Adnan Menderes University
Department of Biosystems Engineering

Opole University of Technology
Department of Processing Technology

Characterisation of thermal processing of olive mill wastes

Ersel Yilmaz

Małgorzata Wzorek

Robert Junga

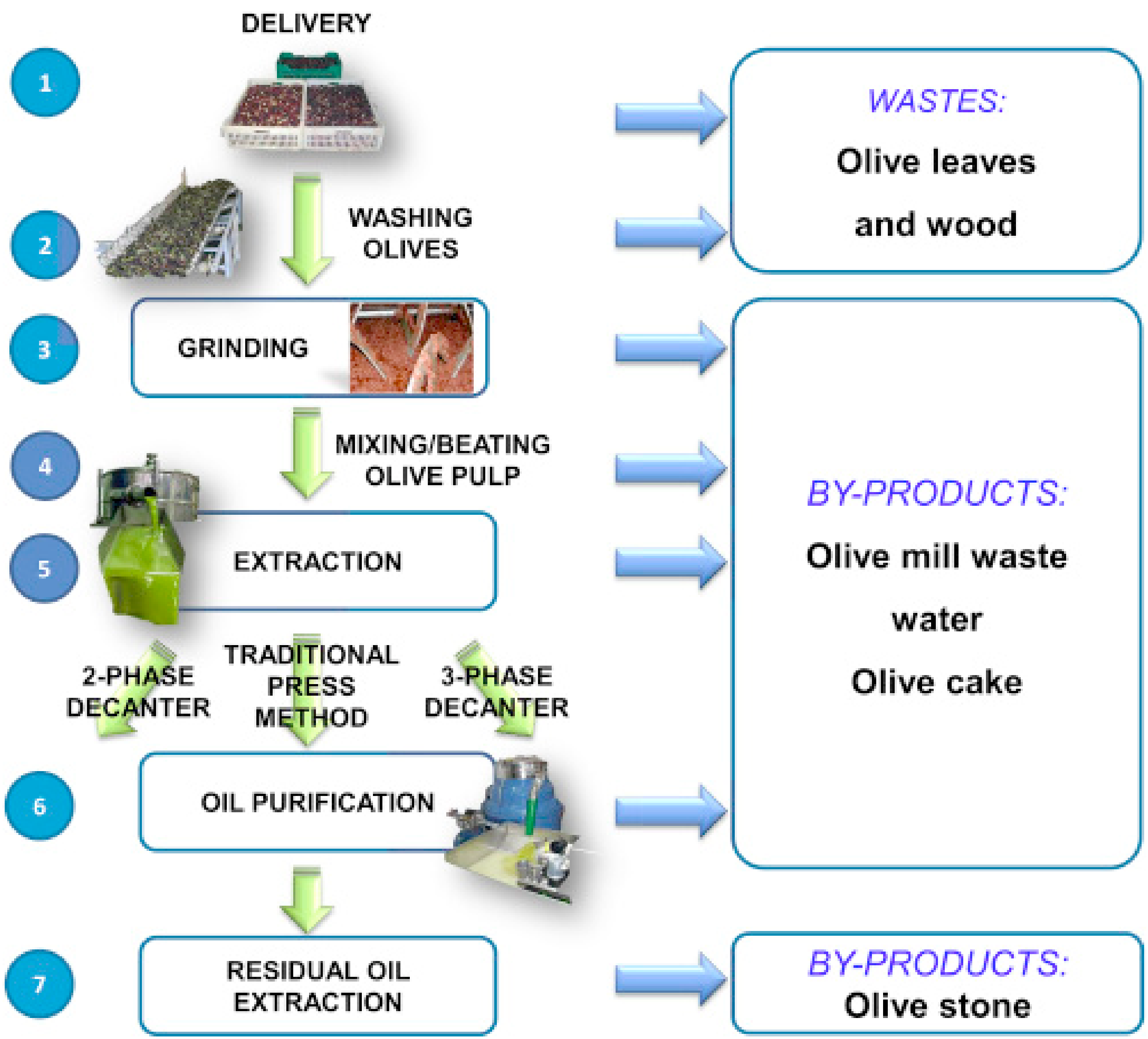
Naxos 2018

Olive oil producing provinces in Turkey

The olive-growing area - 845,542 ha with 1,690,000 olive trees

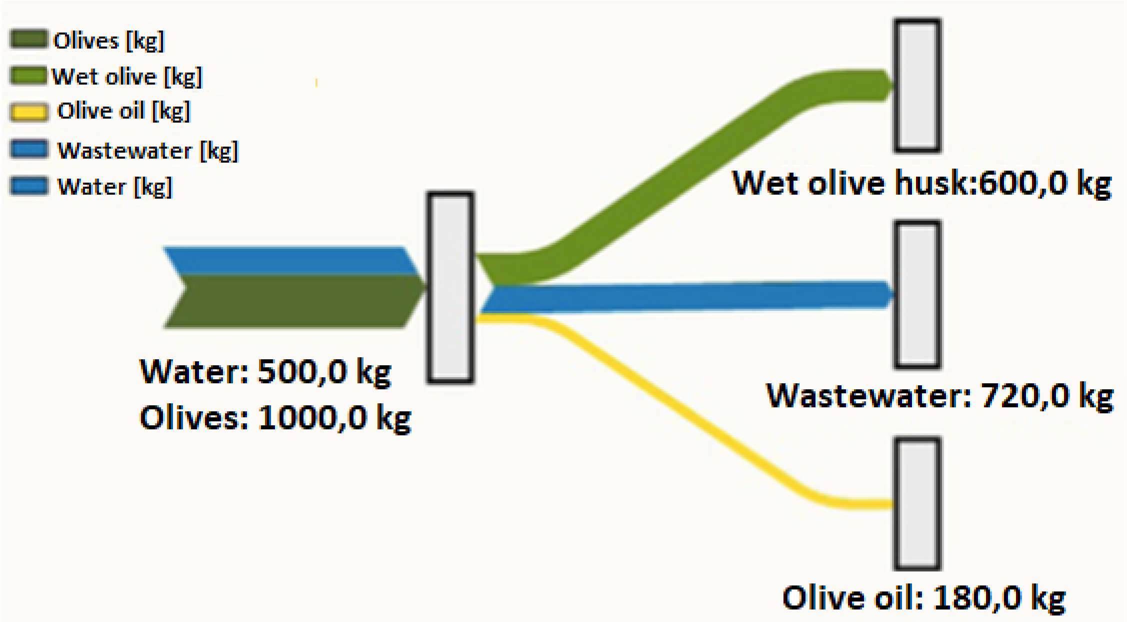
The average production - 527,000 tons of table olives and 1,700, 000 tons of olive oil

Stages of olive production with olive mill by-products



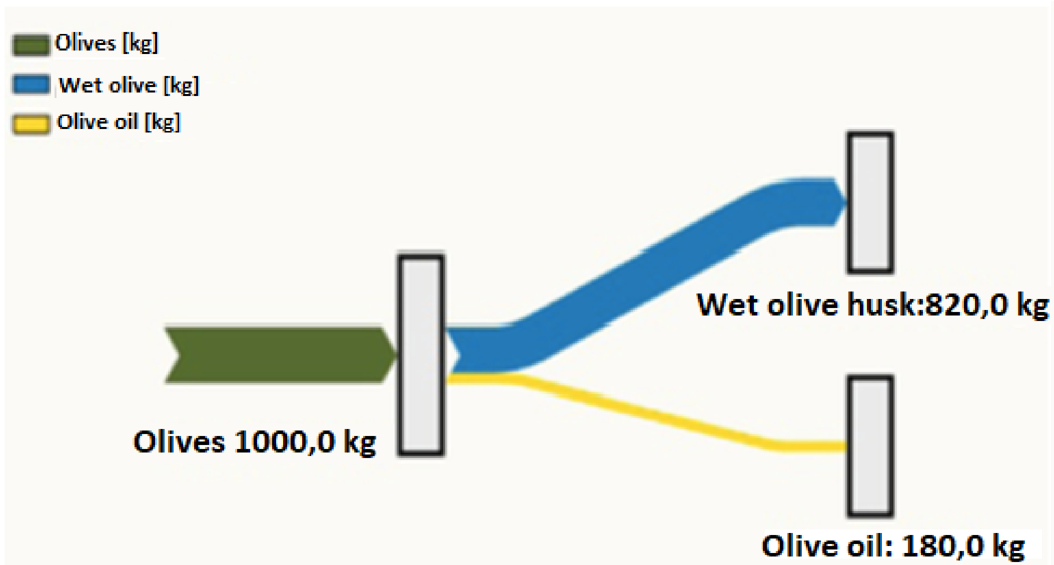
Source: Roselló-Soto E. et al. 2015

Mass balance: 3 – phase process



Source: Christoforou E., Fokaide A.P, Waste Manage., 2016

Mass balance: 2 – phase process



Source: Christoforou E., Fokaide A.P., Waste Manage., 2016

In Turkey 320,000 family enterprises:

- **481 certified olive processing**
- **1,794 are certified olive oil producers**

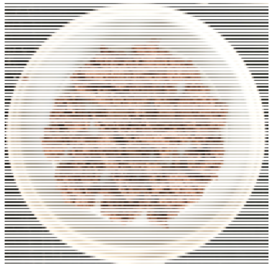
The aim of present work is to study thermal decomposition of different types of olive mill wastes via termogravimetric analyses to determinate the conditions of the combustion process for their application as fuel.

Materials

Olive wastes from different stages of olive oil production and methods were used for research, i.e.:

- small twigs (**OW1**), (diameter >5 mm) separated at the first step of olive oil production when the olives are cleaned prior to milling;
- leaves, named (**OW2)**, separated on sieves before olive cleaning.
- solid olive mill residue from the two-phase decanting method (**OW3**), which is a mixture of stone and pulp of the olive fruit;
- wastewater liquid fraction with oil from the three-phase decanting method (**OW4**).

OW1 and OW2



OW3

OW4

Methods

1. **The energy properties**:

- **moisture -** PN-EN ISO 18134
- **ash -** PN-EN ISO 18122 and PN-ISO 117
- **volatile matter -** PN-EN ISO 18123
- **elementary analysis** using Vario Macro Cube analyser 2.
- **higher heating value (HHV)** with the use of the IKA Calorimeters C 5000 according to PN-EN 14918:2010 and PN-ISO 1928 standard

2. The simultaneous thermal analysis (TG-DTG) was carried out in NETZSCH STA 449 F3 Jupiter device.

- in a dry air atmosphere with the gas flow of 70 mL/min
- temperature up to 800^{o}C
- three heating rates: 6, 8 and 10 K/min

