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# Date Seed Oil as A Potential Natural Additive to Improve Oxidative Stability of Edible vegetable Oils

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SCIENTISTS warn against the dangers of frying food in oil as it releases toxic chemicals linked to cancer and heart disease. The negative effects of synthetic antioxidants lead to searching for a substitute with natural resources. In the present study, fruits of three date palm cultivars; 'Hayani', 'Sewi' and 'Sakouti', were collected at mature stage and date seeds were used for oil extraction. Chemical properties of the oil as well as rancimate measurements were measured to determine the oxidative stability of the oil. Different levels (5, 10. 15 %) of date seed oil were added to crude soybean oil and the oxidative stability for the mixer were then compared to the commercial soybean oil with BHT additive. Pit powder oil content ranged from 8.2-10.6.'Sewi' had the highest total phenols content of phenolic compounds that 183.92 mg among cultivars, while carotenoids content varied (33.5-88.5 mg/kg). The fatty acid compositions of all the cultivars were very similar. Rancimat measurements for all cultivars' oil were higher than that of crude soybean oil. Date seed oil addition at different levels to soybean crude oil increased the rancimat induction time. Treatment of 'Sewi' oil at 15 % was the best treatment among cultivars and was higher than that of the synthetic BHT effect. The results suggested that the seeds from the examined date cultivars as byproducts are good source of oil with high quality that may efficiently used as a natural additive to promote the oxidative stability of other vegetable oil.

**Keywords:** Date seed oil, Natural antioxidant, Heat stability

## Introduction

Date seed is a byproduct of date fruit industry. Previous studies found that date seed are an excellent source of dietary fiber, and has protein and minerals as well as about 8-15% oil (Herchi et al., 2014). Physicochemical characteristics and antioxidant activity of both seed and flesh oil of the date showed that they posse functional properties in the food industry (Herchi et al., 2014). Based on the fatty acid composition of date seed oil, it is suggested the use of this oil for nutritional purpose, as edible cooking oil due to the high stability and resistance of date seed oil to heat treatment which indicate the good storability of this oil. Moreover, different degree of unsaturated fatty acids of date seed oil compared to other vegetable oil make it as potential oil that can be developed for different uses.

During frying process the oil release high concentrations of chemicals called aldehydes, and lead to oil oxidation which have been linked to illnesses including cancer, heart disease and dementia(Grootveld et al., 2001). It is difficult to implement any regulation against the use of this frying oil in the restaurant to increase the safety and quality of fried foods (Paul and Mittal, 1997). In most countries, synthetic antioxidant compounds are added to the food such as oil in order to prolong product shelf life. Antioxidants are components which prevent auto-oxidation of oils and fats occur during cooking and responsible for rancid odors and flavors which reduces nutritional

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quality of the oil (Young and Woodside, 2001). Synthetic Antioxidants such as butylated hydroxyl anisole (BHA), propyl gallate (PG), tertbutyl hydroquinone (TBHQ) and butylated hydroxyl toluene (BHT), are the most frequently used. The level of synthetic antioxidants is regulated and the safety has been tested, however there is always argument because of their possible toxic effects during long-term intake and possibility of being harmful Shahidi (2005). Currently, there is a strong trend to search for an efficient natural source of antioxidants to minimize or avoid the use of synthetic food additives and minimizing damage to our cells (Yanishlieva & Marinova, 2001, Shebis et al., 2013 and Taghvaei & Jafari, 2015).

Recent studies reported that natural antioxidants showed greater anti-oxidant efficiency than synthetic antioxidants Sarkar (2016). Therefore, the use of natural plant extracts; such as olive plant, green tea, sesame, medicinal plants, with antioxidant activities in various edible oils have been tested (Bouaziz et al., 2008, Taha et al., 2014, Leonardis et al., 2007, Suja et al., 2004, Bozkurt, 2006 and Bandak et al., 2011). These natural antioxidants compounds were able to improve the oxidation stability of the vegetable edible oil.

