

Article

The Study of Thermal Properties of Blackberry, Chokeberry and Raspberry Seeds and Oils

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Abstract: The seeds of berry fruits are a component of fruit waste occurring in the production process. Circular economy rules focus on decreasing the amount of waste produced and reusing by-products when it is possible. To determine the possible applications of the studied fruit industry wastes, the thermal properties of berry seeds and of oil extracted from the tested material were examined. Differential scanning calorimetry (DSC), modulated differential scanning calorimetry (MDSC), and thermogravimetry (TG) of blackberry, chokeberry, and raspberry seeds were carried out. The properties of oil extracted in the Soxhlet apparatus were studied by pressure differential scanning calorimetry (PDSC), TG, and gas chromatography (GC) measurements. The results show that berry seeds lipids are from different melting fraction groups with a dominance of low-melting fraction, which consists of mono- and polyunsaturated fatty acids. There are also occurring residues of carbohydrates and inorganic, thermostable substances in the studied seeds. A GC analysis of oil confirms that the polyunsaturated fatty acids (PUFA) are most abundant and amount to $78.72 \pm 0.06\%$ in blackberry seed oil, $73.79 \pm 0.14\%$ in chokeberry seed oil, and $82.74 \pm 0.03\%$ in raspberry seed oil. The PDSC study showed that the most oxidative stable oil is blackberry seed oil, followed by raspberry and chokeberry seed oils. According to the obtained results, berry seeds can be used as a source of oil in food or other production chains. However, more detailed characteristics of berry seed oils are needed to determine their applicability.

Keywords: fruit waste; fruit seeds; thermal analysis; thermogravimetry; differential scanning calorimetry; fatty acid profile



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1. Introduction

Nowadays, agricultural production has to deal with the growing problem of utilizing and reducing food wastes. According to the Food and Agriculture Organization of the United Nations (FAO), up to 45% of the fruits and vegetables produced are wasted [1]. The amount of loss may lead to economic consequences, as well as natural environmental damages [2]. Applying the circular economy model to the food production chain can bring financial and environmental benefits. Especially in fruit processing, the mentioned economic model implies further usage of fruit by-products, as they still consist of bioactive, nutritive compounds [3]. The fruit industry is mainly focused on primary production, but also, a significant amount of fruit is processed into products such as juices or concentrates. During the process of juice pressing, pomace is formed as a by-product and appears to be a major fruit processing waste. Considering berry fruits, this group consists of fruits from *Rubus*, *Ribes*, *Aronia*, *Vaccinium*, and *Fragaria* genera [4]. The FAO estimates that the worldwide berry fruits production (data for 2019) amounts to over 12.2 million tons [5]. The pomace obtained from berry fruits juice pressing may vary depending on berry species,

but generally, they are rich in seeds and skins of fruits. For example, the seeds content in powdered chokeberry pomace was found to be 22.1% [6].

Seeds of berry fruits may be a source of high-quality oil with a high content of polyunsaturated fatty acids (PUFA), which are significant from a nutritional point of view [7,8]. Especially significant is the abundance of α -linolenic and linoleic acids, which are classified as essential fatty acids and must be delivered by food to humans [9]. The oils also contain monounsaturated fatty acids (MUFA) and a limited percentage of saturated fatty acids (SFA) [7,8]. However, a high PUFA content results in the lower oxidative stability of oils which may affect the application of berry seed oils. High tocopherol abundance in berry seed oils [7,8] may have a preventive role in the oxidation process, but only at lower temperatures, due to tocopherol's ability to promote oxidation in high temperatures [10].

To define possible ways of berry seeds usage, it is reasonable to study the properties of seeds and the oil obtained from them. Thermal properties are the most adequate parameters to determine the usefulness of seeds as a source of oil. Differential scanning calorimetry (DSC) and modulated differential scanning calorimetry (MDSC) are applicable tools to describe the thermal transitions of examined samples in micro-scale. They provide information about thermodynamic and kinetic characteristics dependent on the temperature of the material. In food products analysis, DSC helps determine the transitions resulting from the specific composition of foods because different groups of nutrients are specified by various transitions. Considering lipids, it is possible to analyze first-order transitions, e.g., the transformation of the crystalline structures or melting, and also second-order transitions, e.g., setting crystalline structures. That information can be helpful in the determination of the shelf life of products and their rheological properties [11]. Modulated scanning calorimetry is useful in determining the glass transition, which is a parameter describing the transition of a substance from a glassy state to a gummy state. This parameter is specific for a given material and depends on its composition. The material in a glassy state is so viscous that, as a result of limiting the mobility of molecules, most physical changes and chemical reactions in samples are significantly slowed down or do not take place at all. The reduction in the viscosity of such a product may occur as a result of an increase in temperature above the T_g value or an increase in water content. In both cases, the structure of the material is plasticized. As the water content increases, a drastic decrease in T_g is observed, which entails changes in its physical properties [12,13]. Thermogravimetry (TG) is applied to register the decomposition of particular groups of compounds of solid or liquid foods during heating. The following reaction order may be observed in that study. It also gives information about the thermal stability of food products and allows the determination of ash content (thermal stable mineral compounds) in the sample [14]. Pressure differential scanning calorimetry is useful in measuring the oxidative stability of oil. Conditions in an instrument promote the oxidation process, and during that, when the onset time of reaction is reached, the sample of oil releases heat which is recorded as a signal [15]. To refer to the thermal properties of the composition of oil, fatty acids contributions were also studied using gas chromatography (GC). GC is the most commonly used technique to determine fatty acid composition and occurs as a standard method used in studies of oils [16].

The main aim of this study was to analyze the thermal properties of blackberry, chokeberry, and raspberry seeds and oils extracted from the mentioned seeds. In addition, the fatty acid composition and oxidative stability of the extracted oils were analyzed.

2. Materials and Methods

2.1. Chemicals

All reagents and solvents used in the following study were provided by Avantor Performance Materials Poland S.A. (Gliwice, Poland), excluding fatty acid mixture standard used in the GC study, provided by Sigma-Aldrich (Saint Louis, MO, USA).

2.2. Study of Seeds

Dried seeds of blackberry (*Rubus fruticosus*), chokeberry (*Aronia melanocarpa*), and raspberry (*Rubus idaeus*) were examined. Whole seeds and seeds milled in a laboratory mill IKA Tube Mill at 20,000 rpm for 60 s were used.

