



Kinetics and thermodynamic behaviour evaluation of olive residue/recycled polyester pyrolysis

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The growing amounts of plastic and biomass wastes have become a global problem challenging the environmental sustainability. In this regard, waste to energy technologies has gained more importance to convert waste inventory into useful energy and value added products. In this study, pyrolysis characteristics of a textile industry waste (recycled polyester fabric, RPF) and an agricultural waste (olive residue, OR) and their (1/1 wt.%) blend are investigated via thermo-gravimetric analysis (TGA) method. Thermal degradation were examined at heating rates of 10, 30 and 50°C min⁻¹ heated to 1000°C with 100 mL min⁻¹ flow of nitrogen. Kinetic analysis of pyrolysis has been performed with Flynn-Wall-Ozawa (FWO) method. Experimental and theoretical TGA profiles compared and some synergistic interactions have obtained during co-pyrolysis. The activation energies are determined as 254.22, 203.22, 231.72 kJmol⁻¹ for RPF, OR and RPF/OR blend, respectively. The results of kinetics analysis and evaluation of the thermodynamic parameters (activation energy, enthalpy, Gibb's free energy and entropy) have shown that co-pyrolysis of OR and RPF is promising alternative for sustainable bioenergy production.

Keywords: Co-pyrolysis, Kinetics, Olive residue, Recycled polyester fabric, Thermodynamic parameters, Thermo gravimetric analysis

Continuous growth in population, industrial and technological developments have fostered the global energy demand in the last decades. The utilization of fossil fuel resources for energy generation has led tremendous increase in greenhouse gas emission to the atmosphere and hence raised the environmental concerns. According to the International Energy Agency, global energy needs will expand by 30% in 2040 compared to its value in 2017¹. The scenarios on future energy requirements point out the urgent need for the rise of renewable sources, sustainable technology solutions and energy efficiency measures.

Biomass is an environmentally friendly option for meeting the global energy demand and at the same time for managing the waste inventory². Biomass is estimated to supply 15–25% of the world's primary energy demand in 2050 (Ref 3) as a low risk source of renewable energy⁴⁻⁶. The use of plastic derived materials on the other hand, has risen in the recent decades due to their application in many areas, such as textiles, building materials, packaging, electronics, automotive industries, etc. The synthetic fibers such as recycled polyesters are commonly used in textile and apparel sector. Recycled fibers have ecological

advantages over virgin fibers, which made them more favorable for sustainability of the textile industry⁷. World Apparel & Footwear Life Cycle Assessment Database⁸ and The Higg Materials Sustainability Index⁹ provide specific data based on life cycle assessments and environmental performance of materials used in textile and apparel sector. As plastics are highly durable materials with long life span, they become a treat for the environment.

In view of above, there is need for converting waste into renewable energy for environmental protection¹⁰. Pyrolysis is one of the conventional thermochemical technologies for solid waste conversion to bio-oil, syngas and biochar. Thermo gravimetric analysis (TGA) on the other hand, is a precise and simple method to investigate the thermal degradation and kinetic analysis of fuels¹¹. Even several research have been carried out on pyrolysis of different waste materials and their blends, high dependency of the pyrolysis process on fuel structure and operating conditions have remained the problem unsolved¹². Assessment of technical feasibility of pyrolysis of biomass with other waste materials requires investigation of possible synergetic

interactions. Especially, co-pyrolysis process is less conducted subject in literature. Thermal behaviour and kinetic analysis of some biomass/plastic waste¹³⁻¹⁷ were reported. However, no study has been published in literature on thermal behaviour during olive residue and recycled polyester fabric co-pyrolysis. Therefore, this study aims to investigate the kinetics and thermodynamic behaviour of olive residue (OR) and recycled polyester fabric (RPF) and their blend by using thermo gravimetric analysis (TGA) method. Kinetic study was conducted for optimization of thermo chemical conversion of raw materials and the blend. Flynn-Wall-Ozawa (FWO) is conversion integration method was employed to fit TGA data. The activation energies (E_A) and pre-exponential factors (A) derived from the kinetic model were analysed. Thermodynamic behaviour of the fuels were examined by calculation of the properties such as enthalpy (ΔH), Gibb's free energy (ΔG) and entropy (ΔS) were also determined using the TGA data.

