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Kinetic and thermodynamic studies of the oil extracted from Phoenix seeds

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SUMMARY: In this work, phoenix (*Firmiana simplex* L.) seed oil from Sterculiaceae was extracted using ultrasound-assisted and Soxhlet methods, and physicochemical properties and fatty acid composition were compared and analyzed. The kinetic and thermodynamic properties of the extraction process of Phoenix seed oil were also evaluated. The results showed that the common physicochemical properties of the oil samples extracted by the ultrasound-assisted method were lower than those of the Soxhlet extraction method. In the range of 293 K to 323 K, the effective diffusion coefficient of Phoenix seed oil was significantly different, and varied from $5.18\times10^{-13}m^2\cdot s^{-1}$ to $1.29\times10^{-12}m^2\cdot s^{-1}$. The entropy and enthalpy changes in the extraction were positive with values of 33.17 J/(mol·K) and 7.15 kJ/mol, respectively. This work provides the theoretical basis for the development of extraction process parameters and the design of an extraction process for Phoenix seed oil.

Keywords: *Fatty acid composition; Physicochemical properties; Soxhlet extraction method; Ultrasound extraction method.*

RESUMEN: ***Estudios cinéticos y termodinámicos del aceite extraído de las semillas de Phoenix***. En este trabajo se extrajo aceite de semilla de fénix (*Firmiana simplex* L.) de Sterculiaceae mediante métodos de ultrasonido y soxhlet, respectivamente, y se analizaron y compararon las propiedades fisicoquímicas y la composición de ácidos grasos. También se evaluaron las propiedades cinéticas y termodinámicas del proceso de extracción del aceite de semilla de Phoenix. Los resultados mostraron que las propiedades físico-químicas comunes de las muestras de aceite extraídas por el método asistido por ultrasonido eran más bajas que las del método de extracción soxhlet. En el rango de 293 K a 323 K, y el coeficiente de difusión efectivo del aceite de semilla de Phoenix fue significativamente diferente y varió de $5{,}18\times10^{-13}$ $m^2\cdot s^{-1}$ a $1{,}29\times10^{-12}$ $m^2\cdot s^{-1}$. Los cambios de entropía y entalpía de la extracción fueron positivos con valores de 33.17 J/(mol·K) y 7.15 kJ/mol, respectivamente. Este trabajo proporciona la base teórica para el desarrollo de los parámetros del proceso de extracción y el diseño del mismo del aceite de semilla de Phoenix.

Palabras Clave: *Composición en ácidos grasos; Método de extracción por ultrasonido; Método de extracción Soxhlet; Propiedades físico-químicas*

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1. INTRODUCTION

The Phoenix (*Firmiana simplex* L., a family of Sterculiaceae) is an ornamental tree found in many provinces of China (Woo *et al*., 2016). Phoenix tree leaves can be used as feedstock for biomass carbon (Tian *et al*., 2018). Phoenix tree seeds, an undeveloped woody plant resource, are also known as tung ma pea and lady's finger fruit, and have the functions of moving Qi, strengthening the spleen, stopping bleeding, and lowering blood pressure. They are effective for dietary discomfort, spleen deficiency, and stomach diarrhea. The primary fatty acids in Phoenix seed oil have been determined as sterculic acid, palmitic acid, oleic acid, and linoleic acid. In a previous study (Sun and Li, 2016), 23% sterculic acid was found in Phoenix seed oil. Sterculic acid, a cyclic propylene fatty acid, inhibits the formation of mono olefin fatty acids very effectively (James *et al*., 1968). It can be used to make isostearic acid in advanced lubricants and cosmetics. At the same time, sterculic acid can be used as a highly effective pesticide.

