Kinetic study of oil extraction from olive foot cake

By **S. Meziane, H. Kadi[1]*** and **O. Lamrous[2]**

Université Mouloud Mammeri, 15000 Tizi-Ouzou, Algérie.
[2] Laboratoire de Physique et de Chimie Quantique, Faculté des Sciences,
Université Mouloud Mammeri, 15000 Tizi-Ouzou, Algérie.
*Corresponding author: H.Kadi, B.P 70, Poste Annane, 15010 TIZI-OUZOU, ALGERIA.
e-mail: hocinekadi@yahoo.fr

RESUMEN

Estudio cinético de la extracción de aceite de orujo

La cinética de extracción de aceite de orujo puede ser explicada por un modelo basado en dos etapas. La primera etapa corresponde a un simple lavado del aceite de la superficie de las partículas. En la segunda etapa, la extracción esta controlada por dos mecanismos: difusión lenta desde las células rotas y difusión muy lenta desde las células intactas.

Los coeficientes cinéticas de este modelo matemático se calculan usando los resultados experimentales obtenidos con hexano y alcohol etílico comercial para diferentes tamaños de partícula.

PALABRAS-CLAVE: Aceite de orujo - Difusión - Extracción - Solvente.

SUMMARY

Kinetic study of oil extraction from olive foot cake

The kinetics of oil extraction from olive foot cake can be explained by a model based on two stages. The first step corresponds to a simple washing of the oil from the particle surface. In the second step, the extraction is controlled by two mechanisms: slow diffusion from broken cells and very slow diffusion from intact cells.

The kinetic coefficients of this mathematical model are calculated using the experimental results obtained from hexane and commercial ethyl alcohol for different particle sizes.

KEY-WORDS: Diffusion - Extraction - Olive foot cake oil - Solvent.

1. INTRODUCTION

The oil of olive foot cake is of important economic interest. For this reason, much work has been done to improve the yield of this oil recovered by solvent (Cana Munoz *et al.*, 1976; Kmieciak *et al.*, 1991; Kadi and Fellag, 2001).

Numerous theories have been proposed to explain the mechanism of oil recovery by solvent from oil cakes and oilseeds. So, the effect of the nature of the solvent (Hensarling and Jack, 1983; Kmieciak *et al.*, 1991), particle size (Othmer and Agarwal, 1955; Becker and McKee, 1978; Patricelli *et al.*, 1979; So and Macdonald, 1986; Wiese and Snyder, 1987; Schneeberger *et al.*, 1988), temperature (Becker and McKee, 1978; Patricelli *et al.*, 1979; So and Macdonald, 1986; Schneeberger *et al.*, 1988) and moisture (Cana Munoz *et al.*, 1976, Patricelli *et al.*, 1979) on the yield has been demonstrated . However, it is worth mentioning that the molecular diffusion does not correspond to experimental results (Othmer and Agarwal, 1955; Patricelli *et al.*, 1979; So and Macdonald, 1986). On the contrary, Schneeberger *et al.* (1988) showed that the kinetics of oil extraction by solvents in hazelnut cells which are not deteriorated is controlled by diffusion kinetics. It seems that the best mechanism adapted to oil cakes is described in two stages. The first is relative to the oil being at the grain surface and recovered by a simple washing and the second stage corresponds to a diffusion process which is able to take place in one or two phases.

Although many studies have been developed on oil extraction from olive foot cake, not one of them is based on the equations of mass transfer. Our objective in this paper is to present a study of the kinetics of solvent extraction of this residual oil in an agitated isotherm reactor working in a discontinuous regime.

2. MATERIAL AND METHODS

The olive foot cake used was taken from a continuous centrifugation system. Its initial moisture content was 48.0% which was reduced by drying to an interval ranging between 5 and 10%. The oil content of the sample was 6.50%. It was determined by an exhaustive extraction using hexane in a soxhlet apparatus.

The sample was ground using an electric cereal mill with millstones "S.A.M.A.P" type F100. Average

particle sizes obtained were: 1.69; 1.03 and 0.69 mm. The results are summarized in table 1.