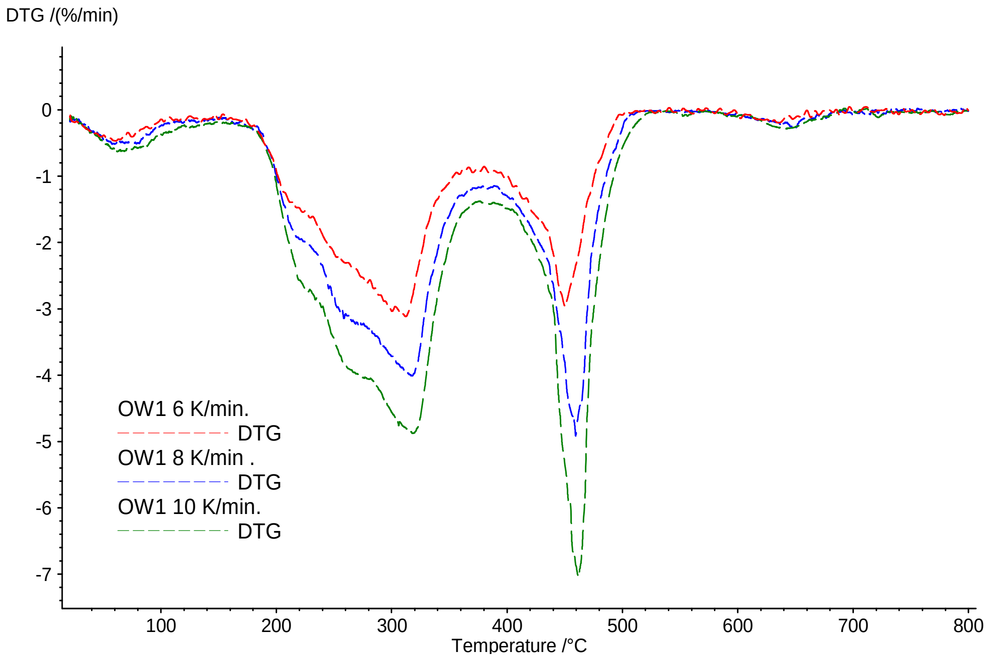
3. Modelling of kinetic with application of isoconversional methods (model free): Friedman (FR) and Ozawa-Flynn-Wall (OFW)

Energy parameteres of olive mill wastes

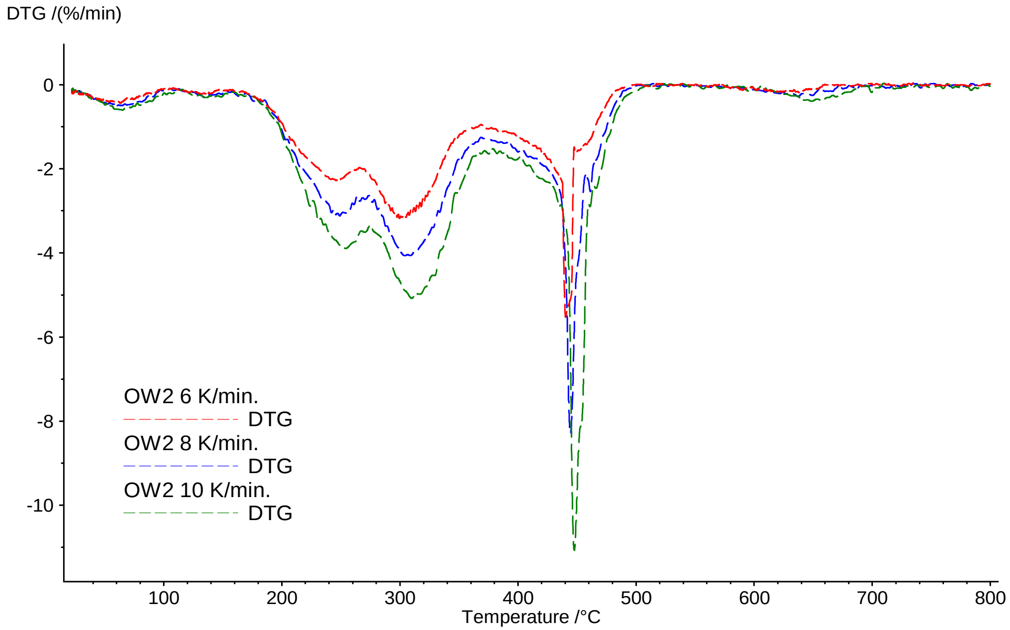
Samples	Proximate analysis wt.% Moisture	Ash d.m.	Voltaire matter d.m.	Ultimate analysis wt.% C	H	N d.m.	S	O	HHV MJ/kg
OW1	19.16	5.10	55.32	45.11	6.34	0.89	0.08	47.58	17.87
OW2	19.55	5.69	55.00	48.41	6.85	1.64	0.16	42.94	20.12
OW3	53.49	3.03	51.57	51.37	6.62	0.85	0.05	41.11	20.88
OW4	84.24	14.19	65.66	46.23	6.12	1.06	0.17	46.42	18.71

