AGRO-INDUSTRIAL WASTES:

D ETICS

Navas C.[a], (eboredo María[b]

[a] Instituto de I acultad de Ingeniería, Universidad N San Juan, Argentina.

[b] Instituto de I encia y Tecnología de Materiales, (CON del Plata, Buenos Aires, Argentina.

Agro-industrial waste

Olive wet husk OWH

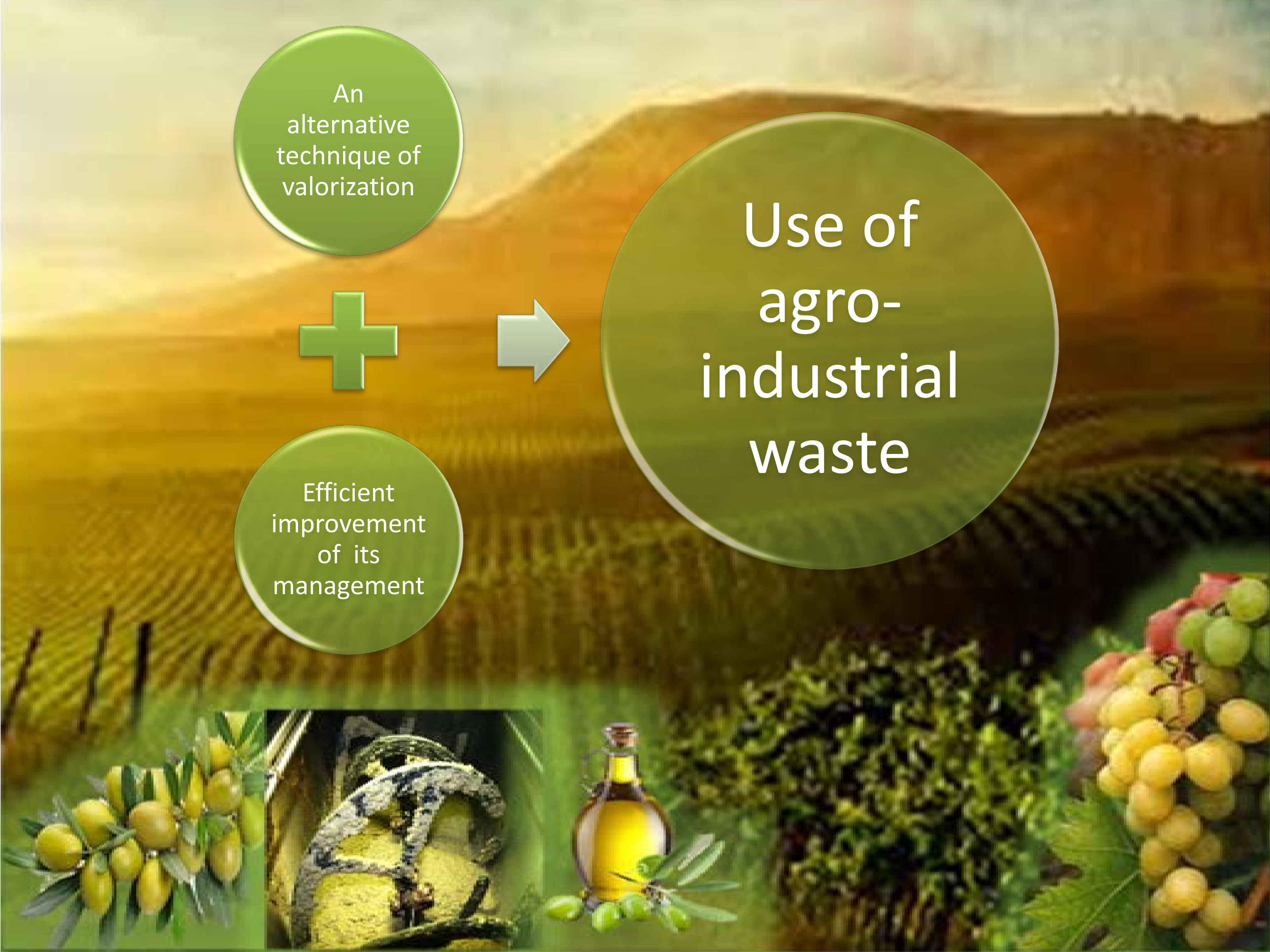
- Constitutes more than 80% of the olives consumed in the production of oil
- Material slightly porous, plastic and susceptible to compression

Olive pits OP

- They are used as combustion energy source
- They are also used to produce activated carbon and other chemicals at laboratory scale

Grape Stalks GS

- Represent between 2.5 and 5.5% of the mature grape bunch
- It is chemically composed of tissues experiencing a process of lignification along the progress of maturation


An alternative technique of valorization
Efficient improvement of its management
Use of agro-industrial waste

OBJECTIVE

To study the temperature effect on the drying kinetics of the materials as a previous conditioning stage before incorporating the particles into a polymeric matrix.

The drying of these wastes before the processing of the composite is an important factor because the water in the particle surface acts a separating agent in the particle-matrix interface.

MATERIALS AND METHODS

The olive wet husk from the manufacture of olive oil was provided by the company Frávega, Pocito

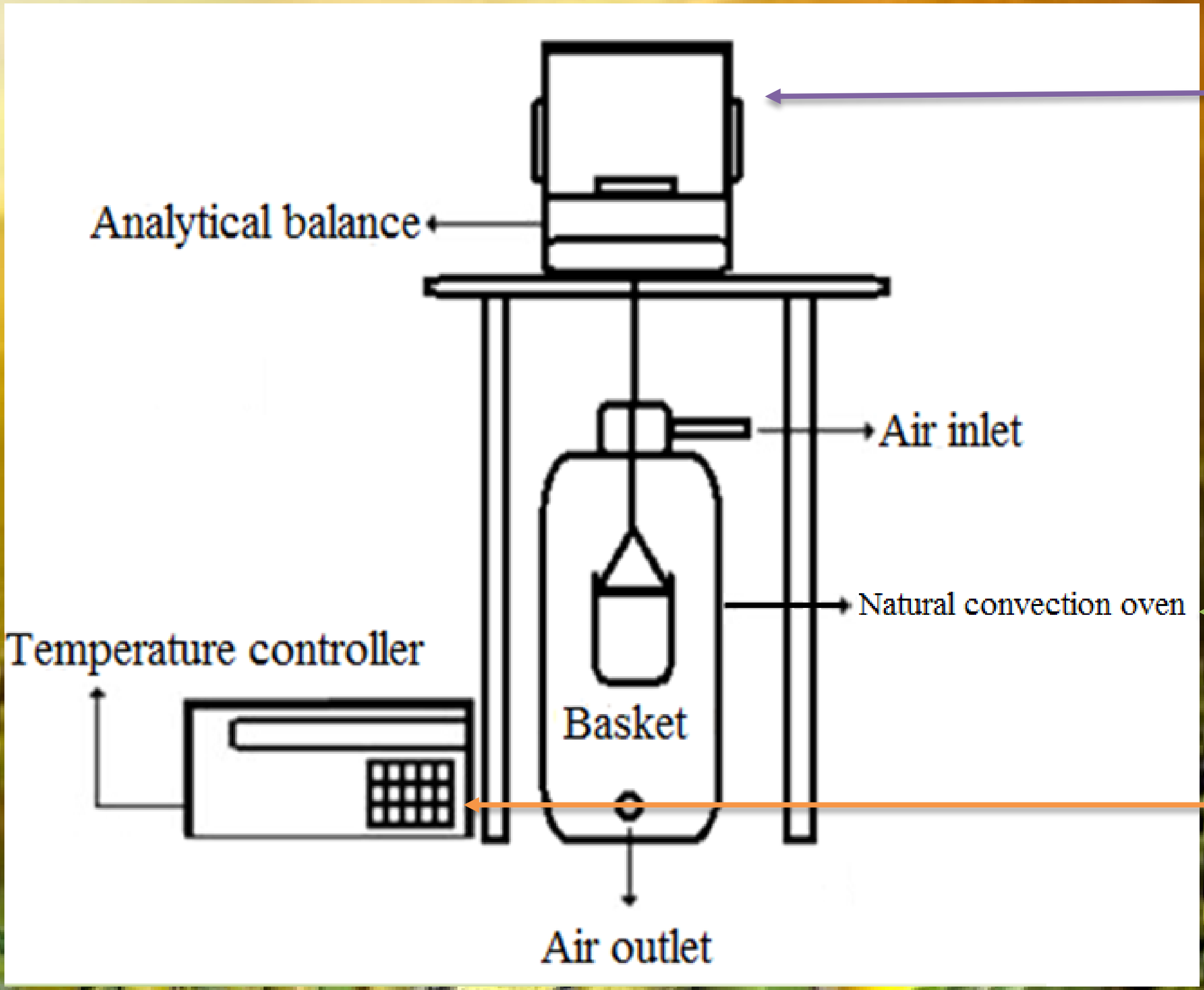
The OWH was used as a slurry, such as received, with a moisture content of 70%.

