Middle-East Journal of Scientific Research 24 (10): 3302-3306, 2016
ISSN 1990-9233

DOI: 10.5829/idosi.mejsr.2016.3302.3306

Determination of Thermophysical Properties of Edible Oil at High Temperature Using Differential Scanning Calorimetry (DSC)

[1]M.T.H. Bhuiyan, [2]M.N. Chowdhury, [3]Rehana Akter,
[1]Md. Hafijur Rahman, [1]Md. Afjalur Rahman and [3]Mala Khan

[1]Department of Physics, Pabna University of Science and Technology, Pabna, Bangladesh
[2]Department of Basic Sciences and Humanities, University of Asia Pacific, Dhaka, Bangladesh
[3]Designated Reference Institute for Chemical Measurement, BCSIR, Dhaka, Bangladesh

Abstract: Differential scanning calorimetry (DSC) is used to study the thermal behavior of edible oil at elevated temperature. The DSC method was based on the heating thermogram of edible oil samples at a scanning rate of 10°C/min from 40°C to 500°C. Three peaks were found at three different temperature points in the heating thermogram which represent the three thermophysical parameters smoke point, flash point and fire point of edible oil. The smoke point, flash point, fire point and their corresponding enthalpies (ΔH) were measured. Marginal differences in thermal phenomena were found between unheated and long time heated samples. Oxidative stability and flash point enthalpy of long time heated samples have found increases.

Key words: Edible oil · DSC · Smoke point · Flash point · Fire point and Thermophysical properties

INTRODUCTION

Edible oils (e.g. palm oil, soybean oil or vegetable oil) are continuously used for deep-fat frying in fast-food shops and restaurants for 12 to 100 hours at temperatures of about 200°C to 220°C. Repeated heating of edible oil causes for different thermodynamical reactions such as hydrolysis, oxidation and polymerization processes and as a consequence the composition of oil changes [1-3]. Free fatty acids can accelerate oxidation process of the edible oil. Decomposition and condensation of hydroperoxides also produce multitude of nonvolatile monomeric products, including di- and tri-oxygenated esters and dimeric and polymeric materials, especially at elevated temperature. Many of these dimers and polymers are known to be rich sources of volatile carbonyl compounds and decrease the flavor and oxidative stability of soybean oil [4]. These high-molecular-weight materials also can produce a series of physical and chemical changes to the oil and food products, including increased viscosity, polarity, free-fatty acid content, development of dark color and an increased tendency of the oil to foam [5].

The smoke point varied considerably with the degree of refining, especially the removal of free fatty acids and also with the mode of oil extraction [6]. The flash point of soybean oil, the temperature at which vapors coming from the oil will catch fire from an ignition source, were reported as 304°C [7], 326–331°C [6], 174°C [8], 318°C [9] and 320°C [10]. Fire points (i.e., self-ignition) temperatures (SITs) for soybean oil by using the Cleveland Cup method, which uses a brass cup, was reported to be 356–363°C [6] and 400°C using a stainless-steel cup apparatus [11]. The burning rate of soybean oil was 4.3g/m^{2}sec, flame height 129 mm and irradiance 0.153 kW/m^2 [11]. Kowalski [12] studied the self-ignition temperature in a differential scanning calorimeter (DSC) heated at rates of (40–90)°C /min and under 800 kPa–2800 kPa of oxygen pressure and found values of 260°C –290°C for soybean oil. He found the addition of copper wire to the sample decreased the self-ignition temperature by 5°C –15°C. The self-ignition temperature was inversely related to oxygen pressure. Wakakura [13, 14] used a scanning calorimeter at an oxygen pressure of 980 kPa with soybean oil spread on glass wool and on bulk and found self-ignition temperatures of 147°C and 376°C respectively. Another researcher reported that the amount of sample and Oxygen inside sample holder has significant impact on the size and shape and reproducibility of DSC thermograms [15].

Corresponding Author: M.T.H. Bhuiyan, Department of Physics, Pabna University of Science and Technology, Pabna, Bangladesh

DSC methods are fast, reliable, do not need any solvents and require very small quantity of samples (few milligrams). In addition, there are theoretical models for analyzing data from DSC experiments. Some studies have been conducted on thermophysical property of edible oil with DSC at low temperatures. Determination of smoke point, flash point and fire point temperatures of edible oil along with their respective enthalpies using DSC have not yet been reported. The objective of this work is to determine the thermophysical properties of edible oil at high temperature using Differential Scanning Calorimetry (DSC) and hence to investigate the effect of repeated heating of edible oil at high temperature.

