



## Thermal analysis and kinetics of biomass samples

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### ABSTRACT

In this research, combustion behavior of agricultural residues known as miscanthus, poplar wood, and rice husk was investigated using thermal analysis techniques. Differential scanning calorimeter (DSC) and thermogravimetry (TG-DTG) techniques were used. Combustion experiments were performed at five different heating rates (5, 10, 15, 25, and 50 °C/min). The reaction regions, ignition and burnout temperatures, heat flow rate values of biomass samples are determined. Activation energy of the biomass samples are calculated using three different iso-conversional methods. It is observed that all three agricultural residues show similar combustion characteristics. The results indicate that the reactivity of biomass fuels is due to the combustion of light compounds; however the energy release from biomass fuels is mainly due to the combustion of fixed carbon.

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### 1. Introduction

The energy issue is an extensively discussed subject. The concerns about the future of energy supply are increasing. The use of agricultural wastes can assist in addressing these concerns, especially for those countries having such resources. In different regions of the world, there are many agricultural wastes. There are more than 3000 biomass power plants worldwide with a capacity of more than 40,000 MW with generating capacities between 1 and 80 MW due to the limited availability of biomass fuels within an economical shipping distance [1]. The utilized biomass fuels are agricultural residues and energy crops. Rice husk is one of the common agricultural residues in Turkey. Miscanthus and poplar are promising energy crops which can be grown to provide energy in power plants. The utilization of these residues in existing thermal power plants or new plants can help for the energy supply of Turkey or countries having such biomass resources.

There are many published articles on the pyrolysis of biomass samples; however publications on the combustion of different biomass fuels are limited, especially for the combustion of miscanthus, poplar, and rice husk using DSC and TGA. Mansary and Ghaly [2] studied the combustion of rice husk in air atmosphere. They observed two reaction regions and relatively higher ash content for rice husk. Biagini et al. [3] investigated the devolatilization kinetics of rice husk and they characterized the rice husk as high volatile matter with relatively higher ash which

can be a possible renewable alternative energy source. Karampinis et al. [4] investigated the combustion properties of miscanthus and poplar. They characterized miscanthus and poplar as reactive fuels with high volatile matter and low ash content properties. Kok et al. [5–7] applied differential scanning calorimeter (DSC) and thermogravimetry (TG-DTG) on combustion of different origin fossil fuel samples. Reaction regions and mechanisms, effect of heating rate, metallic additives and clay content on the kinetics of the fossil fuel samples were studied. Özgür et al. [8] performed combustion tests on miscanthus and poplar and they observed that the combustion of those biomass fuels is highly exothermic and can serve as an appropriate fuel feedstock.

Since there is limited research on combustion characteristics of miscanthus, poplar, and rice husk, this study was performed to generate miscanthus, poplar, and rice husk combustion data and to comment on those biomass fuels' applicability to biomass combustion.

### 2. Materials and methods

The combustion experiments were performed using differential scanning calorimeter (DSC) and thermogravimetry (TG-DTG). The biomass samples used in this research is prepared according to the ASTM Standards (D 2013–72). The experiments are carried out with the powdered sample (~10 mg) whereas the air flow rate (50 ml·min<sup>-1</sup>) was kept constant during the experiments. All the experiments were conducted in the temperature range of 20–600 °C at five different heating rates as 5, 10, 15, 25, and 50 °C min<sup>-1</sup>. Experiments were performed twice to ensure repeatability and experiments showed good repeatability with standard errors ±1 °C (within a confidence interval of 95%). Properties of biomass fuels are given in Table 1.

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**Table 1**  
Proximate and ultimate analysis of biomass samples.

