SOLVENT EXTRACTION OF NIGELLA-SATIVA OIL FROM BLACK SEED

E.E.Ebrahiem

Chemical Engineering Department, Minia University, El-Minia, Egypt.

ABSTRACT

Extraction of Nigella-Sativa Oil from its black seeds using petroleum ether (boiling range 60-80 °C) was investigated. The maximum amount of Nigella- Sativa oil content obtained was 42.01% (by weight of the seed). Thermodynamic and kinetic studies yielded results that show the parameters necessary for the extraction of the oil. The ultimate capacity of the petroleum ether (60-80 °C) as a solvent increased with temperature. The rate parameter for different temperatures is correlated by the equation $K_T = -0.088\,(T\,K)^{0.011}$ The major part of oil was extracted from seeds surface rather than from its pores (the activation energy was found to be = 2.146 kJ/mol) of oil extracted. The extraction-rate parameter for various solvent-feed ratios (S/F) agrees with the equation $K_{(S/F)} = 1/0.995\,(S/F)^{-0.142}$. Also, the relation between the extraction-rate parameter and the mixing intensity can be represented by $K_{r.p.m.} = -1.688\,(r.p.m.)^{0.806}$. The values of the free energy and the enthalpy were evaluated.

Keywords: Extraction, Thermodynamics and Kinetics, Activation Energy, Mixing intensity, Nigella-Sativa Oil.

INTRODUCTION

A large spectrum of valuable substances are extracted from natural raw materials of vegetable origin. Among them, Nigella-Sativa oil extracted from black seeds.

Karawya *et al.* [1] stated that the Arabian authors reported that the black-seeds are useful mainly in headache, respiratory appression, asthma and expelling the urinary calculus, as well as lactagogue, emmenagogue and diuretic. In Egyptian folk medicine it is stated that the seeds are used as carminative and are added as flavouring agent to bread, while its expressed oil is used in asthma, respiratory appression and cough. Khanna *et al.* [2] showed that oil from the seeds of Nigella-Sativa exhibited CNS (central nervous system) depressant and potent analgesic effects in rats and mice. El-Tahir *et al.* [3] studied the respiratory effect of volatile oil of the black seed of Nigella-Sativa in guinea pigs and elucidated the mechanism of action. Aqel [4] studied the calcium antagonistic effect of the volatile oil of Nigella-Sativa seeds. He found that the volatile oil of Nigella-Sativa seeds inhibited the contractions of guinea pig tracheal smooth muscle induced by histamine stimulation and the contractions of rabbit tracheal smooth muscle induced by acetylcholine stimulation. This inhibition was dose dependent and reversible. Also, the volatile oil inhibited the contractions of guinea pig and rabbit tracheal smooth muscles induced by high K^+ solution. Meanwhile, the volatile oil did not inhibit the contractions of guinea pig and rabbit tracheal smooth muscle induced by histamine and acetylcholine, respectively in Ca^{+2} free solution. Karawya *et al.* [1] studied the essential oil and lipids of Nigella-Sativa seed and their biological activity. They found that the main constituent of essential oil are:

ρ-cymene (31.5%), thymoquinone (30.9%), α-pinene (13.6%), β-pinene (5.2%) limonene (13.6%), carvacrol (3%) and thymohydroquinone (0.9%). Further, the oil showed significant antimicrobial and antifungal activities. Nergiz *et al.* [5] studied the chemical composition of Turkish Nigella-Sativa seeds. They reported the proximate chemical composition of the fatty acids, sterols of extracted oil, the content of total polyphenols and tocopherols of the oil and an analysis of water-solution vitamins and minerals in the seeds. Al-Jassir *et al.* [6] reported that proximate analysis of black cumin seeds showed a composition of 20.85% protein, 38.20% fat, 4.64% moisture, 4.37% ash, 7.94% crude fiber and 31.94% total carbohydrates. Aboutabl *et al.* [7] studied the aroma volatiles of Nigella-Sativa seeds. They reported that the oil from Nigella-Sativa seeds was analyzed by capillary gas chromatography coupled to a mass spectrometer and 67 compounds were identified. The oil contained 46% monoterpenes, the main components of which are: ρ-cymene 31.7% and α-pinene 9.3%. The oil also contained 25% carbonyl compounds, mainly thymoquinone (24.5%). Phenols (1.7%), alcohols (0.9%) and esters (16%) were also present. Sener *et al.* [8] found that Nigella-Sativa seed contained 26.6% oil of which the major fatty acids were linoleic (64.60%) and palmitic (20.40%). The unsaponifiable matter gave 5 spots on TLC of which were sterols, the major one being β -sitosterol. A commercial oil may have been adulterated with sunflower oil based on properties and fatty acids composition.

