[Turkish Journal of Chemistry](https://journals.tubitak.gov.tr/chem)

Volume 24 | Number 3 Article 5

1-1-2000

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Turk J Chem
24 (2000) , 247 – 253.


# Kinetics and Thermodynamics of Oil Extraction from Sunflower Seeds in the Presence of Aqueous Acidic Hexane Solutions

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Received 29.04.1999

Oil extraction was performed in aqueous HCl, $H_2SO_4$ and $H_3PO_4$ solutions with n-hexane ($C_6H_{14}$) at 30, 40, 50 and 60°C using 10 gr of sunflower seeds over 1 h with 10-min. sampling intervals. The optimum acid concentration was wt. 10% for each acid, and the highest oil yield was obtained in the extraction procedure with n-hexane containing $H_2SO_4$. The extraction process was observed with regard to the percent oil yield versus time, and the reaction order was found to be first-order kinetics by the differential method. The activation energy for the oil extraction kinetics of sunflower seeds with 10% $H_2SO_4$ was found to be $E_a$=4.2 kJmol$^{-1}$, and the activation thermodynamic parameters at 60°C were $\Delta H^{\neq}$=1.43 kJmol$^{-1}$, $\Delta S^{\neq}$=-309.3 Jmol$^{-1}$K$^{-1}$ and $\Delta G^{\neq}$=104.4 kJmol$^{-1}$. The enthalpy value was $\Delta H$=11.2 kJmol$^{-1}$, and the other thermodynamic parameters at 60°C were $\Delta S$=36.75 Jmol$^{-1}$K$^{-1}$ and $\Delta G$=-1.07 kJmol$^{-1}$.

**Key Words:** Hexane, kinetics, oil extraction, sulfuric acid, sunflower seed, thermodynamics.

## Introduction

There are several techniques for removing oil from oilseeds, including the wet process, the dry process, and solvent extractions. For many years, commercial-grade hexane has been the solvent of choice for the extraction of oil from oilseeds.

Rao et al.[1] and Hassanen[2] studied extraction of oilseed model systems with alcohols, and showed that when the moisture level in flakes was below 3%, aqueous ethanol was an effective extraction solvent. Aqueous ethanol with a tribasic acid, such as phosphoric or citric, was used as an alternative solvent to hexane for the extraction of glanded cottonseed by Hron et al.[3]

Wan et al.[4] found alternative hydrocarbon solvents for cottonseed extraction and they recommended 2 hydrocarbon solvents, heptane and isohexane, as potential replacements for hexane.

Hexane and isopropanol were compared as solvents for use in ambient-temperature equilibrium extraction of rice bran oil[5]. Oil extraction by ethanol from partially defatted pressed sunflower seeds in pulsed and nonpulsed extractors was compared by Sineiro et al.[6].

It is well recognized that the rate of solvent extraction is controlled by the solid particle size[7]. Snyder et al.[8] indicated that particle size not only has an effect on extraction rate, but it also increases the amount of oil extracted. Nieh and Snyder[9] studied extraction rate, a countercurrent extraction system and oil quality for the solvent extraction of oil from soybean flour.

The kinetics of oil extraction from oilseeds and by-products from industries which use corn is dependent on a number of factors[10,11]. These include the composition and morphology of the raw material, and the structural and mechanical properties of the flakes after hydrothermal treatment and milling before preparation of the material for extraction[12−15]. During the extraction itself, the most important conditions are the temperature and duration of the extraction, as well as the polarity of the solvent used for extraction[16,17].

Karlovic et al.[18] investigated the effect of temperature and moisture content on the kinetics of oil extraction from corn germ flakes prepared by a dry degermination process.

Ibemesi and Attah[19] extracted the seeds of rubber [*Hevea brasiliensis* (Kuth) Muell. Arg.] and melon (Colocynthis vulgaris Schrad) using different solvents at various temperatures, and they determined the temperature coefficients and enthalpy changes accompanying the extraction process. They obtained $\Delta H$ values within the range 4-13.5 kJmol$^{-1}$.