MATERIALS AND METHODS

The thermophysical properties of edible oil at high temperature were measured using the DSC (Model: DSC-60, Shemadzu) instrument. All samples have prepared in our laboratory by reheating fresh crude palm oil and soyabean oil at 220°C for several times with the help of a magnetic stirring electric heater. Around 5 mg of each sample is placed in the aluminum sample vessel. The sample vessel is then placed on the sample platform while an empty aluminum vessel was placed on the reference platform. To determine the oxidation point, flash point, fire point and their corresponding enthalpies (ΔH), the instrument is operated at temperatures ranging from 40°C to 500°C and scan rate of 10°C /min. Nitrogen is passed through the heating chamber at atmospheric pressure and a flow (purge) of 30 mL/min is measured at the bypass outlet. Prior to measurements, the DSC is calibrated for temperature and energy sensitivities as specified in the manual. The DSC instrument is fully computer controlled with rapid energy compensation and equipped with automatic data analysis software (TA60) to determine thermophysical properties from the heat flow data. The analyses are carried out using standard and instrumental methods.

RESULTS AND DISCUSSION

Thermal analyses of DSC thermograms provide information about the temperatures and enthalpies of smoke point, flash point and fire point of either whole fat or its fractions. The changes in individual fat fractions gives rise to the appearance of additional peaks, the division of broad initial peaks to multiple narrow peaks and the shifting of some peaks to higher temperature values (Besbes et al., 2005). Thus change in thermal profile is multidirectional and the degree of fat deterioration can be estimated based on discrepancies between the profile of fresh fat and the examined one. Any endothermic or exothermic event is registered as a peak in the thermograph and its area is proportional to the enthalpy gained or lost, respectively [16-18].

According to literature smoking point and flash point temperatures of edible oil should be found near 250°C and 300°C respectively and its drop down due to heating. From the DSC thermographs (Fig. 2) of edible oils it is evident three characteristic peaks: first one is a small endothermic peak found near around 200°C and second and third peaks are noticeably large and found as coupled exothermic & endothermic peak near around 360°C and 400°C respectively. First endothermic peak might be due to oxidation (smoke point) of oil samples and second one might be due to flash point and the last one might be due to fire point temperature. The other insignificant smaller peaks were not analyzed. The temperature is calculated from extrapolating the tangent drawn on the steepest slope of DSC thermograms which is obtained by plotting heat flow versus temperature data.

Smoke Point: Knowing the smoke point of edible oil is important because heating of oil to the point where the oil begins to smoke produces toxic fumes and harmful free radicals. It is also defined as loss of small molecular fragments due to evaporation. Figure 1 presents the calorimetric curves of typical edible oils (palm oil and soybean oil) of different samples. The bottom flat line in curve demonstrates only small fluctuations and no significant exo- and endothermic effects. The figure shows the onset temperature (T_{on}) for smoke point in the range of 140°C - 170°C and offset temperature (T_{Off}) in the range of 190°C-220°C. Table 1 shows the onset temperature, offset temperature, maximum temperature and smoke point enthalpies for different oil samples. Onset temperature (T_{on}) of oxidation is the temperature during which primary oxidation products begin to form in the edible oil matrix, whereas offset temperature (T_{off}) and maximum temperature (T_{max}) represent the termination temperature and the temperature at which a rapid increase in the rate of oxidation of the oil matrix occurred respectively.

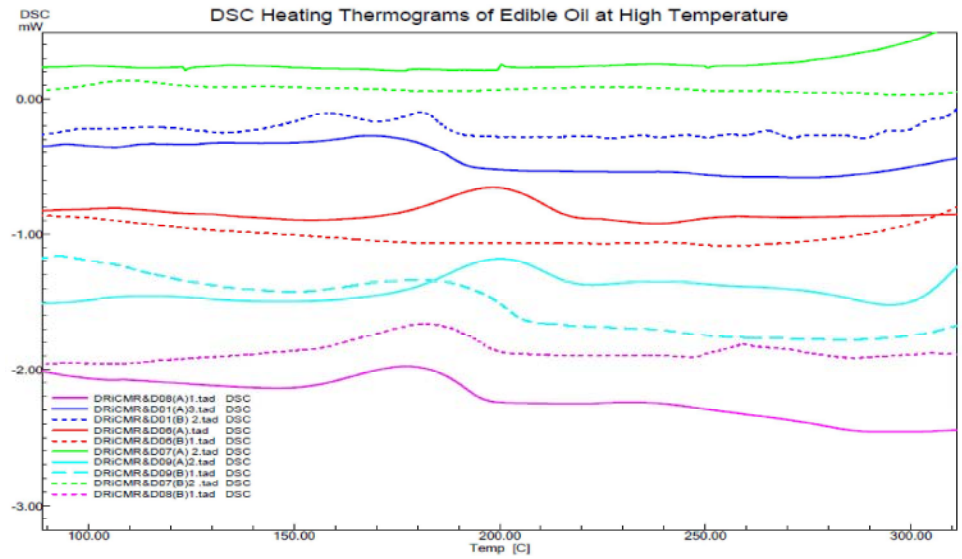

Fig. 1: DSC heating thermograms (zooming view for smoke point) of unheated (solid line) and heated (dotted line) edible oils.