d.m. – dry mass

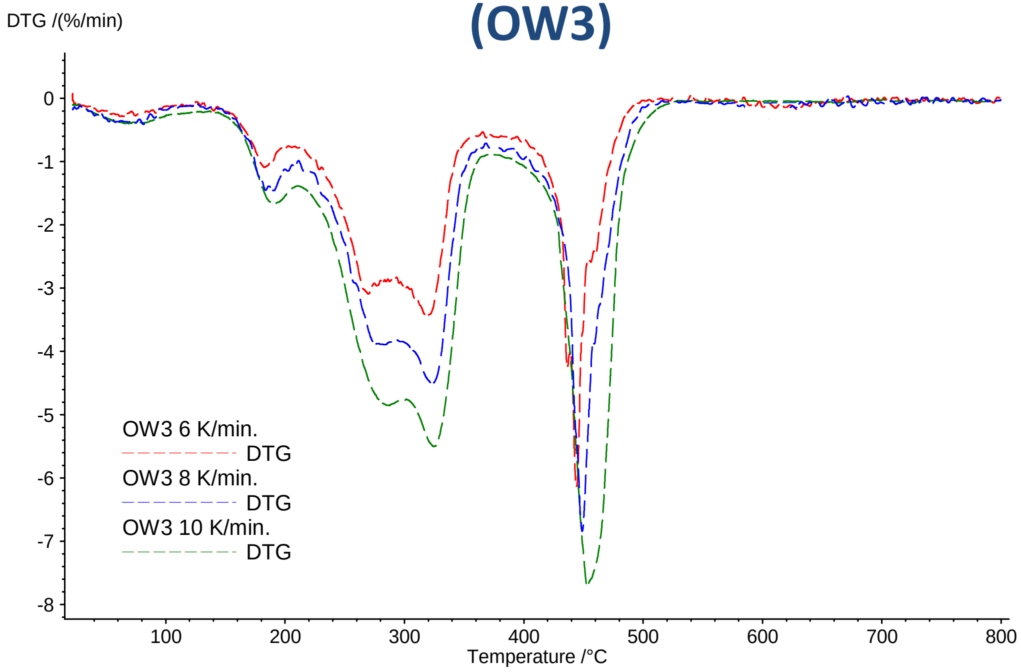
DTG curves of twigs (OW1)



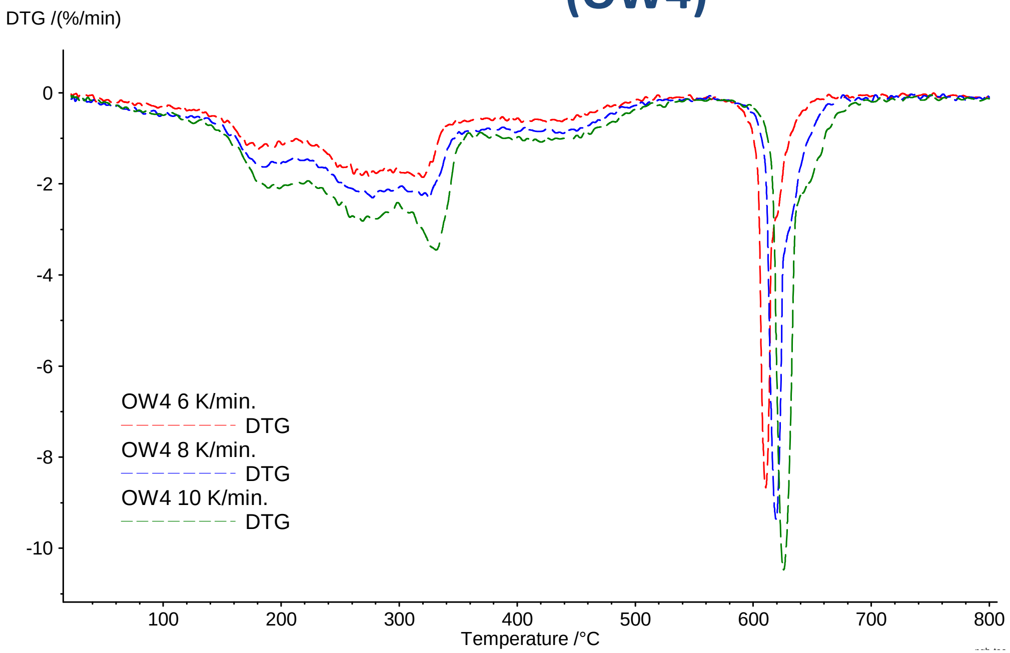
DTG curves of leaves (OW2)