In the present study, oil extraction from sunflower seeds in aqueous hydrochloric acid (HCl), sulfuric acid ($H_2SO_4$) and ortho-phosphoric acid ($H_3PO_4$) solutions with n-hexane ($C_6H_{14}$) was investigated. The aim of the study was to find the optimum acid concentration and most effective acid from HCl, $H_2SO_4$ and $H_3PO_4$, and,in physicochemical terms, to determine the kinetic and thermodynamic parameters of oil extraction from sunflower seeds.

## Experimental

**Sunflower seeds:** The sunflower seeds were purchased from a local market. For the extraction process, the seeds were shelled, dried in an oven at 60°C to constant weight and then ground with a kitchen grinder to a mesh size of 120. The moisture content of the unground and ground sunflower seeds was 10.5% and 6.5%, respectively.

**Solvent and acid solutions:** The n-hexane ($C_6H_{14}$, 99%, 86.18 g/mol, 0.66 g/mL), hydrochloric acid (HCl, 37%, 36.46 g/mol, 1.19 g/mL), sulfuric acid ($H_2SO_4$, 98%, 98.08 g/mol, 1.84 g/mL) and ortho-phosphoric acid ($H_3PO_4$, 85%, 98.00 g/mol, 1.71 g/mL) were supplied by Merck (Darmstadt, Germany). Aqueous acid solutions for each acid were prepared as wt. 0% (without acid, only with distilled water), 5%, 10%, 15%, 20%, 25% and 30%.

**Extraction procedure:** Ground sunflower seed (10.0 g) was put in a three-necked flask (500 mL) with a round bottom containing 100 mL of hexane and 100 mL of acid solution (for each acid solution). The large neck in the middle of the flask was connected to a reflux condenser. A thermometer was placed in one of the two side necks, and the other side neck was used for the addition of the oil sample with a 1-mL pipette during the extraction process. The flask was submerged in a temperature-controlled water bath. The following temperatures were used: 30, 40, 50 and 60°C.

The total extraction time was 60 min. Miscella samples (1 mL) were collected in preweighed flasks after 10, 20, 30, 40, 50 and 60 min of extraction. The amount of oil extracted in each time interval was determined gravimetrically by measuring the mass of the residue in the flask after removal of the solvent by distillation.

## Results and Discussion

The percent oil yield values for the different acid solutions at 60°C are shown in Figure 1 for oil extraction from sunflower seeds. As seen in Figure 1, the oil yields peaked (optimum value) at the 10% concentration for each acid and decreased inversely to acid concentration after this optimum value. At this optimum acid value, since the acid reduced the particle size of the seeds and increased the surface area, it decreased the hexane penetration path lengths and resulted in an increase in the amount of oil extracted.

Since the highest oil yield was obtained with $H_2SO_4$ over HCl and $H_3PO_4$ and the most effective acid was $H_2SO_4$, the kinetic and thermodynamic parameters were calculated according to the values at a 10% acid concentration. The percent oil yields for 10% $H_2SO_4$ at various temperatures are given in Table 1 for sunflower seed oil extraction.

**Table 1.** Percent oil yield (sunflower seed) at various extraction temperatures for 10% $H_2SO_4$ containing n-hexane.

| | Oil Yield (%), Y | | | |
|---|---|---|---|---|
| t/min | 30°C | 40°C | 50°C | 60°C |
| 10 | 13.81 | 15.45 | 17.32 | 19.65 |
| 20 | 14.59 | 16.36 | 18.41 | 20.96 |
| 30 | 15.41 | 17.33 | 19.59 | 22.35 |
| 40 | 16.28 | 18.36 | 20.84 | 23.84 |
| 50 | 17.20 | 19.44 | 22.16 | 25.42 |

A reaction rate equation for oil extraction from sunflower seeds can be written as:

$$\frac{dY}{dt} = kY^n \tag{1}$$

where Y is the percent oil yield; t is the time of extraction (min); k is the extraction constant; and n is the reaction order. Since the percent oil yield increased in the course of time, the terms dY/dt have a positive sign.

