

EXPERIMENTAL EVIDENCE OF OIL EXTRACTION RATE DEPENDENCE ON BOTH EXTRACTION TIME AND GENERATIVE MATERIAL STRUCTURE

ABSTRACT

Background : A kinetic and thermodynamic study of the extraction of oils from pumpkin seeds, sesame seeds and Moringa seeds has been carried out for the first time and has shown that the extraction is an exothermic balanced phenomenon and has made it possible to determine the kinetic constants in the three cases.

These kinetic constants can provide an indication of the organic structural organization of the seeds generating these oils (crystalline → smectic → nematic → amorphous). In addition, they made it possible to calculate the enthalpies, the entropies and a comparison of all these kinetic and thermodynamic parameters was made in the 3 cases.

Aim and Objective : It is demonstrated in this work for the collective imagination that the speed of extraction of oils from pumpkin seeds, sesame seeds and Moringa seeds depends not only on the extraction time, but also on the organic structural organization of seeds generating these oils under given temperature and pressure conditions using petroleum ether as extractant solvent .

Methodology : The measurements and calculations have been our methodology of work .The comparison between kinetics and thermodynamics parameters of the three species have been done . The figures have been plotted by means of excell program. The Study has been performed in dilute medium.

Results : The results are satisfactory and are hereby commented . The oils extraction rates of these three species of seeds, kinetic constants, enthalpies and entropies are calculated and compared.

Conclusion : The kinetic and thermodynamic study of the extraction of oils from pumpkin, sesame and Moringa seeds has shown that the extraction is an exothermic balanced phenomenon and therefore the energy released by this operation can be used to perform mechanical or electrical work . As for the kinetic constants, they are greater in an amorphous body where the entropy is greater. In such a case, the oil is more easily extracted under determined temperature and pressure conditions for a given solvent. Under these conditions, the extraction is dependent not only on time, but also on the structural organization of the material generating the oil. Also, the rate constant can give information on the differentia-

Keywords : Kinetics constant, enthalpy of extraction, entropy .

1. INTRODUCTION

In our previous work, it was shown the chemical compounds that make up gourd seeds, sesame seeds and Moringa seeds [1,2,3]

These compounds are of particular importance in the health of the population as recommended by several studies [4,5,6,7,8,9,10,11,12]. The major concern of Lacopa -PCC was to provide the country (DRC) in a rational way with appropriate technology to solve the eternal problem of knowledge transfer in order to be able oneself to produce large quantities of oil for the population and why not for the world.[13,14,15]

The title of this work announces what is intuitively known by any researcher in this field, but which we have the honor to prove by experimental evidence.

In this same register of concerns, KUNYIMA method [1,2,3] has been developed and successfully applied to the extraction of oils from these three kinds of seeds which have extraordinarily proven nutritional and therapeutic virtues; and we took the opportunity to recommend them for a mechanized culture to the rulers of DRC. It should be remembered that the DRC has a very rich and diverse plant heritage in a favorable climate all year round so that it constitutes a source of wealth creation not only for its population, but also for Africa and for the world.

This work compares the evolution of the extraction speed of oil from pumpkin seeds, sesame seeds and Moringa seeds with the extraction time in petroleum ether at the temperature of 56 ° C for pumpkin and Moringa seeds, 54 ° C for sesame seeds.

The kinetic constants were calculated at these temperatures and have been commented on. They are all different and seem to reflect the differences in structure between different seeds. The two constants measured at 56 ° C can be compared, except that calculated at 54 ° C for sesame seeds which nevertheless give an idea of its evolution in the same direction as the others, especially since the difference of 2 ° C is not great. We made this comparison in the discussion without being afraid to distort our reasoning.

2. MATERIALS AND METHOD

The materials and method have been mentioned in previous work where Soxhlet extraction was used [1,2,3].

This work uses the kinetic constants calculated in previous work and uses the following formula to calculate the speed of the Extraction.

$$X = m_e = m_o (1 - e^{-kt}) \quad [1,16]$$

$$m_o - m_e = m_o e^{-kt}$$

$$v = dX/dt = km_o e^{-(kt)} = km_o((m_o - m_e))/m_o$$

$$v = dX/dt = k(m_o - m_e)$$

Work formula

where v is the extraction speed in g / h

k is the kinetic constant or rate constant

m_o = extractable mass of oil in petroleum ether (it is considered constant).

m_e = mass extracted of oil at a time t expressed in hours (h).

