

Correlation between Vegetable Oil Oxidation Kinetics and Triacylglycerol Compositions Based on Thermogravimetry

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Abstract: Thermogravimetry (TG) and derivative thermogravimetry (DTG) were used to investigate the thermal oxidative properties of six normal vegetable oils. The influence of different heating programs on the weight changing curves was studied and the onset oxidation temperature (T_{on}) and peak oxidation temperature (T_p) were located from the DTG curves. Through the application of Ozawa – Flynn – Wall iso-conventional method, the oxidation kinetic properties of oils were deduced and the correlation between thermal behaviors and triacylglycerol composition was analyzed. The results showed that both T_{on} and T_p were increased with the raise of heating rate and T_p was varied more sensitively, which indicated that the reactions occurred around T_p could be more acuminous to the change in surroundings. Varying degrees of correlation were found between thermal behaviors and triacylglycerol distribution; T_{on} and $E_a(T_{on})$ were found to be positively correlated with high saturated triacylglycerols but negatively correlated with high unsaturated ones. Similar results were found between T_p , $E_a(T_p)$ and various components but with weaker correlations. Specific correlation was depended on the type of fatty acid chains on glycerol skeletons. Thus, predictions of oil thermal stability could be done according to the triacylglycerol profiles. Thermogravimetry analysis was praised for trace sample size, fast operation and high sensitivity, which would show promising prospect in oil processing and quality control.

Key words: vegetable oil; oxidation kinetics; thermogravimetry; derivative thermogravimetry; correlation

0 Introduction

Vegetable oil is not only considered as an important part of the human dietary pattern, but also a major raw material in food processing industry. However, being exposed to light, heat or catalytic metals during storage, transportation and processing, vegetable oil is susceptible to oxidative deterioration, which is commonly known as the free radical chain mechanism. After a series of complicated reactions, the primary oxidation products finally lead to the formation of off-flavor compounds (aldehyde, ketone, acid) and toxic epoxides^[1-2], resulting in decreased sensory acceptability and nutritional value. Consuming oxidized oil could also induce multiple physiological disorders in human bodies, such as damage in enzyme system and accelerated lipid peroxidation^[3]. Therefore, monitoring and controlling the oil oxidation process has long been a major hotspot in oil theoretical

research. To detect the oil oxidation degrees, numerous methods have been proposed, such as iodometry, ferric thiocyanate method, thiobarbituric acid (TBA), active oxygen method (AOM), Schall oven method and Rancimat^[4-5]. Being one commonly used thermal analysis instrument, thermogravimetry (TG) can precisely record the mass variation of sample under different heating time or temperature. With the help of hypersensitized scale, the TG method could be applied to evaluate the oil oxidative stability, to determine the oil oxidative induction time, enthalpy change of reaction, initial decomposition temperature, etc^[6-7]. Compared with traditional methods, TG showed advantages of trace sample size, quick operation, and free of organic reagents. Thus it has been gradually applied in oil processing, quality control and new-type antioxidant research and development.

Oil oxidation is complex reactions which involve

multiple external and internal factors. Among them, the triacylglycerols (TAG) in oil represents not only the existence form of fatty acid but also the major substrate in oil deterioration. Thus, close relationship must exist between the oil oxidative process and its TAG compositions^[8]. During oil oxidation, several complex reactions including oxidation, fission and aggregation happened simultaneously, resulting quality changes in sample. Through recording these variations accurately, the TG method could monitor the intact oxidation progress. And with the combination of kinetic modeling, deduction of kinetic parameters and correlation study with chemical compositions, the oxidative properties of vegetable oil could further be elucidated^[9-14]. VECCHIO et al.^[9] compared the thermal decomposition kinetics of extra virgin olive oil as well as 4 saturated and unsaturated TAGs using TG and DTG. TOMASSETTI et al.^[14] also reported the degradation processes of 5 saturated mono-, di- and tri-glycerides with these two methods. While, these existing studies showed uncomplete characterization of the oxidation course and uncomprehensive consideration of chemical compositions. Thus the goal of this paper is to determine the TG and DTG curves of various vegetable oils under different temperature programs and with the combination of temperature location, kinetic parameters calculation and Pearson correlation study, the relationship between oxidative properties and chemical compositions could be further discussed.

1 Materials and Methods

1.1 Materials and instruments

Totally 6 oil samples were chosen according to their different fatty acid compositions and unsaturation degrees: palm oil from Yijiang (Zhangjiagang) Cereal and Oil Industry Co., Ltd.; olive oil from Shanghai Dongsan Enterprise Development Co., Ltd.; sunflower oil from Shandong Xiwang Food Co., Ltd.; soybean oil from Zhangjiagang Zhongliang Donghai Cereal and Oil Industry Co., Ltd.; sesame oil from Tianjin Jiali Cereal and Oil Industry Co., Ltd. All the oil samples were purchased from local markets with similar manufacture date, consistent purification degree and labels showing free of artificial antioxidants. These oil samples were stored at 4°C in brown bottles without

headspace before analysis. Hexane, carrene, acetone and acetonitrile are of chromatographic grade.

STA449 F3 simultaneous thermoanalyzer coupled with bottom mounted electronic balance, mass flowmeter and NETZSCH – Propeus – 6.1 data analysis software (Netzsch, Bavaria, Germany); Eksigent HPLC – TripleTOF 4600 system, AB SCIEX, CA, USA; ZORBAX SB a C18 column (250 mm × 4.6 mm, 5 μm, Agilent Technologies, USA).

1.2 Experimental method

1.2.1 Thermogravimetry analysis

Oxygen (99.99%, 80 mL/min) was used as the purge gas and nitrogen (99.99%, 20 mL/min) as the protective gas. To ensure constant interaction with the oxygen stream and uniformity of heat conduction, an oil sample of (3.0 ± 0.5) mg was weighed into an aluminum pan hermetically sealed with a pinhole lip in the center^[13]. The systems were equilibrated at 30°C for 5 min and then heated to 400°C at 5 heating rates (5.0°C/min, 7.5°C/min, 10.0°C/min, 12.5°C/min, and 15.0°C/min) to generate the TG and DTG curves under each program.

1.2.2 Confirmation of temperatures and deduction of kinetic parameters

Since the tiny sample size here gives minor variation of TG curves during oxidation, the corresponding DTG curves were obtained by operating a first-order derivative of the TG data^[9, 14]. The onset oxidation temperature (T_{on}) was regarded as when the DTG curve deviated away from the baseline and the peak oxidation temperature (T_p) was obtained when the DTG curve bottomed out after the 1st peak (Fig. 1)^[9, 11, 15].

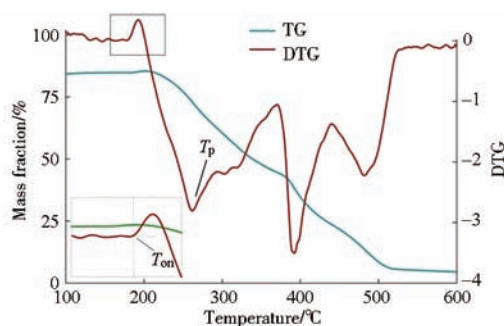


Fig. 1 Confirmation of the onset oxidation temperature and peak oxidation temperature of TG curve

Under the non-isothermal condition in this study, the oil oxidation kept proceeding in the excess state of O_2 , which means the process was independent of the

O₂ concentration and followed a first order reaction^[9, 11, 13]. Using the Ozawa – Flynn – Wall iso-conventional method and temperature parameters (T_{on} , T_p) obtained, the activation energy (E_a) and pre-exponential factor (A) were calculated using following equations.

$$\lg \beta = a \frac{1}{T} + b \quad (1)$$

Where β is the heating rate, K/min; T is the corresponding temperature T_{on} or T_p , K.

Through plotting $\lg \beta$ against $\frac{1}{T}$, the activation energy (E_a , J/mol) and pre-exponential factor (A , min⁻¹) can be directly computed using Eq. (2) ~ (3).

$$a = -0.4567 \frac{E_a}{R} \quad (2)$$

$$b = -2.315 + \lg \left(A \frac{E_a}{R} \right) \quad (3)$$

Where a and b are the slope and intercept of Eq. (1), respectively, R is the universal gas constant (8.314 J/(mol·K)).

1.2.3 Determination of triacylglycerols

The TAG composition was identified using HPLC coupled with a tandem quadrupole mass spectrometer and a C18 column. TAG separation was performed using n-hexane and dichloromethane as mobile phase A (1:1) and acetone and acetonitrile as mobile phase B (5:95). As previously reported, the energy needed to break a fatty acid at sn-2 is larger than that at sn-1 or sn-3^[18-20]. Thus the TAG variety at the glycerol skeleton can be inferred from the ion peak intensity and m/z number difference in the APCI spectrogram. Quantification could also be done through area normalization. The following elution program was performed: 0 ~ 20 min, held at 20% A; 20 ~ 35 min, increased to 80% A; 35 ~ 45 min, decreased back to 20% A. The column temperature and flow rate were set at 40°C and 0.6 mL/min.

