PYROLYSIS AND COMBUSTION BEHAVIOUR OF VARIOUS FUELS IN OXYGEN-ENRICHED AIR AND CO_2 ATMOSPHERES

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ABSTRACT

PYROLYSIS AND COMBUSTION BEHAVIOUR OF VARIOUS FUELS IN OXYGEN-ENRICHED AIR AND CO_2 ATMOSPHERES

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Oxy-fuel combustion technology, which is based on burning coal in a mixture of oxygen and recycled flue gas (RFG), is suggested as one of new promising technologies for capturing CO_2 from power plants.

In this thesis study, the pyrolysis and combustion behaviour of various fuels including imported coal, petroleum coke, two different types of indigenous lignites, olive residue and their blends with different proportions in air and oxy-fuel conditions were investigated by using non-isothermal thermogravimetric method (TGA) coupled with Fourier-transform infrared (FTIR) spectrometer.

Pyrolysis tests were carried out in nitrogen and carbon dioxide environments, which are the main diluting gases of air and oxy-fuel environment, respectively. Pyrolysis results reveal that weight loss profiles are similar up to high temperature zone in both pyrolysis environments, indicating that CO_2 behaves as an inert gas in this temperature range. However, further weight loss takes place in CO_2 atmosphere

after 700^{o}C due to CO_2-char gasification reaction which is observed in pyrolysis of all fuel samples.

Combustion experiments were carried out in four different atmospheres; air, oxygen-enriched air environment (30 % O_2 – 70 % N_2), oxy-fuel environment (21 % O_2 – 79 % CO_2) and oxygen-enriched oxy-fuel environment (30 % O_2 – 70 % CO_2). Combustion experiments show that replacing nitrogen in the gas mixture by the same concentration of CO_2 does not affect the combustion process significantly but leads to slight delay (lower weight loss rate and higher burnout temperature) in combustion. Overall comparison of weight loss profiles shows that higher oxygen content in the combustion environment is the dominant factor affecting the combustion rather than the diluting gas. As O_2 concentration increases profiles shift through lower temperature zone, peak and burnout temperatures decrease, weight loss rate increases and complete combustion is achieved at lower temperatures and shorter times.

Pyrolysis and combustion behaviour of three different fuel blends were also investigated. Results reveal synergistic interactions in combustion tests of all blends in all combustion environments.

During pyrolysis and combustion tests gaseous products CO_2, CO, H_2O, CH_4, SO_2 and COS were identified in flue gas and analyzed by using FTIR. Results indicate that higher CO and COS formation take place during pyrolysis tests due to gasification reaction in CO_2 atmosphere at high temperature zone. Gaseous species evolution trends in combustion tests are found specific for each fuel. However, evolution trends slightly shift to lower temperatures in oxygen-enriched conditions.

Keywords: Oxy-fuel combustion, oxygen-enriched combustion, CO_2 capture, TGA-FTIR, coal blends, lignite-biomass blends.

ÖZ

OKSİJENCE ZENGİN HAVA VE CO_2 ORTAMINDA ÇEŞİTLİ YAKITLARIN PİROLİZ VE YANMA ÖZELLİKLERİNİN İNCELENMESİ

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Kömürün, oksijen ve geri dönüşümlü baca gazı (RFG) karışımında yanmasına dayanan oksi-yakıt yanma teknolojisi, enerji santrallerinden CO_2 gazının yakalanması için günümüzde umut vaat eden yeni teknolojilerden biri olarak önerilmektedir.

Bu tez çalışmasında, ithal kömür, petrokok, yerli linyitler, pirina ve bu yakıtları içeren çeşitli karışımların, hava ve oksi-yakıt koşullarında piroliz ve yanma davranışları termogravimetrik analiz yöntemi (TGA) ve buna bağlı olan Fourier dönüşümü kızılötesi spektrometresi (FTIR) kullanılarak incelenmiştir.

Piroliz testleri hava ve oksi-yakıt koşullarının seyreltici gazları olan sırasıyla azot ve karbon dioksit ortamlarında gerçekteştirilmiştir. Piroliz testlerinde elde edilen sonuçlara göre, kütle kayıp profillerinin her iki piroliz ortamında da yüksek sıcaklıklara kadar benzer davranışlar sergilediği görülmüş ve bu durum CO_2 gazının bu sıcaklık aralığında inert bir gaz şeklinde hareket ettiğini göstermiştir.

Ancak karbon dioksit ortamında 700^{o}C'den sonra kömür-CO_2 gazlaşma reaksiyonu sebebiyle kütle kaybının devam ettiği görülmüştür.

Yakma testleri ise hava, oksijence zengin hava ortamı (30 % O_2 – 70 % N_2), oksi-yakıt ortamı (21 % O_2 – 79 % CO_2) ve oksijence zengin oksi-yakıt ortamı (30 % O_2 – 70 % CO_2) olmak üzere dört farklı atmosferde yapılmıştır. Yakma testlerinde elde edilen sonuçlar yanma atmosferindeki azot gazının, aynı hacimdeki karbon dioksit gazıyla yer değiştirilmesi sonucunda yanma prosesinin belirgin bir şekilde etkilenmediğini; ancak CO_2 gazının yanmada bir miktar gecikmeye (kütle kayıp hızında düşüş ve tam yanma sıcaklığında artış) yol açtığı göstermiştir. Kütle kayıp profillerinin karşılaştırılması sonucunda, yanma prosesine N_2 gazının CO_2 ile yer değiştirmesinden ziyade, en baskın etkenin yanma atmosferindeki yüksek oksijen konsantrasyonu olduğu anlaşılmıştır. Oksijen konsantrasyonunun artmasıyla yanma profilleri daha düşük sıcaklıklara doğru kaymış, maksimum kütle kayıp hızları artmış ve bu noktaya denk gelen maksimum sıcaklıklar düşmüş, tam yanmaya daha düşük sıcaklıklarda ve daha kısa sürede ulaşılmıştır.

Yapılan çalışmada üç farklı çeşit yakıt karışımının da piroliz ve yanma özellikleri incelenmiştir. Buna göre karışımı oluşturan yakıtların tüm ortamlardaki yanma testleri sırasında etkileştiği (sinejik etki) görülmüştür.

Piroliz ve yanma testleri sonucunda, baca gazında CO_2, CO, H_2O, CH_4, SO_2 ve COS tespit edilmiş ve FTIR yöntemi kullanılarak analiz edilmiştir. Piroliz testlerinde, CO_2 ortamında gerçekleşen gazlaşma reaksiyonu sonucunda CO ve COS gazlarının yüksek sıcaklıklarda belirgin bir şekilde arttığı görülmüştür. Yakma testlerinde yakıtların yapısına göre farklı oluşum profilleri elde edilmiştir. Yanma sırasında tespit edilen gazların yüksek oksijen konsantrasyonuna sahip ortamlarda daha düşük sıcaklıklarda oluştuğu söylenebilir.

Anahtar Kelimeler: Oksi-yakıt yanma, oksijence zengin ortamda yanma, CO_2 yakalama, TGA-FTIR, kömür karışımları, linyit-biyokütle karışımları.

To my great family and knowledge

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CHAPTER 1

INTRODUCTION

1.1 General

Today, energy requirement of the world and demand for electric power continues to increase due to population growth, developments in economy and technology. In electric power production, coal provides the largest share due to its abundant and widely distributed reserves. With 826 billion tonnes of proved coal reserves, coal combustion is expected to dominate the energy production for at least the next few decades [1]. Coal combustion dominates the electricity generation sector worldwide with its 41 % share in fuel sources [2]. Higher prices and lower reserves of oil and natural gas make coal-fired generation economically more attractive especially for coal rich countries.

Significant rise in energy demand leads to increase in anthropogenic CO_2 emissions. Since pre-industrial era, CO_2 level in the atmosphere has increased from 280 ppmv to 388 ppmv [3]. Figure 1.1 compares world CO_2 emissions by sector in 2008. Generation of electricity and heat was the largest CO_2 produced sector, which was responsible for 41 % of the world CO_2 emissions in 2008 [4].

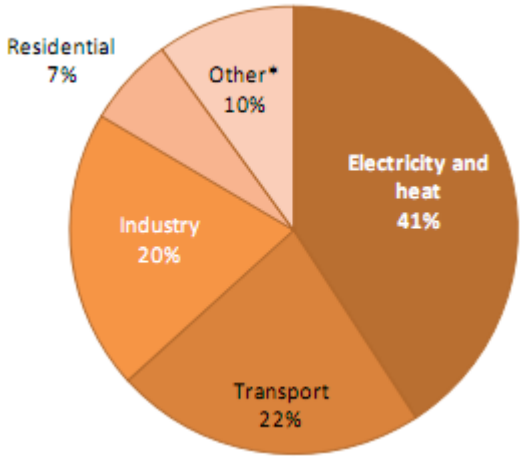

Figure 1.1: World CO_2 emissions by sector in 2008 [4]

Growing concern about greenhouse gas emissions and their potential impact on climate change necessitates reduction of CO_2 emissions from coal fired power plants which accounts for 16 % of world CO_2 emissions [2, 4]. CO_2 emission reduction regulations are driven by international initiatives such as the International Panel on Climate Change (IPCC) and Kyoto Protocol, which was also signed by Turkey in February 2009.

Various solutions can be applied to reduce CO_2 emissions from existing coal fired power plants, such as improving energy efficiency, making use of renewable fuels such as biomass, switching to lower carbon fuels, blend and burn different kinds of solid fuels. However, a significant reduction in CO_2 emissions can be achieved by capturing CO_2 generated from coal utilization from stack gases and storing (sequestering) it [5]. Various technologies and new pathways are being developed for CO_2 capture and storage from coal fired plants. The most attractive technologies for carbon capture and storage (CCS) can be classified in three main categories that are post-combustion, pre-combustion and oxy-fuel combustion [5-8].

