

Pyrolysis and Combustion Behaviour of Ternary Fuel Blends in Air and Oxy-fuel Conditions

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Abstract

Pyrolysis and combustion behaviours of imported coal (medium volatile bituminous coal), an indigenous lignite (high sulphur and ash content), petcoke (high calorific value) and their 60/30/10 wt.% ternary blends in air and oxy-fuel conditions were investigated by using thermogravimetric analyser (TGA) connected to Fourier transform infrared (FTIR) spectrometer. Pyrolysis tests were carried out in nitrogen and carbon dioxide environments, which are the main diluting gases of the air and oxy-fuel conditions, respectively. Pyrolysis test results of the blend and its parent fuels show that weight loss profiles display similar trends up to 700°C in both pyrolysis atmospheres. However, at higher temperatures, further weight loss is observed due to char-CO₂ gasification reaction in CO₂ atmosphere. FTIR formation profiles of the blend also shows that gasification reaction results in significant increase in CO and COS formation. Overall comparison of DTG curves of the blend and its parent fuels during pyrolysis reveals that the blend follows the same trend as lignite owing to the fact that the pyrolysis behaviour of the blend is dictated by lignite due to its significantly high volatile matter content. Different trends in theoretical and experimental pyrolysis profiles and their corresponding characteristic temperatures show the presence of interactions between parent fuels during co-pyrolysis of the ternary blend. Combustion experiments were carried out in air, oxygen-enriched air environment (30% O₂ - 70% N₂), oxy-fuel environment (21% O₂ - 79% CO₂) and oxygen-enriched oxy-fuel environment (30% O₂ - 70% CO₂). Overall comparison of the combustion profiles indicates that effect of oxygen concentration on combustion characteristics is more significant than that of diluting gas in the combustion environment. In oxygen-enriched conditions, combustion profiles shift to lower temperatures, peak and burnout temperatures decrease, and rate of weight loss increases. Theoretical and experimental combustion profiles of the blend mainly display different trends under all combustion conditions. Deviations in experimental curves from expected behaviour indicate synergy between imported coal, petcoke, and lignite during co-combustion of the ternary blend.

1. Introduction

Today, demand for electric power continues to increase due to population growth, and technological and economical development. With 826 billion tonnes of proved coal reserves, coal combustion has an important role in energy production worldwide [1]. Coal blending is becoming an increasingly common technique used in coal-fired power plants as it provides improvement in the combustion behaviour of coals, fuel flexibility and reduction in fuel cost while meeting the requirements of environmental legislations. The uncertainties associated with combustion characteristics of blends arise from non-additive properties of the components of the blend and may result in unexpected problems in practice [2,3]. Therefore, combustion behaviour of coal blends should be tested in laboratory or pilot scale level before using this application in commercial utilities.

Co-firing of the fuels with different characteristics requires a fuel flexible combustion technology. Within available technologies, fluidized bed combustion (FBC) is usually indicated to be the best choice for co-firing due to its fuel flexible features, long residence times, and uniform combustion temperatures, and also for high combustion efficiency and availability with low emissions [4].

Anthropogenic CO₂ production, driven by fossil fuel combustion, leads to growing concern about greenhouse gas emissions and their potential impact on climate change. This situation necessitates investigation of alternative technologies for reduction of CO₂ emissions from power plants. Oxy-fuel combustion technology is suggested as one of the new promising technologies for capturing CO₂ from power plants and has been reviewed in detail recently [5-7]. This technology is based on burning coal in a mixture of oxygen and recycled flue gas (RFG) leading to CO₂ concentrations greater than 95% in the exhaust gas. Recycled flue gas is used to control flame temperature and supply the volume of missing N₂. FBC systems are one of the best options for oxy-fuel combustion applications as significant reduction in the amount of recycled flue gas can be achieved through the external solid heat exchangers for combustion temperature control [8].

Before co-firing tests in FBC combustors, combustion characteristics of the parent fuels and their blends need to be determined under oxy-fuel conditions by using non-isothermal thermo-gravimetric analysis (TGA) technique. TGA is an inexpensive and simple method that has been widely used in studying the pyrolysis and combustion behaviors of fuels and evaluating the relative burning properties of fuel samples [2, 9].

