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Effect of Deep Frying on Fatty Acid Composition and Polymer Content in Sunflower and Soybean Oils

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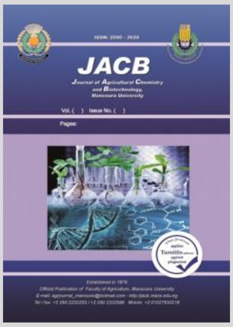

ABSTRACT

The purpose of this investigation was to study the influence of deep frying for Farm Frits Potato fingers at 180 ºC on oxidation and thermal degradation in sunflower and soybean oils. Changes in fatty acid composition, refractive index, acid value, peroxide value, thiobarbituric acid (TBA), and polymer content were used to estimate the oxidation and thermal degradation in investigated oils. The changes in fatty acid composition were observed in both of them whereas saturated fatty acid (SFA) increased, particularly palmitic and stearic acid, as well as mono unsaturated fatty acids (MUFA) increased, particularly oleic acid. In contrast, poly unsaturated fatty acids (PUFA) decreased, particularly linoleic acid and linolenic acid, as a result of thermal oxidation, which was produced as oil was exposed to high temperatures through frying, but the rate of change in fatty acid profile in soybean oil was higher than in sunflower oil. Also, results showed that peroxide value, acid value, thiobarbituric acid and polymer content were increased in sunflower and soybean oils but the rate of increment in soybean oil was higher than in sunflower oil. Finally, sunflower oil exhibited high oxidative stability in comparison to soybean oil during deep frying.

Keywords: Fatty acid composition - peroxide value - acid value - polymer content sunflower oil - soybean oil.

INTRODUCTION

Frying process is one of the most popular cooking methods to make pleasant foods with golden color, delicious flavor and desired texture through a complete inundation of items in frying oil (Yu *et al.,* 2018). Customers prefer deep-fat fried products as they have a pleasant flavor, color, and crisp texture (Boskou *et al*., 2006). The priority of fried foods is attributed to the rapid and appropriate method for food preparation, and also because, after frying, foods exhibit the desired sensory properties of texture, flavor, palatability, and color, which are highly acceptability by consumers (Dobarganes *et al*., 2000). The different factors that influence the performance and frying oil stability may be classified into two categories: external and internal. External influences include fryer type, frying temperature, frying duration, and oxygen presence. Internal impacts include the fatty acid profile, minor component amounts, and minor component composition (Aladedunye, 2015). Oil degradation is influenced by a number of factors. One of the most important impacts of frying oil quality is the frying process, as well as effects such as the oil's characteristics and composition, and the food's interaction with the frying oil (Aladedunye, 2015 and Rossell, 2001). Hydrolysis, oxidation, isomerization, polymerization, and cyclization are examples of complex reactions. These interactions produce volatile and nonvolatile chemicals that alter the frying oil's sensory, functional, and nutritional properties as a result of the frying process, which was conducted at extremely high temperatures (150-180 ºC) in the presence of substrate, food stuff water content, and oxygen (Alireza *et al*., 2010). Volatile and non-volatile compounds including free fatty acids, aldehyde, lactones, hydrocarbons, diglycerides, monoglycerides, glycerol, trans isomers, monomers, and polymers of triglycerides can form, during frying process (jung *et al*., 2014). The volatile chemicals are dissolved and destroyed, while non-volatile decomposition products accumulate in the frying oil, causing additional deterioration. These substances are absorbed by fried foods, enter the diet, and have an impact on public health (Che Man *et al*., 2003 and Romero *et al*., 1998). Furthermore, some of these accumulating products have been associated to harmful health impacts by inhibiting enzymes, destroying vitamins, and perhaps generating mutations or causing troubles in digestive system (Clark and Serbia, 1991). As a result, in order to protect the health of the public, it's necessary not only to monitor the quality of the oils used, but also to evaluate their stability under ordinary frying conditions (Diop *et al*., 2014). Therefore, this investigation was carried out to determine the changes in fatty acid composition, polymer content and some physicochemical properties of sunflower and soybean oils during frying at 180 ºC.

MATERIALS AND METHODS

Materials:

Oils

Refined soybean and sunflower oils in polyethylene terephthalate (PET) bottles were obtained from oil tec. Company for Oils and Detergents, Sadat City, Egypt.