Conventional technologies for removing CO_2 from the stack gas in the existing coal fired power plants are expensive since CO_2 is diluted (typically about 14 % by volume on a dry basis). The cost of gas separation can be reduced by increasing the concentration of CO_2 in the flue gas. This can be achieved by increasing the oxygen concentration in the feed stream by using oxy-fuel combustion technology which is based on burning coal in a mixture of oxygen and recycled flue gas (RFG) leading to CO_2 concentrations up to 98 % in the exhaust gas [9]. Many other techno-economic assessment studies reported that oxy-fuel combustion could be demonstrated as cost effective method of CO_2 capture in CCS technologies.

Many laboratory and pilot scale studies were carried out within the last two decades about this technology. These investigations reveal that it is possible to burn coal in O_2/CO_2 atmosphere. Oxy-fuel combustion technology is a near zero emission technology which can be adapted to both new and existing coal fired power plants. Therefore, oxy-fuel combustion is considered as a favourable option in carbon capture and storage technologies to reduce CO_2 emissions from coal-fired power plants but more research is still required to fully understand this technology.

1.2 Aim and Scope of the Thesis

Oxy-fuel combustion has been studied extensively for pulverized coal combustion, but to date has received relatively less attention for fluidized bed combustion (FBC) systems. Benefits of fluidized bed combustion (FBC) technology such as the ability to burn wide variety of fuels efficiently and to control pollutant emissions without flue gas treatment systems have led to a steady increase in its commercial use over the past decades. Advantage of oxy-fuel firing in FBC technology is that significant reduction in the amount of recycled flue gas can be achieved through the external solid heat exchangers for combustion temperature control [10].

Before firing tests in FBC combustors, combustion characteristics of the various fuels 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 behaviours of fuels and evaluating the relative burning properties of fuel samples [11-17]. In spite of significant ongoing research in this area, there is limited number of studies on oxy-fuel combustion properties of indigenous lignites, biomass, petroleum coke and their blends with various proportions.

Therefore, the objective of this study has been to investigate pyrolysis and combustion behaviour of various fuels in air (O_2/N_2) and oxy-fuel (O_2/CO_2) conditions by using TGA technique combined with Fourier Transform Infrared (FTIR) spectroscopy to analyze the gaseous species evolved. In an attempt to fulfill this aim, pyrolysis and combustion characteristics of five different types of fuels including imported coal, petroleum coke, two different types of indigenous lignites, olive residue as biomass and their various blends have been studied and reported in this thesis.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 General

In the first part of this section, carbon capture and storage technologies including pre-, post- and oxy-fuel combustion and their main processes are briefly summarized. In the following part, oxy-fuel combustion, which is the focus of this study, is explained in detail. This section is concluded with the specific oxy-fuel studies that were carried out by using thermogravimetric analysis technique.

2.2 Pathways to Capture CO_2

In the past two decades, there has been a growing concern about increase in CO_2 emission and its potential impact on climate change. As coal-fired power plants accounts for about 16 % of CO_2 emissions, researchers have focused on improving clean and efficient technologies in CO_2 reduction in the recent years. There are several options to reduce CO_2 emissions, such as increasing power plant efficiency or using fuels with lower fossil carbon content. However, these options will not achieve the required reductions in CO_2 emissions. The capture of CO_2 from coal-fired systems, that is, Carbon Capture and Storage (CCS) technologies may contribute significantly for solution of this problem. The identified technologies for

carbon capture are classified as post-, pre- and oxy-fuel combustion. Main operations concerned with these technologies are described in Figure 2.1.

Post-combustion includes the separation of CO_2 from the flue gas by chemical absorption with chemical solvents and solid minerals such as monoethanolamine (MEA) or a sterically hindered amine (KS-1). Chemically active agents that are used to scrub CO_2 are regenerated by heating to release CO_2. Considerable energy is required to regenerate these solvents, which leads to 10-14 % points drop in efficiency of power plants. Low concentration of CO_2 in the flue gas (~14 %) results in increase in capture equipment sizes and high capital costs [18, 19].

Pre-combustion comprises Integrated Gasification Combined Cycle (IGCC) power plants with carbon capture and storage units. Coal is gasified under high pressure in order to obtain syngas containing CO, CO_2 and H_2. CO is converted into CO_2 by water-gas shift reaction. CO_2 is separated from the gas and remaining H_2 is used for combustion in a gas turbine. IGCC is considered as a promising technology because of its economics and plant efficiency characteristics; however, it requires high capital costs in plant constructions. Moreover, it is not possible to retrofit existing power plants for IGCC-CCS process [18, 20].

Oxy-fuel combustion process is based on increasing the concentration of CO_2 in the flue gas. Conventional technologies for removing CO_2 from the stack gas in the existing coal fired power plants are expensive since CO_2 is diluted (typically about 14 % by volume on a dry basis). The cost of gas separation can be reduced by increasing the concentration of CO_2 in the flue gas. This can be achieved by increasing the oxygen concentration in the feed stream by using oxy-fuel combustion technology which is based on burning coal in a mixture of oxygen and recycled flue gas (RFG) leading to CO_2 concentrations up to 95 % in the exhaust gas. Many other techno-economic assessment studies reported that oxy-fuel combustion should be the most cost and energy efficient technology in CCS.

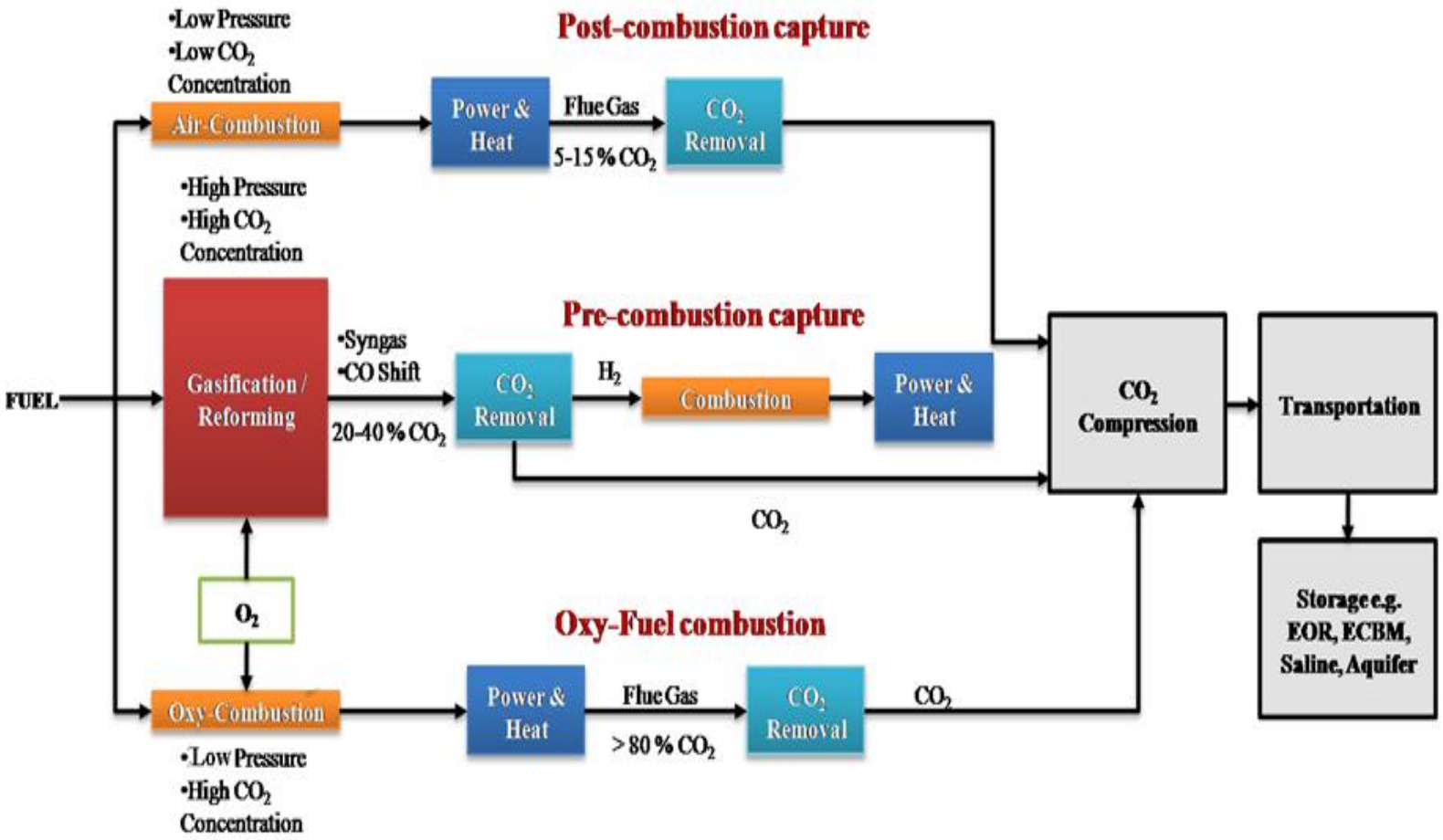

Figure 2.1: Pathways to capture CO_2.

However, main disadvantage of this technology is the requirement of air separation unit (ASU) for pure O_2 [6, 9, 18, 21-23].

There are no full-scale plants using CCS technologies in operation, however, there is a significant ongoing research in this area. There are many large-scale and pilot scale CCS projects worldwide currently. These projects are listed in Appendix A [18].

Recent techno-economic studies have compared the pre-, post- and oxy-fuel combustion technologies in terms of efficiency, the contributions to increased costs, and the cost of electricity (COE) with a CO_2 tax or penalty. These studies reveal that efficiency penalties vary from 7 % to 10 %. CO_2 compressions and solvent regeneration in post combustion or pure oxygen production in pre- and oxy-fuel combustion systems are the main contributors to efficiency losses. Current knowledge on economical comparisons of these three capture technologies shows that there is no significant difference in cost [18, 20, 22].

As one of three main CO_2 capture approaches, oxy-fuel combustion has received a lot of attention in the recent years as it has potential to produce significantly high CO_2 concentration in the flue gas, which provides easier sequestration of CO_2 from flue gases in coal-fired power plants. Therefore, oxy-fuel combustion, which is considered to be a promising and cost effective option for reduction of CO_2 emissions, is the focus of this study.

