# Kangar (*Gundelia tehranica*) seed oil: Quality measurement and frying performance

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**Summary**

Performance of extracted edible oil from Kangar (*Gundelia tehranica*) seed including crude oil, tocopherols free oil, butylated hydroxytoluene (BHT) added oil (200 mg·kg$^{-1}$) and tertiary butyl hydroquinone (TBHQ) added oil (200 mg·kg$^{-1}$) during potato slices frying at 180 °C, 190 °C and 200 °C, totally for 12 h, were investigated. According to instrumental analysis by high performance liquid chromatography (HPLC) and gas chromatography (GC), the crude oil contained notable levels of tocopherols, tocotrienols and unsaturated fatty acids as well as lowest levels of free fatty acids, conjugated dienes, conjugated trienes, carbonyl and anisidine in comparison with other supplemented oils. Although oil stability index decreased during frying process in all examined samples, crude oil was demonstrated to be the most stable oil. The low temperature dependency of oxidation reaction and concentration of the activated complex and, consequently, the slowest rate of oxidation during frying of crude oil were demonstrated by the recorded values of activation energy (5.645 kJ·mol$^{-1}$, 11.280 kJ·mol$^{-1}$ and 24.260 kJ·mol$^{-1}$), frequency factor (0.058 h$^{-1}$, 0.659 h$^{-1}$ and 2.305 h$^{-1}$), enthalpy (1.667 kJ·mol$^{-1}$, 7.301 kJ·mol$^{-1}$ and 20.280 kJ·mol$^{-1}$), entropy and free energy of activation, during 1 h, 6 h and 12 h, respectively. Based on obtained results, the Kangar seed oil, in crude oil form, can be employed for food frying process.

**Keywords**

frying oil; *Gundelia tehranica* seed; kinetic parameters; oxidation stability

Kangar (*Gundelia tehranica*) as a member of the Asteraceae plant family is spread in countries from Turkey to the south to Israel and north-eastwards to Turkmenia, eastwards to Iraq, Iran and until Afghanistan [1–5]. It is one of the naturally growing plants, which can grow in mountainous and steep lands of Iran [1, 4]. Different parts of Kangar, such as seeds and stems, are used in food applications [1, 7], as a traditional medical approach, dry seeds being used to treatment of vitiligo, a disease that causes the loss of skin colour in blotches. It has antibacterial, anti-inflammatory, hepatoprotective, antioxidant, antiplatelet and hypolipemic activities [6]. According to MATTHÄUS and ÖZCAN [7], extracted oil from Kangar flower buds contains high amounts of linoleic acid, oleic acid and palmitic acid. KHANZADEH et al. [2] showed that Kangar seed oil contains a high level of unsaturated oil, which can be melted at room temperature. According to that report, the main unsaponifiable lipids were stigmasterol and β-sitosterol.

In deep-frying as a common process for the preparation and production of different types of

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foods, as result of chemical phenomena such as hydrolysis, oxidation and polymerization, the quality of the used frying oil can be deteriorated [8]. In order to decrease the extent of oxidative reactions during the frying process, incorporation of an antioxidant agent such as tertiary butylhydroquinone (TBHQ) and butylated hydroxytoluene (BHT) into edible oil can be considered as the most prevalent approach. Due to serious concern regarding the possible toxicity, their application in high amounts is not acceptable. On the other hand, the addition of small amounts might not provide enough protection for edible oils under severe frying conditions [9]. Thus, application of natural antioxidants with strong antioxidant activity could be proposed as a suitable alternative [10].

As far as we know, there is no published paper regarding the oxidative stability of Kangar seed oil during the frying process. In addition, in order to predict the oxidative stability of edible oils in different frying conditions, kinetics of the process should be investigated [11, 12]. Considering the available literature, the physicochemical quality of Kangar oil was not sufficiently investigated [2, 7]. Therefore, the purpose of the current study was to demonstrate the practical application of Kangar seed oil as a frying oil. Also, the obtained results for frying performance of crude oil were compared with common edible oils.

## MATERIAL AND METHODS

### Materials

Kangar (*Gundelia tehranica*) seed samples were collected at the final stage of their maturity (July 2015) from mountains located at Yasuj, Iran. Voucher specimen of the species (HSBU-2017101) was deposited at the Herbarium of Medicinal Plants and Drugs Research Institute, Shahid Beheshti University, Tehran, Iran. All chemicals and solvents of analytical grade were purchased from Merck (Darmstadt, Germany) and Sigma (Saint Louis, Missouri, USA).

### Oil extraction

After drying in the shade, seeds were ground to a powder with a grinder 320P (Pars Khazar, Rasht, Iran). The powders were extracted with *n*-hexane (1 g : 4 ml) by agitation in a dark place at laboratory temperature for 48 h. The solvent was evaporated to dryness under reduced pressure at 40 °C. The obtained oil was kept in sealed glass bottles in a freezers (–18 °C) until analysis.

### Oil characterization

Peroxide value, iodine value and unsaponifiable matter were determined according to available national standard methods of Iran [13–15].

