INVESTIGATION OF SPONTANEOUS COMBUSTION TENDENCY OF VEGETABLE OILS BY THE MEANS OF DIFFERENTIAL THERMAL ANALYSIS

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Research article

Abstract: The potential of vegetable oils to undergo violent thermal oxidation is long-known problem. The process of this oxidation is investigated by the means of differential thermal analysis. Polyurethane foam was saturated with Tung oil rich in unsaturated fatty acids at three different mass rations, and airflow at three different rates is introduces to the sample to ensure sufficient volume of air for oxidation. The samples were thermally stressed both dynamically and isothermally. The results were compared to results of standard differential Mackey test.

Keywords: DTA, Tung Oil, Unsaturated oils, Spontaneous combustion, Self-heating, Mackey Test.

Introduction

Several materials are susceptible to spontaneous heating, which in turn may lead to spontaneous combustion. These materials produce heat under various circumstances. If the heat is not allowed to dissipate, it can continue to increase in temperature until the heat is sufficient to spontaneously ignite or ignite nearby combustibles (Chandler 2009).

Spontaneous ignition, sometimes called spontaneous combustion, is a well-known chemical phenomenon in fire investigation (Haan 2011). Spontaneous ignition is sometimes used as a synonym of autoignition, however there is a fundamental distinction that should be made clear (Cox 1995). Spontaneous ignition is the result of the material reacting exothermically without any heat source. Autoignition is the ignition of a material by surrounding temperature in the absence of an external source of ignition: it is a non-piloted ignition, meaning that the ignition is not caused by a piloted source of ignition such as a flame or a spark (Haan 2011). Autoignition does not necessarily occur as a result of a chemical or biological process.

Spontaneous combustion of unsaturated vegetable oils

Drying oils such as linseed oil, tung nut, or fish oil are all susceptible to spontaneous heating. The reaction is dependent on the percentage of the oil in contact with oxygen along with the ability to dissipate heat (Chandler 2009).

In a saturated hydrocarbon, all the available carbon atoms contain the maximum number of hydrogen atoms. Saturated hydrocarbons do not have a tendency for spontaneous combustion. In an unsaturated hydrocarbon, not all the available carbon atoms contain the maximum number of hydrogen atoms; some are bonded to other carbon atoms. Such a compound can accommodate additional hydrogen atoms by breaking those carbon-carbon bonds. Therefore, unsaturated hydrocarbons have a tendency towards spontaneous combustion (O'Connor & Redsicker 1996).

In particular, tung oil (TO) is extracted from the tung tree seeds and is composed mainly of a-elaeostearic acid (77 - 82 %) containing three conjugated double bounds, oleic acid (3.5 - 12.7 %) with one double bond and linolenic acid (8 - 10 %)

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with three non-conjugated double bonds (Meiorin et al. 2012; Mosiewicki et al. 2009; Meiorin et al. 2015).

The Differential Mackey test

The first model of Mackey test was constructed in 1895. For his first test, Mackey used 7 grams of cotton wetted by 14 grams of oil. The sample was then curled into a cylinder by using a stainless steel net, and placed into the oven heated to 100 °C by means of a water bath. Air supply to the sample was provided just through the leaks in the oven. The sample was heated for 5 hours up to the emergence of flame combustion. The readings led Mackey to the conclusion that the period of 1.5 or 2 hours is enough to observe the oils in question. The first model exhibited a lot of imperfections and had to be improved (Vytenis Babrauskas 2003; Hrušovský 2014).

Fig. 1 Device for Differential Mackey Test

The latest type of Mackey device (Fig. 1) uses two samples placed in stainless steel baskets, one of which serves as a reference sample. The result is a thermal analysis of the reference and monitored samples, and so-called SHV value (Spontaneous Heating Value) (Hrušovský 2014). The spontaneous heating value of a material is a measure of the ability of that material to undergo self-heating reactions while supported by a cellulosic or other fibrous material in air. It is an index of autoignition tendency of the substance under such conditions (Nadkarni 2000). The sample, which can be either solid or liquid, is saturated on or rolled into surgical gauze. The sample, as well as a reference sample of surgical gauze, is heated slowly, and any temperature differences are noted. This method allows for changing conditions as convenient and suitable for the particular sample. For example, the method calls for saturating 20 g gauze with 10 g liquid, but then states that "For simulation of self-heating of oily wastes and similar materials, it may be necessary to use sample to gauze ratios as high as 2:1 (Lentini 2012). Tests may be conducted for durations of 4 to 72 h or longer if desired (ASTM D3523-92 2012).

Spontaneous heating values determined by the present test method are regarded only as qualitative measurements of self-heating which occurs under the conditions of the test. The test method does not purport to produce a quantitative measure of the enthalpy of reaction of the sample with air at a given test temperature. Such data can be obtained by the use of an adiabatic calorimeter (ASTM D3523-92 2012).

A weakness of the test which eventually became apparent was the time limit on the specified temperature rise. The addition of anti-oxidant could extend the induction period for oxidation sufficiently to enable an otherwise "unsafe" oil to pass the test (Bowes 1984).