Oxy-fuel combustion has been studied extensively for different types of coals, but to date has received relatively less attention for coal blends, which is fuel flexible and cost effective option in CO₂ emissions reduction. Therefore, in this study, pyrolysis and combustion behaviours of a highly reactive, low cost local lignite, relatively difficult to burn imported coal and petcoke and their 30/60/10 wt. % ternary blend are investigated in air and oxy-fuel conditions by using TGA-FTIR combined system. Weight percentages of the individual fuels in the blend were selected on the basis of their calorific values, ash and sulphur contents. All fuel samples are heated up to 950°C in order to simulate their behaviour in fluidized bed combustion systems.

2. Experimental

2.1 Samples

Imported coal, petcoke and indigenous lignite were used in pyrolysis and combustion tests in this study. Proximate, ultimate and ash analyses of the fuels together with their calorific values are given in Table 1. Analyses were performed according to ASTM standards. The imported coal is classified as medium volatile bituminous coal according to its fixed carbon percentage, calculated on a dry, ash-free basis as stated in the literature [10]. It is a high rank coal that has high calorific value, low volatile matter and sulphur content. The indigenous lignite used in this study is from Çan town of Çanakkale province in Turkey and is characterized by its low calorific value and high ash and sulphur contents. It is a highly reactive coal due to its high volatile matter content. Petcoke is a carbonaceous solid residual by-product of the oil refining process. It has high calorific value with low ash and high sulphur contents. It is difficult to ignite fuel due to absence of inherent oxygen and low volatile matter content. As can also be seen from the table petcoke ash contains high CaO and SO₃ contents. Presence of NiO and V₂O₅ in the petcoke ash and absence of these oxides in imported coal and lignite can also be noted. Blend samples were prepared by mixing imported coal, lignite and petcoke in the proportion of 60:30:10.

Table 1: Proximate, ultimate and ash analyses of fuels.

	Imported Coal	Petcoke	Lignite
Proximate Analysis (As received basis, % by wt.)			
Moisture	8.15	0.54	16.35
Ash	11.21	3.77	28.78
Volatile Matter	18.1	13.51	29.79
Fixed Carbon	62.54	82.18	25.08
Ultimate Analysis (As received basis, % by wt.)			
C	72.87	86.13	37.31
H	3.77	3.26	3.30
O	2.15	0.00	10.01
N	1.63	1.99	0.91
S _{Combustible}	0.22	4.34	3.33
Ash	11.21	3.74	28.78
Moisture	8.15	0.54	16.35
S _{Total}	0.3	4.71	3.49
LHV(MJ/kg)	27.04	33.17	9.89
Ash Analysis (% by wt.)			
SiO ₂	54.08	9.60	43.13
Al ₂ O ₃	28.65	2.19	18.20
Fe ₂ O ₃	5.16	1.62	15.78
CaO	2.91	30.57	7.63
MgO	0.83	1.19	0.48
Na ₂ O	0.00	0.00	2.00
K ₂ O	2.33	0.77	0.63
SO ₃	5.08	46.73	11.08
TiO ₂	0.96	0.00	1.07
NiO	0.00	1.05	0.00
V ₂ O ₅	0.00	6.28	0.00

2.2 Experimental Setup and Method

Pyrolysis and combustion behaviour of imported coal, petcoke, indigenous lignite and their blend was determined by using TGA-FTIR combined system. Fig. 1 shows a schematic diagram of the experimental setup consisting of Perkin Elmer Pyris STA 6000 thermogravimetric analyzer, Spectrum 1 FTIR spectrometer and a mass flow controller (MFC) for each gaseous species. Detail of experimental setup and method used can be found elsewhere [11, 12].

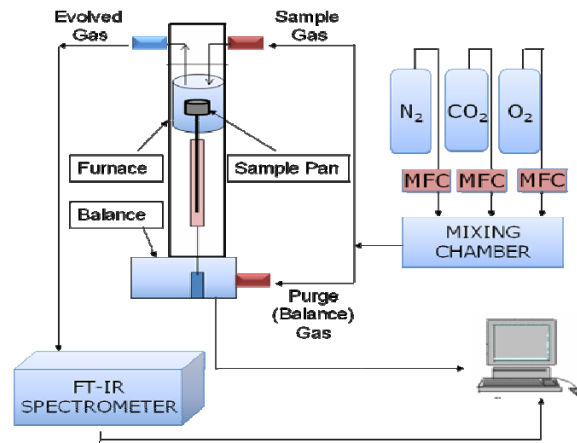


Figure 1: Schematic diagram of experimental setup.