The grape stalks were provided by Bodegas Graffigna, San Juan.

The olive pits from the manufacture of olive oil and canned olives, were provided by the company Frávega, Pocito.

The fresh wastes employed were kept in cooler until use.

Drying equipment



CONVECTION DRYING

moisture removing process by simultaneous transfer	• Heat • Mass
by means of evaporation between	• The product • The drying air
caused by	• Temperature difference • Velocity of the convective air

Drying

$$M_R = \frac{M - M_e}{M_0 - M_e}$$

Test condition

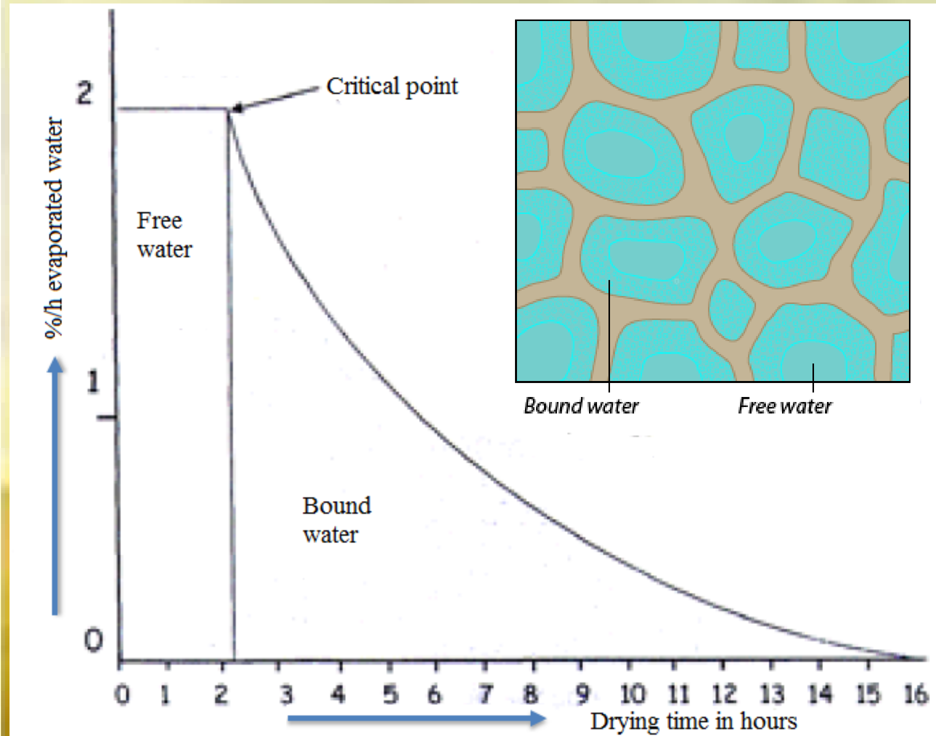
- 3 different temperatures: 60, 80 and 100 °C.
- At higher temperatures protein denaturation processes may occur
- Case of OWH a superficial darkness

Bed height in basket and the corresponding weights

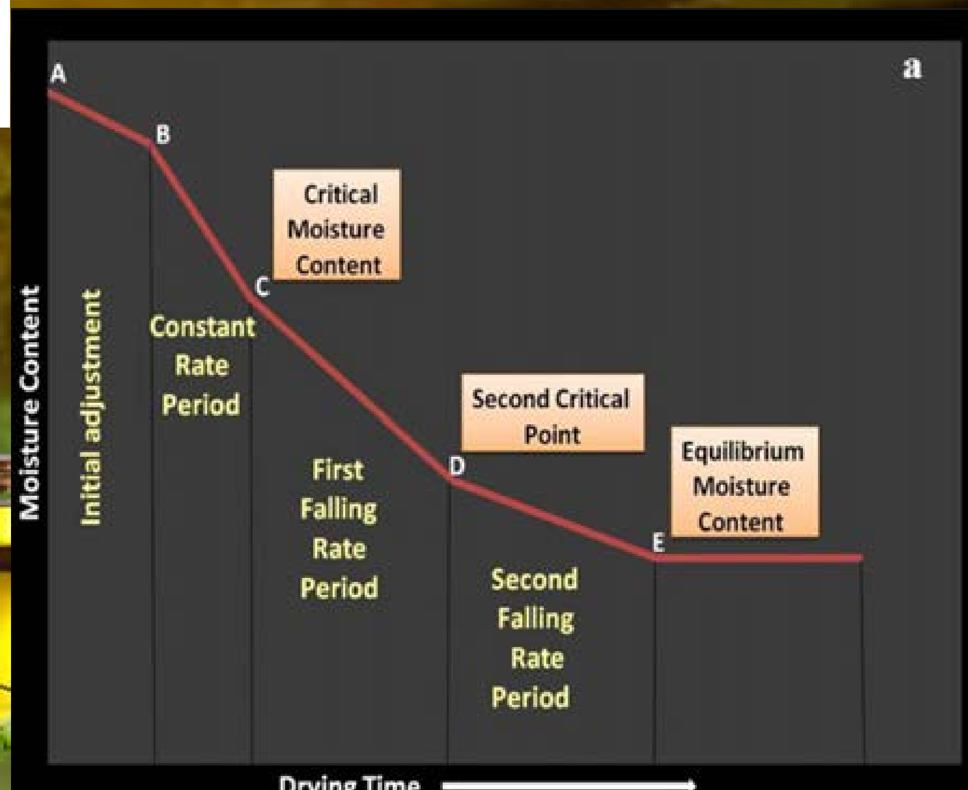
- OWH 2 cm; 20g
- OP 7cm; 55g and GS 7cm; 29g

Moisture loss at different time intervals

- 1 min for the first 180 min
- 2 min for the following 120 min
- 4 min until reaching Me



$$D_R = \frac{M_1 - M_2}{t_2 - t_1}$$



Mathematical modeling

Drying kinetics described with 3 types of models :

- Theoretical models are based on the process of diffusion (Fick's second law) or simultaneous equations of heat and mass transfer
- The semi-theoretical models are derived from general simplifications of Fick's second law solution
- Empirical models fitting all drying data well, but neglect the basics of the process

M_R

- Lewis or Exponential model $M_R = \exp(-kt)$
- Henderson and Pabis model $MR = \text{a} \exp(-kt)$
- Page model $M_R = \exp(-kt^N)$
- Two-term exponential model $M_R = a_1 \exp(-k_1 t) + a_2 \exp(-k_2 t)$
- Logarithmic $M_R = \text{a} \exp(-kt) + c$
- Approximation of diffusion model $M_R \text{ a} \exp(-kt) + (1 - \text{a}) \exp(-kbt)$

Determination of the effective diffusivity

Fick's second law of diffusion

$$\frac{dMR}{dt} = D_{eff}\frac{d^2MR}{dx^2}$$

When the internal mass transfer is the controlling mechanism and the one-dimensional transport in an infinite plate is assumed

