The oxidative stability of fat in three dark chocolates at different stages of manufacturing process.

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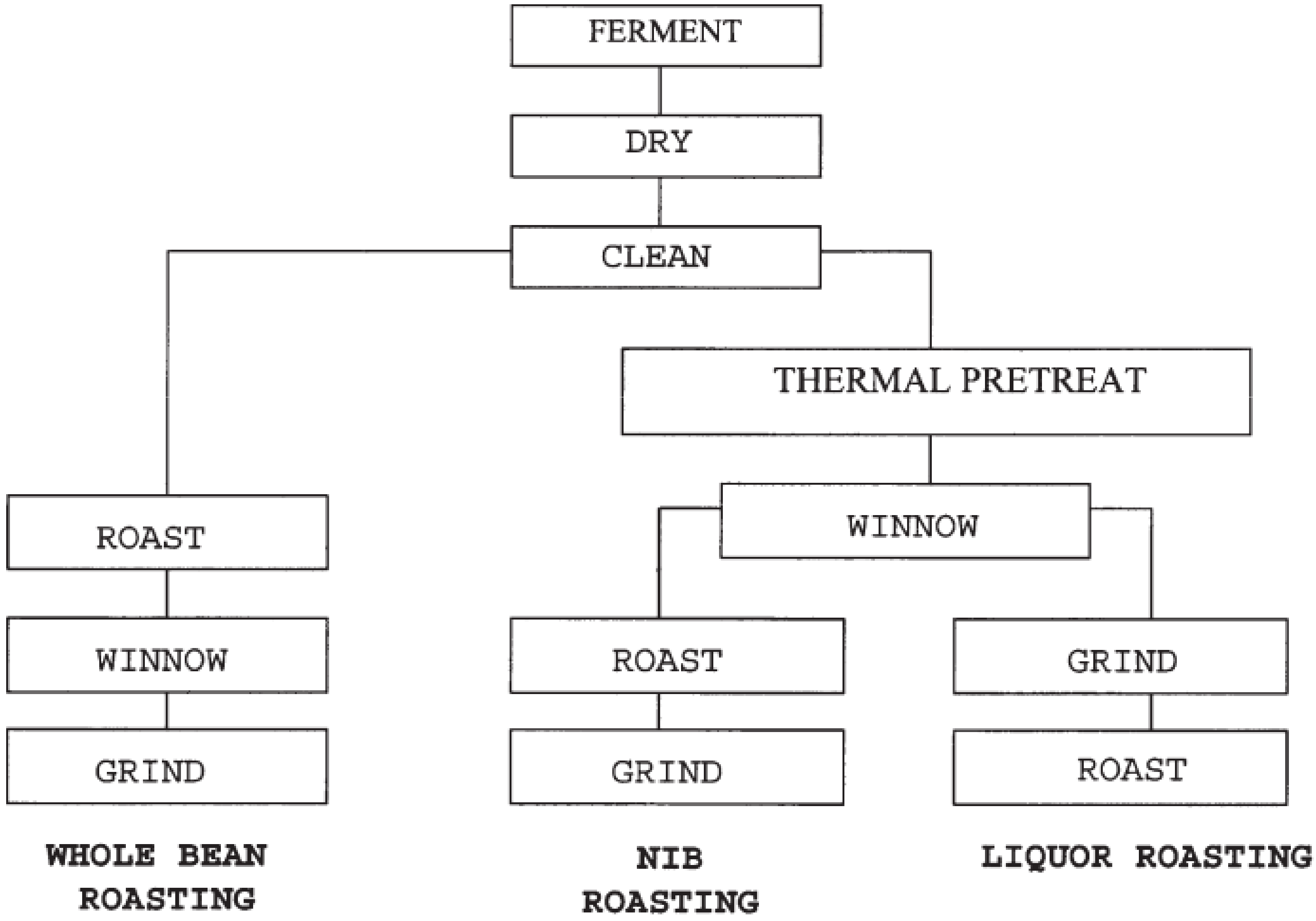
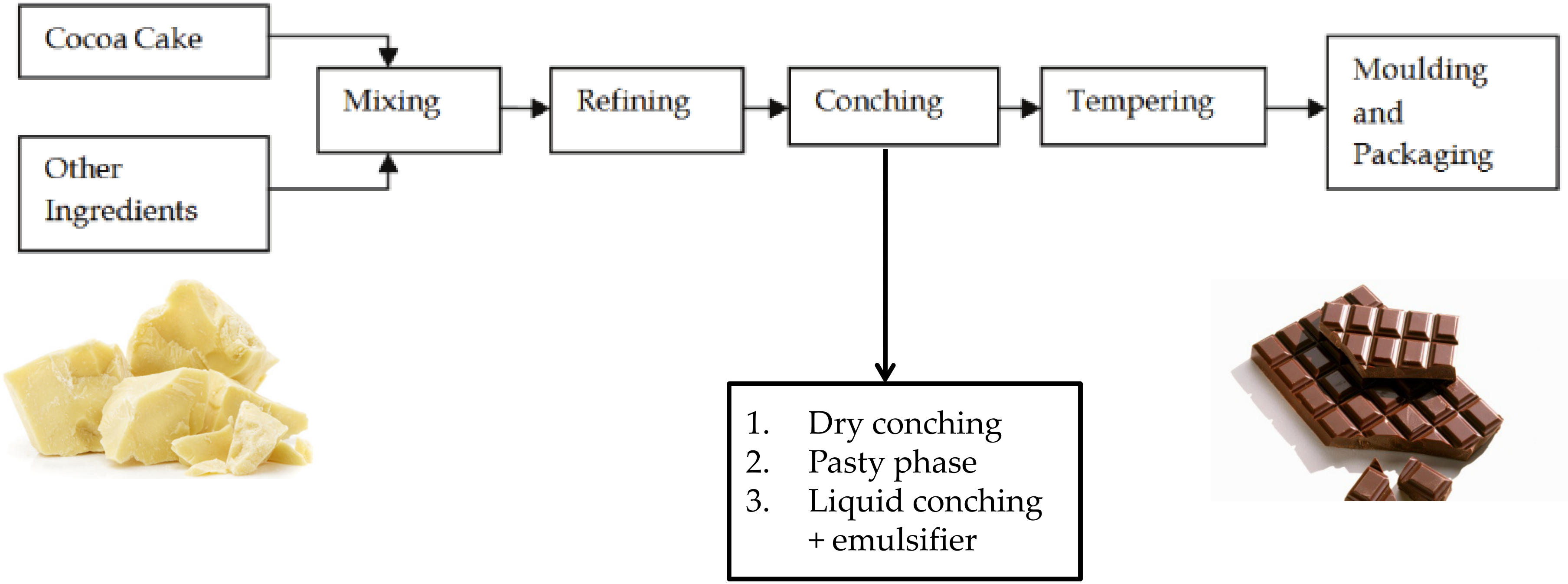
FLOW DIAGRAM ILLUSTRATING THE THREE DIFFERENT METHODS OF ROASTING COCOA BEANS *