2.3 Oxy-fuel Combustion Technology

Oxy-fuel combustion technology has been firstly evaluated by Abraham et al. to produce CO_2 gas for Enhanced Oil Recovery (EOR) in the early eighties [24]. However, after mid-90s, this technology received renewed interest due to growing concern about greenhouse gas emissions.

Oxy-fuel combustion technology involves the combustion of coal in the mixture of oxygen and recycled flue gas (RFG), instead of air, in order to increase concentration of CO_2 in the flue gas for easy separation. CO_2 concentration in the flue gas can be increased from 14 % up to 95 % by volume, with this technology. RFG is used to make up the volume of missing N_2, control the flame temperature and heat flux profiles [6, 25].

Figure 2.2 demonstrates major process steps of a coal-fired oxy-fuel power plant. Oxygen is separated from air by using air separation unit (ASU). Pure oxygen stream is then mixed with recycled stream of flue gas from the boiler and coal is burned in this resulting gas stream. After combustion in the boiler, the released flue gas is transferred to cleaning equipment. Main cleaning equipments include filter, condenser and flue gas desulphurization (FGD) units for removal of fly ash, water vapour and sulphur, respectively. The cleaned flue gas is partially recycled to boiler and rest of the stream containing clean CO_2 gas is sent to storage units.

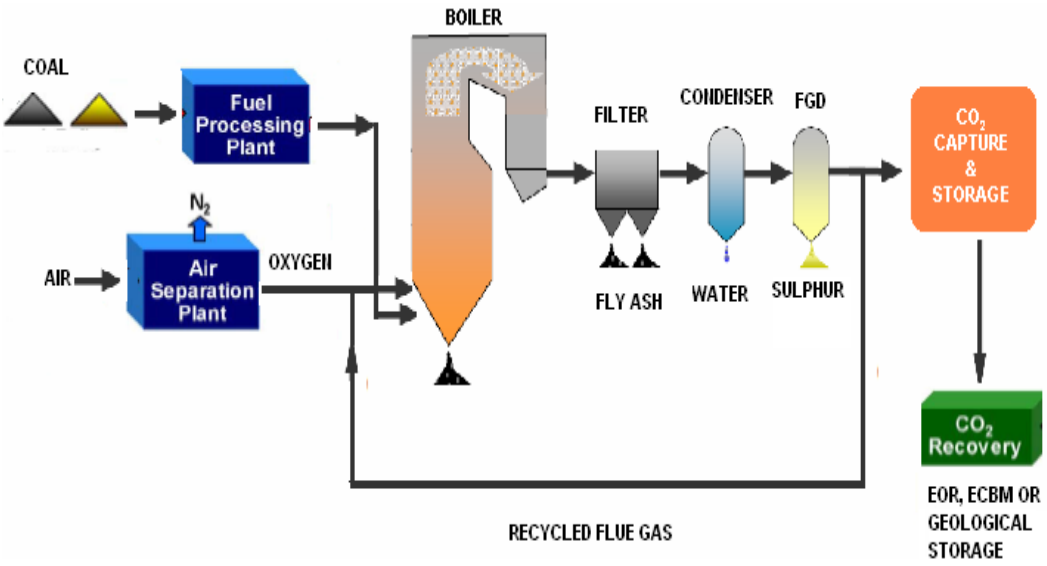

Figure 2.2: Possible configuration of a coal-fired oxy-fuel power plant

Many laboratory and pilot scale studies on oxy-fuel combustion technology have been reported by different researchers and organizations in the open literature up to date. These studies have been summarized by Toftegaard et al. recently, including the information on experimental conditions and aim of each research group [18].

These studies reveal that, oxy-fuel combustion differs from air combustion in combustion characteristics such as burning stability, char burnout, gas temperature profiles and heat transfer due to differences in gas radiative and thermo-physical properties between CO_2 and N_2, which are the main diluting gases in oxy-fuel and air combustion, respectively. Substituting CO_2 with an equal volume N_2 leads to larger specific heat capacity in combustion environment that results in lower flame temperatures and delayed combustion in oxy-fuel conditions compared with those in air conditions. Devolatilization, ignition and burnout take place at lower rates in oxy-fuel conditions [6, 23, 26-29]. Previous studies on oxy-fuel combustion mainly revealed that similar temperature profiles with air case are achieved at higher oxygen concentrations between 25 and 42 vol. % depending on fuel and boiler type [9, 23, 30].

Oxy-fuel combustion also differs from air-firing case in gaseous emissions such as; CO, NO_x, SO_2 and SO_3. It has been reported in the literature that increase in CO_2 concentration in the combustion environment leads to increase in CO emissions in the near flame zone which may cause the risk of CO corrosion [18, 31]. Numerous studies on NO_x emissions in oxy-fuel combustion reveal that it is possible to achieve almost 70-80 % reduction in NO_x emissions compared to combustion in air through near elimination of thermal and prompt NO_x formation as levels of molecular nitrogen is significantly lower in oxy-fuel conditions [22, 24, 28, 32]. However, increase in oxygen concentration results in higher NO_x levels as temperature of combustion environment increases. In order to avoid this effect, various options such as; oxygen staging or increasing oxygen purity is suggested in the open literature [28]. Studies on sulphur oxides shows that release of sulphur from coal is

not affected significantly with the replacement of nitrogen by carbon dioxide. However, sulphur induced corrosion risk appears even at low temperatures (below the acid dew point) in oxy-fuel operation systems including flue gas recirculation without prior SO_2 removal as the amount of SO_3 in the boiler can reach high values. Moreover, SO_3 formation is promoted in oxygen enriched conditions and high water contents in the flue gas if it is recycled before condenser [9, 18, 23].

2.4 Oxy-fuel Combustion Studies by Thermogravimetric Analysis

In the study of Li et al. [25], thermogravimetric technique were used to investigate pyrolysis and combustion behaviour of a pulverized Chinese bituminous coal in oxy-fuel conditions. Effect of pyrolysis environment, oxygen level, particle size and heating rate on pyrolysis and combustion processes and release of gaseous compounds in those conditions were reported. Pyrolysis tests were carried out under N_2 and 21 % N_2 – 79 % CO_2 mixture while combustion tests were performed in air and O_2/CO_2 mixtures with oxygen concentrations of 21, 30, 40, and 80 %. For these tests, approximately 10 mg of pulverized coal samples were heated from room temperature to 1000^{o}C with a heating rate of 30^{o}C/min and gas flow rate of 80 ml/min. In order to clarify the effects of heating rate and particle size additional combustion tests were carried out at heating rates of 10, 20, 30^{o}C/min and particle sizes < 48, 48 – 74, 74 – 90 μm. Gaseous species evolved in pyrolysis and combustion tests were analysed by using FTIR spectrometer. In N_2/CO_2 mixtures, additional gasification stage was observed in pyrolysis profiles of pulverized coal samples at high temperature zone. Under oxygen concentrations corresponding to that of air, combustion was delayed and in elevated oxygen levels, DTG curves shift to lower temperatures. Decrease in particle size led to increase in burning rate and decrease in burnout while heating rate had no significant effect on combustion process.

Liu et al. [33] reported a comparative study on combustion behaviour of two different coal chars in O_2/N_2 and O_2/CO_2 by using thermal analysis methods. Coal chars, which were prepared by using high volatile bituminous coal and anthracite, were burned in the mixtures of O_2/N_2 and O_2/CO_2 with oxygen levels of 3, 6, 10, 21, 30 %. Combustion tests showed that replacing N_2 with the same amount of CO_2 did not result in significant differences in combustion behaviour of char samples as combustion temperature of the sample is controlled by electrical heating in TGA technique. Therefore it was concluded that sample temperature is not affected by combustion environment. Four different methods were used in determination of activation energies of the char samples. Activation energy values were found to be in agreement with those in literature for both bituminous and anthracite chars. Kinetic analysis of the char samples revealed that in oxygen – carbon dioxide mixtures, combustion rate of the char samples were found to vary approximately linearly with the oxygen concentration.

Four different types of Australian coals were analyzed by using drop tube furnace (DTF) to measure coal burnout and thermogravimetric analyzer (TGA) to determine the reactivity of coal/char samples in the study of Rantham and his co-workers. In DTF pyrolysis tests apparent volatile yields of all the four coals were found higher in CO_2 environment compared to those in N_2. TGA pyrolysis tests revealed similar behaviour up to 1030 K in both N_2 and CO_2 environments. After 1030 K, significant increase in mass loss rate was observed. This significant increase and higher apparent volatile yields in CO_2 atmosphere were attributed to CO_2-char gasification reaction. DTF combustion tests were carried out in O_2/N_2 and O_2/CO_2 mixtures with oxygen concentrations in the range 3 to 21 % and 5 to 30 %, respectively. In combustion tests, coal burnout was observed to increase in elevated oxygen levels for all four coals. For coals C and D, coal burnouts were observed to be similar in air and oxy-fuel conditions at the same oxygen levels in contrast to coals A and B. For coals A and B higher burnouts were obtained in oxy-fuel conditions compared to that in air conditions. Coal chars were prepared at 1673K in nitrogen environment by using DTF and combusted in TGA for reactivity analysis. TGA combustion tests

were performed in O_2/N_2 and O_2/CO_2 mixtures with oxygen concentrations of 2, 5, 10, 21 and 50 %. Almost identical combustion behaviours were displayed in O_2/N_2 and O_2/CO_2 mixtures at oxygen concentrations of 5 % and above. However, in 2 % O_2/CO_2 conditions, effect of gasification was significant. At elevated oxygen levels, higher maximum reactivity and lower burnout temperatures were obtained [29].

