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Conservation Study of the Argan Oil by Thermogravimetry

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The arganier, typically Moroccan wood, offers innumerable services: excellent wood and coal for heating, real grazing by its foliage, excellent fodder by the pulp of fruit and source of oil by the seeds. The argan oil, to edible or cosmetic use and owing to its wealth in essential fatty acids (linoleic acid (33.15%) and oleic acid (46.65%)), is able to reduce the rate of blood cholesterol and to warning the atherosclerosis. Our work is a contribution to the determination of the characteristics of this particular oil. The studies showed that the oil preserves relatively well by resisting several months to the oxygen owing to the presence of polyphenols and tocopherols. It becomes degradable easily when it is carried to 64°C for several days.

INTRODUCTION

The argan tree is existing only in Morocco. The almond, contained in the nucleus of the fruit, serves to the preparation of argan oil. This preparation has been made by an artisanal method (crushing, pressing of almonds, extracting to the hot water). The oil is brown in colour and has the taste of hazelnut. The extraction from the almond, by means of organic solvent (hexane), gives a flat and limpid oil (without particular taste)[1, 2].

Argan oil takes part in the resorption of the deficit of Morocco in fat matters. Concerning sources of Moroccan origin, one can note beside an important production of olive oil, we produce sunflower oil, rape, corn and argan oil. Its production being strictly family, one cannot evaluate it quantitatively. One can recognize to argan oil in many cosmetic virtues, pharmaceutical and food.

The main characteristics of this oil have been determined by method AFNOR and UICPA[2] that have put in obviousness the fat acid presence, the glyceridic structure and the insaponifiable. Argan oil has not been studied since the last two decades, but wealth of essential fat acids: oleic acid [C18 : 1] (46.65%) and linoleic acid [C18 : 2] (33.15%), and its capability to reduce the sanguine cholesterol rate and thus give a warning of atherosclerosis[3] have made it a subject of interest.

In the present work, we have approached the study of the thermal stability of oil in function of the time of aging and the temperature. Techniques used are: thermogravimetric analysis[4] (variation of mass loss according to the temperature) and infrared spectroscopy. These techniques have been used to study the reactivity of argan oil in function of temperature and time of aging parameters.

EXPERIMENTAL

Influence of the aging time: In this work we have used a thermobalance of sensitivity (40×10^{-6} g) to detect the mass loss, by pyrolysis, of 5 mg of argan oil. The degradation is realized in dynamic regime, from ambient until 600°C, under an atmosphere of nitrogen at a rate of 16 cm^3/min with a heat rate of 10°C/min. Fig. 1 represents variations of the mass loss (%) according to the temperature where m_0 and m(t) are the initial mass of the sample and at temperature t respectively.

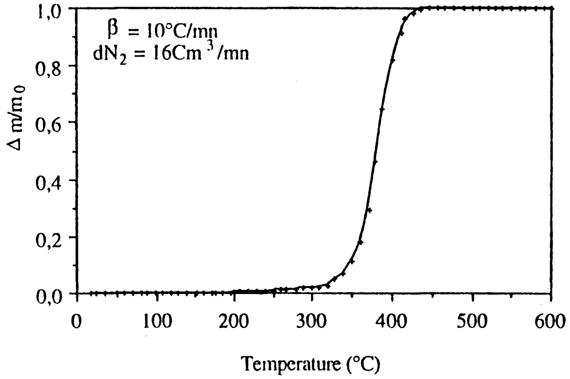

Fig. 1. Thermal degradation (%) of argan oil

According to this thermogram, the degradation of argan oil in volatile products started at 250°C and ended at 420°C. It concerns a stable oil without humidity and without residue; its decomposition becomes rapid only when its temperature exceeds 350°C. We have sought to know its reactivity after having preserved it, during variable duration, at the ambient temperature or at 64°C.