*Stephen T. Beckett, The Science of Chocolate, RSC, 3rd edition

FLOW DIAGRAM ILLUSTRATING THE STAGES OF DARK CHOCOLATE PRODUCTION **



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THE METHODS TO ASSESS OXIDATIVE STABILITY OF LIPIDS

• peroxide value (PV) - that measures volumetrically the concentration of hydroperoxides
• anisidine value (AV) - that measures the aldehyde levels, in particular unsaturated aldehydes, in an oil or fat
• spectrophotometric measurements in the UV region
• gas chromatography (GC) analysis – that measures the amount of volatile compounds

Various different reactions during lipid oxidation, occur simultaneously at different rates. These reactions release heat that can be measured using differential scanning calorimetry (DSC).

• thermal analysis using PDSC - that measures oxidation induction time, OIT (isothermal mode)
• thermal analysis using PDSC - that measures oxidation induction temperature, OIT (non-isothermal mode, constant heating rate)

MAIN LIPID OXIDATION REACTIONS ***

Radical formation

$$A\text{-}B \xrightarrow{\text{Homolysis}} I^{\bullet}$$

Initiation

$$R\text{-}H + I^{\bullet} \longrightarrow R^{\bullet} + I\text{-}H$$

Propagation

$$R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + R\text{-}H \longrightarrow ROOH + R^{\bullet}$$