The oil contained in of Phoenix seed was determined to be 27.8%, which was higher than that of date palm seed (5-11%), corn (2.7-5.4%), and soybean (17.37%) (Sun and Li, 2016; Mrabet *et al*., 2015; Bauman *et al*., 1963; Politiek *et al*., 2002). However, Phoenix seeds, which produce a woody oil with a high yield, have not been developed and used in China. With the depletion of non-renewable energy sources in recent years, the development of economical and environmentally-friendly alternatives to traditional energy sources has become the focus of research (Demirbas, 2016). Due to low tailpipe emissions, and the fact that it is renewable and environmentally friendly, biodiesel has been a promising alternative (Gusniah *et al*., 2019). At present, some edible oils have been used as the feedstocks to produce biodiesel (Atapour and Kariminia, 2011), which can aggravate the imbalance between energy consumption and food consumption. Therefore, some non-edible oils, such as Phoenix seed oil, have shown great potential for biodiesel production (Liu *et al*., 2021; Sun and Li, 2020; Li *et al*., 2021; Sun *et al*., 2019; Zhou *et al*., 2021).

Vegetable oils are rich in various minerals and essential fatty acids (Zhao *et al*., 2021). Pressing, the water enzyme method, ultrasound-assisted (Komartin *et al*., 2021) and solvent extraction are often used to extract vegetable oils. In the cold pressing method, the minor active substances and protein are not destroyed. However, the residual oil rate in the meal is very high and the oil extraction rate is low. The water enzyme method is a mild method, in which no solvent is used and the process is environmentally- friendly. However, emulsification, high enzyme requirement and high production costs are the main issues. Ultrasound-assisted extraction is a green method which promotes mass diffusion and solvent penetration, and makes oil extraction easier (Barba *et al*., 2016). Therefore, ultrasound-assisted extraction has been considered an alternative to conventional solid-liquid extraction, which results in high extraction yield and short extraction time (Mrabet *et al*., 2022). Solvent extraction is a method with a high extraction rate of oils and fats, which has been widely used in industry because of its high economic efficiency.

The kinetic and thermodynamic characteristics of the Phoenix seed oil extraction process are currently not available. The diffusion coefficient and extraction temperature are the important factors for the extraction characteristics of oil. As a new type of woody oil, it is of practical significance to determine the oil diffusion coefficient and reaction activation energy, which can provide a theoretical basis for the formulation and design of the extraction process of Phoenix seed oil.

In this work, two methods (ultrasound-assisted and Soxhlet extraction) were used and compared to extract Phoenix seed oil from Phoenix seeds. The physicochemical characteristics and fatty acid composition of Phoenix seed oil extracted by the two methods were compared and analyzed. The extraction model was established and the oil diffusion coefficient and reaction activation energy of the extraction process of Phoenix seed oil were also evaluated.

2. MATERIALS AND METHODS

2.1. Materials

Phoenix tree (*Firmiana simplex* L.) seeds were provided by Anhui Bozhou Seed Industry Co. Ltd. (Anhui, China). N-hexane and anhydrous ethyl ether were purchased from Tianjin Guangfu Technology Development Co. Ltd (Tianjin, China).

2.2. Extraction of Phoenix seed oil

The Soxhlet extraction and ultrasound-assisted extraction methods were used to extract the oil samples.

Through preliminary experimental exploration, the optimal processes for oil extraction by the two methods were determined. Before extraction, the impurities in Phoenix seeds were removed. Then the Phoenix seeds were milled with a grinder and passed through a 40-mesh sieve to obtain a seed powder with an average particle size of 0.45 mm. The Soxhlet extraction method was carried out as follows: 10 g of dried and constant weight Phoenix seed powder were weighed into a round bottom flask. Next, the oil was extracted from the seed powder using n-hexane as solvent for 12 hours. N-hexane was then removed using a rotary evaporator, until no solvent was evaporated. With n-hexane being the optimal solvent, a solid-liquid ratio of 1:10 (m/v), a 15-minute extraction period, and a microwave power of 200 W were the settings for the ultrasound assisted method. A vacuum pump was used to filter the extract, and the filtrate was evaporated using a rotary evaporator.

2.3. Physical and chemical property analysis

The acid value (AV), refractive index (20 °C), peroxide value (PV), color, saponification value (SV), and phospholipid content (P) of Phoenix seed oil were determined according to the AOCS's methods Cd 3a-63, Cc 7-25, Cd 8-53, Cc 7-25, Cd 3-25, and Ca 12-55, respectively (Firestone, 2009).