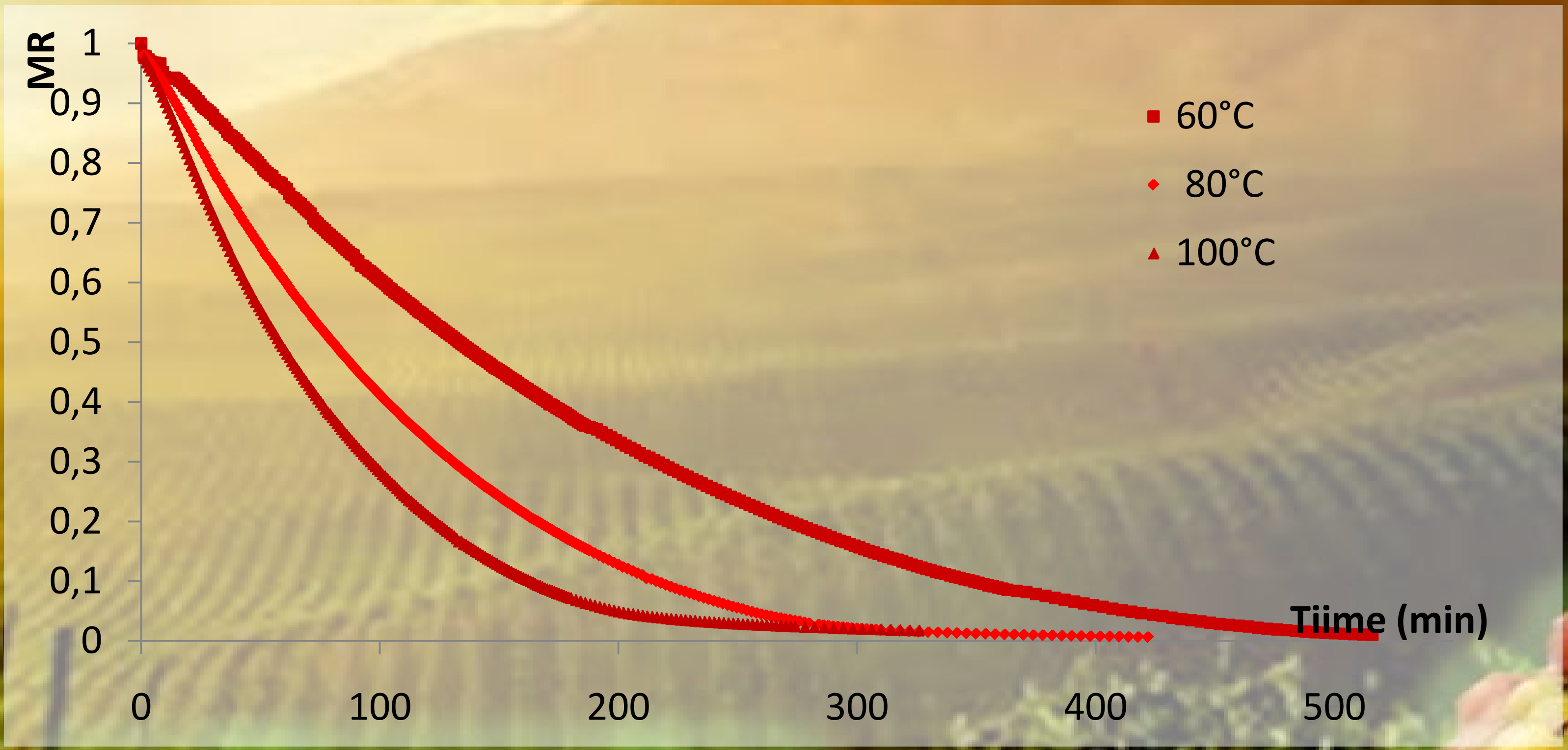
$$M_R = \frac{8}{\pi^2}\sum_{i=0}^{\infty}\frac{1}{(2i+1)^2}exp\left[\frac{-(2i+1)^2 D_{eff}\pi^2 t}{4L^2}\right]$$

Considering only the first term

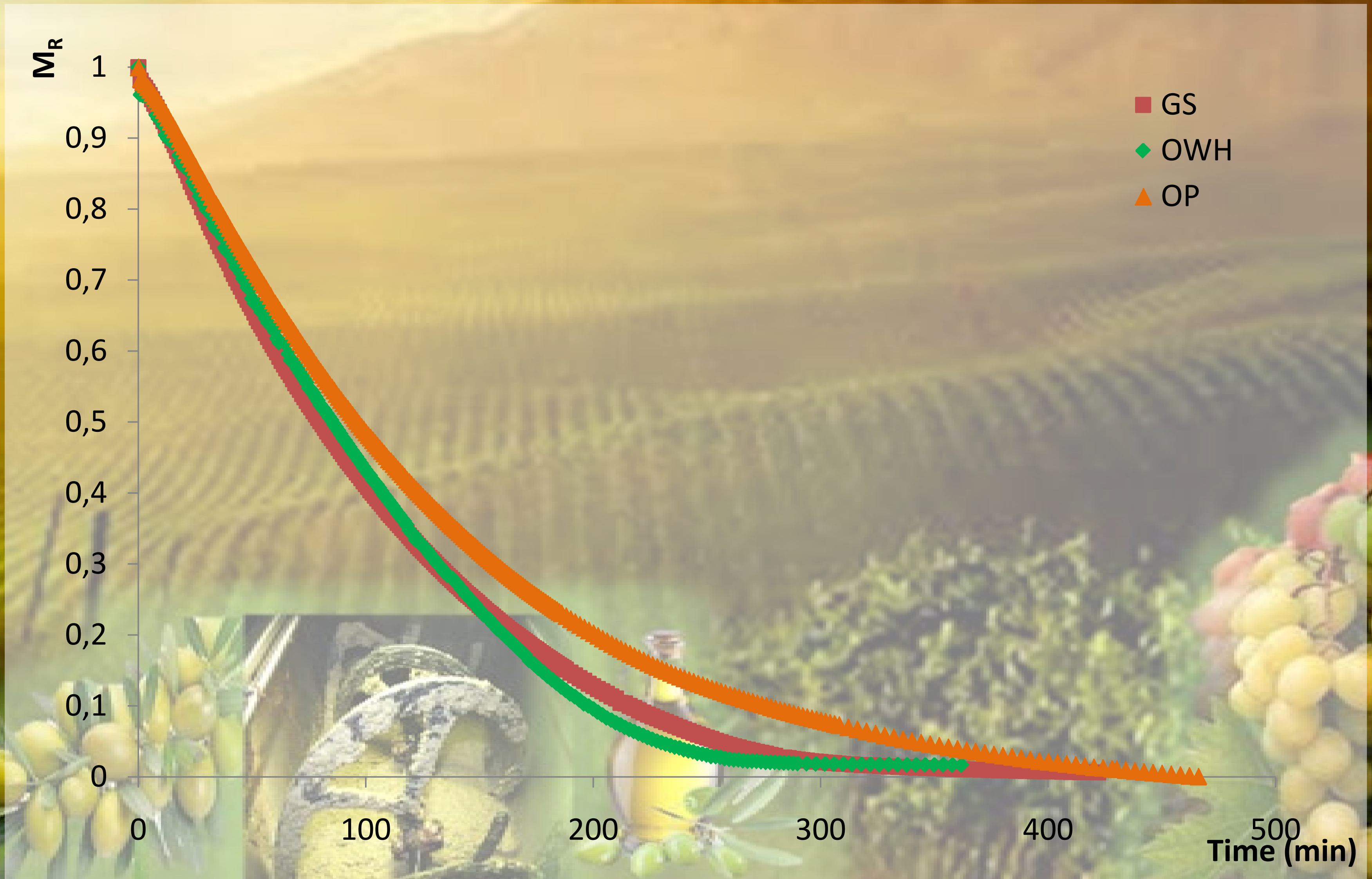
$$M_R = \frac{8}{\pi^2}exp\left[\frac{-D_{eff}\pi^2 t}{4L^2}\right]$$


RESULTS AND DISCUSSION

Experimental moisture ratio as a function of drying time for different temperatures GS



Experimental moisture ratio as a function of drying time for different materials for 80°C



Material	Air drying tem. (°C)	Me	Me average
Olive pits	60	35,40	34,36
	80	34,01	
	100	33,67	

Material	Air drying tem. (°C)	Me	Me average
Grape Stalk	60	13,81	13,26
	80	13,43	
	100	12,53	

Material	Air drying tem. (°C)	Me	Me average
Olive wet husk	60	7,22	6,85
	80	6,51	
	100	6,81	