Experimental section

Feedstock

In this study, OR and RPF were used as raw materials. The olive oil production prevails in the Mediterranean basin, Turkey is the fourth largest olive oil producer in the world. Olive residue is the residual of olive oil processing plant (Fig. 1a). It was obtained from a local olive oil plant located in Nazilli, Aydın, Turkey. Turkey is also a leading country in textile manufacturing with high export share. The total value of fabrics exported in 2015 was about USD 5 billion. The waste fabrics also constitute high waste potential. Recycled polyester fabric (RPF) was provided from a textile company in Denizli, Turkey (Fig. 1b). The proximate and elemental analyses of the samples have shown in Table 1. ASTM D3173, ASTM D 3175, ASTM D

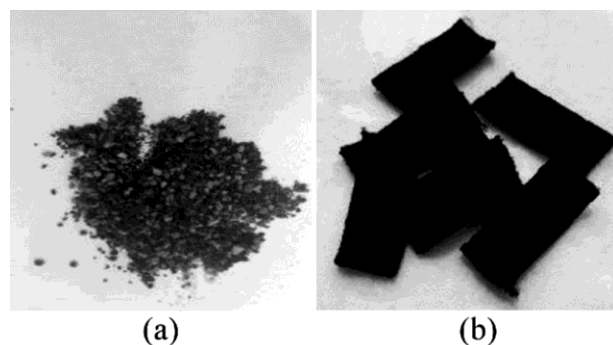


Fig. 1 — Raw materials

3174 methods were used to determine Moisture (M), volatile matter (VM), ash contents of the samples, respectively. The elemental composition (C, H, S, N) was obtained by LECO CHNS-932 elemental analyser.

TGA Experiments

Thermogravimetric (TGA) and derivative thermogravimetric (DTG) analysis of the waste materials OR and RPF were conducted by TG analyzer (Seiko SII TG/DTA 7200) under 100 mL/min nitrogen gas flow, heated from 20 to 1000°C. Heating rates of 10-30-50°C min⁻¹ were used during the experiments. The replication of the experiment has been carried out for three times for each sample to reduce the experimental errors. Standard deviation in the experiments was ± 5 .

Kinetic Model

Kinetics of biomass pyrolysis rely on the reaction temperature on decomposition characteristics with respect to time. Arrhenius relation, $k(T)$ is generally expressed as given below;

$$k(T) = A \exp(-E/RT) \quad \dots (1)$$

where $T(K^{-1})$ is temperature, $k(T)$ is the reactivity, $A(s^{-1})$ is the pre-exponential factor, $E_a (Jmol^{-1})$ describes the activation energy and $R (8.314 KJmol^{-1} K^{-1})$ represents the gas constant. Thermal degradation kinetics is derived from the equation;

$$d\alpha/dt = k(T)f(\alpha) \quad \dots (2)$$

$$d\alpha/dt = A \exp(-E/RT) f(\alpha) \quad \dots (3)$$

where t denotes time, $f(\alpha)$ is function of the reaction which depends on the rate of conversion α

The conversion term is expressed as;

$$\alpha = (W_0 - W_t) / (W_0 - W_f) \quad \dots (4)$$

where W_0 is the initial and W_f is the final weight of the sample. W_t denotes the sample weight at temperature T .