### Frying procedure

The method of Erkan et al. [11] was applied to remove naturally occurring tocopherols from Kangar seed oil. Synthetic antioxidants BHT and TBHQ were added to Kangar seed oil (without tocopherols) at their legal domestic limits (200 mg·kg$^{-1}$ each active ingredient). Consequently, Kangar seed oil samples including crude oil, tocopherols free oil, oil samples supplemented with BHT and TBHQ were prepared for further analysis. Using a mechanical slicer, the peeled, washed potatoes were cut to slices of 0.4 cm thickness and 3 cm width, and submerged in water until the day of use. A domestic deep-fat fryer with a 2.5 l vessel was used for the deep-fat frying process. The frying process was carried out for 12 h at 180 °C, 190 °C, and 200 °C, using thermostatic temperature control. When the oil reached the mentioned temperatures, 150 g of potato chips for each batch cycle was fried. Each batch cycle of frying was 5 min. In other words, 12 batch cycles were performed every hour. After each batch cycle, oil samples were collected and filtered into a screw-capped vial and stored at 4 °C. The volume of oil was not refilled during the entire frying period. The samples were analysed in triplicate and the results were reported as mean ± standard deviation.

### Determination of tocopherols and tocotrienols

The composition of tocopherols and tocotrienols of Kangar seed oil were determined using high-performance liquid chromatography (HPLC) in Alliance system (Waters, Milford, Massachusetts, USA) with a Phenomenex Luna 5 $\mu$m $NH_2$ column (10 nm, 250 mm × 4.5 mm; Phenomenex, Torrance, California, USA) equipped with a fluorescence detector operating at an excitation wavelength of 290 nm and an emission wavelength of 330 nm. The volume of injection was 10 $\mu$l. The mobile phase was hexane–isopropanol (98.5 : 0.5, v/v) at a flow rate of 1 ml·min$^{-1}$.

### Determination of fatty acid composition

Transesterification of fatty acids into their corresponding fatty acid methyl esters (FAMEs) was done by vigorous shaking of oil in hexane (0.3 g in 7 ml) with 2 ml of 7 mol·l$^{-1}$ methanolic KOH at 50 °C for 10 min. FAMEs were analysed by gas chromatography (GC) in HP-5890 (Agilent, Palo Alto, California, USA) equipped with

a CP 88 3400 capillary column of fused silica (120 m in length × 0.25 mm in internal diameter, 0.25 $\mu$m film thickness; Varian, Palo Alto, California, USA) using a flame ionization detector (FID). The used carrier gas was helium with a flow rate of 0.8 ml·min$^{-1}$. The oven temperature gradient was 5 °C each 5 min from 160 °C to 200 °C. Temperatures of the injector and the detector were 210 °C and 300 °C, respectively [16, 17].

#### Free fatty acid contents

The contents of free fatty acids (FFAs) were determined according to official method of the American Oil Chemists' Society [18], the results were expressed as grams of oleic acid per kilogram of oil.

#### Carbonyl value

The carbonyl value (*CV*) demonstrates the secondary oxidation products produced as a result of degradation of hydroperoxides, which are more stable than peroxides. These secondary products are considered to be the main contributors to rancidity, which could reduce the nutritional value of fried products. *CV* of the examined oil samples was assessed using 2-propanol and 2,4-decadienal as solvent and standard, respectively [19, 20].

#### Conjugated dienes and conjugated trienes

In order to determine the conjugated dienes (CD) and conjugated trienes (CT), diluted Kangar seed oil samples with isooctane were prepared. Afterwards, absorbance was recorded at 234 nm and 268 nm for CD and CT values, respectively, using UV/Visible Spectrophotometer (Philips, Cambridge, United Kingdom) [21].

#### Anisidine value

The stability of Kangar seed oil during frying was also measured by determination of secondary oxidation products as anisidine value (*AnV*). Hydroperoxides, as primary oxidation products, could be converted to secondary products form (aldehydic components), which are determined by *AnV*. Determination of *AnV* was carried out spectrophotometrically at 350 nm (UV/Visible Spectrophotometer) by evaluation of the absorbance of solutions of Kangar seed oil (from 0.500 g ± 0.001 g to 4.000 g ± 0.001 g) dissolved in 25 ml isooctane and treated with 1 ml *p*-anisidine reagent. The solvent with the *p*-anisidine reagent in the reference cuvette was used as blank [22].

#### Oil/oxidative stability index

Rancimat instrument (Model 734; Metrohm, Herisau, Switzerland) was used to assess the oil stability index (*OSI*). Three grams of each oil sample at a temperature of 120 °C were exposed to air at a flow rate of 15 l·h$^{-1}$ according to the recommended procedure by Koprivnjak et al. [23] during 1 h, 6 h and 12 h after the frying process.

#### Kinetic data analyses

Temperature coefficients ($T_C$, expressed in reciprocal degrees Celsius) were calculated from the slopes of the following linear regression equation:

$$\log OSI = aT + b \tag{1}$$

$$T_C = a \tag{2}$$

where $T$ is temperature (in degrees Celsius), and $a$ and $b$ are the slope and intercept of the equation, respectively.

Also, the $Q_{10}$ number, which indicates the increase in reaction rate due to a 10 °C rise in temperature, was calculated using the equation derived from the Eq. (1):

$$Q_{10} = 10^{-10T_C} \tag{3}$$

The effect of temperature on the rates of oxidation was evaluated by means of the Arrhenius equation:

$$\log k = \log A - \left(\frac{E_a}{2.303RT}\right) \tag{4}$$

where $k$ (in reciprocal hours) is the reaction rate constant, $R$ is the molar gas constant (8.3143 J·mol$^{-1}$K$^{-1}$), $T$ is the absolute temperature (in Kelvin), $E_a$ is the activation energy (in kilojoule per mol) and $A$ is the frequency factor (in reciprocal hours).

