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Evaluation of the Self-Heating Tendency of Vegetable Oils by Differential Scanning Calorimetry

ABSTRACT: The evaluation of the self-heating propensity of a vegetable (or animal) oil may be of significant importance during the investigation of a fire. Unfortunately, iodine value and gas chromatographic-mass spectrometric analysis do not lead to meaningful results in this regard. To the contrary, differential scanning calorimetry (DSC), which does not measure the chemical composition of the oil, but rather its thermodynamic behavior, produces valuable results. After a thorough literature review on the autooxidation of vegetable oils, several oils with different self-heating tendencies were analyzed using a Mettler-Toledo differential scanning calorimeter DSC 25 between 40°C and 500°C. Analyses were carried out both under air and nitrogen atmosphere to identify the phenomena due to autooxidation reactions. Using DSC, it was possible to observe the induction period of the oil (when available), the three different exothermic events, and the autoignition temperature (relatively independent of the oil type).

KEYWORDS: forensic science, fire investigation, spontaneous combustion, spontaneous ignition, fatty acids, thermodynamics

Spontaneous ignition is a common cause of fire. Different reactions, of biological or chemical origins, can lead to such a phenomenon. Among chemical reactions, the self-heating of vegetable (and animal) oils is well-known and has been reported in the literature as the cause of many fires (1–3). The self-heating of a vegetable oil is due to an autooxidation of its fatty acids, which increases the material's temperature in the absence of any external heat source. When the autoignition temperature of the material or its substrate is reached, spontaneous ignition occurs. Even though this explanation appears simple, several chemical and physical conditions must be met for a vegetable oil to spontaneously ignite (4).

When determining the cause of a fire, the fire investigator must rely upon the application of thermodynamics to develop and test the different hypotheses regarding the production of the initial activation energy (5,6). When dealing with a fire suspected of having been caused by spontaneous ignition, the investigator must also comprehend the chemistry and physics of the self-heating process of a vegetable oil. In any case, the testing of the different hypotheses must include the evaluation of the oil as a source of energy as well as its configuration in the particular scenario.

The investigator has few tools available to evaluate evidence, generate data, and test hypotheses in a spontaneous ignition case involving vegetable oils. Similar to regular fire debris analysis from which the presence of ignitable liquid residues is determined, it is possible to analyze fire debris samples for the presence of vegetable (or animal) oil residues (VOR). A complete review of VOR analysis has been recently published (7,8). However, the determination of the presence of VOR does not imply in any manner that a phenomenon of spontaneous ignition took place: It merely answers the question of whether vegetable oil residues are present in the debris. Likewise, when confronted with a specific scenario, the investigator often wants to determine the propensity of an oil to undergo self-heating and, under the right conditions, spontaneous

ignition. If an exemplar oil is available (i.e., if the oil suspected to have been involved in the fire is known and a comparison sample is obtained), then the investigator can conduct separate analyses on that oil. Gas chromatographic-mass spectrometric (GC-MS) analysis provides the investigator with the composition of the oil in terms of its fatty acid content; however, it typically does not take into account additives that may be present in the oil and that can significantly influence its self-heating capability (8). Thus, the investigator can rely on laboratory reconstruction experiments that evaluate the self-heating propensity of an oil. Laboratory-scale calorimetric tests, such as the Mackey test, are standardized and often used; however, they are long and cumbersome to undertake (9,10). Additionally, they may not be very representative of the conditions under which the fire is thought to have occurred.

As a consequence, the evaluation of the self-heating capability of a vegetable oil is seldom carried out in the scope of an investigation, and the hypotheses regarding the cause of the fire are rarely tested to their fullest extent. This is mostly due to the fact that, in many fires, no exemplar sample of the questioned oil is available. However, when such an exemplar sample is available, the development of a faster and simpler technique to evaluate the self-heating propensity of a vegetable oil could be interesting for the fire investigator. In such an instance, he/she may be more inclined to test the different hypotheses, thus leading to a more thorough and scientific investigation.

One such technique that appears very promising in this regard is differential scanning calorimetry (DSC). In this research, DSC is evaluated as a technique to determine the thermodynamics associated with different vegetable oils and, more particularly, their propensity toward self-heating.

Fundamentals of the Autooxidation of Vegetable Oils

Thermodynamic Considerations

The self-heating phenomenon of vegetable oils originates in the oxidation of the fatty acids present in them. Because this oxidation

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reaction is exothermic, it generates heat directly in the material. In turn, the heat released may be sufficient to provide the activation energy necessary to bring the material or its substrate to its auto-ignition temperature. However, two main conditions must be fulfilled:

- oxygen must be able to penetrate the core of the material in order to guarantee the continuity of the oxidation reactions, and
- the system must be a quasi-isolated medium in order to minimize the heat loss to its surroundings.

The material must be permeable to air, so that oxygen can reach the molecules undergoing the oxidation. Such a condition is generally satisfied only when the material is solid and porous. Liquid oil samples undergo a very limited oxidation at their surface only. This oxidation is usually negligible when compared to their volume, and the heat generated through this process is easily dissipated into the bulk of the material and its surroundings. Therefore, such an oxidation at the surface of a liquid cannot lead to a noticeable self-heating of the oil. However, if a liquid is adsorbed or absorbed onto a solid matrix, the surface/volume ratio of the liquid phase dramatically increases. As a result, contact with oxygen is facilitated and the reaction's heat release rate is highly increased.

An isolated system corresponds to a medium that does not interact with its surroundings: no exchange of work, heat, or matter takes place between the system and its environment. The isolated system is a purely theoretical concept that is approached in some specific situations, such as with some dewar-type insulated recipients, but that can never be reached. The quasi-isolated system is close to the isolated system in the sense that it only allows for a very limited exchange of heat, work, or matter with its surroundings. It is a system much more realistically encountered. Most of the heat produced in the core of such a system cannot dissipate into the environment. As a result, the heat accumulates and increases the system's internal energy level, thus increasing its temperature. The key element to consider is the heat release rate (produced by the exothermic reaction) versus the rate of the heat dissipation into the surroundings. The more isolated the system, the lower the heat dissipation rate. As soon as the heat release rate is greater than the heat dissipation rate, the temperature of the system increases. As the temperature increases, the kinetics of chemical reactions producing the heat are intensified, thus augmenting the heat release rate. This situation is called thermal runaway, and it may generate sufficient heat to eventually increase the system's combustible materials to its autoignition temperature (11).