Heating rate $\beta (Kmin^{-1})$ is defined as;

Table 1 — Proximate and ultimate analysis of OR, and RPF samples		
Proximate analysis (as received basis) wt. %	OR	RPF
Moisture	6.54	0.62
Volatile Matter	76.12	87.19
Ash	4.19	0.04
Fixed Carbon	13.15	12.15
Ultimate analysis (dry basis) wt. %		
C	49.62	62.80
H	7.15	4.30
N	1.06	0.07
S	0.14	0.04
O	43.03	32.79

$$\beta = dT/dt \quad \dots (5)$$

Equation (2) can be transformed into;

$$d\alpha/dt = (A/\beta) \exp(-E/RT) f(\alpha) \quad \dots (6)$$

$f(\alpha)$ is described in the integrated form of as;

$$G(\alpha) = \int d(\alpha)/f(\alpha) = (A/\beta) \int \exp(-E/TR) dT \quad \dots (7)$$

Iso-conversional methods provide feasible estimation of activation energy due to their high validity for model-free approaches. Flynn-Wall-Ozawa (FWO) method provides a linear correlation at different heating rates. FWO kinetic method is described as^{18,19};

$$\ln\beta = \ln [(AE_a)/(Rg(\alpha))] - 5.331 - 1.052 (E_a/TR) \quad \dots (8)$$

E_a can be calculated from the $\ln\beta$ vs. $1/T$ plot for a given value of conversion. The slope of the plot is equal to $-1.052 E_a/R$. The pre-exponential factor (A), Enthalpy (ΔH), Gibbs free energy (ΔG), and entropy (ΔS) were determined from equation given below;

$$A = \beta E_a \exp(E_a/(RT_{max}))(1/(RT_{max}^2)) \quad \dots (9)$$

$$\Delta H = E_a - RT \quad \dots (10)$$

$$\Delta G = E_a + RT_{max} \ln [(k_b T_{max})/(hA)] \quad \dots (11)$$

$$\Delta S = (\Delta H - \Delta G)/T_{max} \quad \dots (12)$$

where T_{max} is the peak temperature, K_B is the Boltzmann constant ($1.381 \times 10^{-23} \text{ JK}^{-1}$) and h is the Plank constant ($6.626 \times 10^{-34} \text{ Js}$).

Results and Discussion

Thermal degradation process and mechanism of the pyrolysis reaction of solid fuels can be comprehensively examined by TGA method. The mass loss of the sample with respect to temperature indicated by the TG curves and the corresponding mass loss rates were obtained by the derivative-TG curves. Pyrolytic behaviours of the OR and RPF were illustrated Fig. 2 under different heating conditions. Thermal decomposition of OR and RPF were obtained to be different from each other. As can be seen from the figure, thermal decomposition of OR occurred at lower temperatures than RPF. This can be attributed to complicated structure of biomass compared to polyester. Polyester fabric has much lower moisture content than biomass, hence its decomposition occurs rapidly at higher temperatures compared to biomass. Devolatilization of OR has seen to occur in 200–400°C temperature range, whereas devolatilization of RPF occurred at higher temperatures, in between 300 and 500 °C.

Devolatilization of polyester at higher temperatures was also observed for other plastic materials²⁰. In the derivative-TG curve of biomass, the peak in between 200-400°C was associated with hemicellulose and cellulose decomposition and the peak in the shoulder shape seen in between 400-550°C represented lignin decomposition, which decomposes in a longer temperature range. 10-40% product yield has obtained after OR pyrolysis. The effect of heating rate on pyrolysis was also demonstrated in Fig. 2. The figure has shown shifting of maximum temperature to higher values with increasing the heating rate. Thermal degradation of RPF has seen to start at 385°C and has reached to maximum at 440°C^{21,25}

Theoretical and experimental co-pyrolysis data revealed that some positive synergy occurred between the OR and RPF. Different results were obtained from individual materials due to synergic interactions. As seen from the TG data in Fig. 3, weight loss during co-pyrolysis was greater than the theoretical mean values, which are calculated from single fuels.