1.2.4 Statistical analysis

All the tests were done in triplicate. The mean value, standard deviation, significant difference (Turkey multiple test, 95% confidence level) and Pearson correlation between thermal oxidation properties and TAG composition were conducted using the SPSS software (Version 22.0, SPSS Inc., Chicago, IL, USA). Kinetic linear fitting was

performed using Sigma Plot (Version 12.5).

2 Results and discussion

2.1 Determination of oil sample oxidation progress using TG/DTG

Fig. 1 shows the TG and DTG curves of olive oil under the heating rate of 5°C/min. The mass variation of oil sample during thermal decomposition could be exactly monitored through the DTG data. As previously illustrated, the oil oxidation progress mainly goes through three stages among 100 ~ 600°C: 160 ~ 280°C refers to the decomposition of saturated and unsaturated fatty acid chains (in some cases the first stage may prolong to 350°C, as shown in Fig. 2); 280 ~ 400°C refers to the oxidation of volatile components; 400 ~ 600°C refers to the reaction of carbon residues^[9, 14]. During the whole oil oxidation, the 1st stage mainly involved the free radical chain reaction of the fatty acid at glycerol skeleton. Thus, two temperatures, i. e., T_{on} and T_p were chosen here to present different oxidative gradations.

Totally 6 oil samples were heated under non-isothermal conditions using 5 heating rates (5.0°C/min, 7.5°C/min, 10.0°C/min, 12.5°C/min, and 15.0°C/min) and the corresponding DTG curves are shown in Fig. 2. Olive oil, sunflower oil, corn oil and sesame oil share similar peak type which is narrow and small, while palm oil and soybean oil show the curve which is much more complanate. As the heating rate increased, all DTG peaks from 6 oil samples shifted towards higher temperatures, which is in agreement with previous studies^[12, 14, 21]. As also shown in Tab.1, both T_{on} and T_p increased as the heating rate rose. For instance, the T_{on} and T_p of sunflower oil at 5°C/min were 163.22°C and 308.15°C, respectively, while they became 178.18°C and 348.80°C at 15.0°C/min. When being heated at lower rate, the sample in aluminum pan could interact with the purge gas consistently, but when warmed at higher rate, the thermal oxidation inside the pan became violent and the vapor produced could not escape out timely, resulting in irregular change of sample mass^[22].

2.2 Confirmation of temperature parameters and kinetic deduction

According to the method described in section 1.2.2,

the T_{on} and T_p of 6 vegetable oil samples under different heating rates were located based on their TG and DTG curves (Tab. 1). As early report, T_{on} was proposed to be closely correlated with the formation of peroxides during oxidation while T_p is related with the termination stage^[23]. As Tab. 1 shows, both T_{on} and T_p rose up as the heating rate ascended, indicating the increasement of oil oxidative temperatures. What can also be perceived from Tab. 1 is that T_p varied more notably

than T_{on} , for olive oil, when β increased from 5.0°C/min to 15.0°C/min, the T_{on} increased by 17.8°C while T_p varied by 31.42°C. Similar trends were also found by MONTEAGUDOS et al.^[11] when they studied the non-isothermal kinetics of anhydrous milk fat rich in conjugated linoleic acid. This phenomenon may imply that the reactions happened around T_p could be more vulnerable to the change in surroundings.

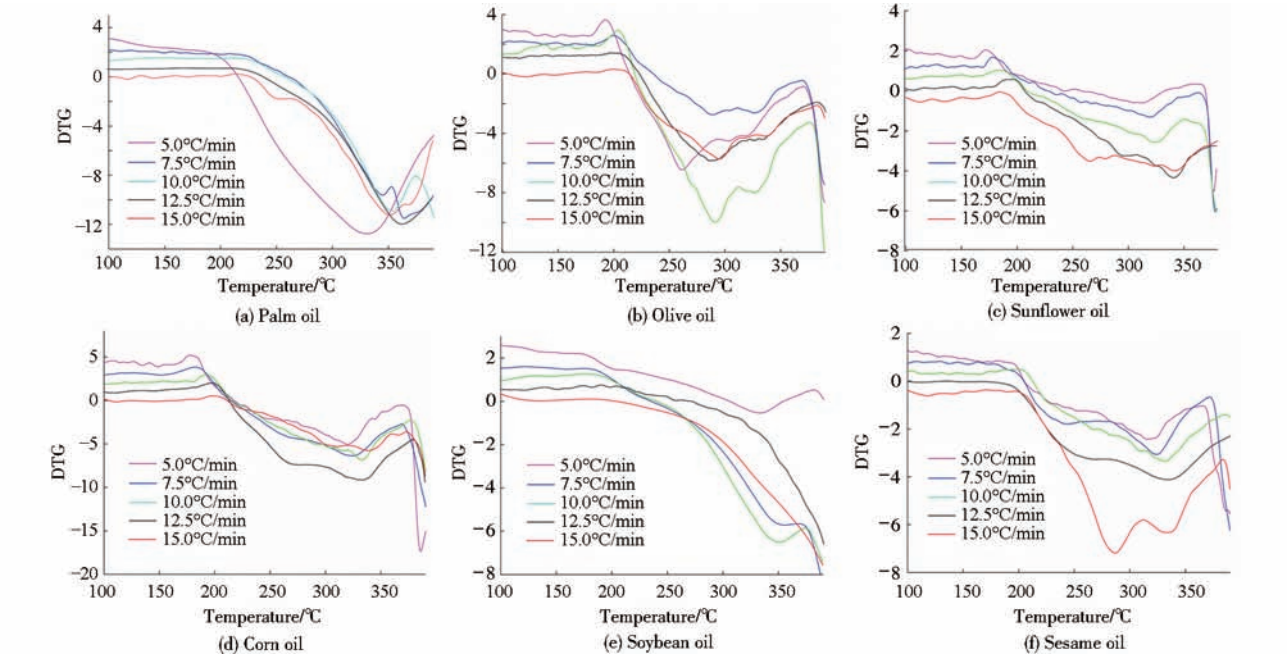


Fig. 2 DTG curves of vegetable oil samples at different heating rates

Tab. 1 Onset oxidation temperature and peak oxidation temperature of oil samples under different heating rates °C

	Heating rate/(°C·min ⁻¹)	Palm oil	Olive oil	Sunflower oil	Corn oil	Soybean oil	Sesame oil
T_{on}	5.0	199.91 ± 0.89 ^a	179.43 ± 1.40 ^e	163.22 ± 0.27 ^f	168.51 ± 0.53 ^e	172.72 ± 0.83 ^d	182.80 ± 0.33 ^b
	7.5	204.25 ± 0.75 ^a	182.09 ± 0.64 ^e	171.36 ± 1.41 ^e	174.07 ± 0.17 ^d	183.27 ± 0.42 ^c	187.62 ± 0.27 ^b
	10.0	209.26 ± 0.42 ^a	189.46 ± 0.15 ^e	175.37 ± 0.48 ^f	179.62 ± 0.50 ^e	188.22 ± 0.92 ^d	191.64 ± 1.15 ^b
	12.5	212.50 ± 0.22 ^a	193.40 ± 0.46 ^e	181.63 ± 0.60 ^e	184.51 ± 1.22 ^d	195.25 ± 0.21 ^b	—
	15.0	214.32 ± 1.02 ^a	197.25 ± 1.27 ^e	178.18 ± 0.26 ^e	187.80 ± 0.25 ^d	197.89 ± 1.03 ^c	200.19 ± 0.58 ^b
T_p	5.0	332.01 ± 0.85 ^a	266.06 ± 0.37 ^c	308.15 ± 0.14 ^d	310.07 ± 0.64 ^d	329.07 ± 0.21 ^b	313.18 ± 0.35 ^c
	7.5	344.92 ± 0.57 ^a	286.46 ± 0.70 ^d	323.26 ± 0.35 ^b	318.47 ± 0.85 ^c	—	322.94 ± 0.69 ^b
	10.0	353.23 ± 0.38 ^a	292.94 ± 0.46 ^d	327.72 ± 0.71 ^d	337.96 ± 0.35 ^c	356.90 ± 0.55 ^b	336.54 ± 0.15 ^c
	12.5	362.48 ± 1.02 ^a	295.53 ± 0.12 ^e	344.14 ± 0.58 ^c	338.84 ± 0.13 ^d	358.82 ± 0.48 ^b	340.48 ± 0.77 ^c
	15.0	—	297.48 ± 0.98 ^e	348.80 ± 0.89 ^b	351.94 ± 0.49 ^a	—	347.08 ± 0.30 ^b

Notes: The values followed by the same superscript letters in the same row are not significantly different ($p>0.05$), vice versa. “—” means that the temperature is undesirable due to the irregular migration of thermal gram.