Drying rate curves at different temperatures for GS

T (°C)	Model	Grape Stalk						Olive wet husk					
		Constants		R^2	$\chi 2$	E_{RMS}	$E_{MD\ (\%)}$	Constants		R^2	$\chi 2$	E_{RMS}	$E_{MD\ (\%)}$
60	**Lewis** **M_R = exp (-kt)**	K:	0,0055	0,9885	9,68E-04	3,11E-02	31,40	K:	0,0053	0,9734	2,29E-03	4,78E-02	77,75
	Henderson y Pabis **M_R = a exp(-kt)**	a:	1,053	0,9928	6,11E-04	2,46E-02	25,52	a:	0,0058	0,9820	1,55E-03	3,93E-02	65,15
		K:	0,0059					K:	0,0058				
	Page **M_R = exp(-kt^N)**	K:	0,0021	0,9988	1,04E-04	1,02E-02	11,47	K:	0,0012	0,9960	3,42E-04	1,84E-02	31,40
		N:	1,187					N:	1,295				
	Two-term exponential **M_R = a1 exp (-k1t) + a2 exp(-k2t)**	a1:	0,527	0,9927	6,15E-04	2,46E-02	25,52	a1:	0,3345	0,9820	1,56E-03	3,93E-02	65,17
		K1:	0,0059					K1:	0,0058				
		a2:	0,527					a2:	0,7398				
		K2:	0,0059					K2:	0,0058				
	Logarithmic **M_R = a exp(-kt) +c**	a:	1,145	0,9991	7,47E-05	8,60E-03	8,10	a:	1,32	0,9988	9,94E-05	9,92E-03	22,67
		K:	0,0046					K:	0,0036				
		c:	-0,1242					c:	-0,3				
	Diffusional approach **MR =a exp(-kt) + (1-a) exp(-kbt)**	a:	0,00024	0,9884	-2,75E-01	3,11E-02	0,10	a:	5,10E+00	0,9984	6,64E-02	2,56E-01	76,83
		K:	0,0056					K:	0,0086				
		b:	0,9868					b:	0,9123				

T (°C)	Grape Stalk							Olive wet husk						
	Model	Constants		R^2	$\chi2$	E_{RMS}	$E_{MD\ (\%)}$	Constants		R^2	$\chi2$	E_{RMS}	$E_{MD\ (\%)}$
80	**Lewis** **M_R = exp (-kt)**	K:	0,009262	0,9910	7,30E-04	2,70E-02	32,43	K:	0,0091	0,9791	1,96E-03	4,42E-02	61,50
	Henderson y Pabis **M_R = a exp(-kt)**	a:	1,051	0,9942	4,71E-04	2,16E-02	26,58	a:	1,065	0,9841	1,49E-03	3,84E-02	51,251
		K:	0,009778					K:	0,0098				
	Page **M_R = exp(-kt^N)**	K:	0,004268	0,9987	1,02E-04	1,01E-02	12,69	K:	0,0025	0,9959	3,86E-04	1,96E-02	19,656
		N:	1,163					N:	1,27				
	Two-term exponential **M_R = a1 exp (-k1t) + a2 exp(-k2t)**	a1:	0,5254	0,9941	4,75E-04	2,16E-02	26,64	a1:	0,5321	0,9839	1,50E-03	3,84E-02	51,43
		K1:	0,009775					K1:	0,0098				
		a2:	0,5254					a2:	0,5321				
		K2:	0,009771					K2:	0,0098				
	Logarithmic **M_R = a exp(-kt) +c**	a:	1,108	0,9992	6,10E-05	7,76E-03	9,80	a:	1,153	0,9944	5,26E-04	2,28E-02	33,30
		K:	0,008026					K:	7,51E-03				
		c:	-0,0867					c:	-0,1257				
	Diffusional approach **MR =a exp(-kt) + (1-a) exp(-kbt)**	a:	0,01364	0,9909	-2,90E-01	1,19E+01	0,07	a:	0,1842	0,9789	-5,61E-01	4,42E-02	0,20
		K:	0,009262					K:	0,0091				
		b:	1					b:	1				

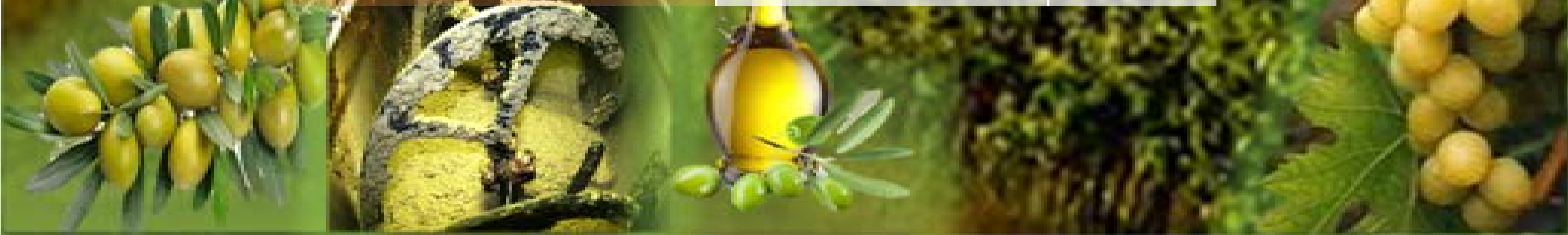
T (°C)		Grape stalk						Olive wet husk					
	Model	Constants		R^2	$\chi2$	E_{RMS}	$E_{MD (\%)}$	Constants		R^2	$\chi2$	E_{RMS}	$E_{MD (\%)}$
100	**Lewis** **M_R = exp (-kt)**	K:	0,01269	0,9949	4,01E-04	2,00E-02	16,35	K:	0,01149	0,9756	2,32E-03	4,80E-02	104,22
	Henderson y Pabis **M_R = a exp(-kt)**	a:	1,045	0,9969	2,41E-04	1,55E-02	12,34	a:	1,089	0,9834	1,58E-03	3,95E-02	0,16
		K:	0,01327					K:	0,01256				
	Page **M_R = exp(-kt^N)**	K:	0,007152	0,9995	4,11E-05	6,39E-03	7,10	K:	0,002672	0,996	3,42E-04	1,84E-02	30,57
		N:	1,127					N:	1,321				
	Two-term exponential **M_R = a1 exp (-k1t) + a2 exp(-k2t)**	a1:	0,3304	0,9969	1,59E-04	1,55E-02	12,33	a1:	0,591191	0,9835	1,59E-03	3,95E-02	83,12
		K1:	0,01327					K1:	0,012557				
		a2:	0,7142					a2:	0,497831				
		K2:	0,01327					K2:	0,012557				
	Logarithmic **M_R = a exp(-kt) +c**	a:	1,059	0,9982	1,39E-04	1,17E-02	14,71	a:	1,144	0,9917	7,90E-04	2,79E-02	69,48
		K:	0,01225					K:	0,0103				
		c:	-0,0295					c:	-0,0872				
	Diffusional approach **MR =a exp(-kt) + (1-a) exp(-kbt)**	a:	5,096	0,9984	1,29E-04	1,13E-02	15,06	a:	0,85559264	0,9756	2,34E-03	4,80E-02	104,16
		K:	0,008651					K:	0,0114922				
		b:	0,9123					b:	1,00000321				

Material	Olive Pits											
T (°C)	60						80					
Model	Constants		R^2	$\chi 2$	E_{RMS}	$E_{MD\ (\%)}$	Constants		R^2	$\chi 2$	E_{RMS}	$E_{MD\ (\%)}$
Lewis M_R = exp (-kt)	K:	0,004747	0,9896	4,62E-04	2,15E-02	25,42	K:	0,007527	0,994	4,98E-04	2,23E-02	46,92
Henderson y Pabis M_R = a exp(-kt)	a:	1,068	0,9961	1,84E-04	1,35E-02	0,02	a:	1,049	0,9970	2,52E-04	1,58E-02	37,875
	K:	0,005174					K:	0,007952				
Page M_R = exp(-kt^N)	K:	0,001707	0,9999	9,12E-06	3,01E-03	4,23	K:	0,003747	0,9998	1,43E-05	3,77E-03	16,893
	N:	1,196					N:	1,143				
Two-term exponential M_R = a1 exp (-k1t) + a2 exp(-k2t)	a1:	0,5336	0,9960	1,86E-04	1,36E-02	17,55	a1:	0,5191	0,9969	2,53E-04	1,58E-02	37,91
	K1:	0,005171					K1:	0,00795				
	a2:	0,5336					a2:	0,5291				
	K2:	0,005172					K2:	0,007948				
Logarithmic M_R = a exp(-kt) +c	a:	1,111	0,9986	4,08E-05	6,36E-03	6,28	a:	1,08	0,9991	7,46E-05	8,59E-03	15,47
	K:	0,004526					K:	0,007087				
	c:	-0,06268					c:	-0,04962				
Diffusional approach M_R =a exp(-kt) + (1-a) exp(-kbt)	a:	1	0,9896	4,65E-04	2,15E-02	25,42	a:	0,8519	0,9939	5,02E-04	2,23E-02	46,91
	K:	0,004747					K:	0,007548				
	b:	1					b:	0,9819				

