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Assessment of lipid oxidation in cottonseed oil treated with phytonutrients: Kinetic and thermodynamic studies

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ABSTRACT

Cottonseed oil was oxidized under accelerated conditions at four different temperature values (110, 120, 130 and 140 °C) through Rancimat method. The temperature dependence of oxidation reaction was expressed by Arrhenius equation. Reaction rate constant (k), activation energy (Ea), activation enthalpy (ΔH^{++}), activation entropy (ΔS^{++}) and Gibbs free energy of activation (ΔG^{++}) for the oxidative stability of the cottonseed oil were calculated according to both Arrhenius model and Eyring equation of activated complex approach. The relevant oil was also treated with gallic acid, rutin and carotenoid in order to improve the shelf-life of the product. Moreover, tertbutyl hydroquinone (TBHQ) was also applied into the oil as control. Furthermore, the quality parameters of the cottonseed oil was also evaluated with respect to phenolic (TP), flavonoid (TF) and carotenoid (TC) contents and free radical scavenging activity (FRSA). Fourier Transformed Infrared-Attenuated Total Reflectance (FTIR-ATR) was also used to evaluate the functional groups of the oil. Depending on the fundamental thermodynamic parameters ($\Delta H^{++} > 0$, $\Delta G^{++} > 0$ and $\Delta S^{++} < 0/\Delta S^{++} > 0$), the nature of the oxidation reaction in the pure and treated cottonseed oils proves that it is an endothermic and non-spontaneous process. The predicted shelf-life of the oils ranged from 46 to 639 days at ambient conditions.

1. Introduction

Rancidity of edible oils under several storage conditions or overexposure to heat is resulted from oxidation reactions caused by autoxidation chain reactions. Therefore, antioxidative additives are applied into the related products to inhibit or delay the concerned deterioration (Oroian and Escriche, 2015). These bioactive substances act as hydrogen atom donors, and convert the toxic materials to less reactive species. The antioxidant radical (A·) formed in this way is stabilized by the displacement of the unpaired electron on the aromatic ring with the oxygen atom. This chain reactions including initiation (1), propagation (2 and 3) and termination (4–6) steps can be summarized as written below (Aluyor and Ori-Jesu, 2002; Yanishlieva and Marinova, 2001):

$$\begin{matrix} R\bullet \\ RO\bullet \\ ROO\bullet \end{matrix} + AH \rightarrow \begin{matrix} RH \\ ROH \\ ROOH \end{matrix} + A\bullet \quad (1)$$

$$\begin{matrix} RO\bullet \\ ROO\bullet \end{matrix} + A\bullet \rightarrow \begin{matrix} ROA \\ ROOA \end{matrix} \quad (2)$$

$$ROO\bullet + RH \rightarrow ROOH + \quad (3)$$

$$A\bullet + O_2 \rightarrow AOO\bullet \quad (4)$$

$$AOO\bullet + RH \rightarrow R\bullet + AOOH \quad (5)$$

$$A\bullet + RH \rightarrow AH + R\bullet \quad (6)$$

Lately, consumption of natural antioxidants have been very popular such as phytonutrients (polyphenols, flavonoids and carotenoids) in order to substitute the synthetic antioxidants such as BHA (Butylated hydroxyanisole), BHT (butylated hydroxytoluene) and TBHQ (tertbutyl hydroquinone) for extending the shelf-life of the products (Bodoira et al., 2017). Table 1 presents the most common additives used as potential antioxidant for the application into the edible oils.