The aim of this study is to discuss the kinetics and thermodynamics of the extraction of Nigella-Sativa oil from its black seeds.

MATERIALS AND METHODS

Materials

The black seeds (Nigella-Sativa) were washed thoroughly by subjecting the seed surface to a water spray. The wet seeds were then dried by air stream and finally the seeds were crushed into small particle size to break its hard cover [9,10] Different solvents were tested, n-hexane, absolute alcohol, methylene chloride, dimethyl formamide and petroleum ether using soxhlet apparatus, and it was found that the petroleum ether (boiling range 60-80 °C) gave the highest extraction yield through this work.

Equilibria of Oil Extraction

Quick fit bottles (250 ml), each containing 2 g of crushed black seed were used. An appropriate amount of petroleum ether (60-80 °C) was added to each of the bottles which were then sealed. The samples were brought to the extraction temperature and shaken at 150 r.p.m. in a thermostatic water-bath shaker for at least 105 min. Extracts were obtained, and the oil content in the extract was measured spectrophotometrically [11] (MSE Spectro-plus MKIA supplied by MSE Scientific Instruments, England) using 0.5 cm light path glass cell. All measurements were made at a wavelength $\lambda_{max.}$ = 390nm. Extraction samples were replicated three times for each of the experimental conditions. The final results are given as mean values of replicated samples. The same procedure was used to obtain equilibrium data at other regulated temperatures of extraction.

Rate of Oil Extraction

A 2 g sample of black seed was extracted in a sealed bottle shaked by a thermostatic shaking water-bath. The temperature of the extractor was maintained in a water-bath at the required extraction temperature. Extraction was terminated after a desired period of time and the oil content was determined. The same procedure was repeated of each of the extraction times [11]

Oil Content

The total Nigella-Sativa oil-content was determined by exhausting selective amount of black seeds with different batches of pure solvent (keeping temperature at 45 °C and time for 3 hr for each batch) and the

amount of extract obtained in each batch was calculated

RESULTS AND DISCUSSION

The Effect Temperature on the Extraction Rate

Figure 1 shows the effect of temperature on the extraction rate of Nigella-Sativa oil, from which it is seen that the rate of oil extraction from the bulk seeds increased with increasing temperature. It also shows that the increase in the rate of extraction of oil at higher temperature reduced the time necessary to attain equilibrium. However, the maximum rate of extraction was obtained at a temperature of 60 °C. Attention must be taken that the boiling range of petroleum ether is 60-80 °C. In Figure 1, at any temperature, the rate of extraction was almost constant to 50 minutes of the extraction time, and then over 50 minutes the increment in the rate of extraction is very minor.

For mass transfer studies, the rate process may be expressed in terms of square root of time [12] On this basis, the relationship between the amount of Nigella-Sativa oil extracted (C_t/C_o (C_o is the initial concentration in seed) and $t^{0.5}$ at different temperatures are depicted in Figure 2.

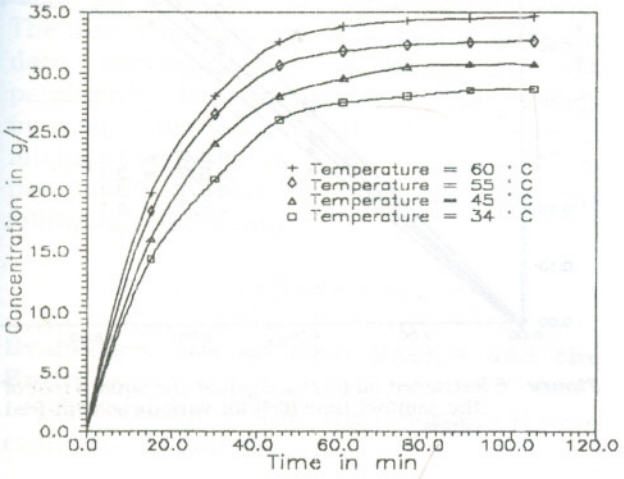

Figure 1 Influence of temperature on the extraction rate of N. Sativa oil (S/F =2:1, 150 rpm)

