Studies on the anti-oxidative ability of quinones in natural ester based insulating liquids for transformers

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Abstract. Due to the unsaturated olefinic structure of natural esters, their antioxidation ability is generally poorer than that of the mineral oils, thus certain antioxidants were commonly added as the additives to improve the oxidative stability of natural ester for their service as transformer oils. The present study reported the influences of adding quinones as additives on the oxidative stability of versatile natural esters. It was found that, under the accelerated oxidation conditions, added quinones could improve the oxidative stability of these tested natural esters through decreasing their acidic values, viscosity increase and dielectric losses to certain extent, thus providing a new category of antioxidants to improve the oxidative stability of natural ester based transformer oils.

1. Introduction
With the rapid depletion of the fossil feedstock, utilizing renewable biomass to partly replace those fossil resources in industrial applications has been well acknowledged. As an example, natural esters have been gradually employed as the alternative to the mineral oils in transformer applications, and they demonstrated multiple merits when compared with the mineral oils including high burning point, extended transformer lifetime, excellent biodegradation and sustainability.[1] Certainly, their excellent biodegradation originates from their glyceryl ester structures. Because of the presence of plenty unsaturated olefinic bonds in these natural esters, it makes them easy to degradation when exposure to the environment; however, it also leads to their oxidative stability much poorer than the corresponding mineral oils in service. Accordingly, based on inhibiting the common free radical chain oxidation which was believed to be responsible for their oxidative degradation,[2,3] certain antioxidants like 2,6-dibutyl-4-methylphenol were added to these natural esters as additives to improve their oxidative stability, and several commercial natural ester oil based transformer oils have been explored including BIOTEMP® and Envirotex FR3®, etc.[4-6]

The challenge is that, although the oxidative degradation of natural oils under the transformer conditions obeys the general free radical chain oxidation as well as those in other oxidation processes, in view of its specific working conditions, for example, emerging of copper wires in the transformer
oils, the mechanism for its oxidative degradation may have some differences from those under other conditions such as oxidation of plant oils during food cooking. Therefore, understanding the degradation mechanism of these natural oils under transformer conditions will definitely benefit the designing of the specific antioxidants, thus promoting the exploration of the new generation of the natural oil based transformer oils for industrial applications. Most recently, these laboratories investigated the oxidative mechanism of soybean oil under the accelerated oxidation conditions, and it was found that copper activated dioxygen to generate the superoxide radical played the significant role in soybean oil oxidation. As evidence, adding 1,4-benzoquinone, a superoxide radical scavenger, as additives can sharply inhibit the oxidation event as well as adding 2,6-dibutyl-4-methylphenol.[7] Continuing on this study, here we present the influences of versatile quinones on the oxidative stability of different natural esters under accelerated oxidation conditions for transformer oil application.

2. Experimental section

2.1. Materials and analytical methods
Soybean oil was purchased from Yihai Kerry, and copper wires came from China Electric Power Research Institute (CEPRI), and the copper content of the copper wires is 99.95%. All the other oils and quinones including 1,4-benzoquinone (CAS: 106-51-4), anthraquinone (CAS: 84-65-1), 3,5-di-tert-butyl-1,2-benzoquinone (CAS: 3383-21-9), 2,5-dimethyl-1,4-benzoquinone (CAS: 137-18-8) and 2-methyl-1,4-benzoquinone (CAS: 553-97-9 were purchased from Sinopharm Chemical Reagent Co., Ltd; the quinones were used without further purification. The air gas was purchased from Wuhan Huaerwen Industrial Co., Ltd. The oil oxidation tests were conducted with the transformer oil oxidation stability tester (HY206), Viscosity was measured with SYD-265D-1 Kinematic Viscosimeter at 40 °C, the acid value of the oil was measured by automatic oil acid value analyzer (SZH-1), and the dielectric loss of the oil sample was measured by Oil dielectric loss resistivity meter (AI-6000).

2.2. Accelerated oxidation tests of soybean oil with different quinones
To remove the oxide film from the copper wires (0.1 mm x 91 cm, equal to 7.28 g) prior to the oxidation tests, they were first treated with dilute hydrochloric acid for 0.5 h at room temperature, and then washed with clean water and dried in vacuum. 1 wt% of quinones were added as the antioxidants into the oxidation tube. Next, according to the NB/SH/T 0811-2010 standard, the copper wires were spirally added into the oxidation tube, and 25(± 0.1) g of soybean oil was also added. Then, dry air was introduced into the oxidation tube, and its flow rate was controlled at 2.5(±0.25) mL/min. The tube was next heated in transformer oil oxidation stability tester (HY206) at 120 °C for 48 h. The total acid value, kinematic viscosity and dielectric loss of the soybean oil were measured after oxidation tests.