Pyrolysis tests were carried out under nitrogen and carbon dioxide atmospheres which are the diluting gases of air and oxy-fuel environments, respectively. Four combustion tests were performed in air environment to investigate the effect of combustion environment on burning process of imported coal, petcoke, lignite and their blends. The base case was considered as combustion in air environment. In oxygen-enriched air case the sample is burned in 30% O₂ – 70% N₂ atmosphere. In oxy-fuel combustion tests, the volume of N₂ used in the base case was replaced with an equal volume of CO₂. In the last case, combustion of fuel samples were investigated in oxygen-enriched oxy-fuel environment, that is, in 30% O₂ – 70% CO₂ atmosphere.

TGA and DTG profiles obtained during pyrolysis and combustion experiments were used to determine pyrolysis and combustion behaviour and some characteristic temperatures such as initial decomposition temperature (T_{in}), peak temperature (T_{max}), ignition temperature (T_{ig}) and burnout temperature (T_b) of the fuel samples. Theoretical DTG curves of the blend samples were plotted in order to investigate the interactions between fuel samples and influence of blending on characteristic temperatures. The curves were calculated by applying the additive rule using the profiles of individual components according to their ratio in the blend [13]. Moreover, formation profiles of evolved gaseous components including CO₂, CO, H₂O, CH₄, SO₂ and COS are also reported in the scope of FTIR analysis.

3. Results and Discussion

3.1 Pyrolysis tests of fuel samples

Pyrolysis plays crucial role in determining flame stability, ignition and product distributions. Pyrolysis tests were carried out in both N₂ and CO₂ environments, which are the main diluting gases of air and oxy-fuel environments, in order to investigate the possible impacts of those gases on pyrolysis process. Pyrolysis behaviours of blend and its parent fuels under N₂ and CO₂ environments and the theoretical pyrolysis behaviour of the blend calculated by using additive rule are compared in Fig.2. The pyrolysis characteristics of the blend and its parent fuels are summarized in Table 2.

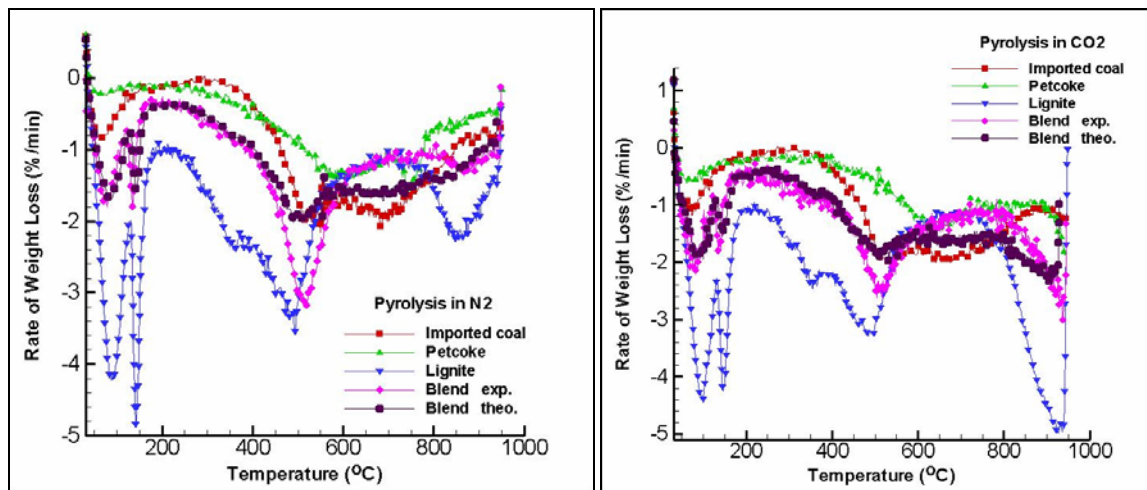


Figure 2: Pyrolysis profiles of the blend and its parent fuels in N_2 and CO_2 atmospheres.

In the DTG profiles of the fuel samples, the first weight loss step corresponds to moisture release within the first $200^\circ C$ temperature zone. Second weight loss step represents volatile matter release within $200-700^\circ C$. Similar trends are obtained in both pyrolysis atmospheres, however, at high temperature zone in CO_2 atmosphere, additional weight loss steps are observed due to CO_2 – char gasification reaction [14, 15].

