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Experimental Evidence of the Dependence of Oil Extraction Rate on Extraction Time and Structure of Generative Material

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Authors' contributions

This work was carried out in collaboration among all authors. Author ABK designed and supervised the study, wrote the protocol, performed the statistical analysis of this paper, he did the references and wrote the first manuscript. Author HMK is the experimentalist of the results of this paper, preformed the statistical analysis of this paper and he is PhD student in the Laboratory of Physical Organic, Food Chemistry and Physical Cardiochemistry (LACOPA-PCC). Author PLK discussed the results of the study, managed the proof reading and correction of manuscript. All authors read and approved the final manuscript.

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ABSTRACT

Background: Kinetic and thermodynamic studies of the extraction of oils from pumpkin seeds, sesame seeds and Moringa seeds have been carried out at temperatures of 56 and 54°C. The extraction process was found to be exothermic and the kinetic constants in the three cases determined. It was also observed that the rate of extraction was dependent on extraction time and structural organization of the seeds. The kinetic constants are expected to provide information on the structural organization (crystalline, smectic, nematic or amorphous) of the seeds generating these oils. The enthalpies and entropies of extraction were calculated and a comparison of the kinetic and thermodynamic parameters obtained in the 3 cases was made.

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Aim and Objective: This work was designed to extract oils from pumpkin, sesame and Moringa seeds and to determine the kinetics and thermodynnamics of the extraction process at the given temperatures using petroleum ether as solvent.

Methodology: Ten grammes of seeds powder have been introduced in cellulose porous cartridge of 33 X 205 mm and all has been put in soxhlet extractor. In a 1000 mL thrice necked bahloon-flash fitted of a thermometer, 450 mL of petroleum ether (40°-60°c, ϱ=0,65 kg/L) have been introduced as solvent. The fitting out of soxhlet has been done on heating skull cap (mark thermo scientific) in fixing temperature at 56°C(or 54°C for sesame) in balloon flask during a given extraction time. To maintain the temperature constant during the experiment, the heating skull cap has been covered of aluminium paper as heat insulating. The ambient temperature has been kept at 22-23°C. After a given extraction time, the cartridge has been taken up to be dried in the drying oven at 50°C during 24 hours in order to get rid of traces of solvent. The oil-solvent mixture collected in the 1000 mL thrice necked balloon-flask is submitted to rotary evaporator to remove the solvent and the balloon flask with extracted oil is introduced in the drying oven at 105°C during 3 hours to eliminate totally all the traces of humidity.

After this step the balloon flask with oil is cooled in a dessicator and weighed. The difference between the balloon flask containing oil and the empty balloon flask determines the extracted oil mass at a t time in gramme.

Results: The kinetic constants, enthalpies and entropies of the extraction process of the oils from the three different seeds were calculated and compared. In all cases, the rate of oil extraction was found to be directly proportional to time of extraction and structure of the seeds.

Conclusion: The kinetic and thermodynamic study of the extraction of oils from pumpkin, sesame and Moringa seeds show that the extraction was an exothermic balanced phenomenon. The energy thus 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 extracted was much more under the same temperature and pressure conditions for a given solvent. Under these conditions, the extraction was dependent not only on time, but also on the structural organization of the material generating the oil.

Keywords: Kinetic constant; enthalpy of extraction; entropy of extraction; Kunyima method.

1. INTRODUCTION

In our previous work [1,2,3], it was shown that gourd seeds like, pumpkin, sesame and Moringa are made up of Chemical compounds. These compounds are of particular importance in the health of the populace 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) with appropriate technology that solves the timeless problem of knowledge transfer in order to produce large quantities of oil for the populace and the world at large if possible [13,14,15].