2.3. Accelerated oxidation tests for soybean oil with different amounts of 1,4-benzoquinone
In a typical procedure, different amounts of 1,4-benzoquinone (0.1 wt%, 0.5 wt%, 1 wt%, 2 wt%) were added in 25 mL of soybean oil which was charged into an oxidation tube containing a copper wire. Dry air was introduced into the oxidation tube, and its flow rate was controlled at 2.5(±0.25) mL/min. Then, the reaction mixtures were heated in the transformer oil oxidation stability tester (HY206) at 120 °C for 48 h. The total acid value, kinematic viscosity and dielectric loss of the soybean oil were measured after oxidation tests.

2.4. Accelerated oxidation tests for soybean oil at different temperature
In a typical procedure, 252.5 mg (1 wt%) of benzoquinone were added in 25 mL of soybean oil which was charged into an oxidation tube containing a copper wire. Dry air was introduced into the oxidation tube, and its flow rate was controlled at 2.5(±0.25) mL/min. Then, the reaction mixtures were heated
in the transformer oil oxidation stability tester (HY206) at different temperature for 48 h. The total acid value, kinematic viscosity and dielectric loss of the soybean oil were measured after oxidation test.

2.5. **Accelerated oxidation tests of different natural esters with 1,4-benzoquinone**

In a typical procedure, 252.5 mg (1 wt%) of 1,4-benzoquinone were added in 25 mL of natural esters which was charged into an oxidation tube containing a copper wire. Dry air was introduced into the oxidation tube, and its flow rate was controlled at 2.5(±0.25) mL/min. Then, the reaction mixtures were heated in the transformer oil oxidation stability tester (HY206) at 120 °C for 48 h. The total acid value, kinematic viscosity and dielectric loss of the soybean oil were measured after oxidation test.

3. **Results and discussion**

3.1. **Accelerated oxidation tests of soybean oil in the presence of different quinones**

To investigate the influences of versatile quinones on the oxidative stability of natural ester based transformer oils, soybean oil was first selected as the model of natural ester, and different quinones were added as the additives to investigate its influence on the total acidic value, viscosity and dielectric loss of soybean oil after oxidation tests. Meanwhile, to mimic the transformer conditions, certain amounts of copper wires were emerged into the soybean oil, and the oxidation tests were conducted at the elevated temperature with certain rate of air flow according to the DL/T 1811 standard.[8] The results are summarized in Table 1; as shown, to match the DL/T 1811 standard, after the oxidation test, the total acidic value should be no higher than 0.6 (KOH mg/g), viscosity increasing less than 30%, and dielectric loss less than 0.5%. In the control experiment without additives added, after the oxidation test, the total acidic value of soybean oil was 0.455, its viscosity increase was 26.8%, and the dielectric loss was 0.357% (Table 1, entry 1). When using 1,4-benzoquinone as the additives, it gave the total acidic of 0.234, viscosity increase of 29.3% with dielectric loss of 0.312%, matching the DL/T 1811 standard (Table 1, entry 2). Since adding benzoquinone to soybean oil may naturally increase its viscosity, to address this issue, the viscosity increase was also directly measured after dissolving benzoquinone to soybean oil (without accelerated oxidation test), and it was found that its viscosity increased 11.3% (Table 1, entry 2). Thus, the viscosity increase of 29.3% after the oxidation test was not completely caused by the oxidation event, but also included the increase caused by dissolved benzoquinone. After eliminating the increase caused by dissolving the benzoquinone, its viscosity increase in the oxidation test should be much less than 26.8% in control experiment (Table 1 entry 1), that is, 18% (29.3%-11.3%=18%, Table 1 entry 2). As disclosed in previous studies,[7] the improved oxidative stability of soybean oil by adding quinone could be attributed to that the added quinones, for example, 1,4-benzoquinone, may have scavenged the superoxide radical which was generated through copper wire activated dioxygen, thus inhibiting the initiation of free radical chain oxidation of soybean oil in oxidation tests. Similarly, using anthraquinone as the additives also provided the data matching the standard, giving total acidic value, viscosity increase and dielectric loss of 0.236, 29.8% and 0.201%, respectively (Table 1, entry 3). In the case of using 3,5-di-tert-butyl-1,2-benzoquinone, 2,5-dimethyl-1,4-benzoquinone or 2-methyl-1,4-benzoquinone as additives, while the total acidic values and dielectric losses still matched the standard, their viscosity increases were slightly out of the range, giving 31.3%, 30.2% and 32.0%, respectively (Table 1, entries 4-6). It is worth mentioning that these viscosity increases also included the increase caused by dissolving the corresponding quinones in soybean oil (see the data in parentheses in Table 2). After eliminating the naturally increased viscosity caused by dissolving quinones, the viscosity increases after oxidation tests of soybean oil by adding these quinones were still less than 30%, matching the DL/T 1811 standard.
Table 1. The influence of different quinones on the oxidative stability of soybean oil in oxidation tests.