Potatoes

The finger potatoes (frozen farm frits with dimensions 9×9×60 mm) were obtained from Almahalawy's market, Cairo, Egypt.

Methods:

Frying Process:

A known amount (2 kg) of each oil was heated to 180 °C in a thermostatically temperature-controlled fryer

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(SASHO Deep Fryer-SH 308). Farm frits (200 g) were then fried for an extended 8 minutes. After each frying cycle, the oils were allowed to cool for 7 minutes, totaling 240 minutes of frying time. Frying oil samples (100 g) were taken every 30 minutes, cooled to room temperature, and then frozen at -18°C for further analysis. The fresh oil (zero time) was also kept at-18 °C for the next experiments (Karakaya and Şimşek, 2011).

Frying process was conducted in the laboratory of biochemistry department-Faculty of Agriculture, Al-Azhar University, Cairo, Egypt.

Identification of fatty acid profile of oils by GLC:

Fatty acid profile was analyzed (in the laboratory of oils and fats- Food Technology Research Institute - FTRI) as described in procedure of ISO 12966-2 (2017).

Physicochemical properties of sunflower and soybean oils during frying at 180 ºC.

According to AOAC (2005), refractive index at 25ºC, acidity (as oleic acid %) and peroxide value (meq.O_2/kg oil) were estimated.

Pearson (1976) method was used to estimate the malonaldehyde compound content (mg/kg oil), while Wu and Nawer (1986) method was used to estimate polymer content % in investigated oils.

These analysis were conducted in the laboratories of biochemistry department-Faculty of Agriculture, Al-Azhar University, Cairo, Egypt

Statistical analysis:

All data were first analyzed by one way ANOVA. Duncan's multiple rang test was used for the determination of the significant differences between values; the p-value <0.05 as the level of the significance.

RESULTS AND DISCUSSION

Fatty acid profile of sunflower and soybean oils before frying

Data in Table (1) exhibit the fatty acid profile of sunflower and soybean oils before frying. The fatty acid profiles of oils were classified into 3 main groups, i.e.; major (>10%), minor (< 10%) and trace (< 1%). Sunflower oil contained oleic acid ($C_{18:1}$) and linoleic acid ($C_{18:2}$) were accounted as major constituents, where their proportions were 24.31and 62.22, respectively. While, C16:0, C18:0 and C18:3 were presented as minor amount, where their proportions were 7.27and 3.78and 1.04, respectively; whereas, C14:0, C16:1, C17:0, C17:1, C20:0 , C20:1 and C22:0 in trace amounts, where their proportions were 0.08, 0.09, 0.05, 0.02, 0.27, 0.15 and 0.72, respectively. These findings are similar to those found in earlier research by Uslu and Özcan (2018) and Ozulku *et al.*, (2017).

Soybean oil contained C16:0, C18:1 and C18:2 were accounted as major constituents, where their proportions were 11.08, 21. 1 and 55.07, respectively. While, C18:0 and C18:3 were presented as minor quantities, where their proportions were 4.1 and 7.55, respectively; whereas, C14:0, C16:1, C17:0, C17:1, C20:0 , C20:1 and C22:0 in trace amount, where their proportions were 0.07, 0.09, 0.10, 0.05, 0.30, 0.18 and 0.31, respectively. These findings are similar to those found in earlier research (Kaur *et al.*, 2020 and Ozulku *et al.*, 2017). Both linoleic acid and α-linolenic acid are necessary in human diets, and must be supplied from food (Pardauil *et al.*, 2017). Saturated fatty acids with shorter chain lengths, such as Caprylic C_8, Capric C_{10} and lauric acid C_{12}, were not identified in soybean and sunflower oils. Because they raise LDL cholesterol, these short chain fatty acids increase the risk of coronary heart disease (Siri-Tarino *et al*., 2010). Soybean oil is an excellent source of PUFAs (ω 6 and ω 3), which are essential for public health (Saini and Keum, 2018).