The reports on date seed oil as a source of antioxidants is limited, therefore more research should be conducted to provide evidence for developing of edible products (Abdul Afiq et al., 2013 and Nehdi et al., 2010). The main objective of this study was to reduce the use of synthetic antioxidantsin the edible oilby using seed oil of three well known varieties of date palm as a source of natural antioxidant to promote the oxidative stability of the crud soybean oil.

## Materials and Methods

*Plant materials preparation and oil extraction*

Three date palm cultivars; grown in southern Egypt were used in this study. Randomly, fruits from soft cultivar 'Hayani', semi-dry cultivar 'Sewi' and dry cultivar 'Sakouti' at ripe stage, were collected. Fruits were washed with bleach, rinsed three times with distilled water and patted dry. Uniform group of fruits was subjected to physical evaluation such as: fruits weight, date flesh and pit weight, flesh and pit percentage and ration, and chemical measurements such as moisture contents, total soluble solids (TSS), titratable acidity and pH of the pulp juice. The other group of fruits was cleaned and their pits were separated using sharp knife edge. Pits were then dried using an air oven dryer at 70°C for 24 hr, and milled with a hammer mill and sieved to obtain a fine pit powder for further use. The moisture, oil and ash contents of the pit powder were measured according to (AOAC 1990 a,b, AOAC, 2000). And the oil was extracted with hexane over 8 h in a Soxhlet apparatus was carried out according to a method of (Besbes et al., 2004a).The obtained pit oils were drained and then The extracted oils were stored at- 20 °C until further analysis.

*Fatty acid analysis*

The evaluation of fatty acids of the extracted date seed oils were determined by Gas Chromatography according to methods for preparing the FAME from fats and oils (ES, ISO 5508 (1990).

*Oil chemical properties*

The extracted date seed oils were analyzed for acid value which was determined as described by the British Standards Institution (BS EN ISO 660: 2009).Total phenols in date seed oil were determined colorimetry at 725 nm with the Folin-Ciocalteau reagent as done by Gutfinger (1981). Carotenoid and chlorophyll were calorimetrically determined as described (Minguez-Mosquera et al., 1991).

*Mixtures of soybean oil and date seeds oil preparation*

Soybean oil was kindly provided from the (Nile oil and detergents company, Sohage, Egypt) the oil was clear, crude and did not have any synthetic antioxidants used as a control sample,BHT was added to crude soybean oil at a rate of 250 ppm, three different levels (5 %,10% and 15%) of date seed oils from all cultivars individually were mixed with soybean crude oil and stirred at room temperature, the produced mixture were used for oxidative stability measurement(Rancimat).

*Oxidative stability*

Oxidative stability was evaluated by the Rancimat method. Stability was expressed as the oxidation induction time measured with the Rancimat 679 apparatus (Metrohm AG, Herison, Switzerland). The induction time was defined as the time necessary to reach the inflection point of the conductivity curve (Halbault et al., 1997).

## Results and Discussion

*Physical and chemical characteristics of the date fruits*

In the present study, fruits from three cultivars

of date palm: 'Hayani','Sewi' and 'Sakouti', grown in southern Egypt were evaluated for the fruit characteristics, as an indication of the fruit ripening stage (Fig. 1). Physical and chemical measurements of the fruit such as fruit, flesh, pit weight, flesh/fruit, pit/fruit percentage and flesh/pit ratio are presented in Table 1. Fruit and pit weight of 'Hayani' was significantly the highest followed by 'Sewi' and 'Sakouti'. 'Sewi' fruit had the highest pit weight while the 'Hayani' had highest flesh weight. That eventually resulted in significant differences between cultivars, as it was the highest for flesh/fruit (91.5%), and pit/fruit (14.5%) in 'Sakouti' and 'Sewi' respectively. 'Sewi' cultivar had a bigger pit that reflected on the value of the Flesh/pit ratio to be the lowest (5.95) compared to the other cultivars (Table 1). This data agreed with previous reports that date fruit characteristics depends on variety and environmental conditions (Goda, 1990 and Al-Hooti et al., 1995).

