Thermochemical Conversion Behavior of Turkish Lignite/Poppy Capsule Pulp Blends in N₂ and CO₂ Atmospheres

Isıl ISIK GULSAC

1 Tubitak Marmara Research Center, Energy Institute, p.k. 21 41470 Gebze Kocaeli, Turkey

Highlights

• Co-pyrolysis characteristics of two different Turkish lignites and a biomass were investigated.
• Kinetic parameters and decomposition products were obtained.
• Experimental data indicated a synergistic effect.

Abstract

In this study, Thermogravimetric Analyzer coupled with Fourier Transform Infrared Spectroscopy (TGA-FTIR) was used for the determination of the thermochemical conversion reactivity of two different types of Turkish lignite coal (Tunçbilek and Orhaneli-Gümüşpınar) and poppy capsule pulp (PCP) mixtures under pyrolysis conditions at nitrogen (N₂) and carbon dioxide (CO₂) atmospheres. Activation energies (Eₐ) and pre-exponential factors (A) were determined according to Coats-Redfern method and first-order reaction model. In CO₂ atmosphere, all samples exhibited an extra weight loss around 800 - 850 °C, different from the N₂ atmosphere, due to the reactive nature of CO₂ during thermal decomposition. FTIR analysis confirmed this finding, at high temperatures CO formation were observed in the CO₂ atmosphere. In all mixtures, the third zone experimental decomposition temperature is lower than that obtained theoretically in N₂ atmosphere, showing that there might a synergistic interaction between the PCP and the lignite samples. The Eₐ of PCP/Tunçbilek lignite mixtures are smaller than the Eₐ of their parent components indicating synergy in N₂ and CO₂ atmospheres. However, initial and maximum decomposition temperatures for the parent components remain unchanged for these mixtures. Moreover, especially at temperatures higher than 600 °C, Eₐ for biomass/lignite mixtures found lower than the theoretical values, due to the possible synergistic interactions between PCP and coal samples. According to FTIR analysis, CO, CH₄, CHₙ and ether/amine components were detected. Gaseous pyrolysis product compositions were highly dependent on temperature, and gas species formation was consistent with the weight loss of samples.

1. INTRODUCTION

Global energy needs will increase by 1.3% annually due to economic and population growth and will be approximately 30% more than today by 2035 [1]. This need is mainly provided from fossil-based energy sources that are known to cause environmental problems such as climate change and CO₂ emissions. Thus, the interest in renewable resources is increasing day by day. Renewable sources are expected to contribute to 25-33% of global energy supply by 2050 [2,3]. In Turkey, 50-65 Mtoe (million tons of oil equivalent) agricultural waste and 11.05 Mtoe animal waste are produced per year. Still, unfortunately, 60% of this waste is capable of being used for energy production. The energy that can be obtained from agricultural and animal wastes have the potential to meet Turkey’s 22-27% of the annual energy consumption [4]. Turkey is one of the primary producers of poppy (Papaver somniferum L) in the world, with the 53% share of the legal poppy cultivation area. This critical industrial plants’ seed is used for food purposes, and its capsule is the raw material of morphine and other alkaloids. Afyon Alkaloids Factory, located in Afyonkarahisar, Turkey, is the world’s largest factory with a poppy capsule processing capacity of 25,000 tons/year. Poppy capsule pulp (PCP) is the significant process waste of this factory; 20,000 tons of this material are produced per year [5]. Thus, the evaluation of this biomass for energy purposes is considered...
to be very necessary. However, there are a few studies on the thermochemical conversion of PCP. Hopa et al. studied the effects of temperature on bio-oil yield and its calorific value obtained from the pyrolysis of PCP in a fixed-bed reactor [6]. In another study, they investigated the pyrolysis and co-pyrolysis behavior and bio-oil yields of sugarcane bagasse, PCP, and rice husk mixtures in a fixed bed reactor [7].

Thermochemical conversion processes developed for coal and biomass mixtures can reduce fossil fuel consumption and contribute to the spread of commercial-scale applications of biomass. Pyrolysis is the primary step of all thermochemical processes, such as combustion, gasification, and liquefaction. Therefore, knowing the devolatilization behavior and reactivity of biomass/coal blends under pyrolysis conditions using thermogravimetric methods is very important to design, optimize and operate thermochemical conversion processes, such as combustion or gasification [8]. The kinetic data obtained can be used in computational fluid dynamics (CFD) simulations to model these processes. Co-pyrolysis characteristics and synergic behavior potential of biomass-coal mixtures have been the subject of many studies [9-16]. In these studies, for different coal and biomass samples, the effects of pyrolysis heating rate [9-10, 14], material particle size [10], and coal/biomass weight ratio [11, 13, 15-16] are examined in N₂ gas atmosphere. Investigation of thermal decomposition behavior in the CO₂ environment is essential for the design of oxy-combustion and gasification systems, since pyrolysis gives information on ignition and reactivity [12]. Yuzbasi and Selcuk investigated the pyrolysis and combustion behavior of Can lignite-olive residue blends in N₂ and CO₂ atmospheres [12]. Cho et al. examined the effect of CO₂ atmosphere in co-pyrolysis of sub-bituminous coal mixtures with cellulose and xylan [17]. Rodina et al. studied the thermal decomposition of Spanish sub-bituminous coal/cynara blends in N₂, air and CO₂/O₂ atmospheres [18]. Irfan et al. determined the gasification kinetics of bituminous coal/palm shell blends in air and CO₂/O₂ atmospheres [19]. Toptas et al. investigated the combustion characteristics of Soma lignite/torrified biomass samples [20]. In the literature, as far as we know, no study investigating the pyrolysis characteristics, reactivity and on-time evolved gas analysis of PCP and coal blends in N₂ and CO₂ atmospheres has been found.