Fig. 2 shows that lignite devolatilizes at lower temperatures with higher weight loss rate due to its high volatile matter content compared to imported coal and petcoke. Overall comparison of DTG curves reveals that experimental curve of blend reveals close resemblance with lignite as lignite dominates pyrolysis behaviour of the blend with its significantly higher volatile matter content. Pyrolysis behaviour of blend shows that peak height decreases and the peak position shifts to higher temperatures with the presence of imported coal and petcoke. Theoretical blend curve displays some deviations from experimental behaviour. Each devolatilization steps of imported coal, petcoke and lignite appears in theoretical curve of blend with lower weight loss rate in both pyrolysis conditions. These differences are considered to be due to interactions (synergy) between parent fuels during pyrolysis process [16, 17].

Table 2: Pyrolysis characteristics of fuel samples.

		T_{in}	T_{max}	$(dm/dt)_{max}$	Weight loss up to 950°C
Imported Coal	Pyrolysis in N₂	465.2	517.0	2.0	21.1
	Pyrolysis in CO₂	463.9	528.4	2.0	23.2
Petcoke	Pyrolysis in N₂	514.9	582.3	1.4	14.4
	Pyrolysis in CO₂	570.9	638.7	1.3	17.0
Lignite I	Pyrolysis in N₂	230.8	482.9	3.6	41.0
	Pyrolysis in CO₂	216.7	481.0	3.16	50.3
Blend Exp.	Pyrolysis in N₂	389.6	512.5	3.1	27.1
	Pyrolysis in CO₂	392.3	512.1	2.4	30.0
Blend Theo.	Pyrolysis in N₂	405.4	500.1	2.1	26.5
	Pyrolysis in CO₂	409.2	532.2	2.0	30.3

The evolution profiles of the gaseous species including CO₂, CO, H₂O, CH₄, SO₂ and COS, from the pyrolysis of blend in nitrogen and carbon dioxide are shown in Fig. 3. In the formation profile of CO₂, three peaks are displayed at around 400, 550 and 750°C during pyrolysis in N₂ atmosphere. The first peak represents CO₂ release due to devolatilization of lignite component while second one may account for volatile matter release of imported coal and petcoke together. The last peak shows CO₂ release as a consequence of calcite decomposition of petcoke component at high temperature zone as also reported in the literature [18, 19]. In both environments, H₂O is identified in the first 200°C due to moisture release. After 200°C, further H₂O formation is observed as result of condensation of phenols [19]. Methane formation takes place between 400-800°C. Certain amount of SO₂ is also formed as a result of the high sulphur content of lignite and petcoke in the blend at around 350°C and 500°C with similar trends in both pyrolysis conditions. After 700°C, distinctive increase is observed in CO and COS formation profiles in CO₂ atmosphere due to CO₂ – char gasification reaction.