Duan et al. [34] investigated pyrolysis of coals in CO_2 atmosphere to have better understanding of combustion characteristics and gas evolution mechanisms in oxy-fuel conditions by using TGA-FTIR combined system. Formation of SO_2, and NO_x related species such as, H_2S, COS, SO_2, HCN and NH_3 were reported. About 10 mg bituminous coal samples having particle size less than 100 µm were used in pyrolysis tests. Samples heated from room temperature to different end temperatures; 700, 800, 900 and 1000^oC with different heating rates; 10, 30, 50 and 70^oC. TGA tests showed that replacing N_2 with CO_2 in pyrolysis environment had no significant effect on initiation of volatile matter release and rate of weight loss up to 480^oC. In N_2 atmosphere, calcite decomposition was observed after 760^oC, however, in CO_2 environment, calcite decomposition was prevented. At higher heating rates, volatile yields decreased, however, at higher end temperatures volatile yields increased to due the effect of coal gasification. In FTIR analysis, reactions between H_2S and CO_2 led to COS formation in CO_2 atmosphere. Conversion of fuel-N to HCN was favoured by gasification of char in CO_2 conditions.

In another study of Duan et al. [35] effect of oxy-fuel conditions on sulphur formation behaviour of a bituminous coal and its char displayed in pyrolysis and combustion experiments was reported. Samples were heated from room temperature to 1173 K with a heating rate of 30 K/min. Pyrolysis tests revealed that COS formation was identified in CO_2 rather than N_2 environment. Higher SO_2 formation was observed when oxygen concentrations were identical in the combustion environment (21 % O_2/79 % N_2 and 21 % O_2/79 % CO_2). It was reported that elevated oxygen levels enhance organic sulphur decomposition rate and conversion of H_2S to SO_2, which resulted in faster SO_2 formation in oxygen-enriched

environments. X-ray photoelectron spectroscopy (XPS) test results demonstrated that sulphur retention ability increased with the increase in oxygen levels in combustion environment.

In the report of Alstom Power Inc. [36] about engineering feasibility and economics of CO_2 on an existing coal fired plant, TGA tests were performed to obtain reactivity parameters of Conesville and Pittsburgh coals. About 4-6 mg of samples were placed over a pan almost a monolayer in order to mitigate the effects of oxygen mass transfer control phenomena during combustion. In each condition 50 cc/min of analysis gases were mixed with 50 cc/min balance N_2 gas, which was used to protect balance from over heating. Combustion tests were carried out in three different environments; base case (air), constant mass case and constant volume case. Constant mass and volume cases refer to replacement of N_2 with an equal mass and volume of CO_2 gas, respectively. Slight differences in TGA combustion efficiency profiles were reported as experimental error for this type of testing. Peak temperatures obtained from DTG profiles of the coals were found to be in the range of 472 – 479^{o}C for all test conditions. This narrow range was considered to be indicative of similar reactivity characteristics of these two coals in air or any of the O_2/CO_2 mixture.

Oxy-fuel characteristics and combustion kinetics of high ash Indian coals were studied in TGA by Saravanan and his co-workers [37]. Pyrolysis tests were carried out in N_2 and CO_2 environments while combustion tests were performed in air and O_2/CO_2 mixtures having oxygen concentrations of 20, 30 and 40 %. Coal samples were heated from room temperature to 1000^{o}C with a heating rate of 10^{o}C/min and gas flow rate was kept at 40 ml/min for each tests. Char-CO_2 gasification was observed above 800^{o}C in pyrolysis tests. Combustion tests showed that two of the coals displayed similar behaviour in 30 % O_2 – 70 % CO_2 mixture with those in air conditions while in the case of the other coal weight loss profiles obtained in air environment laid between weight loss profiles of 20 % O_2 – 80 % CO_2 and 30 % O_2 – 70 % CO_2 mixtures. Therefore, it was concluded that to achieve similar temperature

profiles with air case, O_2/CO_2 proportion need to be considered according to fuel type. In kinetic analysis Arrhenius model was used and calculated activation energies were found within the range from 19 to 33 kJ/mol.

Haykiri-Acma et al. [38] studied reactivity and burnout characteristics of biomass-lignite blends in air and pure oxygen conditions by using TGA and DSC methods. Two different biomass species, sunflower seed shell and hazelnut shell and Soma-Denis lignite were selected for combustion tests. Fuel samples having particle size less than 250μm, was heated from room temperature to 900^{o}C with a heating rate of 40^{o}C/min at a flow rate of 100 ml/min. Biomass-lignite blends were prepared with 5, 10 and 20 wt.% biomass in the blend. It was reported that in pure oxygen maximum weight loss rates shift to lower temperature zone and burnout time shortens. In co-firing tests, presence of biomass led to expected conversion degrees at lower temperatures and better burnout levels. Moreover, excess heat arising from combustion of lignite in pure oxygen could be controlled by co-firing lignite with biomass.

CHAPTER 3

EXPERIMENTAL

3.1 General

In the first part of this chapter, materials used in pyrolysis and combustion tests and their characteristics including proximate, ultimate and ash analyses are reported. This was followed by description of the experimental set-up and the method in detail.

Experiments have been carried out in Middle East Technical University Central Laboratory within the scope of research project 109M401 financed by The Scientific and Technical Research Council of Turkey (TÜBİTAK).

3.2 Materials

Five different types of fuels including imported coal, petcoke, two different types of indigenous lignites and olive residue were selected for pyrolysis and combustion tests.

Representive samples of fuels were subjected to proximate, ultimate and ash analysis. Proximate analysis was carried out with LECO TGA-701. Ultimate analysis as performed by using LECO CHNS-932. Calorific values of the fuels were measured

by using AC-500 bomb calorimeter. Analyses were performed according to ASTM standards. The Jeol JSM-6400 scanning electron microscope (SEM) configured with a Noran energy dispersive spectrometer (EDS) was utilised for determination of ash composition. Proximate, ultimate and ash analyses together with calorific values of the fuels are briefly summarized in Table 3.1.

Table 3.1: Fuel Analyses

Proximate Analysis (As received basis, % by wt.)	**Imported Coal**	**Petroleum Coke**	**Lignite I**	**Lignite II**	**Olive Residue**
Moisture	8.15	0.54	16.35	48.77	6.07
Ash	11.21	3.77	28.78	17.56	4.24
Volatile Matter	18.1	13.51	29.79	22.93	75.69
Fixed Carbon	62.54	82.18	25.08	10.74	14.00
Ultimate Analysis (As received basis, % by wt.)					
C	72.87	86.13	37.31	20.40	47.17
H	3.77	3.26	3.30	1.89	5.99
O	2.15	0.00	10.01	9.66	34.78
N	1.63	1.99	0.91	0.70	1.62
$S_{Combustible}$	0.22	4.34	3.33	1.02	0.13
Ash	11.21	3.74	28.78	17.56	4.24
Moisture	8.15	0.54	16.35	48.77	6.07
S_{Total}	0.3	4.71	3.49	2.33	0.13
LHV(MJ/kg)	27.04	33.17	9.89	6.34	16.85
Ash Analysis (% by wt.)					
SiO_2	54.08	9.60	43.13	24.01	31.19
Al_2O_3	28.65	2.19	18.20	10.58	5.29
Fe_2O_3	5.16	1.62	15.78	5.15	5.17
CaO	2.91	30.57	7.63	25.00	17.52
MgO	0.83	1.19	0.48	4.26	2.51
Na_2O	0.00	0.00	2.00	0.69	5.21
K_2O	2.33	0.77	0.63	0.86	27.95
SO_3	5.08	46.73	11.08	28.68	2.64
TiO_2	0.96	0.00	1.07	0.78	2.52
NiO	0.00	1.05	0.00	0.00	0.00
V_2O_5	0.00	6.28	0.00	0.00	0.00

The imported coal is classified as medium volatile bituminous coal according to its percentage of fixed carbon, calculated on a dry, ash-free basis as stated in the literature [39]. It is a high rank coal that has high calorific value, low volatile matter and oxygen content. Imported coal ash is dominated by oxides of silicon and aluminium.

Petcoke is a carbonaceous solid residual by-product of the oil refining coking process. As crude oil is refined, lighter fractions or products, such as gasoline and jet fuel, are driven off leaving a residual oil of relatively little value. In refineries with cokers, this residual oil is processed further to yield additional amounts of light products, along with petcoke. Petcoke has high calorific value and fixed carbon content; therefore, it is used to make heat recovery in energy production. It has lower ash and higher sulphur contents compared to the other fuels. Absence of inherent oxygen and low volatile matter content result in difficult ignition. Owing to the increasing demand for heavy oil processing the production of petcoke is increasing. High availability, high calorific value and low prices make petcoke attractive as an alternative fuel in energy production [40-42]. Petcoke ash is dominated by CaO and SO_3. Moreover, NiO and V_2O_5 are detected in petcoke ash but not in the ashes of other fuels.

Lignite is not only the world's most abundant fossil fuel, but also one of the two major indigenous sources of energy in Turkey with an estimated quantity of 12.4 billion tons of reserves [43]. Therefore, in this study two different kinds of indigenous lignites representing the majority of the reserves are selected for pyrolysis and combustion experiments. Lignite I is a typical indigenous lignite from Çan town of Çanakkale province in Turkey. As can be seen from

Table 3.1, it is characterized by its low calorific value, high ash content and high total sulphur content. Lignite II is another indigenous lignite from Konya province that is characterized by its high moisture content, low calorific value and higher CaO content in its ash.

Biomass is a renewable energy resource as it can be considered as a carbon neutral fuel [44]. Olive residue is selected for pyrolysis and combustion experiments in this study, which is a specific type of biomass from olive oil production process. It is the remaining part of olive after milling and extraction of the olive oil. As Turkey is one of the main olive producers with 774,000 ha of olive groves and 1,464,248 tons of annual production, significant amount of olive residue is produced [45]. Olive residue contains significant amount of oxygen and volatile matter. It has low moisture and ash content.

3.3 Experimental Set-up

In the present work, thermogravimetry (TGA) / differential thermogravimetry (DTG) were used to determine pyrolysis and combustion characteristics of fuel samples. It is a rapid, inexpensive and simple method that has been widely used in studying the pyrolysis and combustion behaviour of various fuels and evaluating the relative burning properties of fuel samples [13, 15, 46, 47]. For determination of evolved gases during pyrolysis and combustion experiments, TGA system was coupled with Fourier transform infrared (FTIR) spectrometer, which has many applications in the open literature [25, 35, 48-52].