The present study of the aging has focused on a quantity of argan oil that has been left in a bottle (glass) during some times at the ambient temperature or at 64°C. In this study one takes account of the time of stay of the sample in mentioned conditions to the moment of its pyrolysis. In Fig. 2 we have represented the degradation of oil preserved during several days or several months. The superposition of the thermogravimetric curves indicates that the conservation of

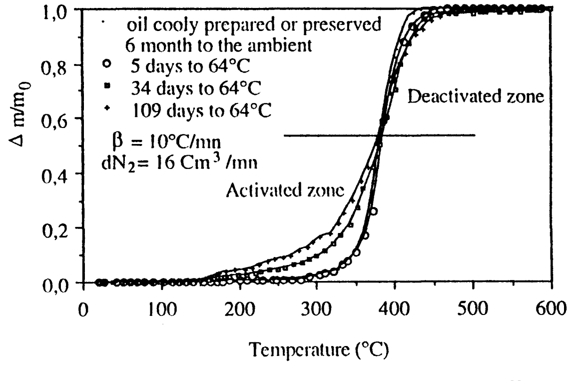

Fig. 2. Mass loss (%) by pyrolysis of argan oil conserved in different manners

oil to the ambient does not modify its reactivity; on the other hand, when it is carried to 64°C during an enough long duration, it becomes easily to debase. According to Charrouf and Guillaume[5], this resistance of argan oil to the oxygen of the air is due to the presence of β, γ, δ tocopherol and polyphenols. But according to the present study (Fig. 2), the pyrolysis of an argan oil, aged to 64°C, during more of 5 days, observes that oil in question presents two type transformations: with the time of aging, the first ($0 < \Delta m/m_0 < 56\%$) is accelerated and second ($56 < \Delta m/m_0 < 100\%$) is delayed. The two phenomenon succeeding and evolving in opposed senses in the explored interval of 5–109 days.

Influence of the heat rate: We know that this oil, according to the utilization, can be heated to different temperatures. Where the interest to study its reactivity by pyrolysis, according to the heat rate.

The heat rate as one factor is most important of the dynamic thermogravimetry. So as to determine the influence of the factor on pyrolysis of argan oil, a series of experiments, led on 5 mg of argan oil, has been realized to $\beta = 5$; 10; 15 and 25°C/min, under a nitrogen atmosphere of 16 cm^3/min. The TG thermograms obtained (Fig. 3), representing the mass loss according to the temperature, are similar for all heat rate and place in an order increasingly accelerated. The rate of degradation depends therefore on the heat rate and consequently the pyrolysis is an activated phenomenon.

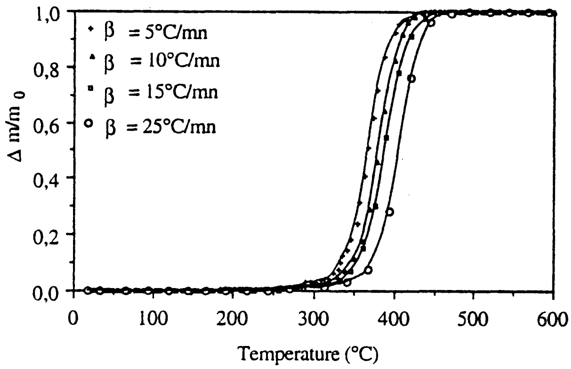

Fig. 3. Weight loss (%), by pyrolysis, of argan oil following the heat rate

Taking account of preceding results, the kinetic study of degradation of argan oil in dynamic regime, can be led is on an oil prepared by pressure to cold of almonds or on a commercial oil. To determine the kinetic of pyrolysis we have sought to determine until what degrees of mass loss ($\Delta m/m_0$) this reaction preserves the same mechanism when the heat rate changes. By representing mass loss in a mark some coordinated reduce (Fig. 4), all losses become independent the heat rate, a "same kinetic regime" covers therefore the totality of the transformation. Consequently, according to Delmon[6], we can apply kinetic studies to all the pyrolysis reaction some is the heat rate employee.

In the kinetic study on dynamic regime of solid/gas systems, several mathematic models can be applied[6–8] to determine the activation energy and the frequency factor.