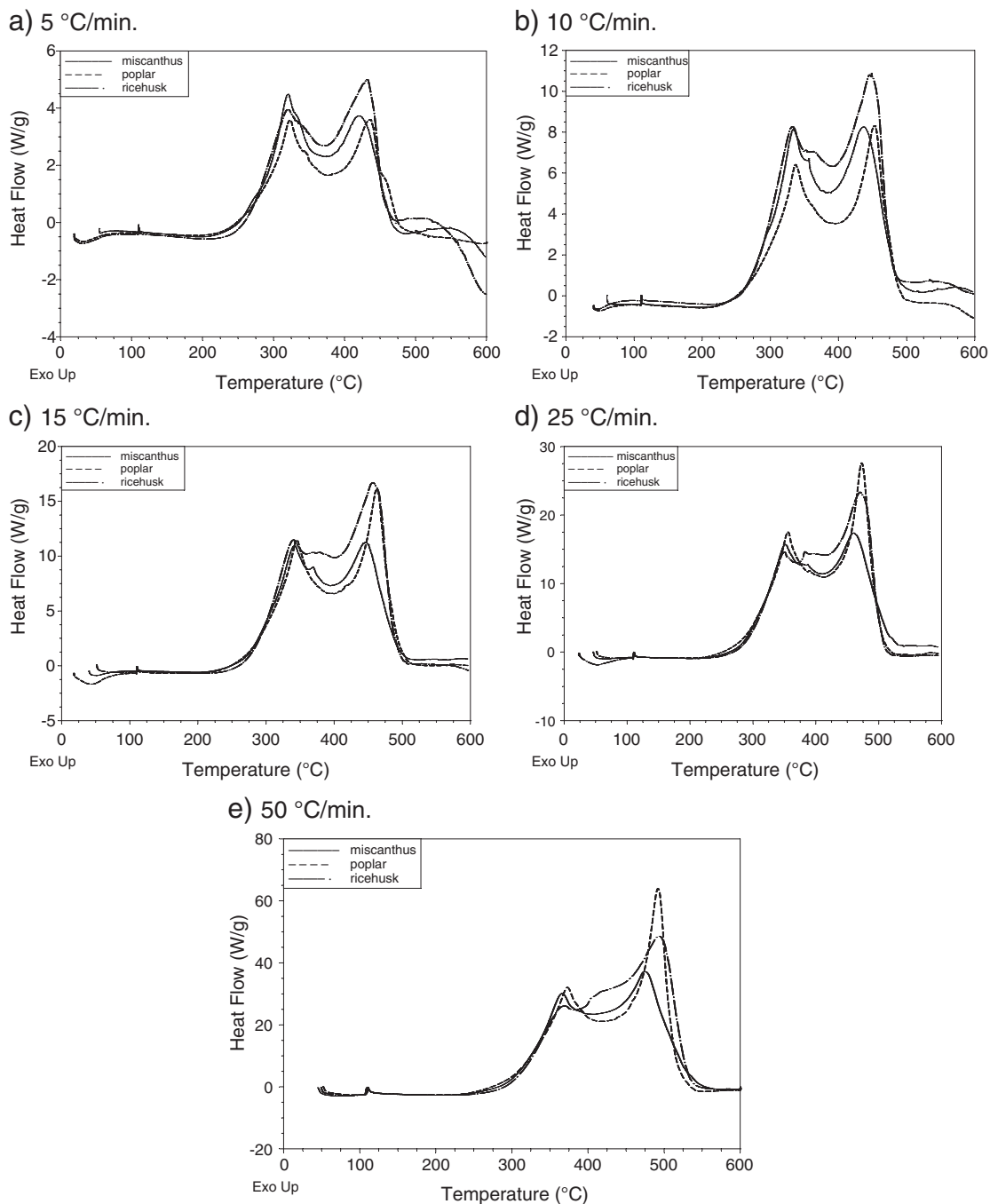
Proximate analysis					
Sample	Moisture cont. (%)	Volatile matter (%)	Fixed carbon (%)	Ash content (%)	
Miscanthus	2.0	80.5	16.0	1.5	
Poplar wood	1.0	74.0	24.0	1.0	
Rice husk	2.4	64.1	22.4	11.1	
Ultimate analysis					
Sample	C (%)	H (%)	N (%)	S (%)	O (diff.) (%)
Miscanthus	45.52	5.93	0.13	0.10	48.32
Poplar wood	45.44	6.03	0.36	0.09	48.08
Rice husk	41.15	5.42	0.29	0.13	53.01

### 3. Results and discussion

Theoretically, combustion of biomass fuel can be initiated whenever oxygen comes in contact. Temperature, composition of the biomass fuel and the air supply dictate the nature of combustion process.

