Oxidation of oils studied by isothermal calorimetry

Instruments to which this note applies: I-Cal Flex, Biocal

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Target use: oil oxidation, rancidity

Introduction

Oil oxidation is the general name for chemical reactions in oil involving oxygen. In oils for human consumption, oxidation will give rancidity and off-flavors, but in other applications, such as oils used in paints, oxidation is a wanted process that results in the hardening of the paint.

All oil is in a state of oxidation - you cannot stop it completely - but its rate is dependent on many factors, such as the type of oil, temperature, light, and the concentration of minor components such as natural and synthetic anti-oxidants and trace metal ions [1]. Oxidation processes in oils are mainly studied by measuring the concentrations of reaction products, such as hydroperoxide (peroxide value) [2]

As oxidation processes are accompanied by significant heat production, hence isothermal calorimetry is well adapted to investigate such processes. Of the few such studies that have been published, Dridi et al. [3] presents research with similar results as encountered in this application note.

Materials and methods

Three different oils were used:

- O1 - Raw linseed oil for human consumption
- O2 - Rapeseed oil for human consumption
- O3 - Raw linseed oil for paint production

All samples had the same mass of 3 g of oil.

The measurements were made at 70°C in an I-Cal Flex isothermal calorimeter with samples placed in 20 mL PE-HD vials. The calorimeters had been calibrated electrically and baselines had been measured with empty vials before the measurement. A Tian correction with calculated time constants was applied, but did not change the result significantly, which is attributable to the fact that the oxidation processes are rather slow (Note: for an explanation of the Tian correction, see Application Note AN-G01).

The following measurements were made (see Fig. 1):

- Empty vial (0-12 h).
- O1 (0-12h – green curve). This sample was aerated at 7 h. the aeration was made by taking up the vial out of the

calorimeter, opening the lid and letting the headspace be refreshed with air, closing the lid and putting the vial down in the calorimeter again.
- O1 (0-12 h – blue curve).
- O2 (0-7 h).
- O3 (7-12 h)

Results and discussion

Figure 1 shows the results. It is seen that significant amounts of heat are produced by all oils, and that O2 seems to be the least reactive, which is expected as rapeseed oil is a non-drying oil, while raw linseed oil is a drying oil (although not at all as reactive as so called boiled linseed oil, which is used in paints).
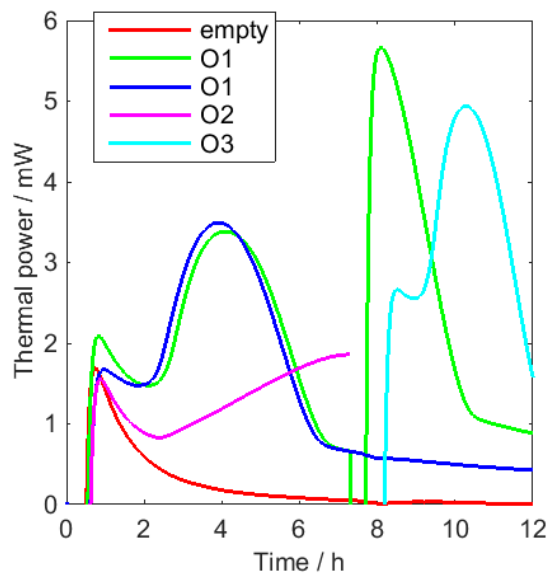

Fig. 1 – Oil oxidation results.

In Fig. 1 it is clearly seen that the signal from the empty vial takes a long time to reach the baseline. This is a true thermal power produced in the vial. Most probably it is oxidation/crystallization?? of the polyethylene polymer in the vial and it is a process that takes place in all PE-HD of the used brand when they are heated to 70 °C for the first time. If cooled to room temperature and heated a second time, this

heat is not seen (not shown). So, although PE-HD vials can be used up to XX °C, they are not as inert as for example glass vials, which may be preferable to use at higher temperatures.