Through applying the above T_{on} and T_p values into Ozawa – Flynn – Wall iso-conventional method, the linear relationship between $\lg \beta$ and $\frac{1}{T}$ could be potted. Take corn oil as an example (Fig. 3), its linear equation could be expressed as following: $y = -4\,909x + 11.83$ with the determination coefficient of 0.993 8.

Except for individual cases, the coefficients of the other oil samples were all above 0.94 (Tab. 2), stating the desirable fitness of OFW method. Thus the kinetic parameters were calculated using Eq. (1) ~ (3) and shown in Tab.2. The activity energies of the 6 oil samples at T_{on} were: palm oil, 132.50 kJ/mol; olive oil, 95.16 kJ/mol; sunflower oil, 90.69 kJ/mol;

corn oil, 89.32 kJ/mol; soybean oil, 71.29 kJ/mol; sesame oil, 106.44 kJ/mol. Their corresponding E_a at T_p were: palm oil, 92.73 kJ/mol; olive oil, 77.77 kJ/mol; sunflower oil, 74.37 kJ/mol; corn oil, 71.98 kJ/mol; soybean oil, 84.79 kJ/mol; sesame oil, 89.89 kJ/mol. Considering the complexity of oil systems and various reactions that happened simultaneously, the E_a values obtained here should be recognized as the apparent activation energy presenting by the numerous reactions happening around the temperature^[22, 24]. The values of E_a stand for the ease of reaction and can be used as one index to evaluate oil oxidative stability. When using T_{on} as the temperature, the oil stability order would be: soybean oil, corn oil, sunflower oil, olive oil, sesame oil and palm oil.

When using T_p that would be: corn oil, sunflower oil, olive oil, soybean oil, sesame oil and palm oil. This is slightly different from the orders using T_{on} , which indicated that one single parameter could not characterize comprehensively and multiple indexes from different reaction stages would be desired^[26].

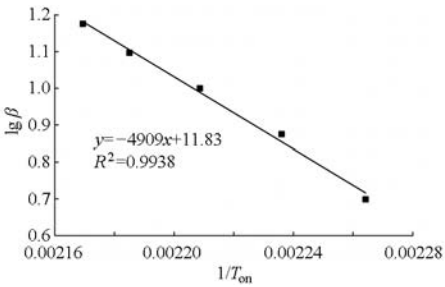


Fig.3 Linear relationship between onset oxidation temperature and heating rate of corn oil

Tab.2 Kinetic parameters of vegetable oil samples

	Parameters	Palm oil	Olive oil	Sunflower oil	Corn oil	Soybean oil	Sesame oil
T_{on}	$\lg \beta$ vs $1/T_{on}$	$y = -7\,282x + 16.10$	$y = -5\,230x + 12.30$	$y = -4\,984x + 12.11$	$y = -4\,909x + 11.83$	$y = -3\,918x + 9.478$	$y = -5\,850x + 13.55$
	$E_a / (\text{kJ} \cdot \text{mol}^{-1})$	132.50	95.16	90.69	89.32	71.29	106.44
	A / min^{-1}	1.63×10^{14}	3.60×10^{10}	2.44×10^{10}	1.30×10^{10}	7.24×10^7	5.72×10^{11}
	R^2	0.9928	0.9573	0.8940	0.9938	0.9920	0.9812
T_p	$\lg \beta$ vs $1/T_{on}$	$y = -5\,096x + 9.123$	$y = -4\,274x + 8.594$	$y = -4\,087x + 7.745$	$y = -3\,956x + 7.517$	$y = -4\,660x + 8.434$	$y = -4\,940x + 9.135$
	$E_a / (\text{kJ} \cdot \text{mol}^{-1})$	92.73	77.77	74.37	71.98	84.79	89.89
	A / min^{-1}	2.46×10^7	1.13×10^6	1.28×10^6	7.84×10^5	5.50×10^6	42.61×10^7
	R^2	0.9976	0.8934	0.9680	0.9480	0.9676	0.9852

2.3 Correlation between thermal oxidative properties and TAG composition

The TAG analysis of oil samples are summarized in Tab.3. According to the unsaturated degrees of fatty acid chains on the glycerol skeleton, the TAGs could be divided into trisaturated triacylglycerol (TSTAG), monosaturated triacylglycerol (MSTAG), desaturated triacylglycerol (DSTAG) and triunsaturated triacylglycerol (TUTAG). As shown in Tab.3, vegetable oils from different plan origins exhibited various TAG distributions and typical TAG moieties. The palm oil is rich in palmitic acid (C16:0) and oleic acid (C18:1)^[27] and its typical TAG is POO (31.77%) and PPO (28.41%). Its TSTAG (5.24%, undetectable in other 5 samples), MSTAG (50.35%) and DSTAG (42.52%) levels are also higher than the other oil samples while its TUTAG (1.89%) content is the lowest among oils^[20]. Olive oil is laden with oleic acid and ROO type TAGs, such as OOO (38.37%), OOL (18.18%) and POO (15.27%). Sunflower oil and corn oil shares similar

TAG profile, which has large amount of LLL + OLLn (39.91%, 28.44%) and OLL + OLPo (23.57%, 25.22%). Sunflower oil also exhibits highest level of TUTAG (72.52%). Soybean oil presents approximately 5% of linoleic acid and thus has significantly larger content of LLLn (9.12%)^[18]. Sesame oil shows uniform TAG profile and higher levels of MSTAG (33.31%) and DATAG (7.39%).

Through applying Pearson correlation analysis between thermal oxidative parameters (T_{on} , T_p and E_a) and TAG distributions, the correlation coefficients were obtained, values of which presents the impact of different TAGs on oil oxidative stabilities^[9]. To ensure the reliability of analysis, only contents larger than 1% were considered.

As the results shown in Tab.4, various degrees of correlation are observed between different TAGs and T_{on} , T_p and E_a . The E_a values at T_{on} shows positive correlation with higher saturated TAGs, such as MPL (0.83), PPL (0.89) and PPP (0.83) but negatively correlate with higher unsaturated ones, such as OLL +