Measurement of oxidative stability would long months of storage time at ambient conditions (Franco et al., 2016). However, time is of great importance to industrial processes. Therefore, some instrumental methods have been emerged to measure the resistance of the fat containing products against this oxidation problem under accelerated conditions due to prompt hydroperoxide decomposition at raised temperature values (at > 100 °C for less than 24 h) (Farhoosh et al., 2008; Farhoosh and Hoseini-Yazdi, 2014; Kowalski et al., 2004; Ostrowska-Ligeza et al., 2010; Polavka et al., 2005; Velasco et al., 2004). Rancimat is a simple acceleration method, where measurements are conducted continuously without requiring any analytical analyses such as

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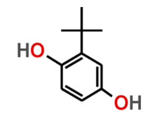
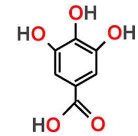
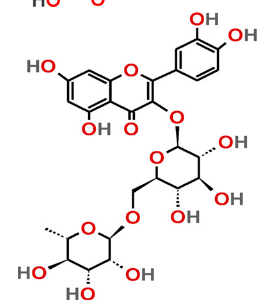
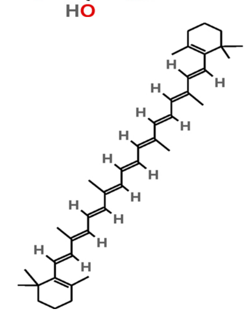
Table 1
Synthetic and natural antioxidants applied in this study.

Additive	Synthetic/natural	Molecular formula	Moleular weight (g/mol)	Molecular Structure
TBHQ	Synthetic	$C_{10}H_{14}O_2$	166.22	
Gallic acid	Natural	$C_7H_6O_5$	170.12	
Rutin	Natural	$C_{27}H_{30}O_{16}$	610.52	
β-carotene	Natural	$C_{40}H_{56}$	536.89	

titrations (Hasenhuettl and Wan, 1992). It only contains three operational variables such as sample quantity, flow rate of air and temperature for the determination of oxidative stability of the related products (Farhoosh, 2007).

The number of kinetic and thermodynamic studies of lipid oxidation held by Rancimat method is extremely low. Anwar et al. used this instrument to determine the oxidative stability of the cottonseed oil in addition to several fat containing food products at 110, 120 and 130 °C, respectively (Anwar et al., 2003). Taghvaei et al. evaluated the stability of the oil after extracting the cottonseeds by means of microwave (Taghvaei et al., 2014). Taking this matter into account, Arrhenius equation has been applied in order to describe the oxidation process as a function of temperature. Thermodynamic parameters are also necessary to predict the lipid oxidation under several conditions for developing the formulations for better quality by comprehending the oxidation reaction in the related product. Apart, kinetic studies on the interaction of peptides and their metal complexes with different additives were also performed in the absence and presence of different media (Kumar et al., 2016a,b, 2014; Kumar and Rub, 2017). To the best of our knowledge, cottonseed oil has not been examined in respect of Arrhenius kinetics as well as thermodynamics parameters under Rancimat test conditions.

2. Materials and methods

2.1. Materials

Cottonseed oil sample was purchased from a local market. Ethanol (> 99.5%), methanol (> 99.8%), hexane (> 99%), sodium nitrite and aluminium chloride were supplied from Merck (Darmstadt, Germany). ABTS (2,2′-azino-bis- (3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt), sodium carbonate, Folin-Ciocalteu, (+)-catechin, gallic acid, rutin, TBHQ and β-carotene were provided from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Treatment of the oil with phythonutrients

The relevant edible oil was enriched by only 200 ppm (parts per million) solid additives due to the limitations of some authorities on additives (Taghvaei and Jafari, 2015), even though increasing the additive amount would have enhanced the resistance of oil oxidation more. Otherwise, the more the additive, the longer the induction time and the more stable the oil is to oxidation. The concerned quantity has also been proved to be safe with respect to toxic effects, where De Leonardis et al. reported that phenolic additives did not inhibit cell growth at the doses of 100–200 ppm depending on their cytotoxicity assay, when they stabilized lard by natural phenolic antioxidants (De Leonardis et al., 2007). The phythonutrients and synthetic antioxidants were added into the oil and blended by the homogenizer at 7000 rpm (random per minute) for 115 s.

2.3. Extraction of antioxidants from treated oil

After addition of hexane into the oil samples, extraction was conducted at 7000 rpm for 60 s by means of methanol. Extraction was repeated twice. Hexane was used to wash the mixture after combining the extracts. Finally, the washed extracts were filtered through a syringe filter (0.45 µm). The samples maintained at −20 °C in dark.