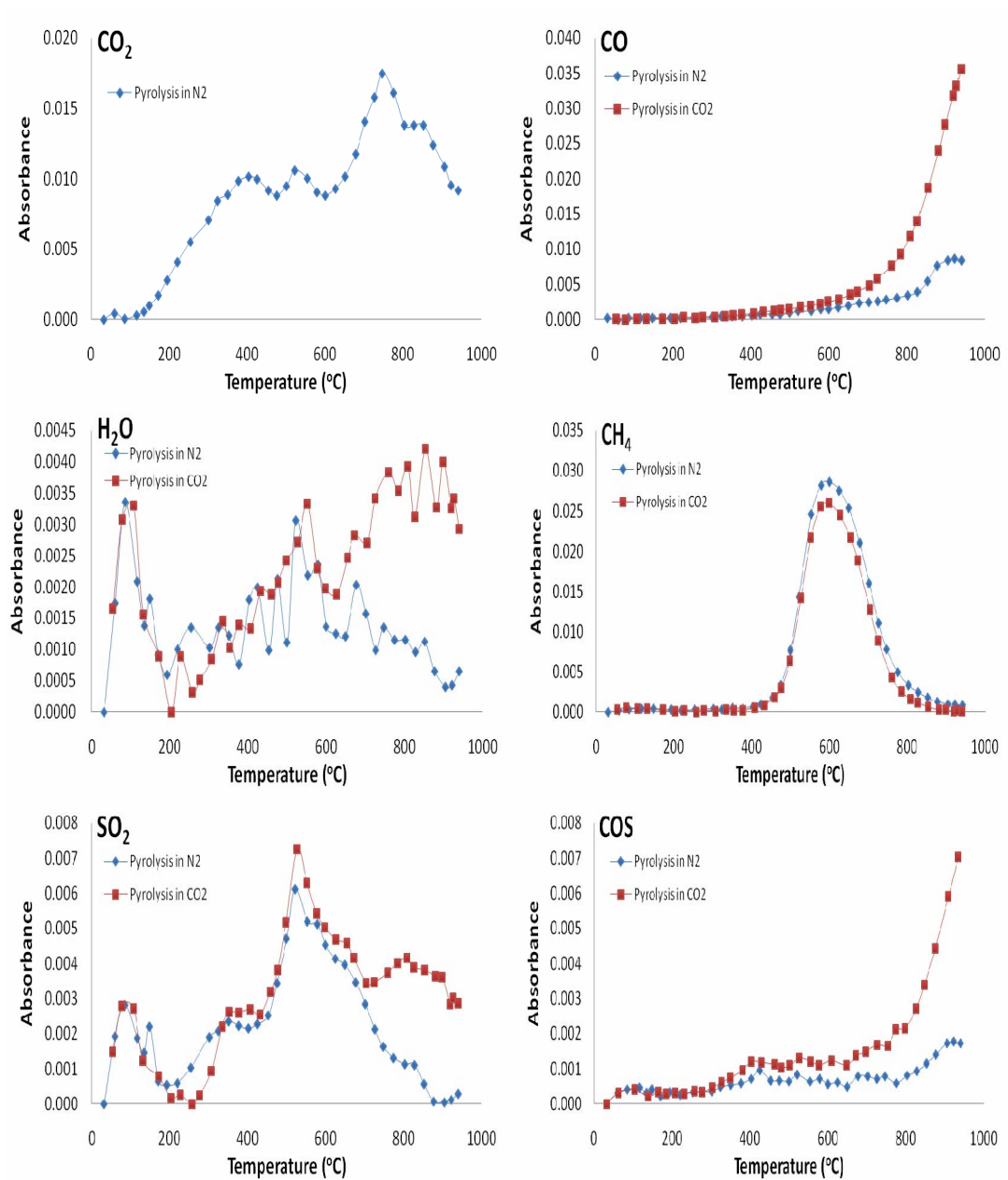


Figure 3: Formation profiles of evolved gases during pyrolysis tests of blend

3.2 Combustion tests of fuel samples

Combustion profiles of imported coal/petcoke/lignite blend under different combustion environments are shown in Fig. 4. Combustion characteristics of parent fuels and their blend are displayed in Table 3.

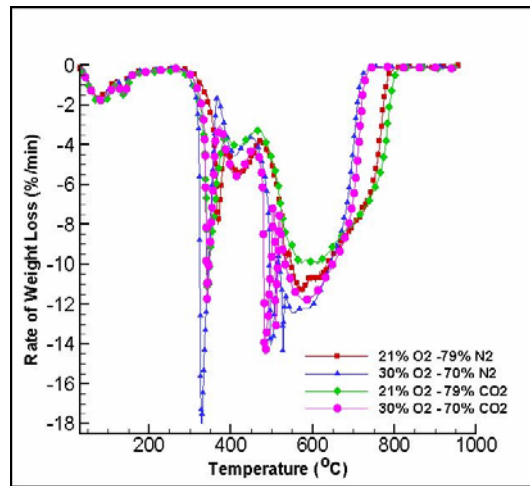


Figure 4: Combustion profiles of the blend in different combustion atmospheres

In air and oxy-fuel cases, after moisture release in the first 200°C temperature zone, three different weight loss steps are displayed in the DTG curves of the blend. In the temperature range of 300-450°C, two different weight loss steps account for combustion of highly reactive lignite component. In this interval, volatile matter and char combustion steps of lignite are discretely separated. The main peak between 450-700°C is attributed to combustion of imported coal and petcoke in both conditions. In this temperature interval, rate of weight loss is lower and burnout temperatures are higher in oxy-fuel conditions as higher heat capacity of CO₂ leads to delay in combustion (Table 3). The effect of oxygen concentration is found to be more significant than that of the diluting gas (N₂ or CO₂) on the combustion profiles. Table 3 and Fig. 4 reveal that at elevated oxygen levels, weight loss rates increase and characteristic temperatures including T_{ig} , T_{max} and T_b decrease. In oxygen-enriched conditions, additional peaks appear in the main combustion peak of imported coal and petcoke after 450°C. These additional peaks represent weight loss due to burning of volatiles in imported coal and petcoke. The presence of oxygen in the combustion environment leads reduction in force of the fusion layer around solid particle, which results in easier release of volatile matter [20]. Therefore, additional peaks appear in DTG curves in oxygen-enriched conditions.

