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Thermochemical Conversion Behavior of Turkish Lignite/Poppy Capsule Pulp Blends in N_2 and CO_2 Atmospheres

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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.

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Keywords

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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 (N_2) and carbon dioxide (CO_2) atmospheres. Activation energies (E_a) and pre-exponential factors (A) were determined according to Coats-Redfern method and first-order reaction model. In CO_2 atmosphere, all samples exhibited an extra weight loss around 800 - 850 ° C, different from the N_2 atmosphere, due to the reactive nature of CO_2 during thermal decomposition. FTIR analysis confirmed this finding, at high temperatures CO formation were observed in the CO_2 atmosphere. In all mixtures, the third zone experimental decomposition temperature is lower than that obtained theoretically in N_2 atmosphere, showing that there might a synergistic interaction between the PCP and the lignite samples. 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. However, initial and maximum decomposition temperatures for the parent components remain unchanged for these mixtures. Moreover, especially at temperatures higher than 600 °C, the E_a 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, CH_4, 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 CO_2 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

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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 N_2 gas atmosphere. Investigation of thermal decomposition behavior in the CO_2 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 N_2 and CO_2 atmospheres [12]. Cho et al. examined the effect of CO_2 atmosphere in co-pyrolysis of sub-bituminious coal mixtures with cellulose and xylan [17]. Rodilla et al. studied the thermal decomposition of Spanish sub-bituminious coal/cynara blends in N_2, air and CO_2/O_2 atmospheres [18]. Irfan et al. determined the gasification kinetics of bituminious coal/palm shell blends in air and CO_2/O_2 atmospheres [19]. Toptaş 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 N_2 and CO_2 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-Gümüşpınar (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 and higher 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-Gümüşpınar 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 (N_2) and carbon dioxide (CO_2) 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*

Initial weight (m_0)	~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 (E_a) 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 a 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:

$$x = \frac{mo - m}{mo - mf} \tag{2}$$

where m_o 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:

$$k = A\exp(-\frac{Ea}{RT}) \tag{3}$$

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

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

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

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:

$$\int_0^x \frac{dx}{(1-x)^n T^2} = \frac{AR}{bE_a}\left[\exp\left(\frac{-E_a}{RT}\right) - \exp\left(\frac{-E_a}{RT_0}\right)\right]. \tag{6}$$

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

$$\int_0^x \frac{dx}{(1-x)^n T^2} = \frac{AR}{bE_a}\left[\exp\left(\frac{-E_a}{RT}\right)\right]. \tag{7}$$

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-Gümüşpınar 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.%)			
	Original Basis		
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.%)			
	Dry Basis		
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 N_2 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-Gümüşpınar 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-Gümüşpınar 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-Gümüşpınar lignite and PCP sample are higher than Tunçbilek coal. The weight loss observed at temperatures higher than 640 °C in N_2 atmosphere is associated to the thermal breakdown of carbonates in literature [10-11].