2.2.1. Water Activity Measurements of Seeds

The water activity of the dried seeds was measured using a hygrometer Rotronic HygroLab C1 at a temperature of 25 ± 0.3 °C.

2.2.2. DSC Study of Seeds

DSC measurements were carried out using TA DSC Q200 differential scanning calorimeter (TA Instruments, New Castle, DE, USA). The cell of a calorimeter was purged with 50 mL/min nitrogen and calibrated with standard pure indium. The samples (12–13 mg) of milled seeds were hermetically sealed in aluminum pans, and an empty sealed aluminum pan was used as a reference. Samples were brought to -70 °C and then heated at a heating rate of 2 °C/min to a temperature of 160 °C. Curves of heat flow (W/g) as a function of temperature were obtained as results. The diagram was registered and interpreted by Universal V4.5A (TA Instruments, New Castle, DE, USA) software [17].

2.2.3. MDSC Study of Seeds

Modulated DSC measurements using TA DSC Q200 differential scanning calorimeter (TA Instruments, New Castle, DE, USA) were conducted to determine the glass transition temperature of the examined seeds. The cell was purged with 50 mL/min nitrogen and calibrated with pure indium standard. The samples (12–13 mg) of milled seeds were sealed hermetically in aluminum pans, and an empty sealed aluminum pan was used as a reference. Samples were cooled to 20 °C and then kept in isothermal conditions to equilibrate for 5 min. After that, the samples' thermal and dynamic properties during heating from 20 to 120 °C with a constant heating rate of 2 °C/min with an amplitude of ± 1 °C and a period of modulation lasting 60 s were registered. Obtained curves were analyzed from their total, reversible and non-reversible heat flow. Glass transition temperatures were determined by extrapolating two baselines and manually setting the mid-point of the transition on the curve. The analysis of the curves was taken using Universal V4.5A (TA Instruments, New Castle, DE, USA) software [18].

2.2.4. TG/DTG Study of Seeds

Thermogravimetric analysis was carried out using a Discovery TGA thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). The samples (7–8 mg) of milled and whole seeds were put in tared platinum pans. Nitrogen and oxygen at a flow rate of 25 mL/min, a temperature range of 50–700 °C, and with a heating rate of 10 °C/min were used. The obtained TG curves were a graphical illustration of temperature dependence on mass loss; the first-derivative of function was calculated using the TG software [19].

2.3. Study of Oil Obtained from Seeds

2.3.1. Extraction of Oil

Soxhlet extraction was conducted in a classical apparatus by the standard method [20]. Ten grams of ground seeds with 150 mL of hexane were used. The obtained extract was dried with anhydrous magnesium sulfate and filtered. The solvent was evaporated from the filtrate using BÜCHI Rotary Evaporator at 40 °C; the obtained lipid fraction was then dried under a nitrogen atmosphere to remove hexane residue.

2.3.2. GC Analysis of Extracted Oils

The profile of fatty acids was analyzed using The YL6100 GC gas chromatograph apparatus (Young Lin Bldg., Anyang, Hogye-dong, Korea) coupled with a flame ionization detector and equipped with a 30-m long BPX 70 capillary column (SGE Analytical Science,

Milton Keynes, UK) with an inner diameter of 0.22 mm and a film thickness of 0.25 μm . The chromatograph used the split injection mode at a 1:100 ratio. The injector and detector temperatures were kept at 225 °C and 250 °C, respectively. The oven temperature was programmed starting at 60 °C for 5 min; then it was increased up to 180 °C at a rate of 10 °C/min, followed by an increase up to 230 °C at a rate of 3 °C/min and was maintained at this temperature for 15 min. Nitrogen was applied as a carrier gas, with a flow rate of 1 mL/min. The fatty acids from samples were converted to fatty acid methyl esters (FAME) using methanolic KOH solution according to PN-EN ISO:2001 [21]. FAMES were identified by retention time compared to the standard FAMES mixture. A quantitative analysis was done by the procedure of area normalization, and the results were calculated as a percentage of each fatty acid.

2.3.3. PDSC Study of Extracted Oils

PDSC measurements were conducted using a DSC Q20 TA Instrument (TA Instruments, New Castle, DE, USA). Samples (3–4 mg) of oil were put in aluminum pans; the empty pan was used as a reference. Both pans were placed in the cell under an oxygen atmosphere (50 mL/min flow rate) with an initial pressure of 1400 kPa. The experiment was carried out in isothermal conditions of 120 °C. The induction time of the samples was determined based on the maximum rate of oxidation. Diagrams were registered and analyzed using TA Universal Analysis 2000 software [15].

2.3.4. TG/DTG Study of Extracted Oils

Seed oils were examined in the Discovery TGA thermogravimetric analyzer, using methodology as described for the seeds [19].

2.4. Statistical Analysis

Measurements were taken in triplicate. Results are given as the means \pm standard deviation. The one-way ANOVA was carried out using the Statistica 13.3 (StatSoft, Kraków, Poland) software. A *p*-value of 0.05 was chosen to consider significant differences according to Tukey's post-hoc test.

3. Results and Discussion

3.1. Study of Seeds

3.1.1. Water Activity of Seeds

Water activity is a useful parameter to evaluate the effectiveness of the drying process. In the case of food material, spoilage disqualifies the product from possible usage. It is claimed that under a value of 0.8 for water activity, microorganisms are not able to grow [22]. Presented in Table 1, measurements of water activity showed the lowest values for blackberry seeds, followed by similar values for chokeberry and raspberry seeds. All of the examined samples reached lower values than the determined limit value, so it may be concluded that studied seeds are microbiologically safe.

Table 1. Water activity of studied berry seeds.

Source of Seeds	a_w
Blackberry	0.156 ± 0.002^a
Chokeberry	0.227 ± 0.001^b
Raspberry	0.237 ± 0.004^c

a_w —water activity; mean values with different letters (^{a–c}) in the columns are significantly different at $\alpha = 0.05$.

Moreover, what is important when considering seeds as a source of oils, is that the increased moisture may increase the oxidative reactions in the material. That may result in a shorter shelf-life of the product and a lower stability. Products containing high values of PUFAs may especially be susceptible to oxidation during storage in conditions of high a_w values [23].