Termination

$$ROO^{\bullet} + ROO^{\bullet} \longrightarrow ROOR + O_2$$

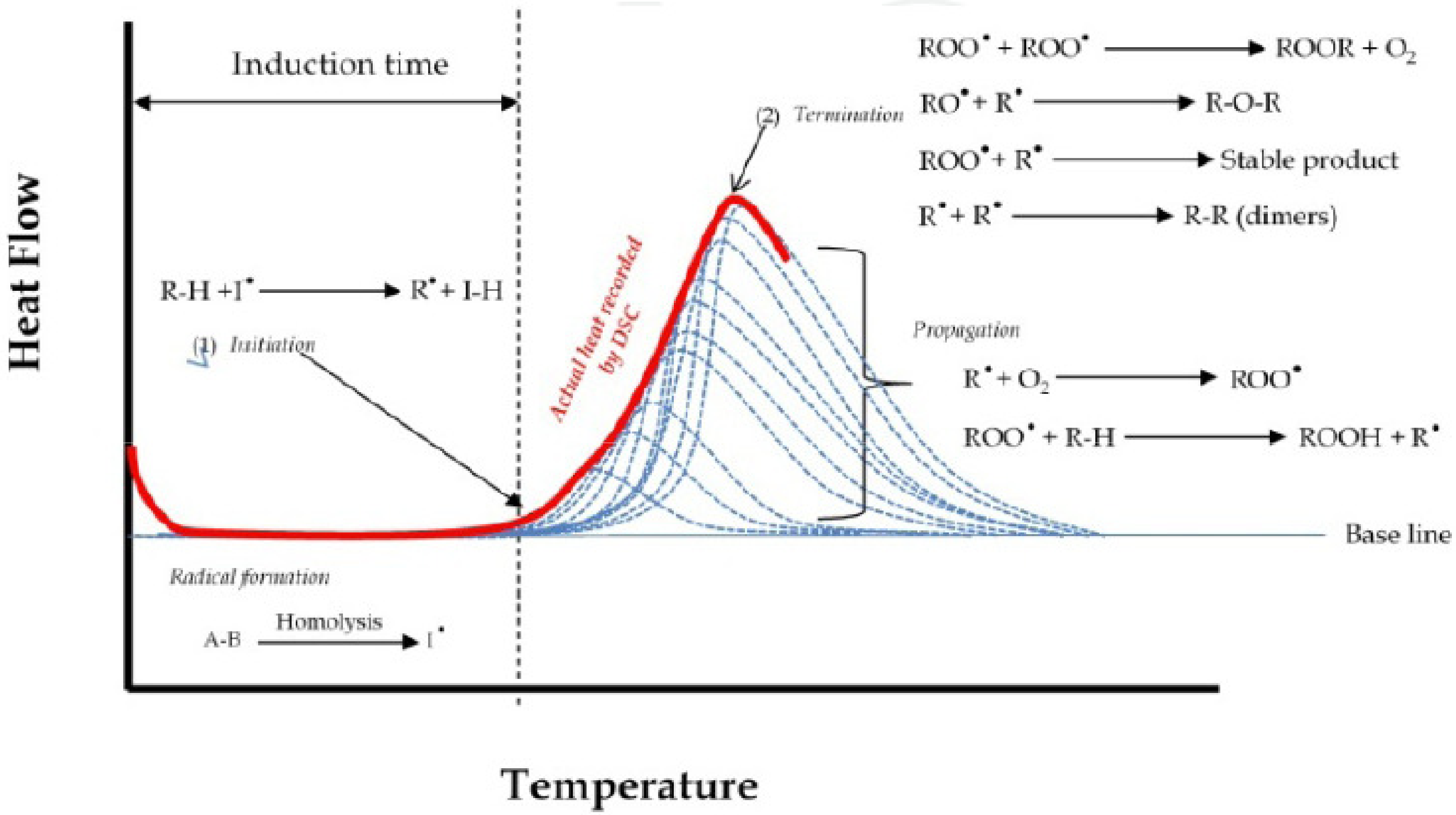
$$RO^{\bullet} + R^{\bullet} \longrightarrow R\text{-}O\text{-}R$$

$$ROO^{\bullet} + R^{\bullet} \longrightarrow \text{Stable product}$$

$$R^{\bullet} + R^{\bullet} \longrightarrow R\text{-}R \text{ (dimers)}$$

*** Saldańa, M.D.A.; Martínez-Monteagudo, S.I. B. Oxidative Stability of Fats and Oils Measured by Differential Scanning Calorimetry for Food and Industrial Applications. In Applications of Calorimetry in a Wide Context – Differential Scanning Calorimetry, Isothermal Titration Calorimetry and Microcalorimetry; Elkordy, A.A., Eds.; InTech: Rijeka, Croatia, 2013; pp. 445–468.

IDEAL THERMOGRAM OF NON-ISOTHERMAL OIL OXIDATION ****



**** Saldańa, M.D.A.; Martínez-Monteagudo, S.I. B. Oxidative Stability of Fats and Oils Measured by Differential Scanning Calorimetry for Food and Industrial Applications. In Applications of Calorimetry in a Wide Context – Differential Scanning Calorimetry, Isothermal Titration Calorimetry and Microcalorimetry; Elkordy, A.A., Eds.; InTech: Rijeka, Croatia, 2013; pp. 445–468.