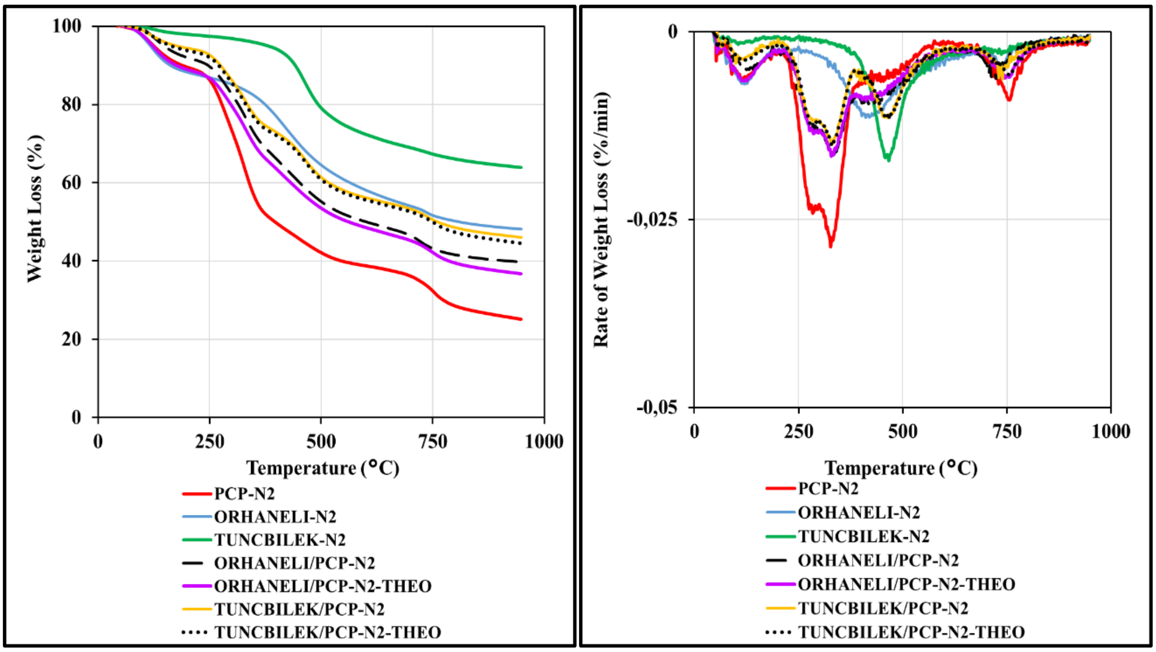
Initial decomposition temperatures (T_{in}), peak temperatures (T_{max}), maximum weight loss rates ($(dm/dt)_{max}$) in DTG curves given in Table 4 and 5 are used to determine the pyrolysis characteristics of the samples. T_{in} is the temperature at which the rate of weight loss reaches 1%/min after 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 second 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 N_2 and CO_2 atmospheres. The results were given in Figures 1 and 2.

$$Mass\ loss\ (theoretical) = x_1 \times mass\ loss_1 + x_2 \times mass\ loss_2 \tag{8}$$

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.



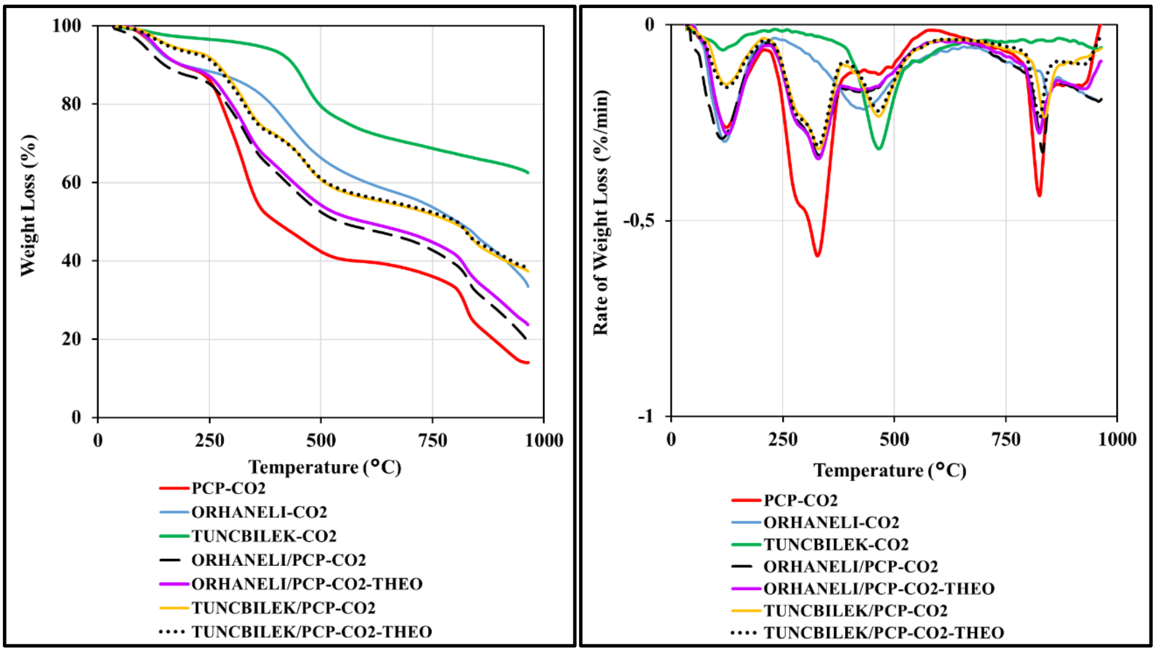
(a) (b)