3.1.2. Differential Scanning Calorimetry of Seeds

DSC curves of the heating of blackberry, chokeberry and raspberry milled seeds from -70 °C to 160 °C are shown in Figure 1. For blackberry and raspberry seeds, the curves are comparable; the chokeberry seeds' heating curve has a different course. Despite the differences, all of the diagrams include four maximum points. Considering blackberry and raspberry seeds, one exothermic and three endothermic peaks are seen on the diagram. An endothermic peak appearing first at -40.35 °C for blackberry and at -40.01 °C for raspberry is due to the low-melting fraction of triacylglycerols (TAGs) occurrence. Low-melting fractions generally consist of mono- and polyunsaturated fatty acids. Next, maximum signals and exothermic peaks (overlapping effect) of around -38 °C represent the thermal transition connected with crystallization of polymorphic forms of TAGs. The endothermic maximums around -20 °C appear due to middle-melting and high-melting fractions of TAGs which are represented by fatty acids of different structures, containing both unsaturated and also saturated fatty acids. Similar shapes of DSC curves of blackberry and raspberry seeds were reported by Micić et al. [24]. The authors observed the same thermal transitions occurring due to the phase transitions of oil present in seeds and also described a phenomenon of polymorphism of fat in seeds as a cause of specific shape of the diagram in the region of temperatures at -50 °C to -10 °C. Oomah et al. [25] reported similar DSC tracings for raspberry oil extracted from raspberry seeds with distinctive transitions correlated to the polymorphism of raspberry seed fat. Moreover, considering the polymorphism phenomenon, it is concluded that the first endothermic peak is a result of the melting of the less stable α crystal form, and the exothermic signal comes from crystallizing the more stable β form of the oil.

On the DSC curve for chokeberry seeds, three endothermic peaks are observed. The maximum signal at a temperature of around -18 °C is present due to middle-melting and high-melting fractions of TAGs containing unsaturated and saturated fatty acids, as well as in the case of blackberry and raspberry seeds.

The following two peaks at temperatures of around 137 °C and 140 °C occur as a consequence of carbohydrates transformation. Additionally, for blackberries and raspberries at a temperature of 140 °C, an endothermic peak is seen, which is a consequence of the carbohydrates' thermal transition. According to Majewski et al. [26] and Sójka et al. [27], the carbohydrates fractions of raspberry and chokeberry seeds are mainly fiber, so it can be claimed that the signals around 120 °C and 140 °C on the DSC curve come from fiber decomposition.

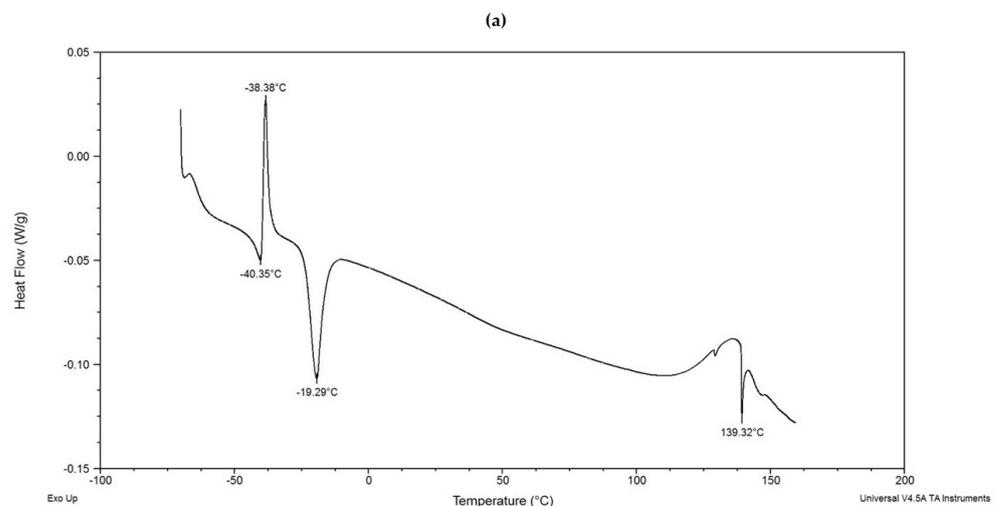


Figure 1. Cont.

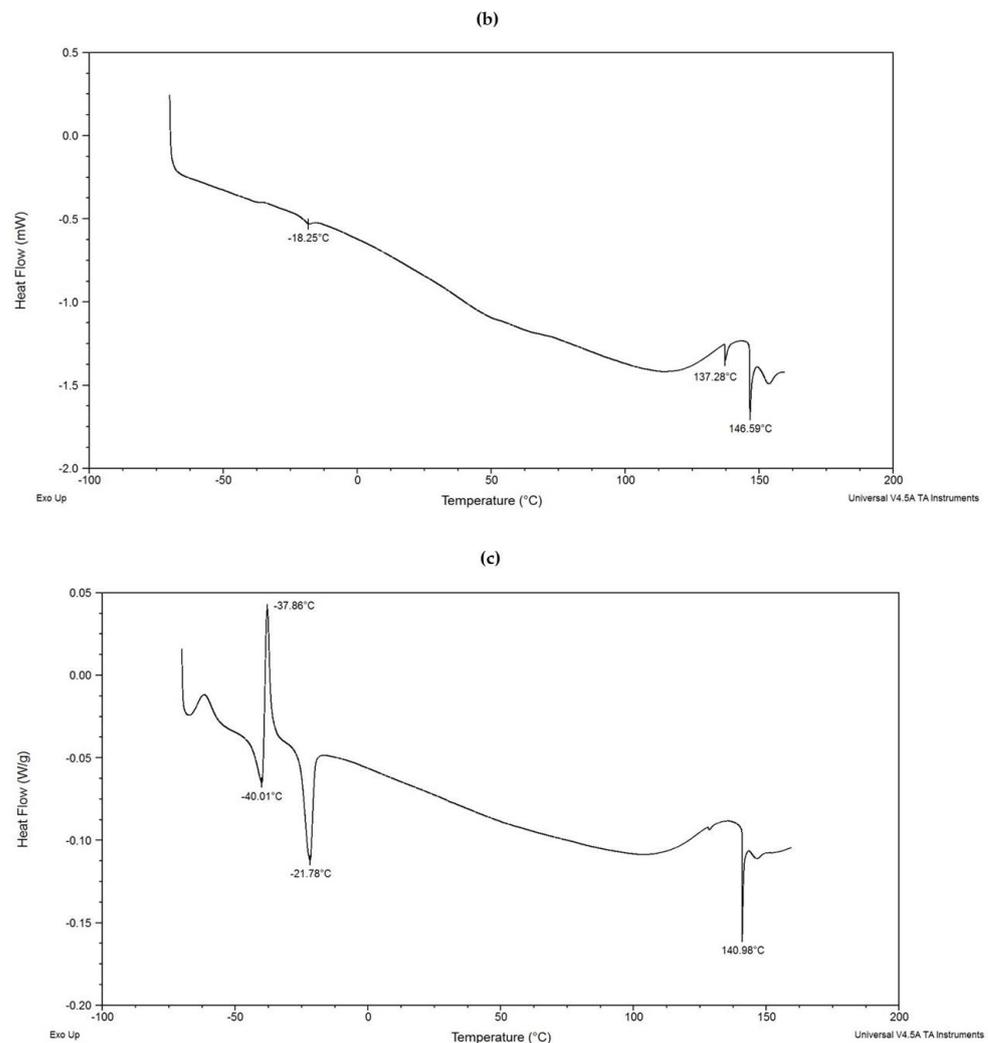


Figure 1. DSC curves for (a) blackberry, (b) chokeberry, (c) raspberry seeds.

