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Combustion of Turkish lignites and olive residue: Experiments and kinetic modelling

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HIGHLIGHTS

- Combustion characteristics of two lignites and a biomass are investigated.
- Lignites present lower reactivity and combustibility compared to the biomass.
- Lignites present higher burnout temperatures compared to the biomass.
- Tunçbilek lignite presents the highest apparent activation energy.
- Soma lignite and olive residue had similar apparent activation energy values.
- Increasing heating rate increased combustibility and burnout temperatures.

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ABSTRACT

This study investigated the combustion behavior and kinetics of Turkish fuels. Two lignite coals from Tunçbilek and Soma region, and olive residue, were used, all within a size range of 106–125 μm. Experiments were performed in a thermogravimetric analyzer (TGA) coupled with a differential thermal analyzer (DTA), under three different heating rates, namely 15, 20, and 40 °C/min. Based on the weight loss (TG) and derivative weight loss (DTG) curves, the characteristic temperatures were determined, three different conversion stages were identified, and a combustibility index was calculated for the major stage of combustion. In addition, combustion kinetics parameters of each fuel were determined using the Coats-Redfern method. Experimental results revealed that all three fuels went through a decomposition stage followed by the combustion stage(s). Tunçbilek and Soma lignite had one major combustion stage at an approximate peak temperature of 500 °C, while olive residue had two distinct stages for combustion at peak temperatures of 290 °C and 423 °C. Burnout temperatures of olive residue were always lower than either of the lignites, and an increase in heating rate from 20 to 40 °C/min shifted the burnout to higher temperatures. Combustibility index of lignites was similar at low heating rates, whereas at higher heating rates the combustibility of Tunçbilek was approximately twice that of Soma lignite. Olive residue presented values of combustibility which were at least fivefold those of the lignites. During the major stage of combustion and at 20 °C/min, Tunçbilek lignite had the highest apparent activation energy of approximately 100 kJ/mol, while Soma lignite and olive residue had similar apparent activation energies of approximately 40 kJ/mol. Increasing heating rate clearly increased the reactivity, combustibility, and burnout temperatures of all fuel samples. Apparent activation energies decreased with a shift in the heating rate from 20 to 40 °C/min, whereas between 15 and 20 °C/min the values were approximately constant.

1. Introduction

The abundance of low quality coals and solid waste biomass and subsequent low prices generates a high interest in the large scale burning of these fuels. Turkey presents a large extraction of lignite coal (~30% of the total primary energy supply in 2014),

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and abundant biomass residues as a consequence of a strong agricultural production [1]. In Turkey, legislation has been enacted to prevent the burning of solid biomass waste in open-air burn pits or domestic stoves, prompting the large-scale burning of these fuels [2]. Turkish lignite coals are characterized by a low fixed carbon content, high ash and moisture content, and high sulphur content. Agricultural solid waste biomass typically present high volatile matter content, low calorific value, and high content of alkali metals. The high amount of sulphur and alkali metals contribute largely to the formation of ash deposits in superheater tubes and the adherence of low melting point fly ash to the surfaces of the boiler, whereas the high ash and moisture content may originate difficulties in flame stabilization [3,4]. Whereas individual burning of these fuels can be problematic, co-firing lignite with biomass presents considerable advantages that include an increase on the overall reactivity of the combustion process [4], and the reduction on the emission of pollutants [2]. In addition, it is relatively easy to retrofit existing pulverized coal boilers to burn coal and/or biomass [5]. Nonetheless, the retrofitting of the boiler is likely to introduce changes in the fluid dynamics and temperature distribution in the near burner region, and a good knowledge of the burning characteristics of the fuels becomes crucial to ensure flame stabilization along with a sufficient residence time to minimize pollutant emissions. Studies focused on coal [6–13] and biomass [9,10,13–20] have provided relevant fundamental data for fuel characterization. Within this scope, thermogravimetric techniques have been applied to characterize the combustion process of Turkish lignites and biomass [21–27], although most studies fail to fully characterize the combustion behavior.

Empirical methods are commonly applied to determine the characteristic temperatures that describe the combustion process (decomposition temperature, ignition temperature, peak(s) temperature(s), and burnout temperature). The ignition of biomass typically occurs in the interval 200–250 °C [21,23], regardless of the biomass type, whereas lignites tend to ignite at temperatures within 200–300 °C, depending on the volatile matter content [8,13,21,27,28]. After ignition, the majority of low rank coals and biomass undergo devolatilization and volatile combustion during the first weight loss stage (200–400 °C), followed by char combustion above 500 °C [9,22,26]. For some low rank coals, however, combustion takes place in one single stage [22,28]. Biomass fuels generally experience burnout at temperatures ranging from 500 to 600 °C [23,26], and less frequently up to 800 °C [22]. The burnout temperatures of lignite coals burning in air are typically in the order of 500–600 °C [11,21,25,27], but can also reach 750 °C [24].