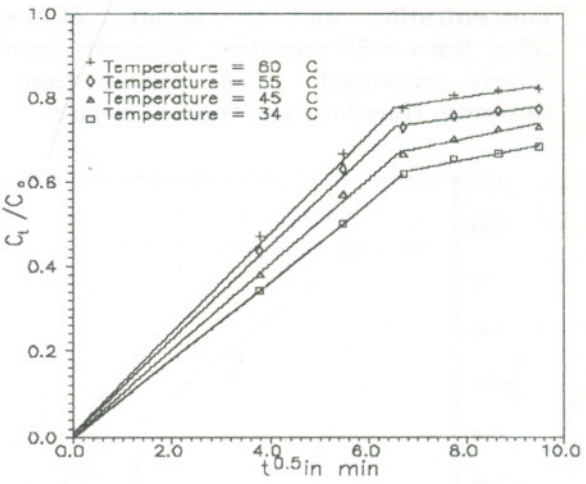

Figure 2 Extracted oil (C_t/C_o) against the square root of the contact time ($t^{0.5}$) for various temperatures.

The examination of Figure 2 shows that it consists of two straight lines, with different slopes. Different slopes represent two different modes of extraction.

The first linear portion of the relation with higher slope may be explained according to Chien *et al.* [11] as oil is extracted from vegetable raw materials only from the surface of a shrinking unextracted core. The major part of oil (≈ 95%) is extracted from surface of the seed. The lower slope of the second part of the relation may be due to the slow diffusion of petroleum ether into the particles and/or diffusion of oil out of the particles. An activation energy of 2.146 kJ/mol was calculated from the data depicted in Figure 3 (K is the slope of the first linear portion of the curves in Figure 2). This illustrates that the oil uptake by the petroleum ether is a diffusion-controlled process [13]

The Effect of Solvent-Feed Ratio (S/F) on the Rate of Extraction.

Figure 4 shows the behaviour of extraction rate with different solvent-feed (S/F) weight ratios, the concentration of Nigella Sativa oil in solvent decreased with increasing the of S/F ratio. Vice versily , as in Figure 5, the amount of oil extracted increased with increasing the S/F ratio at the same time. The increment in both the

concentration and the amount of the oil after time = 50 minutes were very small or nearly constant. This proves that the optimum time for extraction is 50 min.

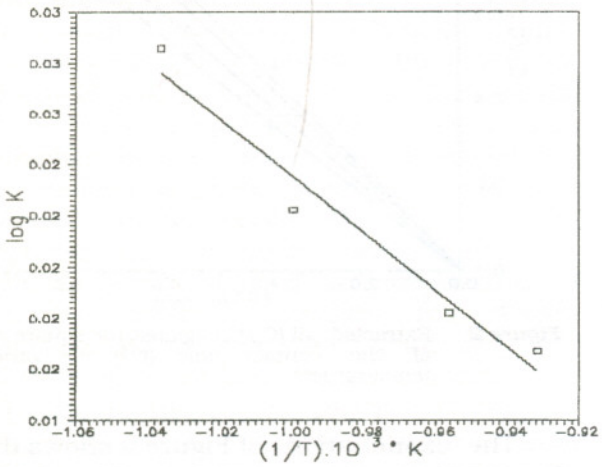

Figure 3 Plot of the logarithm of the rate parameter (K) versus the reciprocal of the absolute temperature (1/T) for N. Sativa oil extraction

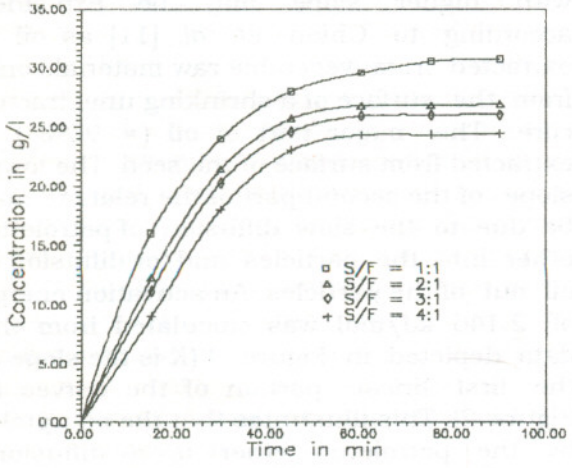

Figure 4 Influence of solvent-feed ratios on the extraction rate of N. Sativa oil. (T=40 °and 150 rpm).