Because the heat release rate of exothermic autooxidation reactions of vegetable oils is quite low, this normally prevents the possibility of inducing the ignition of combustible materials, unless specific conditions are met. As mentioned above, the presence of a quasi-isolated system and sufficient oxygen availability are the two basic necessary conditions to increase the system's temperature. A heat release rate greater than the heat dissipation rate is the third condition needed for this autoignition. Finally, sufficient materials to sustain the reaction long enough to produce enough energy to bring the mass to its autoignition temperature is also necessary. This is called the critical mass. When all of these conditions are met, thermal runaway occurs to the point of autoignition, and fire breaks out. As an example, when liquid linseed oil is soaked on cotton wicks wrapped together in towels, dissipation of heat in the core of the system occurs more slowly than heat production, and the temperature increases. On the contrary, if the same cotton wicks soaked with linseed oil are spread apart and placed flat on a

tabletop, the heat dissipation rate will be greater than the heat release rate, and no increase in temperature will occur.

Chemical Reactions

The autooxidation of vegetable oils is a process that can be described as occurring in three different steps: initiation, propagation, and termination (12).

The initiation step consists of the reaction of the fatty acid chain with a free radical ($R\bullet$), as shown in Fig. 1a. The origin of the free radical is rarely explained in the literature; however, some authors have reported the natural presence of hydroperoxides (ROOH), which decompose to form free radicals (13). The radical attacks a C-H bond, most likely one from a methyl group present between two double bonds (most common configuration). The resulting chain is stabilized in a resonance configuration.

During the propagation stage, the new radical reacts with oxygen to form a peroxy radical ($ROO\bullet$) as shown in Fig. 1b. In turn, this radical reacts either with another radical to form a nonradical species (a case of termination) or with a hydrogen atom from another fatty acid, thus forming a hydroperoxide (ROOH) and a new alkyl

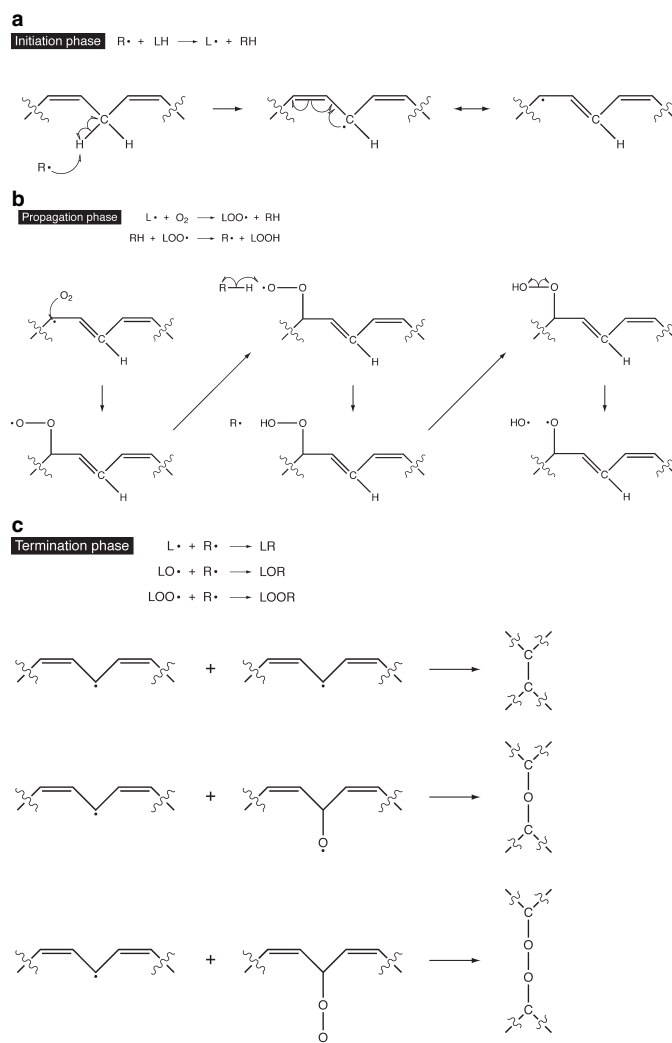


FIG. 1—(a) Initiation phase of the autooxidation of fatty acids (12). (b) Propagation phase of the autooxidation of fatty acids (12). (c) Termination phase of the autooxidation of fatty acids (12).

radical ($R'\bullet$), as in the initiation stage. This last option occurs only rarely because its kinetics are several orders of magnitude lower than those of the reaction of oxygen (O_2) with an alkyl radical (14). Alternatively, a hydroperoxide can also lose a hydroxyl radical ($\bullet OH$), thus leaving an oxy radical ($RO\bullet$).

In the termination step, two radicals react together to form a stable product. Because the resulting links take place between fatty acid chains, it is a cross-linking reaction. The bonds formed can be of either carbon-to-carbon (C–C), ether (C–O–C), or peroxide (C–O–O–C) types, as shown in Fig. 1c (13,15). Other bond formations, including the creation of a ring structure between two fatty acids, have been described in the literature. However, they are beyond the scope of this article (16). Note that bonding can occur between two fatty acids from the same triglyceride, in which instance no polymerization of the oil takes place, or between fatty acids of different triglycerides, in which polymerization of the oil occurs (16). Other oxidations take place and lead to the production of ketones, alcohols, acids, and other products (14).