3.1.3. MDSC of Seeds

To investigate the stability of the berry seeds, it is reasonable to determine the glass transition temperature. The parameter has been proven to be an effective indicator of food quality changes during storage. Food products are expected to be fairly stable below the T_g , but when the temperature rises above T_g , a solid structure is transformed to a supercooled liquid state with a time-dependent flow. The amorphous matrix may exist either as a very viscous glass or as a more liquid-like rubber [28]. At a glass transition temperature, changes occur from the glass state to the rubbery state [29].

In the present study, DSC curves of reversing heat flow versus temperature were recorded to determine the glass transitions' temperatures of samples. Experimental values of the glass transition temperatures presented in Table 2 are reported with parameters indicating their onset, midpoint, and endpoint values to define the width of the transition. Based on the obtained results, it can be stated that in the case of samples of berry seeds, a single glass transition was observed. The onset glass transition temperature of the samples in the study ranged from $28.26\text{ °C} \pm 0.17$ for raspberry seeds to $73.66\text{ °C} \pm 1.46$ for blackberry seeds, the midpoint T_g was $29.31\text{ °C} \pm 0.11$ and $74.09\text{ °C} \pm 1.23$ for raspberry and blackberry seeds, respectively, and the endpoint T_g was $30.36\text{ °C} \pm 0.15$ for raspberry seeds and $74.11\text{ °C} \pm 1.41$ for blackberry seeds. It is worth mentioning that the glass transition temperature reached the highest value for blackberry seeds, which were characterized by the lowest value of water activity. In the case of raspberry seeds, for which the highest water activity was determined, the glass transition temperature had the lowest value. Obtained

results confirmed the statement that the glass transition temperatures of materials are mainly dependent on the water activity and chemical composition of the material [30–32]. Based on the obtained results, it can be stated that an increase in water activity of studied samples caused a decrease in T_g values.

Table 2. Experimental glass transition temperatures of studied berries seeds.

Source of Seeds	T_g Onset (°C)	T_g Midpoint (°C)	T_g Endpoint (°C)
Blackberry	73.66 ± 1.46	74.09 ± 1.23	74.11 ± 1.41
Chokeberry	55.14 ± 0.89	55.27 ± 0.78	55.40 ± 1.08
Raspberry	28.26 ± 0.17	29.31 ± 0.11	30.36 ± 0.15

3.1.4. TG/DTG of Seeds

The results of the TG analysis are TG curves with calculated and graphically presented first derivatives, which refers to a mass loss of sample as a consequence of thermal decomposition, presented in Figure 2. The pyrolysis behaviors of all the studied seeds were similar. Considering milled seeds tested under a nitrogen atmosphere, small mass losses of up to 3% occurred first, at temperature ranges of 50–140 °C; these were a consequence of water and volatile compounds' evaporation from samples. The next two incidents of mass losses at temperatures of 120–230 °C were connected to carbohydrates degradation. The largest decomposition of samples (49% for blackberry seeds, 44% for raspberry seeds, and 30% for chokeberry seeds) occurred at temperatures of 300–500 °C and were due to the further pyrolysis of organic compounds: carbohydrates and also fat. As it comes to whole seeds tested under a nitrogen atmosphere, the mass losses resulting from thermal decomposition occurred in a different range of variability for temperatures. The first degradation, due to water and volatile compounds evaporation, was present up to a temperature of around 160 °C. Second mass losses at around 160–300 °C were combined with carbohydrates pyrolysis. The two largest mass losses at temperatures of 300–375 °C and 375–550 °C were due to fat and further organic compounds degradation. Duman et al. obtained comparable courses of thermogravimetric curves for cherry seeds; the weight losses were observed at a temperature range of 200–500 °C, although the highest mass losses were registered at temperatures characteristic of saccharides decomposition [33]. In the TG study conducted under a nitrogen atmosphere, 27–36% of the mass of the sample remained undegraded in the range of temperatures from the following study. The remaining part was ash, containing thermostable inorganic compounds. The TG analysis under an oxygen atmosphere resulted in curves with three to four weight losses for milled seeds. Chokeberry and blackberry seeds were decomposed in four main steps; chokeberry seeds—with first two losses of about 3% at 50–125 °C and 12% at 125–240 °C and two following almost equal losses of 42% at 240–370 °C and at 370–515 °C of 41% weight; blackberry seeds—with a loss of over 7% at 50–190 °C, 8% at 190–240 °C, and the next two similar as in the samples of blackberry seeds: 44% at 240–370 °C and 36% at 370–515 °C. In the case of the raspberry seeds TG curve, three weight losses were registered, around 14% of the mass was lost at 50–220 °C, 48% at 20–380 °C, and 35% at 380–500 °C. The first events occurring at lower temperatures of up to 125 °C for chokeberry and 190 °C for blackberry seeds are a result of moisture and volatile compounds evaporation from the sample. Following events of decomposition at temperatures that range up to 515 °C are connected to organic compounds degradation, i.e., saccharides and lipids.