The batch extraction was carried out in a cylindrical reactor of 600 ml ($\emptyset_r$ = 85 mm; h = 106 mm) supplied with a mechanical agitator. The agitation turbine in stainless steel was equipped with 4 blades tilted to 45° ($\emptyset_b$ = 51 mm). The solid-liquid separation was performed under reduced pressure. The miscella was distilled by means of a rotary evaporator.

The extractions have been carried out under the following conditions:

– kinetic study: solvent-to-solid ratio, $\frac{L}{S}$ = 4; extraction temperature, T = 25°C; agitation speed, V_a = 800 rpm; extraction time, t: from 0 to 60 min
– study at equilibrium: $\frac{L}{S}$ = 4; T = 25°C; t = 150 hours

The weight of the cake submitted to extraction was always 50 g. Each yield value calculated was the average of three tests for the kinetic study and five tests for the equilibrium study.

The HPLC grade hexane and ethyl alcohol 96.0 % (v/v) purity were used in all oil extraction experiments. Their average densities were 0.664 and 0.806, respectively. These solvents are Prolabo products.

3. MATHEMATICAL MODEL

The mechanism of oil extraction from oleaginous seeds assumes that the oil transfer from the solid phase to the liquid phase is carried out in two simultaneous processes: a predominant washing process and a diffusion process.

Patricelli *et al.* (1979), working on uninterrupted oil extraction from sunflower seeds, proposed a model where the concentration C_t at any time is given by the equation:

$$C_t = C_e^w (1 - \exp(-k_w t)) + C_e^d (1 - \exp(-k_d t))$$

where,

C_e^w: oil concentration to equilibrium in the solvent due to the washing step
C_e^d: oil concentration at equilibrium in the solvent due to the diffusion step
k_w: mass transfer coefficient for the washing step
k_d: mass transfer coefficient for the diffusion step

The final oil concentration in miscella at time equal to infinity:

$$C_e = C_e^w + C_e^d$$

The model applied by So and Macdonald (1986) for the oil extraction from canola (rapeseed) derives from the preceding model. It considers the possibility of two distinct steps of diffusion inside the seed.

– slow, unhindered diffusion of oil held in the ruptured cells of the seed
– a very slow, hindered diffusion of oil held within unruptured cells of the seed.

The transfer equation is then written:

$$C_t = C_e^w (1 - \exp(-k_w t)) + C_e^{d1} (1 - \exp(-k_{d1} t)) + C_e^{d2} (1 - \exp(-k_{d2} t))$$

at equilibrium

$$C_e = C_e^w + C_e^{d1} + C_e^{d2}$$

The value C_e corresponds to the concentration at equilibrium. It has been determined experimentally.

In this study, we have then tried to determine the applicability of these two mathematical models to the oil extraction from olive foot cake by studying the extraction yield according to time for different particle sizes and solvents. This yield ρ_t, calculated on a dry basis, can be expressed by the equation:

Model I: $\rho_t = \rho_t - \rho_e^w \exp(-k_w t) - \rho_e^d \exp(-k_d t)$
with $\rho_e = \rho_e^w + \rho_e^d$

Model II: $\rho_t = \rho_e - \rho_e^w \exp(-k_w t) - \rho_e^{d1} \exp(-k_{d1} t) - \rho_e^{d2} \exp(-k_{d2} t)$
with $\rho_e = \rho_e^w + \rho_e^{d1} + \rho_e^{d2}$

where,
ρ_e: oil yield of the extraction to equilibrium
ρ_e^w: oil yield to equilibrium for the washing step
ρ_e^d: oil yield to equilibrium for the diffusion step
1 and 2: relative indexes at the first and the second diffusion

The oil yields at equilibrium according to the particle size and nature of the solvent (ρ_e) have been determined experimentally. The kinetic coefficients k_w, k_{d1} and k_{d2} as well as the oil yields at equilibrium ρ_e^w, ρ_e^{d1} and ρ_e^{d2} have been calculated numerically with a non-linear least squares fitting method using program "Origin 7.0".