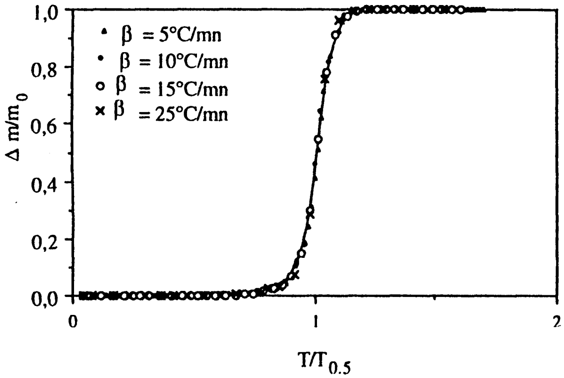

Fig. 4. Argan oil thermograms pyrolysis represented in a mark some coordinated reduce

Experimental data of instantaneous rates for each heat rate (Fig. 5) suggest that argan oil behaves thermically as if it was formed an alone product.

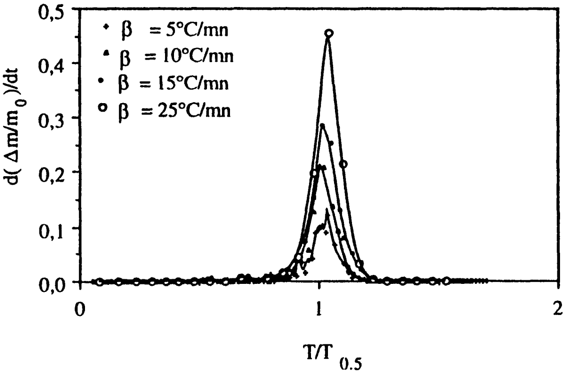

Fig. 5. Instantaneous rate pyrolysis of argan oil according to $T/T_{0.5}$ to different rate heats

The maximum rate [v_{max} (%/min)] of argan oil pyrolysis and its corresponding temperature evolve according to the heat rate, on the other hand the corresponding mass loss (%) remains practically constant and equal to 51% (Table-1).

TABLE-1

VARIATION OF THE INSTANTANEOUS v_{max} PYROLYSIS OF ARGAN OIL AND ITS CORRESPONDING TEMPERATURE ACCORDING TO THE HEAT RATE

Heat rate (β) (°C/min)	5	10	15	25
v_{max} (%/min)	12.3	21	28.5	46
Tv_{max} (°C)	368	380	388	405

We can use a simple expression as an instantaneous degradation rate:

$$\frac{d}{dt}\frac{\Delta m}{m_0} = Kf\left(\frac{\Delta m}{m_0}\right)$$

where K represents the rate constant, according to Arrhénius, and $f\left(\frac{\Delta m}{m_0}\right)$ the law of transformation[9].

For a given mass loss $\left(\frac{\Delta m}{m_0}\right)$, the function $f\left(\frac{\Delta m}{m_0}\right)$ checks the same value (Fig. 4).

One can write: $$v_{max} = \frac{d}{dt}\frac{\Delta m}{m_0} = Kf\left(\frac{\Delta m}{m_0}\right) \qquad (1)$$

With $$K = K_0\, e^{-E/RT}$$

To one $\frac{\Delta m}{m_0} = 65\%$ has $f\left(\frac{\Delta m}{m_0}\right) = A = 1{,}059$; then:

$$v_{max} = K_0\, e^{-E/RT} \qquad (2)$$

In a logarithm basis, the representation of the equation (2) leads to:

$$\log v_{max} = \log K_0A - E/RT \qquad (3)$$

The right, representing the function (3) (Fig. 6), allows to determine activation energy and the product K_0A.

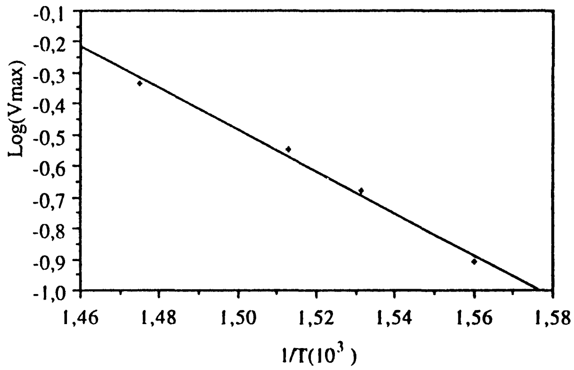

Fig. 6. Representation of v_{max} of argan oil pyrolysis of function its temperature in the mark [log v_{max} = f(1/T)].