Safety calorimeter SEDEX

The SEDEX (Fig. 2) was originally developed as an apparatus for the sensitive detection of the initial temperature of exothermic processes in substances and reaction mixtures under industrial operating conditions. The device is exceptionally versatile and finds universal use for investigating the thermal properties of substances in the chemical industry. The modern design of the apparatus not only allows more reliable and efficient safety measurements of the usual type but also permits investigations which were not possible up to now (Hakl 1981).

Fig. 2 Safety calorimeter SEDEX

This adiabatic calorimeter can collect a lot of useful and practical information on the reactions taking place in a substance, e.g. the safe upper temperature limit, gas production and heat production from the reaction. The acquired data can be used to predict the behavior of a substance or mixture of substances in larger quantities, thereby avoiding potentially dangerous situations (Hrušovský 2014; Geissmann n.d.).

The sophisticated design of the oven and the flexibility of the Combilab system permit the versatile use of the SEDEX apparatus. Therefore, in the following sections only the typical possible uses of the device will be described. Other working procedures are either possible without any further modifications, or they can be employed with a simple addition to the control system and its appropriate extension (Hakl 1981).

The device can perform five methods of measurement, which include Scanning, Isoperibol steps, Isoperibol Long term, Adiabatic Analysis and IsoARC.

It is combinatory equipment for several areas of use with large test quantities. Different measurement cells and different control systems allow many combinations, which can be used particularly for routine operations, but can also be used for scientific purposes in research. Functions such as DTA (but sequential; comparison test is first measured as calibration run), ARC, DPSC, all with or without pressure measurement are possible under different background conditions and with different test quantities. Tests can sometimes be stirred and gassed. Pressure ranges up to 200 bar or more are possible. Longterm isoperibol experiments (self-heating experiments) are also provided for, as are pure adiabatic and over adiabatic experiments. Even wire basket experiments can be carried out in SEDEX (Meier 1998).

Materials and methods

Tung oil rich in unsaturated fatty acids was chosen for the investigation of spontaneous combustion and the process of self-heating under various conditions. The aim of this study was to compare the data obtained by differential thermal analysis conducted in safety calorimeter SEDEX and the data obtained by standard differential Mackey test.

Differential Mackey test

The standard procedure according to ASTM D 3523- 92 (Reapproved 2012) suggest to use 10 g of oil susceptible to self-heating and apply it on 20 g of surgical gauze, then 20 g of pure surgical gauze is used as reference sample.

Since we focused also on the effect of mass ratio of the porous material and oil on the process of self-heating, it was decided to apply 10, 20 and 40 g of oil on 20 g of surgical gauze to achieve the mass rations of 2:1, 1:1 and 1:2. The tests were stopped after the sample temperature decreased to the temperature of reference sample. Properties of the Tung oil are listed in Tab. 1.

Tab. 1 Properties of Tung oil

Boiling point	148 - 200 °C
Ignition point	64 °C
Flash point	289 °C
Density	0,94 g/cm^3
Iodine value	158
Acid number	5,38 mg KOH/g
Saponification value	190 mg KOH/g

Differential thermal analysis

Polyurethane foam was chosen as suitable carrier for the oil, since the volume of the standard stainless steel sample vessel for SEDEX safety calorimeter is only 20 ml. This material was chosen also because it has homogenous structure, which allows even spread of the oil through the whole body of the carrier. It was important to choose such carrier that would be porous enough and wouldn't degrade along the used temperature range. Suitable polyurethane foam with density of 20 kg/m^3 was chosen. General properties of the polyurethane foam are listed in Tab. 2.

Tab. 2 Properties of polyurethane foam

Ignition point	270 - 280 °C
Flash point	400 - 410 °C
Heat of combustion	26,9 MJ/Kg[1]
Mass burning rate	0,068 kg/m^2.s[1]
Density	20 kg/m^3

Sample of 10 mm thick polyurethane foam was cut in such way, to fit in to the sample vessel and the thermocouple of the device could be inserted in to the sample. The pure sample of the polyurethane foam was thermally loaded from room temperature to 400 °C, at heating rate of 45 K/h to determine its thermal stability. The sample did not show any significant thermal decomposition which would manifest in steep peak, but was slowly decomposing from proximately 250 °C. However, the highest

 DOI 10.1515/tvsbses-2015-0007

temperature for dynamic heating was set to 200 °C for certainty.

Each fresh sample of polyurethane foam was weighted and soaked in the Tung oil. After it was fully soaked, the remaining oil was pressed out. Three mass rations were used as in the Mackey test. The samples were thermally loaded from room temperature to 200 °C, at heating rate of 45 K/h. After this set of trials, fresh samples were isothermally heated at 100 °C. Samples with the mass ratio which showed the greatest rise in the temperature were isothermally heated at 100 °C, but with modified sample vessel. The sample vessel was equipped with air inlet, and air flow regulator. Measurements were conducted under the air flows of 5, 10 and 15 ml/min to determine the airflow that would be the most favorable for the self-heating.