Figure 4 shows the data fitting of DTG plots of OR and RPF with Flynn-Wall-Ozawa (FWO) method. Calculated kinetic parameters are shown in Table 2. Activation energy (E_a) which can be defined as the minimum amount of energy required to start a reaction or in other terms reactivity of the fuel¹². As can be seen from Table 2, activation energy has increased with conversion due to presence of endothermic reactions. The addition of biomass in

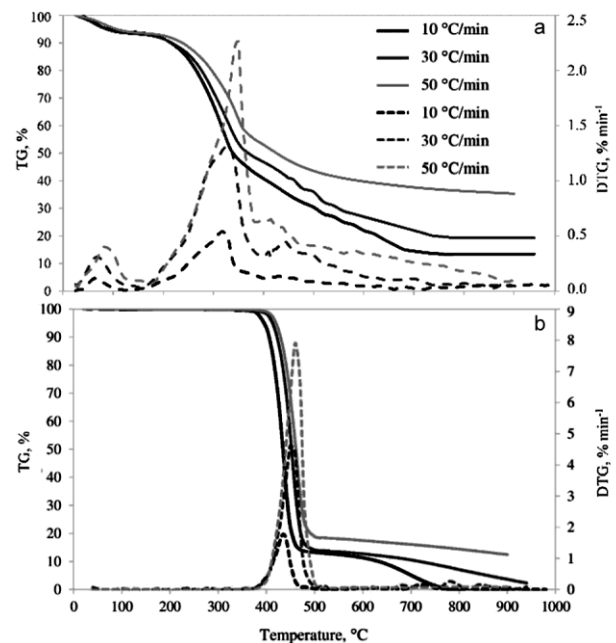


Fig. 2 — TG and DTG curves of (a) OR and (b) RPF

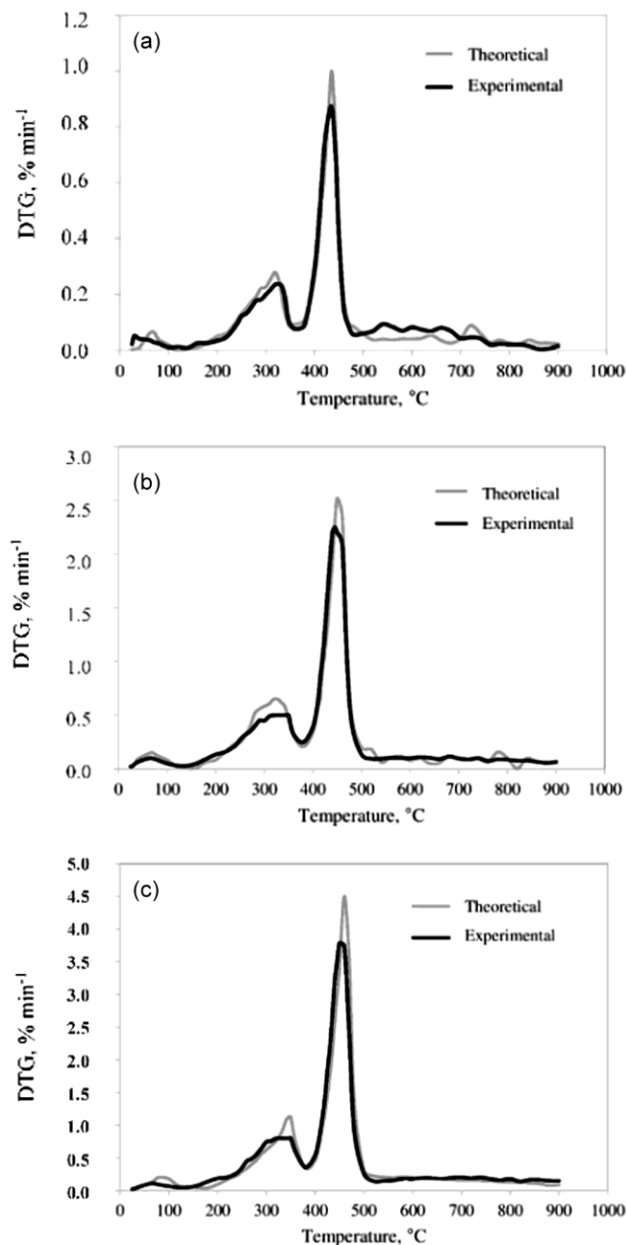


Fig. 3 — Comparison of theoretical and experimental results of OR/RPF co-pyrolysis at different heating rates (a) $10\text{ }^{\circ}\text{C min}^{-1}$, (b) $30\text{ }^{\circ}\text{C min}^{-1}$ and (c) $50\text{ }^{\circ}\text{C min}^{-1}$.