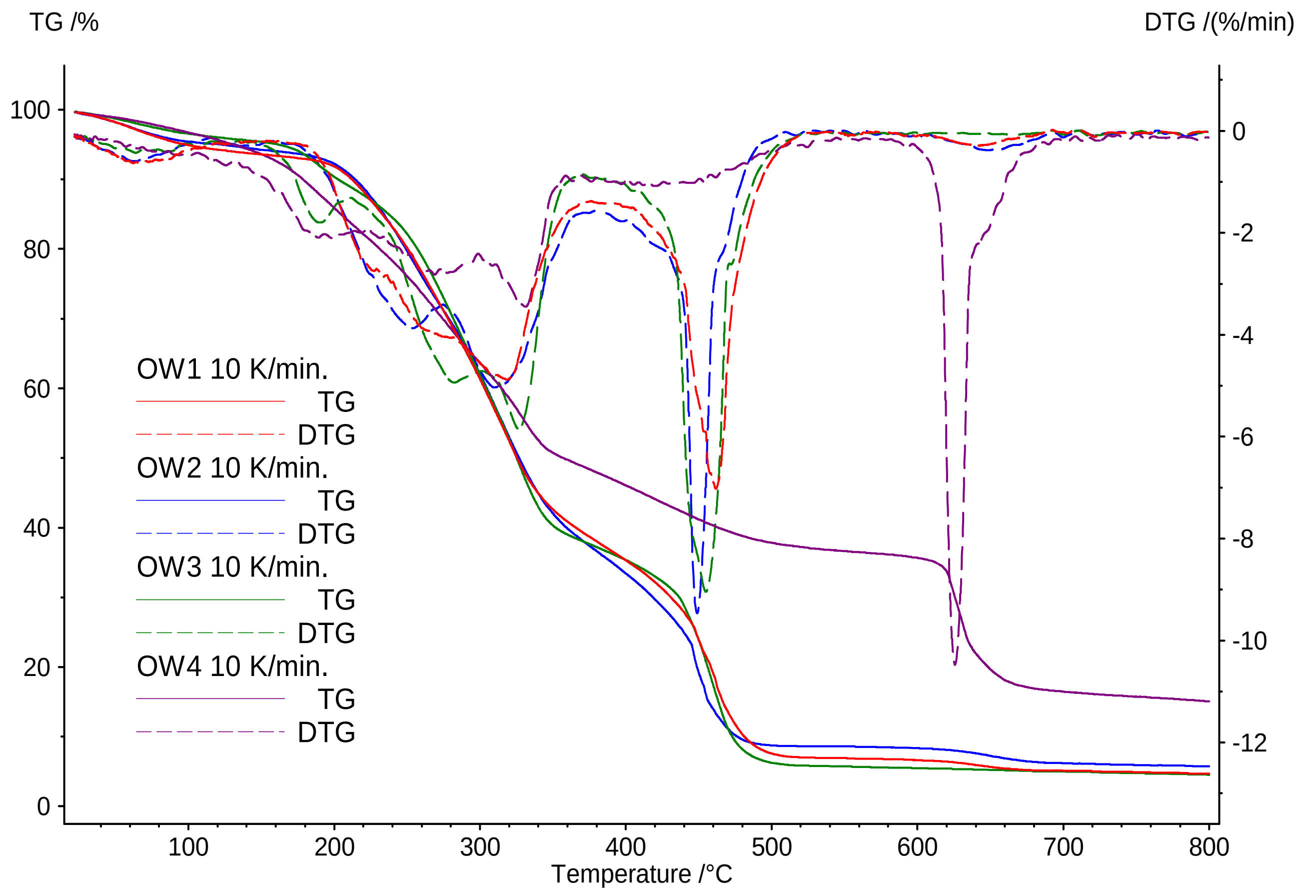
DTG curves of two-phase process (OW3)



DTG curves of three-phase process (OW4)



TG/DTG curves of olive waste samples



Temperature ranges of combustion stages

Sample	Stage IIb °C	Stage IIc °C	Stage IId °C	Stage III °C
6 K/min				
OW1	-	-	170-375	375-512
OW2	-	166-267	267-368	368-498
OW3	133-203	203-290	290-361	361-504
OW4	213-293	293-354	354-515	515-662
8 K/min				
OW1	-	-	171-379	379-516
OW2	-	171-270	270-374	374-501
OW3	133-210	210-293	293-367	367-519
OW4	214-302	302-355	355-520	520-673
10 K/min				
OW1	-	-	172-380	380-524
OW2	-	174-275	275-378	378-511
OW3	140-210	210-301	301-372	372-527
OW4	220-300	300-360	360-524	524-693

in the case of stage IIa, the initial temperature cannot be determined as the tested samples were dried

Characteristic combustion parameters for the olive mill wastes

Sample	T_i Initial tem.	T_b End of combustion tem.	t_b Time of combustion	Stage IIa		Stage IIb		Stage IIc		Stage IId		Stage III	
				DTG_{max}	T_{max}	DTG_{max}	T_{max}	DTG_{max}	T_{max}	DTG_{max}	T_{max}	DTG_{max}	T_{max}
	°C	°C	min	%/min	°C	%/min	°C	%/min	°C	%/min	°C	%/min	°C
6 K/min													
OW1	207	512	46.6	-	-	-	-	-	-	-3.06	311.9	-3.05	450.6
OW2	205	498	48.0	-	-	-	-	-2.28	249.1	-3.18	299.6	-5.53	440.3
OW3	167	504	55.1	-	-	-1.09	182.7	-3.09	269.8	-3.44	319.0	-6.13	444.1
OW4	160	662	82.8	-1.25	179.8	-1.83	275.2	-1.86	319.9	-0.65	425.8	-8.67	610.5
8 K/min													
OW1	210	516	34.7	-	-	-	-	-	-	-4.01	317.9	-4.92	459.5
OW2	207	501	35,9	-	-	-	-	-3.12	249.0	-4.06	304.2	-8.30	444.4
OW3	167	519	42.5	-	-	-1.46	190.4	-3.89	283.1	-4.51	323.2	-6.84	448.9
OW4	167	673	61.9	-1.63	185.8	-2.31	277.5	-2.30	325.3	-0.89	438.7	-9.36	619.31
10 K/min													
OW1	210	524	28.2	-	-	-	-	-	-	-4.88	317.7	-7.02	461.6
OW2	213	511	28.5	-	-	-	-	-3.89	254.1	-5.08	309.9	-11.07	447.7
OW3	174	527	33.7	-	-	-1.67	189.9	-4.85	287.2	-5.50	324.1	-7.71	453.2
OW4	167	693	50.9	-2.10	198.3	-2.82	268.9	-3.45	331.3	-1.08	420.1	-10.47	625.7