For AV, 2 g oil and 20 mL mixed solvents (ethanol/ether, 1:2, v/v) were added to a 100-mL conical flask. Then, 0.2 mL 1% phenolphthalein was used as the indicator. After that, the oil solution was titrated with 0.1 N of KOH until a pink color was observed. The AV was calculated as follows:

$$AV = 56.1 \times V \times N / M \quad \text{(Eq. 1)}$$

where 56.1 represents the molecular weight of KOH; V and N represent the volume and concentration of KOH used for titration, respectively; and M represents the mass of the oil sample.

Refractive index is defined as the ratio of the speed of light in a sample to that in the vacuum (or air) at a particular wavelength. The refractive index of the oil sample was determined by an ABBE refractometer at 20 °C. Color was determined by the Rovipon colorimetric method. The color of the light passing through an oil sample with a known light range is matched to the color of the light passing through a standard glass chromatograph under the same light source.

For PV, 1 g of oil sample was weighed and added to a 100-mL conical flask. Then 20 mL mixed solvents of chloroform and glacial acetic acid (1:2, v/v), and 1 mL of saturated KI were added to the oil sample and completely mixed. After that, 20 mL of distilled water were added, and 1 ml of 1% starch solution was added and used as the indicator. Afterwards, the oil sample mixture was titrated using 0.01 N $Na_2S_2O_3$ solution. The PV was calculated as follows:

$$PV = V_{Na2S2O3} \times N_{Na2S2O3} \times 1000 / M \quad \text{(Eq. 2)}$$

where V and N represent the volume and concentration of $Na_2S_2O_3$ used for titration, respectively; and M represents for the weight of the oil sample.

For SV, 2.0 g of oil sample were weighed into a conical flask. Next, 25 mL of a 0.5 N ethanol-KOH solution were added, and then the oil sample was completely mixed. The oil solution was refluxed in a water bath for one hour. A Phenolphthalein indicator was added into the hot solution, which was titrated with 0.5 N HCl until a colorless solution appeared. The blank experiment was also used for the determination. The SV was obtained as follows:

$$SV= (A-B) \times N \times 56.1/ M \quad \text{(Eq. 3)}$$

where A and B represent the volumes of HCl consumed by the blank sample and the oil sample, respectively; N represents the concentration of HCl; and M represents the weight of the oil sample.

For P, 3.0 g of oil sample were weighed into a crucible. Then 0.5 g of zinc oxide was added, and heated on an electric furnace until the oil was completely carbonized. The crucible was put into a muffle furnace at 550-600 °C to ash for 2 hours. After the sample had been completely converted to ash, 5 mL of distilled water and 5 mL of hydrochloric acid were added to the crucible and heated gradually over low heat to a slight boil. After boiling for 5 minutes, the furnace was immediately turned off. After the solution in the crucible was cooled down to room temperature, the solution was filtered into a 100 mL

flask. 50% KOH solution was then added. After a white precipitate had appeared, hydrochloric acid solution was added to make the precipitate disappear gradually, and 2 additional drops were added. At the same time, a blank control was prepared. Next, 10 mL of the solution, 8 mL of hydrazine sulfate solution and 2 mL of sodium molybdate solution were accurately pipetted, and placed in a water bath for 10 minutes. After the mixture was cooled to room temperature, the distilled water was added to adjust the volume, which was stood for 10 minutes. The prepared sample was moved into the cuvette. The UV spectrophotometer was zeroed with a blank solution, and the absorbance was measured at 650 nm. The P was calculated as follows:

$$P\ (\%) = 10\ (A\text{-}B) / (M \times V) \quad \text{(Eq. 4)}$$

where A and B represent the phosphorus content of the oil sample and blank control; M represents the weight of the oil sample; V represents the volume of the measured sample.