In differential scanning calorimeter (DSC) and thermogravimetry (TG-DTG) experiments, two different exothermic reaction regions were observed (Figs. 1 and 2). First region is due to the combustion of light volatile matters which provides reactivity of biomass fuels. Second region represents the combustion of fixed carbon. It is observed that as heating rate increases, the starting and end point temperature of interval increases due to thermal lag (Table 2).

In differential scanning calorimeter (DSC) experiments, the first shoulder is due to the combustion of light volatile matters which



**Fig. 1.** DSC curves of biomass samples at different heating rates.

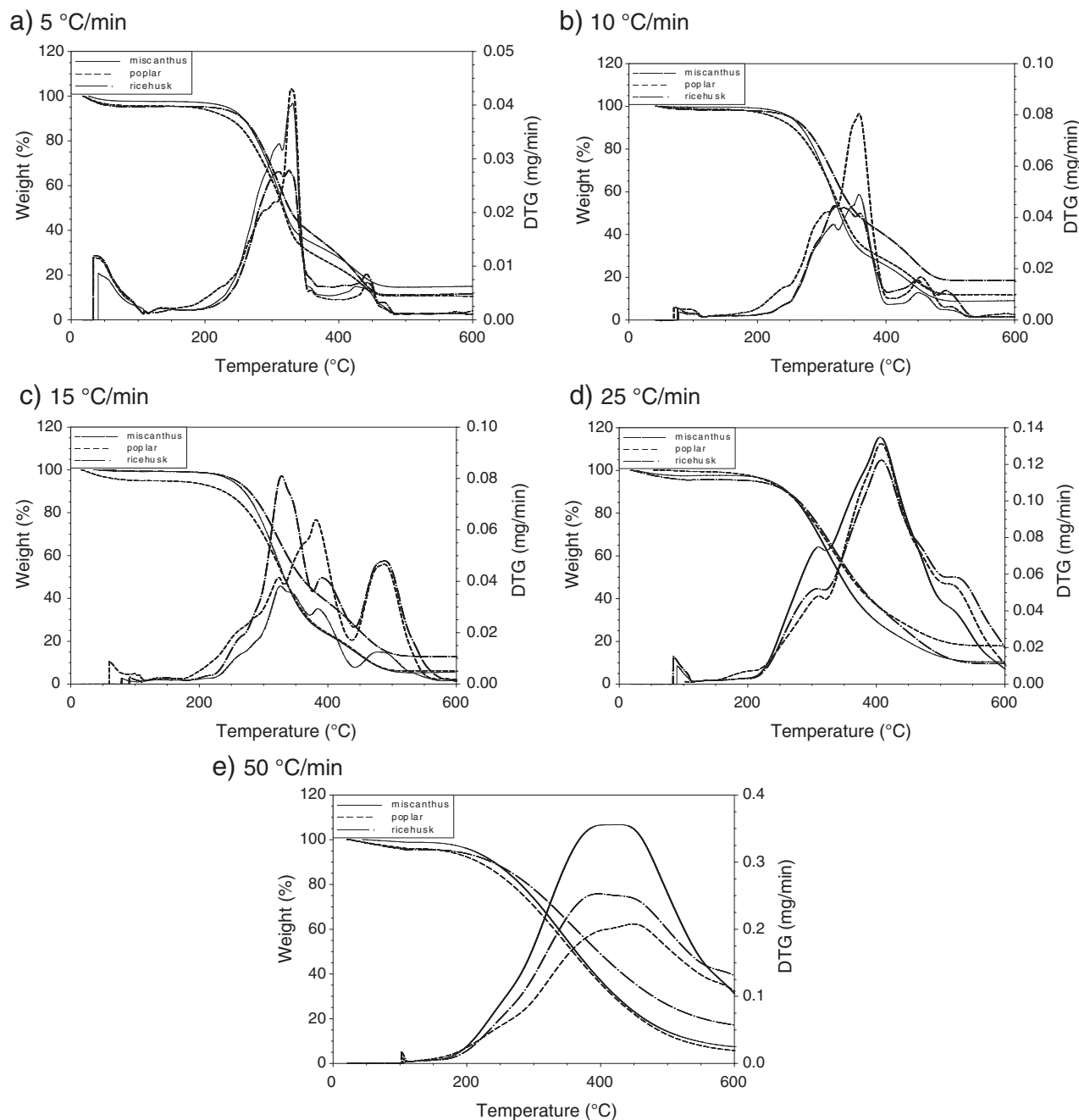


Fig. 2. TG–DTG curves of biomass samples at different heating rates.

provides reactivity of biomass fuels. Second shoulder is caused by the combustion of fixed carbon. The ignition and burnout temperatures were obtained from DSC profiles of biomass samples to characterize the samples, which can give clues about the combustion behavior of samples. The change of ignition and burnout temperature of biomass fuels with respect to heating rate were presented in Fig. 3. Among the tested samples, rice husk has the highest ignition temperature. Miscanthus and poplar have very close ignition temperature values although poplar has a slightly lower ignition temperature. Although poplar has a lower volatile matter content compared to that of