Using the values in Table 1 and applying the Differential Method[20], plots of ln $\left(\frac{dY}{dt}\right)$ versus ln Y for 10% $H_2SO_4$ were drawn and were found to be linear by means of Equation 1. A first-order kinetics was found from the values of n obtained from the slopes of the straight lines in Figure 2, and the reaction rate constants were calculated from the slopes (Table 2). Thus, the oil extraction kinetics from the sunflower seeds can be described by the following equation obtained after integration of Equation 1:

$$Y_t = Y_u e^{kt} \tag{2}$$

where $Y_t$ is the percent extracted oil content at time $t$; and $Y_u$ is the percent unextracted oil at time zero. This equation is similar to that of D.Karlovic et al.[21].

**Table 2.** Values of the reaction rate constants for sunflower seed oil extraction with 10% $H_2SO_4$ containing n-hexane at various temperatures.

| t/°C | $k \times 10^3/\text{min}^{-1}$ |
|---|---|
| 30 | 5.49 |
| 40 | 5.75 |
| 50 | 6.17 |
| 60 | 6.44 |

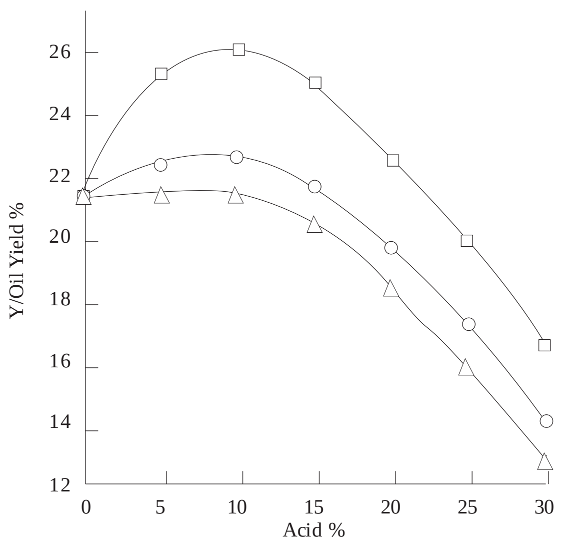


**Figure 1.** Effect of acid concentrations on percent of oil yield (Y) for sunflower seed oil extraction at 60°C: ○: HCl, □: $H_2SO_4$ and △: $H_3PO_4$.

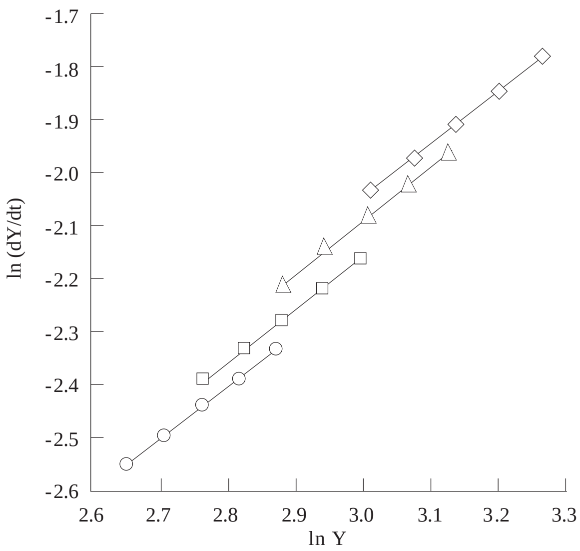


**Figure 2.** A plot of ln $\left(\frac{dY}{dt}\right)$ versus ln Y: ○: 30°C, □: 40°C, ◇: 50°C and △: 60°C for 10% $H_2SO_4$ containing n-hexane.