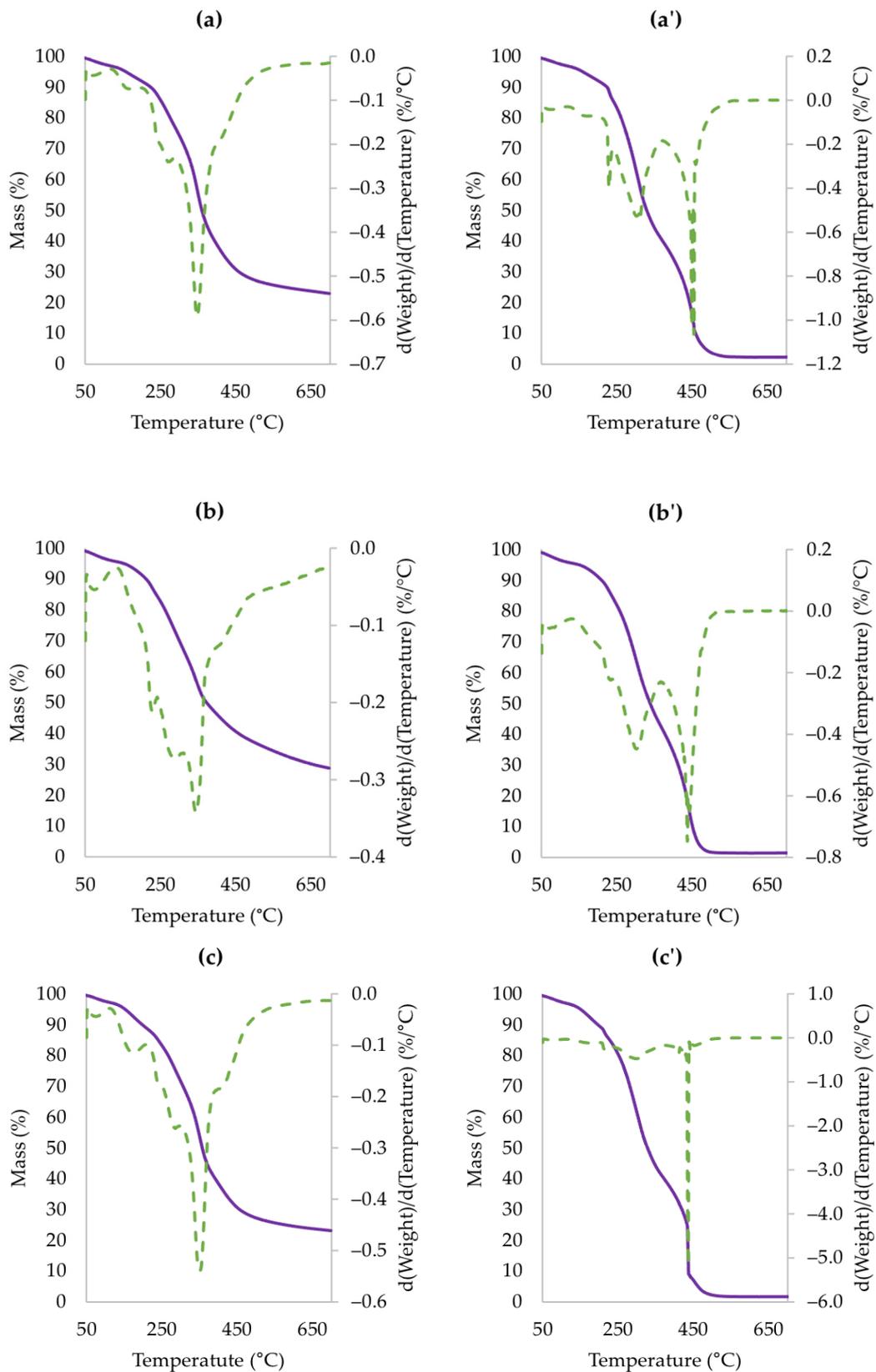


Figure 2. Examples of TG/DTG curves of milled (a) blackberry, (b) chokeberry, (c) raspberry seeds under nitrogen atmosphere, and of milled (a') blackberry, (b') chokeberry, and (c') raspberry seeds under oxygen atmosphere.

Whole seeds of all fruits were pyrolyzed and registered three main weight losses. However, ranges of temperatures of single degradations were different for the studied

seeds. Blackberry seeds lost around 26% at 50–325 °C, 20% at 325–375 °C and 51% at 375–475 °C. For chokeberry seeds, a first weight loss of 26% was noticed at 50–300 °C, a second of 29% at 300–400 °C, and a last of 39% at 400–475 °C. Raspberry seeds at a temperature range of 50–180 °C lost about 7% of mass, at 180–375 °C 36%, and at 375–475 °C lost over 52% of weight. Whole seeds do not contain as many saccharide residues as milled seeds, which may be contaminated with the remains of fruit material, which is the cause of decomposition events occurring at temperatures characteristic to lipids degradation.

In contrast to analysis under a nitrogen atmosphere, in an oxygen atmosphere, ash constituted up to 5.8% in samples of milled blackberry seeds.

3.2. Study of Oil Obtained from Seeds

3.2.1. Oil Extraction Efficiency

Fat extraction yields from milled seeds were as follows: 12.43% for blackberry seed oil, 8.19% for chokeberry seed oil, 14.25% for raspberry seed oil. According to Bada et al. [34], oil yield obtained by extraction in a Soxhlet apparatus using hexane as a solvent ranged from 15.68% for blackberry and 10.55% for raspberry seed oils. Wajs-Bonikowska et al. [35] yielded 11.8% blackberry seed oil in that method, although the process was carried for 8 h. In the same study, ethanol was used as a solvent in a comprehensive run and resulted in a higher oil yield than hexane.

3.2.2. Gas Chromatography (GC) of Extracted Oils

The results of the gas chromatography study are chromatograms; the blackberry seed oil chromatogram is presented as an example in Figure 3. The fatty acids profile of extracted berries seed oils is presented in Table 3. Based on the obtained results, it can be seen that the studied oils are rich in unsaturated fatty acids, especially polyunsaturated fatty acids. In raspberry seed oil, unsaturated fatty acids percentage is the highest from studied oils and values at a level of over 94%. In all of the extracted fats, the main group of unsaturated fatty acids are polyunsaturated fatty acids. The percentage of monounsaturated fatty acids ranges from $11.95 \pm 0.00\%$ to $18.21 \pm 0.06\%$ for raspberry seed oil and chokeberry seed oil, respectively. For the extracted oils, the most abundant fatty acid was linoleic acid (C 18:2) with values of $62.53 \pm 0.06\%$, $67.62 \pm 0.04\%$, and $51.44 \pm 0.04\%$ for blackberry, chokeberry, and raspberry seeds oils, respectively. The second most frequent fatty acid considering blackberry and raspberry seed oils was α -linoleic acid, with percentages ranging from $16.19 \pm 0.01\%$ for blackberry seed oil and $30.56 \pm 0.04\%$ for raspberry seed oil, in the case of chokeberry seed oil, oleic acid ranged from $17.48 \pm 0.04\%$.