Table 1. Fatty acid profile of sunflower and soybean oils before frying

(FA %)	Sunflower oil	Soybean oil
C14:0	0.08	0.07
C16:0	7.27	11.08
C16:1	0.09	0.09
C17:0	0.05	0.10
C17:1	0.02	0.05
C18:0	3.78	4.1
C18:1	24.31	21.1
C18:2	62.22	55.07
C18:3	1.04	7.55
C20:0	0.27	0.30
C20:1	0.15	0.18
C22:0	0.72	0.31
SFAs	12.17	15.96
MUFAs	24.57	21.42
PUFAs	63.26	62.62

Physicochemical properties of Sunflower and Soybean oils before frying.

It is important to investigate the physicochemical properties of edible oils in order to determine their quality and consumer desirability, as well as the healthy, safe quality features of these lipids and the products cooked or prepared with them. Table (2) shows the physicochemical properties assessments of fresh oils under investigation, physiochemical properties of oil samples are refractive index, acid value, peroxide value, thiobarbituric acid and polymer content. The general feature of oils reflects good properties, acceptable levels of acidity and peroxides.

Table 2. Physicochemical properties of Sunflower and Soybean oils before frying

Parameters	Sunflower oil	Soybean oil
Refractive index	1.4724	1.4729
Peroxide value (meq/kg)	0.55	0.86
Acid value	0.021	0.030
Thiobarbituric acid (TBA)	0.006	0.010
polymer content %	0.00	0.00

Changes in fatty acid profile of sunflower and soybean oils during frying

The fatty acid content (FAC) of oils plays a significant role in preserving the characteristics of the oil throughout the frying operation (Kaur *et al*., 2020). According to the results presented in Table 3, changes in the fatty acid profile of sunflower and soybean oils were observed with increasing time of frying. The amounts of PUFAs, which are essential in human nutrition, were slightly reduced as the frying time was increased, whereas SFA and MUFA were slightly enhanced in both of them. There had been a slight increase in SFAs and MUFA opposite to a decline in PUFA during 4 hours of frying. In sunflower and soybean oil, however, considerable increases in SFA and MUFA, particularly palmitic, stearic acid and oleic acid, and decreases in PUFA, particularly linoleic acid and linolenic acid, were found during the fourth hour of frying. Our findings are consistent with those of Abd Razak *et al*. (2021) and Ramadan *et al*. (2006) who observed a reduction in linoleic acid levels and an increment in palmitic and stearic acid levels after two days of frying in two different vegetable oil blends. The breakdown of (PUFA) in vegetable oils during deep frying might be the cause of the alterations in fatty acid profile.

Table 3. Changes in fatty acid profile of sunflower and soybean oils during frying

(FA %)	Sunflower oil					Soybean oil				
	Frying time (min)									
	0	60	120	180	240	0	60	120	180	240
C14:0	0.08	0.09	0.10	0.12	0.12	0.07	0.08	0.09	0.09	0.11
C16:0	7.27	7.35	7.44	7.55	7.68	11.08	11.28	11.44	11.60	11.89
C16:1	0.09	0.09	0.10	0.10	0.11	0.09	0.09	0.09	0.09	0.09
C17:0	0.05	0.05	0.06	0.06	0.07	0.10	0.11	0.11	0.11	0.11
C17:1	0.02	0.02	0.02	0.02	0.02	0.05	0.05	0.05	0.06	0.06
C18:0	3.78	3.81	3.85	3.91	3.98	4.1	4.20	4.32	4.41	4.51
C18:1	24.31	24.43	24.53	24.63	24.70	21.1	21.19	21.27	21.32	21.40
C18:2	62.22	61.98	61.74	61.49	61.23	55.07	54.76	54.50	54.26	53.92
C18:3	1.04	1.02	0.99	0.91	0.85	7.55	7.45	7.32	7.24	7.08
C20:0	0.27	0.28	0.28	0.30	0.32	0.30	0.30	0.31	0.31	0.31
C20:1	0.15	0.15	0.15	0.16	0.17	0.18	0.18	0.18	0.18	0.19
C22:0	0.72	0.73	0.74	0.75	0.75	0.31	0.31	0.32	0.33	0.33
SFAs	12.17	12.31	12.47	12.69	12.92	15.96	16.28	16.59	16.85	17.26
MUFAs	24.57	24.69	24.80	24.91	25.00	21.42	21.51	21.59	21.65	21.74
PUFAs	63.26	63.00	62.73	62.4	62.07	62.62	62.21	61.82	61.50	61.00