2.4. Total fatty acid and sn-2 fatty acid composition

FA methyl esters were prepared using potassium hydroxide-methanol in a hexane system in accordance with AOCS Ce-1b 89 (2007). The fatty acid methyl esters were analyzed using GC-MS, and the analytical procedure was the same as in the previous research (Sun and Li, 2016). The fatty acid at the sn-2 position was analyzed according to the Luddy *et al*. (1964) method with some modifications. 0.6 mL of sodium cholate solution, 2 mL of Tris-HCl buffer (1 mol/L, pH 8.0), and 0.4 mL of $CaCl_2$ were added to 0.1 g oil sample. The mixture was then combined for 1 minute in a water bath at 40 °C with 25 mg of pancreatic lipase. Finally, 1 mL of 6 mol/L HCl was added to terminate the reaction, after which 1 mL of n-hexane was added and centrifuged for separation. The supernatant was aspirated with a syringe and spotted at 1.5 cm from the bottom of the laminate. The unfolding agent was poured into the unfolding tank, and the plate was placed in the unfolding tank, which was unfolded until the solvent was 1 cm from the top of the plate. The band of the thin layer plate having glycerol monoester was scraped off for subsequent methylation operation, and the gas chromatography analysis was performed after methylation as previously described.

2.5. Kinetic study of the oil extraction

The initial stage of oil extraction is the stage where the diffusion phenomenon did not start. The kinetic model of the non-equilibrium reaction system was applied to a modified model of Fick's diffusion law with the following equation:

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} A_n \exp(-B_n t) \quad \text{(Eq. 5)}$$

where t is diffusion time; M_t is the oil extraction ratio (Phoenix seed oil/ Phoenix seeds, kg/kg) when the diffusion time is t; M_∞ is the oil extraction ratio (Phoenix seed oil/ Phoenix seeds, kg/kg) after equilibrium.

2.6. Thermodynamic study of the oil extraction

The oil extraction time should be longer than 12h, and the absolute temperatures were 293K, 303K, 313K and 323K, respectively. The extraction equation of the equilibrium constant was as follows:

$$K = \frac{(R_e)_{miscella}}{(R_e)_{soild}} \quad \text{(Eq. 6)}$$

where K is the extraction equilibrium constant; $(Re)_{miscella}$ is the extraction rate at extraction equilibrium; $(Re)_{soild}$ is the residual oil rate at extraction equilibrium.

Van't Hoff's equation was as follows:

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \text{(Eq. 7)}$$

where K is the extraction equilibrium constant for each temperature condition; ΔS^0 is the entropy change; ΔH^0 is the enthalpy change; R is the general gas constant.

Gibbs free energy equation for the extraction was as follows:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{(Eq. 8)}$$

2.7. Statistical analysis

All of the experiments were carried out three times, and the results were analyzed and processed

using SPSS 20.0 and Origin 9.0 software. The results were expressed as mean ± SD. ANOVA analysis was used to analyze the differences in means. And $p < 0.05$ indicated that there was a significance difference.

3. RESULTS AND DISCUSSION

3.1. Physicochemical properties analysis

As shown in Table 1, the PV, P, SV, and AV of the oil extracted by the ultrasound-assisted method were 0.37±0.04 mmol/kg, 0.12±0.03%, 188.73±1.76 mg KOH/g, and 47.60±1.35 mg KOH/g, respectively, which were lower than the oil using Soxhlet extraction method (1.42±0.30 mmol/kg, 0.48±0.05%, 195.11±2.46 mg KOH/g, and 51.43±1.75 mg KOH/g). High AV was found for Phoenix seed oil, which was significantly higher than that of corn oil (5.13±0.51 mg KOH/g), camellia seed oil (3.7 mg KOH/g), or soybean oil (< 2.0 mg KOH/g) (Wang *et al*., 2021; Chen *et al*., 2017). The high AV of Phoenix seed oil was due to the hydrolysis of endogenous lipases in the seeds. These were also confirmed by the experiment which, after the seeds were stored for one year, a higher AV (60.3 mg KOH/g) of the oil extracted from the seeds was found (Li *et al*., 2021). Compared with Soxhlet extraction method, the lower peroxide value, phospholipid content, saponification value, and acid value of Phoenix seed oil obtained by the ultrasound-assisted method may be due to the fact that the high temperature and long oil extraction time were used in the Soxhlet extraction method, which resulted in some oxidation and hydrolysis of the oil. Similar oxidation and hydrolysis were found during the extraction of papaya seed oil by Samaram *et al*. (2014). Phospholipids have antioxidant properties, and Phoenix seed oil has a low phospholipid level when compared to other oils (such as soybean oil, which has a phospholipid content of 3.2%). This makes Phoenix seed oil difficult to store (Gustone, 2002).