Enthalpies ($\Delta H^{++}$) and entropies ($\Delta S^{++}$) of activation were determined by regressing log $k/T$ versus the inverse of temperature ($T$) via the equation derived from the activated complex theory:

$$\log\left(\frac{k}{T}\right) = \log\left(\frac{k_B}{h}\right) + \left(\frac{\Delta S}{2.303R}\right) - \left(\frac{\Delta H}{2.303RT}\right) \tag{5}$$

where $k_B$ is the Boltzmann constant ($1.380658 \times 10^{-23}$ J·K$^{-1}$, the ratio between $R$ and Avogadro's number, $6.022 \times 10^{23}$ mol$^{-1}$) and $h$ is Planck's constant ($6.6260755 \times 10^{-34}$ J·s). From the slopes and intercepts of the lines, the values of $\Delta H^{++}$and $\Delta S^{++}$were calculated.

$$\Delta H^{++} = \frac{1}{2.303R} \tag{6}$$

$$\Delta S^{++} = \log\left(\frac{k_B}{h}\right) + \left(\frac{1}{2.303R}\right) \tag{7}$$

Finally, for a reaction at a given temperature,

the free energy of activation ($\Delta G^{++}$) could be written in terms of $\Delta H^{++}$and $\Delta S^{++}$ by the equation [24, 25]:

$$\Delta G^{++} = \Delta H^{++} - T\Delta S^{++} \quad (8)$$

### Statistical analysis

The data were analysed using one-way ANOVA, and significant differences between groups were determined using Duncan's multiple range test. All statistical analyses were performed using SPSS 16.0 for Windows (SPSS, Chicago, Illinois, USA). Differences were considered significant at $p < 0.05$.

## RESULT AND DISCUSSION

### Physicochemical properties

The physicochemical characteristics of Kangar seed oil are presented in Tab. 1. The amount of extracted seed oil was 264.0 g·kg$^{-1}$ ± 8.0 g·kg$^{-1}$, which is comparable to other oilseeds such as *Sinapis arvensis* (262 g·kg$^{-1}$) [26].

The observed iodine value of Kangar seed oil (1370 g·kg$^{-1}$ ± 10 g·kg$^{-1}$) is similar to those reported for sunflower oil (1 250–1 360 g·kg$^{-1}$) and soybean oil (1 200–1 430 g·kg$^{-1}$) [27]. Consequently, the Kangar seed oil can be considered as semi-drying oil [2].

Saponification value of Kangar seed oil was determined to be 175 g·kg$^{-1}$ ± 2 g·kg$^{-1}$. The range from 182 g·kg$^{-1}$ to 198 g·kg$^{-1}$ can be considered as an average range for most of the edible oils [2].

The content of free fatty acids was found on a low level when compared with similar edible oils [27].

### Content of fatty acids

Data on fatty acid content are presented in Tab. 1. Kangar seed oil was found to contain mainly linoleic acid (572.9 g·kg$^{-1}$ ± 4.9 g·kg$^{-1}$), followed by oleic acid (248.4 g·kg$^{-1}$ ± 1.3 g·kg$^{-1}$) acid, which contributed by 82.1% of the unsaturated fatty acids. KHANZADEH et al. [2] reported linoleic and oleic acid contents of Kangar seed oil to be 546 g·kg$^{-1}$ and 280 g·kg$^{-1}$, respectively. The contents of linoleic acid and oleic acid in sunflower oil were reported to be 554 g·kg$^{-1}$ and 302 g·kg$^{-1}$, respectively, and soybean oil contained 508 g·kg$^{-1}$ and 264 g·kg$^{-1}$ linoleic acid and oleic acid, respectively [28].

It was observed that, with prolonging the frying period to 12 h, the unsaturated fatty acids (UFA) content decreased, while saturated fatty acids (SFA) content increased (Tab. 2). During 12 h of frying, the oil sample showed a higher

**Tab. 1.** Physico-chemical properties of Kangar seed oil.

| Characteristic/Compound | Content/value |
|---|---|
| Kangar seed oil [g·kg$^{-1}$] | 264.0 ± 8.0 |
| Free fatty acid value[g·kg$^{-1}$] | 0.8 ± 0.1 |
| Saponification value [g·kg$^{-1}$] | 175 ± 2 |
| Iodine value [g·kg$^{-1}$] | 1370 ± 10 |
| Peroxide value [meq·kg$^{-1}$] | 0.92 ± 0.03 |
| **Tocopherols and tocotrienols** | |
| α-Tocopherol [mg·kg$^{-1}$] | 649.0 ± 1.6 |
| β-Tocopherol [mg·kg$^{-1}$] | 39.0 ± 0.9 |
| γ-Tocopherol [mg·kg$^{-1}$] | 47.0 ± 1.0 |
| δ-Tocopherol [mg·kg$^{-1}$] | 16.4 ± 0.5 |
| α-Tocotrienol [mg·kg$^{-1}$] | 13.0 ± 0.6 |
| β-Tocotrienol [mg·kg$^{-1}$] | 3.2 ± 0.4 |
| γ-Tocotrienol [mg·kg$^{-1}$] | 5.3 ± 0.7 |
| δ-Tocotrienol [mg·kg$^{-1}$] | 6.1 ± 0.9 |
| **Fatty acids** | |
| C8:0 (caprylic acid) [g·kg$^{-1}$] | 39.5 ± 1.0 |
| C9:0 (pelargonic acid) [g·kg$^{-1}$] | 9.7 ± 3.0 |
| C16:0 (palmitic acid) [g·kg$^{-1}$] | 97.2 ± 6.1 |
| C18:0 (stearic acid) [g·kg$^{-1}$] | 19.0 ± 1.0 |
| C18:1 (oleic acid) [g·kg$^{-1}$] | 248.4 ± 1.3 |
| C18:2 (linoleic acid) [g·kg$^{-1}$] | 572.9 ± 4.9 |
| C21:0 (heneicosanoic acid) [g·kg$^{-1}$] | 9.3 ± 0.7 |