Figure 3.1 shows a schematic diagram of the experimental setup consisting of Perkin Elmer Pyris STA 6000 thermo-gravimetric analyzer, Spectrum 1 FTIR spectrometer and a mass flow controller (MFC) for each gaseous species. TGA and FTIR were connected by a heated line with a temperature of 270^{o}C in order to

prevent the condensation of gases. FTIR spectra were collected with 4 cm^{-1} resolution, in the range of 4000-700 cm-1 IR absorption band.

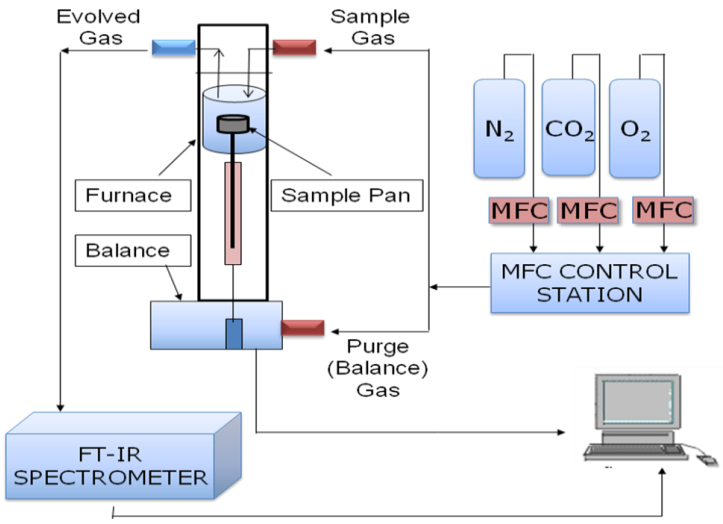

Figure 3.1: Schematic diagram of the experimental setup.

3.4 Experimental Method

About 12 mg of coal sample with particle size less than 100 µm was held initially at room temperature for 1 min and then heated with a heating rate of 40°C/min from room temperature up to 950°C during each experiment. In pyrolysis tests, samples were held at 950°C for an additional 60 mins. The required combustion environments were formed by mixing two gases in the desired ratio by using two different mass flow controllers in order to regulate the flow rates of the gases. The total gas flow was set to 70 ml/min for pyrolysis and 45 ml/min for combustion experiments.

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. The base case was considered as combustion in air environment. In oxygen-enriched air case the sample is burned in 30 % O_2 – 70 % N_2 atmosphere. In oxy-fuel combustion tests, the volume of N_2 used in the base case was replaced with an equal volume of CO_2. In the last case, combustion of fuel sample was investigated in oxygen-enriched oxy-fuel environment, that is, in 30 % O_2 – 70 % CO_2 atmosphere.

TGA and DTG profiles obtained during pyrolysis and combustion experiments were used to determine some characteristic parameters such as initial decomposition temperature (T_{in}), peak temperature (T_{max}), ignition temperature (T_{ig}) and burnout temperature (T_b). T_{in} represents the initiation of weight loss and is defined as the temperature at which the rate of weight loss reaches 1 %/min after initial moisture loss peak in DTG profile [12]. T_{max} is the point at which maximum reaction rate occurs. Different from initial decomposition temperature, ignition temperature T_{ig} is defined as the temperature at which coal starts burning. It is taken as the temperature at which the weight loss curves in the oxidation and pyrolysis experiments diverge [25, 46, 53]. The last characteristic temperature considered is burnout temperature, which represents the temperature where sample oxidation is completed. It is taken as the point immediately before reaction ceases when the rate of weight loss is 1 %/min [13].

Theoretical DTG curves of the blend samples were plotted in order to investigate the interactions between coal and biomass 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 [54-56].

A linear relation between spectral absorbance at a given wavenumber and concentration of gaseous components is given by Beer's Law. In this study, the points of absorbance at a certain wavenumber are plotted against temperature in order to obtain a formation profile for each evolved gas observed in the spectra

during experiments. The IR wavenumbers of CO_2, CO, H_2O, CH_4, SO_2 and COS are 2360, 2112, 1540, 3016, 1340 and 2042 cm^{-1}, respectively. Formation profiles of NO_x related species such as NO and NO_2 are not reported due to overlap of their absorption bands with the characteristic absorption bands of water in the range of 3900-3500 and 1900-1350 cm^{-1}.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 General

This study is based on investigation of pyrolysis and combustion behaviour of various fuels in air and oxy-fuel conditions. The effect of diluting gas and oxygen concentration on pyrolysis and combustion characteristics are studied by using TGA-FTIR combined system. In this chapter, TGA-FTIR test results are analyzed by using weight loss and derivative weight loss profiles (TGA/DTG) profiles. Characteristic parameters are calculated by the method defined in Chapter 3 and presented for each fuel and their blend. Moreover, gas formation profiles of the evolved gases identified in FTIR spectra of the fuel samples are also given.

Pyrolysis as the preliminary process of coal combustion plays a crucial role in determining flame stability, ignition, and product distributions [57]. The possible impacts of different gases on pyrolysis process necessitate the investigation of devolatilization behaviour of fuel in both N_2 and CO_2 environments. Devolatilization of fuels may differentiate in volatile composition, volatile yield and possible CO_2 – char reaction at high temperature range. Therefore, pyrolysis tests were carried out under both nitrogen and carbon dioxide atmospheres, which are the diluting gases of air and oxy-fuel environments, respectively.

Oxy-fuel combustion was found to differ from air combustion in heat transfer, combustion characteristics and emissions due to the presence of CO_2 in high concentrations in oxy-fuel combustion conditions. Therefore, in order to investigate effects of combustion environment, combustion tests were carried out under air (base case), oxygen-enriched conditions (30 % O_2 – 70 % N_2), oxy-fuel conditions (21 % O_2 – 79 % CO_2), oxygen-enriched oxy-fuel conditions (30 % O_2 – 70 % CO_2) for all fuel samples.

4.2 Imported Coal

As mentioned previously, imported coal is a high rank, medium volatile bituminous coal with high calorific value and low volatile matter content. Pyrolysis and combustion characteristics of imported coal are explained in the next two sections.

4.2.1 Pyrolysis of Imported Coal

Pyrolysis behaviour of imported coal in N_2 and CO_2 environments is shown with TGA and DTG curves in Figure 4.1.

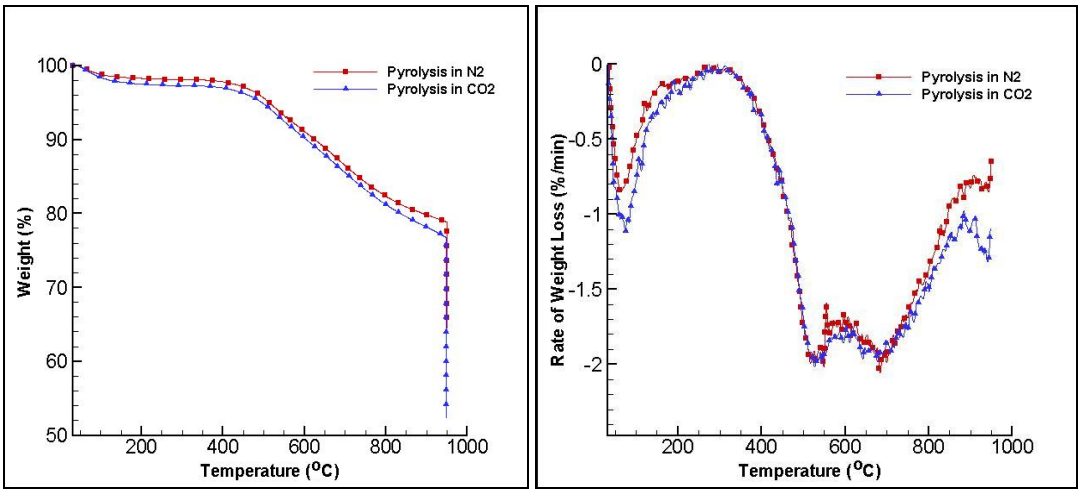

Figure 4.1: TGA and DTG profiles of imported coal during pyrolysis in N_2 and CO_2 atmospheres

As can be seen from figures, similar behaviours are observed in pyrolysis of imported coal samples under N_2 and CO_2 atmospheres up to around 750°C, which indicates that CO_2 behaves as an inert atmosphere until a certain temperature. After moisture release in the first 200°C temperature zone, pyrolysis continues with the release of volatile matter content in the range of 200–750°C. In 250–490°C temperature interval, it is known that primary pyrolysis takes place which includes the release of larger fraction of volatiles, mainly light species and gases; CO_2, light aliphatic gases, CH_4 and H_2O. Tar and hydrocarbons evolve between 490 and 640°C. During secondary pyrolysis additional gas formation such as CH_4, CO and H_2 from ring condensation is mainly observed [17, 57]. The major difference in pyrolysis of imported coal samples in these two different atmospheres is observed after 750°C with the separation of TGA profiles. In 700–950°C temperature range, additional peak is displayed in DTG profile of imported coal obtained in CO_2 atmosphere as shown in Figure 4.1. Sharp peak observed in DTG profile of pyrolysis in CO_2 environment can be attributed to char–CO_2 gasification reaction as also confirmed by higher total weight loss in CO_2 atmosphere as shown in confirmed by other studies [25, 29, 33, 34].