Because the autooxidation is initiated by the breakage of a C–H bond along the alkyl chain of fatty acids, the strength of that C–H bond significantly influences the occurrence and rate of the reaction. As a matter of fact, the strength of the C–H bond is, in and of itself, affected by the presence of double bonds on adjacent carbon atoms. These double-bonded atoms weaken the C–H bonds of the adjacent carbon atoms, thus decreasing the bond dissociation energy necessary to break them (17). Different configurations, along with their respective bond dissociation energies, are shown in Fig. 2.

As such, the autooxidation of vegetable oils is highly dependent on the presence of double bonds. The easier the C–H bond breaks, the more likely the chain reaction is to take place. Thus, the more polyunsaturated fatty acids an oil contains, the greater its propensity to autooxidize and thus, to self-heat (18). Litwinienko and Kasprzycka-Guttman reported that the ratio of the rates of oxidation of mono-, di-, and triunsaturated esters was 1:3:12 (19). Gunstone and Hilditch reported 1:12:25 for the rates of oxidation of oleic (C18:1), linoleic (C18:2), and linolenic (C18:3) acids, respectively (20). Christie reported even higher ratios (21).

Induction Period and Additives

In addition to fatty acids, vegetable oils contain other substances, such as colorants, perfumes, or emulsifiers, some of which are naturally present and others that are added during the manufacturing process. Among these substances, there are two classes of

compounds that significantly influence the oil's tendency to self-heat. These are:

- antioxidants, and
- drying agents.

Vegetable oils contain some natural antioxidants and, often, artificial antioxidants are added to the composition. This is particularly true for edible oils, for which the oxidation must be prevented as much as possible. There are several natural and artificial antioxidants that can be found in vegetable oils, such as citric acid, tocopherol (vitamin E), butylated hydroxyanisole (BHA), and butylated hydroxytoluene (BHT) (22–24). Currently, the Food and Drug Administration limits the use of BHA and BHT to 0.02% in vegetable and animal oils in the United States (25).

The free radicals created during the initiation phase first react with the natural or added antioxidants present in the oil. These antioxidants have a much greater reactivity and affinity for the free radicals, thus taking priority over the propagation phase of the autooxidation process. The time period during which the antioxidants react with the free radicals is called the induction period (23). As long as the induction period is taking place, antioxidants inhibit the propagation of the autooxidation kinetic chain by abstracting free radicals. It is only after these antioxidants are consumed that the free radicals start to react with the fatty acid chains (13).

By contrast, it is possible to treat the oil in order to accelerate the induction period or to neutralize the naturally present antioxidants. The addition of metal catalysts to the oil allows for an acceleration of the induction period because they favor the production of peroxy radicals (13). Also, the addition of some driers decrease the activation energy necessary for the hydroperoxides to initially decompose (13). There are many different driers that can be added to the oil, most of which are salt metals based on cobalt, zirconium, or manganese. It is crucial to understand that as soon as a metal salt is added to an oil, the oil becomes inedible.

Alternatively, it is possible to subject the oil to a particular treatment, which helps to neutralize its natural antioxidant content. Under these circumstances, the oil will have already undergone its induction period and will be ready to start autooxidation. There are several treatments available in this regard. Historically, the oil was boiled—whence the term boiled linseed oil originates—which results in the simple reaction of the antioxidants with free radicals. More modern treatments include the subjection to ultraviolet light or the addition of driers. The term boiled is no longer representative of the process used to suppress the induction period of the oil, but rather of the oil's condition. As such, ASTM D 260–86 standard sets the specifications necessary for a linseed oil to bear the denomination boiled (26).

The three stages of the autooxidation reaction described earlier occur neither simultaneously nor at the same rate. Litwinienko and Kasprzycka-Guttman demonstrated that the reaction scheme was sequential and autocatalyzed (27).

Measure of an Oil's Propensity to Self-Heat

Methods

Accurately measuring an oil's propensity to self-heat is not an easy process. First, because the tendency of an oil to self-heat to the point of spontaneously igniting is highly dependent on parameters unrelated to the oil's chemical and physical properties, it is not easy to clearly define the dangerousness associated with a given oil. The industry typically uses a scale of low, moderate, or high tendency to self-heat. Second, there is not a unique standard

$\dot{C}-C=C$	86.3 ± 1.5
$\dot{C}-C=C-C$	85.6 ± 1.5
$C=C-\dot{C}-C=C$	76 ± 3
$\dot{C}-C=C-C=C$	83 ± 3
$C-\dot{C}-C=C$	82.5 ± 1.3

FIG. 2—Bond dissociation energies for different configurations expressed in kcal/mol. The energy relates to the breakage of a C–H bond at the location indicated by the free radical (shown with the dot on the C) (17).

method widely used to quickly and easily measure this tendency, and the expression of the results is even less standardized.

In many cases for which self-heating of a given oil is suspected, an exemplar sample of the oil involved may be available based on the investigation. However, it is exceptional to find reliable information regarding the exact composition of this oil and even less reliable information regarding its tendency to self-heat. Interestingly, in most cases where an oil manufacturer is the defendant in a legal proceeding, the manufacturer often describes the oil's tendency to self-heat as low or even nonexistent. Thus, the fire investigator is left alone to generate reliable data on an oil's tendency to self-heat. So, the question remains as to which method is the most reliable and the easiest to carry out in order to measure the self-heating propensity of an oil.

In the food industry, the iodine value (IV) is a variable that has been used for many years to characterize vegetable oils (21). It represents the level of unsaturation of an oil's fatty acid content. Unfortunately, it has been erroneously used to estimate the susceptibility of an oil to undergo self-heating based on the wrong premise that the higher the IV, the more likely an oil is to oxidize (28). Because the IV does not take into account the position of the double bonds on the fatty acids, it may not be directly correlated to the self-heating capability of an oil (7). Moreover, the IV does not take into account the presence of any additives. Even though IVs are widely available for different types of oil and are likely found in the documentation accompanying an oil, this information does not help the fire investigator to estimate the oil's propensity to self-heat.