During repeated frying, fatty acids containing double (π) bonds are more susceptible to thermal degradation and oxidative deterioration (Debnath *et al*., 2012; Hassanien and Sharoba, 2014). In comparison to soybean oil, there was a minor alteration in fatty acid profile of sunflower oil after the first, second, third and fourth hours of frying, as indicated in Table 3. Throughout two days of frying, Hassanien and Sharoba (2014) indicated that cotton seed oil exhibited a higher alterations in fatty acid profile (a raise in palmitic $C_{16:0}$ and stearic $C_{18:0}$ acids and a reduction in linoleic) than sunflower and palm olein oil (a reduction in linoleic and an increment in palmitic and stearic acids proportions). Earlier studies have reported that increasing the number of repeated frying periods or frying cycles causes an increase in SFA and MUFA. In contrast, a reduction in PUFA in oils (Sharoba and Ramadan, 2012; Multari *et al*., 2019 and Zribi *et al*., 2014).

Changes in physical and chemical properties of sunflower and soybean oils during frying.

Refractive index

The refractive index is a useful analytical indicator for the degree of oil unsaturation, and as the number of conjugated double bonds in the oil increased, thus increased the refractive index (Ali and El Anany, 2014). Data presented in Table 4, indicates that the refractive index of sunflower and soybean oils increased gradually with increasing time of frying. This increase may be attributed to conjugated unsaturation which, was formed as frying oils are exposed to extreme heat during frying, similar findings were reported by Tabasum *et al*. (2012); Ali and El Anany (2014) and Hashem *et al*. (2017). The frying process is widely recognized for converting some non-conjugated double bonds to conjugated double bonds. As a result of this case, the refractive index increased (Ali and El Anany, 2014).

Acid Value

Free fatty acids are considered as an important indicator for hydrolysis in fats and oils during processing, storage and frying (Shahidi, 2005). Oil is exposed to oxygen and moisture at high temperatures, during frying thus lead to hydrolysis of triacylglycerol. As a result, free fatty acids are produced. As a result, free fatty acids are produced. The released fatty acids are more susceptible to thermal oxidation, resulting in an unpleasant odor and off flavor in the frying oil and products (Horuz and Maskan, 2015). The alterations in acid values of sunflower and soybean oils during frying are shown in Table 5, the initial acid values of oils before frying ranged from 0.021 for sunflower oil to 0.030 for soybean oil, revealing that they are of high quality. Generally, gradual increases in the acid values were observed in the investigated oils with increasing frying time, but soybean oil exhibited an acid value higher than sunflower oil at the end of the frying process. Similar findings of an increment in the acid value of frying oils with an increment in frying cycles were demonstrated in earlier studies (Kaur *et al*., 2021; Debnath *et al*., 2012; Zribi *et al*., 2014). Ramadan *et al*. (2006) also found an increase in the FFA level after two days of frying in two different vegetable oil blends. Release of free fatty acids consider as indicator for triacylglycerol hydrolysis during frying (Karimi *et al*., 2017).

Table 4. The changes in refractive index of sunflower and soybean oils during frying

Frying time (min)	Refractive index	
	Sunflower oil	Soybean oil
0	1.4724	1.4729
30	1.4729	1.4741
60	1.4738	1.4748
90	1.4746	1.4755
120	1.4755	1.4763
180	1.4764	1.4770
210	1.4770	1.4785
240	1.4783	1.4796

Table 5. The changes in acid value of sunflower and soybean oils during frying

Frying time (min)	Acid value	
	Sunflower oil	Soybean oil
0	$0.021^{Ag}\pm0.001$	$0.030^{Ah}\pm0.000$
30	$0.030^{Bg}\pm0.000$	$0.065^{Ag}\pm0.003$
60	$0.062^{Bf}\pm0.005$	$0.111^{Af}\pm0.001$
90	$0.094^{Be}\pm0.002$	$0.195^{Ae}\pm0.003$
120	$0.120^{Bd}\pm0.003$	$0.275^{Ad}\pm0.003$
180	$0.162^{Bc}\pm0.002$	$0.365^{Ac}\pm0.005$
210	$0.211^{Bb}\pm0.002$	$0.488^{Ab}\pm0.005$
240	$0.329^{Ba}\pm0.007$	$0.579^{Aa}\pm0.001$

Where*:* Mean values in the same row (as a capital letter) or column (as a small letter) with the same letter are not significantly different ($p<0.05$).