Values are expressed as mean ± standard deviation. Peroxide values are expressed as milliequivalents of oxygen per kilogram of oil. Free fatty acids are expressed as grams of oleic acid per kilogram of oil.

**Tab. 2.** Effect of frying time on Kangar oil fatty acid composition.

| Content [g·kg$^{-1}$]: | Frying time | | |
|---|---|---|---|
| | 1 h | 6 h | 12 h |
| C8:0 | 39.0 ± 1.0$^{a}$ | 38.1 ± 1.2$^{a}$ | 37.7 ± 1.4$^{a}$ |
| C9:0 | 9.5 ± 0.4$^{a}$ | 9.3 ± 0.8$^{a}$ | 9.2 ± 0.6$^{a}$ |
| C16:0 | 103.2 ± 1.3$^{c}$ | 115.1 ± 1.1$^{b}$ | 126.2 ± 1.5$^{a}$ |
| C18:0 | 20.2 ± 0.7$^{c}$ | 41.7 ± 2.1$^{a}$ | 61.8 ± 1.9$^{a}$ |
| C18:1 | 259.4 ± 1.1$^{c}$ | 273.8 ± 3.2$^{b}$ | 285.4 ± 2.4$^{a}$ |
| C18:2 | 557.8 ± 3.5$^{a}$ | 513.0 ± 1.4$^{b}$ | 481.2 ± 1.6$^{c}$ |
| C21:0 | 9.5 ± 0.9$^{a}$ | 10.1 ± 0.8$^{a}$ | 10.0 ± 0.3$^{a}$ |
| ΣSFA/ΣUFA | 0.222 | 0.272 | 0.319 |
| 18:2/16:0 | 5.40 | 4.46 | 3.81 |

Means with the same lowercase letters are not significantly different at $p < 0.05$.
ΣSFA – sum of saturated fatty acids, ΣUFA – sum of unsaturated fatty acids.