THE METHODOLOGY - THE FAT EXTRACTION *****

30 g of cocoa mass

day 1

- GRIND
- HOMOGENISATION $CHCl_3/CH_3OH$ (1/1 v/v)
- HEATING at 60˚C / 20 min
- + 100 mL $CHCl_3$ HOMOGENISATION
- + 70mL 1M KCl LEFT OVER NIGHT

day 2

- PHASE SEPERATION
- DRYING with $MgSO_4$
- SOLVENT EVAPORATION

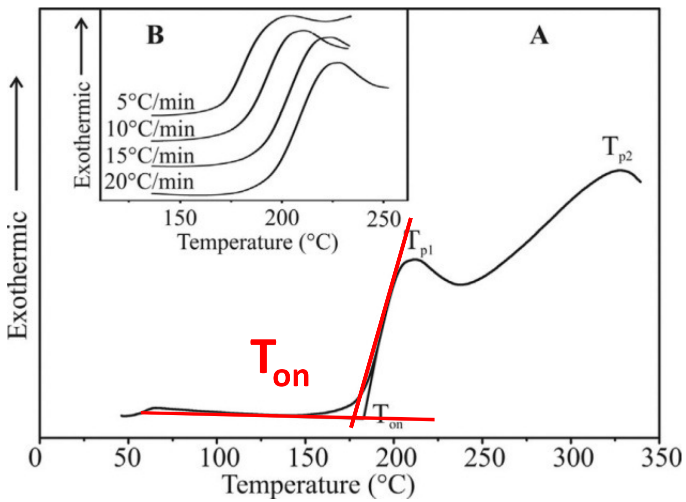
TOTAL YIELD = 32%

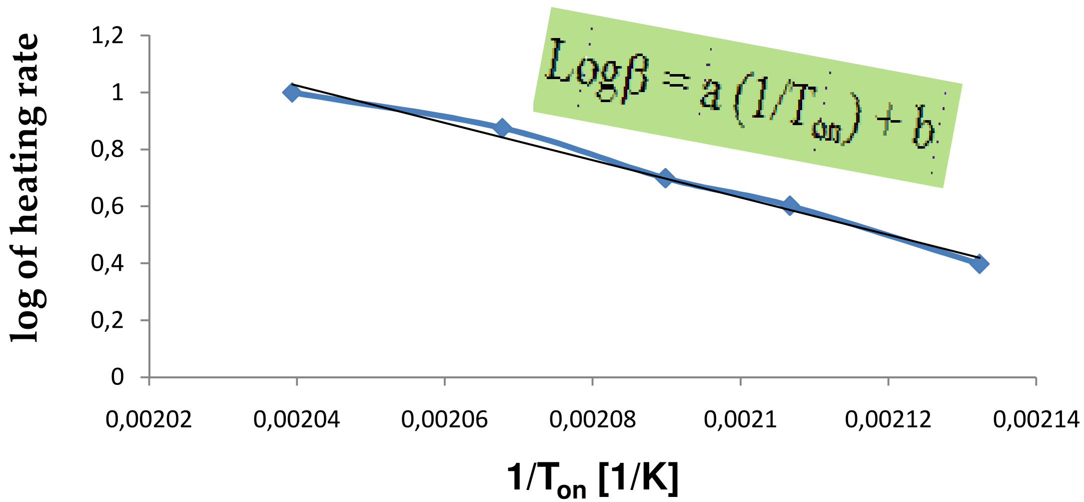
***** Boselli, E., Velazco, V., Caboni, M. F., & Lercker, G. Pressurized liquid extraction of lipids for the determination of oxysterols in egg-containing food. *J Chromatography* A., **2001**, 917, 239-244

THE METHODOLOGY

THE OZAWA-FLYNN-WALL'S METHOD

For the extracted fats the kinetics of the oxidation process was determined using a PDSC apparatus in an oxygen atmosphere using the following sample heating rates: 2.5°C/min, 4°C/min, 6°C/min, 7.5°C/min, 10°C/min, 12.5°C/min, 15°C/min.





$$E_a = -2.19\, R\, \frac{d \log \beta}{d(1/T)} \qquad Z = \frac{\beta Ea\, e^{\frac{Ea}{RT}}}{RT^2}$$

All measurements were performed in triplicate, starting from extraction. Standard deviations were calculated using Excel 2010.

THE RESULTS AND DISCUSSION

The higher the activation enrgy of oxidation the more stable to exidation the fat is.