The activation energy was calculated with the Arrhenius equation[20]:

$$k = Ae^{-E_a/RT} \tag{3}$$

where k is the reaction rate (extraction) constant, A is the Arrhenius constant or frequency factor; $E_a$ is the activation energy; R is the universal gas constant, and T is the absolute temperature.

A plot of ln k vs 1/T gives a straight line whose slope represents the activation energy of extraction, $-E_a/R$, and whose intercept is the Arrhenius constant, ln A (Figure 3). Thus, the activation energy and the Arrhenius constant were calculated. These were $E_a = 4.2$ kJ mol$^{-1}$ and A = 4.83 $\times 10^{-4}$ s$^{-1}$, respectively.

The activation thermodynamic parameters were calculated in the following equations according to the transition state theory[20]:

$$A = \frac{RT}{Nh} e^{\Delta S^{\neq}/R} \tag{4}$$

$$\Delta H^{\neq} = E_a - RT \tag{5}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{6}$$

where N is the Avogadro constant; h is the Planck constant; $\Delta S^{\neq}$ is the activation entropy; $\Delta H^{\neq}$ is the activation enthalpy; and $\Delta G^{\neq}$ is the activation free energy or Gibb's energy. These activation thermodynamic parameters are shown in Table 3 for each temperature.

**Table 3.** The activation thermodynamic parameters for sunflower seed oil extraction with 10% $H_2SO_4$ containing n-hexane at different temperatures.

| T/K | $\Delta S^{\neq} Jmol^{-1}K^{-1}$ | $\Delta H^{\neq}/kJmol^{-1}$ | $\Delta G^{\neq}/kJmol^{-1}$ |
|---|---|---|---|
| 303 | -308.6 | 1.68 | 95.2 |
| 313 | -308.8 | 1.60 | 98.3 |
| 323 | -309.1 | 1.52 | 101.4 |
| 333 | -309.3 | 1.43 | 104.4 |

The thermodynamic parameters for sunflower seed oil extraction were determined using the expressions[19]:

$$K = \frac{Y_T}{Y_u} \tag{7}$$

$$\ln K = -\frac{\Delta G}{R}\frac{1}{T} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \tag{8}$$

where K is the equilibrium constant; $Y_T$ is the percent oil yield at temperature T; $Y_u$ is the percent unextracted oil; ΔH is the enthalpy change; ΔS is the entropy change; and ΔG is the free energy or Gibb's energy.

Upon comparing our ΔH value with a similar value in the literature, that of Ibemesi and Attah[19], who produced plots of ln $Y_T$ vs 1/T, it can be seen that the plot in our paper gives a straight line whose slope represents the enthalpy change of extraction, $-\Delta HR$. Thus, the enthalpy change was calculated to be $\Delta H = 11.2$ $kJmol^{-1}$ for sunflower seed oil extraction with 10% $H_2SO_4$ (Figure 4). The ΔH value obtained was in agreement with the range of $4 - 13.5 kJmol^{-1}$ in the literature, indicating the physicochemical nature of the oil extraction process.