Theoretical and experimental combustion profiles of the blends with their parent fuels are compared in Fig. 5. DTG curves mainly display different trends, which may be due to synergistic interactions between parent fuels in all combustion environments. In theoretical DTG curves of the blend samples, lignite combustion is not distinguished due to its lower proportion in the blend. However, as lignite burns separately from imported coal and petcoke, its combustion peak is clearly demonstrated in experimental DTG curves in contrast to expected behaviour. The positive effect of blending is observed at higher temperatures. In this temperature zone, the main combustion peaks of imported coal and petcoke have higher weight loss rates and lower corresponding peak temperatures than those in theoretical conditions. All these results are indicative of interaction of the component coals during combustion in all cases.

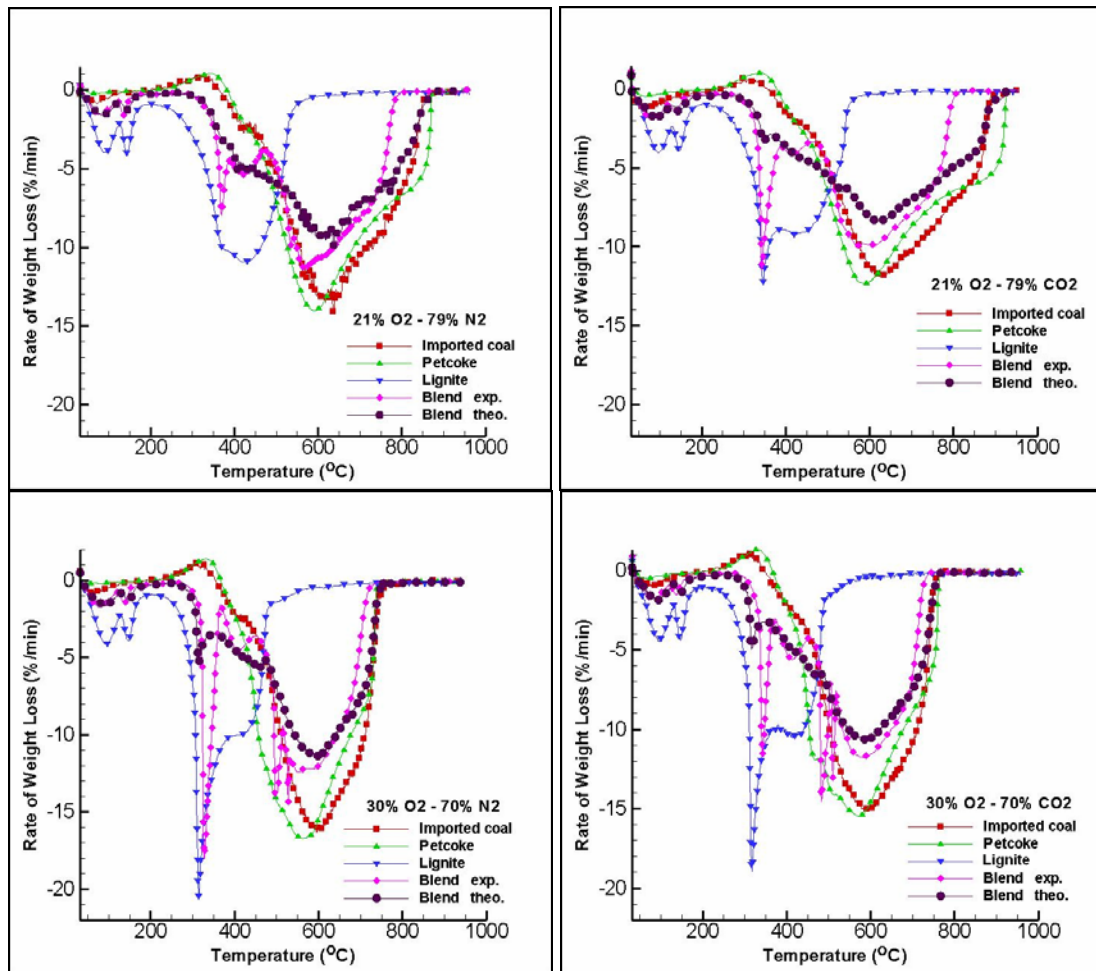


Figure 5: Combustion profiles of the blend and its parent fuels in different combustion environments

Table 3: Combustion characteristics of fuel samples.