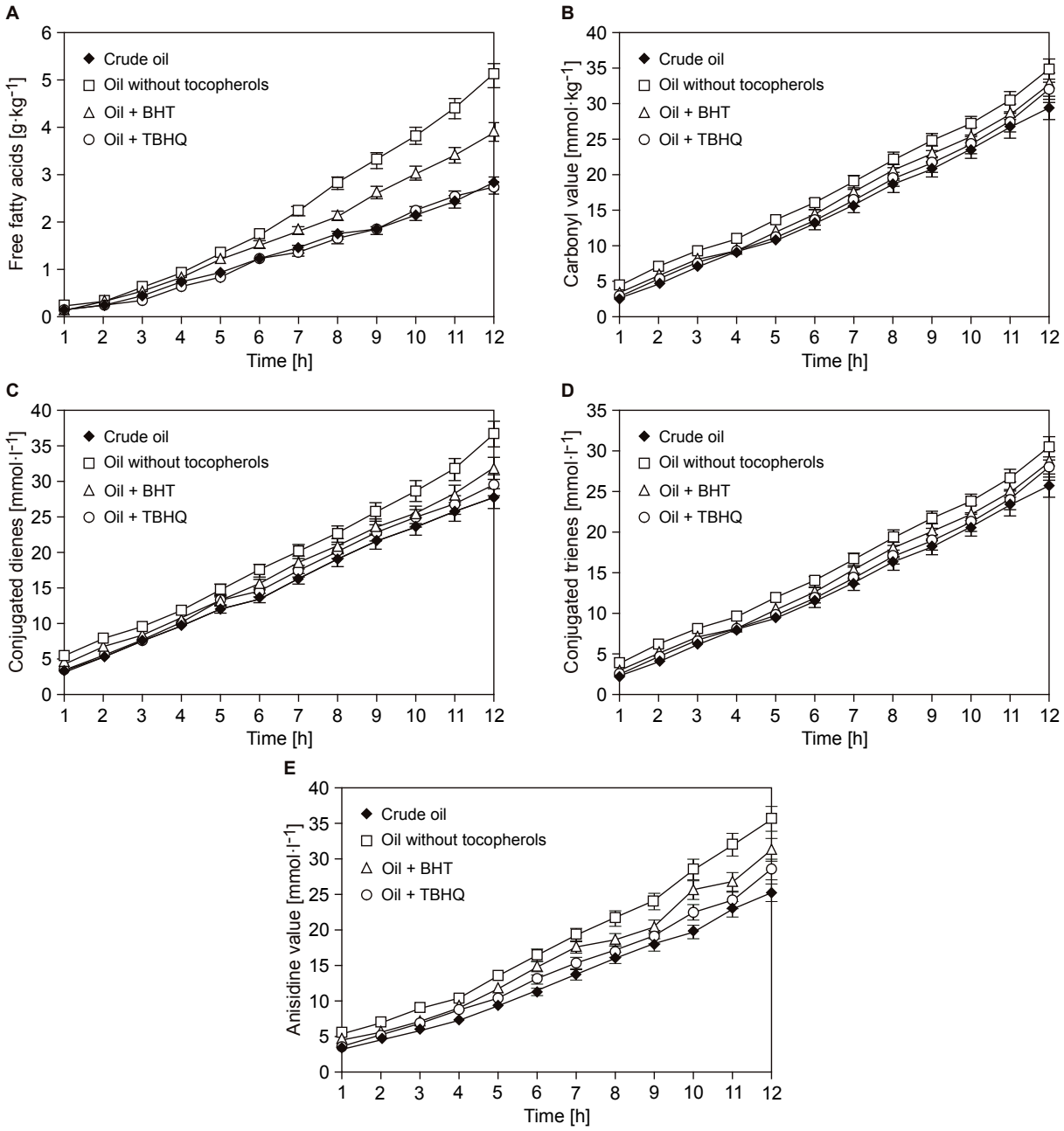


**Fig. 1.** Oxidation parameters of Kangar seed oil during frying at 180 °C.

A – Free fatty acid (FFA), B – Carbonyl value (CV), C – Conjugated diene value (CDV), D - Conjugated triene value (CTV), E – Anisidine value (AnV).

value of ratio SFA/UFA, which indicates oxidation of unsaturated fatty acids during the frying time. The smaller ratio of SFA/UFA is taken as good from nutritional aspect. The C18:2/C16:0 ratio can be considered as an indicator of the deterioration level [12]. Our results revealed that the ratio of linoleic to palmitic acid was reduced to 3.81 at the end of frying time. These results are similar to those of TALPUR et al. [29] who observed a decrease in both ratios of linoleic and linolenic to palmitic acids during frying of maize oil samples. The increase in saturated fatty acids may be attributed to the destruction of double bonds by polymerization and/or oxidation [8].

### Content of tocopherols

Crude Kangar seed oil can be considered as a rich source of tocols (tocopherols and toco-

trienols), with α-tocopherol being the most abundant tocopherol (649.0 mg·kg$^{-1}$ ± 1.6 mg·kg$^{-1}$), followed by γ-tocopherol (47.0 mg·kg$^{-1}$ ± 1.0 mg·kg$^{-1}$) and then β-tocopherol (39.0 mg·kg$^{-1}$ ± 0.9 mg·kg$^{-1}$) (Tab. 1). Among tocopherols, α-tocopherol has received the most attention in connection with vitamin E properties, but also the other isomers are recognized as having an important antioxidant activity [26, 27]. Tocotrienols are known to possess a higher antioxidant activity than tocopherols and they may have anticancer properties [30, 31]. The most abundant tocotrienol in Kangar seed oil was α-tocotrienol (13.0 mg·kg$^{-1}$ ± 0.6 mg·kg$^{-1}$). In comparison with previously published articles, the determined tocols content of Kangar seed oil was higher than of other vegetable oils such as sunflower or cottonseed oil [32].

#### Free fatty acids

The changes in FFAs of the oil samples during frying at 180 °C are shown in Fig. 1A. FFAs are quickly oxidized, and they catalyse additional oxidation of polyunsaturated fatty acids by activation and solubilization of catalytic metal salts [33]. The greatest increase in FFAs was observed in tocopherol-free oil samples, which confirms that unprotected Kangar seed oil (tocopherols-free oil) is more susceptible to degradation during frying in comparison with samples with added artificial or natural antioxidants. At the end of the frying period, the FFA levels of the oil without tocopherols, crude, BHT and TBHQ oils were 5.1 g·kg$^{-1}$, 2.8 g·kg$^{-1}$, 3.9 g·kg$^{-1}$ and 2.7 g·kg$^{-1}$, respectively. Consequently, adding of synthetic antioxidants and removing of tocopherols caused a decrease and increase in FFAs content during frying, respectively. Obtained results are in good agreement with previously conducted investigations [34, 35].

#### Oxidation stability

Many factors could affect the formation of carbonyl compounds during the frying process such as the frying time, temperature and/or antioxidant content [20, 36]. The changes in *CV* during the frying process are demonstrated in Fig. 1B. With increasing frying time, a rapid increase ($p < 0.05$) in *CV* of all Kangar seed oil samples was observed. *CV* of the oil without tocopherols, crude, BHT and TBHQ oil samples increased from 1.36 mmol·kg$^{-1}$ to 34.60 mmol·kg$^{-1}$, 29.10 mmol·kg$^{-1}$, 32.60 mmol·kg$^{-1}$ and 31.70 mmol·kg$^{-1}$ after 12 h of frying at 180 °C, respectively. However, none of the reported *CV* values of the oil samples exceeded the recommended level (50 mmol·kg$^{-1}$), which is set in Japan [37]. The low levels of *CV* in crude oil samples could correspond to tocopherol and tocotrienol compounds, which could act as antioxidants (Tab. 2) [37, 38].