Figure 6, shows the rate process as given in Figure 2 but for different S/F ratios. The slope of the first portion can be defined as rate parameter (K).

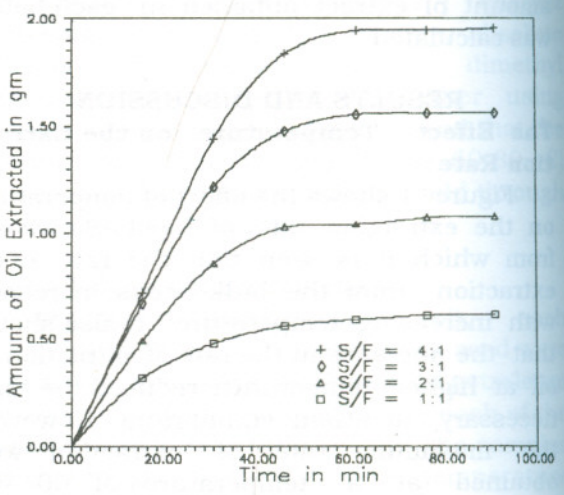

Figure 5 Amount of Extracted oil against the contact time for various solvent-feed ratios (T=40°C, 150 rpm).

The solvent-feed ratio dependence of K was determined by plotting log (S/F) as shown in Figure 7. The straight line indicates that the relationship between rate parameter K and solvent -feed ratio can be expressed as:

$$K_{(S/F)} = 1/0.995\ (S/F)^{-0.1423}$$

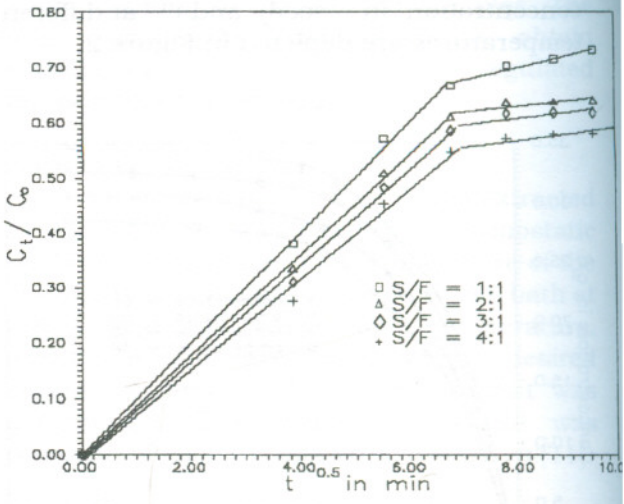

Figure 6 Extracted oil (C_t/C_o) against the square root of the contact time ($t^{0.5}$) for various solvent-feed ratios.

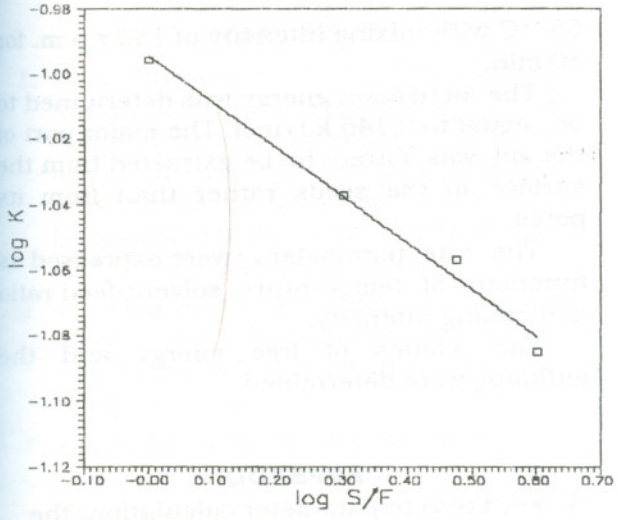

Figure 7 Plot of the logarithm of the rate parameter (K) versus the logarithm of the solvent-feed ratio (S/F) for N. Sativa oil extraction.

The Effect of Agitation (r.p.m.) on the Rate of Extraction.

Figure 8 shows the behavior of extraction rate with different r. p.m. The concentration of Nigella-Sativa oil increases with increasing the of the mixing intensity rate which can also support that the extraction is a diffusion controlled process.