Results and discussion

Results from differential Mackey test (Fig. 3) show, that the optimal mass of the Tung oil applied to the 20 g of surgical gauze is 10 g, which is the mass ratio of 2:1. Spontaneous combustion occurred under the conditions in differential Mackey test apparatus in two cases of samples (10 g and 20 g of oil). The sample containing 40 g of oil was too much wetted, therefore there was no good oxygen distribution and the insulation properties of the sample were too low for spontaneous combustion to occur. The sample with 10 g of oil reached maximal temperature of 616 °C with Self-heating value (SHV) of 522. Second highest temperature of 420 °C was reached by the sample containing 20 g of oil with Self-heating value (SHV) of 328. The lowest temperature of 175 °C reached sample containing 40 g of oil with self-heating value (SHV) of 81.

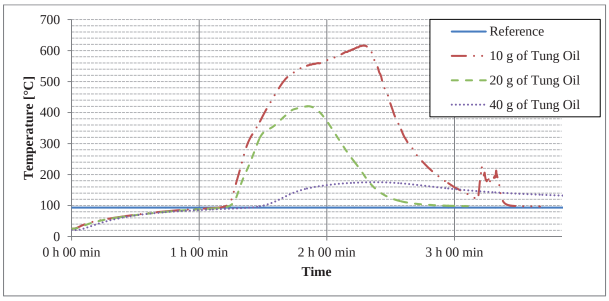

Fig. 3 Results of Mackey Differential Test for different masses of Tung oil

Different results were achieved during the differential thermal analysis in SEDEX. It must be taken into account that these measurements were carried out under completely different conditions. Firstly, the standard stainless steel sample vessel of SEDEX is a closed type vessel, therefore there is no airflow through the sample. Secondly, different type of porous material was chosen as carrier for the oil. The differential temperature Delta T was evaluated, since the SEDEX is constructed for analysis of smaller samples and therefore is more sensitive.

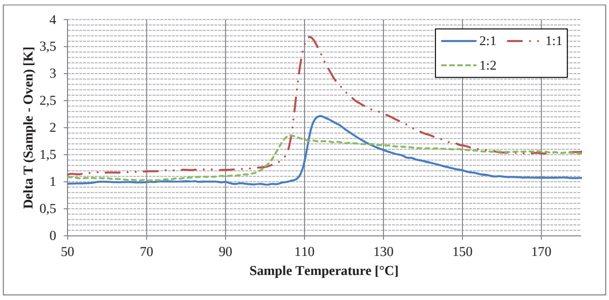

Fig. 4 Results of differential thermal analysis at heating rate of 45 K/h for samples of different mass rations of polyurethane foam and Tung oil

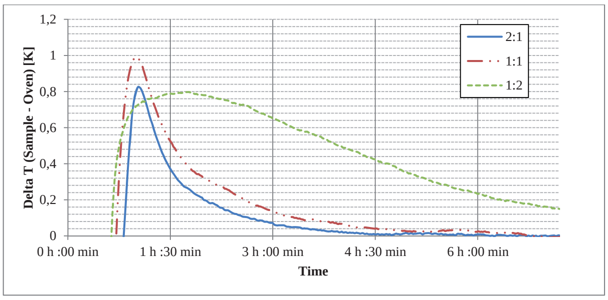

Fig. 5 Results of isothermal differential thermal analysis at 100 °C of samples of different mass rations of polyurethane foam and Tung oil

The results both from dynamic and isothermal heating (Fig. 4 and Fig. 5) show, that in this case the mass ratio of polyurethane foam and Tung oil of 1:1 was the most favorable towards the process of self-heating. This could have been caused by higher density of the polyurethane foam or the oxygen shortage. Only small differential temperatures between the oven temperature and the sample were reached, due to the deficiency of oxygen.

The applied air flow had only insignificant effect on the process of self-heating during the isothermal treatment of the sample with mass ratio of 1:1. As the results (Fig. 6) show, the most favorable was the airflow of 15 ml/min. However, the difference between the influences of the airflow velocities on the maximal temperature differences of samples and oven temperature is negligible.

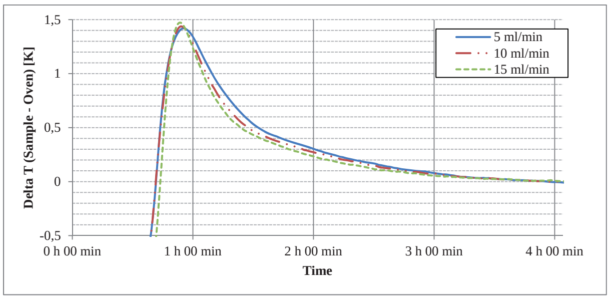

Fig. 6 Results of isothermal differential thermal analysis at 100 °C of samples of polyurethane foam and Tung oil at different airflows

Conclusion

On the basis of measured data it can be stated, that the safety calorimeter SEDEX can be used for the determination of the propensity of material towards self-heating. However, there is no certain method that can be used on calorimeter SEDEX using the standard stainless steel vessel that would reproduce the results obtained by Mackey differential test. Each method has its own advantages and drawbacks.

Acknowledgment

This work was supported by the Slovak Research and Development Agency under the contract No. APVV-0057-12.

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