Tab.3 Triacylglycerol compositions of vegetable oil samples

TAG	Palm oil	Olive oil	Sunflower oil	Corn oil	Soybean oil	Sesame oil
LLnLn	—	—	—	—	1.86 ± 0.03 ^a	—
LLLn	—	—	—	1.09 ± 0.05 ^b	9.12 ± 0.06 ^a	0.21 ± 0.01 ^c
MPP	0.48 ± 0.03 ^a	—	—	—	—	—
LLL + OLLn	—	1.68 ± 0.06 ^e	39.91 ± 0.07 ^a	28.44 ± 0.14 ^b	23.53 ± 0.09 ^c	11.15 ± 0.05 ^d
OLL + OLPo	—	6.92 ± 0.09 ^d	23.57 ± 0.14 ^a	25.22 ± 0.04 ^a	19.67 ± 0.16 ^b	17.34 ± 0.14 ^c
LLP	—	1.74 ± 0.11 ^e	10.44 ± 0.09 ^c	14.12 ± 0.05 ^b	16.51 ± 0.07 ^a	8.43 ± 0.10 ^d
MPL	2.31 ± 0.06 ^a	—	—	—	—	—
OOL	0.91 ± 0.02 ^c	18.18 ± 0.14 ^a	5.61 ± 0.11 ^d	8.38 ± 0.15 ^c	6.79 ± 0.05 ^d	15.67 ± 0.05 ^b
PLO + SLL	9.05 ± 0.05 ^b	6.51 ± 0.07 ^d	8.80 ± 0.06 ^c	9.08 ± 0.03 ^b	10.96 ± 0.09 ^a	8.40 ± 0.05 ^c
PPL	8.60 ± 0.01 ^a	1.90 ± 0.09 ^c	0.98 ± 0.04 ^c	1.21 ± 0.07 ^d	1.79 ± 0.03 ^c	5.52 ± 0.02 ^b
OOO	0.98 ± 0.03 ^f	38.37 ± 0.10 ^a	3.43 ± 0.07 ^d	4.78 ± 0.06 ^c	2.37 ± 0.06 ^c	14.93 ± 0.07 ^b
SLO	5.51 ± 0.09 ^a	2.63 ± 0.03 ^c	3.52 ± 0.06 ^b	2.59 ± 0.04 ^c	2.26 ± 0.12 ^d	3.18 ± 0.15 ^b
POO	31.77 ± 0.12 ^a	15.27 ± 0.06 ^b	1.50 ± 0.03 ^e	2.42 ± 0.08 ^d	2.38 ± 0.01 ^d	11.12 ± 0.09 ^c
PPO	28.41 ± 0.06 ^a	1.41 ± 0.05 ^c	1.07 ± 0.08 ^d	1.63 ± 0.11 ^b	0.95 ± 0.03 ^c	0.47 ± 0.02 ^f
SOO	4.06 ± 0.04 ^a	2.65 ± 0.03 ^b	0.53 ± 0.10 ^d	0.42 ± 0.03 ^d	0.65 ± 0.05 ^d	1.63 ± 0.05 ^c
PSO	2.26 ± 0.05 ^a	1.78 ± 0.08 ^b	—	—	0.63 ± 0.02 ^c	1.44 ± 0.03 ^b
MMM	0.51 ± 0.01 ^a	—	—	—	—	—
PPP	4.25 ± 0.02 ^a	—	—	—	—	—
AOO	—	0.35 ± 0.03 ^b	—	0.50 ± 0.06 ^a	—	0.51 ± 0.08 ^a
SSO	0.90 ± 0.08 ^a	0.45 ± 0.05 ^b	—	—	—	—
OOB	—	—	0.64 ± 0.06 ^a	—	0.48 ± 0.03 ^b	—
TSTAG	5.24 ± 0.11 ^a	—	—	—	—	—
MSTAG	50.35 ± 0.07 ^a	29.15 ± 0.06 ^c	25.43 ± 0.05 ^d	29.13 ± 0.05 ^c	33.24 ± 0.04 ^b	33.31 ± 0.04 ^b
DSTAG	42.52 ± 0.15 ^a	5.54 ± 0.11 ^c	2.05 ± 0.09 ^d	2.84 ± 0.03 ^c	3.37 ± 0.11 ^b	7.39 ± 0.08 ^b
TUTAG	1.89 ± 0.04 ^f	65.15 ± 0.07 ^c	72.52 ± 0.07 ^a	67.91 ± 0.06 ^b	63.34 ± 0.06 ^d	59.30 ± 0.08 ^c

Notes: M, myristic acid (C14:0); P, palmitic acid (C16:0); Po, palmitoleic acid (C16:1); S, stearic acid (C18:0); O, oleic acid (C18:1); L, linoleic acid (C18:2); Ln, linolenic acid (C18:3); A, arachidic acid (C20:0); B, behenic acid (C22:0).

OLPo (− 0.73). Its correlation with MSTAGs and DSTAGs is due to the moieties of unsaturated fatty acid chains, where positive correlate with the ones rich in oleic acid such as POO (0.90) but negative correlate with the ones rich in linoleic acids, such as LLP (− 0.81). Previous studies have reported that the saturated —CH₂— chains can inhibit radical attack towards fatty acid chains and thus enhance the TAG stabilities^[28]. Similar trends are also observed between the T_{on} values and TAG distributions even with highly significant correlations (MSTAG, 0.92). Therefore, the oil oxidative stabilities could be anticipated according to its chemical composition and T_{on} value. The T_p values present positive correlation with TSTAG as well as related TAGs but negative correlation with TUTAG and related moieties, such as OOO (− 0.92). Howbeit, no notable correlation is observed between T_p , MSTAG, DSTAG and other component. The E_a values at T_p also show weakened correlation with TAG components, of which the reason could be that the TAG oxidative reactions around T_p already entered the

Tab.4 Correlation analysis between thermal oxidation properties and triacylglycerol compositions of oil samples

TAG	T_{on}	$E_a(T_{on})$	T_p	$E_a(T_p)$
LLnLn	− 0.19	− 0.63	0.40	0.16
LLLn	− 0.23	− 0.66	0.41	0.11
LLL + OLLn	− 0.88 *	− 0.63	0.19	− 0.64
OLL + OLPo	− 0.89 *	− 0.73	0.09	− 0.62
LLP	− 0.75	− 0.81 *	0.33	− 0.40
MPL	0.84 *	0.83 *	0.46	0.62
OOL	− 0.15	− 0.24	0.78	− 0.17
PLO + SLL	− 0.15	− 0.33	0.86 *	0.21
PPL	0.94 * *	0.89 *	0.44	0.88 *
OOO	0.06	− 0.03	− 0.92 * *	− 0.16
SLO	0.73	0.90 *	0.41	0.56
POO	0.96 * *	0.90 *	0.09	0.68
PPO	0.83 *	0.83 *	0.45	0.60
SOO	0.93 * *	0.84 *	− 0.05	0.64
PSO	0.92 * *	0.72	− 0.09	0.75
PPP	0.84 *	0.83 *	0.46	0.62
TSTAG	0.84 *	0.83 *	0.46	0.62
MSTAG	0.92 * *	0.77	0.55	0.81
DSTAG	0.90 *	0.87 *	0.43	0.69
TUTAG	− 0.91 *	− 0.84 *	− 0.47	− 0.73

termination stage and series of secondary products have formed, which contributed to the sample mass. Furthermore, the oils evolved in this study contain small amount of natural antioxidants, such as tocopherol and polyphenol. There was no significant correlation between oil thermal kinetics and total phenol content since these compounds might had degraded before 200°C^[9,29]. Thus they were not considered in this paper.

3 Conclusions

The thermal oxidation properties of normal vegetable oils were studied using TG and DTG method. Both T_{on} and T_p shifted towards higher temperatures when heating rate increased and the later varied more notably. Through applying Ozawa – Flynn – Wall iso-conventional method, the kinetic modeling and calculation were conducted. The results showed satisfied fitness and the kinetic parameters (E_a , A) obtained can be used to present oil thermal stabilities. Meanwhile, by evaluating the correlations between oil thermal oxidative properties and TAG distributions, both T_{on} and $E_a(T_{on})$ showed positive correlation with higher saturated TAGs while negative correlation with higher unsaturated ones and the p values were determined by the fatty acid chains varieties. The T_p and $E_a(T_p)$ were also positive correlated with TSTAG but negatively correlated with TUTAG. Their correlations with MSTAG, DSTAG and other components were slightly weakened. This preliminary exploration of the “thermal oxidative property-chemical composition” illustrated the impact of multiple components on oil oxidation progress, which could be used for predicting oil stability, controlling oil processing, refining and storage condition.

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基于热重法的植物油氧化动力学-甘油三酯相关性研究

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摘要: 通过热重(TG)及微商热重(DTG)法研究了6种常见植物油的热氧化特性,分析了不同温控程序对质量变化曲线的影响,通过微商热重曲线确定了不同升温速率下的氧化起始温度(T_{on})和氧化峰值温度(T_p),结合Ozawa-Flynn-Wall等转化率法对油脂的氧化动力学特性进行推导,并对油脂热氧化特性与其甘油三酯组成与分布的相关性进行了分析。研究表明:随着升温速率的增加, T_{on} 和 T_p 均随之升高且 T_p 变化更为敏感;植物油的热力学特性与其甘油三酯组成间具有不同程度的相关性,其中, T_{on} 及 T_{on} 处活化能与高饱和度甘油三酯呈正相关而与高不饱和度甘油三酯呈负相关, T_p 及 T_p 处活化能与各组分间具有相似的关系但相关性略有减弱,具体相关性与甘油骨架上脂肪酸链的种类有关。热重分析法所需样品微量、操作快捷、灵敏度高,在油脂加工及质量检测领域具有广阔的应用前景。

关键词: 植物油; 氧化动力学; 热重分析; 微商热重分析; 相关性

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Correlation between Vegetable Oil Oxidation Kinetics and Triacylglycerol Compositions Based on Thermogravimetry

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Abstract: Thermogravimetry (TG) and derivative thermogravimetry (DTG) were used to investigate the thermal oxidative properties of six normal vegetable oils. The influence of different heating programs on the weight changing curves was studied and the onset oxidation temperature (T_{on}) and peak oxidation temperature (T_p) were located from the DTG curves. Through the application of Ozawa-Flynn-Wall iso-conventional method, the oxidation kinetic properties of oils were deduced and the correlation between thermal behaviors and triacylglycerol composition was analyzed. The results showed that both T_{on} and T_p were increased with the raise of heating rate and T_p was varied more sensitively, which indicated that the reactions occurred around T_p could be more acuminous to the change in surroundings. Varying degrees of correlation were found between thermal behaviors and triacylglycerol distribution: T_{on} and $E_a(T_{on})$ were found to be positively correlated with high saturated triacylglycerols but negatively correlated with high unsaturated ones. Similar results were found between T_p , $E_a(T_p)$ and various components but with weaker correlations. Specific correlation was depended on the type of fatty acid chains on glycerol skeletons. Thus, predictions of oil thermal stability could be done according to the triacylglycerol profiles. Thermogravimetry analysis was praised for trace sample size, fast operation and high sensitivity, which would show promising prospect in oil processing and quality control.