To calculate enthalpy and entropy we use the formula similar to that of Arrhenius .[17]

$$k = Ae^{-E/RT}$$

Arrhenius calls E = activation energy in a chemical reaction.

In the extractions there is no chemical reaction, there are interactions.

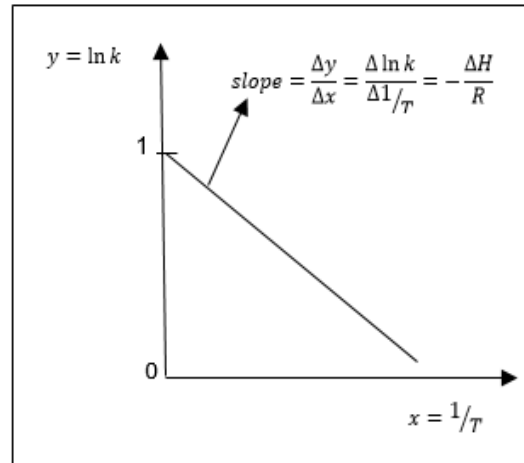
We call E = energy of interactions or energy of extraction

$$\ln k = \ln A - \frac{E}{RT} = \ln A - \frac{\Delta H - T\Delta S}{RT}$$

Suppose that $E = \Delta G$ and $\Delta G = \Delta H - T\Delta S$

$$\begin{aligned} \ln k &= \ln A - \frac{\Delta H}{RT} + \frac{T\Delta S}{RT} \\ &= \ln A + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \end{aligned}$$

$$\ln k = B - \frac{\Delta H}{RT}$$



$$slope = \frac{\ln k_1 - \ln k_0}{\left(\frac{1}{T_1} - \frac{1}{T_0}\right)} = -\frac{\Delta H}{R}$$

$$\text{If } T = \infty \rightarrow \ln k_0 = 0$$

$$\frac{1}{T} = 0$$

$$slope = \frac{\ln k_1}{\frac{1}{T_1}} = -\frac{\Delta H}{R}$$

$$T_1 \ln k_1 = -\frac{\Delta H}{R}$$

$$\Delta H = -RT \ln k$$

Work formula

It is explained under the point results and discussion why $E \neq \Delta G$,

but $E = \Delta H$ and $\Delta G = 0$

Therefore

$$\Delta S = \frac{\Delta H}{T} = -R \ln k$$

The following expression is used to calculate the error on E (ΔH)

$$\ln k = \ln A - \frac{E}{RT}$$

$$\frac{dk}{k} = \frac{dA}{A} - \left[\frac{dE \cdot RT - d(RT) \cdot E}{(RT)^2} \right]$$

$$\frac{dk}{k} = - \frac{RT dE}{(RT)^2}$$

$$\frac{dk}{k} = - \frac{dE}{RT}$$

$$\frac{\Delta k}{k} = \frac{\Delta E}{RT}$$

$$\Delta E = \frac{RT \Delta k}{k}$$

Work for-
mula

It should be noted that this method leads in this case to obtain the values of the extraction energies with 0 as an error because, in fact, the derivative of a constant (kinetic constant) is zero (dk / k)

3. RESULTS AND DISCUSSION

In regard to the extraction of oil pumpkin seeds, Table 1 gives the values of the measured and calculated parameters.

Table 1. Variation of pumpkin oil extraction speed as a function of time.