		T_{in}	T_{max}		$(dm/dt)_{max}$			T_{ig}	T_b	Total weight loss up to 950°C	
Imported Coal	21 % O ₂ - 79 % N ₂	387.4	618.3	-	-	13.3	-	-	446.6	848.4	89.1
	30 % O ₂ - 70 % N ₂	376.7	594.9	-	-	16.1	-	-	422.0	745.0	89.2
	21 % O ₂ - 79 % CO ₂	387.0	629.2	-	-	11.8	-	-	393.0	885.1	93.3
	30 % O ₂ - 70 % CO ₂	371.4	591.1	-	-	15.0	-	-	420.3	752.0	90.3
Petcoke	21 % O ₂ - 79 % N ₂	400.1	589.0	-	-	14.0	-	-	469.5	867.0	96.8
	30 % O ₂ - 70 % N ₂	381.6	562.2	-	-	16.8	-	-	439.7	735.6	95.9
	21 % O ₂ - 79 % CO ₂	398.7	587.6	-	-	12.4	-	-	465.4	923.7	96.7
	30 % O ₂ - 70 % CO ₂	379.5	572.6	-	-	15.5	-	-	434.7	761.8	97.9
Lignite	21 % O ₂ - 79 % N ₂	224.0	-	426.2	-	-	11.0	-	297.1	546.7	59.2
	30 % O ₂ - 70 % N ₂	226.1	314.5	-	-	20.5	-	-	265.3	530.0	59.3
	21 % O ₂ - 79 % CO ₂	225.8	347.1	-	-	12.3	-	-	308.8	550.0	59.6
	30 % O ₂ - 70 % CO ₂	202.8	317.2	-	-	19.0	-	-	264.1	535.6	61.2
Blend Exp.	21 % O ₂ - 79 % N ₂	329.6	368.8	424.1	573.7	7.8	5.4	11.4	363.4	780.2	81.5
	30 % O ₂ - 70 % N ₂	306.9	328.3	403.9	551.2	18.0	4.5	12.4	324.3	715.6	80.8
	21 % O ₂ - 79 % CO ₂	308.1	343.1	410.0	609.9	11.5	4.0	10.0	338.7	795.23	82.3
	30 % O ₂ - 70 % CO ₂	315.3	343.2	411.0	583.5	11.8	5.6	11.8	346.3	725.9	82.9
Blend Theo.	21 % O ₂ - 79 % N ₂	332.8	-	637.8	-	-	10.8	-	360.7	852.8	80.9
	30 % O ₂ - 70 % N ₂	295.7	314.7	595.7	-	5.5	11.5	-	298.1	740.7	81.1
	21 % O ₂ - 79 % CO ₂	316.4	-	630.4	-	-	8.3	-	334.7	887.4	83.2
	30 % O ₂ - 70 % CO ₂	300.5	316.4	591.5	-	4.9	10.7	-	308.4	754.5	82.3

The formation profiles of evolved gases during combustion of the blend in different atmospheres are shown in Fig. 6. The formation profile of CO₂ in oxygen-enriched air atmosphere shifts to lower temperature zone as elevated oxygen levels lead to faster burning and earlier release of CO₂. Two steps are observed in formation profiles of CO₂ gas due to burning of lignite and imported coal-petcoke, consecutively. CO formation takes place between 300-800°C with a shoulder at around 375°C. H₂O formation profiles show that moisture is released first in all combustion environments with further release in the temperature range of 200-800°C. CH₄, SO₂ and COS gases evolve between 250-750°C and reveal two stages in their evolution profiles. Mainly similar formation trends are observed for gases in all combustion cases.