The Results in Figure 9 prove that at lower r. p.m. extraction of oil is only from seed surfaces, and as r.p.m. is increased some oil will also be extracted from pores. The linear portion in this figure gives the data necessary for deducing the rate parameter dependency on the mixing intensity (plotted in Figure 10). The effect of mixing intensity on the extraction-rate parameter can be expressed by the following relationship:

$$K_{r.p.m.} = -1.6883\ (r.p.m.)^{0.8061}$$

Evaluation of the Free Energy and the Enthalpy

The values of the free energy [14] were evaluated as follows:

T temp. in °C	ΔF kcal/ mol
35	19.585
45	20.240
55	20.897
60	21.225

The enthalpy was calculated from the slope of the line in Figure 11 and its value is: $\Delta H = 1.2947\ kcal/g\ mol$

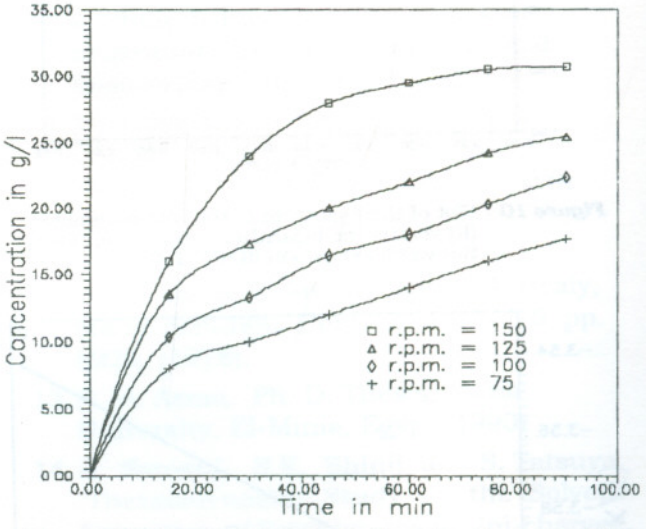

Figure 8 Influence of r.p.m. on the extraction rate of N. Sativa oil at S/F = 2:1and T=40°C.

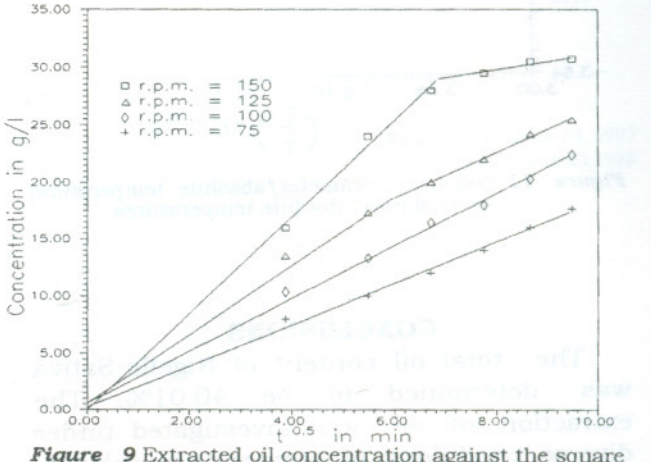

Figure 9 Extracted oil concentration against the square root of the contact time ($t^{0.5}$) for various r. p.m. and S/F = 2:1 and T=40°C.

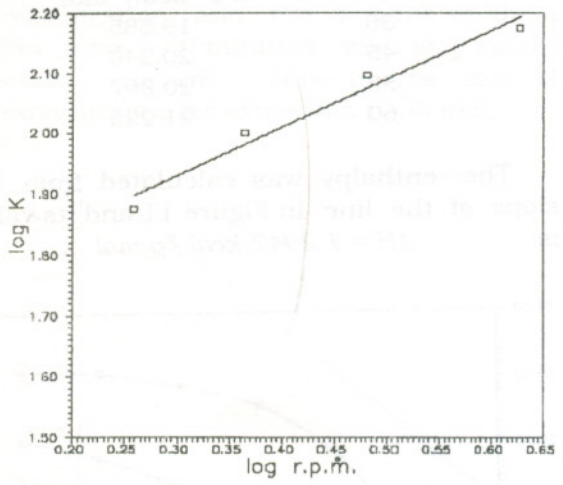

Figure 10 Plot of the logarithm of the rate parameter (K) versus the logarithm of the r.p.m. for N. Sativa oil extraction (S/F = 2:1).