Peroxide value

The production of peroxides and hydroperoxides as a result of the oxidative deterioration of oils is known as PV (Suri *et al*., 2019). The changes in the Peroxide values of sunflower and soybean oils during deep fat frying are given in Table 6, the initial Peroxide value of sunflower and soybean oils before frying ranged from 0.55 meqO_2/kg for sunflower oil to 0.86 meqO_2/kg for soybean oil, Both two fresh oils had a PV of less than 10 meqO_2/kg, which is the permissible limit. From results in table 6, it could be observed that with increasing the frying time the PV of all samples was elevated gradually and significantly, indicating the occurrence of primary oxidation in fatty acids during the frying periods. Similar findings of an increment in peroxide value were reported by Ramadan *et al*. (2006) who found a similar rise in PV after two days of frying in two different vegetable oil blends. Edible oils containing high proportions of (PUFA) were more susceptible to oxidation and had a higher increment in PV as frying time increased. As a result, free radical action on double bonds in PUFA and the aggregation of peroxides and hydroperoxides in vegetable oil during the deep-frying process lead to an increase in PV (Liu *et al*., 2018). In earlier studies, a similar trend in oil PV was observed as deep-frying duration increased (Kaur *et al*., 2021; Liu *et al*., 2019 and Hashem *et al*., 2017).

Table 6. The changes in Peroxide value of sunflower and soybean oils during frying.

Frying time (min)	Peroxide value	
	Sunflower oil	Soybean oil
0	0.55±0.00^{Bh}	0.86±0.00^{Ah}
30	1.05±0.01^{Bg}	1.35±0.01^{Ag}
60	1.90±0.01^{Bf}	2.10±0.01^{Af}
90	2.69±0.01^{Be}	3.29±0.03^{Ae}
120	3.24±0.00^{Bd}	4.52±0.08^{Ad}
180	4.92±0.01^{Bc}	5.91±0.01^{Ac}
210	6.35±0.01^{Bb}	7.72±0.03^{Ab}
240	8.02±0.03^{Ba}	10.20±0.06^{Aa}

Where*:* Mean values in the same row (as a capital letter) or column (as a small letter) with the same letter are not significantly different ($p<0.05$).

TBA Values

The thiobarbituric acid (TBA) test is a reaction between TBA and malonaldehyde, the most common product of secondary oxidation of oil, and it measures aldehyde contents in oil, mainly 2,4-dienals and 2-alkenals, produced from the decomposition of hydroperoxides formed during the oxidation of food lipids. As a result, the TBA value is regarded as a good chemical quality criterion for determining the oxidative state of edible oils and fats, and it represents the degree of stability of any edible oil (Lalas, 1998).

Table 7. The changes in TBA value of sunflower and soybean oils during frying

Frying time (min)	TBA value	
	Sunflower oil	Soybean oil
0	0.006^{Ah}±0.000	0.010^{Ag}±0.000
30	0.063^{Bg}±0.001	0.075^{Ag}±0.001
60	0.110^{Bf}±0.002	0.184^{Af}±0.002
90	0.170^{Be}±0.002	0.271^{Ae}±0.001
120	0.244^{Bd}±0.002	0.461^{Ad}±0.001
180	0.303^{Bc}±0.002	0.452^{Ac}±0.001
210	0.384^{Bb}±0.001	0.535^{Ab}±0.002
240	0.434^{Ba}±0.001	0.620^{Aa}±0.006

Where*:* Mean values in the same row (as a capital letter) or column (as a small letter) with the same letter are not significantly different ($p<0.05$).

Table 7 shows the variations in TBA values of sunflower and soybean oils after deep fat frying. Increasing the frying time caused gradually and significantly an increase in TBA values for all oil samples investigated. The fact that the unstable primary oxidative molecules (i.e., hydroperoxides) breakdown further to produce aldehydes might explain the increment in TBA. The TBA reagent reacts with these carbonyl compounds to create colored compounds that absorb at 532nm (Przybylski and Eskin, 1995). Soybean oil recorded TBA value higher than sunflower oil at the frying duration, whereas soybean oil recorded 0.620 mg malonaldehyde / kg in the contrary sunflower oil recorded 0.434 mg malonaldehyde / kg, similar findings were reported by Hashem *et al*. (2017).