Key words: vegetable oil; oxidation kinetics; thermogravimetry; derivative thermogravimetry; correlation

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引言

植物油既是人群膳食结构中的重要组成部分,也是食品加工业重要的原料之一,然而油脂在储存、运输和加工过程中在光、热、催化金属等条件下易发生氧化劣变,其中以自由基链式反应为主,生成的初级氧化产物(氢过氧化物)经过一系列复杂反应生成醛、酮、酸等低阈值异味分子以及环氧化物等有害产物^[1-2],降低了油脂及其制品的感官可接受度及营养价值。人体食用氧化的油脂会造成机体酶系统损伤,加速体内脂质过氧化,引起一系列生理异常^[3]。因此,对油脂氧化进程的监测及控制一直是油脂理论研究的焦点。近些年来,研究人员提出了一系列检测油脂氧化程度的方法,如碘量法、硫氰酸铁法、硫代巴比妥酸值测定法(TBA法)、活性氧化法(AOM法)、Schall干燥箱法、Rancimat法等^[4-5]。热重仪作为重要的热分析仪器之一,是在程序控温下通过高灵敏度的电子天平记录试样的质量随时间或温度的变化,进而反映样品反应进程的热分析技术,相比传统的测定方法,具有所需样品微量、操作简单快速、无需使用有机溶剂、准确性和灵敏度高等优点。利用该方法可检测并比较油脂的氧化稳定性、测定油脂氧化诱导时间、氧化反应焓变、氧化分解起始温度等^[6-7],在油脂加工及质量监控、新型抗氧化剂研发等领域已逐渐得到应用。

油脂的氧化机制复杂,受诸多外部和内部因素影响。其中,甘油三酯(TAG)既是油脂中脂肪酸的存在形式,也是构成油脂的主要组分(质量分数95%以上),同时也是参与酸败反应的主要物质,因此,油脂的氧化进程与其甘三酯的组成及分布密切相关^[8]。油脂在氧化过程中会发生一系列复杂的氧化、裂变、聚合等反应,质量上发生变化,热重仪通过对这些变化的精确记录,可监测完整的油脂氧化进程,结合动力学模型的建立、反应动力学参数的推导及与组分的相关性研究可进一步阐明油脂的氧化特性^[9-14],如VECCHIO等^[9]通过植物油热重(TG)及微商热重(DTG)在非等温条件下对初榨橄榄油及4种饱和、不饱和甘三酯的热降解动力学进行对比,TOMASSETTI等^[14]则利用该2种方法研究了5种饱和单甘酯、双甘酯和三甘酯的热降解过程。但目前已有的相关研究围绕对象较少,温度参数或动力学参数无法完整表征油脂氧化进程,且对化学组成的考虑尚不全面。因此,本文通过测定不同温控程序下植物油的热重(TG)及微商热重(DTG)曲线的变化,分析各品种植物油的氧化特性,并通过不同温度参数的获取、动力学参数的求解及与样品甘

三酯组成的皮尔森相关性研究,进一步探讨油脂的氧化特性与其组成结构的关系。

1 材料与方法

1.1 材料与仪器

选取脂肪酸组成及不饱和程度各异的6种植物油样品,分别为:棕榈油,益江(张家港)粮油工业有限公司;橄榄油,上海东森企业发展有限公司;葵花籽油,上海嘉里食品工业有限公司;玉米油,山东西王食品有限公司;大豆油,张家港中粮东海粮油工业有限公司;芝麻油,天津嘉里粮油有限公司。油样购于当地超市,生产日期相近,加工精炼等级一致,商品标签上均注明不含有人工添加的抗氧化剂。分析前将油样置于棕色瓶内放在低温(4℃)、避光、无顶空条件下保存。正己烷、二氯甲烷、丙酮、乙腈均为色谱纯。

STA449 F3型同步热分析仪(配有铂金炉、底置式电子天平、质量流量计、NETZSCH-Propeus-6.1数据分析软件),德国耐驰公司;Eksigent HPLC-TripleTOF 4600型高效液相色谱-串联四级杆飞行时间质谱联用仪(配有二元溶剂管理器、自动进样器、柱温箱、APCI电离源),美国AB SCIEX公司;ZORBAX SB型C18反相高效液相色谱柱(4.6 mm × 250 mm, 5 μm),美国Agilent公司。

1.2 实验方法

1.2.1 热重测定方法

以O₂(99.99%, 80 mL/min)为吹扫气体,N₂(99.99%, 20 mL/min)为天平保护气体。为确保样品与O₂的充分接触及热传导的均匀性,避免凹盘内出现温度梯度,将(3.0 ± 0.5) mg油样置于密封(中央有孔)铝盘中^[13],于30℃恒温5 min后以一定速率加热至400℃。考虑到继而动力模型的建立以及STA分析仪加热速率的合适范围,取5个不同升温速率:5.0、7.5、10.0、12.5、15.0℃/min,得到每个升温速率下油脂样品的TG及DTG图谱。

1.2.2 温度参数的确定及动力学参数的推导

由于样品质量较小,在氧化进程中热重曲线变化细微,对质量分数取一阶导数得到相应的微商热重曲线,表征样品质量变化速率与温度的关系^[9,14],以微商热重曲线偏离基线时的温度为氧化起始温度(T_{on}),以曲线起峰后第1次降至最低点时的温度为氧化峰值温度(T_p)^[9,11,15],如图1所示。

在非等温条件下,吹扫气体O₂始终处于过量状态,因此可忽略热氧化进程中O₂的消耗,即油脂氧化过程与O₂的量无关,氧化属于一阶动力学^[9,11,13]。符合Ozawa-Flynn-Wall等转化率方程^[16-17],将每

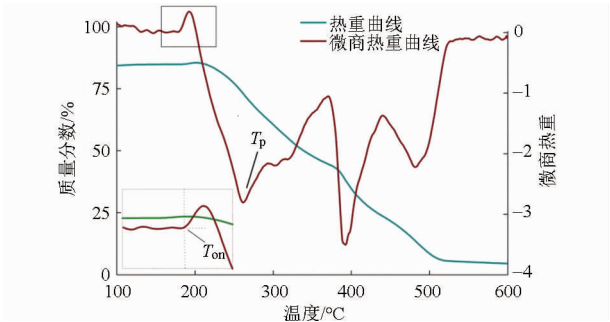


图 1 热重曲线氧化起始温度及氧化峰值温度的确定

Fig. 1 Confirmation of onset oxidation temperature and peak oxidation temperature of TG curve

一样品在 5 个不同升温速率下的 T_{on} 及 T_p 代入方程

$$\lg \beta = a \frac{1}{T} + b \tag{1}$$

式中 β ——升温速率, $^{\circ}\text{C}/\text{min}$

T —— T_{on} 或 T_p , $^{\circ}\text{C}$

以 $\lg \beta$ 对 $\frac{1}{T}$ 拟合所得直线的斜率 a 和截距 b 与活化能 E_a (J/mol) 和前指数因子 A (min^{-1}) 的关系为

$$a = -0.4567 \frac{E_a}{R} \tag{2}$$

$$b = -2.315 + \lg \left(A \frac{E_a}{R} \right) \tag{3}$$

式中 R ——摩尔气体常数, 取 $8.314 \text{ J}/(\text{mol} \cdot \text{K})$

1.2.3 甘油三酯组成测定方法

利用高效液相色谱-串联四极杆飞行时间质谱联用 (HPLC-MS), 以 APCI 为电离源, C18 柱为洗脱柱, 正己烷、二氯甲烷 (体积比 1:1) 为流动相 A, 丙酮、乙腈 (体积比 5:95) 为流动相 B, 分离样品中的甘三酯分子。研究发现, 在甘三酯分子中从 sn-2 位断裂 1 个脂肪酸所需的能量要比从 sn-1 或 sn-3 位上断裂 1 个脂肪酸所需的能量大^[18-20], 因此, 可根据 APCI 质谱图中各种碎片离子峰的强度及质量数差值, 判断甘三酯分子的种类及其甘油骨架上脂肪酸的位置, 进一步通过面积归一法定量确定每种油样中甘三酯的组成及分布。洗脱程序为: 0~20 min, 20% A; 20~35 min, 升至 80% A; 35~45 min, 降至 20% A。柱温设置为 40°C , 流速设置为 $0.6 \text{ mL}/\text{min}$ 。