Time (h)	$m_0(g)$	$m_e(g)$	$v(gh^{-1})$
0	5.3118±0.4193	0.0000±0.0000	8.7171
1	5.3118±0.4193	4.0485±0.8790	2.0732
1.5	5.3118±0.4193	4.6640±0.5862	1.0631
2	5.3118±0.4193	5.1423±0.5888	0.2782
2.5	5.3118±0.4193	5.2212±0.3131	0.1487
3	5.3118±0.4193	5.2587±0.3562	0.0871
3.5	5.3118±0.4193	5.2950±0.4075	0.0276
4	5.3118±0.4193	5.3118±0.4193	0.0000

As it can be seen, Table 1 gives the variation in the extraction speed of gourd seeds oil as a function of the extraction time expressed in hours (h). It can be observed in this table that the extraction speed decreases with the extraction time as shown in figure 1

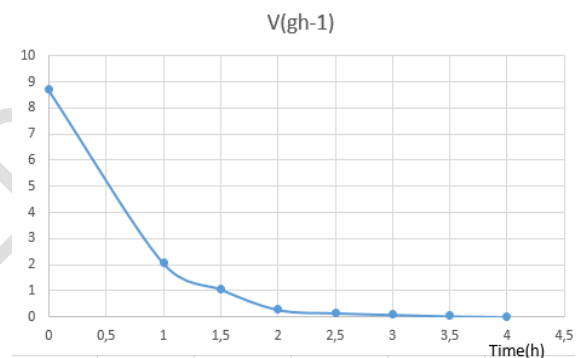


Figure 1. Gourd seeds oil extraction rate versus time.

This decrease in speed seems logical given that the solvent tends to saturation as time passes.

Table 2 gives the values of the experimental parameters for sesame seeds oil.

Table 2. Variation in the speed of extraction of the oil from the sesame seeds as a function of the time.

Time (h)	$m_0(g)$	$m_e (g)$	$v (gh^{-1})$
0	5.3911±0.1753	0.0000±0.0000	8.3778
0.5	5.3911±0.1753	2.0773±0.3029	5.1496
1	5.3911±0.1753	4.7635±0.2632	0.9753
1.5	5.3911±0.1753	5.1920±0.1853	0.3094
2	5.3911±0.1753	5.2522±0.1770	0.2158
2.5	5.3911±0.1753	5.2916±0.1859	0.1592
3	5.3911±0.1753	5.3337±0.1753	0.0892
3.5	5.3911±0.1753	5.3711±0.1753	0.0311
4	5.3911±0.1753	5.3911±0.1753	0.0000

The finding is the same, it is observed the decrease in speed as a function of time showing the saturation of the extracting solvent (petroleum ether) in extracted substance as time passes as it can be seen on figure 2.

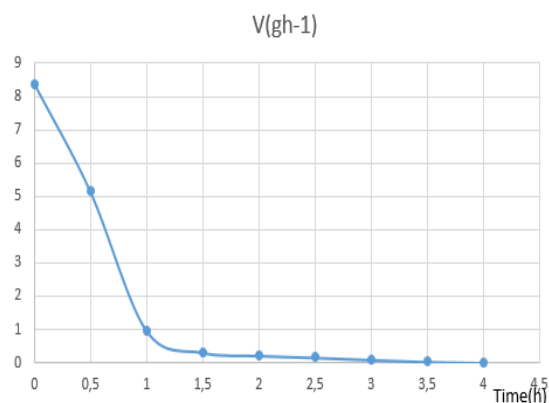


Figure 2. sesame seeds oil extraction rate versus time.

The same is true for Moringa seed oil, of which Table 3 and Figure 3 give the values and the evolution of the parameters.

Table 3. Variation of Moringa seeds oil extraction rate as a function of time

Time (h)	$m_0(g)$	$m_e (g)$	$v (gh^{-1})$
0	2.6105±0.2901	0.0000±0.0000	3.2910
0.5	2.6105±0.2901	1.6457±0.1767	1.2156
1	2.6105±0.2901	2.0361±0.2650	0.7241
1.5	2.6105±0.2901	2.2611±0.0960	0.4405
2	2.6105±0.2901	2.3550±0.1454	0.3221
2.5	2.6105±0.2901	2.5244±0.2889	0.1085
3	2.6105±0.2901	2.5635±0.3031	0.0592
3.5	2.6105±0.2901	2.5831±0.3080	0.0345
4	2.6105±0.2901	2.6105±0.2901	0.0000