T (°C)	Modelo	Olive pits					
		Constants		R^2	$\chi 2$	E_{RMS}	$E_{MD\ (\%)}$
100	**Lewis** M_R = exp (-kt)	K:	0,01014	0,9948	4,32E-04	2,08E-02	14,73
	Henderson y Pabis M_R = a exp(-kt)	a:	1,056	0,9978	1,67E-04	1,29E-02	8,71
		K:	0,01103599				
	Page M_R = exp(-kt^N)	K:	0,005215	0,9999	8,47E-06	2,90E-03	7,24
		N:	1,142				
	Two-term exponential M_R = a1 exp (-k1t) + a2 exp(-k2t)	a1:	0,4990333	0,9989	1,68E-04	1,29E-02	8,71
		K1:	0,01075024				
		a2:	0,55690772				
		K2:	0,01075023				
	Logarithmic M_R = a exp(-kt) +c	a:	1,064	0,9984	1,26E-04	1,12E-02	18,76
		K:	0,01028				
		c:	-0,01669				
	Diffusional approach M_R =a exp(-kt) + (1-a) exp(-kbt)	a:	0,02467	0,9947	7,63E-04	2,75E-02	13,86
		K:	1				
		b:	0,01014				

Coefficient values for effective diffusivity for different drying air temperature

Material	Temperature (°C)	D_{eff}
Grape stalks	60	5,004E-06
	80	5,029E-06
	100	5,036E-06
Olive wet husk	60	4,090E-07
	80	4,109E-07
	100	4,126E-07
Olive pits	60	4,996E-06
	80	5,016E-06
	100	5,020E-06



Effective diffusivity values of several wastes in different drying conditions

Material	Effective diffusivity (m2/s)	Drying conditions
Grape stalks	$5{,}00 \times 10^{-6}$ – $5{,}04 \times 10^{-6}$	Convective drying (60-100°C)
Olive wet husk	$4{,}09 \times 10^{-7}$ – $4{,}13 \times 10^{-7}$	Convective drying (60-100°C)
Olive pits	$4{,}99 \times 10^{-6}$ – $5{,}02 \times 10^{-6}$	Convective drying (60-100°C)
Olive pomace	$1{,}84 \times 10^{-7}$ – $3{,}94 \times 10^{-7}$	Convective drying (1,5m/s, 60-80°C)
Olive pomace	$0{,}68 \times 10^{-7}$ – $2{,}15 \times 10^{-7}$	Fluidized bed dryer (1 m/s,50-80°C)
Olive pits of olive wet husk	$3{,}98 \times 10^{-9}$ – $5{,}97 \times 10^{-8}$	Drying tunnel (1 m/s, 100 - 250°C)
Olive pits of olive pomace	$1{,}17 \times 10^{-7}$ – $2{,}92 \times 10^{-7}$	Convective drying (50 - 150°C, 0,683 m/s)
Grape pomace	$11{,}01 \times 10^{-9}$ – $26{,}05 \times 10^{-9}$	Infrared dryer (100 - 160°C)
Seed grape	$5{,}39 \times 10^{-10}$ – $2{,}09 \times 10^{-11}$	Infrared dryer (50 - 80°C)
Poplar sawdust	$9{,}38 \times 10^{-10}$ – $1{,}38 \times 10^{-9}$	Thermogravimetric method (60-90°C)

CONCLUSIONS

- Drying of different agro-wastes (GS, OWH and OP) was studied. The results indicated that the moisture transferred during drying is controlled mainly by internal diffusion. Page and Logarithmic models showed the best fit at different temperatures and for different materials. The difference in regression coefficients between the two models is very small, so considering its simplicity, Page model can be chosen for all cases.

- D_{eff} and D_R increased both with the increasing of drying temperature, and consequently the drying time decreased. The D_{eff} values were around 5.10^{-6} m^2s^{-1} for GS, $4,09.10^{-7}$ m^2s^{-1} for OWH and $5,02.10^{-6}$ m^2s^{-1} for OP. This suggests that the water diffusion phenomena into the material are significant and depend on the internal structure of the material.

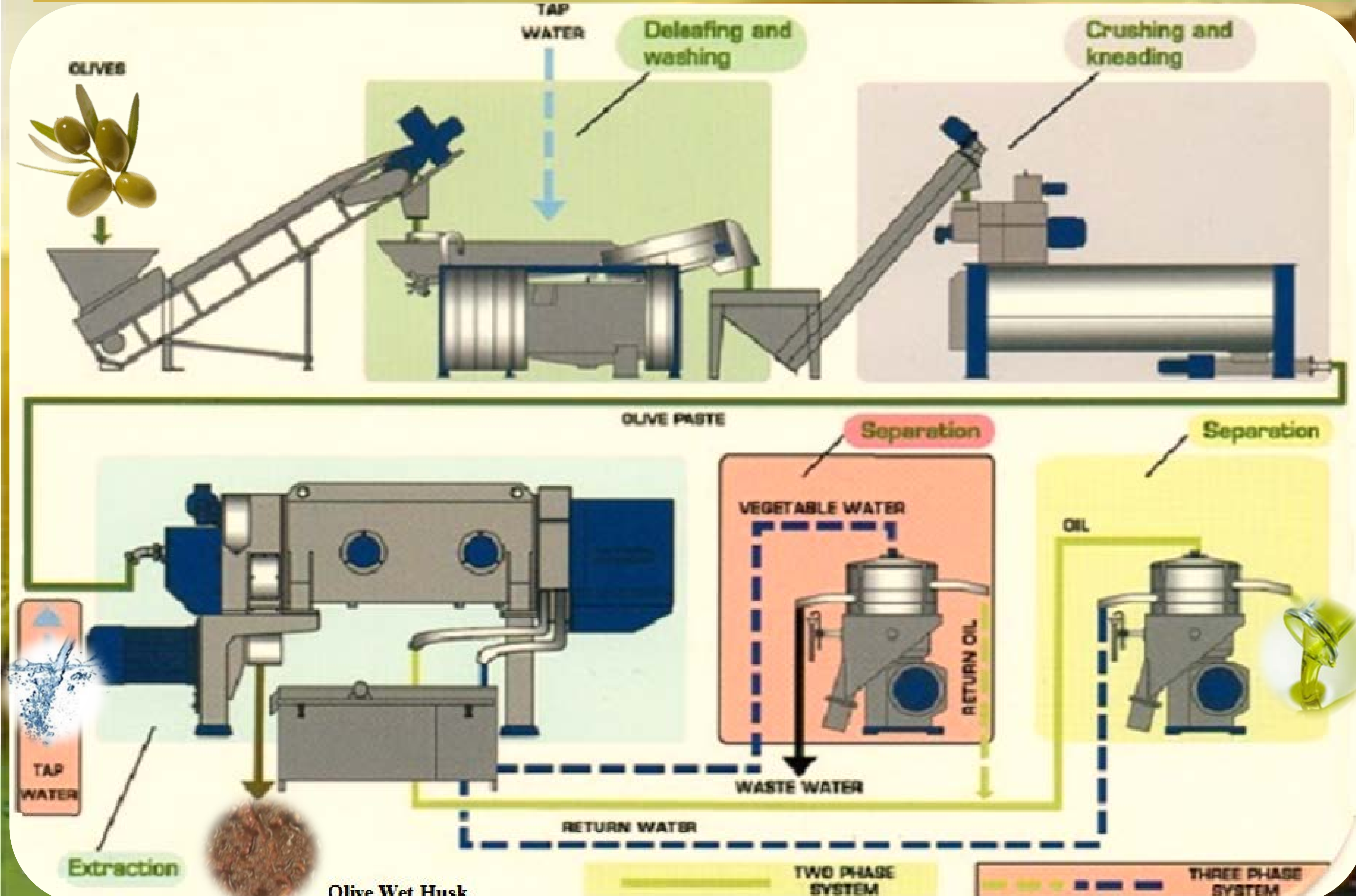
CONCLUSIONS

- The results of this work show that OP present a greater difficulty to be dried.