Table 1
Characteristics of samples and yields of extraction at equilibrium

Average diameter of sample (mm)		1.69	1.03	0.64
Moisture (%)		5.9	5.85	5.48
Oil content at equilibrium (%)*	Hexane	5.82		
	Ethyl alcohol 96.0%	5.22		

* calculated on dry basis

4. RESULTS AND DISCUSSION

4.1. Study at equilibrium

Table 1 presents the oil yield at equilibrium according to granulometry and the nature of the solvent. These results obtained after a contact time of 150 hours show that the yield is independent of the particle size. This conclusion is in agreement with that of So and Macdonald (1986) who studied the oil extraction from canola (rapeseed). These authors showed that the equilibrium is reached after about 3 days for 0.06 mm thickness and after 6 days for 0.76 mm thickness.

As shown in Table 1, hexane appears to be the solvent that gives the best yield. It extracts approximately 10.3% more fat matter than ethyl alcohol 96.0%.

4.2. Kinetic Study

The data from our experiments are first fitted with mathematical model I based on a washing stage and a single diffusion. Figures 1a and 1b show the extraction graphs with ethyl alcohol 96.0% and hexane according to the contact time and for different particle sizes. A first visual analysis especially indicates a good fit for the low

granulometries. Model II, which implies two diffusion stages, gives better results as shown in figures 2a and 2b.

These curves also show that the oil yield increases very quickly with time at the beginning of the extraction. This rapid increase could be explained by the fact that this first stage which in general lasts 3 to 11 min for model I and one half-minute to 6 min for model II corresponds to the washing process from the grain surface.

The second stage is characterized by a yield which increases less and less rapidly. Then, the extraction is only assured by diffusion which is an increasingly slow process.

Tables 2 and 3 give the calculated values of the kinetic coefficients of the washing and diffusion stages for different particle sizes and different
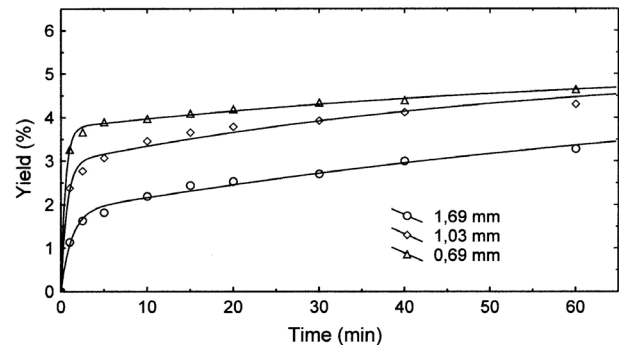

Figure 1a
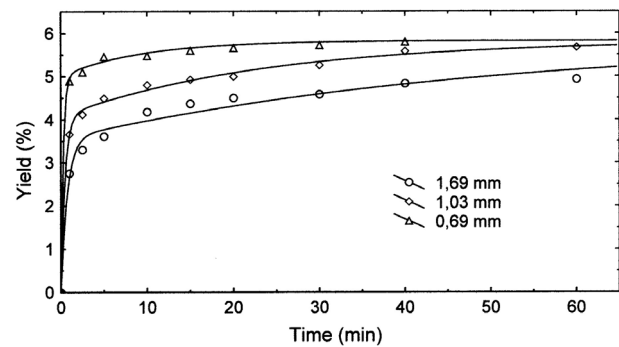Fit of model I to the extraction with ethyl alcohol 96.0% showing the effect of particle size

Figure 1b
Fit of model I to the extraction with hexane showing the effect of particle size

solvents. One can observe that extraction by washing is more effective than that resulting from diffusion. The determination coefficients r^2 indicate a good fit for model I ($0.987 \leq r^2 \leq 1.000$) and a very good fit for model II ($0.991 \leq r^2 \leq 1.000$). In the case of model I, the kinetic coefficients of washing are 33 to 126 times greater than for the diffusion stage. For model II, the washing coefficients are 9 to 151 times greater than those of the first diffusion and those for diffusion 1 are 7 to 47 times greater than for diffusion 2. It should be noted that all the coefficients of washing and diffusion of model II are higher than those of model I, for a given solvent and granulometry.