pyrolysis of polyester appreciably decreased the activation energy.

As shown in Table 2, R^2 of the curves changes in interval of 0.9914 to 1.000. This indicated well-correlation of pyrolysis with FWO method. Activation energy changes with conversion degrees suggested complication of the pyrolysis and co-pyrolysis processes. The apparent activation energy of RPF has found to reduce during co-pyrolysis, which is an

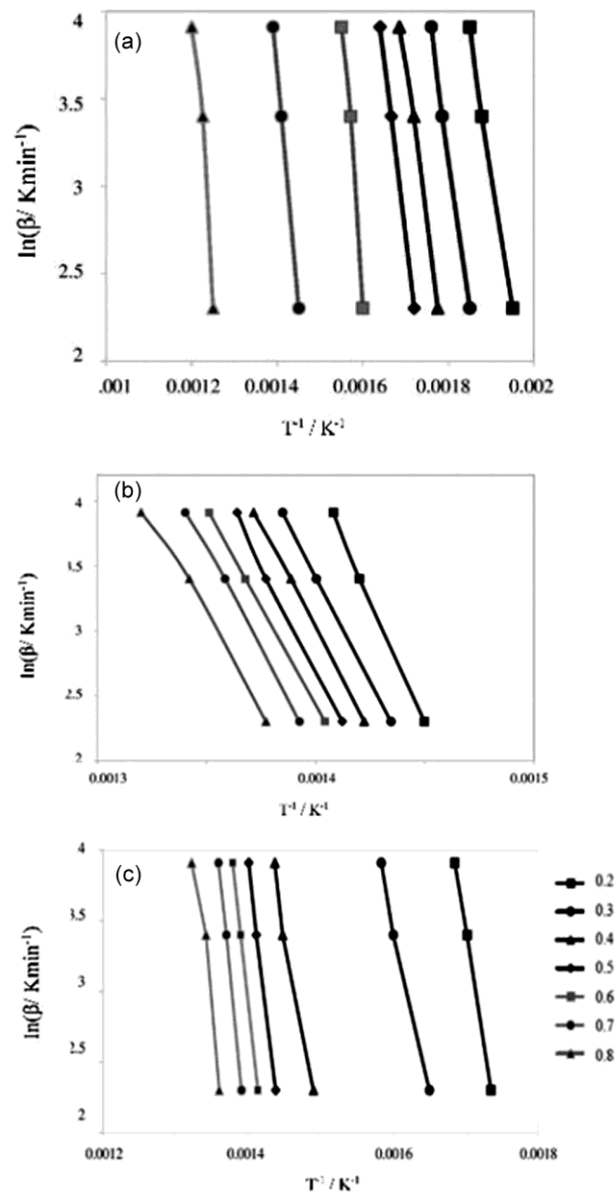


Fig. 4 — Linear correlation for determining E_a of (a) OR, (b) RPF and (c) OR/RPF Blend.

indicative of decrease in energy consumption. The non-additive behaviour of DTG curves obtained from comparison of experimental and theoretical activation energies revealed occurrence of synergy during co-pyrolysis process. Biomass and polyester co-pyrolysis has shown to form synergic effect in many studies²²⁻²⁵.