Absorbance at 232 nm measures the concentration of CD, which represents the level of primary oxidation products. The changes in CD values during frying of the oil samples are shown in Fig. 1C. The absorbance of the crude Kangar seed oil was significantly ($p < 0.05$) different from the tocopherol-free oil, and from oils added synthetic antioxidants. At the end of the frying time, CD values for the crude, without tocopherols, BHT and TBHQ oils were 27.5 mol·l$^{-1}$, 36.6 mol·l$^{-1}$, 31.7 mol·l$^{-1}$ and 29.4 mol·l$^{-1}$, respectively.

Considering the observed results, significant effects on the absorbance at 268 nm for the crude oil was noted in a study of Urbančič et al. [35] (Fig. 1D). At the end of the frying period, this absorbance of tocopherol-free oil was greater in comparison with crude oil, also the concentrations of CT of crude, tocopherol-free, BHT- and TBHQ-added oils were recorded as 19.6 mmol·l$^{-1}$, 27.5 mmol·l$^{-1}$, 24.4 mmol·l$^{-1}$ and 21.7 mmol·l$^{-1}$, respectively. Results revealed that the CD values were considerably higher than CT values due to the high concentration of linoleic acid in the Kangar seed oil [35].

*AnV* increased over 12 h of frying (Fig. 1E). It was also observed for all samples that, during frying *AnV* changed significantly. At 12 h, *AnV* of tocopherol-free oil reached 35.6 mmol·l$^{-1}$ oil, whereas for crude, BHT and TBHQ oil samples, the values were 25.1 mmol·l$^{-1}$, 31.2 mmol·l$^{-1}$ and 28.4 mmol·l$^{-1}$, respectively. An increase of *AnV* in all treatments with a definite pattern correlated with carbonyl, CD and CT values. The following decreasing order of inhibition of *AnV* was observed among the samples: crude > TBHQ > > BHT > oil without tocopherols.

The increase in the rate of oxidation by exposing oil samples to high temperature in the presence of an extreme amount of air could be demonstrated by *OSI* [23]. A decrease of *OSI* in all of the examined treatments was recorded during frying at 180 °C for 12 h (Fig. 2). At the end of the frying process, the *OSI* values were 3.0 h, 0.9 h, 2.3 h and 2.6 h, respectively, for crude, tocopherol-free, BHT- and TBHQ-added oil samples.

#### Kinetic data analyses

The data of oxidation kinetic of oil samples based on *OSI* were obtained during frying at 180–200 °C. The $T_C$ and $Q_{10}$ values, which demonstrate the level of temperature effect on the oxidation rate of lipid systems, are considered to be the quantities representative of edible oils [12]. $T_C$ cal-

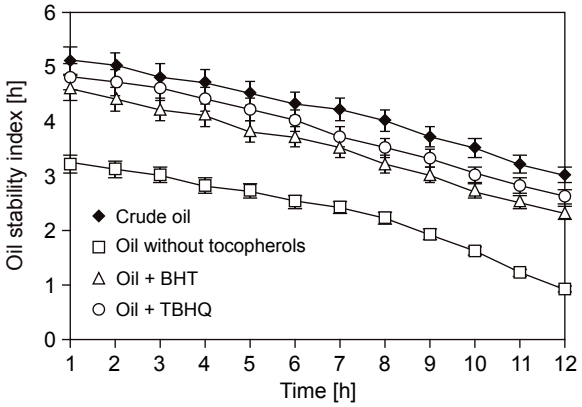


**Fig. 2.** Oil stability index of Kangar seed oil samples during frying at 180°C.

culated in terms of *OSI*, ranged from –0.070 °C$^{-1}$ to –0.015 °C$^{-1}$ and $Q_{10}$ values ranged from 1.41 to 5.01 (Tab. 3). The crude oil demonstrated the lowest $Q_{10}$ value among all treatments. The temperature dependence of lipid oxidation decreased with the presence of tocopherols (lowest reported value) or synthetic antioxidants. In other words, crude oil was the most stable sample during frying. Furthermore, the frying time significantly affected temperature dependence of lipid oxidation. Consequently, $Q_{10}$ and $T_C$ depended on the frying time and the type of antioxidant. HASHEMI et al. [12] reported that $Q_{10}$ and $T_C$ of oil samples containing antioxidants were lower than control during oxidation of a blended vegetable oil.

