, and acid and peroxide values. Antioxidants such as alpha-tocopherol or tert-butylhydroquinone are often added to increase the oxidation stability of biodiesel.

Differential scanning calorimetry (DSC) is a well-established technique to characterize the physical properties of oils including petroleum and vegetable oils. Since the oxidation reaction is exothermic, DSC can be used to study the oxidation stability of biodiesel. The method is called oxidation induction time (OIT), and it has been used to evaluate the oxidative stability of petroleum oil. This test is conducted under accelerated conditions (e.g., high temperature or high pressure) in order to shorten the experimental time to minutes instead of hours or days, which is required under normal storage conditions. The pressurized differential scanning calorimetry is specially designed to conduct the DSC measurement under elevated pressure. It has been used to study polymer phase transition and polymerization reaction and the oxidation stability of lubricating oil.

Oxidation Testing

For the following experiment, OIT testing of four different biodiesel samples using pressure differential scanning calorimetry was performed to determine compliance with ASTM D 6186 standard test methods. Elevated pressure was employed to accelerate the oxidation reaction and suppress the evaporation of the biodiesel at high temperature. Meanwhile, the oxidation onset temperature (OT) was also

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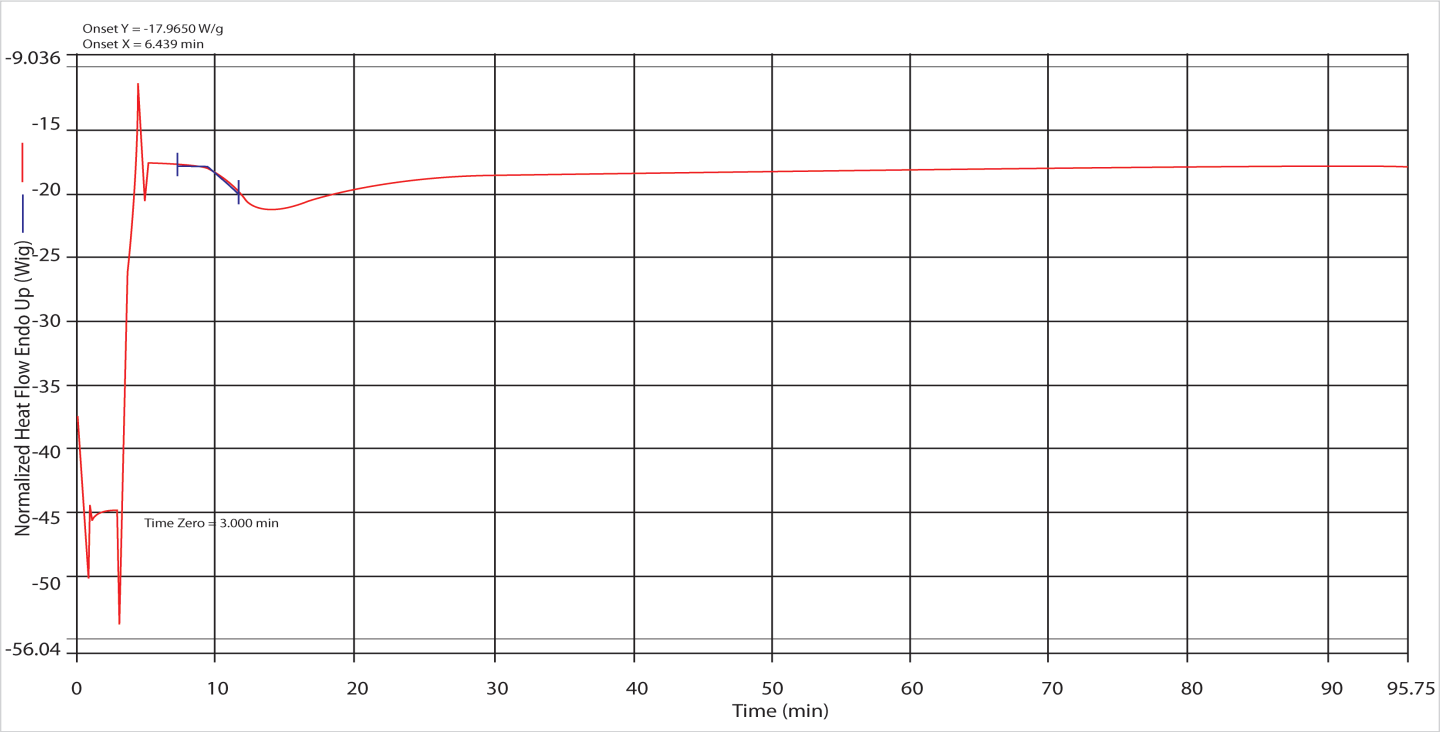

Figure 1. OIT of sample 3 rice biodiesel at 130 degrees Celsius

SOURCE: PERKINELMER

determined using pressurized differential scanning calorimetry.