Total soluble solids and acidity of the fruits are important evaluations of fruit ripening to determine the postharvest quality (Kader et al., 1998). Results of the chemical analysis such as: titratable acidity and pH and TSS of the date pulp juice, moisture contents of the fresh fruit and pit and pit powder as well as oil and ash contents of the pit powder is presented in Table 1. TSS of date pulp juice was highest in 'Sakouti' (67.3) followed by 'Sewi' and 'Hayani' that had (57.9, 52.2) respectively. The pH and the titratable acidity for the 'Sakouti' juice (0.69, 6.2) was significantly different from the other cultivars; (0.46, 7.53) for 'Hayani' and (0.39, 7.29) for 'Sewi' (Table 1). These values were in the normal range for the fresh date fruit at harvest time of all cultivars.

Moisture content and ash of the fruit flesh was not different within the studied cultivars. On the other hand the pit moisture was (30.7, 31.2, 29.8) for 'Hayani', 'Sewi' and 'Sakouti' respectively, which means that the net weight of dried powder is roughly 69.3- 68.8, 70.2) for the three cultivars (Table 1). The oil contents of the pit powder of 'Hayani' cultivars was the highest (10.6%) while there were no differences between the other two cultivars 'Sewi' and 'Sakouti' (8.22, 8.20%) respectively. This substantial amount of oil can be extracted and utilized in different food processing (Nehdi et al., 2010).


**Fig. 1. Fruit, pit and pit powder of three date palm cultivars 'Sewi' , 'Hayani' and 'Sakouti'**

**TABLE 1. Physical characteristic of date palm fruit**

| Fruit characteristics | Cultivar | | |
|---|---|---|---|
| | Hayani | Sewi | Sakouti |
| Fruit weight (g) | 14.9+0.41a | 13.0+0.44b | 11.5+0.39c |
| Flesh weight (g) | 13.40+0.41a | 11.1+0.43b | 10.4+0.35b |
| Pit weight (g) | 1.49+0.06ab | 1.86+0.04a | 0.97+0.04b |
| Flesh/fruit (%) | 89.4+0.62b | 84.8+0.61c | 91.5+0.63a |
| Pit/fruit (%) | 10.1+0.44b | 14.5+0.51a | 8.5+0.22c |
| Flesh/pit ratio | 9.23+0.5a | 5.95+0.21b | 10.8+0.31a |
| Chemical characteristics of the date palm fruit | | | |
| TSS (Total soluble solids) | 52.2+0.57c | 57.9+0.37b | 67.3+0.32a |
| Acidity | 0.46+0.03b | 0.36+0.01b | 0.69+0.03a |
| PH | 7.53+0.01a | 7.29+0.02a | 6.02+0.01b |
| Flesh moisture (%) | 49.1+0.61a | 50.1+0.53a | 47.6+0.47b |
| Fresh pit moisture (%) | 30.7+0.50a | 31.2+0.48a | 29.8+0.33a |
| Pit powder moisture (%) | 4.10+0.08a | 3.10+0.10a | 3.80+070a |
| Pit powder ash (%) | 1.44+0.02a | 1.72+0.04a | 1.13+0.02a |
| Pit oil content (%) | 10.6+0.18a | 8.22+0.21b | 8.20+0.33b |

Values are the mean ± standard error, n=50.

*Chemical characteristics of date seed oil*

Chemical properties of the extractable oil from date seed are presented in Table 3. Date seed oils showed low acid value as 'Sewi' oil date seedhadthe lowest acid value 1.75 and 'Sakouti' 1.78 while 'Hayani' the highest acid value 1.90. The low free fatty acids (FFA) content of the oil indicated that it is edible and could have a long shelf life as low acidity value indicates higher stability of the oil (Boukouada and Yousfi, 2009).