Table 4.1: Pyrolysis Characteristics of Imported Coal

	Pyrolysis in N_2	**Pyrolysis in CO_2**
T_{in} (^oC)	465.2	463.9
$T_{max.-1}$ (^oC)	517.0	528.4
$T_{max.-2}$ (^oC)	-	933.7
$(dm/dt)_{max.-1}$ (%/min)	2.0	2.0
$(dm/dt)_{max.-2}$ (%/min)	-	1.2
Weight loss up to (%)	21.1	23.2

Formation profiles of evolved gases including CO_2, CO, H_2O, CH_4, SO_2 and COS during pyrolysis in N_2 and CO_2 environments are shown in Figure 4.2. CO_2 formation displays an increasing trend in the temperature range of 200-950^oC, with a maximum absorbance value at around 775^oC. This range corresponds to the devolatilization temperature interval as represented in DTG curve of imported coal. Formation of CO_2 in N_2 environment is found to be the major contributor to the evolved gases with its highest absorbance intensity. CO formation is observed to initiate at around 300°C and continue to evolve up to 700°C. CO formation is observed to complete at 850^oC in nitrogen atmosphere, while a distinctive increase is observed in formation profile of CO due to char–CO_2 gasification reaction in CO_2 atmosphere. Water vapour shows an increasing trend especially after 700°C. It is considered to be due to effect of side gasification reactions. Methane formation takes place between 400 – 600°C with slightly higher absorbance intensity in CO_2 environment. In the case of sulphur containing gases, SO_2 and COS formation is identified in the FTIR spectra. Certain amount of SO_2 is formed in two steps at around 600^oC and 900^oC. In CO_2 atmosphere, the absorbance intensity of SO_2 gas is higher than the one in N_2 atmosphere; however, similar trends are observed in both atmospheres. As reported in the literature, COS is formed by reaction of pyrite or sulphur formed during pyrite decomposition with CO [34, 35, 58]. Therefore, COS formation is observed to increase significantly with the initiation of gasification reaction in CO_2 environment. Higher CO concentration in pyrolysis environment leads to the formation of COS in CO_2 atmosphere, in contrast to N_2 atmosphere.

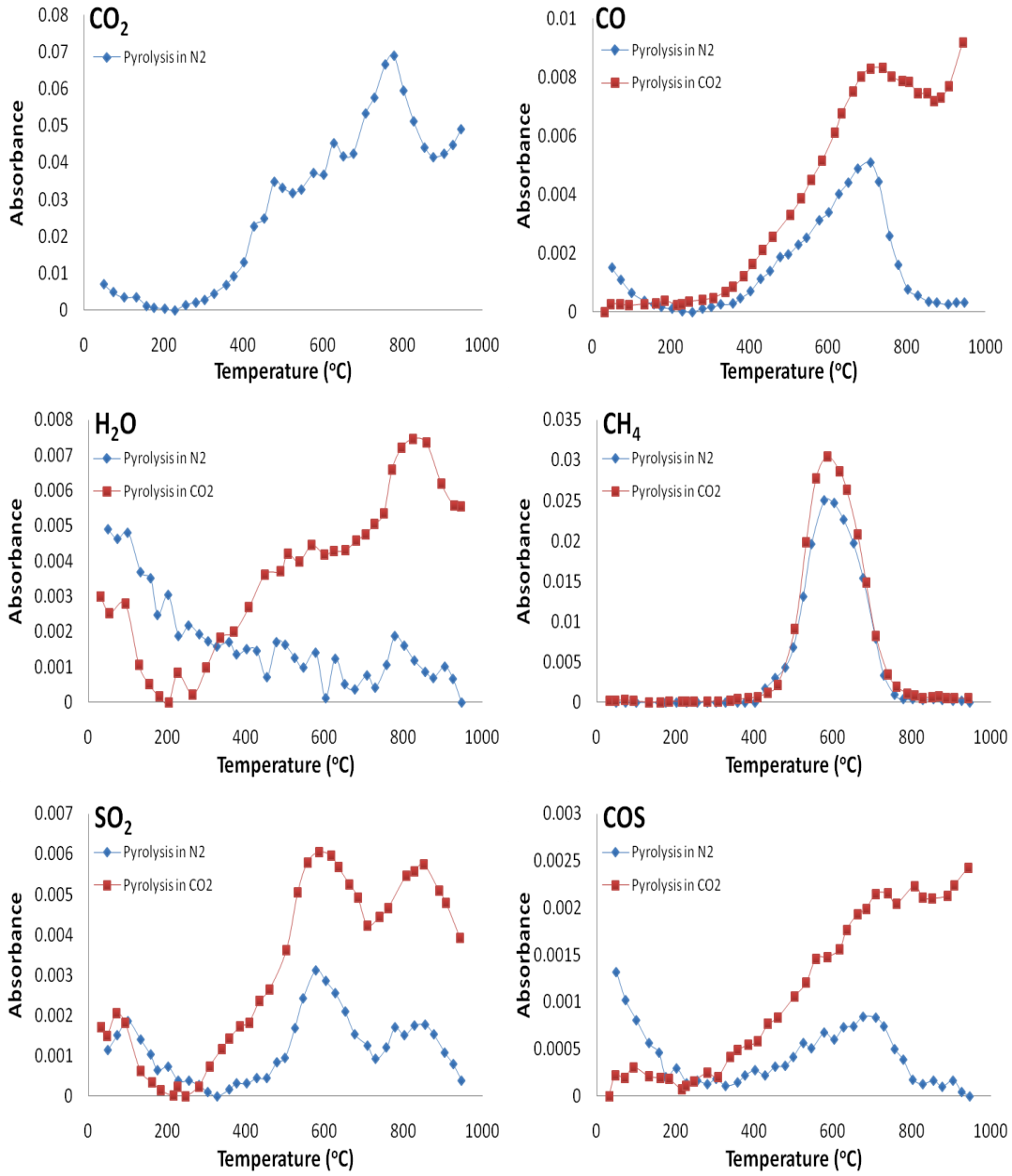

Figure 4.2: Formation profiles of evolved gases during pyrolysis tests of imported coal.

4.2.2 Combustion of Imported Coal

Figure 4.3 shows combustion behaviour of imported coal in air, oxygen-enriched air (30 % O_2 – 70 % N_2), oxy-fuel environment (21 % O_2 – 79 % CO_2), and oxygen enriched oxy-fuel environment (30 % O_2 – 70 % CO_2).

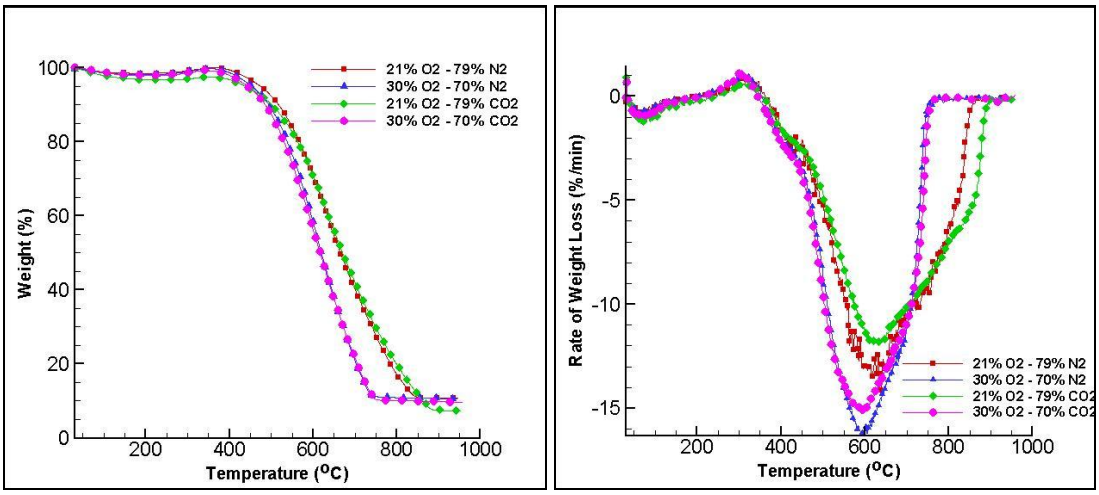

Figure 4.3: TGA and DTG profiles of imported coal in different combustion atmospheres

TGA curves in Figure 4.3 shows that the effect of oxygen concentration is more significant than that of the diluting gas (N_2 or CO_2) on the combustion profiles. While combustion in O_2/N_2 and O_2/CO_2 mixtures with identical oxygen concentrations results in only slight differences in combustion characteristics, elevated oxygen levels in combustion environment shift the weight loss curves to lower temperature zone.

Overall comparison of DTG curves reveal two main weight loss steps in all combustion environments. The first step corresponds to moisture release within the temperature range of 200^{o}C, and the second one accounts for weight loss due to devolatilization of volatile matter and burning of char in the temperature range of

300-850^{o}C. After 200^{o}C, increase to positive values is observed in the rate of weight loss in DTG curves, which is related to the weight gain during heating in the temperature range of 200-400^{o}C [13, 59]. This is considered to be due to oxygen adsorption in the coal structure, which results in formation of oxygenated complex before combustion. In air firing case, as can be seen from the figure, devolatilization and char burning is not sharply separated, however, the shoulder around 400^{o}C can be attributed to volatile release.

Comparison between the DTG curves of imported coal in air and oxy-fuel environments reveals that replacing nitrogen with CO_2 results in lower reactivity and delayed combustion due to lower slope of weight loss rate and higher peak and burnout temperatures. Delayed combustion in CO_2 environment is a physically expected phenomenon that takes place due to higher specific heat of CO_2 leading to lower particle temperature [6, 22, 25]. The shoulder in DTG profile in CO_2 environment after 800^{o}C is also worth noting. This can be attributed to CO_2-char reaction as also confirmed by findings in the literature [33].

Combustion of imported coal in oxygen enriched air environment displays significantly different behaviour than that in air environment despite the similarity in the shape of DTG profiles. Table 4.2 shows that initial decomposition, peak and burnout temperatures are lower in the oxygen enriched air environment. These lower temperatures are indicative of earlier loss of volatile matter, easier ignition and faster approach to complete combustion, respectively. This is also confirmed by higher reactivity of imported coal in oxygen enriched atmosphere due to higher maximum weight loss rate, $(dm/dt)_{max}$, and lower temperature corresponding to the main peak, T_{max}. It can, therefore, be concluded that imported coal burns hotter and faster in oxygen-enriched environment compared to air environment.