| Entries | Quinones                                      | Total acidic value | Viscosity increase | Dielectric loss |
|---------|-----------------------------------------------|--------------------|--------------------|-----------------|
|         |                                               | (KOH mg/g) ≤ 0.6   | ≤ 30%              | ≤ 0.5%          |
| 1       | -                                             | 0.455              | 26.8%              | 0.357%          |
| 2       | 1,4-benzoquinone                              | 0.234              | 29.3%(11.3%)       | 0.312%          |
| 3       | anthraquinone                                 | 0.236              | 29.8%(19.7%)       | 0.201%          |
| 4       | 3,5-di-tert-butyl-1,2-benzoquinone            | 0.102              | 31.3%(21.3%)       | 0.196%          |
| 5       | 2,5-dimethyl-1,4-benzoquinone                 | 0.132              | 30.2%(7.4%)        | 0.247%          |
| 6       | 2-methyl-1,4-benzoquinone                     | 0.051              | 32.0%(17.4%)       | 0.414%          |

Conditions: copper wire (7.28 g), soybean oil (25 g), additives (1 wt %), the flow rate of the air (2.5±0.25 mL/min), 120 °C, 48 h. The data in parentheses represent the viscosity increase caused by adding scavenger directly (prior to the oxidation test).

3.2. Accelerated oxidation tests of soybean oil with different contents of 1,4-benzoquinone

Next, using 1,4-benzoquinone as the additives, the influence of its contents on the oxidative stability of soybean oil in oxidation tests was investigated (Table 2). As shown, adding 0.1% contents of 1,4-benzoquinone had already sharply decreased the total acidic value and dielectric loss when compared with the control experiment without 1,4-benzoquinone added, giving 0.109% of the total acidic value and 0.233% dielectric loss (Table 2, entries 1 and 2). Increasing the loading of 1,4-benzoquinone caused gradually increasing of all of these parameters including the total acidic value, viscosity increase and dielectric loss. The increased total acidic value could be attributed to that the generated hydroquinone from 1,4-benzoquinone during the oxidation process was acidic, while the increased viscosity was possibly related to the poor solubility of 1,4-benzoquinone in soybean oil when its contents increased gradually. As evidence, adding benzoquinone to soybean oil naturally increased its viscosity as displayed in the parentheses of Table 2. For example, adding 2% benzoquinone naturally caused its viscosity increasing 14.7%, while in the oxidation test, it increased 51.5% (Table 2, entry 5).

Table 2. The influence of the content of 1,4-benzoquinone on the oxidative stability of soybean oil in oxidation tests.

| Entries | 1,4-benzoquinone | Total acidic value | Viscosity increase | Dielectric loss |
|---------|------------------|--------------------|--------------------|-----------------|
|         |                  | (KOH mg/g) ≤ 0.6   | ≤ 30%              | ≤ 0.5%          |
| 1       | -                | 0.455              | 26.8%              | 0.357%          |
| 2       | 0.1%             | 0.109              | 25.7%(7.6%)        | 0.233%          |
| 3       | 0.5%             | 0.136              | 27.1%(9.0%)        | 0.248%          |
| 4       | 1%               | 0.234              | 29.3%(11.3%)       | 0.312%          |
| 5       | 2%               | 0.282              | 51.5%(14.7%)       | 0.533%          |

Conditions: copper wire (7.28 g), soybean oil (25 g), the flow rate of the air (2.5±0.25 mL/min), 120 °C, 48 h. The data in parentheses represent the viscosity increase caused by adding scavenger directly (prior to the oxidation test).