Using $E_a$, which is the least amount of energy that must be consumed in order to begin a chemical reaction, is another approach to describe the dependency of the rate of lipid deterioration on temperature [36]. $E_a$ of the frying oil samples varied significantly from 5.645 kJ·mol$^{-1}$ to 187.500 kJ·mol$^{-1}$ (Tab. 4). HASHEMI et al. [12] reported that, according to *OSI*, activation energies of blended oil without antioxidants and with TBHQ were 126.090 kJ·mol$^{-1}$ and 82.470 kJ·mol$^{-1}$, respectively. $E_a$ of control samples was significantly higher than that of oil samples containing antioxidants. Also in the case of crude oil samples, $E_a$ was significantly lower than the reported amounts for oils with synthetic antioxidants. TAN et al. [40] reported that chemical reactions with low $E_a$ were temperature-insensitive and reactions with high $E_a$ were temperature sensitive. Thus, temperature dependency of the oxidation reaction decreased with

**Tab. 3.** Effect of frying time on temperature coefficient and $Q_{10}$ of Kangar oil.

| Sample | $T_C$ [°C$^{-1}$] | | | $Q_{10}$ | | | $R^2$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | Time | | | | | | | | |
| | 1 h | 6 h | 12 h | 1 h | 6 h | 12 h | 1 h | 6 h | 12 h |
| Crude oil | –0.015$^{aA}$ | –0.025$^{bA}$ | –0.035$^{cA}$ | 1.41$^{cD}$ | 1.79$^{bD}$ | 2.24$^{aD}$ | 0.964 | 0.986 | 0.993 |
| Stripped oil | –0.055$^{aD}$ | –0.065$^{bD}$ | –0.070$^{cD}$ | 3.55$^{cA}$ | 4.47$^{bA}$ | 5.01$^{aA}$ | 0.997 | 0.998 | 0.993 |
| Oil + BHT | –0.025$^{aC}$ | –0.040$^{bC}$ | –0.050$^{cC}$ | 1.79$^{cB}$ | 2.51$^{bB}$ | 3.16$^{aB}$ | 0.986 | 1.000 | 1.000 |
| Oil + TBHQ | –0.020$^{aB}$ | –0.020$^{bB}$ | –0.040$^{cB}$ | 1.58$^{cC}$ | 1.99$^{bC}$ | 2.51$^{aC}$ | 0.923 | 1.000 | 1.000 |

Means within a column with the same uppercase lowercase letters are not significantly different at $p < 0.05$. For the same parameters, means within a row with the same lowercase letters are not significantly different at $p < 0.05$. Temperature coefficient and $Q_{10}$ were calculated based on oil stability index.
$T_C$ – temperature coefficient, $Q_{10}$ – temperature acceleration factor, $R^2$ – regression coefficient, BHT – butylated hydroxytoluene, THBQ – tertiary butylhydroquinone.

**Tab. 4.** Effect of frying time on frequency factor and activation energy of Kangar oil.

| Sample | $A$ [h$^{-1}$] | | | $E_a$ [kJ mol$^{-1}$] | | | $R^2$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | Time | | | | | | | | |
| | 1 h | 6 h | 12 h | 1 h | 6 h | 12 h | 1 h | 6 h | 12 h |
| Crude oil | 0.058$^{cD}$ | 0.659$^{bD}$ | 2.305$^{aD}$ | 5.645$^{cD}$ | 11.280$^{bD}$ | 24.260$^{aD}$ | 0.962 | 0.986 | 0.966 |
| Stripped oil | 3.942$^{cA}$ | 7.321$^{bA}$ | 21.240$^{aA}$ | 38.740$^{cA}$ | 67.270$^{bA}$ | 187.500$^{aA}$ | 0.997 | 0.984 | 0.968 |
| Oil + BHT | 0.562$^{cB}$ | 1.999$^{bB}$ | 5.629$^{aB}$ | 10.830$^{cB}$ | 22.360$^{bB}$ | 52.220$^{ab}$ | 0.986 | 0.990 | 0.979 |
| Oil + TBHQ | 0.257$^{cC}$ | 1.112$^{bC}$ | 3.354$^{aC}$ | 8.149$^{cC}$ | 14.930$^{bC}$ | 33.720$^{aC}$ | 0.923 | 0.992 | 0.986 |

Means within a column with the same uppercase lowercase letters are not significantly different at $p < 0.05$. For the same parameters, means within a row with the same lowercase letters are not significantly different at $p < 0.05$. Frequency factor and activation energy were calculated based on oil stability index.
$A$ – frequency factor, $E_a$ – activation energy, $R^2$ –regression coefficient.

**Tab. 5.** Effect of frying time on enthalpy and entropy of Kangar oil.

| Sample | $\Delta H^{++}$ [kJ·mol$^{-1}$] | | | $\Delta S^{++}$ [J·mol$^{-1}$·K$^{-1}$] | | | $R^2$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | Time | | | | | | | | |
| | 1 h | 6 h | 12 h | 1 h | 6 h | 12 h | 1 h | 6 h | 12 h |
| Crude oil | 1.667$^{cD}$ | 7.301$^{bD}$ | 20.280$^{aD}$ | 5645.100$^{cD}$ | –258.300$^{cD}$ | –213.100$^{aD}$ | 0.773 | 0.929 | 0.957 |
| Stripped oil | 34.750$^{cA}$ | 63.280$^{bA}$ | 183.500$^{aA}$ | 38736.100$^{cA}$ | –181.700$^{bA}$ | –149.500$^{aA}$ | 0.994 | 0.983 | 0.864 |
| Oil + BHT | 6.678$^{cB}$ | 18.390$^{bB}$ | 48.230$^{aB}$ | 10828.100$^{cB}$ | –246.400$^{bB}$ | –149.400$^{ab}$ | 0.991 | 0.988 | 0.979 |
| Oil + TBHQ | 4.172$^{cC}$ | 10.950$^{bC}$ | 29.736$^{aC}$ | 8149.100$^{cC}$ | –252.300$^{aC}$ | –191.100$^{aC}$ | 0.820 | 0.990 | 0.984 |