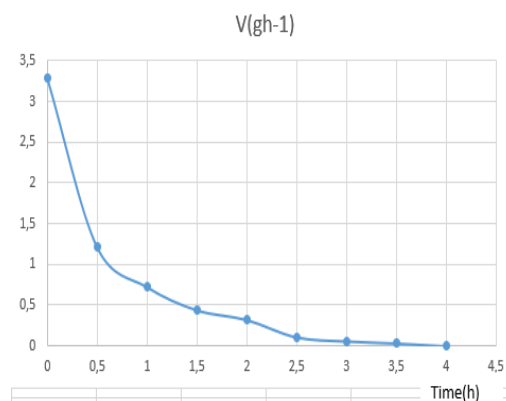


Fig 3. Moringa seeds oil extraction rate versus time

The superposition of the results of the oils of these three species clearly highlights the variation in the extraction speed not only with time but also with the nature of the species engaged in the extraction as shown in Figure 4.

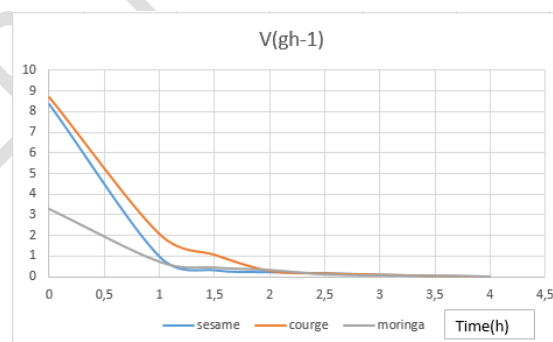


Fig 4. Oils extraction rate versus time.

The kinetic and thermodynamic study undertaken to account for the influence of the structure on the extraction speed has shown that at given temperature and pressure, the kinetic constant depends on the nature of the seeds that generate the oils and therefore on their structures in a well-determined extracting solvent. The rate constants were calculated.

To calculate the extraction enthalpies and the entropies, the Arrhenius relation was used ($k =$

$Ae^{-\frac{E}{RT}}$ [17] where E is the activation energy in a chemical reaction. However, in the case under study, the extractions are not chemical reactions, they are interactions.

E translate therefore the energy put into play in an extraction. The Soxhlet Extraction that we carried out constitutes an extraction operation in a closed system and we know that in such a closed system

$$dG = -SdT + VdP \text{ et } dH = TdS + VdP$$

Since the extraction was carried out at constant temperature and pressure $\Delta G = 0$ and $\Delta H = T\Delta S$

The calculated energy of extraction exists, it has a value, it is not zero as ΔG , but it is equal to ΔH ($E = \Delta H$) and the relationship

$\Delta H = -RT \ln k$ has been used. Therefore : $\Delta S = \frac{\Delta H}{T} = -R \ln k$ served as an entropy calculation. The results of the experiment, the extraction is a balanced exothermic phenomenon and the energy it releases can be used to produce a mechanical work or electrical work. As for obtained values. ΔS , they suggest that the entropy is greater in pumpkin seeds in the sesame seeds which, in turn, have a higher entropy than Moringa seeds.

Indeed, in a crystal, the molecules are organized. In an amorphous body, there is no organization. As it melts, a crystal changes from an organized state to an unorganized state. There are intermediate states between the crystalline state and the amorphous

state. These are the mesomorphic bodies divided into two classes according to the type of organization :

Smectic bodies where the molecules are oriented parallel and on parallel surfaces and nematic bodies where the molecules are oriented parallel but without any other order.

For some bodies, there are successive passages : Crystal \rightarrow smectic state \rightarrow nematic state \rightarrow amorphous state .

The results of the experiment are reported in Table 4 and give us the above information.

Table 4 Kinetic and thermodynamic parameters of the three species

	$k (h^{-1})$	$\Delta H (Jmol^{-1}h^{-1})$	$\Delta S (Jmol^{-1}h^{-1}K^{-1})$
Ground seeds oil	1.6411 ± 0.0712	- 1355.0706 ± 0.0000	-4.1187 ± 0.0000
Sesame seeds oil	1.5540 ± 0.1404	- 1198.3569 ± 0.0000	-3.6647 ± 0.0000
Moringa seeds oil	1.2607 ± 0.0591	- -633.7856 ± 0.0000	-1.9264 ± 0.0000

As for the values of the speed constants, they are consistent with the species studied.