miscanthus, combustion of poplar begins very slightly earlier. This can be probably due to the volatile matter in poplar that includes higher organic matter and lower chemisorbed water. The burnout temperature of rice husk is higher than the other fuels due to the higher ash content which characterizes the burnout process.

In thermogravimetry (TG–DTG) experiments, there are two main reaction regions during the combustion of biomass samples. Combustion of volatiles and devolatilization take place which are more reactive parts and later on combustion of more complex and thermally stable structures and char forming reactions take place. The reactivity of combustion regions is proportional with the height of DTG peak.

The heat liberated during the combustion of biomass samples at different heating rates that is based on the area under DSC curve is also determined and presented in Fig. 4. Since the mass loss occurs continuously during the combustion reaction, the values can be used only for comparison among different biomass samples. It was observed that as heating increases, there is a tendency that heat liberated from reaction decreases due to the long exposure time of samples to heater so that bonds are cracked easily. It was also observed that the heat liberated from rice husk is slightly higher than the other samples at high

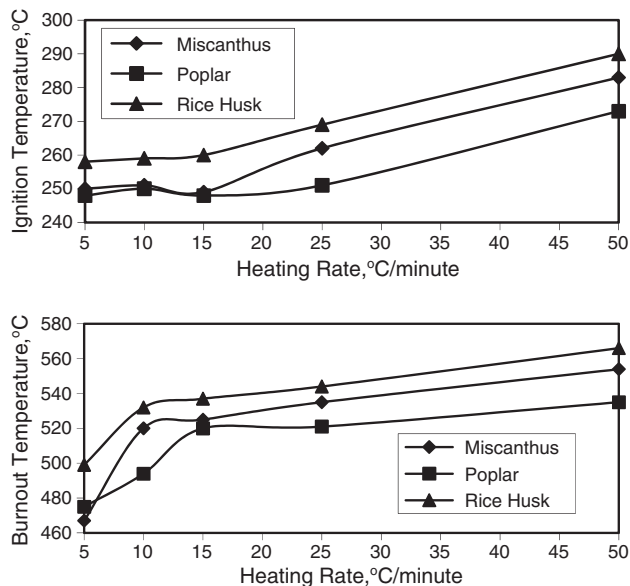
**Table 2**  
Reaction regions of biomass samples at different heating rates.