Kinetic models

The kinetics of the thermal decomposition of the olive mill wastes is based on the non-isothermal experimental method combined with isoconversional (model free)

Arrhenius equation:

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} = k(T)f(\alpha) = Aexp\left(-\frac{E_\alpha}{R\cdot T}\right)f(\alpha) \qquad (1)$$

where: $d\alpha/dt$ - rate of conversion from solid-state to volatile product
A - frequency of reactants collisions, occurring with appropriate orientation to react, 1/s
β - heating rate, K/min
E_α - activation energy, J/mol
T - the reaction temperature, K
k – reaction rate constant
R - 8.314 - stands for universal gas constant, J/mol·K

The degree of conversion α, represents the loss in mass fraction and is defined by the relationship

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \qquad (2)$$

where: m_i - initial mass of the sample
m_t - the mass sample at the time t
m_f - the sample mass at the end of the process

Friedman method (FR)

$$\ln\left(\frac{d\alpha}{dt}\right)_{\alpha,i} = ln[f(\alpha)\cdot A_\alpha] - \frac{E_\alpha}{R\cdot T_{\alpha,i}} \tag{3}$$

where: the index *i* is individual heating rate.

The value of activation energy E_α can be estimated as a slope of a plot of $\ln(d\alpha/dt)_{\alpha,i}$ vs. $1/T_{\alpha,i}$.

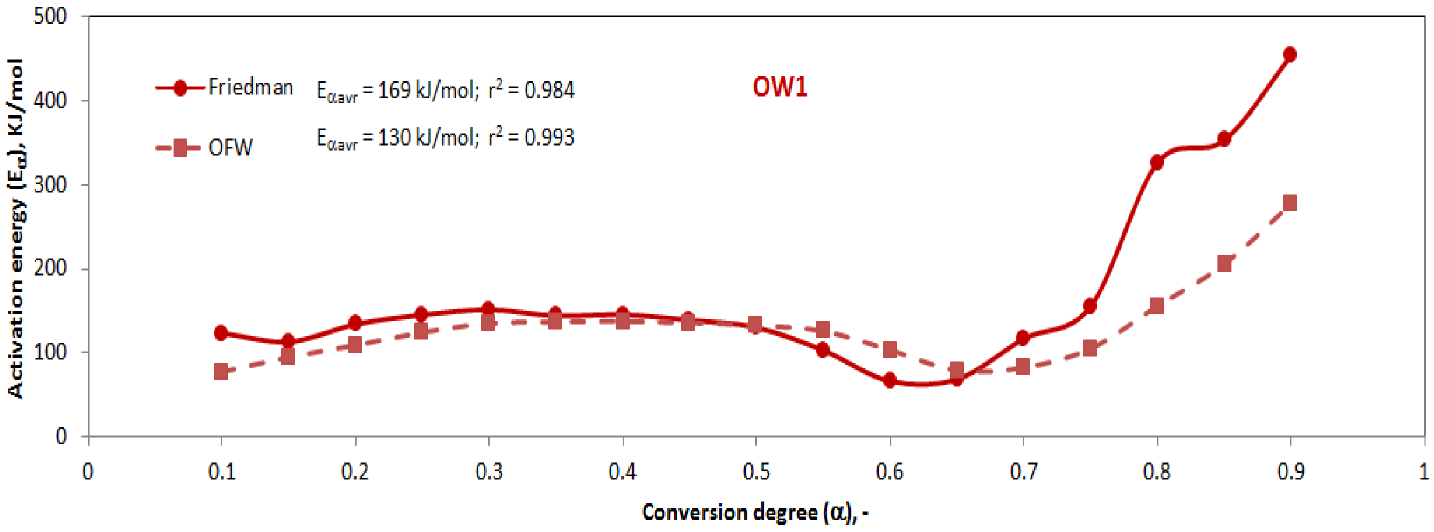
Ozawa - Flynn - Wall method (OFW)

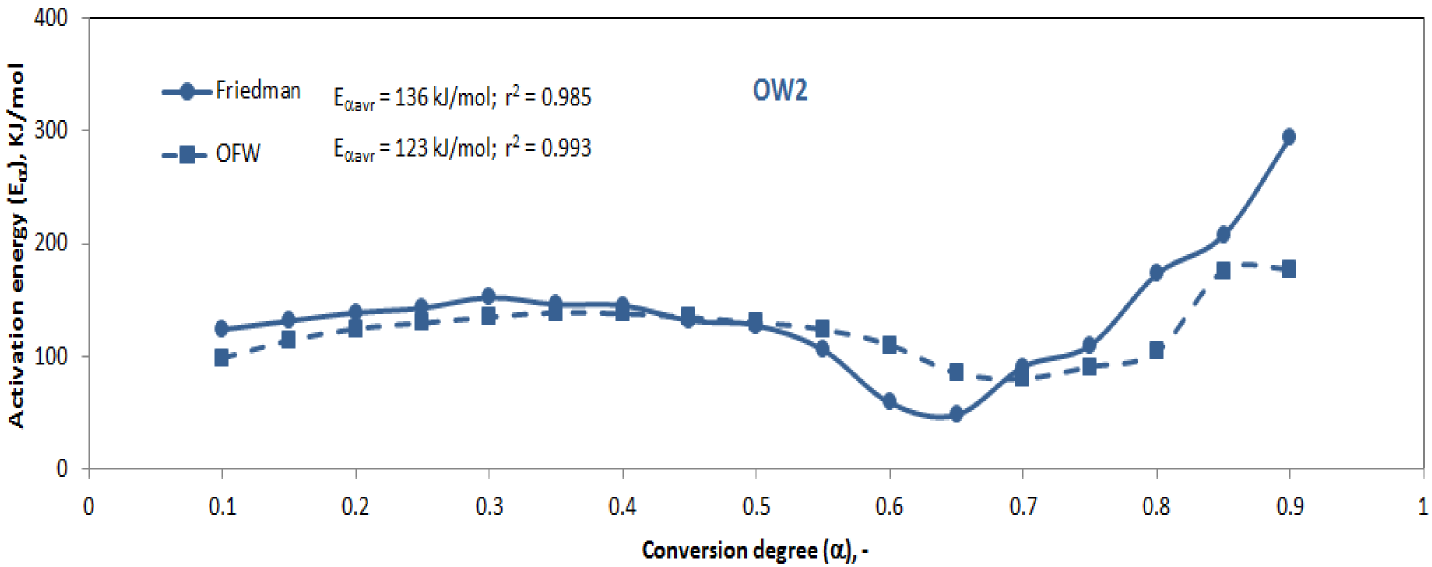
$$ln(\beta_i) = ln\left(\frac{A_\alpha\cdot E_\alpha}{R\cdot g(\alpha)}\right) - 5.3305 - 1.052 = ln\left(\frac{0.0048A_\alpha\cdot E_\alpha}{R\cdot g(\alpha)}\right) - 1.052\left(\frac{E_\alpha}{R\cdot T_i}\right) \tag{4}$$