1.2.4 数据分析

实验均测定 3 次, 采用 SPSS 22.0 统计分析软件对数据的平均值、标准差、差异显著性及热降解特性与甘三酯组成的皮尔森相关性进行分析。其中, 差异显著性分析采用 Turkey 多重检验, 95% 置信水平 ($p < 0.05$), 动力学直线采用 SigmaPlot 12.5 拟合。

2 结果与结论

2.1 DSC 对油脂样品热氧化进程的测定

图 1 是橄榄油在 $5^{\circ}\text{C}/\text{min}$ 速率下的热重及微商热重曲线, 通过微商热重曲线可以清晰地监测油脂样品在热降解过程中的质量变化。已有研究说明, 在 $100 \sim 600^{\circ}\text{C}$ 范围内, 油脂热氧化主要经历 3 个阶段反应: $160 \sim 280^{\circ}\text{C}$ 主要是饱和和不饱和脂肪酸链的降解 (部分油样该阶段反应会持续至 350°C , 如图 2), $280 \sim 400^{\circ}\text{C}$ 对应挥发性物质的氧化, $400 \sim 600^{\circ}\text{C}$ 则是碳质残渣的反应^[9, 14]。其中第 1 阶段主要涉及甘油骨架上脂肪酸链的自由基链式反应, 因此在该温度范围内选择 T_{on} 、 T_p 2 个温度参数表征油脂热降解的不同阶段。

在非等温温控程序下, 分别对 6 种油脂样品在 5 个升温速率 (5.0 、 7.5 、 10.0 、 12.5 、 $15.0^{\circ}\text{C}/\text{min}$) 下进行测定, 所得微商热重曲线如图 2 所示。由图 2 可知, 6 种油脂样品中橄榄油、葵花籽油、玉米油和芝麻油微商热重曲线峰型均窄小, 而棕榈油和大豆油 DTG 曲线则呈现较平坦的趋势, 且随着升温速率的增加, 6 种油样的微商热重峰均向更高温度迁移, 这与已有研究趋势相同^[12, 14, 21]。由表 1 也可知, T_{on} 和 T_p 值均随升温速率升高而升高, 如在 $5.0^{\circ}\text{C}/\text{min}$ 时, 葵花籽油的 T_{on} 和 T_p 分别为 163.22°C 和 308.15°C , 而在 $15.0^{\circ}\text{C}/\text{min}$ 时, 其 T_{on} 和 T_p 分别升至 178.18°C 和 348.80°C (表 1)。但在个别高加热速率 (大于 $10.0^{\circ}\text{C}/\text{min}$) 下 DTG 峰会向相反方向偏移 (图 2c), 出现这种现象的原因是, 当升温速率较低时, 坩埚内油样可与吹扫气体 (氧气) 充分反应, 而当升温速率较高时, 样品内热氧化反应剧烈, 产生的挥发性物质未能及时排出坩埚, 造成样品质量变化的不规律^[22]。

2.2 温度参数的确定及热降解的动力学推导

根据 1.2.2 节中所述的方法, 从 6 种植物油样品的热重及微商热重曲线中确定其在不同温控程序下的氧化起始温度 (T_{on}) 和氧化峰值温度 (T_p), 见表 1。根据已有研究证明, T_{on} 与氧化进程中过氧化物的生成密切相关, T_p 则与氧化终止阶段有关^[23]。由表 1 可知, 随着升温速率的增加, 油脂样品 T_{on} 和 T_p 均随之升高, 说明油脂发生热氧化反应的温度升高, 且 T_p 增加幅度较 T_{on} 大, 如当升温速率由 $5.0^{\circ}\text{C}/\text{min}$ 升至 $15.0^{\circ}\text{C}/\text{min}$ 时, 橄榄油 T_{on} 增幅为 17.8°C , 而 T_p 增幅则为 31.42°C 。MONTEAGUDOS 等^[11] 在对富含共轭亚油酸的无水乳脂肪进行非等温热力学研究中也发现, T_p 变化较 T_{on} 更为敏感, 这一现象说明氧化峰值温度附近发生的反应对外界条件的变化更为敏锐。

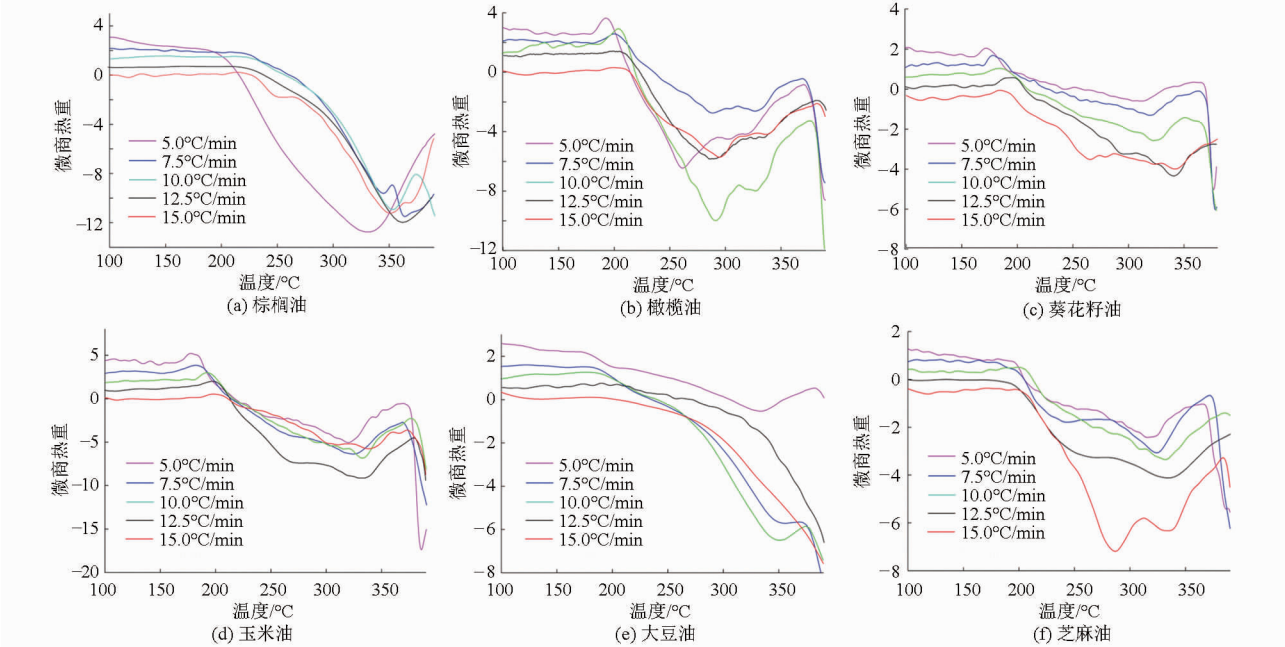


图2 植物油样品在不同升温速率下的微商热重曲线

Fig.2 DTG curves of vegetable oil samples at different heating rates

表1 不同升温速率下植物油样品的氧化起始温度和氧化峰值温度

Tab.1 Onset oxidation temperature and peak oxidation temperature of oil samples at different heating rates							℃
升温速率/(℃·min ⁻¹)		棕榈油	橄榄油	葵花籽油	玉米油	大豆油	芝麻油
T_{on}	5.0	199.91 ± 0.89 ^a	179.43 ± 1.40 ^c	163.22 ± 0.27 ^f	168.51 ± 0.53 ^e	172.72 ± 0.83 ^d	182.80 ± 0.33 ^b
	7.5	204.25 ± 0.75 ^a	182.09 ± 0.64 ^c	171.36 ± 1.41 ^e	174.07 ± 0.17 ^d	183.27 ± 0.42 ^c	187.62 ± 0.27 ^b
	10.0	209.26 ± 0.42 ^a	189.46 ± 0.15 ^c	175.37 ± 0.48 ^f	179.62 ± 0.50 ^e	188.22 ± 0.92 ^d	191.64 ± 1.15 ^b
	12.5	212.50 ± 0.22 ^a	193.40 ± 0.46 ^c	181.63 ± 0.60 ^e	184.51 ± 1.22 ^d	195.25 ± 0.21 ^b	—
	15.0	214.32 ± 1.02 ^a	197.25 ± 1.27 ^c	178.18 ± 0.26 ^e	187.80 ± 0.25 ^d	197.89 ± 1.03 ^c	200.19 ± 0.58 ^b
T_p	5.0	332.01 ± 0.85 ^a	266.06 ± 0.37 ^c	308.15 ± 0.14 ^d	310.07 ± 0.64 ^d	329.07 ± 0.21 ^b	313.18 ± 0.35 ^c
	7.5	344.92 ± 0.57 ^a	286.46 ± 0.70 ^d	323.26 ± 0.35 ^b	318.47 ± 0.85 ^c	—	322.94 ± 0.69 ^b
	10.0	353.23 ± 0.38 ^a	292.94 ± 0.46 ^d	327.72 ± 0.71 ^d	337.96 ± 0.35 ^c	356.90 ± 0.55 ^b	336.54 ± 0.15 ^c
	12.5	362.48 ± 1.02 ^a	295.53 ± 0.12 ^c	344.14 ± 0.58 ^c	338.84 ± 0.13 ^d	358.82 ± 0.48 ^b	340.48 ± 0.77 ^c
	15.0	—	297.48 ± 0.98 ^c	348.80 ± 0.89 ^b	351.94 ± 0.49 ^a	—	347.08 ± 0.30 ^b