The phenolic content of oils assessing the quality of oil as it is correlated with color and the shelf-life of oil, in particularly its resistance to oxidation (Cheikh-Rouhou et al., 2006). In this study, date seed oil of all cultivars showed substantial content of total phenols, the content of total phenolic varied between cultivars. 'Sewi' had the highest content of phenolic compounds that 183.92 mg, while 'Hayani' and 'Sakouti' had 30.98and 36.95 mg respectively. Our results were consistent with that reported by (Besbes et al., 2004b). They reported that phenolic content in date seed oil was relatively high compared to most edible oils except for olive oil, which is considered to be a rich source of phenolic compounds in the Mediterranean diet (Nissiotis and Tasioula-Margari, 2002). This means that date pits oil is good source of phenolic compounds and this content varied according to cultivars due to the genetic variation (Saafi et al., 2008). The differences in chemical composition of both date flesh and seed might be due to the variability of the cultivars and also climatic conditions. Date seed oil had been shown to be rich in the content of polyphenols (Caponio et al., 1999 and Ali & El Anany, 2012).

Color of date seed oil was varied from yellow for both 'Hayani' and 'Sakouti' to intense yellow for 'Sewi', these remarks indicates the presence of a sensible quantity of carotenoids in oils which is responsible for the yellow color of the date seed oil. The color of date seed oil varies from green-yellow to brown-yellow(Boukouada and Yousfi, 2009) or pale-yellow and it is semi-solid (Devshony et al., 1992). Significant quantity of carotenoid pigment in date seed oil and it makes its color a very intense yellow made it more yellow-colored than soybean oil, sunflower oil, olive oil and corn oil (Saafi et al., 2008). Carotenoids content of date seed oils in this study varied from (33.5 mg/kg to 88.5 mg/kg) (Table 2). β-Carotene is the major carotenoid in date seed oil of the 18 date varieties cultivated in the UAE and ranged between 1.18 mg and 2.68 mg/100g (Habib et al.,2013). Carotenoids are beneficial as they simulate the appearance of butter (Oomah et al., 2000).

**TABLE 2. Chemical characteristics of the date seed oil**

| Oil quality index | Cultivar | | |
|---|---|---|---|
| | Hayani | Sewi | Sakouti |
| Acidity(mg KOH g–1) | 1.9 ± 0.04a | 1.75±0.04a | 1.78±0.02a |
| Phenolic (mg/100g) | 30.1±0.21b | 183.92±0.51a | 36.95±0.13b |
| Chlorophyll (mg/kg) | 2.17±0.03a | 1.65±0.05a | 1.47±0.02a |
| Carotenoid (mg/kg) | 33.5±0.31c | 88.5±0.40a | 60.2±0.34b |
| State at room temperature | liquid | liquid | liquid |

**TABLE 3. Fatty acid composition of date seed oil**

| Fatty acid | Cultivar | | |
|---|---|---|---|
| | Hayani | Sewi | Sakouti |
| Caprylic C8:0 | ND | 0.42 | ND |
| Capric C10:0) | 0.44 | 0.52 | 0.35 |
| Lauric C12:0 | 21.8 | 21.37 | 18.78 |
| Myristic C14:0 | 11.85 | 10.75 | 11.3 |
| Palmitic C16:0 | 11.64 | 10.52 | 11.31 |
| Stearic C18:0 | 2.88 | 3.25 | 2.89 |
| Oleic C18:1 ω9 | 41.9 | 44.03 | 44.61 |
| Linoleic C18:2ω6 | 8.19 | 7.56 | 9.14 |
| Linolenic C18:3 | 0.06 | 0.03 | 0.2 |
| Gondoic C20:1ω9 | 0.35 | 0.5 | 0.4 |
| Behenic (C22:0) | 0.36 | 0.33 | 0.30 |
| SFA(saturated fatty acid) | 48.97 | 47.16 | 44.93 |
| UFA (unsaturated fatty acid) | 50.50 | 52.12 | 54.35 |
| MUFA(Mono unsaturated fatty acid) | 42.25 | 44.53 | 45.01 |
| PUFA(poly unsaturated fatty acid) | 8.25 | 7.59 | 9.34 |
| Unsaturated/Saturated | 1.03 | 1.10 | 1.20 |
| Oliec/Linoliec | 5.11 | 5.82 | 4.88 |