3.2. Fatty acid composition analysis

Table 2 shows that the different extraction methods had a minor effect on the composition and content of total fatty acids. However, some small differences in sn-2 fatty acid composition and content were found. Phoenix seed oil has the saturated fatty acid contents

Table 1. Physicochemical properties of Phoenix tree seed oil.

Properties	Ultrasound-assisted	Soxhlet extraction
Refractive index (20 °C)	1.4650 ± 0.0001	1.4662 ± 0.0003
Peroxide value (mmol/kg)	0.37 ± 0.04	1.42 ± 0.30
Phospholipid content (%)	0.12 ± 0.03	0.48 ± 0.05
Saponification value (mg KOH/g)	188.73 ± 1.76	195.11 ± 2.46
Color (Lovibond, 1 inch)	Y 5.8, R 2.5	Y 5.8, R 2.9
Acid value (mg KOH/g)	47.60 ± 1.35	51.43 ± 1.75

The values are the mean ± SD of the two different oil extraction methods used and the results are the average values of three replicates.

Table 2. Fatty acid composition of Phoenix tree seed oil (%, w/w).

Fatty acid	Total fatty acid		Sn-2 fatty acid	
	Ultrasound-assisted	Soxhlet extraction	Ultrasound-assisted	Soxhlet extraction
Palmitoleic acid	1.33 ± 0.09^{a}	1.33 ± 0.07^{a}	1.64 ± 0.06^{b}	1.18 ± 0.07^{c}
Palmitic acid	18.20 ± 0.56^{a}	18.53 ± 0.74^{a}	3.84 ± 0.07^{b}	1.83 ± 0.07^{c}
Malvalic acid	1.00 ± 0.34^{a}	1.00 ± 0.04^{a}	0.29 ± 0.03^{b}	0.22 ± 0.02^{b}
Linoleic acid	33.36 ± 0.21^{a}	32.83 ± 0.43^{a}	50.28 ± 0.03^{c}	48.26 ± 0.28^{b}
Oleic acid	21.52 ± 0.38^{a}	21.63 ± 0.96^{a}	29.20 ± 0.89^{b}	30.62 ± 0.34^{c}
Stearic acid	2.60 ± 0.21^{a}	2.67 ± 0.14^{a}	1.07 ± 0.16^{b}	0.86 ± 0.03^{b}
Sterculic acid	19.30 ± 1.79^{a}	19.43 ± 0.17^{a}	11.55 ± 0.73^{b}	13.80 ± 0.25^{c}
Nonadecenoic acid	0.77 ± 0.25^{a}	0.81 ± 0.04^{a}	0.44 ± 0.03^{b}	0.31 ± 0.02^{b}
Eicosadienoic acid	0.36 ± 0.03^{b}	0.18 ± 0.06^{a}	0.50 ± 0.07^{c}	1.75 ± 0.04^{d}
Others	1.55 ± 0.16^{a}	1.58 ± 0.06^{a}	1.17 ± 0.03^{b}	1.15 ± 0.09^{b}
Saturated fatty acids	20.8 ± 0.21^{a}	21.2 ± 0.08^{a}	4.91 ± 0.04^{b}	2.69 ± 0.05^{c}
Unsaturated fatty acids	77.65 ± 0.45^{a}	77.22 ± 0.09^{a}	93.92 ± 0.13^{b}	96.16 ± 0.04^{c}