This study is conducted to determine the thermal decomposition characteristics, pyrolysis products with respect to temperature and synergistic interaction potentials of two types of Turkish lignite/PCP mixtures with the help of a thermogravimetric analyzer (TGA) and Fourier Transform Infrared spectroscopy (FTIR), for the first time in literature.

2. EXPERIMENTAL

2.1. Characterization of the Coal and Biomass Samples

Poppy capsule pulp (PCP) as process waste of Afyon Alkaloids Factory (Afyonkarahisar, Turkey) and two types of Turkish lignite coal samples; Tunçbilek (Kütahya) and Orhaneli-Gümüşpinar (Bursa), were used in this study. Samples were ground and sieved below 100 µm before the characterization experiments. Proximate analysis was carried out by using LECO TGA 701 Thermogravimetric Analyzer (USA). The ultimate analysis was performed with LECO TRUSPEC CHNS Elemental Analyzer (USA). Their lower heating values, both on an original and dry basis, were measured by LECO AC 600 Semi-Automatic Isoperibol Calorimeter (USA). Analyses were carried out according to the relevant American Society for Testing and Materials (ASTM) standards. Bruker S 8 TIGER (USA) X-Ray Fluorescent (XRF) device was used to determine the inorganic contents of biomass and coal samples.

2.2. TGA-FTIR Analysis

Netzsch STA 449 F3 Jupiter TGA (Germany) coupled with Bruker Tensor II TGA-IR (USA) device was used to determine thermal decomposition characteristics Tunçbilek and Orhaneli-Gümüşpinar lignites, poppy capsule pulp and their 50/50 wt% blends. Within the scope of thermogravimetric analysis, the weight losses, weight-loss rates and thermal decomposition components of the samples were determined in nitrogen (N₂) and carbon dioxide (CO₂) atmospheres as a function of temperature at atmospheric pressure. Experimental conditions are given in Table 1. The TGA outlet gases were sent to the FTIR analyzer via a 200 °C heated line to prevent the condensation of volatiles formed as a result of thermal decomposition. FTIR measurements were performed in a gas cell heated at 200 °C. FTIR spectra were measured at 4 cm⁻¹
resolution, 4000-700 cm⁻¹ IR absorption band. All measurements were repeated three times to ensure repeatability.

**Table 1. Experimental conditions for the thermal decomposition of the samples**

| Parameter                                      | Specification          |
|------------------------------------------------|------------------------|
| Initial weight (m₀)                            | ~20 mg                 |
| Coal/biomass blend ratios (wt./wt.)            | 100:0/50:50/0:100      |
| Gas flow rate                                  | 30 ml/min              |
| Fine powder sample size                        | ≤100 µm                |
| Heating rate                                   | 25 °C/min              |
| Initial-final temperature                      | 25-950 °C              |

2.3. Kinetic Modeling

Data obtained from TGA experiments were used to perform the kinetic analysis of two types of lignite coal samples, poppy capsule pulp, and their blends. The activation energies (Eₐ) and Arrhenius parameters (A) are determined by using Coats-Redfern approximation [21], which has been used in many studies to model the kinetics of coal and biomass decomposition [22].

The kinetics of thermal degradation of coal and biomass samples are complicated, as they involve many chemical and physical processes; such as breaking of bonds and many molecular rearrangements, heat transfer between sample and gas atmosphere and volatile matter transport from the sample interior to the surface, resulting from a large number of reactions in parallel and series and related to the overall mass loss [23]. For this reason, solid-state decomposition of the samples considered based on apparent rate, as given in Equation (1):

\[
\frac{dx}{dt} = kf(x) \tag{1}
\]

where \( k \) is the reaction rate constant, \( dx/dt \) is the conversion rate, and \( x \) is the conversion of the sample, defined as:

\[
x = \frac{m₀ - m}{m₀ - m_f} \tag{2}
\]

where \( m₀ \) is the initial sample weight, \( m \) is the sample weight at time \( t \), and \( m_f \) is the final sample weight at the end of the process.

The reaction rate constant, \( k \), is given by the Arrhenius expression:

\[
k = A \exp \left( -\frac{E_a}{RT} \right) \tag{3}
\]

where \( A \) is a pre-exponential factor (min⁻¹); \( E_a \) is activation energy (kJ mole⁻¹); \( T \) is the temperature (K); \( R \) is the universal gas constant, \( 8.314 \times 10^{-3} \) kJ mole⁻¹ K⁻¹.