In what respects the kinetic modelling of the combustion of solid fuels, authors typically choose either model-free or model-fitting methods. Model free methods can be preferable to avoid modelling of complex reaction mechanisms. Since the chemical kinetic parameters are determined without using any specific model, the eventual errors which may arise from the selection of the reaction model are suppressed. Within the model-free methods, the isoconversional methods such as the Kissinger-Akahira-Sunose (KAS) [14,15,29], the Flynn-Wall-Ozawa (FWO) [6,14,15], or the Friedman method [6,15,18] are largely applied to determine the activation energy as a function of the conversion. In model-fitting, different models are fit to the experimental data and the model which gives the best statistical fit is selected to evaluate the kinetic parameters [9]. Examples of model-fitting methods are the ones developed by Coats and Redfern [30], Freeman and Carroll [31], and Duvvuri et al. [32]. Model-fitting methods are usually easy to apply and enable a better insight into the reaction mechanisms responsible for each stage of combustion. The nucleation models [14,33]; reaction order and geometrical contraction models [9,14,33]; and diffusion models [9,33] are the most commonly applied.

The present study focused on the analysis of the combustion characteristics and kinetics of three different fuels of Turkish origin: two lignites from Tunçbilek and Soma regions, and one olive residue from Balıkesir region. Thermogravimetric analysis was undertaken under different heating rate conditions, to evaluate the influence of the fuel type and heating rate on the combustion behavior and combustion kinetics of Turkish fuels. The characteristic combustion temperatures and a combustibility index were calculated based on the TG/DTG profiles. Additionally, the apparent activation energies were calculated by means of a model-fitting approach and application of the Coats-Redfern method.

2. Methodology

2.1. Turkish fuels characterization

Three distinct Turkish fuels were studied: Tunçbilek (TL) and Soma (SL) lignites, and olive residue (OR). The two lignite coals had origin in the regions of Tunçbilek – Tavşanlı, Kütahya, and Soma-Manisa, and are extensively used in Turkey for electricity generation. Similarly, olive residue is an abundant agricultural residue in Turkey, and the sample used in this study had its origin in the region of Havran, Balıkesir. All samples were sieved down to a size range of 106–125 μm. Each fuel was fully characterized in terms of chemical composition. The proximate analysis was performed by thermogravimetry, and the ultimate analysis was obtained by a TruSpec CHN analyzer. The ash composition of each fuel sample was calculated by X-ray Fluorescence (XRF). The low heating value was calculated by means of a Leco AC 500 calorimeter. The results from proximate and ultimate analysis, ash analysis, and low heating value, are presented in Table 1. Tunçbilek lignite

Table 1
Elemental analysis of the studied fuels.

Parameter	OR	TL	SL
Proximate analysis (wt.%, dry basis)			
Volatile matter	78.7	35.6	38.7
Fixed Carbon[a]	19.0	46.9	32.0
Ash	2.3	17.5	29.3
Ash (upon re-evaluating, wt.%, dry basis)[b]	5.3	15.5	33.3
Ultimate analysis (wt.%, dry ash free)			
C	48.3	57.3	45.3
H	6.2	5.3	3.1
N	0.7	2.1	0.6
S	0.1	1.3	1.3
O[a]	44.7	34.0	49.7
Lignocellulosic composition[c] (wt.%, dry ash free)			
Hemicellulose	9.4	–	–
Cellulose	36.2	–	–
Lignin	54.3	–	–
Ash analysis (wt.%, dry basis)			
SiO_2	16.6	52.7	18.7
Al_2O_3	5.2	22.3	12.8
Fe_2O_3	3.2	15.2	5.2
CaO	26.8	1.5	52.1
SO_3	1.5	0.1	7.2
MgO	6.0	2.2	1.3
P_2O_5	14.3	0.5	0.4
K_2O	18.1	2.7	0.4
Na_2O	7.8	0.2	0.2
Cl	–	–	0.5
Other oxides	0.5	2.6	1.2
Low Heating value (MJ/kg)	18.6	24.1	13.4

[a] Calculated by difference.
[b] Values for lignite coals obtained according to ASTM D3174-12 Standard, and value for olive residue obtained according to the ASTM E1755-01 Standard.
[c] Lignocellulosic composition of olive residue was calculated according to Sheng and Azevedo [35].