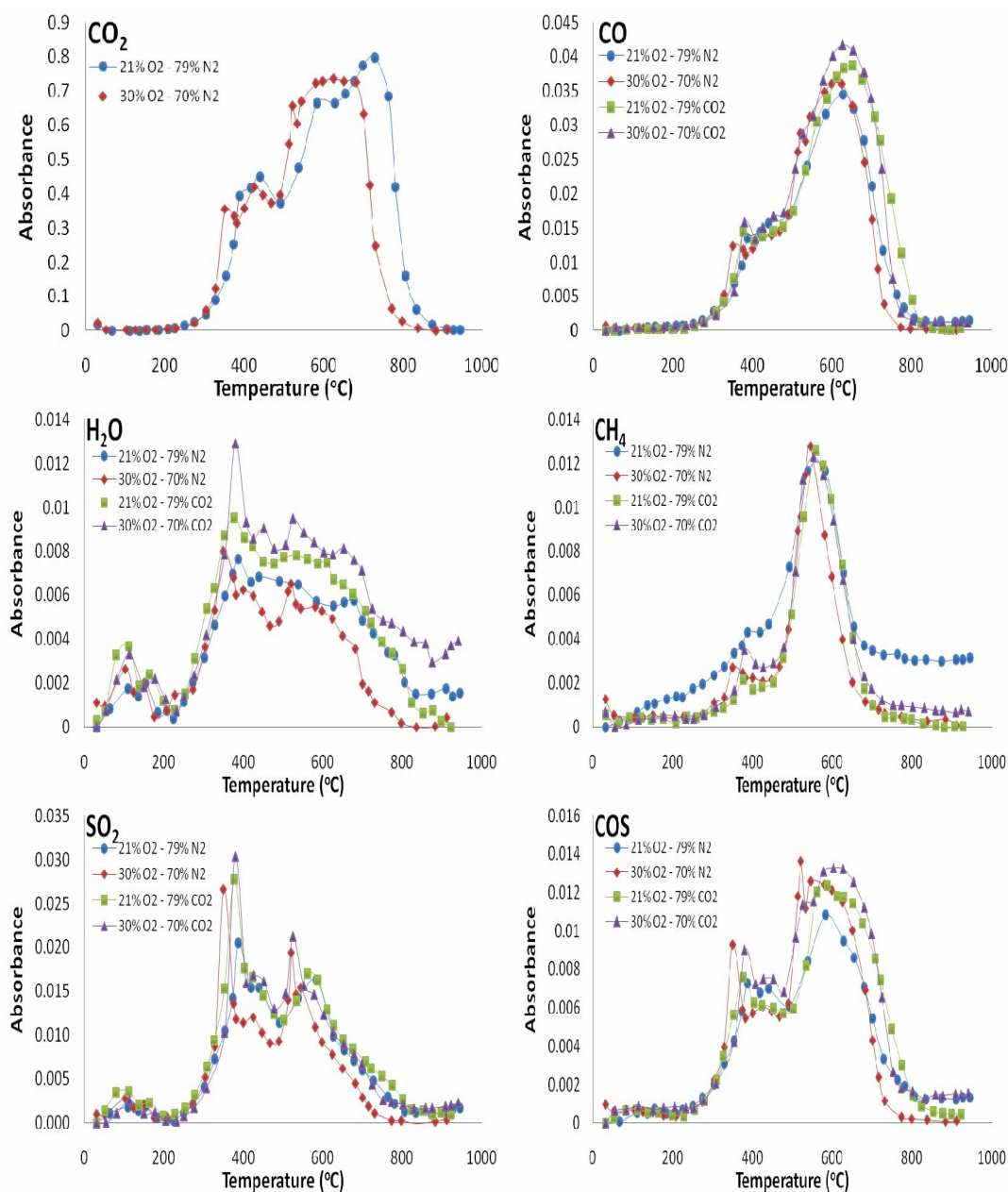


Figure 6: Formation profiles of evolved gases during combustion tests of blend

4. Conclusions

In this study, pyrolysis and combustion characteristics of imported coal, indigenous lignite, petcoke and their 60/30/10 wt. % ternary blend in air and oxy-fuel conditions was reported.

Experiments were carried out by using TGA-FTIR combined system. In pyrolysis tests similarity in weight loss profiles of the fuel samples up to 700°C in both N₂ and CO₂ environments reveal that CO₂ behaves as an inert gas. However, at high temperature zone char-CO₂ gasification reaction is observed which leads to significant increase in FTIR formation profiles of CO and COS gases. Pyrolysis behaviour of the blend is dominated by lignite that has the highest volatile matter content in the parent fuels. Theoretical and experimental DTG curves are compared to investigate the synergistic behaviour of the blend samples. Different characteristic temperatures and trends in theoretical and experimental curves display the synergy between parent fuels during co-pyrolysis. Combustion tests were carried out in O₂/N₂ and O₂/CO₂ mixtures with oxygen concentrations of 21 and 30%. Effect of oxygen concentration is found to be more significant compared to that of diluting gas in combustion environment. At elevated oxygen levels, volatile matter and char burning steps are separated, weight loss rates increase and characteristic temperatures decrease. Comparison between theoretical and experimental combustion curves also reveals that there are interactions between parent fuels during combustion tests. In experimental conditions higher weight loss rates and lower characteristic temperatures are obtained than theoretical ones which indicates the positive effect of coal blending.

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