The heating rate, \( b \), is defined as \( dT/dt \). If Equation (1) is rearranged accordingly:

\[
\frac{dx}{dT} = \frac{A}{b} (1 - x) \exp \left( \frac{-E_a}{RT} \right) \tag{4}
\]

\( f(x) \) is presented as:

\[
f(x) = (1 - x)^n \tag{5}
\]

where \( n \) is the reaction order.
Combination of Equations (4) and (5), with further integration:

\[
\int_0^x \frac{dx}{(1-x)^p} = \frac{AR}{bEa} \left[ \exp \left( \frac{-Ec}{RT} \right) - \exp \left( \frac{-Ec}{RT_0} \right) \right].
\]

Because of \( \exp \left( \frac{-Ec}{RT_0} \right) \approx 0 \) Equation (6) reduces to:

\[
\int_0^x \frac{dx}{(1-x)^p} = \frac{AR}{bEa} \exp \left( \frac{-Ec}{RT} \right).
\]

In this study, decomposition reactions are assumed to follow a first-order reaction kinetics with \( n=1 \), as reported in the literature [18-19].

According to Equation (7), the plot of \( \ln[-1/T^2 \ln (1-x)] \) to \( 1/T \) gives a straight line, and the slope provides activation energy \( (E_a) \). The intercept of the line is \( \ln(A/b)(R/E) \). Thus, the value of the pre-exponential factor \( (A) \) is calculated from the intercept. R-Squares coefficients of determination (COD) for the identified slopes are determined between 0.9312 to 0.9946.

### 3. RESULTS AND DISCUSSION

#### 3.1. Raw Materials Characterization

The results of proximate and ultimate analysis, together with the higher heating values of lignite and PCP samples are given in Table 2. According to Table 2, the fuels show different characteristics in terms of volatile matter, oxygen, nitrogen, sulfur contents, and heating values. Volatile matter content of PCP is higher than lignite samples, and Orhaneli-Gümüşpinar has higher volatile content than Tunçbilek coal on a dry basis. Ash analysis results of the samples are given in Table 3. It is seen that, PCP has higher amounts of calcium, potassium and phosphorus than lignite samples, whereas Tunçbilek lignite has the highest aluminium, silicon and iron contents among the other samples.

**Table 2. Proximate and ultimate analysis and heating values of the samples**

|                          | ORHANELİ-GÜMÜŞPINAR LIGNITE | TUNÇBİLEK LIGNITE | PCP |
|--------------------------|-----------------------------|------------------|-----|
| **PROXIMATE ANALYSIS (wt.%)** |                             |                  |     |
| Moisture                 | 36.16                       | 7.43             | 71.55 |
| Volatile matter          | 30.06                       | 31.57            | 21.09 |
| Ash                      | 6.70                        | 21.43            | 6.54 |
| Fixed carbon             | 27.08                       | 39.57            | NA  |
| **Dry Basis**            |                             |                  |     |
| Volatile matter          | 47.09                       | 34.10            | 74.14 |
| Ash                      | 10.50                       | 23.16            | 22.98 |
| Fixed carbon             | 42.41                       | 42.74            | NA  |
| **ULTIMATE ANALYSIS (wt.%)** |                             |                  |     |
| C                        | 68.46                       | 64.63            | 37.76 |
| H                        | 4.58                        | 4.25             | 4.62 |
| N                        | 0.92                        | 2.45             | 0.97 |
| TOTAL SULPHUR            | 3.51                        | 2.13             | 0.12 |
| O                        | 12.03                       | 3.38             | 33.52 |
| Cl                       | NA                          | NA               | 0.030 |
| **HIGH HEATING VALUES (kcal/kg, (dry basis))** | 6134                        | 5981             | 3358 |
Table 3. Ash analysis results of samples (%, dry basis)

|     | ORHANELİ-GÜMÜŞPINAR LIGNITE | TUNÇBİLEK LIGNITE | PCP |
|-----|-------------------------------|------------------|-----|
| Al  | 1,31                          | 11,4             | 0,08|
| Ca  | 24,8                          | 2,67             | 62,3|
| Fe  | 4,04                          | 7,29             | 0,12|
| Si  | 3,29                          | 24,6             | 2,14|
| K   | 0,11                          | 1,24             | 4,60|
| Mg  | 1,98                          | 2,38             | 2,99|
| Mn  | 0,14                          | 0,09             | 0,03|
| Na  | 0,16                          | 0,09             | 0,09|
| P   | 0,12                          | 0,08             | 1,71|

3.2. Thermogravimetric Analysis

The change of weight and derivative weight loss of lignite samples, PCP, and lignite/PCP blends with respect to temperature in the N₂ atmosphere are given in Figure 1 (a) and (b), respectively. It is seen from Figure 1(a) that, Tunçbilek lignite retained nearly the 64% of its mass at 950 °C, whereas, at the same temperature, Orhaneli-Gümüşpinar and PCP have remaining weights of ~48% and ~25%, respectively. This finding is in accordance with the proximate analysis results in Table 2, especially in terms of volatile matter on a dry basis.