Samples	Reaction type	5 °C/min.	10 °C/min.	15 °C/min.	25 °C/min.	50 °C/min.
<i>DSC</i>						
Miscanthus	Combustion of light volatiles	250–374	251–385	252–396	262–410	283–412
	Combustion of heavy volatiles	374–467	385–520	396–525	410–535	412–554
Poplar	Combustion of light volatiles	248–376	249–394	250–400	251–413	273–420
	Combustion of heavy volatiles	376–475	394–494	400–520	413–521	420–535
Rice husk	Combustion of light volatiles	258–372	259–392	260–400	269–415	290–420
	Combustion of heavy volatiles	372–499	392–532	400–537	415–544	420–566
<i>TG-DTG</i>						
Miscanthus	Combustion of light volatiles	233–368	244–381	246–399	255–425	280–410
	Combustion of heavy volatiles	368–478	381–522	399–531	425–542	410–575
Poplar	Combustion of light volatiles	233–380	238–391	239–402	245–423	265–425
	Combustion of heavy volatiles	380–469	391–505	402–520	423–551	425–585
Rice husk	Combustion of light volatiles	242–367	252–380	253–396	255–415	275–420
	Combustion of heavy volatiles	367–485	380–525	396–542	415–562	420–595

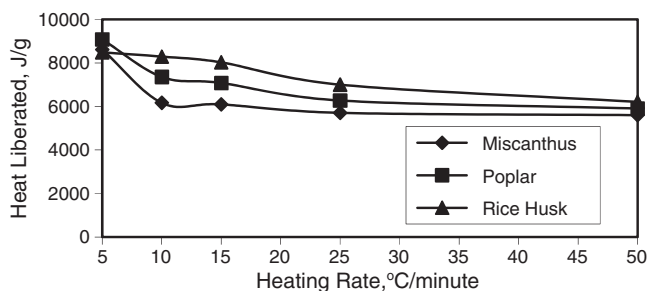
heating rates although carbon and hydrogen contents of rice husk are lower than other samples. This is most probably due to the short contact of miscanthus and poplar with heater at high heating rates which prevents the breaking of bonds completely.

### 3.1. Kinetic analysis

The non-isothermal kinetic study during a combustion process is extremely complex, because of the presence of numerous components and their parallel and consecutive reactions.



**Fig. 3.** Ignition and burnout temperature of biomass samples at different heating rates.



**Fig. 4.** Heat liberated from biomass combustion at different heating rates.

To obtain activation energies of combustion reactions; Ozawa–Flynn–Wall, Kissinger, and ASTM I-II iso-conversional kinetic methods were used.

For Ozawa–Flynn–Wall method [9], several TG–DTG curves are used simultaneously to determine the activation energy values of biomass samples. The TG–DTG curves move to higher temperatures with increasing heating rates. At the same conversion levels, the following relationship is used where activation energy is obtained from the slope of the plot  $\log(\beta)$  vs.  $1/T$  at given conversion levels.

$$[d(\log\beta)/d(1/T)] = 0.4565(E/R) \quad (1)$$

where:  $E$  = activation energy in J/mol,  $R$  = ideal gas constant = 8.314 Jmol<sup>-1</sup> K<sup>-1</sup>,  $T$  = temperature in K (Kelvin = °C + 273) corresponding to the measured heating rate at same conversion,  $\beta$  = heating rate in °C/min.

In Kissinger method [10], the peak temperature from the DSC curve and heating rate for several thermal analysis curves are correlated and the activation energy can be calculated based on the following equation. In this method, activation energy is calculated from the slope of the plot  $\ln(\beta/T_p^2)$  vs.  $1/T_p$ .

$$\left[ \frac{d(\ln\beta/T_p^2)}{d(1/T_p)} \right] = -(E/R) \quad (2)$$

where:  $E$  = activation energy in J/mol,  $R$  = ideal gas constant = 8.314 Jmol<sup>-1</sup> K<sup>-1</sup>,  $T_p$  = peak temperature in K (Kelvin = °C + 273),  $\beta$  = heating rate in °C/min.