- Also OP have higher residual humidity, followed by the grape stalks and olive wet husk. Taking into account that the presence of water on the particle surface avoids a good interaction with the polymer matrices, it could be assumed that, after a convenient drying process, the olive wet husk could have better adhesion to the polymer in the composite, followed by the olive stalks and olive pits.

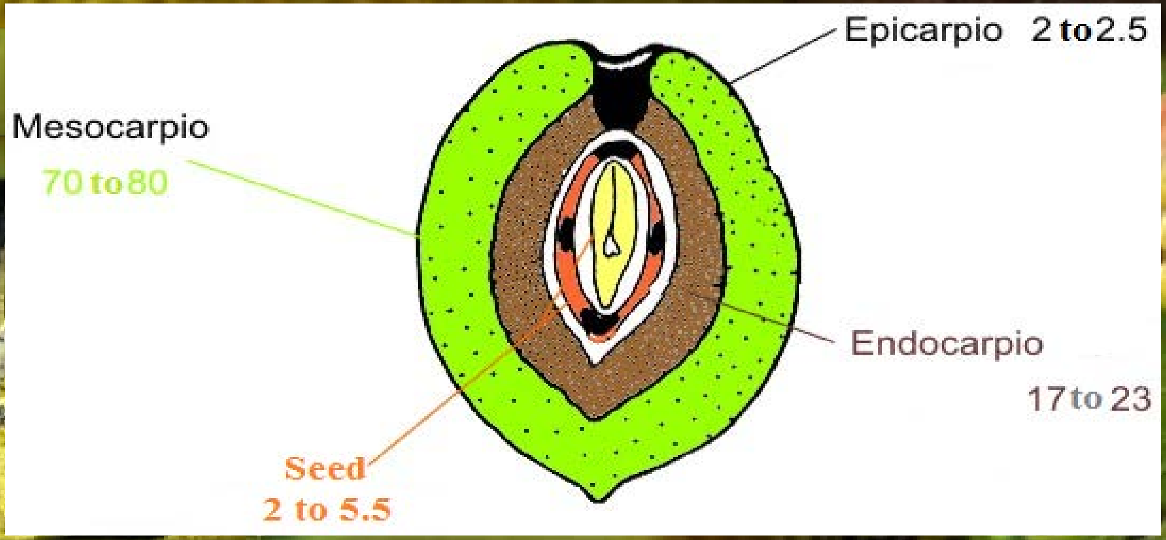
- **THANKS FOR YOUR ATENCION !!!!**

Olive wet husk

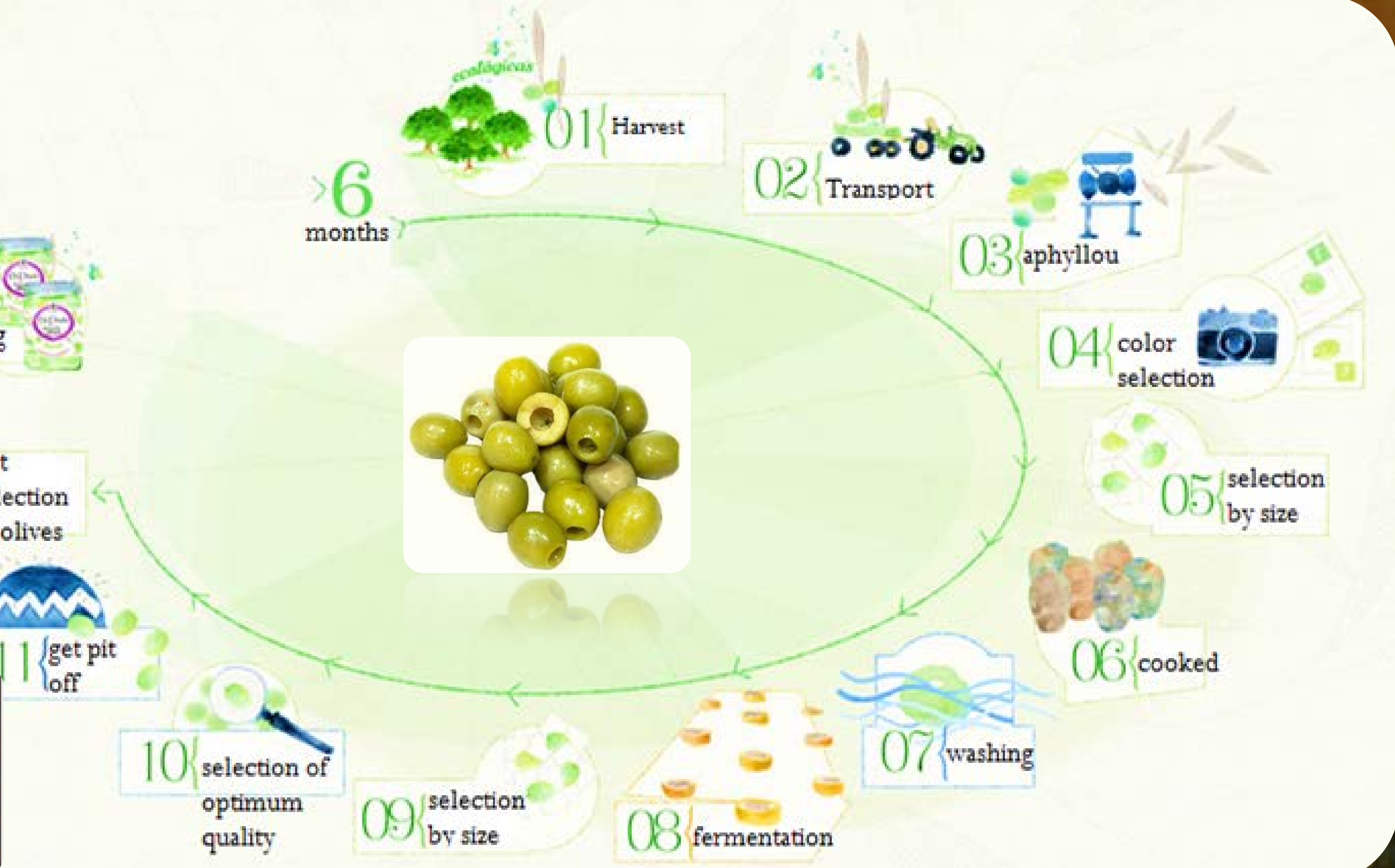


Olive Wet Husk (OWH) typical composition

- 42% milled shell core (endocarp or pit wall)
- 3% crushed seeds
- 21% olive envelope (epicarp or skin) and pulp (mesocarp)
- 9 to 10% a significant amount of residual oil
- 25 to 28 % water