Table 1. Regression analysis of DSC data, activation energies (E_a) and pre-exponential factors of oxidation reaction of fat phase extracted from chocolate masses during raw dark chocolate production process, small manufacturer

Parameter	Cocoa butter	Cocoa liquor	Tempered mass	Chocolate
a	6953	8250	6997	5341
b	15.02	18.08	15.23	12.48
R^2	0.999	0.997	0.999	0.991
E_a/kJ mol^{-1}	126.58[1]	150.19[1]	127.38[1]	97.24[1]
Log Z	13.15	16.14	13.36	10.73
Z / min^{-1}	$1.42x 10^{13}$	1.37×10^{16}	2.29×10^{13}	5.33×10^{10}

[1]Calculations based on onset temperatures.

The stability of initial ingredients: cocoa butter and cocoa liquor showed higher stability than tempered cocoa mass and final chocolate bar. In case of small manufacturer of raw chocolate, the production process affects significantly the value of activation energy of fat oxidation. Raw chocolate is produced from cocoa beans roasted in very low temperature for a short time. No strong thermal treatment of the cocoa beans affects increases themal stability cocoa butter and cocoa liquor.

THE RESULTS AND DISCUSSION

Table 2. Regression analysis of DSC data, activation energies (E_a) and pre-exponential factors of oxidation reaction of fat phase extracted from chocolate masses during classic dark chocolate production process, small manufacturer

Parameter	Cocoa butter	Cocoa liquor	Conched mass	Chocolate
a	6805	5750	5510	5166
b	14.82	13.21	12.80	10.78
R^2	0.996	0.990	0.990	0.960
E_a/kJ mol^{-1}	123.89[1]	104.68[1]	100.31[1]	65.36[1]
Log Z	12.96	11.42	11.03	7.15
Z / min^{-1}	9.16×10^{12}	2.66×10^{11}	1.08×10^{11}	1.40×10^{7}

[1] Calculations based on onset temperatures.

The stability of initial ingredients for classic dark chocolate showed much higher oxidative stability, in case of cocoa butter, and higher stability, in case of cocoa liquor in comparison to conched cocoa mass. The fat from the final chocolate bar had almost twice smaller oxidation stability than cocoa butter that was used in production process. Hence, the production process of classic dark chocolate from small manufacturer affects significantly the value of activation energy of fat oxidation. Cocoa beans used in classic dark chocolate production process are roasted in high temperature at different times depending on a company procedure.

THE RESULTS AND DISCUSSION

Table 3. Regression analysis of DSC data, activation energies (E_a) and pre-exponential factors of oxidation reaction of fat phase extracted from chocolate masses during classic dark chocolate production process, large manufacturer

Parameter	Cocoa butter	Cocoa liquor	Conched mass	Chocolate
a	4528	5876	5768	6682
b	10.77	13.34	14.24	15.16
R^2	0.998	0.998	0.989	0.989
E_a/kJ mol^{-1}	82.43[1]	106.98[1]	105.01[1]	121.65[1]
Log Z	9.09	11.55	12.45	13.31
Z / min^{-1}	1.23×10^9	3.51×10^{11}	2.84×10^{12}	2.04×10^{13}

[1] Calculations based on onset temperatures.

The stability of initial ingredients for classic dark chocolate showed lower oxidative stability, in case of cocoa butter, and comparable stability, in case of cocoa liquor in comparison to conched cocoa mass and final chocolate bar. The fat from the final chocolate bar had significantly higher oxidation stability than cocoa butter that was used in production process. Hence, paradoxically the production process of classic dark chocolate from large manufacturer affects the value of activation energy of fat oxidation in a positive way probably due to addition of an emulsifier declared on the label. Emulsifiers are usually rich in mono- and polyunsaturated fatty acids which naturally prevent thermoxidation of the mixture .

THE CONCLUSION

Cocoa butter is characterized in literature by very high kinetic parameters (E_a, Z) dependent on many factors such as sample pre-treatment, sample preparation, sample size, heating rate and DSC mode. Therefore, the cocoa butter samples analyzed in three different production processes have statistically different values of activation energy indicating different oxidative stability. Despite of that, the stability of fat in the final product – chocolate bar is not dependent from initial stability of the basic ingredients (no correlation) but rather from thermal pre-treatment of these ingredients and process parameters. Moreover, there are also less obvious reasons for the oxidative stability of cocoa butter during chocolate production such as additives. In multicomponent systems, the fat sometimes needs to be extracted from the matrix. Therefore, the lipid oxidative behaviour might be different from its original matrix.

The biggest increase in oxidative stability of the fat in favour of the final chocolate bar was observed for classic dark chocolate from a large producer. The biggest drop in oxidative stability of the fat was observed in case of classic dark chocolate when referred to cocoa butter and in case of raw dark chocolate when referred to cocoa liquor.

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