In the area of $\beta = 5$; 10; 15 and 25°C/min, the activation energy is E = 30.80 kcal/mol. To determine the factor of frequency K_0, Fig. 6 gives $\log K_0T_0 = 9.559$. A polynomial function of 4th degree represents suitably $f(\Delta m/m_0)$ and whose value, for $\Delta m/m_0 = 51\%$, costs to A = 1.059, then $K_0 = 3.62 \times 10^9\ \text{min}^{-1}$.

Infrared Spectrometric Studies

To link the kinetic study to the chemical transformation of oil, we have followed its pyrolysis by spectroscopic analysis. This spectral study has been led on sample before hand in a thermobalance by means of dynamic experiments until a given temperature which equally corresponds a rate of given transformation (Table-2). Samples (A, B, C, D, E) are then returned to the ambient temperature and analyzed by FTIR. The result shows that the initial product contains carboxylic acid functions, alkanes, aldehydes, alcohols and phenols. As the pyrolysis temperature increases, on the one hand the relative intensity of some functions decreases then disappears, on the other hand new functions appear. To make a quantitative function analysis from FTIR, samples have been pyrolysed at fixed temperatures and then analyzed by FTIR to 25°C. Equally we suggest that in spectroscopic analysis, the concentration of the chemical function is linked to the width of the m_i-height of a well solved peak; moreover the virgin oil composition have been given by several authors since 1972 (Table-3) where acids oleic and linoleic are in excess. These compounds, with 18 atoms of carbon, represent 46.65 and 33.15% with one and two double connections (C=C) respectively.

TABLE-2
EVOLUTION OF (%) OF MASS LOSS OF ARGAN OIL ACCORDING TO THE TEMPERATURE

T(°C)	300	320	340	360	380
$\Delta m/m_0$ (%)	2	2,6	8	16	48
N° sample	A	B	C	D	E

TABLE-3
FATTY ACID COMPOSITION OF ARGAN OIL TRIGLYCERIDES (%)

Acid	Traditionally extracted oil[a]	Solvent extracted oil[b]
Myristic	0, 2	0–0.2
Pentadecanoic	–	0–0.1
Palmitic	11.7–14.3	13.5–13.9
Palmitoleic	–	0–0.2
Heptadecanoic	–	0–0.1
Stearic	5–5.9	5.6
Oleic	46.4–48.1	45.2–46.9
Linoleic	31.5–34.9	31.6–34.6
Linolenic	0–0.6	0–0.1
Nonadecenoic	–	0–0.1
Arachidic	–	0–0.4
Gadoleic	–	0–0.5
Behenic	–	0–0.1

[a] From Berrada (1972), Huyghebaert et Hendrick (1974), Belcadi (1994)
[b] From Charrouf (1984), Farines *et al.* (1984a).

During pyrolysis, the molecular chains of this oil can be saturated, fragmented, cyclized, polymerized, . . . etc. Indeed, the analysis of widths to m_i-height of FTIR peaks relative to alkane and alkene functions evolve in opposed senses on the interval 340–360°C, where the disappearance of the alkane functions is accompanied by the training of the alkene functions. Since (A, B, C, D, E) samples having served to the FTIR analysis have been prepared in 340–360°C area, we can conclude that kinetics of oil pyrolysis of argan is globally controlled by the transformation:

$$C—C \longrightarrow C{=}C$$

Conclusion

The thermogravimetric analysis showed that argan oil preserves several months at the ambient temperature without being altered, due to the presence of the β, γ, δ tocopherol, the composition weak in fat acetylenic acidic (0.1%) and the polyphenols. The oil decomposition becomes more significant when it is carried to 64°C. In this case the thermogravimetric curves present an accelerated phase $(0 < \frac{\Delta m}{m_0} < 56\%)$ and a slowed phase $(56 < \frac{\Delta m}{m_0} < 100\%)$. Moreover the virgin or preserved argan oil pyrolysis kinetics is controlled by the saturation phenomenon ($C—C \longrightarrow C{=}C$). These results are confirmed by spectroscopic analysis (FTIR) relative to alkane and alkene functions.

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