The analysis of a vegetable oil's fatty acid content provides extra information to the investigator. This analysis is typically performed by gas chromatography-mass spectrometry after a derivatization of the triglycerides constituting the oil into fatty acid methyl esters (8). The relative amounts of the different fatty acids are known and it is possible to estimate an overall tendency of the oil to self-heat based on the propensity of each fatty acid to autooxidize. Unfortunately, this technique does not take into account the presence of additives (antioxidants or driers). As a result, the estimate may also be far from accurate.

Because the presence of antioxidants or driers substantially influences the propensity of an oil to self-heat, it is crucial to find an analytical technique that is not limited to the fatty acid content, but that also takes into account the presence of additives. Additionally, it would be beneficial to obtain thermodynamics data directly usable within the timeline of the circumstances of the case. This, of course, can only be carried out when an exemplar sample of the questioned oil is available for testing.

Hence, the next step would involve the use of much more cumbersome methods, such as the Mackey test (9). The Mackey test consists of taking a given amount of the questioned oil and mixing it with a combustible material, such as cotton gauze, in order to create a quasi-isolated medium. The material is then heated, and the temperature at the core is measured. Based on the temperature reached within a given timeframe, the material's self-heating propensity is qualified. This test is neither practical nor does it allow for a detailed study of the kinetics of the different phenomena of the autooxidation reaction.

More modern thermoanalytical techniques are often used to study the kinetics of endothermic and exothermic reactions. Among them are DSC, differential thermal analysis (DTA), and thermogravimetry (TG). These have all been applied to the analysis of vegetable oils, mostly from a food chemistry perspective. While these all generate data based on the thermal properties of a substance, DSC seems to offer a very interesting means of studying

the different reactions occurring around the autooxidation of vegetable oils. Compared to noninstrumental thermoanalytical methods, DSC has the following advantages: short analytical time (up to c. 1 h), minimal sample preparation, and only small sample size needed (a few mg) (29).

DSC

DSC is a thermal microanalytical technique, which records thermal changes occurring in a sample while subjected to temperature variations. This analytical technique is based on the Boersma principle. The apparatus is composed of an oven with two pans. The first pan contains the sample to be analyzed and a sensor placed outside the pan records its temperature. In parallel, a second pan, identical to the first one with the exception of being empty, is used as a reference. Another temperature sensor is dedicated to that second pan. The reference material is of high purity and its thermal properties are well known. During the analysis, the temperature of the sample and reference pans are constantly recorded and compared to each other. This comparison leads to the compensation of the influence of the pan's thermal capacities during the scanning calorimetry analysis (30).

The two pans are placed in an oven that is either maintained at a given temperature, or heated at a predetermined rate. A micro-resistance heating device is located under each pan in order to provide energy to either the sample or the reference pan when necessary. During the experiment, the temperature of either the sample or the reference pan is adjusted, so that no temperature difference takes place between the two pans. For example, if a thermal change in the sample occurs (endothermic or exothermic), the temperature of the sample pan will no longer match the temperature of the reference sample. As such, in order to maintain temperature equilibrium between the two pans, energy will be supplied to either the sample pan (in case of endothermic process) or to the reference pan (in case of exothermic process). DSC measures the difference in energy required to maintain a quasi null difference between the sample and reference pans while the oven temperature increases at a given rate (30,31). Figure 3 shows the typical set-up of the two pans in the DSC apparatus used in this experiment.

A small amount of the sample material is placed in a pan and weighed, and the analysis is started. The resulting data is produced in graph form and is called a DSC curve, where the temperature is plotted on the *x*-axis and the difference in energy between the two pans, normalized based on the sample's weight, is plotted on the *y*-axis. In the present research, an exothermic reaction is represented as an increase of the curve (higher value on the *y*-axis), while an endothermic reaction results in a decrease of the curve (lower value on the *y*-axis).

DSC has been used for many years in the food industry to evaluate melting and crystallization phases, among other parameters of vegetable oils (32,33). It has also been used to evaluate the

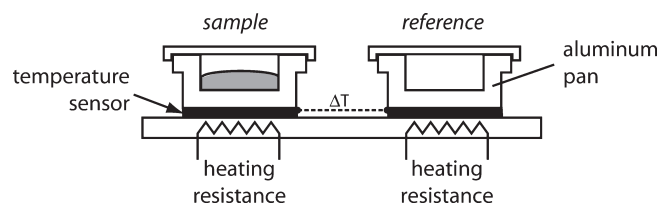


FIG. 3—Illustration of the set-up of a DSC apparatus, with the sample and the reference pans, the temperature sensors, and the heating resistances.

oxidative stability of the oils, mostly from a food degradation perspective (22,29,34–39). As such, many of the published DSC curves range from a negative temperature (°C) to about 100 to 200°C. Few publications actually have studied vegetable oils from a self-heating perspective and have presented DSC curves that reach the autoignition of the oils (14,40). Hellmiss and Schwanebeck also published a paper describing the use of DSC to measure the reaction enthalpy of different materials (41). Their ultimate goal was to calculate the rise in temperature for adiabatic conditions and, thus, determine whether or not a given substance can undergo spontaneous ignition under given conditions. However, all publications seem to agree that DSC is one of the most appropriate techniques used to study the different reactions involved in the autooxidation of vegetable oils. On the basis of this assumption, this study was conducted in order to evaluate the possibility of using DSC to qualify the self-heating potential of a given sample of vegetable oil.

Materials and Methods

Oils

Five different vegetable oils were used in this study: edible linseed oil, boiled linseed oil, safflower oil, corn oil, and peanut oil. The selection of these different types of oil was based on the degree of their saturation, which is often linked to their propensity toward self-heating. Table 1 shows the approximate distribution of the different fatty acids in these oils and their usual propensity to self-heat (7). Boiled linseed oil has a high content in polyunsaturated fatty acids, such as linolenic acid (C18:3) and linoleic acid (C18:2). Its high propensity to undergo autooxidation is well known and is even increased by the presence of drying agents that accelerate the oxidation process. As such, it is often used as a component of paint and coatings to guarantee rapid drying. While the fatty acid composition of edible linseed oil remains very similar to its boiled counterpart, it does not contain any drying agents and has not been treated in any manner to reduce its induction period. Indeed, it contains additional antioxidants to guarantee its stability as an edible product. These two oils have been chosen to obtain a direct evaluation of the effect of the different oils' additives on their tendency to self-heat. Safflower oil has a slightly lower content of polyunsaturated fatty acids. It does not contain any linolenic acid (C18:3), thus it is known to be less subject to autooxidation than linseed oil. Corn oil also has a high linoleic acid content; however, it contains more monounsaturated fatty acids than linseed and safflower oils. Finally, peanut oil has the lowest known tendency to self-heat of the oils on this list. This is due to its relatively low proportion of polyunsaturated fatty acids.