In ASTM methods [11], the reciprocal of temperatures at which the reaction peaks occur are plotted as a function of the log of respective heating rates. In this method, trial and error procedure is used and the activation energy is calculated based on the following equation.

$$E = -2.19R[d(\log_{10}\beta)/d(1/T)] \quad (3)$$

The obtained activation energy values those obtained from three different methods are given in Table 3. It is observed that as ignition temperature of the sample increases, the activation energy for the

**Table 3**  
Activation energy (kJ/mol) values of biomass samples.

Sample	Ozawa–Flynn–Wall	Kissinger	ASTM I	ASTM II
Miscanthus	229.4	135.8	143.2	141.3
Poplar wood	219.2	129.2	138.1	131.9
Rice husk	250.3	145.8	158.7	148.6

combustion of the sample also increases. The sequence of activation energies showed parallel distribution with that of ignition temperatures (Table 3). In general, it is difficult to report specific activation energy of solid fuel combustion reactions since each kinetic method may give different results. Solid fuels are not homogeneous and the results are sensitive to experimental conditions, material characteristics and the kinetic methods used in the calculation. Thus the results can vary accordingly. Therefore, instead of focusing on an activation energy value, one should be interested in the comparative values when using the same kinetic method [12].

#### 4. Conclusions

In this research combustion characteristic tar sand samples were investigated using differential scanning calorimeter (DSC) and thermogravimetry (TG–DTG) at different heating rates. The following conclusions were derived from the research conducted.

- It is found that the biomass samples have two-stage of combustion. In the first stage, the combustion of the light volatiles occurred in the region of 250 °C to 400 °C and in the second stage; the combustion of fixed carbon took place in the region between 400 °C and 500 °C, depending on the biomass sample and heating rate.
- Ignition temperature and burnout temperature of biomass samples are found to increase with increasing heating rate. It is observed that the reactivity of biomass fuels is due to the combustion of light volatiles; however the energy release of biomass fuels is mainly due to the combustion of fixed carbon.

#### Nomenclature

DSC	Differential scanning calorimeter
DTG	Derivative thermogravimetry
E	Activation energy, kJ/mol

mg	Milligram
min	Minute
MW	Megawatt
R	Ideal gas constant, 8.314 Jmol <sup>-1</sup> K <sup>-1</sup>
T	Temperature, K (Kelvin = °C + 273)
TGA	Thermogravimetric Analyzer
p	Peak
β	Heating rate, °C/min.

#### References

- [1] S.V. Loo, J. Koppejan, The Handbook of Biomass Combustion of Co-firing, Earthscan, 2008.
- [2] K.G. Mansaray, A.E. Ghaly, Determination of reaction kinetics of rice husks in air using thermogravimetric analysis, Energy Sources 21–10 (1999) 899–911.
- [3] E. Biagini, A. Fantei, L. Tognotti, Effect of the heating rate on the devolatilization of biomass residues, Thermochemica Acta 472 (2008) 55–63.
- [4] E. Karampinis, D. Vamvuka, S. Sfakiotakis, P. Grammelis, G. Itskos, E. Kakaras, Comparative study of combustion properties of five energy crops and Greek lignite, Energy & Fuels 26–2 (2012) 869–878.
- [5] M.V. Kok, O. Karacan, Pyrolysis analysis and kinetics of crude oils, Journal of Thermal Analysis and Calorimetry 52 (1998) 781–788.
- [6] M.V. Kok, O. Karacan, R. Pamir, Kinetic analysis of oxidation behaviour of crude oil SARA constituents, Energy & Fuels 12–3 (1998) 580–588.
- [7] M.V. Kok, C. Keskin, Comparative combustion kinetics for in-situ combustion process, Thermochemica Acta 369–2 (2001) 143–147.
- [8] E. Özgür, B.G. Miller, S.F. Miller, M.V. Kok, Thermal analysis of co-firing of oil shale and biomass fuels, Oil Shale 29–2 (2012) 190–201.
- [9] J. Kaloustian, T.F. El-Moselhy, H. Portugal, Chemical and thermal analysis of the biopolymers in thyme, Thermochemica Acta 401 (2003) 77–86.
- [10] H.E. Kissinger, Reaction kinetics in differential thermal analysis, Analytical Chemistry 29–11 (1957) 1702–1706.
- [11] ASTM - E698-05. Standard test method for Arrhenius kinetic constants, <http://dx.doi.org/10.1520/E0698-05>.
- [12] P.J. Haines, Principles of Thermal Analysis and Calorimetry, Royal Society of Chemistry, 2002.