Means within a column with the same uppercase letters are not significantly different at $p < 0.05$. For the same parameters, means within a row with the same lowercase letters are not significantly different at $p < 0.05$. Enthalpy and entropy were calculated based on oil stability index.
$\Delta H^{++}$ – enthalpy, $\Delta S^{++}$ – entropy, $R^2$ – regression coefficient.

availability of tocopherols or incorporation of synthetic antioxidants. As a result of the frying time elapsing, the activation energy of all samples was increased. According to the Arrhenius equation, the frequency factor is considered to be the other main kinetic parameter affecting the rate of the oxidation. The frequency factor for oxidation of the Kangar seed oil samples during frying varied significantly from log 0.058 h$^{-1}$ to log 21.240 h$^{-1}$. The frequency factor of control was significantly higher than antioxidants added treatments. The loss of rotational freedom in the transition state due to the presence of tocopherols or synthetic antioxidants can lead to low frequency factors. Additionally, frequency factors of crude oil samples were lower than those of oils containing synthetic antioxidants. The decrease of frequency factor in the presence of antioxidants may be due to the combination of donating hydrogen with antioxidants and the loss of rotational freedom in the transition state [12].

The calculated $\Delta S^{++}$ and $\Delta H^{++}$ for lipid oxidation in all oil samples during frying are summarized in Tab. 5. The $\Delta H^{++}$ and $\Delta S^{++}$ values calculated from *OSI* can be summarized as ranging from 1.667 kJ·mol$^{-1}$ to 183.474 kJ·mol$^{-1}$ and from –258.300 J·mol$^{-1}$·K$^{-1}$ to 149.500 J·mol$^{-1}$·K$^{-1}$, respectively. Farhoosh and Hoseini-Yazdi [41] reported the $\Delta H^{++}$and $\Delta S^{++}$ values based on *OSI* for oxidation of olive oil samples to range from 86.120 kJ·mol$^{-1}$ to 109.930 kJ·mol$^{-1}$ and from –112.150 J·mol$^{-1}$·K$^{-1}$ to –48.200 J·mol$^{-1}$·K$^{-1}$, respectively. The positive sign of enthalpy indicates the endothermic nature of the activated complex formation of the oxidation reaction. According to Tan et al. [40], highly unsaturated oils have a greater enthalpy in comparison with oils with low levels of unsaturated fatty acids. Results showed that enthalpy of crude oil was lower than that of oils containing synthetic antioxidants. It should be mentioned that concentration of the activated complex in crude oil was lower when compared with antioxidants-added oils, so the rate of oxidation reaction during frying was slower. The greater negative entropy value for crude oil showed fewer numbers of species in the activated complex state [12, 39]. Thus, the activated complex for lipid oxidation during frying in crude oil was less probable and, consequently, the oxidation rate was slower. Hashemi et al. [12] indicated that antioxidants decreased enthalpy and entropy of the oxidation reaction. Results also showed that an increase in the frying period increased both enthalpy and entropy of the oxidation reaction and, therefore, increased oxidation rate during frying.

Fig. 3 demonstrates the oxidative stability of the Kangar seed oils as a function of $\Delta G^{++}$ of the activated complexes formation during frying at temperatures from 180 °C to 200 °C. Linear equations could be utilized to explain the relationship between $\Delta G^{++}$ and *OSI*, while the oxidative stability of the Kangar seed oils increased constantly. The Gibbs free energy increased as frying temperature increased because of the endothermic nature of the activated complex formation during

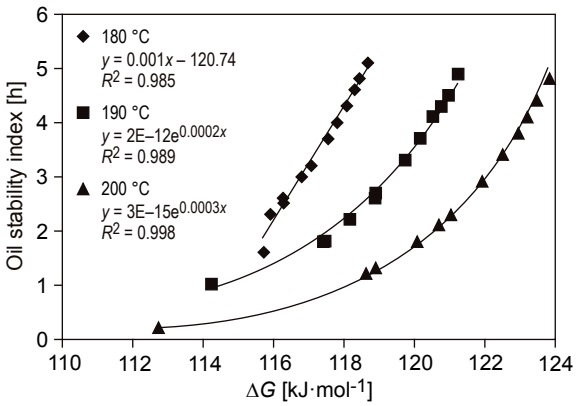


**Fig. 3.** Relationship between the free energy of activation and the oil stability index.

oxidation of the Kangar seed oils and because of decreased disordering of the reactants in the activated complexes [12]. Crude oil samples had higher $\Delta G^{++}$ values in comparison to samples containing antioxidants, showing slower oxidation reaction rates during frying at a constant temperature.

## CONCLUSIONS

It can be concluded that Kangar seed oil is a proper edible oil for frying of foods at high temperatures, with notable nutritional benefits such as high amounts of unsaturated fatty acids and natural antioxidants. The crude oil offered slightly better stability during frying than the oils supplemented with artificial antioxidants BHT or TBHQ. According to kinetic parameters, crude oil showed lower temperature sensitivity than oils containing synthetic antioxidants, a fact that should be considered when using them in high-temperature processes. Due to the observed desirable characteristics of crude Kangar seed oil, possible utilization in the food industry as a stable frying oil, as well as further investigations regarding stability at emerging technologies, are recommended.

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