Table 4.2: Combustion Characteristics of Imported Coal

	21 % O_2-79 % N_2	30 % O_2-70 % N_2	21 % O_2-79 % CO_2	30 % O_2-70 % CO_2
T_{in} (^oC)	387.4	376.7	387.0	371.4
$T_{max.-1}$ (^oC)	618.3	594.9	629.2	591.1
T_b (^oC)	848.4	745.0	885.1	752.0
$(dm/dt)_{max.}$ (%/min)	13.3	16.1	11.8	15.0
T_{ig} (^oC)	446.6	422.0	393.0	420.3
Weight loss up to 950^oC (%)	89.1	89.2	93.3	90.3

The DTG profiles of imported coal in oxygen enriched air and oxygen enriched CO_2 environments reveal close resemblance and slightly lower maximum weight loss rate in the CO_2 environment. Overall comparison of DTG profiles shows that higher oxygen content in the combustion environment is the most effective parameter irrespective of the dilute gas. At higher O_2 concentrations peak and burnout temperatures are lower, weight loss rate is higher and complete combustion is achieved at lower temperatures and shorter time [25, 29, 33, 35, 38, 60]. In oxygen-enriched oxy-fuel conditions, CO_2 gasification shoulder disappears as complete combustion is achieved before 800^{o}C.

Figure 4.4 displays formation profiles of gases evolved in different combustion environments. Gaseous species evolved during combustion tests were found to be CO_2, CO, H_2O, CH_4, SO_2 and COS. CO_2 evolution is observed to initiate at around 300^{o}C and continues up to the end of combustion in air and oxygen-enriched air conditions. Higher oxygen concentration in combustion environment results in shift in CO_2 formation profile to lower temperature zone as elevated oxygen levels lead to faster burning and earlier release of CO_2. The major contributor to the evolved gases is found to be CO_2 with its higher absorbance intensity. CO formation is

identified between 300-900^{o}C and similar trends are displayed in all combustion conditions. In oxy-fuel environment, CO formation is completed at higher temperatures compared to air conditions, due to effect of gasification reaction. In the first 200^{o}C temperature zone, H_2O formation is detected due to moisture release in all cases. In the second part, further H_2O release is observed in all conditions due to coal oxidation reactions. However, H_2O formation is found to be slightly higher in oxy-fuel conditions. Similar trends are displayed in CH_4 gas evolution profiles 400 – 700^{o}C in all cases. SO_2 gas formation is observed during entire combustion period. COS gas evolves in the temperature range of 300-900^{o}C under all combustion conditions. COS formation is completed in higher temperatures in oxy-fuel case similar to CO formation.

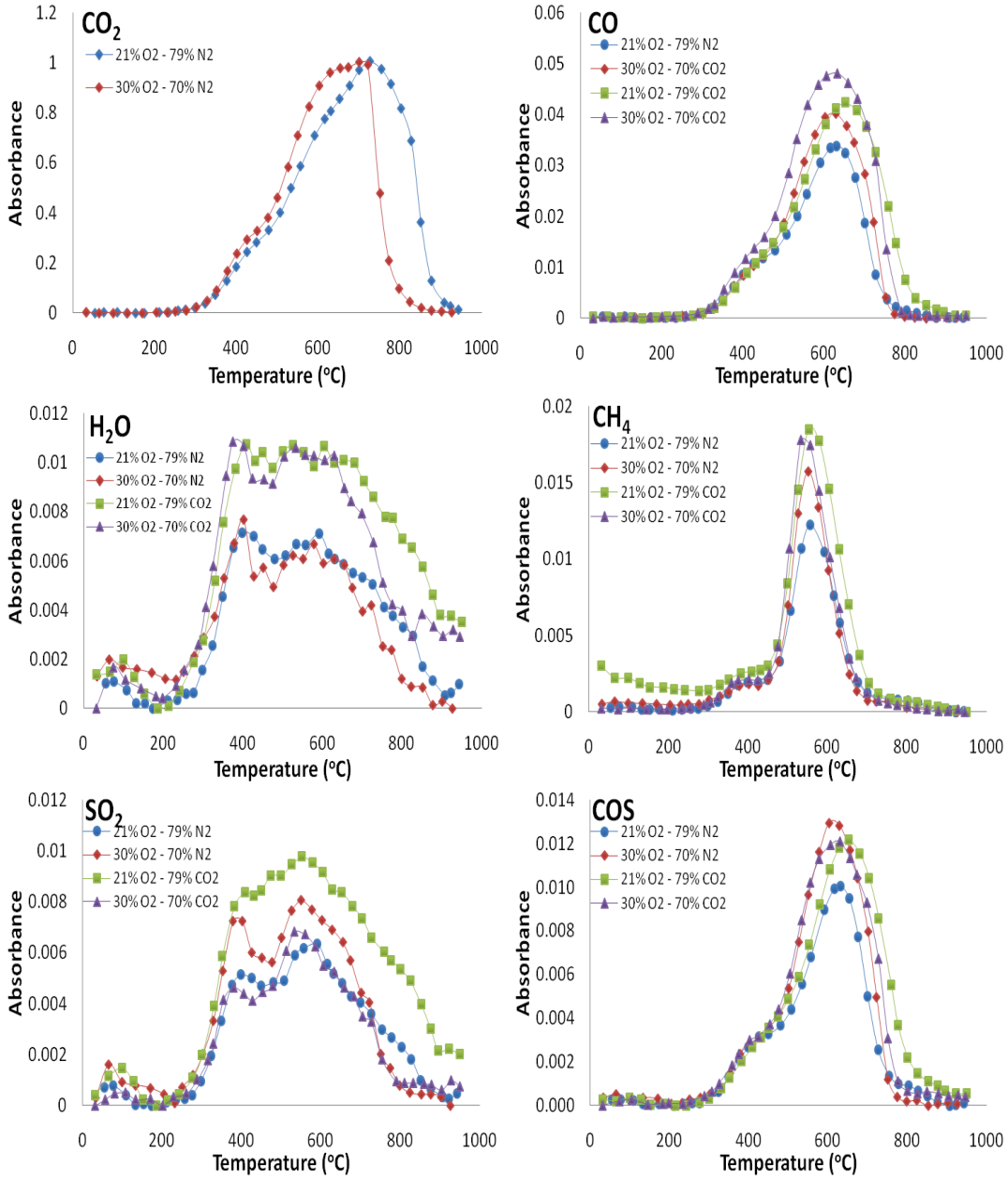

Figure 4.4: Formation profiles of evolved gases during combustion tests of imported coal

4.3 Petcoke

Petcoke is a by-product of oil refining process. Petcoke is typically a carbon-rich fuel that contains low volatile matter and high sulphur content with very low ash.

4.3.1 Pyrolysis of Petcoke

TGA and DTG curves of petcoke under nitrogen and carbon dioxide environment are shown in Figure 4.5. Pyrolysis characteristics determined from these profiles are summarized in Table 4.3.

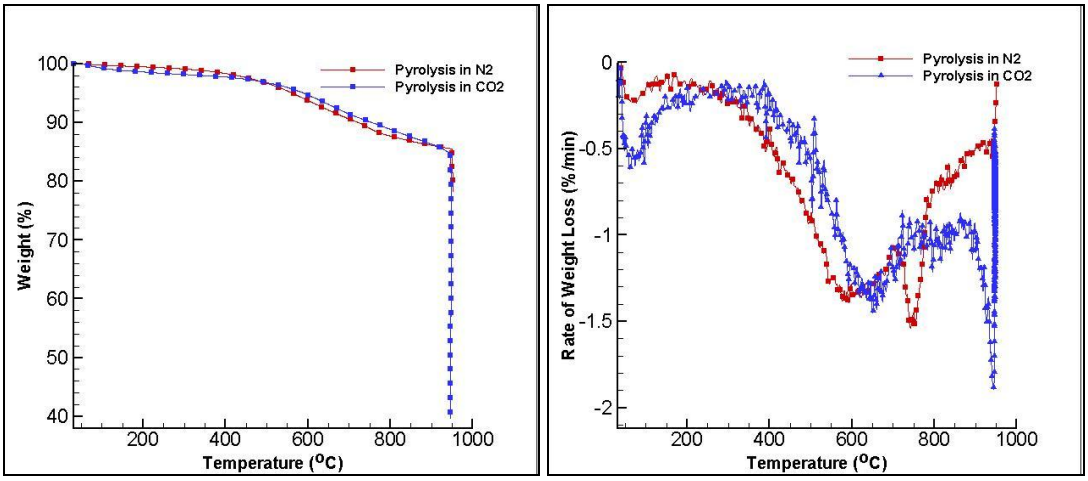

Figure 4.5: TGA and DTG profiles of petcoke during pyrolysis in N_2 and CO_2 atmospheres

As can be seen from TGA curve in Figure 4.5 and Table 4.3 total weight loss of petcoke under CO_2 atmosphere is significantly higher than that in N_2 atmosphere. DTG curves of the petcoke samples show that moisture release takes place with relatively lower weight loss rate due to its lower moisture content in the first 200°C

temperature zone. After moisture release, two main weight loss steps appear in DTG profiles of the fuel samples. First weight loss step within 200-700^{o}C temperature range is attributed to release of volatile matter content. Higher heat capacity of CO_2 gas leads to delay in weight loss profiles, higher initial decomposition and peak temperatures under CO_2 atmosphere. Second weight loss step is represented with additional peaks after 700°C in both atmospheres. In N_2 atmosphere, second peak is attributed to calcite decomposition in N_2 atmosphere. This point can also be confirmed by high CaO content in petcoke ash (Table 3.1) and related studies in the literature [34, 48, 54]. However, the sharp peak observed in CO_2 environment is considered to be due to char-CO_2 gasification reaction.

Table 4.3: Pyrolysis Characteristics of Petcoke

	Pyrolysis in N_2	**Pyrolysis in CO_2**
T_{in} (^{o}C)	514.9	570.9
$T_{max.-1}$ (^{o}C)	582.3	638.7
$T_{max.-2}$ (^{o}C)	742.9	944.2
$(dm/dt)_{max.-1}$ (%/min)	1.4	1.3
$(dm/dt)_{max.-2}$ (%/min)	1.5	1.6
Weight loss up to 950^{o}C (%)	14.4	17.0

Formation profiles of the gases released during pyrolysis of petcoke is represented in Figure 4.6. CO_2 formation takes place in three steps in the temperature range of 200 – 950^{o}C. First two steps are considered to be due to release of volatilities while last step represents the CO_2 release as a result of calcite decomposition reactions. CO formation profile reveals that significant amount of CO is evolved due to char – CO_2 gasification after 800^{o}C. In CO_2 atmosphere water vapour formation is significantly higher than that in N_2 atmosphere in high temperature zone because of

gasification reactions. Methane formation is observed in the temperature range of 500 – 900^{o}C in both pyrolysis conditions. In pyrolysis of high sulphur content petcoke samples, SO_2 formation is identified after 500^{o}C and relatively higher absorbance intensity is observed in CO_2 atmosphere. COS evolution appears at high temperature zone related to CO formation.