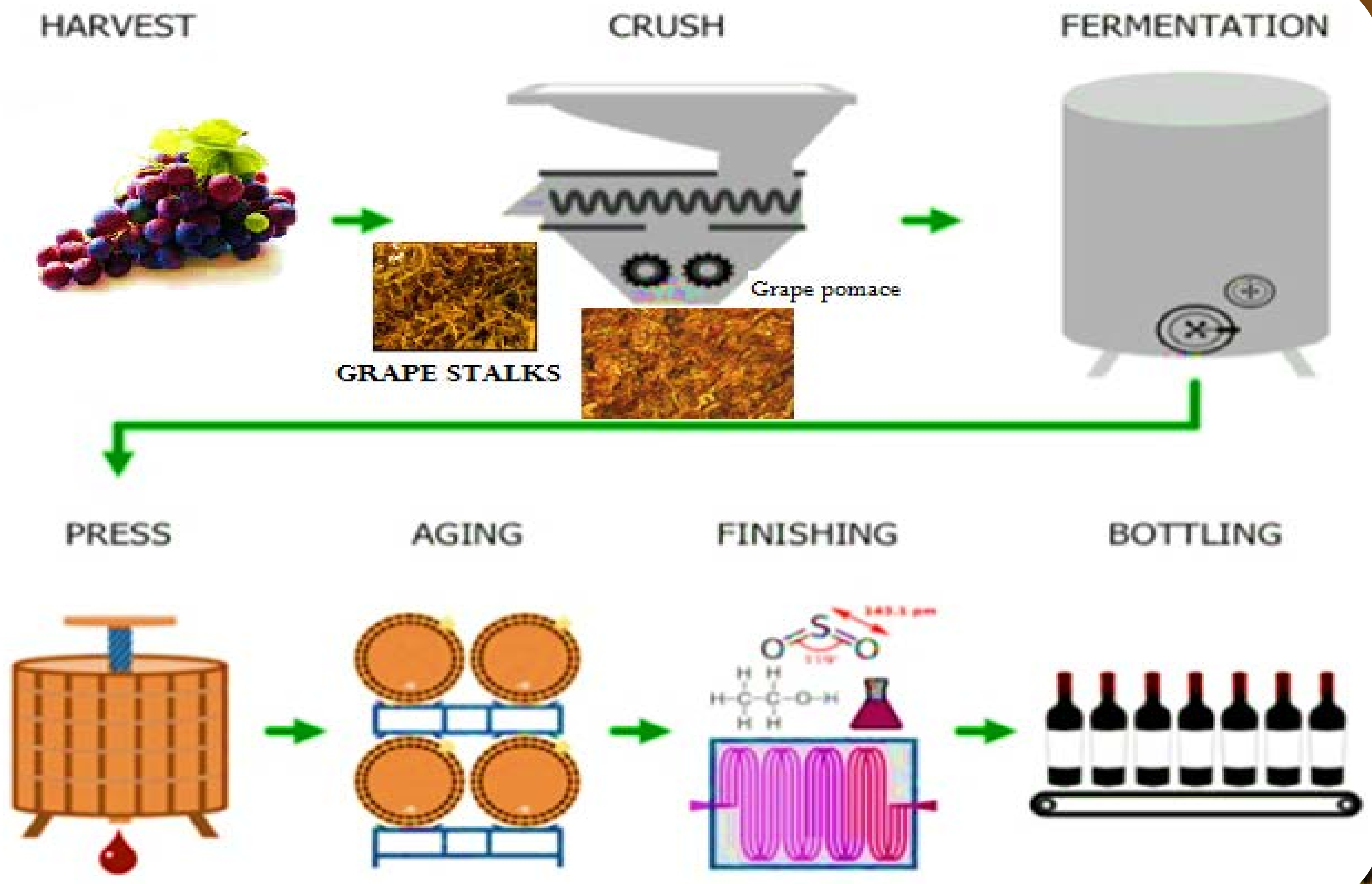


Olive pits

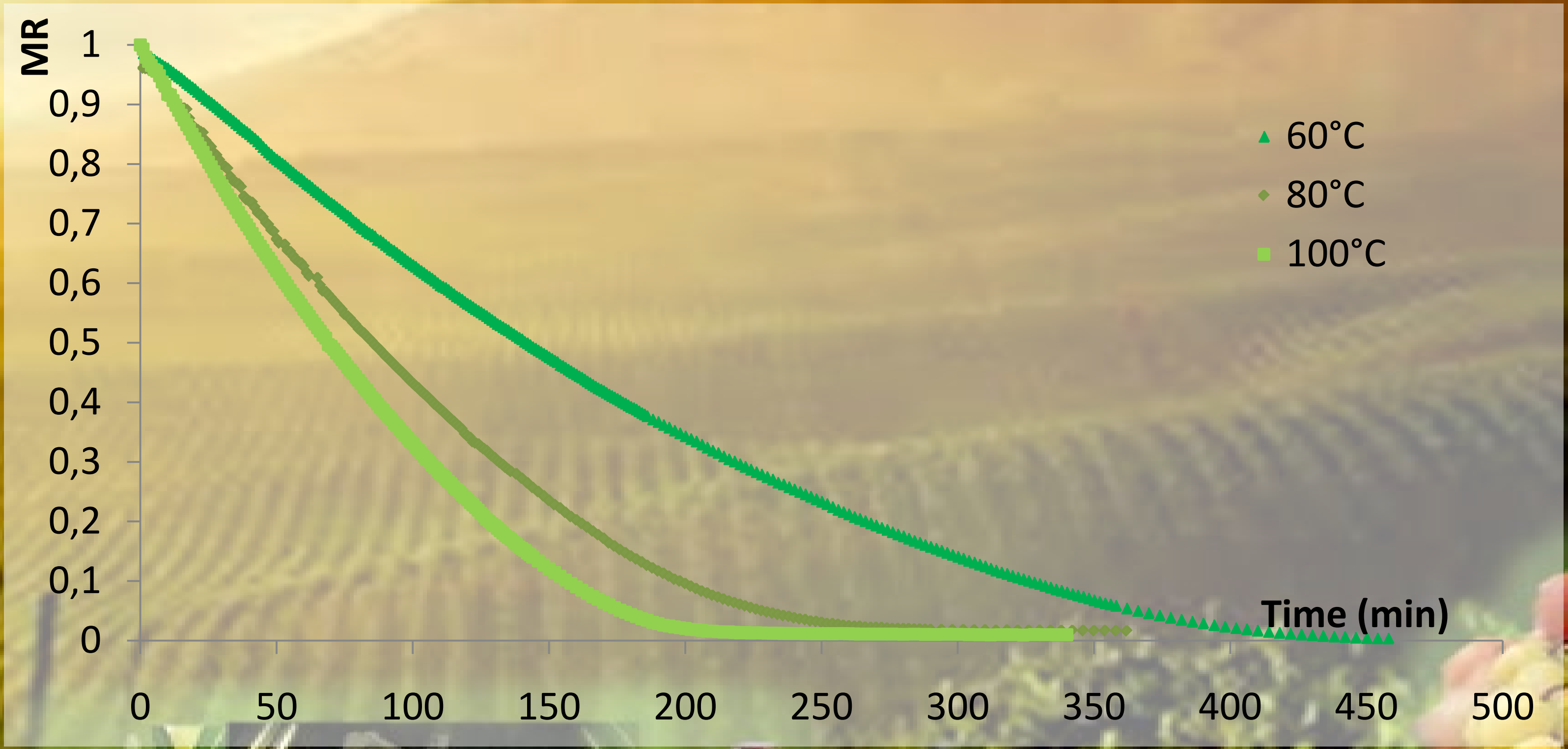


Olive pits

Grape Stlaks

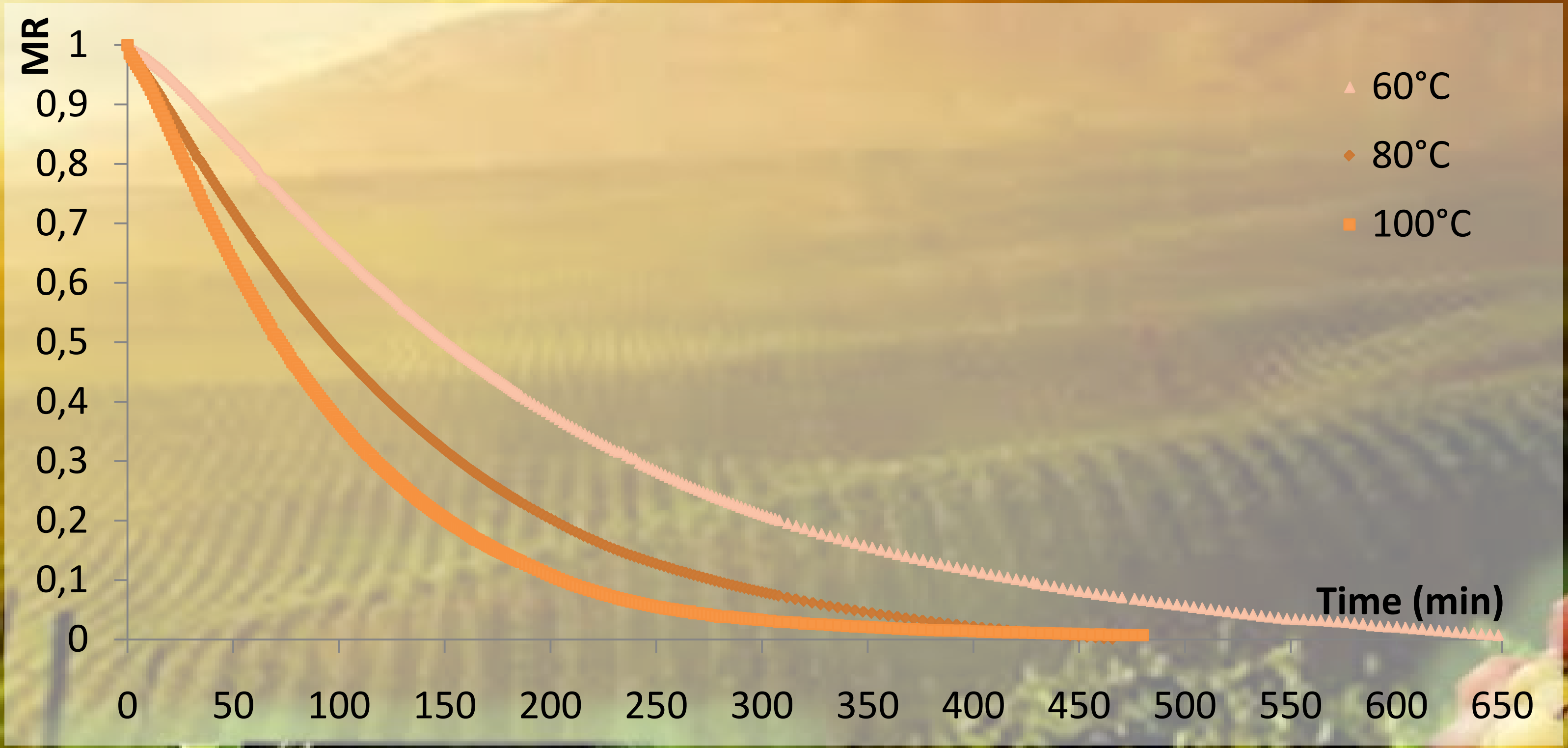


Experimental moisture ratio as a function of drying time for different temperatures OWH



Material	Air drying tem. (°C)	Me	Me averange
Olive wet husk	60	7,22	6,85
	80	6,51	
	100	6,81	

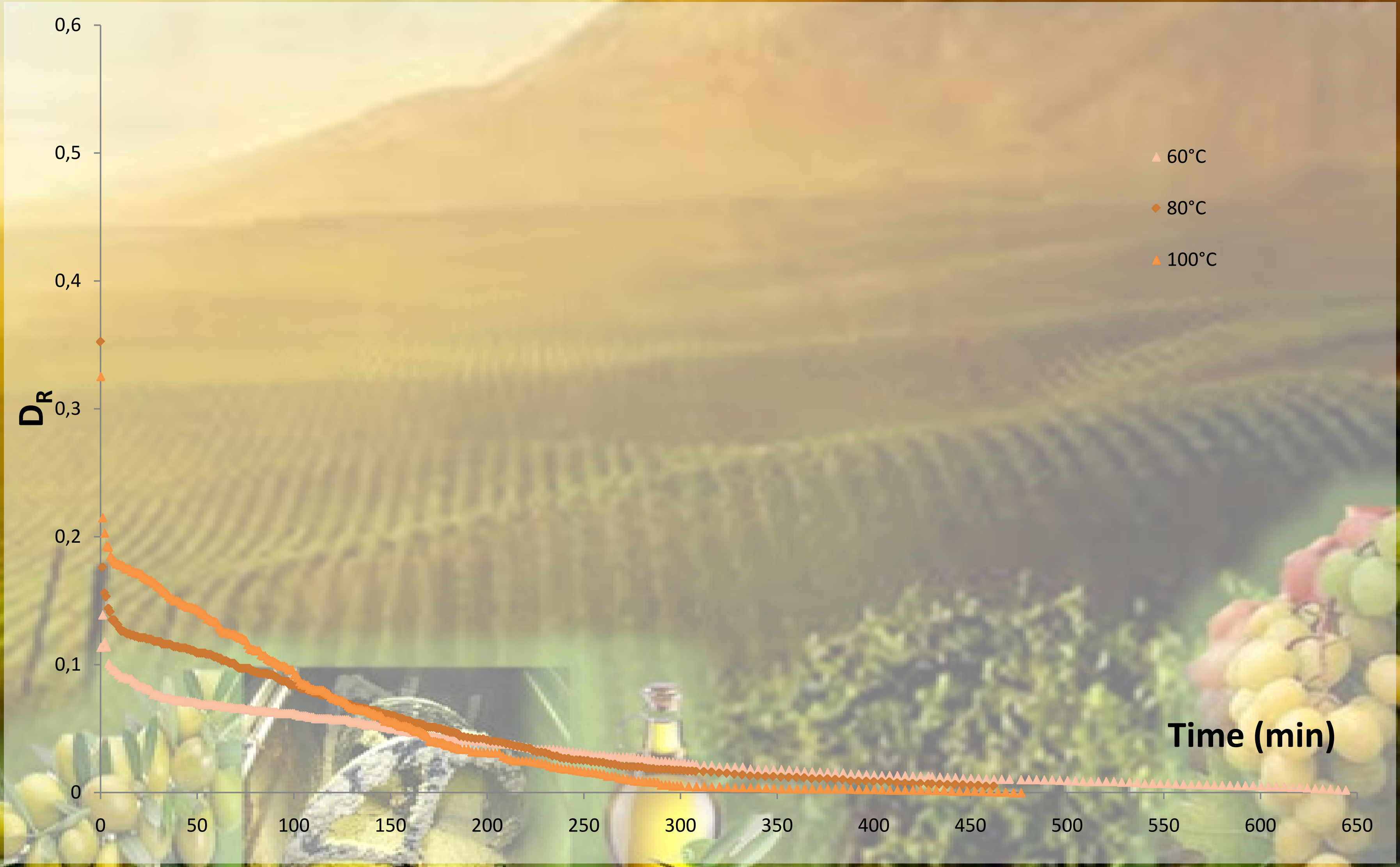
Experimental moisture ratio as a function of drying time for different temperatures OP



Material	Air drying tem. (°C)	Me	Me averange
Olive pits	60	35,40	34,36
	80	34,01	
	100	33,67	

Drying rate curves at different temperatures for OWH

Drying rate curves at different temperatures for OP



CONCLUSION

- Drying of the different agro-wastes (GS, OWH and OP) was studied. The results indicated that the moisture transferred during drying is controlled mainly by internal diffusion. Page and Logarithmic models showed the best fit for the kinetics of drying at different temperatures and for different materials, compared with the other semi-theoretical models tested. The difference in regression coefficients between the two models is very small, however, and considering its simplicity, Page model can be chosen for all cases.
- The effect of drying air temperature was studies in the range of 60-100 ° C for GS, OWH and OP. D_{eff} and D_R increased both with the increasing of drying temperature, and consequently the drying time decreased. The D_{eff} value ranged from 5.10^{-6} m^2s^{-1} to $5,04.10^{-6}$ m^2s^{-1} for GS, from $4,09.10^{-7}$ m^2s^{-1} to $4,13.10^{-7}$ m^2s^{-1} for OWH and from $4,99.10^{-6}$ m^2s^{-1} to $5,02,10^{-6}$ m^2s^{-1} for OP. This suggests that at high temperatures the water diffusion phenomena into the material are significant and depend on the internal structure of the material.
- The results of this work suggest that OP is the material having greater difficulty to be dried, preserving
- higher residual humidity, followed by the grape stalks and olive wet husk. Taking into account that the presence of water on the particle surface avoids a good interaction with the polymer matrices, it could be presupposed that, after a convenient drying process, the olive wet husk could have better adhesion to the polymer in the composite, followed by the olive stalks and olive pits.