The title of this work is intuitively known by any researcher in this field. However, we have the honor to prove this by experimental evidence. In similar researches, KUNYIMA method [1,2,3] has been developed and succesfully applied to the extraction of oils from these three different seeds. These seeds are proven to have nutritional and therapeutic values. We thus recommend them to the rulers of DRC for a mechanized culture. It should be remembered that the DRC has a very rich and diverse plant heritage in a favorable climate all year round which constitutes a source of wealth creation not only for its population, but also for Africa and the entire world. This work compares the extraction speed of oils from pumpkin seeds, sesame seeds and Moringa seeds in petroleum ether at temperatures of 56°C for pumpkin and Moringa seeds, and 54°C for sesame seeds.

The kinetic constants of the extraction were calculated at these temperatures. The values were all different for the different seeds and seem to reflect the differences in the structure of the seeds. The two constants at 56°C are comparable because measured at the same temperature. The calculated constant at 54°C for sesame has been incorporated in the discussion without being afraid to distort our reasoning because it shows its evolution in the same direction and the difference of 2°C is not significant. It is evident that its value at 56°C will be a little bit different.

2. MATERIALS AND METHODS

The materials and method are same as in previous work where soxhlet extraction was used [1,2,3].

The kinetic constants calculated in our previous work were used to calculate the speed rates of extraction using the formula below.

$$x = m_e = m_0\left(1-e^{-kt}\right) \quad [1,16] \tag{1}$$

$$m_0 - m_e = \left(1-e^{-kt}\right)m_o \tag{2}$$

$$v = \frac{dx}{dt} = km_0 e^{-kt} \tag{3}$$

$$v = \frac{dx}{dt} = km_0 \frac{\left(m_0 - m_e\right)}{m_0} \tag{4}$$

$$v = \frac{dx}{dt} = k\left(m_0 - m_e\right) \tag{5}$$

where v is the extraction speed in g_r / h_r,
k is the kinetic constant or rate constant,
m_0 is the extractable mass of oil in petroleum ether (it is usually considered constant).
m_e is the extracted mass of oil at a time t expressed in hours (h_r).

To calculate enthalpy and entropy of extraction a formula similar to that of Arrhenius was used [17].

$$k = Ae^{-\frac{E}{RT}} \tag{6}$$

where $E =$ activation energy of chemical reaction and A integration constant.

But, extraction processes involves molecular interactions and not chemical reaction. Therefore, the E in Arrhenius equation can be called interaction or extraction energy. Hence, on expansion the equation becomes

$$\ln k = \ln A - \frac{E}{RT} \tag{7}$$

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

$$\ln k = \ln A - \frac{\Delta H - T\Delta S}{RT} \tag{8}$$

$$\ln k = \ln A - \frac{\Delta H}{RT} + \frac{T\Delta S}{RT} \tag{9}$$

$$\ln k = \ln A + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{10}$$

$$\ln k = B - \frac{\Delta H}{RT} \tag{11}$$

with $B = \ln A + \frac{\Delta S}{R}$

When $\ln k$ is plotted versus 1/T a straight line is obtained whose slope is -ΔH/R and the intercept is B as it can be seen in Fig. 1.

When $x = \frac{1}{T} = 0$ (T=∞) $\longrightarrow$

$$\ln k = B \tag{12}$$

When $\frac{1}{T} = \frac{RB}{\Delta H}$ $\longrightarrow$

$$\ln k = 0 \ (\ln k0 = 0) \tag{13}$$

$$slope = \frac{\ln k - \ln k0}{\frac{1}{T} - 0} = \frac{\ln k}{\frac{1}{T}} \tag{14}$$

$$\frac{\ln k}{\frac{1}{T}} = -\frac{\Delta H}{R} \tag{15}$$

$$\Delta H = -RT\ln k \tag{16}$$

That means the enthalpy of extraction is directly proportional to $\ln k$.

To each value of $\ln k$ correspond (coincide) a value of extraction enthalpy (ΔH) at a given temperature.

The reason why E is not equated to ΔG (free enthalpy or Gibbs free energy variation) has been explained under results and discussion where it is clearly demonstrated that $E = \Delta H$ and $\Delta G = 0$

Therefore the entropy variation

$$\Delta S = \frac{\Delta H}{T} = -R\ln k \tag{17}$$

The equation 7 is used to calculate the error on $E(\Delta H)$.