TABLE 1—Approximate fatty acid composition of the five different types of oil used in this research (7).

	Saturated		Polyunsaturated Fatty Acids (%)		Known Propensity to Self-Heat
	Fatty Acids (%)	Monounsaturated Fatty Acids (%)	Linoleic Acid (C18:2)	Linolenic Acid (C18:3)	
Edible linseed oil	9	20	17	54	High
Boiled linseed oil	9	20	17	54	High
Safflower oil	9	13	78	0	Moderate
Corn oil	13	28	58	1	Moderate
Peanut oil	18	48	34	0	Low

Sampling and Analyses

Samples of the different oils were prepared for calorimetric measurements carried out by DSC. For each type of oil, a small amount (between 2 and 5 mg) was introduced in a 40- μ L aluminum pan and weighed. The pan was sealed and holes were perforated through its cover. Even though bulk liquid is analyzed (in opposition to an oil absorbed/adsorbed on a solid, porous medium), because the oil's mass is so small, the surface to mass ratio is still high. Enough oxygen is provided through the flowing atmosphere. While these conditions are valid to test for the oil's exothermic events, one must be aware that they differ in some ways from the real conditions found in a fire scenario. First, the medium is not isolated since heat is supplied to it through an external source. However, any energy supplied or produced is recorded. Second, the rate of heat build-up in spontaneous ignition is slower than the thermal ramp used in the experiment. Finally, there is no combustible fuel present other than the oil itself. Under real conditions, the oil is always present with another combustible fuel, such as a rag, whose autoignition temperature may be lower than that of the oil.

A Mettler-Toledo differential scanning calorimeter DSC 25 equipped with a TA4000 ceramic sensor was used in the analyses. The apparatus was calibrated with indium and indium/lead/zinc standards. The analyses were carried out in four different stages:

First, analyses of each type of oil sample were performed between 40 and 500°C at a rate of 10°C/min, while air was flowing at a rate of 100 mL/min in the analytical cell. These analyses were used to identify the region(s) of interest for each type of oil.

Second, experiments were conducted with the same instrumental parameters but by replacing the airflow with a nitrogen flow at the same rate of 100 mL/min. This was done in order to confirm that the observed thermal phenomenon under air atmosphere could really be attributed to an oxidation reaction. Nevertheless, it also controls for endothermic processes that may cancel out (or hinder) a possible exothermic (oxidation) reaction, thus resulting in a flat line instead of a peak in the analysis conducted under the air atmosphere (14).

Finally, the last two sets of experiments were conducted under air atmosphere (at 100 mL/min):

- One between 25 and 250°C, with a temperature range of 5°C/min, for the observation of the first exothermic peak.
- One at 10°C/min with limit temperatures varying for each type of oil. The aim of this second set of experiments was to examine the oxidation phenomena occurring at higher temperatures and the autoignition of the sample.

In this last set, initial and final temperatures applied for each oil type were defined based on the results of the first calorimetric analyses carried out between 40 and 500°C.

Table 2 summarizes the analytical conditions applied for the different sets of experiments. At the end of each experiment, the

TABLE 2—Instrumental parameters for DSC analyses.

Set	Initial Temperature (°C)	Final Temperature (°C)	Heating Rate (°C/min)	Atmosphere and Flow (mL/min)	Number of Analyses Per Oil
1	40	500	10	Air—100	3
2	40	500	10	Nitrogen—100	3
3	25	250	5	Air—100	3
4	Variable, depending on oil type		10	Air—100	1

aluminum pans were removed and visually inspected, and the condition of the remaining material was recorded.

Onset temperatures for the different thermal processes observed were extrapolated using the Mettler-Toledo STARe software, version 6.0 (Mettler-Toledo, Greifensee, Switzerland). With the exception of the fourth set of experiments, all values provided in the results are averages of at least three measures.

Results and Discussion

Overall Observations

The five types of oil studied presented similar calorimetric curves between 40 and 500°C with several exothermic events. The subsequent experiments carried out under a nitrogen atmosphere confirmed that the exothermic events are the results of oxidation reactions and that no endothermic phenomena interfered with them. For both atmospheres and all oil samples, the repetition of the experiments exhibited a very limited intravariability, thus enabling the interpretation of the results and an interoil comparison. The interpretation of DSC curves of vegetable oils is not an easy task, and there are important contradictions in the literature in this regard. As such, only limited definitive conclusions can be drawn from the curves.

Figures 4–8 show the DSC curves obtained for the five oils between 40 and 500°C under both air and nitrogen atmospheres. A first exothermic reaction (identified as P_1 on the figures) occurs just below 200°C for all types of oils and is quite closely followed by a succession of exothermic peaks, suggesting an acceleration of the global kinetics of the reaction. Because the induction period does not constitute an exothermic reaction, it can be assumed that as soon as an exothermic activity is observed, all inhibitors (antioxidants) are consumed and that the induction period is over (23). As such, a good portion of the literature is in agreement that the onset (T_i on the figures) of this first exothermic event corresponds to the end of the induction period and the beginning of the formation of primary products of oxidation (hydroperoxides) (13,19,27,42). However, there are a few exceptions. Gouveia de Souza et al. explained that the different peaks correspond to the three stages of decomposition of polyunsaturated, monounsaturated, and saturated fatty acids (22). Kaisersberger attributed this first peak to the oxidation of unsaturated fatty acids based on his experiments (40).