Green pigments, particularly chlorophyll content was detectable for all the studied varieties.The highest content of chlorophyll was for 'Hayani'(2.17 mg/kg) and the lowest was for 'Sakouti'(1.47 mg/kg) while the content for 'Sewi' was (1.65 mg/kg).

*Fatty acid composition of date seed oil*

The fatty acid compositions of date pits oils from the three studied cultivars are presented in Table 3. The fatty acid compositions of all the cultivars are very similar. The 6 major fatty acids identified in all cultivars were oleic acid (C18:1ω9) with contents of ( 41.90% to 44.61%) followed by lauric acid (C12:0) at (18.78% to 21.80%), myristic acid (C14:0) at (10.75% to 11.85%), palmitic acid (C16:0) at (10.52% to 11.64%), linoleic acid (C18:2ω6) at (7.56% to 9.14%), and stearic acid (C18:0) at (2.88% to 3.25%). Monounsaturated oleic acids, which are the major acids in date seed oils and olive oil, have been shown to reduce the risk of cardiovascular disease (Mart´ınez-Gonz´alezet al., 2015).This results is agreed with those reported by (Akbari et al., 2012,Nehdi et al., 2018).In general, the ratio of Unsaturation/Saturation (US/S) fatty acids ranged (1.03-1.20). The cultivars in this study can be classified as oleic-lauric oils.

*Oxidative stability of date seed oil and their mixtures with soybean oil*

Data for the measurements of the oxidation stability of oils by rancimat for soybean and all studied cultivars, as well as the treatments at

different levels (5, 10 and 15%) are presented in Fig. 2. Generally, the stability of the oil extracted from date seed was higher than the crude soybean oil. The induction time for the soybean oil was 5.3h, while the extracted oil from date seed of different cultivars was 19.7, 20.7 and 25.0 hr for 'Hayani', 'Sakouti'and 'Sewi' oil, respectively.

Addition of synthetic antioxidant Butylated hydroxyl toluene (BHT) to the soybean oil increased the stability as the induction time increased from 5.3 to 12.1 hr. Addition of date seed oil to soybean oil at three different levels generally increased the induction time positively linked to increase the oxidative stability of the oil. Oil from 'Sewi' cultivar at 15 % was the best treatment as it significantly increased the induction time (16.2 hr) more than BHT. The 10% 'Sewi' oil (13.1 hr) and 15% 'Sakouti' oil treatments (12.4 hr) had similar effect as BHT and higher effect than the other treatments. Oil of 'Hayani' cultivar did increase the induction time of the soy bean but not as much as the other treatments. The present study results agreed with previous reports that the seed oil extracted from different date palm cultivars recorded induction time of 21.8 -22.9 hr (Nehdi et al., 2018). The level of monounsaturated fatty acids, carotenoids content and phenolic compounds that transferred from the seed into the extracted oil, may explain the high induction time of date seed oils compared to the other vegetable oil. The higher rancimat of date seed oil inversely proportional to polyunsaturated fatty acids contents (PUFA) detected in the date seed oil (Gharibzahedi et al., 2013). The oxidative stability of date seed oil was high also due to the low content of linoleic and lack of linolenic as a PUFA acid (Biglar et al., 2012). However, some expected lipophilic components of the date seeds could be extracted into the oils and caused the oxidative stability to be increased.