Table 3. Fatty acid profile (%) of berry seed oils.

Fatty Acid	Blackberry Seed Oil	Chokeberry Seed Oil	Raspberry Seed Oil
C 16:0	4.52 ± 0.19	5.44 ± 0.02	2.92 ± 0.03
C 16:1	0.13 ± 0.01	0.15 ± 0.01	0.08 ± 0.01
C 18:0	2.87 ± 0.03	1.39 ± 0.07	1.45 ± 0.03
C 18:1 <i>n</i> -9	12.17 ± 0.01	17.48 ± 0.04	11.74 ± 0.00
C 18:2 <i>n</i> -6	62.53 ± 0.06	67.62 ± 0.04	51.44 ± 0.04
C 18:3 <i>n</i> -3	16.19 ± 0.01	0.92 ± 0.03	30.56 ± 0.04
C 20:0	1.06 ± 0.06	0.81 ± 0.03	0.62 ± 0.03
C 20:1	0.38 ± 0.01	0.25 ± 0.02	0.14 ± 0.01
C 20:2	n.d.	5.26 ± 0.21	0.33 ± 0.01
C 22:0	0.18 ± 0.02	0.38 ± 0.01	0.34 ± 0.02
other	n.d.	0.35 ± 0.00	0.41 ± 0.03
∑ SFA	8.62 ± 0.09	8.02 ± 0.08	5.32 ± 0.04
∑ MUFA	12.67 ± 0.02	18.21 ± 0.06	11.95 ± 0.00
∑ PUFA	78.72 ± 0.06	73.79 ± 0.14	82.74 ± 0.03

(C16:0—palmitic acid, C16:1—palmitoleic acid, C18:0—stearic acid, C18:1—oleic acid, C18:2—linoleic acid, C18:3— α -linolenic acid, C20:0—arachidic acid, C20:1—pauillenic acid, C20:2—eicosadienoic acid, C22:0—behenic acid, ∑PUFA—sum of polyunsaturated fatty acids, ∑MUFA—sum of monounsaturated fatty acids, ∑SFA—sum of saturated fatty acids; n.d.—not detected).

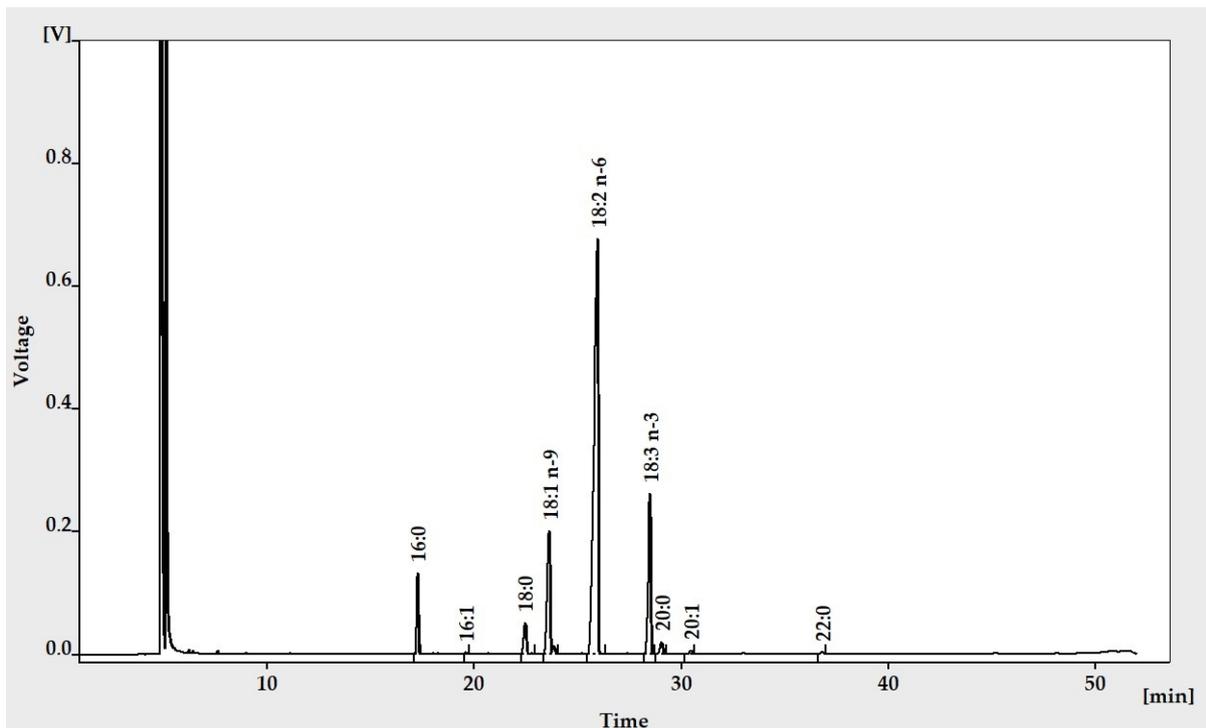


Figure 3. Chromatogram of blackberry seed oil (16:0—palmitic acid, 16:1—palmitoleic acid, 18:0—stearic acid, 18:1—oleic acid, 18:2—linoleic acid, 18:3— α -linolenic acid, 20:0—arachidic acid, 20:1—pauilnic acid, 22:0—behenic acid).

The obtained results are consistent with previous findings. Bada et al. [34] studied the fatty acid composition of blackberry and raspberry seed oils extracted in the Soxhlet apparatus. Blackberry oil consisted of 83.78%, 8.40%, and 6.49% of PUFA, MUFA, and SFA, respectively. In raspberry oil, PUFA accounted for 81.05%, MUFA 12.81%, and SFA 4.13%. In both oils, linoleic acid is the most abundant fatty acid. In another study, the blackberry and raspberry seed oil proportions of fatty acid groups were: 74.94%, 17.87%, and 7.13% in blackberry oil and 82.52%, 13.21%, and 4.23% in raspberry oil for PUFA, MUFA and SFA, respectively [36]. Chokeberry seed oil extracted using chloroform and methanol as solvents consisted of 73.58% of PUFA, 16.91% of MUFA, and 9.51% of SFA, with a linoleic acid occurring as a dominant [37]. The specific fatty acid composition affects oil properties. High values of PUFAs may result in a decreased oxidative stability of the plant oils [38]. However, oils rich in PUFAs show high nutritional value as they are recommended by FAO/WHO as an SFA replacement in diet [39]. Considering novel nutritional indices of fat, PUFA/SFA ratios of berry seed oils, ranging 9.13, 9.20, and 15.55 for blackberry, chokeberry, and raspberry oils, respectively, are values adequate enough to classify berry seed oils as nutritionally valuable [40].