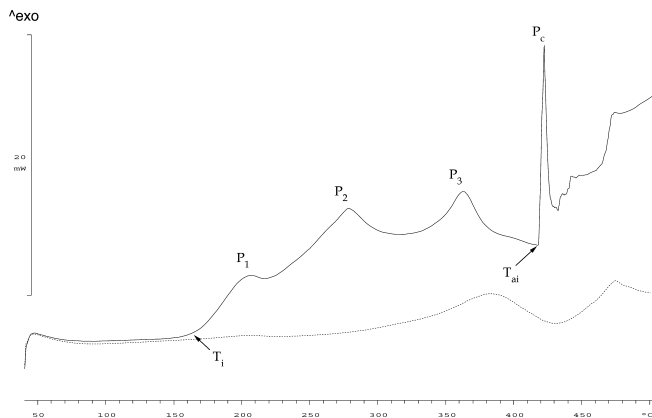


FIG. 4—DSC curve of edible linseed oil under air atmosphere (plain curve) and nitrogen atmosphere (dotted curve). T_i represents the onset of the first exothermic event (the end of the induction period); T_{ai} is the autoignition temperature; P_1 , P_2 , and P_3 are exothermic peaks corresponding to the three exothermic events due to the autooxidation of the oil; P_c is the exothermic peak due to the combustion of the oil. The mention “^exo” shows the direction of an exothermic reaction. mW, milliwatt.

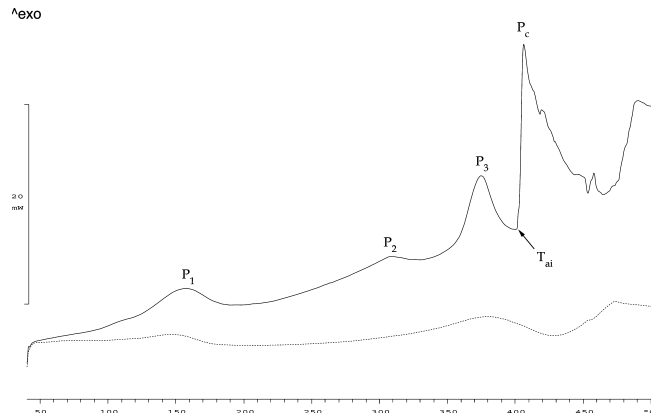


FIG. 5—DSC curve of boiled linseed oil under air atmosphere (plain curve) and nitrogen atmosphere (dotted curve). mW, milliwatt.

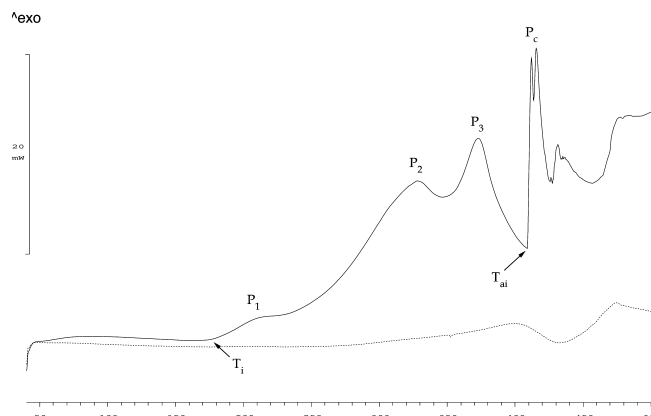


FIG. 6—DSC curve of safflower oil under air atmosphere (plain curve) and nitrogen atmosphere (dotted curve). mW, milliwatt.

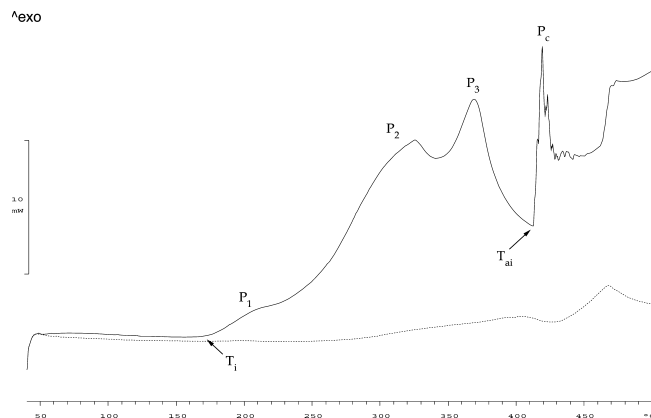


FIG. 7—DSC curve of corn oil under air atmosphere (plain curve) and nitrogen atmosphere (dotted curve). mW, milliwatt.

Ulkowski et al. clearly criticized this alleged misinterpretation and attributed the first peak to the production of hydroperoxides through the reaction of lipids with oxygen and a second peak to their further oxidation and decomposition (14).

In the present experiments, a second peak (identified as P_2 in the figures) can likely be attributed to the decomposition of hydroperoxides, as described in the propagation phase of the autooxidation. This is also an exothermic event and, because the order of the

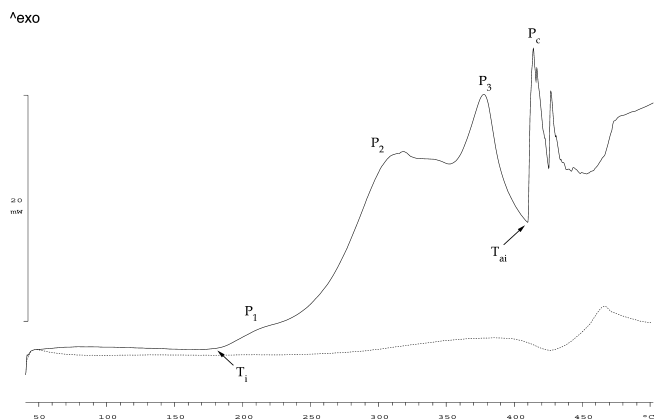


FIG. 8—DSC curve of peanut oil under air atmosphere (plain curve) and nitrogen atmosphere (dotted curve). mW, milliwatt.

reactions is sequential, it follows the initiation phase. The third peak (identified as P_3 in the figures) likely represents the termination phase, which constitutes the polymerization of the oil. According to Litwinienko and Kasprzycka-Guttman, the oxidative polymerization is much slower than the autooxidation process (propagation phase). Therefore, the two exothermic events do not interfere with each other (19). This is compatible with the presence of the two peaks P_2 and P_3 as shown in the DSC curves.