$$\mathrm{g}(\alpha) = \frac{A}{\beta}\int_0^T exp\left(-\frac{E}{R\cdot T}\right)dT \tag{5}$$

The activation energy E_α of the reaction can be estimated as a slope of a plot $\ln(\beta_i)_{\alpha,i}$ against $1/_{\alpha,i}$.

Activation energies E_α for different mass conversion degrees α at the heating rate of 10 K/min





Conclusions

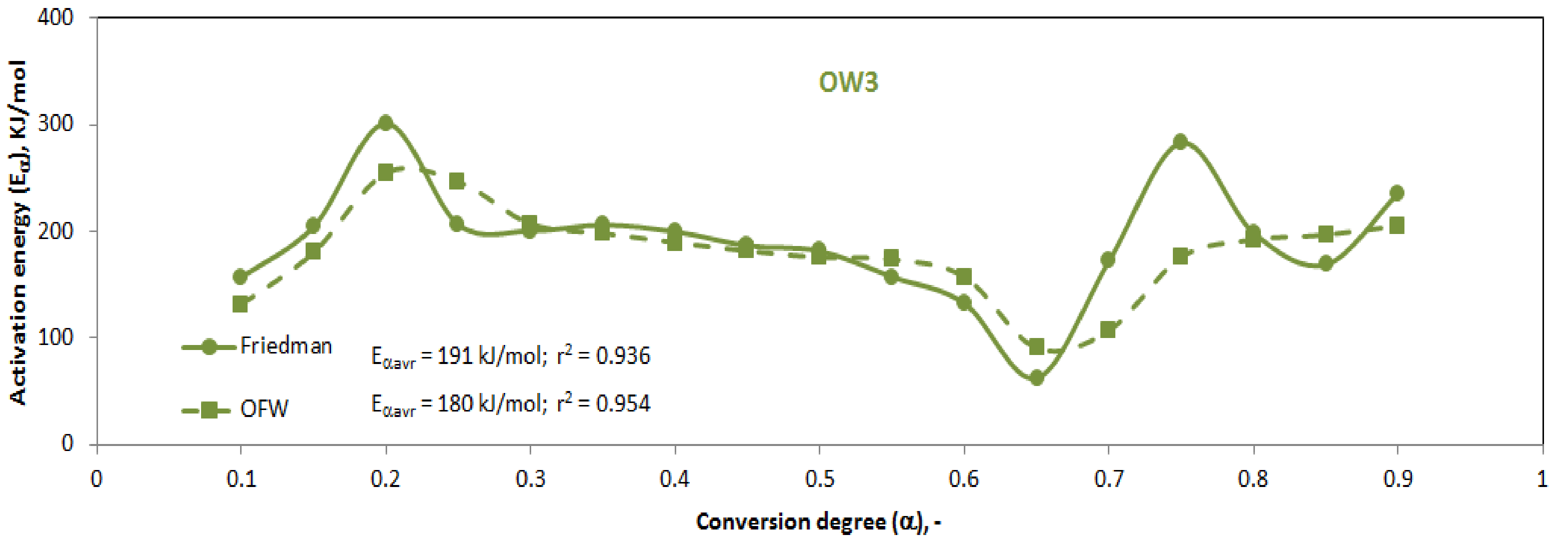
- Olive mill by-products are potential renewable energy sources in Turkey and other countries of the Mediterranean basin. Application of olive mill wastes in energy production can bring benefits for the environment.
- The burning profiles of olive mill wastes for OW1, OW2 and OW3 samples show the characteristic peaks in the range of temperatures typical for biomass degradation (dehydration, devolatilization, gases and char combustion). In the case of OW3, the highest mass loss rate was observed at the char combustion stage instead of in the volatiles liberation stage.
- Based on the obtained combustion results at the heating rates of 6, 8 and 10 K/min, it can be concluded that initial degradation temperature and temperature at which combustion is ended increase along with increase of the heating rate and the total combustion time is reduced.