3.2.3. PDSC of Extracted Oils

PDSC analysis is a tool to determine the value of induction time of an oxidation reaction. This parameter is essential to describe oil stability in conditions of oxidative degradation. In this study, PDSC was conducted at isothermal conditions at a temperature of 120 °C. The PDSC curves for blackberry, chokeberry, and raspberry seed oils are presented in Figure 4.

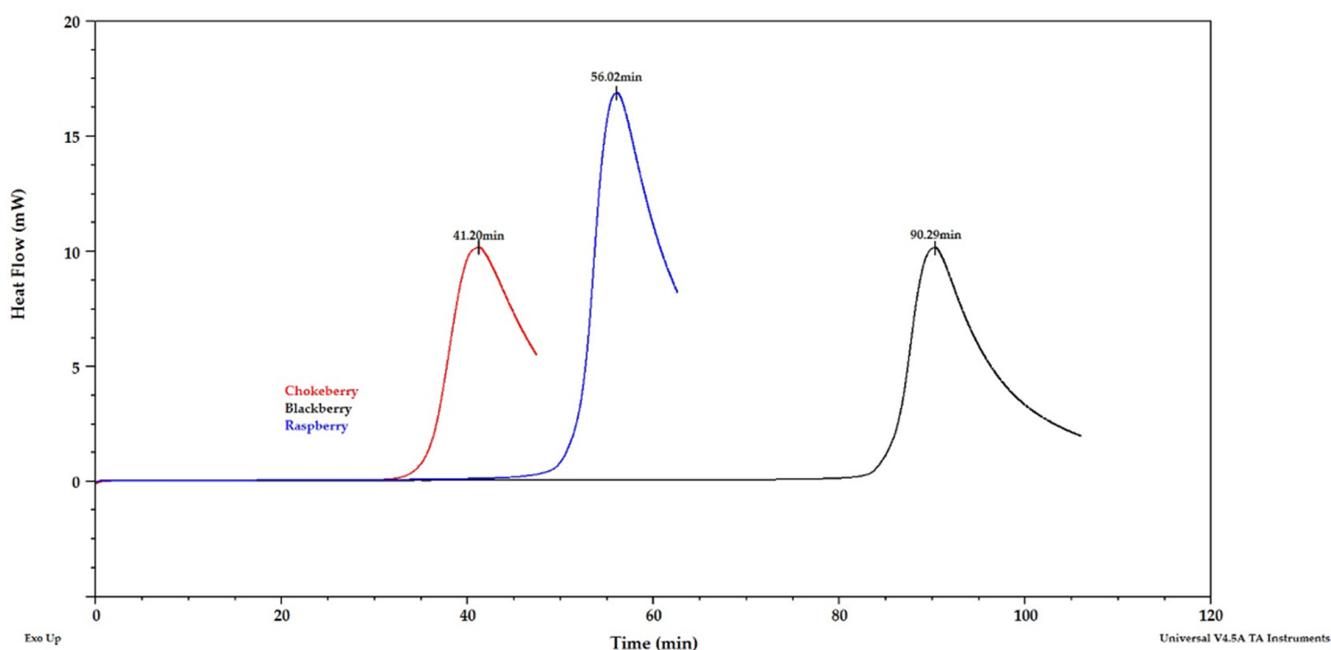


Figure 4. PDSC curves showing oxidation induction times of blackberry, chokeberry, and raspberry seed oils.

It can be observed that values of induction time of oxidation reaction for oils are different. At 120 °C, chokeberry seed oil has the shortest induction time lasting 41.20 min, followed by raspberry seed oil with a result of around 56.02 min. The highest value is seen in blackberry seed oil which amounts to over 90.29 min. The results for chokeberry and raspberry oils from the following study were lower than for rapeseed oils at 120 °C, valued from 66.61–74.78 min in a study by Symoniuk et al. [41] or than soybean oil with a 63.1 min induction time [15]. Ciemniewska-Żytkiewicz et al. reported induction times for hazelnut oil and olive oil, and the results were higher than for berry seed oils in the following study. Times of oxidative reactions ranged from 119.95–191.06 min and 134.15–180.07 min for hazelnut oil and olive oil, respectively [42]. Considering that, the studied berries oils are not as oxidatively stable as hazelnut or olive oil. However, the examined berry oils have higher induction times and may be considered as more stable in 120 °C than the linseed oil studied by Symoniuk et al. with an induction time of 21.20–24.72 min [43], camelina oil with the result of 26.81–35.85 min [44], and sunflower oil with a 33.4 min time of oxidative reaction [15].

3.2.4. TG/DTG of Extracted Oils

Examples of TG/DTG curves of the studied seed oils are presented in Figure 5. TG curves with calculated derivatives of oils under nitrogen atmosphere show a similar course for all of the studied samples. Three mass losses can be noticed. For chokeberry oil, the temperature range of the first decomposition reaches up to 250 °C with around 4% of weight loss, the second reaches temperatures of 250–480 °C with the most significant loss of weight of 94%, and the final loss accounts for over 1%. For blackberry and raspberry oils, temperature ranges are the same, and a first decomposition of around 2.5% and 6% weight of blackberry oil and raspberry oil, respectively, is observed at a temperature of up to 300 °C. In temperatures of around 300–500 °C, over 96% of blackberry oil and 93% of raspberry oil is decomposed. A final loss of less than 1% of weight was noticed at over 500 °C.