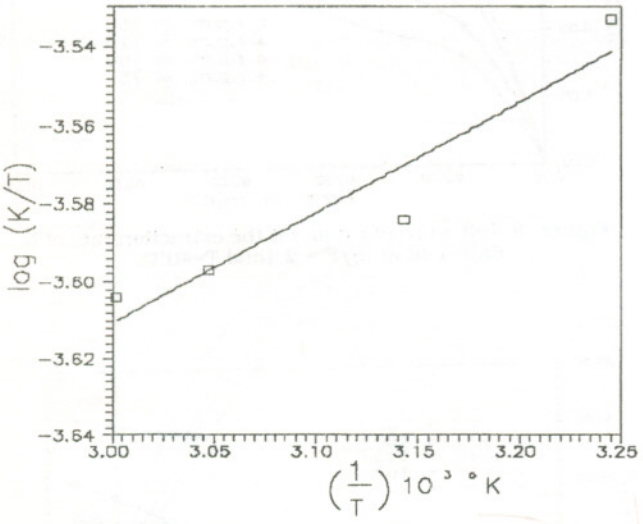

Figure 11 Log (rate-parameter/absolute temperature) vs. reciprocal absolute temperatures

CONCLUSIONS

The total oil content of Nigella-Sativa was determined to be 40.01%. The extraction of oil was investigated under diverse conditions of temperature, solvent-feed ratio and mixing intensity.

The suitable condition for the extraction of the Nigella-Sativa oil that gives a high yield of the oil is by using petroleum ether (60 - 80 ° C) and keeping the temperature at 55 °C with mixing intensity of 150 r.p.m. for 50 min.

The activation energy was determined to be equal to 2.146 kJ/mol. The major part of the oil was found to be extracted from the surface of the seeds rather than from its pores.

The rate parameters were expressed as functions of temperature, solvent-feed ratio and mixing intensity.

The values of free energy and the enthalpy were determined.

APPENDIX

1. For the rate parameter calculation, the following form were used:

$$K = A\,(variable)^{B}$$

where :

A and B are constants for the particular system.

variable may be: mixing intensity, or initial concentration or temperature.

2. Evaluation of activation energy (*E*)

$$K = A \exp(-E/R\,T)$$

where :

A Boltzman constant

R Universal gas constant

3. Evaluation of the free energy [14] :

$$K = \frac{RT}{Nh} \cdot e^{-(\Delta F/RT)}$$

where:

N : Avogadro's number

h : Plank's quantum constant

4. Evaluation of enthalpy [13] :

$$\Delta H = - R \frac{d \ln (K/T)}{d (1/T)}$$

NOMENCLATURE

A Arrhenius constant

C_o Initial concentration of oil in seed (g/l)

E Activation energy (kJ/mol)

K Rate parameter

t time (min)

T temperature (K)

ΔF Free energy change, kcal /mol

ΔH Enthalpy Change, kcal/mol

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استخلاص زيت حبة البركة من الحبيبات السوداء

ابراهيم اسماعيل ابراهيم

قسم الهندسة الكيمائية – جامعة المنيا

ملخص البحث

تم دراسة استخلاص زين حبة البركة السوداء باستخدام الإيثير البترولى (و الذى مدى درجة غليانه من ٦٠_٨٠°م). وتم الحصول على ٤٢,٠١ % من المحتوى الإجمالى للحبيبات من الزيت . ولقد بينت الدراسات الترموديناميكيه والحركيه نتائج متوافقه مع المتغيرات اللازمه لعمليه الإستخلاص . أما سعه الإستخلاص للزيت بواسطة الإيثير البترولى فقد وجد أنها تزداد مع زياده درجة الحراره. كذلك فإن السرعه النوعيه لعملية الإستخلاص فلقد وجد أنها تعتمد على درجة الحراره وفقا والمعادله:

$$K_T = -0.08848\ (T, K)^{-0.1121}$$

وكان معظم الزيت المستخلص من الحبيبات من الطبقه السطحيه أكثر مما هو موجود داخل مسام الحبيبات . كما وجد أن طاقه التنشيط تساوى ٢,١٤٦ كيلو جول /مول أما متغير الإستخلاص للنسب المختلفه من المذيب إلى التغذيه بالحبيبات فلقد وجد أنه يخضع للمعادله :

$$K_{(S/F)} = 1/0.0995\ (S/F)^{-0.1423}$$

أما معدل الإستخلاص فلقد وجد أنه يرتبط بمعدل التقليب حسب المعادله :

$$K_{r.p.m.} = -1.6883\ (r.p.m.)^{0.806}$$

كما تم أيضا تحديد قيم كل من الطاقه الحره والمحتوى الحرارى لعملية الإستخلاص .