From Fig. 1 it is seen that all curves except the green curve after aeration shows similar initial minima that may be the result of each of these measurements being the sum of the decreasing signal from the vials and increasing signals from the oil samples. This has been tested in Fig. 2, in which the vial signal has been subtracted from the first three oil samples. Although this data correction should not be seen as perfect, for example as only one empty vial was used, the result indicates that the thermal power from the oil oxidation initially increases from low values.
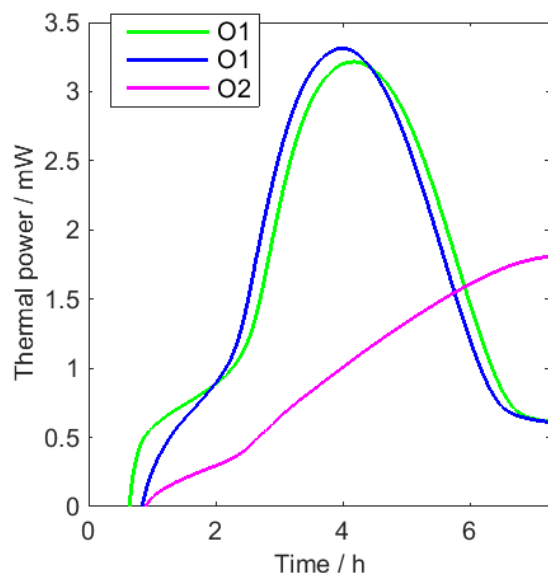

Fig. 2 – Three results from which the thermal power of the PE-HD vial has been subtracted.

All curves except the one for O2 decreases to lower values after a peak in thermal power. This is most probably an effect of oxygen limitations. To investigate this in a little more detail I have redrawn the longest measurement in Fig. 3 with two modifications:

1. I have assumed that the thermal power during the first hour was linearly increasing from zero.
2. I have indicated that the whole measurement could be seen as being composed of two parts.

The integrals of the two part A and B are 39 and 13 J, respectively. This can be compared with the 80 J produced when all the oxygen in a 20 mL vial is consumed (calculated using the ideal gas law and the enthalpy of oxidation of -455 kJ/mol(O_2)). As the sample is small, the head-space oxygen can this support almost 80 J, but part A only produces half of this before the thermal powers drop rapidly to low values. A possible explanation for this is that the first part (A) is the autocatalytic consumption of oxygen already in the oil that is initiated by the increase in temperature, and the second part (B) is the continued consumption of oxygen that diffuses into the oil from the head-space.
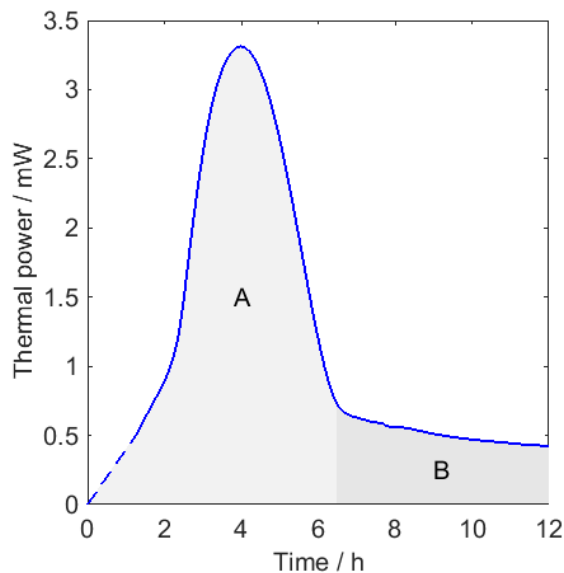

Fig. 3 – The two phases seen in the measurements.

References

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2. Halvorsen, B.L. and R. Blomhoff, Determination of lipid oxidation products in vegetable oils and marine omega-3 supplements. Food Nutr. Res., 2011 55.
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