It is seen from Figure 1(b) that all samples, except Tunçbilek lignite, show three main weight loss steps, in the pyrolysis experimental temperature range. First weight loss between 25-200 °C is attributed to moisture release, and the second weight loss step in 200-600 °C is related to the primary devolatilization of the organic matter. A large fraction of volatiles is formed between 250 and 490 °C, whereas tar and hydrocarbons are known to release between 490 and 640 °C [10]. Additionally, Rosenvold and Dubow stated that weight losses > 550 °C corresponds to cracking and coking reactions [24]. Orhaneli-Gümüşpinar coal and PCP exhibit an additional weight loss at 700 °C and 757 °C, respectively. As it can be seen in Table 3, calcium contents of Orhaneli-Gümüşpinar lignite and PCP sample are higher than Tunçbilek coal. The weight loss observed at temperatures higher than 640 °C in N₂ atmosphere is associated to the thermal breakdown of carbonates in literature [10-11].

Initial decomposition temperatures (T_in), peak temperatures (T_max), maximum weight loss rates ((dm/dt)_max) in DTG curves given in Table 4 and 5 are used to determine the pyrolysis characteristics of the samples. T_in is the temperature at which the rate of weight loss reaches 1%/min after initial moisture release. In other words, it shows weight loss initiation. T_max is the maximum reaction rate temperature [12]. In the study, T_max1 is defined as the maximum temperature for primary devolatilization. T_max2 and T_max3 are the maximum temperatures of secondary and third devolatilization zones, respectively. Maximum weight loss rates are also given regarding to the primary, secondary and tertiary decomposition stages. It is seen from Tables 4 and 5 that, the initial and maximum decomposition temperature of the biomass sample is lower than that of Tunçbilek and Orhaneli lignites. Since, the cellulose, hemicellulose and lignin polymers of biomass samples are held by relatively weak bonds and lower bonding energies, PCP temperature resistance is lesser than lignite samples, resulting in lower decomposition temperatures [9]. Coal is subjected to thermal degradation at higher temperatures compared to biomass due to its aromatic polycyclic hydrocarbons bound to each other by C = C bonds, that are known to be more resistant to thermal degradation [9]. The mass-loss rate peak height is known to be directly proportional to reactivity [10]. It can be seen from Table 4 and 5 that the PCP is more reactive than Tunçbilek and Orhaneli lignites.

Theoretical weight losses and weight-loss rates were calculated according to Equation (8) to determine possible synergistic effects between PCP and lignite samples in N₂ and CO₂ atmospheres. The results were given in Figures 1 and 2.

Mass loss (theoretical) = x₁ × mass loss₁ + x₂ × mass loss₂

(8)
where $x_1$ is the ratio of PCP in blends, mass loss$_1$ is the experimental mass loss of 100% PCP, $x_2$ is the ratio of lignite in the blends and mass loss$_2$ is the experimental mass loss of 100% lignite.

Figure 1(b) shows the experimental and theoretical loss of mass rate behaviors of PCP/lignite samples in $N_2$ atmosphere. It is observed from Figure 1(b) that all the blend samples show the decomposition characteristics of their parent components. As can be seen from the Figure 1 (b) and Table 4, the most significant difference between theoretical and experimental mass loss rates was observed at 700 ° C and after. In PCP/Tunçbilek and PCP/Orhaneli-Gümüşpınar mixtures, the third zone experimental decomposition temperature is lower than that obtained theoretically, showing that there might a synergistic interaction between the PCP and the lignite samples forming the mixtures in $N_2$ environment. Similar situations have been observed in the literature for different coal/biomass mixtures [9, 14-16, 25-26]. Haykiri-Acma and Yaman declared that, the chemical composition (inorganic contents, high O/C and H/C ratios) and high reactivity of biomass samples could be the reason of the synergy in coal/biomass blends [25]. Especially high calcium [9], potassium [9, 25] and phosphorus [25] contents of the parent materials are believed to support devolatilization. According to Table 3, PCP has higher amounts of calcium, potassium and phosphorus than coal samples. Additionally, significant aliphatic hydrocarbon content in lignite samples are accounted for the synergy in coal/biomass co-pyrolysis [9, 16]. According to Li et al. [14] and Wang et al. [26], due to the reactions between coal and hydrogen containing free radicals generated by biomass, the interactions are increased during devolatilization.

![Figure 1](image1.png)  
**Figure 1.** Weight (a) and derivative weight loss (b) curves of Turkish lignites, PCP, and their blends in the $N_2$ atmosphere

|                | $T_{in}$ (°C) | $T_{max1}$ (°C) | $(dm/dt)_{max1}$ | $T_{max2}$ (°C) | $(dm/dt)_{max2}$ | $T_{max3}$ (°C) | $(dm/dt)_{max3}$ |
|----------------|---------------|-----------------|------------------|-----------------|-----------------|-----------------|-----------------|
| PCP            | 219,5         | 326,8           | 0,60             | -               | -               | 755,9           | 0,19            |
| ORHANELİ       | 264,5         | 419,2           | 0,24             | -               | -               | 736,8           | 0,11            |
| TUNÇBİLEK      | 388,4         | 467,8           | 0,32             | -               | -               | -               | -               |
| ORHANELİ/PCP-EXP | 222,3         | 335,1           | 0,32             | -               | -               | 727,9           | 0,12            |