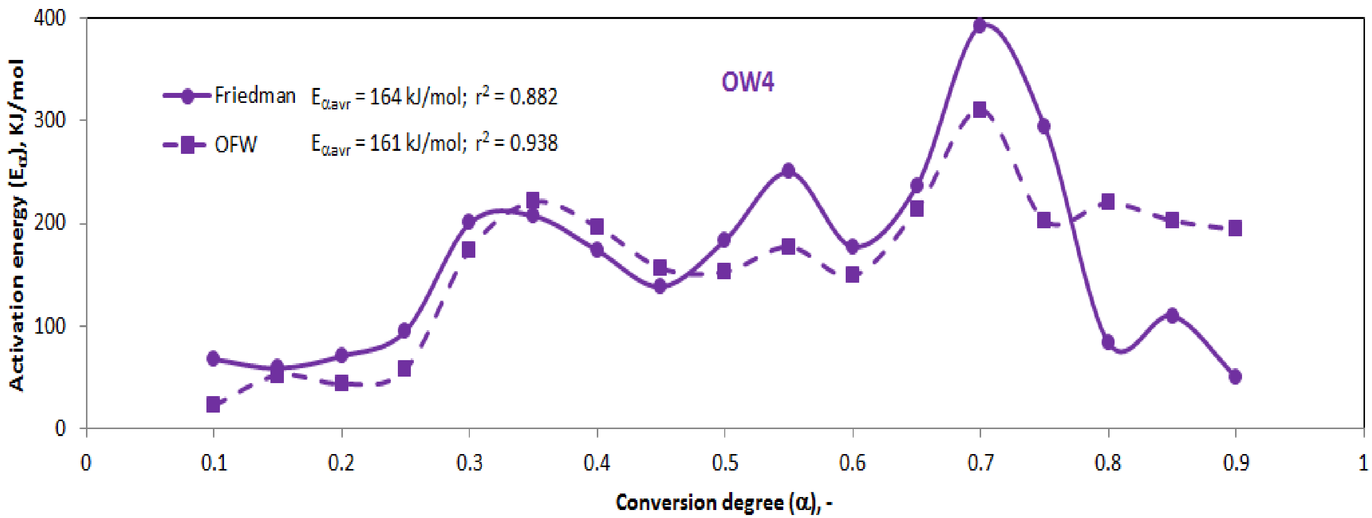
Conclusions

- Average activation energies E_α calculated in accordance with model-free (isoconversional) methods were found to fall within the range of 136-191 kJ/kmol for Friedman and 123-180 kJ/mol for Ozawa-Flynn-Wall method. Those methods demonstrate high compatibility in the range of conversion degree α of up to 0.6.

Thank you for your attention

Activation energies E_α for different mass conversion degrees α at the heating rate of 10 K/min





The thermodynamic parameters

Conversion degrees α	A s^{-1}	ΔH kJ/mol	ΔG kJ/mol	ΔS kJ/mol
		OW1		
0.2	2.45E+05	103	233	-177
0.3	2.15E+07	129	231	-140
0.4	3.32E+07	132	231	-136
0.5	1.43E+07	127	231	-143
0.6	9.16E+04	97	233	-185
0.7	2.42E+03	77	234	-215
0.8	7.44E+08	150	230	-110
		OW2		
0.2	4.95E+06	119	228	-152
0.3	3.00E+07	129	228	-137
0.4	5.14E+07	132	227	-132
0.5	1.29E+07	124	228	-144
0.6	4.00E+05	104	229	-172
0.7	2.06E+03	74	231	-216
0.8	1.43E+05	98	229	-181
		OW3		
0.2	1.76E+16	249	226	31
0.3	5.27E+12	201	227	-36
0.4	2.67E+11	183	228	-61
0.5	2.48E+10	169	228	-81
0.6	1.09E+09	151	229	-107
0.7	1.92E+05	101	231	-179
0.8	4.12E+11	186	228	-57
		OW4		
0.2	4.00E+01	37	296	-289
0.3	5.99E+07	167	286	-133
0.4	1.36E+09	189	285	-107
0.5	3.10E+06	146	287	-157
0.6	1.72E+06	141	287	-162
0.7	1.44E+10	206	284	-87
0.8	3.46E+10	212	284	-80

The thermodynamic parameters

Pre-exponential factor (A_α) in Arrhenius equation

$$A_\alpha = \frac{\beta \cdot E_\propto}{R \cdot T_{max}^2} exp\left(\frac{E_\propto}{R \cdot T_{max}}\right) \qquad (5)$$

Changes of enthalpy (ΔH_α)

$$\Delta \mathrm{H}_\alpha = E_\propto - R \cdot T \qquad (6)$$

Changes of free Gibbs energy (ΔG_α)

$$\Delta \mathrm{G}_\alpha = E_\propto - R \cdot T_{max} \cdot ln\left(\frac{k_B \cdot T_{max}}{h \cdot A_\alpha}\right) \qquad (7)$$

Changes of entropy (ΔG_α)

$$\Delta \mathrm{S}_\alpha = \frac{\Delta H_\alpha - \Delta G_\alpha}{T_{max}} \qquad (6)$$

where *h* is the Plank constant ($6.62607004 \cdot 10^{-34}$ m^2kg/s), k_b is the Boltzmann constant ($1.38064852 \cdot 10^{-23}$ $m^2kg/(s^2K)$), and T_{max} is the temperature at the peak od DTG curve.