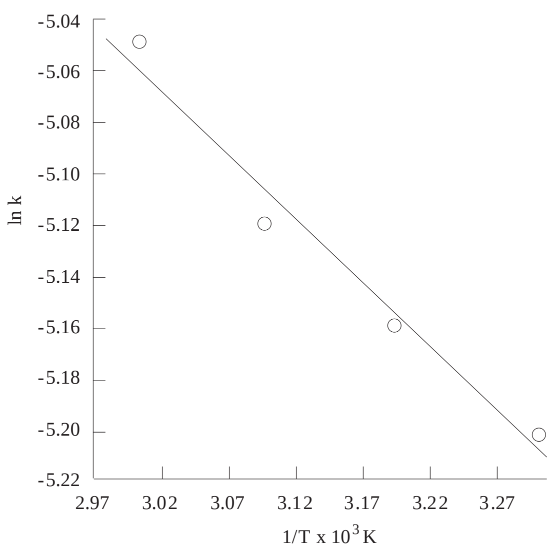


**Figure 3.** A plot of ln k versus 1/T for sunflower seed oil extraction with 10% $H_2SO_4$ containing n-hexane.

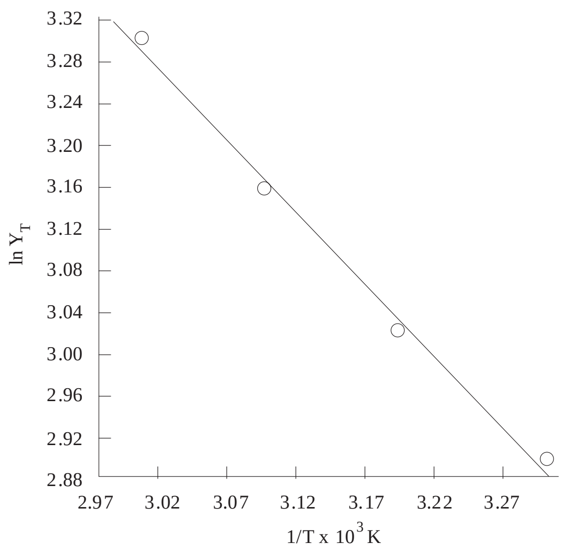


**Figure 4.** A plot of ln $Y_T$ versus 1/T for sunflower seed oil extraction with 10% $H_2SO_4$ containing n-hexane.

Other thermodynamic parameters (ΔG and ΔS) and the equilibrium constant values for sunflower seed oil extraction with 10% $H_2SO_4$ are given in Table 4 for each temperature.

**Table 4.** The equilibrium constants (K) and the thermodynamic parameters (ΔG and ΔS) for sunflower seed oil with 10% $H_2SO_4$ containing n-hexane at various temperatures.

| T/K | K | $\Delta G$/kJmol$^{-1}$ | $\Delta S$/mol$^{-1}$K$^{-1}$ |
|---|---|---|---|
| 303 | 1.39 | -0.83 | 39.60 |
| 313 | 1.41 | -0.90 | 38.69 |
| 323 | 1.45 | -0.99 | 37.78 |
| 333 | 1.47 | -1.07 | 36.75 |

According to these results, the fact that ΔH is positive for sunflower seed oil extraction shows that this process is endothermic. In addition, $\Delta S > 0$ and $\Delta G < 0$ indicate that there is an increase in the entropy change and a decrease in the free energy, that is, this process is spontaneously forward.

The reaction system initially consists of the ground sunflower seed, aqueous acid solution and n-hexane, whereas the oil molecules are extracted from the sunflower seeds during the extraction process, and, therefore, the entropy of the mixture increases in the course of the extraction, that is, the entropy change has a positive value.

# Conclusion

It was found that sulfuric acid, $H_2SO_4$, was more effective and more suitable than HCl and $H_3PO_4$ in the presence of n-hexane for oil extraction from sunflower seeds. The optimum acid value was 10%. The sunflower seed oil extraction process has a first-order kinetics. The activation energy was $E_a$=4.2 kJmol$^{-1}$, and the activation thermodynamic parameters at 60°C were $\Delta H^{\neq}$=-1.43 kJmol$^{-1}$, $\Delta S^{\neq}$=-309.3 Jmol$^{-1}$K$^{-1}$ and $\Delta G^{\neq}$=104.4 kJmol$^{-1}$. The enthalpy value was $\Delta H$ = 11.2 kJmol$^{-1}$, and the other thermodynamic parameters at 60°C were calculated to be $\Delta S$ =36.8 Jmol$^{-1}$K$^{-1}$ and $\Delta G$ =-1.07 kJmol$^{-1}$.

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