The heat released by the first exothermic process contributed to an acceleration of the overall reaction and, thus, to the heat generated. Under real conditions, once this first oxidation process is activated, and, if all of the necessary conditions are present, notably that of a quasi-isolated medium, the heat produced may lead the system to its autoignition temperature (18). In the DSC curves, this autoignition is eventually reached due to the external supply of heat. The autoignition is evidenced by the sharp peak (P_c) present toward the end of the curve, right after the third peak (P_3). The onset of that peak is identified as T_{ai} on the figures.

Edible Linseed Oil

The presence of an induction period is obvious in the DSC curve of the sample of edible linseed oil: up to *c.* 160°C, no heat release is detected by the calorimetric analysis and both curves under air and nitrogen atmospheres remain flat as shown in Fig. 4. Above this temperature (T_i), a first oxidation process occurs, producing heat. This analysis demonstrated that a given amount of energy is required to first bring the oil to T_i in order to commence the self-heating process of the oil. It is important to understand that in a more practical setting the oil does not necessarily need to be raised to 160°C for this exothermic process to occur; however, the energy required to reach the point of deflection T_i must be provided. This can be done at a much lower temperature, but with a corresponding increase of time.

The first exothermic event is followed by two exothermic events (P_2 and P_3) before the autoignition of the oil at 415°C (T_{ai}).

Visual comparison of the sample's remains in the aluminum pan also was performed. At 250°C, the oil changed slightly in color and became dark brown. At 385°C, oxidation further occurred and the sample was almost black, but still greasy. At 500°C, the aspect of the sample clearly indicated that combustion of the sample occurred: black and almost solid residues were present, similar to

char. This visual comparison process confirms that P_c is the exothermic event produced by the combustion of the oil and that T_{ai} corresponds to the autoignition temperature of the oil.

Boiled Linseed Oil

Because boiled linseed oil has been treated in order to suppress its induction period, the DSC curve (see Fig. 5) does not start with a flat line as in Fig. 4. The T_i is thus below 40°C. The DSC curve rises slowly until *c.* 150°C where P_1 , the first peak likely corresponding to the production of hydroperoxides, is found. P_2 would correspond to the decomposition of these hydroperoxides, and P_3 to the polymerization of the oil. The major exothermic peak observed near 400°C (P_c) corresponds to the combustion of the oil. Visual inspection of the sample's remains in the pans also was performed. The same general observations to the ones already made with edible linseed oil were made and support the identification of the different exothermic events as described.

The results obtained for boiled linseed oil confirm its ability to sustain self-heating: even near ambient temperature (below 40°C), the oxidation of the oil is already taking place. This chemical reaction releases heat contributing to an increase of the speed of oxidation. Thus, if the thermodynamic conditions are favorable, i.e., air supply is provided and heat dissipation limited, such an oil can induce the self-ignition of the system in which it is contained.

While the proportion of saturated, monounsaturated, and polyunsaturated fatty acids of both boiled linseed oil and edible linseed oil is quasi-identical, their propensity to start the self-heating process is quite different when considering the DSC analyses. This emphasizes the significant influence of additives—driers or antioxidants—on the autooxidation process. With the case of edible linseed oil, not only are there no metal salts present, because this would render it improper for human consumption, but also it may very well contain additional antioxidants. This corresponds to the presence of the induction period, as shown in Fig. 4.

The exothermic tendency of boiled linseed oil is definitely emphasized when comparing the DSC curve under air and nitrogen atmospheres, which stays almost flat, as shown in Fig. 5.

Safflower Oil

The general shape of the safflower oil DSC curve under air atmosphere (see Fig. 6) is very similar to the one of edible linseed oil. The first exothermic event occurred slightly later (T_i around 170°C), but no exothermic tendency was recorded below this temperature. The slopes under air and nitrogen atmospheres remain comparable until 170°C.

The autoignition temperature of safflower oil occurs slightly below the one of edible linseed oil, with an onset value (T_{ai}) around 410°C. The nature of this exothermic oxidation reaction is corroborated with the visual aspect of the sample's remains in the aluminum pans.

Corn Oil

No evidence of exothermic reaction was recorded from ambient temperature up to *c.* 155°C: Below this temperature, the curves obtained with experiments undertaken under air and nitrogen atmospheres remain utterly parallel, as shown in Fig. 7.

TABLE 3—Mean values and standard deviations for the onset temperature of the first oxidation (T_i) and of the autoignition temperature (T_{ai}) measured in the different experiments. The acronym “n/a” refers to values that could not be measured because the inflection could not be determined.

Vegetable Oil Type	DSC Analytical Conditions	T_i (°C)		T_{ai} (°C)	
		Mean	Standard Deviation	Mean	Standard Deviation
Boiled linseed oil	40–500°C (10°C/min)	n/a	n/a	402.7	0.2
	25–250°C (5°C/min)	n/a	n/a		
Edible linseed oil	40–500°C (10°C/min)	160.3	2.0	416.1	1.7
	25–250°C (5°C/min)	151.6	2.1		
Safflower oil	40–500°C (10°C/min)	176.2	2.0	409.8	2.6
	25–250°C (5°C/min)	166.2	1.2		
Corn oil	40–500°C (10°C/min)	175.4	0.9	409.7	2.3
	25–250°C (5°C/min)	155.6	3.9		
Peanut oil	40–500°C (10°C/min)	184.2	2.8	410.0	1.9
	25–250°C (5°C/min)	164.8	0.7		

Several steps of oxidation (P_1 , P_2 , and P_3) occurred above the temperature of 170°C, showing mainly smooth and not well-defined inflexions. At around 410°C, a sharper exothermic reaction was recorded (T_{ai}), which corresponded to the autoignition of the material. Upon observation of the pans after heating, despite darkening, no change in the nature of the oil occurred up to 385°C. A loss of material was observed at 500°C, leaving only a thin layer of solid black residue.