The values are the mean ± SD of the two different oil extraction methods used and the results are the average values of three replicates. According to Duncan's multiple range test, different superscript letters (a, b, and c) in the same row show significant differences ($p < 0.05$) in the fatty acid composition of Phoenix tree seed oil between the two extraction methods.

of 20.8-21.2% for total fatty acids and 2.69-4.91% for sn-2 fatty acids. Among the saturated fatty acids, the content of palmitic acid was higher than stearic acid. Further, the content of unsaturated fatty acids was up to more than 75%. And the contents of oleic and linoleic acid in the total fatty acids were 21.52-21.63 and 32.83-33.36%, respectively, and the contents of oleic and linoleic acid in sn-2 fatty acids were classified as 29.20-30.62 and 48.26-50.28%. The high contents of oleic and linoleic acid in Phoenix seed oil means it may have the function of lowering LDL (low density cholesterol), which has a significant effect on the prevention and treatment of myocardial infarction, atherosclerosis and other diseases. Table 2 also shows that sn-2 fatty acids were mainly unsaturated (oleic acid and linoleic acid); whereas saturated fatty acids were mainly concentrated on the sn-1 and sn-3 positions, which was compatible with the fatty acid distribution pattern on the glycerol ester of vegetable oils. In addition, compared to other vegetable oils, Phoenix seed oil has two special fatty acids, sterculic acid and malvalic acid, both of which have special physiological effects. Sterculic acid and malvalic acid were mainly distributed on the sn-1 and sn-3 positions in the glycerol ester of Phoenix seed oil.

3.3. Kinetic study

In this study, different extraction temperatures (20, 30, 40 and 50 °C) were used (Figure 1). The initial stage of Phoenix seed oil extraction is the stage in which the oil on the surface of Phoenix seed powder was washed using n-hexane. At this stage, the extraction of oil from the surface of the powder was very fast. The extraction rate increased substantially at 50 °C when the extraction duration was less than 15 minutes. When the extraction time was 15 min, the extraction rate of Phoenix seed oil was 18.84% (50 °C), which was 73% of the extraction rate of Phoenix seed oil when the equilibrium was reached. However, when the extraction time was longer than 30 min, the diffusion phase of the extraction process was reached, and the increasing trend of the extraction rate of Phoenix seed oil was to slow down. When the extraction time was longer than 10 h, the equilibrium stage of the oil extraction was reached, and the maximum extraction rate of Phoenix seed oil (25.81%) was obtained.

When the extraction temperature was 20-50 °C (or 293 K to 323 K), the mass transfer between phoenix seed powder and extraction solvent was accelerated (Figure 1), and the extraction rate of Phoenix seed oil increased as the extraction temperature was raised, which was due to the acceleration of mass transfer between Phoenix seed power and the extraction solvent at a high temperature. However, in the washing stage, the increase trend was pronounced. When the extraction entered the diffusion stage, the temperature had a minor influence on the extraction rate of Phoenix seed oil.

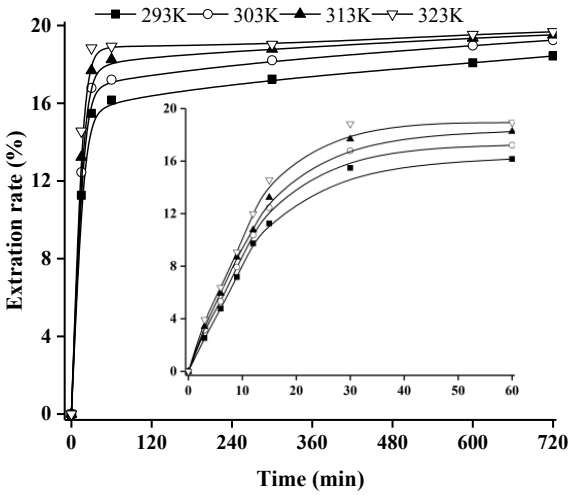

Figure 1. Effect of extraction time on the extraction rate of Phoenix seed oil with a reaction system substrate ratio (Phoenix seeds: hexane, w/v) of 1:10. The results reported are mean values, and the experiments were repeated three times.