*Table 4. Pyrolysis characteristics of samples in $N_2$ atmosphere*
Table 5. Pyrolysis characteristics of samples in CO₂ atmosphere

| Sample Description | T₀ (°C) | T₂₁ (°C) | (dm/dt)max₁ | T₂₂ (°C) | (dm/dt)max₂ | T₂₃ (°C) | (dm/dt)max₃ |
|--------------------|---------|----------|--------------|---------|--------------|---------|--------------|
| PCP                | 225,4   | 327,6    | 0,59         | -       | -            | 826,8   | 0,43         |
| ORHANELİ           | 242,4   | 433,3    | 0,21         | -       | -            | 845,5   | 0,18         |
| TUNÇBİLEK          | 396,5   | 464,5    | 0,32         | -       | -            | -       | -            |
| ORHANELİ/PCP EXP   | 236,7   | 334,3    | 0,33         | -       | -            | 833,0   | 0,32         |
| ORHANELİ/PCP THEO  | 230,5   | 334,3    | 0,34         | -       | -            | 826,7   | 0,27         |
| TUNÇBİLEK/PCP EXP  | 224,8   | 334,3    | 0,31         | 464,6   | 0,23         | 839,2   | 0,23         |
| TUNÇBİLEK/PCP THEO | 225,8   | 327,8    | 0,30         | 464,5   | 0,22         | 826,7   | 0,24         |

Figure 2. Weight (a) and derivative weight loss, (b) curves of Turkish lignites, PCP, and their blends in the CO₂ atmosphere
The change of weight and derivative weight loss of lignite samples, PCP, and PCP/lignite blends with respect to temperature in the CO\(_2\) atmosphere is given in Figure 2 (a) and (b), respectively.

If Figures 1(b) and 2(b) are compared, it is seen that the samples exhibited an extra weight loss around 800 - 850 \(^\circ\) C, different from the N\(_2\) atmosphere. The weight loss observed in the CO\(_2\) atmosphere that occurred above 800 \(^\circ\)C is connected to the reactions between CO\(_2\) and gas, char, as well as tar components formed during decomposition [14, 27-29]. The main reactions can be seen in Reactions (1) - (4) [30]. Since these reactions are highly endothermic, they are not expected to occur at low temperatures.

\[
\begin{align*}
C_nH_m + nCO_2 & \rightarrow 2nCO + m/2H_2 & \text{Reaction (1)} \\
C(s) + CO_2 & \rightarrow 2CO & \text{Reaction (2)} \\
H_2 + CO_2 & \rightarrow H_2 + 2CO & \text{Reaction (3)} \\
CO_2 & \rightarrow CO + 0.5O_2 & \text{Reaction (4)}
\end{align*}
\]

If pyrolysis characteristics of samples shown in Tables 4 and 5 are compared, it is seen that in primary devolatilization stage (200-500 \(^\circ\) C), \(T_{in}\) and \(T_{max1}\) are shifted to slightly higher temperatures in CO\(_2\) atmosphere, generally. This phenomenon is attributed to the difference in physical properties (density, specific heat, radiative capacity, etc.) of N\(_2\) and CO\(_2\) gases. Similar results are obtained in several studies [12, 28, 31]. At elevated temperatures, mass losses occurred around 700 \(^\circ\)C for PCP and Orhaneli samples in N\(_2\) environment are disappeared in CO\(_2\) atmosphere, due to the blockage of calcium carbonate decomposition in high CO\(_2\) concentrations [27, 31]. Maximum weight loss rates occurred above 800 \(^\circ\)C related with char gasification stage are also given in Table 5, as \(T_{max3}\). Similar to N\(_2\) atmosphere, biomass/lignite mixtures show the characteristic decomposition behavior of their parent components in CO\(_2\) atmosphere. The primary devolatilization peak of Orhaneli-Gümüşpinar lignite appeared as shoulder in mixtures.

Figure 2(b) shows the experimental and theoretical loss of mass rate behaviors of PCP/lignite samples in CO\(_2\) atmosphere. Theoretical mass losses and mass-loss rates were calculated using Equation (1) and given in Table 5. It is seen in Table 5 that, in CO\(_2\) environment, experimental \(T_{max3}\) is higher than the theoretical in mixtures, opposite to N\(_2\) atmosphere. Especially in this stage, multiple reactions are known to occur, such as Boudouard, tar cracking, dry reforming, water-gas shift, dehydrogenation, polymerization, etc. The presence of reactive CO\(_2\) environment might suppress the synergistic interactions between PCP and the lignite samples, that discussed previously for N\(_2\) atmosphere.

### 3.3. Kinetic Studies

Tables 6 and 7 show the kinetic parameters of PCP, Orhaneli coal, Tunçbilek Coal and PCP/lignite mixtures in N\(_2\) and CO\(_2\) atmospheres, respectively. During kinetic analysis, the first weight loss related to moisture release is neglected, similar to the literature [32].