3.3. Accelerated oxidation tests of soybean oil under different temperature in the presence of 1,4-benzoquinone

Then, the influence of oxidation temperature was investigated for soybean oil with 1,4-benzoquinone as the additives. As shown in Table 3, lower temperature clearly benefited the oxidative stability of soybean oil for its service in transformer. For example, at 40 °C, after adding 1% content of 1,4-benzoquinone, the total acidic value was only 0.140, viscosity increase was 1.5%, and the dielectric loss was also only 0.129%, much lower than those in the DL/T 1811 standard (Table 3, entry 1). Since the transformers generally work at ambient temperature, these data clearly indicated that adding
1,4-benzoquinone as the additives could substantially improve the oxidative stability of soybean oil for its service as the consulting oil in transformer.

Table 3. The influence of oxidation temperature on the oxidative stability of soybean oil with 1,4-benzoquinone as additives.

| Entries | Temperature (°C) | Total acidic value (KOH mg /g) ≤ 0.6 | Viscosity increase ≤ 30% | Dielectric loss ≤ 0.5% |
|---------|-----------------|----------------------------------------|--------------------------|------------------------|
| 1       | 40              | 0.140                                  | 1.5%                     | 0.129%                 |
| 2       | 60              | 0.141                                  | 2.6%                     | 0.142%                 |
| 3       | 80              | 0.186                                  | 28.8%                    | 0.165%                 |
| 4       | 100             | 0.229                                  | 29.0%                    | 0.202%                 |
| 5       | 120             | 0.234                                  | 29.3%                    | 0.312%                 |

Conditions: copper wire (7.28 g), soybean oil (25 g), benzoquinone (1 wt %), the flow rate of the air (2.5±0.25 mL/min), 48 h.

3.4. Accelerated oxidation tests of different natural esters in the presence of 1,4-benzoquinone

Finally, the influence of 1,4-benzoquinone as additives on the oxidative stability of different natural esters were investigated, and the results are summarized in Table 4. Generally, the total acidic values were significantly decreased by adding 1,4-benzoquinone as additives, and it was much lower than that required by the DL/T 1811 standard. For the viscosity increase, the values from sunflower oil, corn oil and camellia oil were still lower than 30%, while others were slightly higher than the requirement from the standard. The dielectric losses of soybean oil, sunflower oil, and corn oil were lower than 0.5%, while others were higher than the standard required. Also, the obtained data for these parameters for different natural esters were not consistently lower or higher than the standard required, but highly the oil source dependent, possibly related to their chemical compositions. Remarkably, adding 1,4-benzoquinone as additives demonstrated very excellent oxidative stability for corn oil in oxidation tests, giving total acidic value of 0.112, viscosity increase of 28.5% with dielectric loss of 0.487%, which is similar to those for soybean oil (Table 4, entries 2 and 5). In view of the abundance of both soybean and corn oils, this quinone based new antioxidants may have provided the opportunity for them to service as a new generation of the natural ester based consulting oil for transformer usage.

Table 4. The influence of 1,4-benzoquinone on the oxidative stability of versatile natural esters.

| Entries | Natural esters | Total acidic value (KOH mg /g) ≤ 0.6 | Viscosity increase ≤ 30% | Dielectric loss ≤ 0.5% |
|---------|----------------|----------------------------------------|--------------------------|------------------------|
| 1       | soybean oil    | 0.234                                  | 29.3%                    | 0.312%                 |
| 2       | sunflower oil  | 0.202                                  | 33.4%                    | 0.290%                 |
| 3       | rapeseed oil   | 0.273                                  | 32.0%                    | 1.282%                 |
| 4       | corn oil       | 0.112                                  | 28.5%                    | 0.487%                 |
| 5       | camellia oil   | 0.196                                  | 27.0%                    | 2.455%                 |
| 6       | methyl hexadecanoate | 0.133                               | 31.1%                    | 0.777%                 |

Conditions: copper wire (7.28 g), natural esters (25 g), benzoquinone (1 wt %), the flow rate of the air (2.5±0.25 mL/min), 120 °C, 48 h.

4. Conclusions

In summary, this work investigated the influence of different quinones on the oxidative stability of versatile natural esters under the accelerated oxidation conditions. It was found that these quinones can significantly improve the oxidative stability of natural esters in oxidation tests, thus offering new opportunity for exploring a new category of natural ester based transformer oils.
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