Table 2
Coefficients of mass transfer and yields at equilibrium of model I

		MODEL I				
Solvent	Average diameter (mm)	Coefficients of mass transfer (min⁻¹)		Yields at equilibrium (%)		Coefficients of determination
		k_w	k_d	ρ_e^w	ρ_e^d	r^2
Ethyl	1.69	0.81	0.0100	1.84	3.38	0.9923
alcohol	1.03	1.46	0.0185	2.96	2.26	0.9940
96.0%	0.69	1.97	0.0156	3.76	1.46	0.9984
	1.69	1.23	0.0191	3.66	2.16	0.9887
Hexane	1.03	2.08	0.0425	4.08	1.74	0.9976
	0.69	3.57	0.1086	5.00	0.82	0.9996

Table 3
Coefficients of mass transfer and yields at equilibrium of model II

		MODEL II						
Solvent	Average diameter (mm)	Coefficients of mass transfer (min^{-1})			Yields at equilibrium (%)			Coefficients of determination
		k_w	k_{d1}	k_{d2}	ρ_e^w	ρ_e^{d1}	ρ_e^{d2}	r^2
Ethyl	1.69	1.48	0.158	0.0078	1.30	0.83	3.09	0.9986
alcohol	1.03	2.86	0.174	0.0109	2.31	1.17	1.74	0.9997
96.0%	0.69	46.82	0.695	0.0143	2.67	1.16	1.39	0.9998
	1.69	3.20	0.270	0.0132	2.44	1.64	1.74	0.9960
Hexane	1.03	47.62	0.651	0.0367	2.89	1.38	1.55	0.9987
	0.69	60.98	0.403	0.0607	4.66	0.61	0.55	0.9998

Figures 1a, 1b, 2a and 2b also indicate that the particle size has a great influence on the extraction; the yield increases when the particle size decreases. This fact is confirmed by the general increase in all kinetic coefficients given in tables 2 and 3.

The results presented in these tables show that the nature of the solvent has an effect on transfer coefficients. In the case of both models, hexane gives the best transfer coefficients in all the steps of washing and diffusion for the same particle size. This is confirmed by figures 3a, 3b and 3c represented by model II which show that, for a given granulometry, hexane always extracts more oil than ethyl alcohol 96.0%.
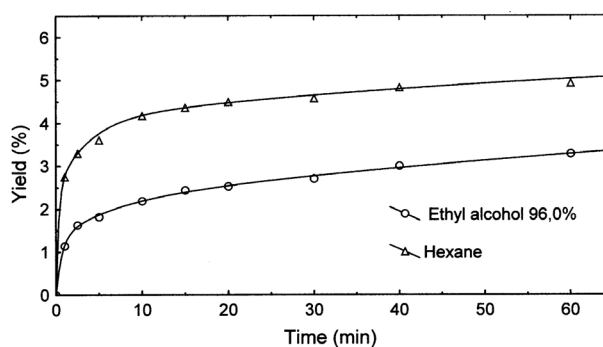

Figure 3a
Fit of model II to extraction with 1.69 mm diameter showing the effect of solvent nature
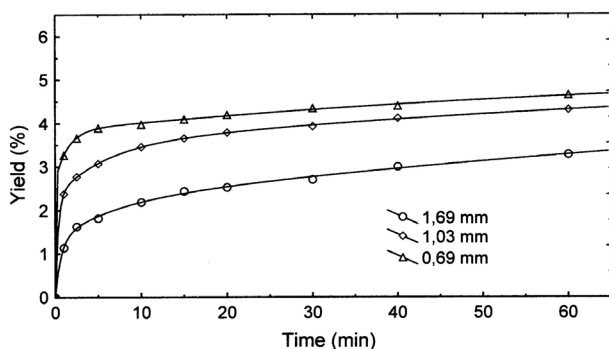

Figure 2a
Fit of model II to the extraction with ethyl alcohol 96.0% showing the effect of particle size
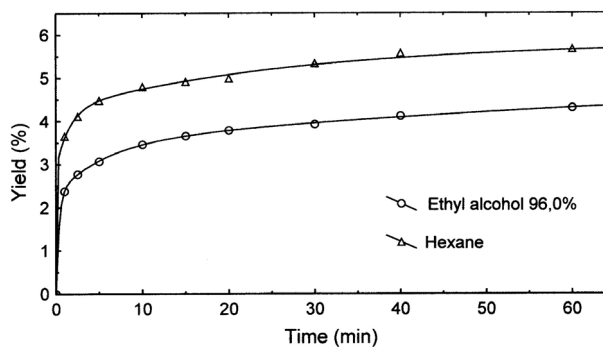