Tunçbilek coal is observed to have higher apparent activation energy (\(E_a\)) than Orhaneli-Gümüşpinar lignite and biomass in N\(_2\) and CO\(_2\) atmospheres. One of the reasons of this observation might be the higher calcium contents in Orhaneli-Gümüşpinar and PCP samples, that is known to show catalytic effects during thermochemical conversion processes [22]. According to the results given in Table 3, Tunçbilek coal has higher amounts of Al and Si than the other fuels, whereas Ca is the dominant mineral in Orhaneli-Gümüşpinar lignite and PCP. Higher volatile matter/fixed carbon ratio of PCP sample also contributes its lower activation energy [22]. Moreover, biomass cellulose, hemicellulose and lignin components are linked together with weak ether bonds that decompose at lower temperatures [16]. Low rank of Orhaneli-Gümüşpinar coal might be one of the reasons of its lower activation energy.

According to Tables 6 and 7, the apparent activation energies of PCP/Tunçbilek lignite mixtures are smaller than the activation energies of their parent components indicating synergy, in N\(_2\) and CO\(_2\) environment. However, initial and maximum decomposition temperatures for the parent components remain unchanged for these mixtures. Moreover, especially above 600 \(^\circ\)C, the experimental activation energies for biomass/lignite mixtures found lower than the theoretical values, due to the possible synergistic interactions.
between PCP and coal samples, in both gas atmospheres. Similar results obtained by other researchers. Wang et al. [26] and Jeong et al. [33] also proposed synergy between coal and biomass samples during co-pyrolysis in N₂ atmosphere, in terms of activation energy.

It is seen from Tables 6 and 7 that Eₐ of primary devolatilization stages are generally lower than the final decomposition steps in N₂ and CO₂ atmospheres, showing that the reactive activities of mineral decomposition step and gasification reactions are lower than the main volatile release step [28]. Activation energy is known to show the minimum energy required for a reaction started and higher value of activation energy means slower reaction rate [33]. The lower value of the activation energy is assigned to the presence of light and active volatile components, whereas the high values of activation energy seen in second and third decomposition steps are the sign of less volatile composition having stronger chemical bonds [27].

It is seen that at temperatures lower than 600 °C, for the primary devolatilization stage, activation energies are lower in CO₂ atmosphere than N₂ atmosphere in all samples, due to the increase in reactivity. At higher temperatures, due to possible different reaction mechanisms, activation energies in CO₂ atmosphere becomes higher than that of N₂ atmosphere.

| Sample          | Temperature range (°C) | Eₐ (kJ/mol) | A (min⁻¹) | R²     |
|-----------------|------------------------|-------------|-----------|--------|
| PCP             | 223 - 379              | 26.37       | 2.35x10⁸  | 0.9832 |
|                 | 698 - 835              | 26.93       | 1.51x10⁹  | 0.9739 |
| ORHANELİ        | 317 - 515              | 14.96       | 2.30x10⁹  | 0.9781 |
|                 | 715 - 760              | 26.21       | 1.42x10⁹  | 0.9912 |
| TUNÇBİLEK       | 387 - 543              | 52.99       | 3.15x10⁷  | 0.9784 |
| ORHANELİ/PCP    | 237 - 372              | 21.93       | 6.28x10⁸  | 0.9946 |
| EXP             | 686 - 800              | 24.55       | 1.52x10⁹  | 0.9882 |
| ORHANELİ/PCP    | 237 - 372              | 18.26       | 1.07x10⁹  | 0.9894 |
| THEO            | 707 - 783              | 26.06       | 1.55x10⁹  | 0.9738 |
| TUNÇBİLEK/PCP   | 218 - 386              | 22.55       | 6.58x10⁸  | 0.9819 |
| EXP             | 395 - 543              | 13.67       | 2.39x10⁹  | 0.9735 |
|                 | 700 - 776              | 22.59       | 2.01x10⁹  | 0.9778 |
| TUNÇBİLEK/PCP   | 225 - 397              | 21.41       | 7.84x10⁸  | 0.9792 |
| THEO            | 405 - 540              | 13.47       | 2.49x10⁹  | 0.9746 |
|                 | 705 - 806              | 24.71       | 1.81x10⁹  | 0.9791 |

| Sample          | Temperature range (°C) | Eₐ (kJ/mol) | A (min⁻¹) | R²     |
|-----------------|------------------------|-------------|-----------|--------|
| PCP             | 223 - 379              | 26.37       | 2.35x10⁸  | 0.9832 |
| ORHANELİ/PCP    | 237 - 372              | 21.93       | 6.28x10⁸  | 0.9946 |
| EXP             | 686 - 800              | 24.55       | 1.52x10⁹  | 0.9882 |
| ORHANELİ/PCP    | 237 - 372              | 18.26       | 1.07x10⁹  | 0.9894 |
| THEO            | 707 - 783              | 26.06       | 1.55x10⁹  | 0.9738 |
| TUNÇBİLEK/PCP   | 218 - 386              | 22.55       | 6.58x10⁸  | 0.9819 |
| EXP             | 395 - 543              | 13.47       | 2.49x10⁹  | 0.9746 |
|                 | 705 - 806              | 24.71       | 1.81x10⁹  | 0.9791 |