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

Table 4. *Pyrolysis characteristics of samples in 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

ORHANELİ/PCP-THEO	223,6	332,3	0,36	-	-	750,3	0,13
TUNÇBİLEK/PCP-EXP	224,4	330,3	0,31	465,4	0,24	738,5	0,13
TUNÇBİLEK/PCP-THEO	225,8	328,9	0,30	468,2	0,23	760,8	0,11



(a) **(b)**

Figure 2. *Weight (a) and derivative weight loss, (b) curves of Turkish lignites, PCP, and their blends in the CO_2 atmosphere*

Table 5. *Pyrolysis characteristics of samples in CO_2 atmosphere*

	T_{in} (°C)	T_{max1} (°C)	$(dm/dt)_{max1}$	T_{max2} (°C)	$(dm/dt)_{max2}$	T_{max3} (°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

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 ° C, different from the N_2 atmosphere. The weight loss observed in the CO_2 atmosphere that occurred above 800 °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.

$C_nH_m+nCO_2 \rightarrow 2nCO+ m/2H_2$	Reaction (1)
$C(s)+CO_2 \rightarrow 2CO$	Reaction (2)
$H_2+CO_2 \rightarrow H_2+2CO$	Reaction (3)
$CO_2 \rightarrow CO+0.5O_2$	Reaction (4)

If pyrolysis characteristics of samples shown in Tables 4 and 5 are compared, it seen that in primary devolatilization stage (200-500 °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 °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 °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-Gümüşpınar 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-Gümüşpınar 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-Gümüşpınar 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-Gümüşpınar 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-Gümüşpınar 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 °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 N_2 atmosphere, in terms of activation energy.

It is seen from Tables 6 and 7 that E_a of primary devolatilization stages are generally lower than the final decomposition steps in N_2 and CO_2 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 CO_2 atmosphere than N_2 atmosphere in all samples, due to the increase in reactivity. At higher temperatures, due to possible different reaction mechanisms, activation energies in CO_2 atmosphere becomes higher than that of N_2 atmosphere.

Table 6. *Kinetic parameters of samples in an N_2 atmosphere*

Sample	Temperature range (°C)	E_a (kJ/mol)	A (min^{-1})	R^2
PCP	223 - 379	26,37	$2,35x10^8$	0,9832
	698 - 835	26,93	$1,51x10^9$	0,9739
ORHANELİ	317 - 515	14,96	$2,30x10^9$	0,9781
	715 -760	26,21	$1,42x10^9$	0,9912
TUNÇBİLEK	387 - 543	52,99	$3,15x10^7$	0,9784
ORHANELİ/PCP EXP	237 - 372	21,93	$6,28x10^8$	0,9946
	686 - 800	24,55	$1,52x10^9$	0,9882
ORHANELİ/PCP THEO	237 - 372	18,26	$1,07x10^9$	0,9894
	707- 783	26,06	$1,55x10^9$	0,9738
TUNÇBİLEK/PCP EXP	218 - 386	22,55	$6,58x10^8$	0,9819
	395 - 543	13,67	$2,39x10^9$	0,9735
	700 - 776	22,59	$2,01x10^9$	0,9778
TUNÇBİLEK/PCP THEO	225 - 397	21,41	$7,84x10^8$	0,9792
	405 - 540	13,47	$2,49x10^9$	0,9746
	705 - 806	24,71	$1,81x10^9$	0,9791