Figure 3b
Fit of model II to extraction with 1.03 mm diameter showing the effect of solvent nature
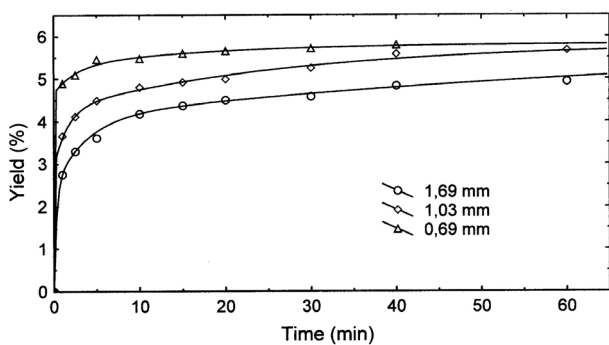

Figure 2b
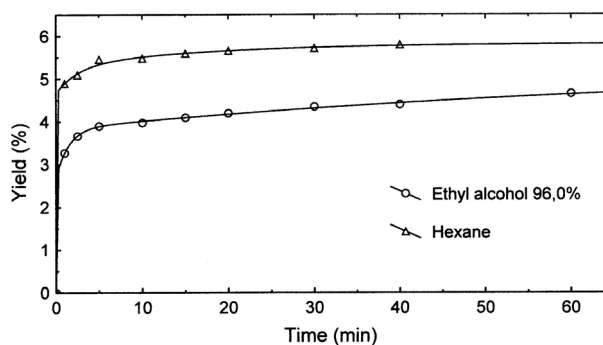Fit of model II to the extraction with hexane showing the effect of particle size

Figure 3c
Fit of model II to extraction with 0.69 mm diameter showing the effect of solvent nature

5. CONCLUSION

The study of oil extraction at equilibrium showed that the yield after 150 hours of contact is independent of the particle size for a given solvent. It also appears that hexane is the solvent which extracts the most fat matter.

The results produced by model I and especially by model II are in agreement with the experimental results. However, model I seems more adequate because it is easier to use: it requires less parameters that model II.

In both models, the predominant mechanism in the extraction process is the washing of oil from the particle surface. This washing which allows the recovery of a significant quantity of oil is finished in about 11 minutes for model I and 6 minutes for model II. The extraction is then assured by the diffusion process only.

It is important to point out as well that the extraction is influenced by particle size and by the nature of the solvent. Hexane gives the highest kinetic coefficients in all cases. These coefficients increase in both models when the particle size decreases. We notice that the amount of extracted oil during the washing stage increases with the decrease of particle size. For extraction with hexane, the decrease in size from 1.69 to 0.69 mm leads to an increase in oil yield from 42.0 to 80.0%. This variation is less significant (25.0 to 51.0 %) in the case of ethyl alcohol.

Both models, while giving good results, do not describe the extraction process such as it occurs since they consider that the steps of washing and diffusion happen simultaneously. However, in reality, the diffusion process of oil in a solvent can only begin when the washing step is finished.

NOMENCLATURE

C_t: oil concentration in the solvent at any time (g oil / 100 g miscella)

C_e: oil concentration to equilibrium after the extraction process has been completed (g oil / 100 g miscella)

C_e^w: oil concentration to equilibrium in the solvent due to washing stage (g oil / 100 g miscella)

C_e^d: oil concentration at equilibrium in the solvent due to diffusion step (g oil / 100 g miscella)

h: height of reactor (mm)

k_d: coefficient of mass transfer for diffusion step (min^{-1})

k_w: coefficient of mass transfer for washing step (min^{-1})

$\dfrac{L}{S}$: solvent-to-solid ratio (ml solvent / g solids)

r^2: coefficient of determination

t: extraction time (min)

T: extraction temperature (°C)

V_a: agitation speed (rpm)

ρ_t: oil yield of the extraction at any time (g oil / 100 g solids)

ρ_e: oil yield of the extraction to equilibrium (g oil / 100 g solids)

ρ_e^w: oil yield to equilibrium for washing stage (g oil / 100 g solids)

ρ_e^d: oil yield to equilibrium for diffusion stage (g oil / 100 g solids)

$\varnothing_b$: diameter of agitator blade (mm)

$\varnothing_r$: diameter of reactor (mm)

1 and 2: relative indexes after first and the second diffusions

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