The instrument used was a PerkinElmer Diamond DSC with a high-pressure cell. The instrument was calibrated using indium under the experimental condition.

The biodiesel tested included samples 1 and 2 from animal sources, sample 3 from rice biodiesel and sample 4 from soy-based biodiesel.

The conditions included a minimum purity of 99.5 percent oxygen and an operation pressure of 500 plus or minus 25 pounds per square inch (psi). The purge rate was 100 plus or minus 10 milliliters per minute (ml/min).

The test temperatures were 210, 180, 155 or 130 degrees Celsius.

The following describes the test method. For OIT test ASTM D 6186, 3 plus or minus 0.2 milligrams of biodiesel was weighted into a new aluminum sample pan without the cover. Beginning at ambient temperature, the test temperature was ramped to 100 degrees Celsius per minute and held for two minutes. The oxygen valve was opened to slowly pressurize the cell to 500 plus or minus 25 psi within two minutes. As soon as the pressure equilibrated, the cell purge rate was checked, adjusted and maintained at 100 plus or minus 10 ml/min. The OIT time was measured from the time the oxygen valve was opened.

For the OT test, 3 to 3.5 milligrams of biodiesel was weighted into a new aluminum sample pan without the cover. The pressure was adjusted to 500 plus or minus 25 psi and the purge rate to 100 plus or minus 10 ml/min. Beginning at ambient temperature, the pressure was held for two minutes then ramped to 220 degrees Celsius at 10 degrees per minute. The onset temperature was calculated and recorded.

Results

Sample 3, rice biodiesel, is used as an example to illustrate the results. The OIT test started at 210 degrees Celsius, following the ASTM D 6186 method. The data indicated that the oxidation reaction happened quickly after the oxygen valve was opened. According to the standard, if the OIT is less than 10 minutes, then lower the temperature to the next level and repeat the experiment. Consequently, the same test was

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Sample	1	2	3	4
Oxidation onset temperature (degrees Celsius)	155	167	155	134

Table 1. OT summary
SOURCE: PERKINELMER

conducted at 180, 155 and 130 degrees Celsius.

The OIT can not be readily measured until 130 degrees Celsius with an OIT of 6.4 minutes, still a relatively short period of time (Figure 1). In this figure, the first minute is the temperature ramp-up from room temperature to test temperature. The next two minutes are isothermal at the test temperature. The oxygen valve was opened at three minutes. From three to five minutes, the cell was gradually pressurized to 500 psi and the purge rate was adjusted to 100 ml/min. Note, the software used takes into consideration the zero time, which is the moment the oxygen valve was opened when performing the OIT calculation.

Further reducing the experimental temperature may result in a longer OIT. When the temperature is set to 110 degrees Celsius the OIT is calculated to be 34.6 minutes. The repeatability of this test was checked by running the same method on sample 3 five times. The results are 6.439, 6.442, 6.326, 6.440 and 6.372 minutes respectively with an average of 6.404 minutes and a standard deviation of 0.053 minutes. The DSC with the high-pressure cell gives highly repeatable results under identical experimental conditions.

Although, generally speaking, it is not possible to correlate the oxidation induction time directly to the oxidation onset temperature, the OT measurement gives another way to look at the oxidation stability of the material. In order to determine the oxidation onset temperature, the sample is scanned from low temperature to high temperature instead of being held isothermally, and the OT is determined as the onset temperature of exothermic reaction. For example, sample 3 was heated from room temperature to 220 degrees Celsius under the same experimental conditions (pressure 500 psi, oxygen 100 ml/min). The onset temperature was found to be approximately 155 degrees Celsius. The OT results for all four samples are summarized in Table 1. Clearly, the OT sequence is sample 2 is greater than sample 1 equals sample 3 which is greater than sample 4.

The OIT results are summarized in Table 2. The measurement temperature was 130 degrees Celsius for samples 1, 3 and 4 and 155 degrees Celsius for sample 2. For sample 2 at 130 degrees Celsius, no obvious OIT was detected within the measurement time of 120 minutes. Again, samples 1 and 3 performed similarly. Note, for samples 2 and 4 the oxidation happened so quickly after the oxygen valve opened that their OIT can not be determined accurately.

Conclusion

The OIT test following ASTM standard D 6186 or OT test can be used to study the oxidation stability of biodiesel. The use of pressure DSC can significantly reduce the experimental time under accelerating conditions. Therefore, pressurized differential scanning calorimetry may be a useful tool to screen different antioxidants or different antioxidant concentrations for biodiesel fuel. ■

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Sample	1	2	3	4
Oxidation induction time (minutes)	6.5 at 130 degrees Celsius	Less than 2 at 155 degrees Celsius	6.4 at 130 degrees Celsius	Less than 2 at 130 degrees Celsius

Table 2. OIT summary
SOURCE: PERKINELMER

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