Table 6. Kinetic parameters of samples in an N₂ atmosphere

Table 7. Kinetic parameters of samples in a CO₂ atmosphere
|                | PCP     | ORHANELİ | TUNÇBİLEK | ORHANELİ/PCP EXP | ORHANELİ/PCP THEO | TUNÇBİLEK/PCP EXP | TUNÇBİLEK/PCP THEO |
|----------------|---------|-----------|-----------|-------------------|-------------------|-------------------|-------------------|
| Temperature   | 225-390 | 270-590   | 396-527   | 236-390           | 236-390           | 224-390           | 224-390           |
| (°C)          | 801-858 | 826-870   | 396-527   | 801-864           | 801-864           | 402-520           | 414-520           |
| Methane (CH₄) | 24,2    | 8,5       | 48,9      | 12,9              | 15,70             | 20,4              | 19,51             |
| (mg)          | 4,1x10⁸ | 7,54x10⁹ | 6,3x10⁷   | 3,00x10⁹          | 2,04x10⁹          | 1,12x10⁹          | 1,17x10⁹          |
| CO₂ (g)       | 0,9801  | 0,9312    | 0,9819    | 0,9836            | 0,9882            | 0,9811            | 0,9789            |
| CO (g)        | 0,9803  | 0,9883    | 0,9779    | 0,9779            | 0,9776            | 0,9771            | 0,9771            |

### 3.4. FTIR Studies

Figure 3 shows FTIR spectra of some of the main gas species with respect to temperature for Orhaneli-Gümüşpinar coal, PCP and their binary mixtures both in N₂ and CO₂ atmospheres, obtained during TGA analysis. The absorbance data of single volatile species are normalized to the same amount sample (20 mg). Thus, evolved gas profiles during pyrolysis can be compared qualitatively. Typical bands used for the component determination are given in Table 8.

It is observed from Figure 3 (a) that carbon monoxide (CO) formation profiles of PCP and lignite samples are different. In N₂ atmosphere, CO release shows maximum around 300 °C in PCP sample. However, most of the CO is evolved at about 700 °C in Orhaneli-Gümüşpinar coal and PCP/lignite mixture. In N₂ atmosphere, CO is known to evolve by the decomposition of the carbonyl group and ether bridge at low temperatures and ether cleavage at high temperatures [27]. CO formation increased significantly in the CO₂ environment, especially above 800 °C, due to the reactions occurring between the gas, char, and tar components and CO₂, that are given through Reactions (1)-(4).

During devolatilization methane (CH₄) (Figure 3 (b)) and alkyl groups (Figure 3 (c)) are especially formed between 200-800 °C and 200-600 °C intervals, respectively. CH₄ and alkyls is known to form by (a) the methylene group (–CH₂-) break (b) the secondary reactions of tar or some light compounds, (c) char polycondensation reactions and (d) the hydrogenation of the generated free radicals [27]. It is observed from the Figures 3 (b) and (c) that, CO₂ presence suppressed the formation of CH₄ and alkyl compounds. In the literature, it is stated that the thermal cracking efficiency of volatile species increased in CO₂ atmosphere, due to the hindering of secondary char formation and polymerization reactions [34]. The most significant release of CH₄, alkyls and ether/amine components are observed between 200 °C and 600 °C during primary devolatilization that corresponds to maximum rate of weight loss, as seen in Figures 1 and...
2. According to Figure 3(d), ether/amine formation is higher in PCP sample due to its greater oxygen content.

Orhaneli-Gümüşpinar/PCP blends show the IR evolution profiles of CH₄ and ether/amine species of their main components. Thus, for these blends, synergistic effect regarding gas emission is not observed in the study.

Table 8. Functional groups determined by FTIR [27]

| WAVE NUMBER (cm⁻¹) | FUNCTIONAL GROUP     | GAS SPECIES       |
|--------------------|----------------------|-------------------|
| 2240-2060          | C - O                | CO                |
| 3000-2700          | C - H                | CH₄               |
| 3115-2675          | C – H of methylene   | CH₄, Hydrocarbons |
| 1300-1000          | C-O/C-N              | Ether/amine       |
4. CONCLUSIONS

Thermochemical conversion reactivity of two different Turkish lignite sample (Tunçbilek and Orhaneli-Gümüşpinar)/PCP mixtures under two different pyrolysis atmospheres are determined using TGA-FTIR. Kinetic parameters (A, E_a) of the samples are calculated by Coats-Redfern Method. The following conclusions are made:

- At higher temperatures than 600 °C, differences in thermal degradation characteristics were observed with the substitution of N_2 by CO_2.
- In N_2 environment, the third experimental decomposition temperatures for all PCP/lignite blends are lower than theoretical values, showing that there might be a synergistic interaction between biomass and the coal samples. Kinetic analysis results support this observation, the E_a for biomass/lignite mixtures are lower than the theoretical values above 600 °C.
- The E_a of PCP/Tunçbilek lignite mixtures are smaller than the E_a of their parent components indicating synergy in N_2 and CO_2 atmospheres.
- FTIR analysis stated that pyrolysis product compositions were highly dependent on temperature, and gas species formation during thermal degradation was consistent with the weight loss of samples. No synergy was observed in terms of evolved gases. The presence of CO_2 decreased the absorbance of CH_4, alkyl and ether/amine components due to its reactive behavior.
- The results of this work may contribute to the design of oxy-fuel combustion and gasification systems, since pyrolysis is the fundamental step of all thermochemical conversion processes.