注:同一行中右上角标小写字母相同者差异不显著($p < 0.05$),不同者差异显著,下同;“—”为热谱图中曲线反方向偏移导致该点不可取。

将表1中的 T_{on} 或 T_p 分别代入Ozawa - Flynn - Wall等转化率方程中,以升温速率 β 的对数值对氧化起始温度 $1/T_{on}$ 或氧化峰值温度 $1/T_p$ 制图,图3是以玉米油为例表示其 $\lg \beta$ 与 $1/T_{on}$ 间的线性关系。由图3可知, $\lg \beta$ 与 $1/T_{on}$ 间具有较好的线性关系,可用方程 $y = -4\,909x + 11.83$ 表示,其决定系数为0.9938。除个别情况外,其他油脂样品线性拟合决定系数也均大于0.94(表2),说明Ozawa - Flynn - Wall等转化率法较适用于本研所得数据。利用式(1)~(3),求得的动力学参数列于表2。通过上述动力学的求解,6种油样在 T_{on} 处的活化能分别为:棕榈油,132.50 kJ/mol;橄榄油,95.16 kJ/mol;葵花籽油,90.69 kJ/mol;玉米油,89.32 kJ/mol;大豆油,71.29 kJ/mol;芝麻油,106.44 kJ/mol。在 T_p 处的活化能分别为:橄榄油,92.73 kJ/mol;橄榄油,

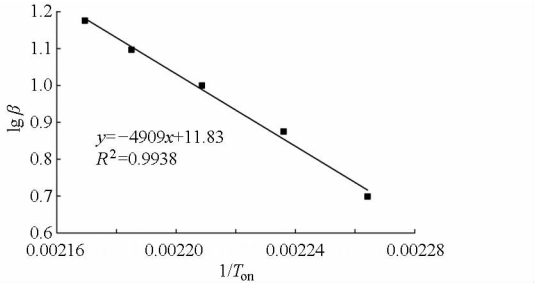


图3 玉米油起始氧化温度与升温速率间的线性关系

Fig.3 Linear relationship between onset oxidation temperature and heating rate of corn oil

77.77 kJ/mol; 葵花籽油, 74.37 kJ/mol; 玉米油, 71.98 kJ/mol; 大豆油, 84.79 kJ/mol; 芝麻油, 89.89 kJ/mol。油脂体系组分复杂,在热降解过程中会同时发生多个反应,因此所得的活化能为油脂样品在该温度附近所发生诸多热氧化反应的表现活化

能^[22, 24]。活化能可表征物质发生反应的难易程度^[25],以活化能的高低评定油脂样品的氧化稳定性从低到高排序, T_{on} 为大豆油、玉米油、葵花籽油、橄榄油、芝麻油、棕榈油; T_p 为玉米油、葵花籽油、橄榄

油、大豆油、芝麻油、棕榈油,这与以 $E_a(T_{on})$ 高低的排序结果略有差异,说明单一指标表征并不全面,而应结合不同阶段的多个指标从多个方面综合评价油脂的氧化稳定性^[26]。

表 2 植物油样品的动力学参数
Tab.2 Kinetic parameters of vegetable oil samples

参数	棕榈油	橄榄油	葵花籽油	玉米油	大豆油	芝麻油
T_{on}	lg β 与 $1/T_{on}$ 关系式	$y = -7\,282x + 16.10$	$y = -5\,230x + 12.30$	$y = -4\,984x + 12.11$	$y = -4\,909x + 11.83$	$y = -3\,918x + 9.478$
	$E_a/(kJ\cdot mol^{-1})$	132.50	95.16	90.69	89.32	71.29
	A/min^{-1}	1.63×10^{14}	3.60×10^{10}	2.44×10^{10}	1.30×10^{10}	7.24×10^7
	R^2	0.992 8	0.957 3	0.894 0	0.993 8	0.992 0
T_p	lg β 与 $1/T_{on}$ 关系式	$y = -5\,096x + 9.123$	$y = -4\,274x + 8.594$	$y = -4\,087x + 7.745$	$y = -3\,956x + 7.517$	$y = -4\,660x + 8.434$
	$E_a/(kJ\cdot mol^{-1})$	92.73	77.77	74.37	71.98	84.79
	A/min^{-1}	2.46×10^7	1.13×10^6	1.28×10^6	7.84×10^5	5.50×10^6
	R^2	0.997 6	0.893 4	0.968 0	0.948 0	0.967 6

2.3 样品热氧化动力学特性与其甘油三酯组成的相关性

对油脂样品的甘油三酯分析结果见表 3,按甘油骨架上连接脂肪酸的不饱和程度可将甘三酯分为三饱和脂肪酸甘三酯(Trisaturated triacylglycerol, TSTAG)、单饱和脂肪酸甘三酯(Monosaturated

triacylglycerol, MSTAG)、二饱和脂肪酸甘三酯(Disaturated triacylglycerol, DSTAG)和三不饱和脂肪酸甘三酯(Triunsaturated triacylglycerol, TUTAG)。由表 3 可知,不同植物源的油脂具有不同的甘三酯分布及特征甘三酯。其中,棕榈油由于富含棕榈酸(C16:0)和油酸(C18:1)^[27],其特征甘三酯为 POO

表 3 植物油样品的甘油三酯质量分数
Tab.3 Triacylglycerol compositions of vegetable oil samples

甘油三酯组成	棕榈油	橄榄油	葵花籽油	玉米油	大豆油	芝麻油
LLnLn	—	—	—	—	1.86 ± 0.03 ^a	—
LLLn	—	—	—	1.09 ± 0.05 ^b	9.12 ± 0.06 ^a	0.21 ± 0.01 ^c
MPP	0.48 ± 0.03 ^a	—	—	—	—	—
LLL + OLLn	—	1.68 ± 0.06 ^c	39.91 ± 0.07 ^a	28.44 ± 0.14 ^b	23.53 ± 0.09 ^c	11.15 ± 0.05 ^d
OLL + OLPo	—	6.92 ± 0.09 ^d	23.57 ± 0.14 ^a	25.22 ± 0.04 ^a	19.67 ± 0.16 ^b	17.34 ± 0.14 ^c
LLP	—	1.74 ± 0.11 ^e	10.44 ± 0.09 ^c	14.12 ± 0.05 ^b	16.51 ± 0.07 ^a	8.43 ± 0.10 ^d
MPL	2.31 ± 0.06 ^a	—	—	—	—	—
OOL	0.91 ± 0.02 ^c	18.18 ± 0.14 ^a	5.61 ± 0.11 ^d	8.38 ± 0.15 ^c	6.79 ± 0.05 ^d	15.67 ± 0.05 ^b
PLO + SLL	9.05 ± 0.05 ^b	6.51 ± 0.07 ^d	8.80 ± 0.06 ^c	9.08 ± 0.03 ^b	10.96 ± 0.09 ^a	8.40 ± 0.05 ^c
PPL	8.60 ± 0.01 ^a	1.90 ± 0.09 ^c	0.98 ± 0.04 ^e	1.21 ± 0.07 ^d	1.79 ± 0.03 ^c	5.52 ± 0.02 ^b
OOO	0.98 ± 0.03 ^f	38.37 ± 0.10 ^a	3.43 ± 0.07 ^d	4.78 ± 0.06 ^c	2.37 ± 0.06 ^c	14.93 ± 0.07 ^b
SLO	5.51 ± 0.09 ^a	2.63 ± 0.03 ^c	3.52 ± 0.06 ^b	2.59 ± 0.04 ^c	2.26 ± 0.12 ^d	3.18 ± 0.15 ^b
POO	31.77 ± 0.12 ^a	15.27 ± 0.06 ^b	1.50 ± 0.03 ^e	2.42 ± 0.08 ^d	2.38 ± 0.01 ^d	11.12 ± 0.09 ^c
PPO	28.41 ± 0.06 ^a	1.41 ± 0.05 ^c	1.07 ± 0.08 ^d	1.63 ± 0.11 ^b	0.95 ± 0.03 ^c	0.47 ± 0.02 ^f
SOO	4.06 ± 0.04 ^a	2.65 ± 0.03 ^b	0.53 ± 0.10 ^d	0.42 ± 0.03 ^d	0.65 ± 0.05 ^d	1.63 ± 0.05 ^c
PSO	2.26 ± 0.05 ^a	1.78 ± 0.08 ^b	—	—	0.63 ± 0.02 ^c	1.44 ± 0.03 ^b
MMM	0.51 ± 0.01 ^a	—	—	—	—	—
PPP	4.25 ± 0.02 ^a	—	—	—	—	—
AOO	—	0.35 ± 0.03 ^b	—	0.50 ± 0.06 ^a	—	0.51 ± 0.08 ^a
SSO	0.90 ± 0.08 ^a	0.45 ± 0.05 ^b	—	—	—	—
OOB	—	—	0.64 ± 0.06 ^a	—	0.48 ± 0.03 ^b	—
TSTAG	5.24 ± 0.11 ^a	—	—	—	—	—
MSTAG	50.35 ± 0.07 ^a	29.15 ± 0.06 ^c	25.43 ± 0.05 ^d	29.13 ± 0.05 ^c	33.24 ± 0.04 ^b	33.31 ± 0.04 ^b
DSTAG	42.52 ± 0.15 ^a	5.54 ± 0.11 ^c	2.05 ± 0.09 ^d	2.84 ± 0.03 ^e	3.37 ± 0.11 ^b	7.39 ± 0.08 ^b
TUTAG	1.89 ± 0.04 ^f	65.15 ± 0.07 ^c	72.52 ± 0.07 ^a	67.91 ± 0.06 ^b	63.34 ± 0.06 ^d	59.30 ± 0.08 ^e