The date seed extracted oil in this study falls within the definition of CODEX STAN. of edible vegetable oils that are known as the foodstuffs which are composed primarily of glycerides of fatty acids being obtained only from vegetable sources. They may contain small amounts of other lipids such as phosphatides, of unsaponifiable constituents and of free fatty acids naturally present in the fat or oil. Also, MPOB (2014) approved that vegetable oils, animal fats or a mixture of both can serve as the frying medium. In order to select the frying medium suitable for deep-frying, the important attributes to be considered are the ability of the fats/oils to withstand the high temperature of deep frying as well as stable against the oxidation and polymerisation. The oil must have a high resistance to oxidation and gumming, low free fatty acid rise and smoking, low rate of foaming, low rate of darkening, low melting point (except for special purpose) and

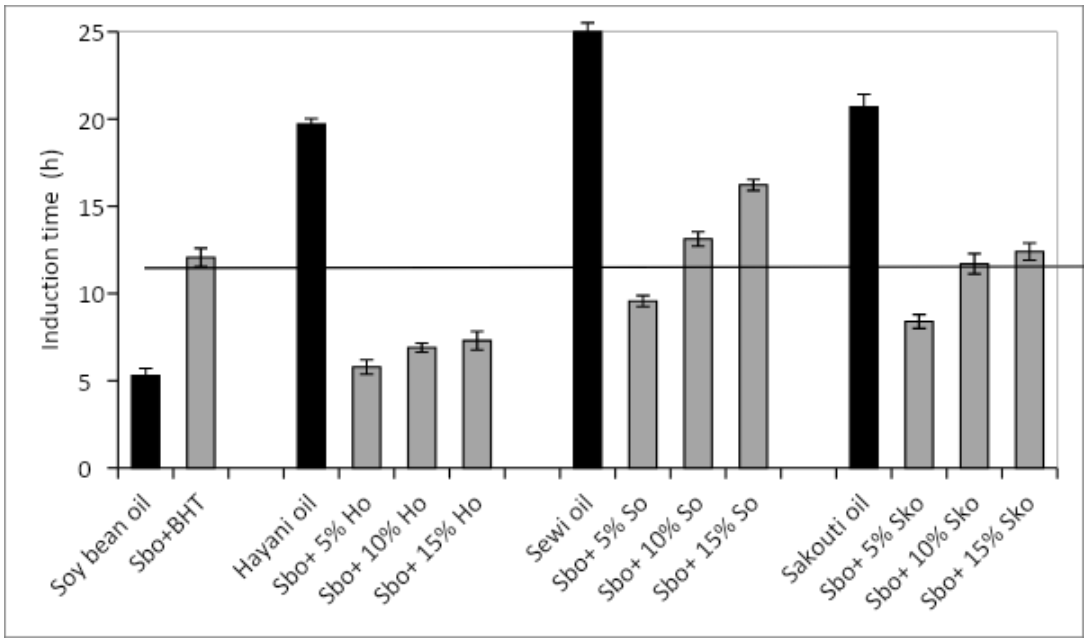


**Fig. 2. Induction period of date seed crude oils as well as soybean crude oil, and the treatment of soybean oil with BHT or different levels of date seed oils measured by Rancimat test.**
**# Sob =soybean oil, BHT= Butylated hydroxyl toluene, Ho=Hayani oil, So= Sewi oil, Sko= Sakouti oil**

nutritionally good fatty acid composition.A blend of palm oil and vegetable oils such as groundnut oil, cottonseed oil and soyabean oil enhances the stability of the liquid vegetable oils (MPOB, 2014). The extracted oils in the present study cover successfully MPOB criteria's.

CODEX Comitee on Fats and oils (CCFO), 2017, agreed to request CAC38 to approve a new work on the revision of the Standard for Named Vegetable Oils (CODEX STAN, 210-1999) to include a new category named "Palm Oil – High Oleic Acid" containing 48-58 % oleic acid. The committee noted that ranges for percent oleic acid (C18:1) in mid and high oleic acid oils contained in the Standard for Named Vegetable Oils (CODEX STAN 210-1999) are 43.1 - 71.8 Mid Oleic Acid Sunflower Seed Oil –75 - 90.7 – High Oleic Acid Sunflower Seed Oil, 70.0 - 83.7 High Oleic Acid SafflowerSeed Oil –. palm oil containing 48-58% oleic acid be called "Palm Oil - Mid Oleic Acid "according to these reports the extracted oils in this study could be named a Mid Oleic Acid oils.