Table 7. *Kinetic parameters of samples in a CO_2 atmosphere*

Sample	Temperature range (°C)	E_a (kJ/mol)	A (min^{-1})	R^2

PCP	225-390	24,2	$4{,}1x10^8$	0,9801
	801-858	63,2	$1{,}25x10^8$	0,9803
ORHANELİ	270-590	8,5	$7{,}54x10^9$	0,9312
	826-870	18,4	$8{,}19x10^9$	0,9883
TUNÇBİLEK	396-527	48,9	$6{,}3x10^7$	0,9819
ORHANELİ/PCP EXP	236-390	12,9	$3{,}00x10^9$	0,9836
	801-864	29,4	$3{,}39x10^9$	0,9723
ORHANELİ/PCP THEO	236-390	15,70	$2{,}04x10^9$	0,9862
	801-864	32,58	$2{,}38x10^9$	0,9881
TUNÇBİLEK/PCP EXP	224-390	20,4	$1{,}12x10^9$	0,9811
	402-520	10,8	$3{,}97x10^9$	0,9712
	807-876	38,8	$1{,}23x10^9$	0,9779
TUNÇBİLEK/PCP THEO	224-390	19,51	$1{,}17x10^9$	0,9789
	414-520	10,89	$3{,}76x10^9$	0,9776
	801-864	41,64	$8{,}82x10^8$	0,9771

3.4. FTIR Studies

Figure 3 shows FTIR spectra of some of the main gas species with respect to temperature for Orhaneli-Gümüşpınar coal, PCP and their binary mixtures both in N_2 and CO_2 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 N_2 atmosphere, CO release shows maximum around 300 °C in PCP sample. However, most of the CO is evolved at about 700 °C in Orhaneli-Gümüşpınar coal and PCP/lignite mixture. In N_2 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 CO_2 environment, especially above 800 °C, due to the reactions occurring between the gas, char, and tar components and CO_2, that are given through Reactions (1)-(4).

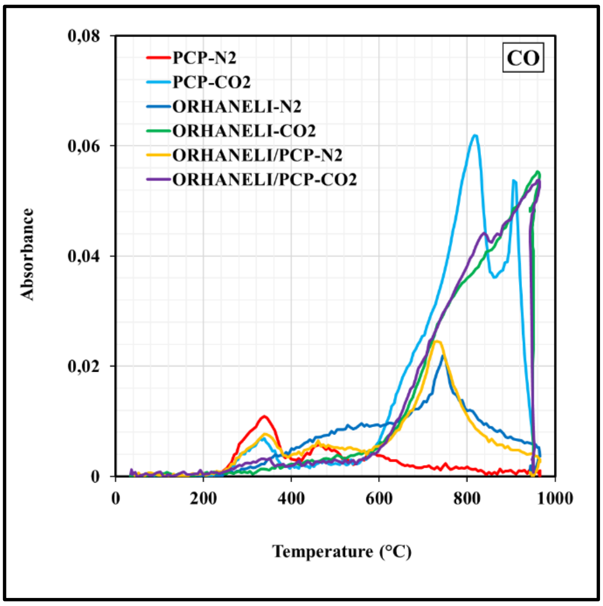
During devolatilization methane (CH_4) (Figure 3 (b)) and alkyl groups (Figure 3 (c)) are especially formed between 200-800 °C and 200-600 °C intervals, respectively. CH_4 and alkyls is known to form by (a) the methylene group ($–CH_2$-) break (b) the secondary reactions of tar or some light compounds, (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, CO_2 presence suppressed the formation of CH_4 and alkyl compounds. In the literature, it is stated that the thermal cracking efficiency of volatile species increased in CO_2 atmosphere, due to the hindering of secondary char formation and polymerization reactions [34]. The most significant release of CH_4, 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