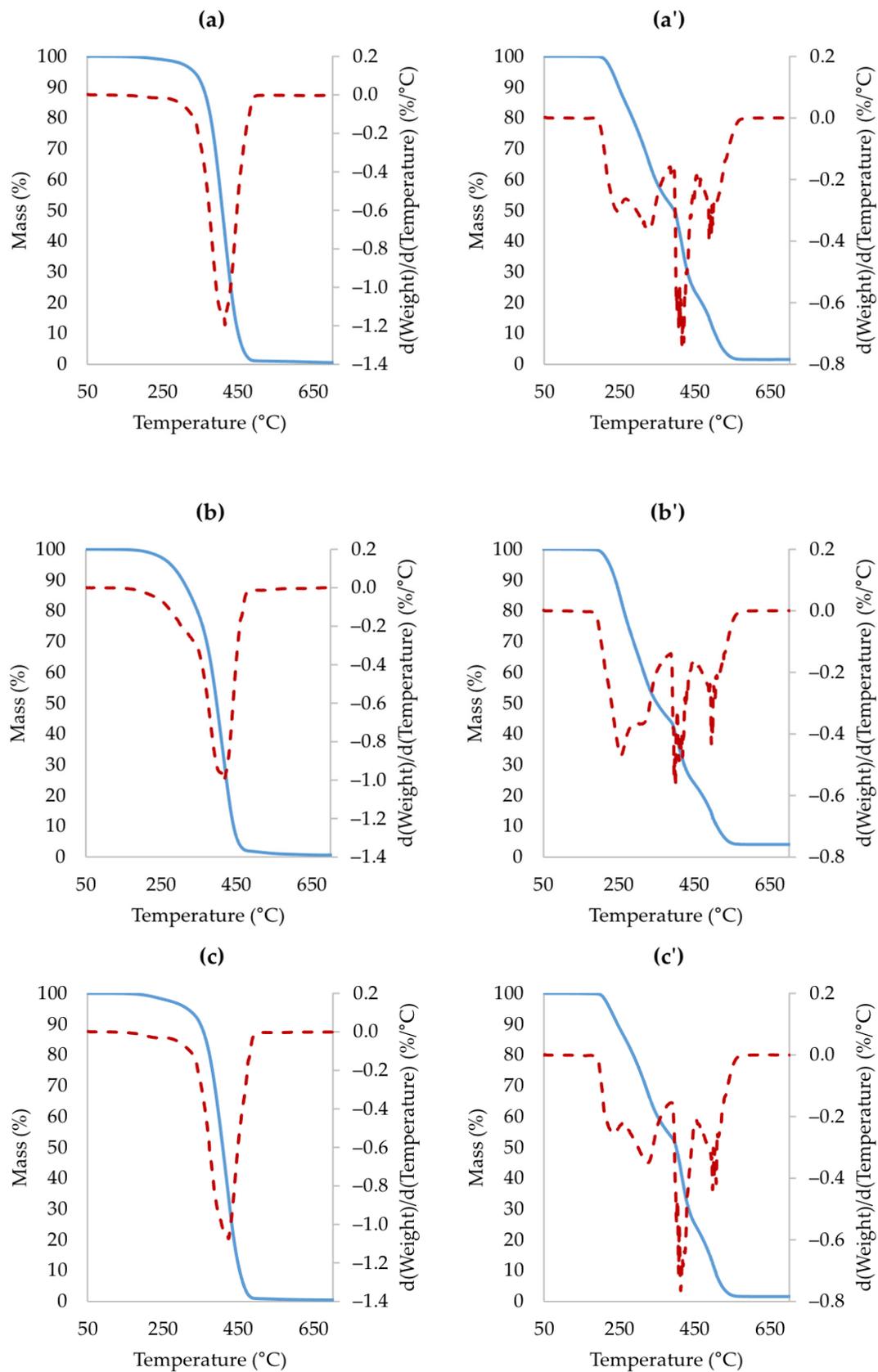


Figure 5. The examples of TG/DTG curves of (a) blackberry, (b) chokeberry, (c) raspberry seed oils under nitrogen atmosphere, and (a') blackberry, (b') chokeberry, (c') raspberry seed oils under an oxygen atmosphere.

Under an oxygen atmosphere, there are also three noticeable events at the same temperature ranges for all of the oils. First, at 200–380 °C, the highest mass loss amounts to 47%, 49%, and 57% of raspberry, blackberry, and chokeberry, respectively. The next decomposition occurring at 380–450 °C contributed to a loss of 20% of chokeberry oil, 27% of blackberry oil, and 29% of raspberry oil weights. The following mass loss amounts to 20–23% within oils.

The results are in agreement with the study of *Citrullus colocythis* by Nehdi et al. [45] carried out in the air atmosphere. The degradation in oil started after reaching a temperature above 286 °C, and it decomposed in four stages at temperatures: 377.4 °C, 408.4 °C, 434.9 °C, and 559.2 °C. Moreover, results of the TG study of sunflower oil were shown. Degradation of sunflower oil began at a temperature above 247 °C and it was also degraded in a four-stage weight-loss with maximum signals at 352.7 °C, 419.7 °C, 437.4 °C, and 541.7 °C. The temperatures of oil degradation in the following study are lower than for *C. colocythis* and sunflower oils due to differences in fatty acid composition. *C. colocythis* and sunflower oils contain more SFA and MUFA than berry seed oils and can be characterized by increased thermal stability.

4. Conclusions

Seeds from berry fruits are a waste product that can be reused to fortify the final product or to obtain high-quality oil in food or other industries. Applied methods of thermal properties studies are appropriate to determine the stability and quality of seeds and oils extracted from seeds. All of the studied seeds have similar properties determined in DSC, MDSC, and TG analyses. Slight differences in the thermal and physical properties of berries seeds are determined by their chemical composition and water activity. The DSC study revealed that berry seeds are composed of low-melting, middle-melting, and high-melting fractions of triacylglycerols and that the polymorphism phenomenon of fat occurs in raspberry and blackberry seeds. Moreover, the properties of seeds are affected by residues of carbohydrates in samples, which is seen in the results of the DSC and TG studies. However, the thermal decomposition of seeds during the TG analysis is incomplete due to the content of inorganic, thermally stable compounds in the material. Oils extracted from berries seeds have a high contribution of PUFA, with a dominance of linoleic acid and a low contribution of SFA, and that impacts their thermal and oxidative stabilities. Blackberry oil with the highest content of SFA has the highest oxidative stability, which was noticed in the PDSC study. That dependence does not apply to chokeberry and raspberry seed oils, as raspberry seed oil has the lowest percentage of SFA but is still more stable than chokeberry oil. This may be related to the specific fatty acid composition of chokeberry oil, with the highest linoleic acid content among all studied oils. Additionally, in the TG analysis of oils, main weight losses are contributed to PUFA degradation. The oils can be recovered and further used as they are rich in essential fatty acids and have an adequate PUFA/SFA ratio up to 15.55 for raspberry seed oil. Further research is needed on the properties of oils obtained from berries by-products to determine their possible applications and changes during technological processing or storage.

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