Predictive oxidative evaluation of lipid samples using Differential Scanning Calorimetry

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Introduction

Lipid molecules are currently attracting attention due to their pharmaceutical and technological applications (1) and, playing a structural role, lipids are present in the membrane composition of various microorganisms (2). However, oxidative stability is a main bottleneck in their utilization and application. Thus, this study proposes using Differential Scanning Calorimetry (DSC) technique under oxygen atmosphere as a predictive oxidation status tool, based on the Ozawa-Flynn-Wall method by heating commercial oils at different rates and determining the Oxidation Induction Temperature (OIT) (3). The oxidation effective activation energy (Ea) and its kinetic parameters, such as the pre-exponential factor (A) (i.e., frequency of molecules collision) and the constant reaction rate (k) can also be calculated (4).

Objectives

To study the oxidative stability of olive oil (OL), coconut oil (CO), sunflower oil (SF) and petrolatum (PE), using DSC and exposing these samples to dynamic studies under an O_2 flow and assessment of kinetic parameters. The measurement of the kinetic pre-exponential factor (A) and the Ea value, as well as OIT value will bring information to predict the oxidative stability of a lipidic sample. This method could be useful for the determination of lipids suitability for food or pharmacological applications: for example if a elaboration process (i.e. temperature) would cause degradation. It may also be assayed with microbial lipids (e.g. yeasts at different fermentation points) or cells exposed to pollution factors to understand how these oxidation kinetic factors are affected.

Methods

Dynamic Analysis

Detection of **the oxidation peak**

Development of **fast and reliable method**

Determination of

OIT - Oxidation Induction Temperature
Ea – Effective Activation Energy

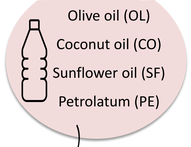
$$Ea = -2.19\,R\frac{d\log\beta}{dT^{-1}}$$

A – Pre Exponential Factor
k – Reaction Rate

$$k = A\,exp^{\left(\frac{-Ea}{RT}\right)}$$

The heat released by the oxidized oil is recorded as the heat flow signal.

Method Validation with



The reaction kinetics follows an Arrhenius type equation:

$$\frac{d\alpha}{dt} = A\,exp^{\left(\frac{-E_a}{RT}\right)} f(\alpha)$$

- **R** is the universal gas constant (8.31 J/mol K);
- **T** is the oxidation induction temperature (T_{onset});
- **f(α)** is the reaction model.

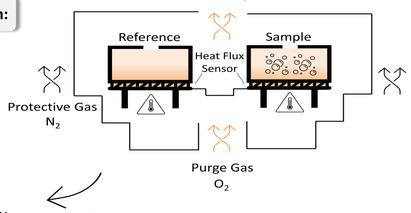


Figure 1. Illustration of Differential Scanning Calorimetry (DSC) thermo-analytical technique under oxygen atmosphere.

Table 1. Main set parameters of DSC applied methodology.

Temperature (°C)	Heating rate β (°C/min)	Gas flow (mL/min)	Time (min)
20	---	50	5
500	**5, 10, 15 and 20**	50	48

Results

Table 2. Obtained oxidation temperature onset (T_{on}) for SFO, OL, CO and PE.

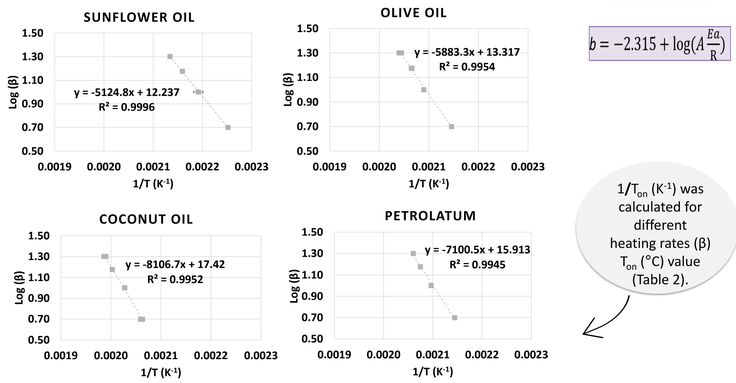
T_{on} (°C)							
SFO		OL		CO		PE	
Average	SD	Average	SD	Average	SD	Average	SD
184.88	8.69	206.24	8.95	221.64	6.26	204.50	6.80

The effective Activation Energy (Ea) and The Pre-exponential Factor (A) are determined directly from the slope (a) and intercept (b):

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

$$a = -0.4567\frac{Ea}{R}$$

$$b = -2.315 + \log\left(A\frac{Ea}{R}\right)$$



$1/T_{on}$ (K^{-1}) was calculated for different heating rates (β) T_{on} (°C) value (Table 2).

Figure 2. Plot of Log(β) against 1/T for each studied oil.

- For SF, the OIT value was 184.88±8.69 °C, suggesting that it is oxidized at lower temperatures (Table 2);
- CO was more resistant to oxidation, probably due to its inherent composition (minor concentration of unsaturated fatty acids that are more susceptible to peroxidation) (Table 2);

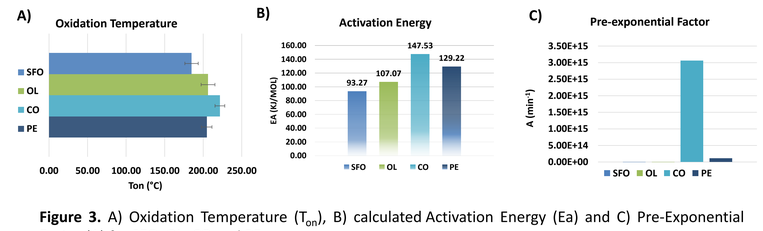


Figure 3. A) Oxidation Temperature (T_{on}), B) calculated Activation Energy (Ea) and C) Pre-Exponential Factor (A) for SFO, OL, CO and PE.

Table 3. Kinetic parameters obtained for different heating rates (β) for SFO, OL, CO and PE.

	Oxidation Kinetic Parameters			
	SFO	OL	CO	PE
Ea (kJ/mol)	93.27	107.07	147.53	129.22
log(A) (min^{-1})	10.50	11.52	15.49	14.04
k (460K) (min^{-1})	0.80	0.23	0.05	0.23
A (min^{-1})	3.18E+10	3.33E+11	3.06E+15	1.09E+14

- OL, PE and CO presented the following OIT values: 206.24±8.95 °C, 204.50±6.80 °C and 221.64±6.26 °C, respectively. Interestingly, for SF, the OIT value was 184.88±8.69 °C, suggesting that it is oxidized at lower temperatures (Table 2).
- In fact, both the kinetic pre-exponential factor (A = $3.18x10^{10}$ min^{-1}) and the calculated Activation Energy (Ea = 93.27 KJ/mol) for SF are in agreement with the obtained OIT value (Table 3).
- Different oils presented different kinetic oxidation parameters (Figure 3).

Conclusions

Overall, as stated by the obtained results, DSC OIT is a fast and reliable method to measure parameters related to oxidative stability of lipophilic samples. The main achieved conclusion was that CO was more resistant to oxidation and therefore more stable than SF, OL and PE. The prediction of thermal oxidative stability using OIT DSC technique can be applied to expect the oxidative stress resistance in microorganisms.

References

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