Table 1: Onset temperatures, Maximum rate temperatures, Offset temperatures and smoke point enthalpies of different edible oils in multiple heated and unheated oils.

Sample ID	Onset temperature in (°C)	Offset temperature in (°C)	Maximum Rate temperature in (°C)	Enthalpy (ΔH) in J/g
DRiCMR&D01(A)	148.67	193.93	171.96	6.11
DRiCMR&D01(B)	141.53	189	180.68	7.12
DRiCMR&D06(A)	170.61	210.14	191.39	10.04
DRiCMR&D06(B)	-	-	-	-
DRiCMR&D08(A)	152.35	196.45	177.33	10.66
DRiCMR&D08(B)	153.27	199.5	181.78	10.83
DRiCMR&D09(A)	175.80	218.51	199.42	6.62
DRiCMR&D09(B)	159.88	207.87	179.41	9.07

From Table 1 it is seen that different edible oil has different smoke point temperatures. Experimental results also suggest that onset temperature (T_{on}), offset temperatures (T_{Off}) and maximum rate temperatures (T_{max}) for long time heated edible oils have increased for most of the samples. A high T_{on} indicates a high oxidative stability of the edible oil matrix therefore high smoke point temperature. Lower T_{on} and T_{off} indicates thermally unstable matrix to oxidation. Oxidation curve in the DSC thermograms have broaden for long time heated oil samples comparative to the fresh (i.e., unheated) samples.

Smoke point enthalpy (ΔH) of the edible oils depends on the availability of Oxygen gas into the sealed sample holder pan. Greater amount of Oxygen gas is responsible for greater Oxidation reaction, therefore greater enthalpy. Moreover, for some samples, no observable oxidation curve in the DSC heating thermogram was noticed and it might be due to lack of sufficient Oxygen to initiate oxidation reaction inside the sample pan. Oxidation stability of edible oils decreases due to long time heating.

Flash Point Characteristics: The temperature at which vapors coming from oil will catch fire from an ignition source is defined as flash point of edible oil. The characteristic second curve in the DSC thermogram (Fig. 2) is responsible for the flash point event of the edible oil for both heated and unheated edible oil samples. The exhalations of vapors of natural fats and oils usually occur over a considerable temperature range. The values of onset temperature (T_{on}), offset temperature (T_{off}) and maximum rate temperature of flash point are measured and all the values are given in Table 2. Flash point enthalpies are also calculated throughout the complete process and all the values are presented in Table-2. The second significant peak, which is exothermic in character, in the DSC thermograph (Fig. 2) is the characteristic curve for the ignition process of edible oils.

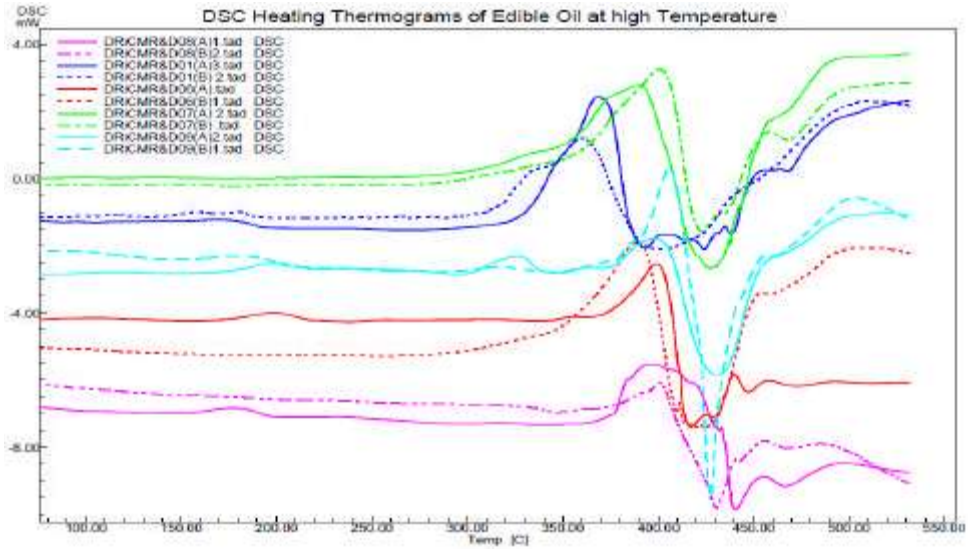

Fig. 2: DSC heating thermograms of unheated (solid line) and heated (dotted line) edible oils

Table 2: Onset temperatures, Maximum rate temperatures, Offset temperatures and flash point enthalpies of different edible oils in multiple heated and unheated oils.