According to the kinetic model of Fick's diffusion law by Eq. 5, the kinetic data obtained from the experiments were curve-fitted and the regression coefficients are shown in Table 3. The experimental data showed high correlation ($R^2 > 0.97$), which indi-

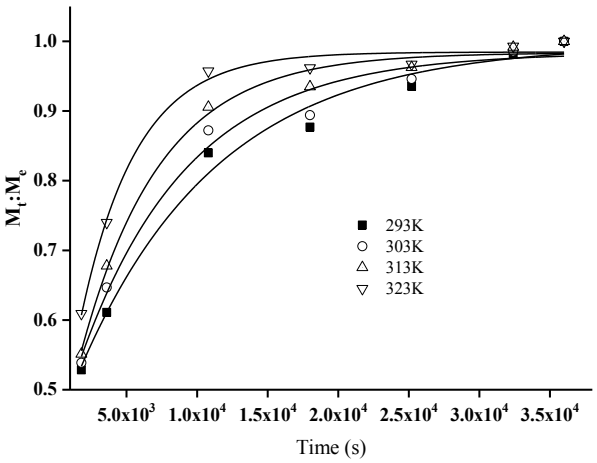

Figure 2. Extraction kinetic curve of Phoenix seed oil. The results reported are mean values, and the experiments were repeated three times.

Table 3. Parameters of Fick's diffusion law kinetic model.

Parameters	Absolute temperature (K)			
	293	303	313	323
A	0.5553[a]	0.5514[a]	0.5878[b]	0.5944[b]
$B_1(s^{-1})$	$1.01x10^{-4}$	$1.30 x10^{-4}$	$1.76 x10^{-4}$	$2.52 x 10^{-4}$
R_e	18.83[a]	19.25[ab]	19.52[b]	19.68[b]
R^2	0.982	0.978	0.989	0.989

The results reported are mean values, and the experiments were repeated three times. Values with different letters in the same row are significantly different at $p < 0.05$ according to one-way ANOVA followed by Duncan's multiple range test.

cated that the kinetic model could be used to characterize the extraction kinetics of Phoenix seed oil. The curve fit of Phoenix seed oil kinetic data is shown in Figure 2.

As shown in Table 3, Fick's diffusion law kinetic model parameter B_1 was the crucial factor for the effective diffusion coefficient of Phoenix seed oil extraction. The diffusion coefficient increased as the extraction temperature was raised. This indicated that the diffusion coefficient of Phoenix seed oil increased as well at the higher extraction temperature. The effective diffusion coefficient of Phoenix seed oil extraction at 20 °C was 5.18×10^{-13} $m^2 \cdot s^{-1}$. The effective diffusion coefficient of Phoenix seed oil extraction at 50 °C was 1.29×10^{-12} $m^2 \cdot s^{-1}$. The effective diffusion coefficient of rapeseed oil extracted with hexane was 1.3×10^{-12} $m^2 \cdot s^{-1}$ - 3.0×10^{-12} $m^2 \cdot s^{-1}$ (Fernandez *et al*., 2012). The effective diffusion coefficient of sunflower seed oil extracted with hexane was 2.06×10^{-12} $m^2 \cdot s^{-1}$ - 5.03×10^{-12} $m^2 \cdot s^{-1}$ (Perez *et al*., 2011). The effective diffusion coefficient of Phoenix seed oil extraction was lower than that of canola and sunflower seed oils, which may be due to the presence of cyclic acrylic acid in Phoenix seed oil.

3.4. Thermodynamic study

From the Van't Hoff equation (Eq. 7), the extraction equilibrium coefficient of Phoenix seed oil was used to characterize its extraction thermodynamics. The thermodynamic constants of Phoenix seed oil extraction were calculated from Eq. 6, as shown in Table 4. The equilibrium coefficient of Phoenix seed oil extraction increased with the increase in temperature, which indicated that the extraction was an endothermic process. Meanwhile, the increase in extraction temperature could accelerate the mass transfer between the oil in the Phoenix seed powder and the extraction solvent, which was beneficial to the increase in the extraction rate of Phoenix seed oil.