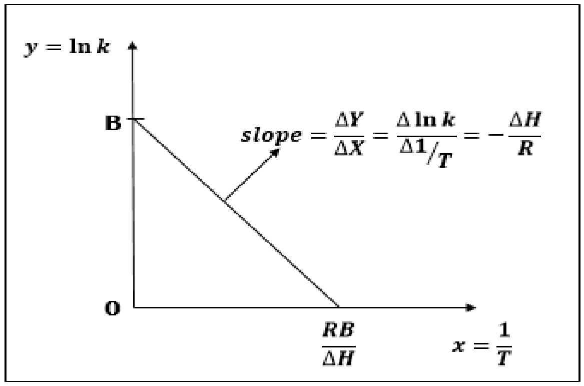

Fig. 1. $y = -\frac{\Delta H}{R} * \frac{1}{T} + B$

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

$$\frac{dk}{k} = \frac{dA}{A} = -\left[\frac{dE.RT - d(RT)E}{(RT)^2}\right] \tag{18}$$

$$\frac{dk}{k} = -\frac{RTdE}{(RT)^2} \tag{19}$$

$$\frac{dk}{k} = -\frac{dE}{RT} \tag{20}$$

$$\frac{\Delta k}{k} = -\frac{\Delta E}{RT} \tag{21}$$

$$\Delta E = \frac{RT\Delta k}{k} \tag{22}$$

It should be noted that this method helps to obtain the values of the extraction energies with 0 as an error, since the derivative of a constant (kinetic constant) is zero $\left(\frac{dk}{k}\right)$.

All the figures have been plotted by means of origin 9.2 program.

3. RESULTS AND DISCUSSION

Table 1 gives the values of the measured and calculated parameters for the extraction of oil from pumpkin seeds.

Table 1 shows the values of the rate of extraction; the corresponding time, extractable and extracted masses of pumpkin gourd seeds oil. It is observed in this table that the extraction speed decreases with the extraction time.

Table 1. The values of rate of oil extraction, time of extraction and other parameters involved in the extraction of oil from pumpkin seeds using petroleum ether as solvent

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

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

Table 2. Values of the speed and times of extraction as well as the extractable and extracted masses of oil for sesame seeds

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

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

The experimental results obtained (Table 2 and Fig. 3) are similar to those of pumpkin seeds. The decrease in rate of extraction as a time increased shows the saturation of the extracting solvent in the extracted substance.

Table 3 and Fig. 4 give the data obtained for Moringa seeds oil extraction. These values follow similar trend to those obtained previously.

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 Fig. 5.

Kinetic and thermodynamic studies were undertaken to account for the influence of structure on the extraction speed. The results show that at a given temperature and pressure, the kinetic constant depends on the nature and structural arrangement of the seeds that generate the oils. The extraction enthalpies and entropies were calculated using the Arrhenius relation:

$$k = Ae^{-\frac{E}{RT}}$$ [17]

Table 3. Values of extraction rate and the corresponding times for the extraction of Moringa seeds oil