Sample ID	Onset Temp. (T_{on}) in °C	Offset Temp. (T_{off}) in °C	Maximum rate temp. (T_{max}) in °C	Enthalpy (ΔH) in (J/g)
DriCMR&D01(A)	377	392	388	125
DRiCMR&D01(B)	309.9	404.6	393	56.5
DRiCMR&D06(A)	322	391	379	150
DRiCMR&D06(B)	310.5	408	384.5	143
DRiCMR&D07(A)	345	407.5	389.5	284
DRiCMR&D07(B)	345.5	416.5	403	152.5
DRiCMR&D08(A)	341	400.5	377	127.36
DRiCMR&D08(B)	370.16	403.5	389.16	76.315
DRiCMR&D09(A)	369	404	390.37	24
DRiCMR&D09(B)	386	417	405.73	22

By analyzing the DSC heating thermograms it is found that the onset (T_{on}), offset (T_{off}) and maximum rate (T_{max}) temperatures of flash point of different edible oil are different and they are found at around 350°C, 400°C and 380°C respectively. Enthalpy throughout the complete ignition processes are also measured and found different for different samples. One important characteristic for edible oil is that flash point enthalpy of long time or multiple times heated edible oils decreases compared to the unheated oil sample. The decrease in the enthalpy is ascribed to changes in fat composition caused by high heat treatment. Another significant relation is also observed and that is the onset temperature of flash point decreases for multiple times heated oils compared with unheated edible oil. On the other hand, maximum rate temperatures of the multiple time heated oil sample have increased compared to the unheated oil samples.

Fire Point Characteristics: The temperature at which vapors coming from oil will catch fire itself without any ignition source is defined as fire point of edible oil. Fire point temperature of edible oil is defined as self-ignition temperatures (SITs). It could be affected by multiple times heating of edible oil at high temperature. High temperature heat treatment is a reason for breakdown of unsaturated fats into saturated fats and creation of different byproducts i.e., volatile and nonvolatile and toxin compounds. The third significant curve (Fig. 2), which is endothermic in character, in the DSC thermogram is a consequence of fire point process of the edible oil for both heated and unheated samples. From Fig. 2 it is seen that offset temperature of flash point process and onset temperature of fire point process are coupled in a complex fashion i.e., one is merged into another. Maximum rate of self burning is not changed much for long time multiple

times heated sample compared to unheated samples [Table 3]. Though for some samples have shown increment in fire point temperature and decrement in fire point temperature is found in marginal scale. Similar trend of increment and decrement is also observed in case of fire point enthalpy and some change is found in great amount.

Table 3: Maximum rate temperatures and fire point enthalpies of different edible oils in multiple heated and unheated conditions.

Sample ID	Maximum rate temp. (T_{max}) in °C	Enthalpy (J/g)
DRiCMR&D01(A)	410.62	72.71
DRiCMR&D01(B)	409.92	83
DRiCMR&D06(A)	399.9	128
DRiCMR&D06(B)	426	147
DRiCMR&D07(A)	424	164
DRiCMR&D07(B)	426.5	77
DRiCMR&D08(A)	436	162
DRiCMR&D08(B)	430.8	169
DRiCMR&D09(A)	434.5	114
DRiCMR&D09(B)	426.12	112

CONCLUSION

Thermophysical properties of edible oils at high temperature are affected by long time heating and it can be determined using DSC instrument. DSC method offers a more effective alternative for the monitoring of the edible oil due to its appreciable time-saving, use of small samples with minimal preparation and absence of toxic chemicals. Though, changes in oxidation enthalpy of long time heated samples are observed and no meaningful information is obtained. It might be due to the fact that since the oxidation enthalpy is directly connected with the amount of sample and Oxygen gas inside the sample pan and in this study sample holder was not sealed with Oxygen gas in controlled way. At high temperature reproducibility of the experimental result is a bit difficult because it is related with the amount of sample and rate of heating.

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