ACKNOWLEDGEMENTS

The experimental part of this study is supported by the Presidency of the Republic of Turkey, Strategy and Budget Directorate, within the scope of Advanced Coal Conversion Technologies (2016K121340) project.

CONFLICTS OF INTEREST

No conflict of interest was declared by the author.

REFERENCES

[1] BP Energy Outlook, https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/energy-outlook/bp-energy-outlook-2017.pdf (2017).

[2] Survey of Energy Resources, World Energy Council Report, https://www.worldenergy.org/assets/downloads/ser_2010_report_1.pdf (2010).

[3] Yao, D.D., Hu, Q., Wang, D.Q., Yang, H.P., Wu, C.F., Wang, X.H., et al. “Hydrogen production from biomass gasification using biochar as a catalyst/support” Bioresource Technology, 216: 159–164, (2016).

[4] Doğan, M., “Enerji Kaynakları Çevre Sorunları ve Çevre Dostu Alternatif Enerji Kaynakları” Standard Dergisi, 39(468): 28-36, (2000).
torrefied biomass and their blends with lignite

Toptas

atmospheres

gasification of coal, biomass and their blends in air (N2/O2) and different oxy-fuel (O2/CO2) atmospheres” Energy, 37: 665-672, (2012).

Irfan, M. F., Arami-Niya, A., Charakrabarti, M. H., Daud, W.M.A.W, Usman, M. R., “Kinetics of gasification of coal, biomass and their blends in air (N2/O2) and different oxy-fuel (O2/CO2) atmospheres” Energy, 37: 665-672, (2012).

Toptas, A., Yildirim, Y., Duman, G., Yanik, J., “Combustion behavior of different kinds of torrefied biomass and their blends with lignite” Bioresearch Technology, 177: 328-336, (2015).
[21] Coats, A.W., Redfern, J.P., “Kinetic parameters from thermogravimetric data” Nature, 201: 68-69, (1964).

[22] Magalhaes, D., Kazanç, F., Riaza, J., Erensoy, S., Kabakh, Ö., Chalmers, H., “Combustion of Turkish lignites and olive residue: experiments and kinetic modelling” Fuel, 203: 868-876, (2017).

[23] Kök, M. V., “Coal pyrolysis: thermogravimetric study and kinetic analysis” Energy Sources, 25: 1007-1014, (2003).

[24] Rosenvolld, R. J., Dubow, J. B., “Thermal analysis of Ohio bituminous coals” Thermochimica Acta, 53: 321-332, (1982).

[25] Haykiri-Acma, H., Yaman, S., “Interaction between biomass and different rank coals during co-pyrolysis” Renewable Energy, 35: 288-292, (2010).

[26] Wang, J., Zhang, S., Guo, X., Dong, A., Chen, C., Xiong, S., Fang, Y., Yin, W., “Thermal behaviors and kinetics of Pingshuo coal/biomass blends during co-pyrolysis and co-combustion” Energy & Fuels, 26: 7120-7126, (2012).

[27] Tang, Y., Ma, X., Wang, Z., Wu, Z., Yu, Q., “A study of the thermal degradation of six typical municipal waste components in CO2 and N2 atmospheres using TGA-FTIR” Thermochimica Acta, 657: 12-19, (2017).

[28] Chen, J., Mu, L., Cai, J., Yao, P., Song, X., Yin, H., Li, A., “Pyrolysis and oxy-fuel combustion characteristics and kinetics of petrochemical wastewater sludge using thermogravimetric analysis” Bioresource Technology, 198: 115-123, (2015).

[29] Lai, Z., Ma, X., Tang, Y., Lin, H., “Thermogravimetric analysis of the thermal decomposition of MSW in N2, CO2 and CO2/N2 atmospheres” Fuel Processing Technology, 102: 18-23, (2012).

[30] Zhang, H., Xiao, R., Wang, D., He, G., Shao, S., Zhang, J., Zhong, Z., “Biomass fast pyrolysis in a fluidized bed reactor under N2, CO2, CO, CH4, and H2 atmospheres” Bioresource Technology, 102: 4258-4264, (2011).

[31] Wen S., Yan, Y., Lin, J., Buyukada, M., Evrendilek, F., “Pyrolysis performance, kinetic, thermodynamic, product and joint optimization analyses of incense sticks in N2 and CO2 atmospheres” Renewable Energy, 141: 814-827, (2019).

[32] Moliner, C., Bosio, B., Arato, E., Ribes, A., “Thermal and thermo-oxidative characterisation of rice straw for its use in energy valorisation processes” Fuel, 180: 71-79, (2016).

[33] Jeong, H. M., Jee, M. W., Jeong, S. M., Na, B. K., Yoon, S. Y., Lee, J. G., Lee, W. J., “Pyrolysis kinetics of coking coal mixed with biomass under non-isothermal and isothermal conditions” Bioresource Technology, 155: 442-445, (2014).

[34] Ma, Z., Chen, D., Gu, J., Bao, B., Zhang, Q., “Determination of pyrolysis characteristics and kinetics of palm kernel shell using TGA–FTIR and model-free integral methods” Energy Conversion and Management, 89: 251-259, (2015).