注:M,肉豆蔻酸(C14:0);P,棕榈酸(C16:0);Po,棕榈油酸(C16:1);S,硬脂酸(C18:0);O,油酸(C18:1);L,亚油酸(C18:2);Ln,亚麻酸(C18:3);A,花生酸(C20:0);B,山嵛酸(C22:0)。

(31.77%) 和 PPO (28.41%); 且 其 TSTAG (5.24%)、MSTAG (50.35%)、DSTAG (42.52%) 含量均高于其他样品,而 TUTAG (1.89%) 含量低于其他样品,且除棕榈油外其他油样均不含 TSTAG; 橄榄油富含油酸^[20], 因此其含 ROO 型甘三酯较多, 如 OOO (38.37%)、OOL (18.18%) 和 POO (15.27%); 葵花籽油和玉米油甘三酯组成相似, 均含有较多的 LLL + OLLn (39.91% , 28.44%) 和 OLL + OLPo (23.57% , 25.22%), 其中 葵 花 籽 油 TUTAG (72.52%) 含量高于其他样品; 大豆油一般含 5% 左右亚油酸^[18], 因此较其他油样 LLLn (9.12%) 含量显著增多; 芝麻油甘油酯分布较均匀, 且含有较多的 MSTAG (33.31%) 和 DSTAG (7.39%)。

对油脂甘三酯组成及分布与其热降解过程中的热力学参数(氧化起始温度 T_{on} 、氧化峰值温度 T_p 、活化能 E_a) 进行皮尔森相关性分析, 相关系数的正负及大小代表不同组分对油脂氧化稳定性的影响程度^[9], 为保证结果的可靠性, 对所有样品中质量分数均低于 1% 的甘三酯不予考虑, 具体结果见表 4。

由表 4 可知, 油脂不同的甘三酯组成与其 T_{on} 、 T_p 及 E_a 间有着不同程度的相关性。其中, 油脂在 T_{on} 处的活化能与高饱和度甘三酯呈显著正相关, 如 MPL (0.83)、PPL (0.89)、PPP (0.83), 而与不饱和程度较高的甘油酯呈负相关, 如 OLL + OLPo (-0.73), 但与 MSTAG 及 DSTAG 的相关性则与甘三酯中不饱和脂肪酸链的种类有关, 其中与含油酸链较多的甘油酯呈显著正相关, 如 POO (0.90), 而与含亚油酸链较多的甘油酯呈负相关, 如 LLP (-0.81)。研究证明, 饱和-CH₂-可抑制自由基对脂肪酸链的攻击, 提高甘三酯的氧化稳定性^[28]。油脂的氧化起始温度与甘三酯组成间的相关性与 T_{on} 处活化能的结果相似, 且与多个组分相关性极显著, 如 MSTAG (0.92), 因此可根据油脂的化学组成推断其氧化起始温度的高低进而预判油脂的热稳定性。油脂的氧化峰值温度 T_p 同样与 TSTAG 及相关甘三酯呈正相关, 而与 TUTAG 及相关组分呈负相关, 如 OOO (-0.92), 但 T_p 与 MSTAG 及 DSTAG 组分相关性不显著, 油脂在 T_p 处活化能与各组分的相关性与 $E_a(T_{on})$ 相似但相关性有所减弱, 产生上述现象的原因可能是氧化峰值温度附近甘油三酯的降解已进入末期, 并转化成一系列次级氧化产物, 样品质量变化同时受后者积累的影响。此外, 本研究所用植物油样中会含有一定量的天然抗氧化成分, 如酚类物质(生育酚、多酚等), 但已有研究证明油脂的热力学特性与其总酚含量及分布相关性不显著, 因上述酚类物质在 200℃ 前已发生降解并挥发, 对

表 4 植物油样品热氧化特性与其甘三酯组成的相关性分析
Tab.4 Correlation analysis between thermal oxidation properties and triacylglycerol compositions of vegetable oil samples

甘油三酯组成	T_{on}	$E_a(T_{on})$	T_p	$E_a(T_p)$
LLnLn	-0.19	-0.63	0.40	0.16
LLLn	-0.23	-0.66	0.41	0.11
LLL + OLLn	-0.88 *	-0.63	0.19	-0.64
OLL + OLPo	-0.89 *	-0.73	0.09	-0.62
LLP	-0.75	-0.81 *	0.33	-0.40
MPL	0.84 *	0.83 *	0.46	0.62
OOL	-0.15	-0.24	0.78	-0.17
PLO + SLL	-0.15	-0.33	0.86 *	0.21
PPL	0.94 **	0.89 *	0.44	0.88 *
OOO	0.06	-0.03	-0.92 **	-0.16
SLO	0.73	0.90 *	0.41	0.56
POO	0.96 **	0.90 *	0.09	0.68
PPO	0.83 *	0.83 *	0.45	0.60
SOO	0.93 **	0.84 *	-0.05	0.64
PSO	0.92 **	0.72	-0.09	0.75
PPP	0.84 *	0.83 *	0.46	0.62
TSTAG	0.84 *	0.83 *	0.46	0.62
MSTAG	0.92 **	0.77	0.55	0.81
DSTAG	0.90 *	0.87 *	0.43	0.69
TUTAG	-0.91 *	-0.84 *	-0.47	-0.73

注: * 表示相关性在 0.05 水平上显著, ** 表示相关性在 0.01 水平上显著。 T_{on} 、 T_p 均以 5℃/min 进行分析, 其他升温速率情况下所得结果相近。

后续热谱图影响微弱^[9,29], 因此本研究未予考虑。

3 结束语

利用热重及微商热重法, 对常见植物油的热氧化特性进行了探究, 通过分析不同温控程序对热重及微商热重曲线的影响, 发现氧化起始温度和氧化峰值温度均随着升温速率的升高而增大, 且 T_p 比 T_{on} 变化更为敏感。利用 Ozawa - Flynn - Wall 等转化率方程对油脂样品进行了动力学推导及求解, 拟合结果理想, 所得热力学参数 (E_a , A) 均可表征油脂的热氧化稳定性。同时, 通过分析油脂热氧化特性与其甘三酯组成及分布间的相关性, 发现氧化进程中 T_{on} 及 $E_a(T_{on})$ 多与高饱和度甘三酯含量呈正相关, 而与高不饱和程度甘三酯含量呈负相关, 且相关性与甘油酯中脂肪酸链的种类有关; T_p 与 $E_a(T_p)$ 同样与 TSTAG 呈正相关, 与 TUTAG 呈负相关, 但与 MSTAG 及 DSTAG 有关组分相关性有所减弱。对“热氧化特性-化学组成”相关性的探索初步明晰了不同组分对油脂热氧化进程的影响, 并为油脂热稳定性的预判, 油脂加工、精炼及储藏条件的控制提供一定的实验依据。

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