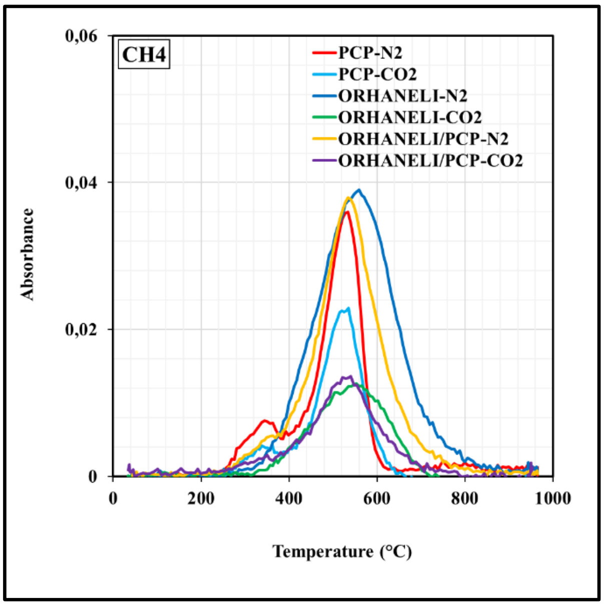
2. According to Figure 3(d), ether/amine formation is higher in PCP sample due to its greater oxygen content.

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

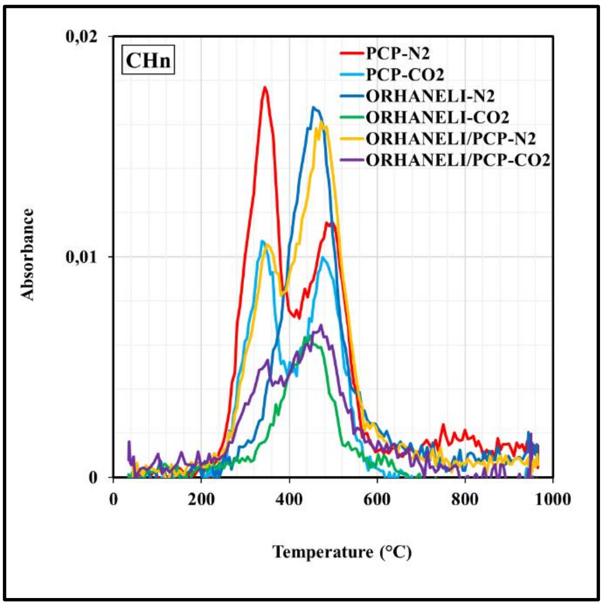
Table 8. *Functional groups determined by FTIR [27]*

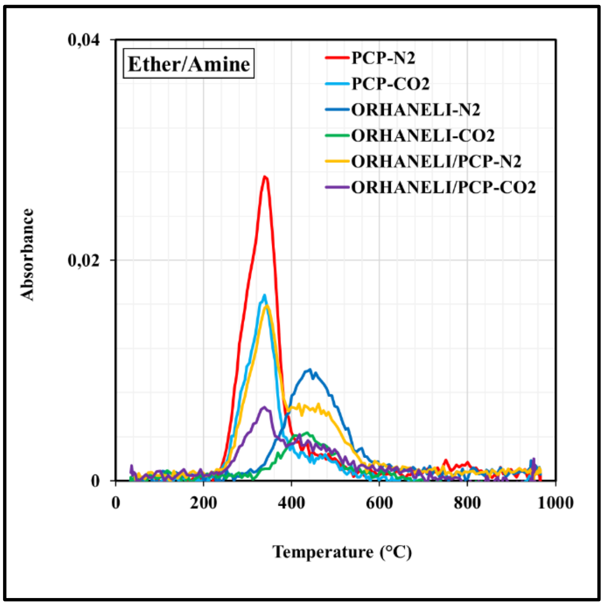
WAVE NUMBER (cm^{-1})	FUNCTIONAL GROUP	GAS SPECIES
2240-2060	C - O	CO
3000-2700	C - H	CH_4
3115-2675	C – H of methylene	CH_n-Hydrocarbons
1300-1000	C-O/C-N	Ether/amine





(a) (b)





(c) (d)

Figure 3. *IR evolution profiles of gaseous species throughout pyrolysis of samples (a) CO (b) CH_4 (c) CH_n (d) Ether/Amine*

4. CONCLUSIONS

Thermochemical conversion reactivity of two different Turkish lignite sample (Tunçbilek and Orhaneli-Gümüşpınar)/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 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.

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CONFLICTS OF INTEREST

No conflict of interest was declared by the author.

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