Their change suggests that the kinetic constant which is a measure of the ease with which the solvent extracts the oil is greater for pumpkin seed oil than for sesame seeds oil and the latter exhibits a kinetic constant greater than Moringa seeds under the same temperature and pressure conditions for a given solvent.

Thus , in a more amorphous structure and therefore more disordered , the oil extraction is easier.

4. CONCLUSION

The kinetic and thermodynamic study of the extraction of oils from pumpkin seeds, sesame seeds and Moringa seeds has shown that the extraction of oils from these seeds is an exothermic balanced phenomenon. Therefore, the energy released by this operation can be harnessed to perform mechanical or electrical work.

As for the kinetic constants, they are greater in a more amorphous body where the entropy is greater for a given temperature, pressure and solvent.

In such an amorphous body, oil extraction takes place more easily and the oil extraction speed is dependent not only on the extraction time but also on the structure of the oil generating material.

The rate constant can give indications about the structure.

5. REFERENCES

1. Kunyima A.B, Kaseya H.M, Lusamba S.N, Kunyima P.K., Matter Transfer in Liquid-solid Extraction of Democratic Republic of Congo Gourd Seeds Oils by "Kunyima Method". Chemical Science International Journal/American Chemical Science Journal. 2018; 24(4): 1-12.
2. Kunyima A.B, Kaseya H.M, Ntumba M.D and Lusamba S.N., Democratic Republic of Congo Moringa Seeds Oil Extraction: Kunyima Method Application. International Research Journal of Pure & Applied Chemistry. 2019; 18(3): 1-10
3. Kunyima A.B, Kaseya H.M, Lusamba S.N., Mulaji C.K. and Ataweza B.M., Kunyima Method Validity in Sesame Seeds Oil Extraction "Democratic Republic of Congo". Chemical Science International Journal 2021; 30(1): 11-17
4. Otto Fruhwirth G, et al. Fluorescence screening of antioxidant capacity in pumpkin seed oils and other natural oils. European Journal of Lipid Science and Technology. 90055. 2003.
5. Ryan E, et al. Phytosterol, squalene, tocopherol content and fatty acid profile of selected seeds, grains, and legumes. Plant Foods for Human Nutrition. 2007;62(3).
6. Glew RH, et al. Amino acid, mineral and fatty acid content of pumpkin seeds (*Cucurbita* spp) and *Cyperus esculentus* nuts in the Republic of Niger. Plant Foods for Human Nutrition. 2006;61(2).
7. Descazeaud A. Medical treatment of BPH. Prog Urol. 2009;19(12):890-892.
8. Rouprêta M. et al. Sexual dysfunctions linked with prostatic diseases. Prog Urol. 2012;22:S14-S20.
9. Bardon Y, et al. The prostate, a symbol of male vulnerability: A qualitative survey AUF-IPSOS. Prog Urol. 2006;16:324-327.
10. Kabele Ngiefu C. Contribution to the chemical study of oleaginous plants of the Republic of Zaire. PhD Thesis. National University of Zaire (UNAZA); 1975.
11. Rachel Poirot, et al. Fast batch to continuous solid-liquid extraction from plants in continuous industrial extractor. Chemical Engineering & Technology. 2007;30(1).
12. Mehdi Laoufi et Salah Dounit. Modeling of material transfer during a solid-liquid extraction. Annals of

Science and Technology.
2013;5(2).

13. Garnier A. Calculation of chemical reactors. Chemical Engineering Laval University; 2006.
14. Vignes JP, Trambouze PJ. Diffusion and chemical reaction in a tubular reactor in a laminar regime. Chemical Engineering Science. 1962;17(2).
15. Kolajo TE, Onilude MA. Design and construction of a low temperature chemical reactor for biomass pretreatment. International Journal of Engineering Research & Technology (IJERT). 2016;5(01).
16. Yves Cherruault. Biomathematics. 1st edition. Academic Presses of France; 1983.
17. David RH Jones, Michael F. Ashby. Engineering Materials 1 (Fifth Edition), 2019, pp. 367-379; Butterworth-Heinemann; UK.

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