Polymer content %

The changes in the polymer content of sunflower and soybean oils during the frying process are tabulated in table 8, an increase in the polymer content of all oil samples under this study was observed with prolonging the frying time. The highest value for polymer content was recorded for soybean oil (0.756 %) at the end of frying period. On the other hand, sunflower oil had significantly the lowest values 0.629 at the end of frying period. These results are in agreement with Adel *et al*. (2015) and Hashem *et al*. (2017) who reported that Polymer content% increased gradually during frying and were strongly correlated with prolonging the frying period. Formation of dimers and polymers depends on the oil type, frying temperature, and number of frying. As the number of frying and the frying temperature increase, the amounts of polymers increased (Cuesta *et al*., 1993 and Takeoka *et al*., 1997).

Table 8. The changes in Polymer content % of sunflower and soybean oils during frying.

Frying time (min)	Polymer content %	
	Sunflower oil	Soybean oil
0	0.00^{g}	0.00^{h}
30	0.025^{Bg}±0.000	0.049^{Ag}±0.001
60	0.068^{Bf}±0.029	0.110^{Af}±0.008
90	0.180^{Be}±0.004	0.233^{Ae}±0.003
120	0.269^{Bd}±0.000	0.362^{Ad}±0.004
180	0.379^{Bc}±0.003	0.482^{Ac}±0.003
210	0.492^{Bb}±0.003	0.598^{Ab}±0.004
240	0.629^{Ba}±0.002	0.756^{Aa}±0.006

Where*:* Mean values in the same row (as a capital letter) or column (as a small letter) with the same letter are not significantly different ($p<0.05$).

CONCLUSION

As the frying time was extended, changes in chemical characteristics, fatty acid composition and polymer content of sunflower and soybean oils were detected. For various parameters, the characteristics of the investigated oils significantly changed as frying time increased with increasing frying time, soybean oil exhibited a significant shift in FFA content, PV, TBA, polymer content, and SFAs than sunflower oil, which might be attributed to soybean oil's high levels of linolenic fatty acid content.

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تأثير القلي العميق على الأحماض الدهنية ونسبة البوليمر في زيت زهرة الشمس وزيت فول الصويا

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الغرض من هذه الدراسة هو دراسة تأثير القلي العميق لأصابع بطاطس فارم فريتس عند درجة حرارة 180 مº على الأكسدة والتحلل الحراري في زيت زهرة الشمس وزيت فول الصويا. وقد استخدمت التغيرات في تركيب الأحماض الدهنية ومعامل الإنكسار ورقم الحموضة ورقم البيركسيد وحامض الثيوباربتيوريك ونسبة البوليمر لقياس الأكسدة والتحلل الحراري في الزيوت محل الدراسة. وقد لوحظ تغيرات في تركيب الأحماض الدهنية في كلاهما حيث زادت نسبة الأحماض الدهنية المشبعة لا سيما حمض البالمتيك وحمض الإستياريك, وكذلك الأحماض أحادية عدم التشبع لا سيما حمض الأوليك, وبالعكس قد انخفضت نسبة الأحماض الدهنية غير المشبعة لا سيما حمض اللينوليك وحمض اللينولينك كنتيجة للأكسدة الحرارية الناتجة بسبب الحرارة العالية التي تعرض لها الزيت اثناء التحمير, لكن معدل التغيرات في تركيب الأحماض الدهنية لزيت فول الصويا كان أعلى منه في زيت زهرة الشمس, كما أظهرت النتائج زيادة كل من رقم البيروكسيد ورقم الحموضة وحامض الثيوباربيتيورك ونسبة البوليمر في زيت فول الصويا وزيت زهرة الشمس ولكن كانت نسبة الزيادة أعلى في زيت الصويا مقارنة بزيت زهرة الشمس، وأخيرا فإن زيت زهرة الشمس أظهر ثباتا تأكسديا اعلى من زيت فول الصويا أثناء التحمير العميق.