Time (h)	m_o(*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

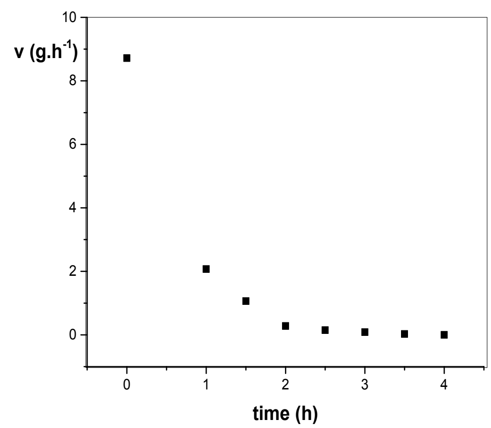

Fig. 2. Plot of extraction rate versus time for Gourd seeds oil

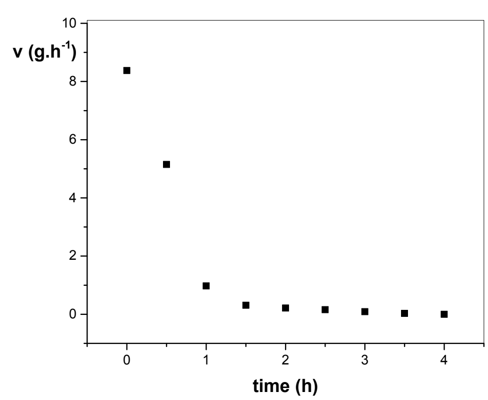

Fig. 3. Plot of sesame seeds oil extraction rate versus time

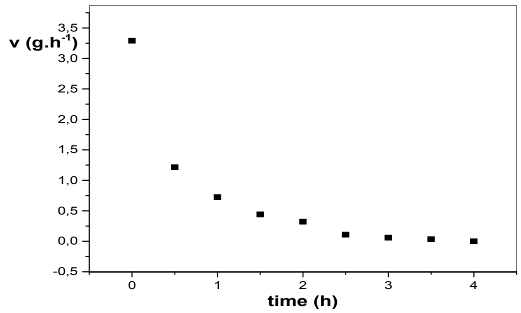

Fig. 4. Extraction rate versus time of extraction of Moringa seeds oil

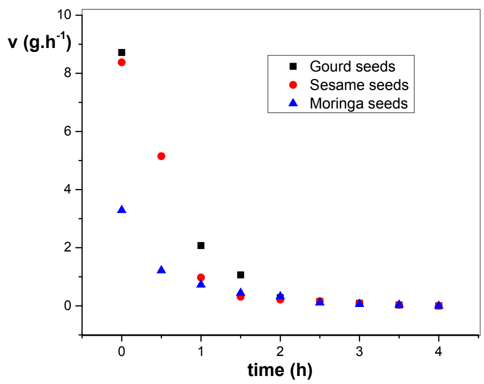

Fig. 5. Plots of rates of oil extraction versus time for the three seeds analysed

The Soxhlet extraction that we carried out constitutes an extraction operation in a closed system and in such a closed system

$$dG = -SdT + VdP \tag{23}$$

$$dH = TdS + VdP \tag{24}$$

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

The energy required for extraction is not zero as ΔG, but equal to the change in enthalpy, ΔH

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

The entropy change of the extraction is related to the enthalpy change by

$$\Delta S = \frac{\Delta H}{T} = -R \ln k \tag{25}$$

The values of change in enthalpy and entropy for the extraction of the oils from the different seeds are tabulated in Table 4. These experimental values are negative for all the seeds studied. It means that the energy released in the extraction process can be used to produce a mechanical or electrical work. However the magnitude of the energy involved in extraction, ΔH and that of agitation, ΔS, are largest for pumpkin seeds and least for moringa. The energetic situation for sesame is in between (Pumpkin → Sesame → Moringa).

The values of ΔS suggest also that the entropy is greater in pumpkin seeds than in sesame seeds where the disorder is higher than in Moringa seeds.

Indeed, in crystal, the molecules are organized. In an amorphous body, there is no organization. In melting, 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: smetic bodies where the molecules are oriented parallel and on unparallel surfaces and nematic bodies where the molecules are oriented parallel but without any other order.

Table 4. Kinetic and thermodynamic parameters obtained from the extraction of oils from the three species of seeds studied

	$k\left(h^{-1}\right)$	$\Delta H\left(Jmol^{-1}h^{-1}\right)$	$\Delta S\left(Jmol^{-1}h^{-1}K^{-1}\right)$
Grourd 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

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

As for the values of the rate 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 seeds oil than for sesame seeds oil and the latter exhibits a kinetic constant greaterthan Moringa seeds under the same temperature and pressure conditions for a given solvent.

Thus, in a more amorphous and therefore more disordered structure, 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. The oil extraction speed was also found to be dependent not only on the extraction time but also on the structure of the material generating oil. This assertion was possible through the evaluation of rate constants of the extraction process.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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