Peanut Oil

Comparison of curves obtained with DSC analysis of peanut oil under air and nitrogen atmospheres revealed that no exothermic process occurred between ambient temperature and the first inflexion (T_i) around 170°C (see Fig. 8).

In the same manner observed with the previous samples, after the first exothermic inflexion, two other exothermic steps were recorded (P_2 and P_3) with smooth inflexion until approximately a temperature of 410°C (T_{ai}), where a sharp exothermic reaction occurred (P_c). Visual observations of the sample's remains in the aluminum pans were also consistent with the aforementioned conclusions.

Final Comments

The results of the different analyses were considered for the evaluation of the self-heating abilities of different oils by focusing on the first exothermic inflexion and the sharp inflexion corresponding to the autoignition temperature. Table 3 presents the measured onset values for these points (T_i and T_{ai}) for each oil sample, recorded for the analyses conducted between 40 and 500°C at 10°C/min, and between 25 and 250°C at 5°C/min (only the first onset value).

The difference between the onset values of the first oxidation obtained for the two sets of analytical parameters reflects the thermal lag that occurs by changing heat rates (43). As an example, other authors report an onset value of 90°C for linolenic acid at a rate of 5°C/min and a value of 130°C at a rate of 40°C/min (23). Since thermal lag increases with heating rate, the onset values determined at 5°C/min are closer to the actual T_i temperatures of the oils in a real case scenario. However, it is still probably far from real values because it only takes about 25 min to reach T_i in the DSC analysis, when it rarely takes less than a couple of hours in a real case setting.

The comparison of the different curves based on the increasing saturation level of the oil (linseed—safflower—corn—peanut) is also interesting. Besides the slight increase in T_i , a shift of the total area constituted by peaks 1, 2, and 3, toward the right is noticeable. Of all figures, peaks 1, 2, and 3 are most distinct in Fig. 4. In Figs. 7 and 8, peak 1 has almost disappeared into the slope of peak 2. Also, the height of peaks 2 and 3 increase as they shift to the right. This shift is likely due to the increased saturation of the oils' content: the more saturated the oil, the later the release of thermal energy.

Finally, it should be noted that the autoignition temperature (T_{ai}) is almost identical for all oils and does not depend on the level of saturation in the oils. This was expected, because the combustion of vegetable oils does not involve the same chemical reactions as the autooxidation. While some variations may occur in the autoignition temperatures of vegetable oils, most of them are expected to remain around 400°C. This value is still pertinent and should be considered for each specific scenario, even though one must remember that, in many instances, it is not the oil that catches fire first, but the solid material with which it is mixed.

This study demonstrated that DSC is suitable for evaluating the propensity of an oil to undergo self-heating. Not only is this ability correlated to the oil's saturation level and its content in polyunsaturated fatty acids, most particularly linolenic acid, but also to its additive package. Thus, despite identical proportions of saturated, monounsaturated, and polyunsaturated fatty acids (in particular in linolenic acid), boiled linseed oil and edible linseed oil exhibited different DSC curves. The first oil showed an exothermic reaction starting near ambient temperature, while the second one had a T_i around 150°C at 5°C/min. Most importantly, by using DSC one may observe whether or not an induction period is present. As such, it directly informs whether or not an oil is ready to start its self-heating process, a crucial piece of data for hypothesis testing of fire cause scenarios.

Unfortunately, it is not possible to use DSC with the present parameters directly to extract quantitative thermodynamic data and apply them to a real case. The onset temperature for the first peak is not representative of the temperatures involved in a real case. Also, it does not really answer the question of whether an oil can provide sufficient energy to lead to spontaneous ignition. As a matter of fact, in this particular setting, the oil will eventually autoignite as the temperature is controlled and increased by the apparatus.

Future research should explore the possibility of extracting energy values from the DSC curves. This would require a particular pan setting, which would allow for exact quantitative measurement of the energy released by the exothermic reactions. Also, the advantage of DSC over DTA is that one analysis encompasses all of the kinetic information that would normally take several DTA runs (13). However, future research should also explore the use of DTA, as it may reveal pertinent information to fire investigation applications, in particular. As a matter of fact, a DTA apparatus does not provide external energy to augment the temperature of the system. As such, only the energy released by the autooxidation of the oil is used to increase the oil's temperature. Thus, it may truly reveal if the heat released by an oil's autooxidation is sufficient to lead the oil to its autoignition temperature.

Conclusion

These results emphasize the need to perform calorimetric analyses of vegetable oils in order to assess their self-heating capability. The study of the composition and the proportion of saturated and

unsaturated fatty acids or the determination of the iodine value are not sufficient to evaluate an oil's propensity to self-heat. This assertion relies on the fact that commercial products suspected to have induced spontaneous ignition in real fire cases do not contain solely pure oil, but also erratic amounts of additives that can radically change the propensity of the final product to self-heat, either by promoting or by inhibiting oxidation processes.

Nonisothermal DSC analysis constitutes a fast, simple, and reliable method of testing the oxidizability and exothermic reaction propensity of real oil products made from pure oil mixed with additives. By comparing DSC curves obtained under oxidizing and inert atmospheres, such as air and nitrogen, respectively, this method proved to be sensitive and to provide satisfactory intravariability.

The results obtained by applying this method to different types of oil not only demonstrated that the self-heating ability of an oil is undeniably correlated to its degree of unsaturation, but that the influence of additives could be critical. As a direct consequence, this study demonstrated the usefulness of calorimetric analyses in the evaluation of the self-heating propensity of a questioned oil. Finally, it also led to promising results which may stimulate further research in the analysis of vegetable (and animal) oils using calorimetric techniques.

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