The requirements in the Standard for Named Vegetable Oils (CODEX STAN) are to ensure consumer protection in terms of food safety and authenticity of the products. Further studies are needed to ensure that the extracted oil from date palm seed is healthy and safe for human consumption.

## Conclusion

The extraction of date oils from seed as by-product of date industry may contribute in reuse some of the date seed waste in many of date-producing countries. Date seed oils had high monounsaturated fatty acids, carotenoids and phenolic compounds contents than other commonly consumed oils, indicatingthe higher oxidative stability. This high oxidative stability makes it great natural additive to the other crude vegetable oil to improve its heat stability, and might be a promising substitute for the commercially used synthetic antioxidant such as BHT. Our results suggest that the synthetic antioxidant could be safely replaced by natural source of antioxidant found in date seed oil especially from Sewi and 'Sakouti' cultivars.

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## Conflict of Interest

The authors declare that there is no conflict of interest.

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## قدرة زيت نوى نخيل البلح كمضادات اكسدة طبيعية على تحسين الثبات ضد الاكسدة للزيوت الغذائية

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زاد الاهتمام بين العلماء في الآونة الأخيرة بخطورة زيوت القلى وما تنتجه عملية القلى من مواد ضارة في الغذاء وما يرتبط بها من امراض القلب والسرطان .ان التأثيرات السلبية لمضادات الاكسدة الصناعية أدت الى البحث عن بديل طبيعى لها. في هذه الدراسة تم استخدام نوى نخيل البلح لثلاثة أصناف وهى السيوى والسكوتى والخيانى في مرحلة النضج التام. تم دراسة الخصائص الكيميائية للزيت المستخرج من نوى الثمار و قياس ثباته ضد الأكسدة بقياس الرانسمات . بعد ذلك تم خلط زيت النوى المستخرج بثلاث تركيزات وهى ٥٪ و١٠ ٪و١٥٪ الى زيت الصويا الخام وتم استخدام ال BHT كمضاد أكسدة صناعى لمقارنته بزيت النوى. أوضحت النتائج ان نسبة الزيت تراوحت في مطحون النوى من ٨,٢ الى ١٠,٦ ٪. وكان الصنف السيوى هو الأعلى في تركيز المركبات الفينولية في الزيت بالنسبة لباقى الاصناف والتي وصلت الى ١٨٣,٩٢ مجم . بينما تراوح تركيز الكاروتينات بين ٣٣,٥ و٨٨,٥ مجم /كجم . وكان تركيب الاحماض الدهنية للزيت المستخرج متشابه في الأصناف الثلاثة وكان قياس الرانسمات لكل أصناف الزيت أعلى منها بالنسبةلزيت الصويا الخام. واوضحت النتائج ان إضافة زيت نوى النخيل بنسب مختلفة الى زيت الصويا سببت زيادة ثبات الزيت ضد الاكسدة بقياس الرانسيمات لهذه المخاليط . وكانت عملية إضافة ١٥٪ من زيت نوى الصنف السيوى هى افضل معاملة بين كل الأصناف والتركيزات فى المخاليط وكان كذلك أفضل من مضاد الأكسدة الصناعى BHT . لذا فان الدراسة تقترح ان زيت نوى نخيل البلح محل الدراسة يمكن ان تستخدم كنواتج ثانوية ذات قيمة مرتفعة وبكفاءة كمصدر لمضادات الاكسدة الطبيعية والتي يمكن ان تزيد ثبات الزيوت الغذائية الأخرى منخفضة الثبات.