Thermodynamic parameter have presented in Table 2. Activation energy obtained from FWO methods were used in determination of the other thermodynamic parameters. Enthalpy (ΔH) term

Table 2 — Kinetic Parameters for the pyrolysis of OR, RPF and their blend

Sample	Conversion	$E_a(kJmol^{-1})$	$A (s^{-1})$	R^2	$\Delta H (kJ mol^{-1})$	$\Delta G (kJ mol^{-1})$	$\Delta S (Jmol^{-1} K^{-1})$
OR	0.2	133.16	4.73×10^8	0.9945	127.83	187.71	-93.50
	0.3	150.02	1.27×10^{10}	0.9953	144.7	187.08	-66.18
	0.4	157.59	5.51×10^{10}	0.9914	152.26	186.81	-53.96
	0.5	214.78	3.48×10^{15}	0.9965	209.46	185.17	37.93
	0.6	257.01	1.15×10^{19}	0.9988	251.68	184.21	105.36
	0.7	256.69	1.09×10^{19}	0.9995	251.37	184.22	104.86
	0.8	253.3	5.68×10^{18}	0.9931	247.98	184.29	99.45
RPF ²⁵	0.2	301.98	2.04×10^{25}	0.9989	296.08	218.57	109.22
	0.3	255.84	6.92×10^{16}	1.0000	249.94	167.25	116.53
	0.4	251.89	3.50×10^{16}	0.9995	245.99	167.34	110.83
	0.5	260.83	1.64×10^{17}	0.9977	254.93	167.15	123.70
	0.6	239.19	3.85×10^{15}	1.0000	233.29	167.65	92.51
	0.7	244.90	1.04×10^{16}	0.9988	239.00	181.07	81.62
	0.8	224.93	3.23×10^{14}	0.9942	219.03	168.00	71.90
Blend (1:1 wt %)	0.2	236.70	2.97×10^{25}	0.9953	232.90	127.62	230.88
	0.3	197.18	7.36×10^{25}	0.9957	193.39	128.31	142.71
	0.4	212.99	5.14×10^{22}	0.9932	209.20	128.02	178.01
	0.5	236.70	2.97×10^{25}	0.9946	232.90	127.62	230.88
	0.6	252.32	1.95×10^{27}	0.9952	248.53	127.48	265.68
	0.7	247.25	5.02×10^{26}	0.9937	243.46	127.46	254.39
	0.8	238.89	5.35×10^{25}	0.9913	235.10	127.59	236.77

describes the amount of energy required for structural degradation of solid fuel. Enthalpy has obtained to increase with the degree of conversion. Low differences in activation energy and enthalpy values denote high feasibility of the pyrolysis and co-pyrolysis processes. Pre-exponential factor (A) is a key parameter to explain the reaction chemistry during optimizing the pyrolysis process. Lower values of A ($<10^9$) suggest formation of surface reaction, however the pre-exponential factor values in this study have found to be greater than 10^9 , which have indicated the complexity of the degradation process of waste materials under consideration.²⁴The indicator of degree of system disorder is defined by entropy term. During OR pyrolysis entropy has increased with the degree of conversion, which was attributed to the high reactivity of the system that accelerates formation of activated complex^{6,15,26}. The amount of available energy upon pyrolysis and co-pyrolysis can be described by Gibb's free energy (ΔG).The calculated values of ΔG have shown that OR/RPF blend has high remarkable potential for bioenergy production.

Conclusion

The results of this study revealed that co-pyrolysis of recycled polyester fabric and olive residue is beneficial for energy production. TGA-DTG plots of OR/RPF blend show synergistic effect during pyrolysis of OR/RPF blend. The activation energies calculated by FWO method were obtained as 203.22,

254.22 and 231.72 $kJmol^{-1}$ for OR, RPF and their blend, respectively. The FWO kinetic model described by one reaction could be used as a first approximation of thermal decomposition of OR/RPF pyrolysis. Thermodynamic parameters signify the potential of the blend to contribute sustainable energy production.

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