Table 4. Thermodynamic constants for the extraction of Phoenix seed oil at different extraction temperatures.

Temperature (K)	$(R_e)_{miscell}$	$(R_e)_{solid}$	K	lnK
293	18.43[a]	6.54[a]	5.45[b]	1.04[a]
303	19.25[b]	2.82[a]	3.58[b]	1.21[b]
313	19.52[b]	5.72[b]	5.29[b]	1.28[b]
323	19.68[b]	3.37[b]	3.72[b]	1.31[b]

The results are mean values, and the experiments were repeated three times. Values with different letters in the same column are significantly different at $p < 0.05$ according to one-way ANOVA followed by Duncan's multiple range test.

Table 5. Thermodynamic parameters of Phoenix seed oil extraction.

Temperature (K)	ΔH^0 (KJ/mol)	ΔS^0 ($Jmol^{-1}K^{-1}$)	ΔG^0 (KJ/mol)
293	7.15	33.17	-2.57[a]
303	7.15	33.17	-2.90[a]
313	7.15	33.17	-3.23[b]
323	7.15	33.17	-3.56[b]

The results reported are mean values, and the experiments were repeated three times. Values with different letters in the same column are significantly different at $p < 0.05$ according to one-way ANOVA followed by Duncan's multiple range test.

From Equations 7 and 8, it can be determined that the changes in Gibbs free energy, enthalpy and entropy during the extraction of Phoenix seed oil at different temperatures were obtained, as shown in Table 5. During the extraction of Phoenix seed oil, energy absorption was required to break through the hindrance of oil transfer from the solid to liquid phases. The entropy and enthalpy changes in the extraction were 33.17 J/(mol·K) and 7.15 kJ/mol, respectively, which also showed that the process was an endothermic process. This was mainly because the transfer of oil from the solid phase to the liquid phase was hindered during the extraction

process of Phoenix seed oil, which required energy absorption. These were slightly lower than the extraction of other vegetable oils. The entropy and enthalpy changes in coconut oil extraction were 36.73 J/(mol·K) and 12.16 kJ/mol, respectively (Sulaiman *et al*., 2013). The entropy and enthalpy changes in olive oil extraction were 59.33 J/(mol·K) and 12.91 kJ/mol, respectively (Meziane and Kadi, 2008). Compared to the extractions of coconut oil and olive oil, the enthalpy and entropy changes in Phoenix seed oil extraction were lower, which indicated that less heat was absorbed during the extraction of Phoenix seed oil and that the extraction could be performed at a low temperature. The enthalpy and entropy changes in the n-hexane extraction of Phoenix seed oil were positive and the Gibbs free energy was negative, which indicated that the extraction of Phoenix seed oil is a heat-absorbing, irreversible, and spontaneous process.

4. CONCLUSIONS

In this paper, the ultrasound-assisted and Soxhlet extraction methods were used to extract Phoenix seed oil, and the physicochemical properties and fatty acid composition of the extracted Phoenix seed oils were compared. The peroxide value, phospholipid content, saponification value, and acid value of the oil extracted by the Soxhlet extraction were higher than those of the oil using the ultrasound-assisted method. The different extraction methods had a minor impact on the composition and content of total fatty acids. However, there are some small differences in sn-2 fatty acid composition and content. In the extraction temperature ranging from 20 (293 K) to 50 °C (323 K), the effective diffusion coefficient of Phoenix seed oil was significantly different and increased from 5.18×10^{-13} $m^2\cdot s^{-1}$ to 1.29×10^{-12} $m^2\cdot s^{-1}$. The entropy and enthalpy changes of the extraction using n-hexane were positive with the values of 33.17 J/(mol·K) and 7.15 kJ/mol, respectively. However, the Gibbs free energy of the extraction using n-hexane was negative, with a value of -3.56 KJ/mol at an extraction temperature of 50 °C. This indicated that solvent extraction of Phoenix seed oil using n-hexane is a spontaneous and heat-absorbing process. This research could provide the theoretical information for the oil extraction and the design of the extraction process for Phoenix seed oil.

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