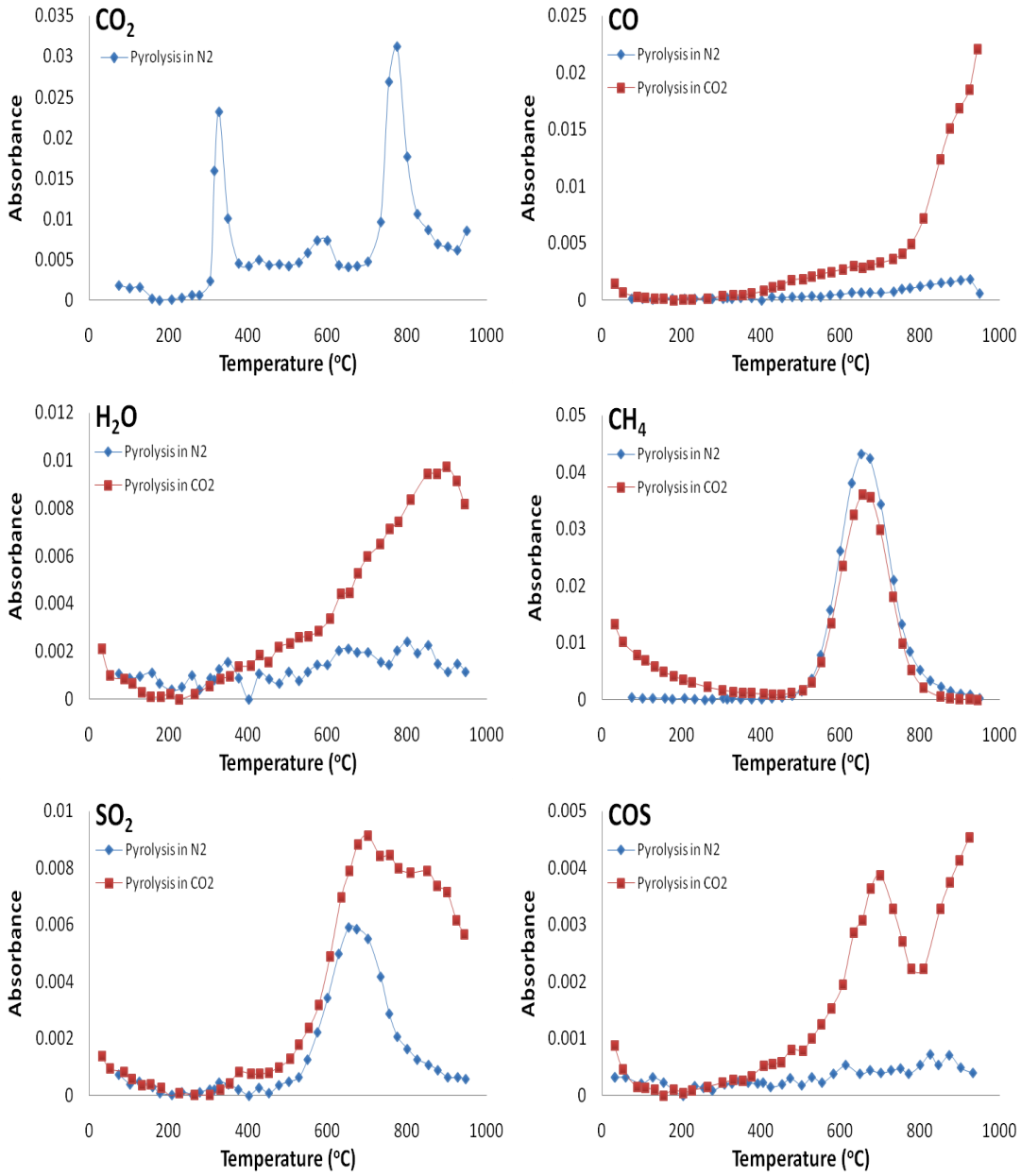

Figure 4.6: Formation profiles of evolved gases during pyrolysis tests of petcoke

4.3.2 Combustion of Petcoke

TGA and DTG profiles evaluated in combustion tests of petcoke are represented in Figure 4.7.

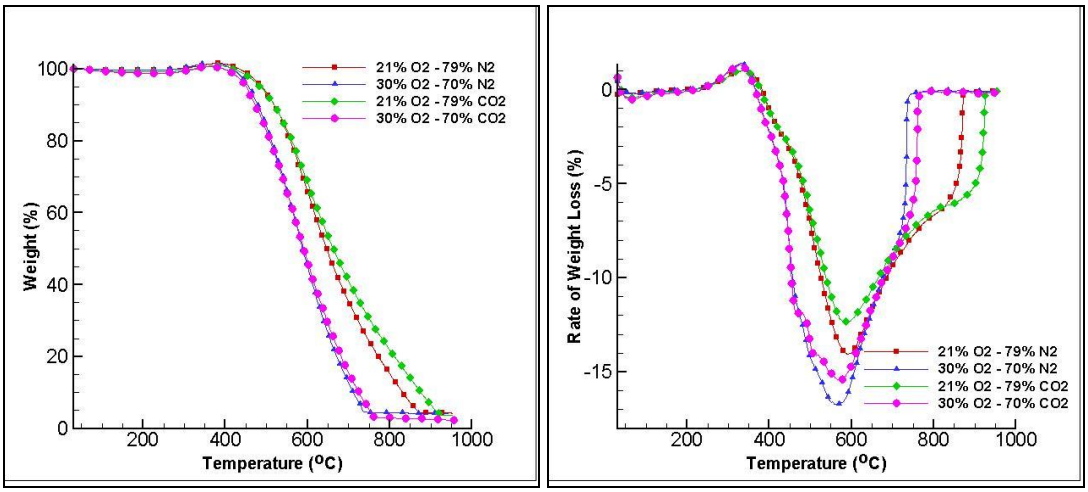

Figure 4.7: TGA and DTG profiles of petcoke in different combustion atmospheres

Different combustion behaviours of petcoke are observed in all combustion conditions. Effects of oxygen concentration and diluting gas (N_2 and CO_2) on combustion are clearly displayed in TGA curves of Figure 4.7. Weight loss profiles reveal that elevated oxygen levels lead to shift in combustion curves to lower temperatures. Moreover, CO_2, as a diluting gas in the combustion environment, causes delay in combustion and results in combustion of petcoke samples at slightly higher temperatures.

Overall comparison of DTG curves in Figure 4.7 reveals that weight loss takes place at one main step. Moisture release is not observed in the first 200°C temperature zone due to absence of moisture in petcoke samples in contrast to other fuels. However, after 100°C, weight gain is observed to initiate that is caused by oxygen adsorption before combustion procedure until 350°C as also observed in

combustion of imported coal. After weight gain, initial decomposition starts at around 400°C and weight loss reaches to its maximum value at around 590°C in air and oxy-fuel environments. After 800°C, distinctive shoulders are observed in DTG profiles in both conditions, which is attributed to thermal decomposition of carbonates. In oxy-fuel case, the calculated characteristic temperatures such as T_{in}, T_{max} and T_{ig} are found almost the same with air case as reported in Table 4.4. Replacing nitrogen with carbon dioxide in combustion environment results in delayed combustion; lower weight loss rate, higher peak and burnout temperatures.

Table 4.4: Combustion Characteristics of Petcoke

	21 % O_2-79 % N_2	**30 % O_2-70 % N_2**	**21 % O_2-79 % CO_2**	**30 % O_2-70 % CO_2**
T_{in} (°C)	400.1	381.6	398.7	379.5
$T_{max.}$ (°C)	589.0	562.2	587.6	572.6
T_b (°C)	867.0	735.6	923.7	761.8
$(dm/dt)_{max.}$ (%/min)	14.0	16.8	12.4	15.5
T_{ig} (°C)	469.5	439.7	465.4	434.7
Weight loss up to 950°C (%)	96.8	95.9	96.7	97.9

In oxygen-enriched conditions, main peak is observed in a narrower temperature interval between 350 – 750°C. In oxygen-enriched conditions, calcite decomposition is not observed as complete combustion is achieved before the temperature interval of thermal decomposition reactions. All characteristic temperatures such as T_{max}, T_{in}, T_{ig} and T_b are lower and weight loss rate is higher in elevated oxygen levels.

Highest relevant temperatures are observed in combustion of petcoke compared to other fuels. These findings are in agreement with the studies reported in the literature about petcoke studies [41, 42, 53, 61]. Petcoke has the highest initial decomposition temperature and is the hardest fuel to ignite and reach to total burnout with its highest ignition and burnout temperatures, respectively.

Formation profiles of the gases evolved in combustion tests of petcoke are demonstrated in Figure 4.8. CO_2 formation is observed to initiate at around 300^oC and end with the completion of combustion. The formation profile of CO_2 in oxygen-enriched air atmosphere shifts to lower temperature zone due to the effect of elevated oxygen levels. The major contributor to the evolved gases is found to be CO_2 with its higher absorbance intensity. CO formation takes place in the temperature range of 300 – 800^oC and similar trends are observed in formation profiles when oxygen concentrations are identical in combustion environment. Water vapour is evolved between 300-900^oC with similar formation trends in all combustion cases. Methane gas is identified mainly between 500-750^oC. Combustion of high sulphur content petcoke samples reveal that SO_2 gas is evolved in two steps at around 600^oC and 900^oC in air and oxy-fuel cases while SO_2 release takes place in one-step at around 500^oC in oxygen-enriched conditions. COS formation is detected between 350 – 800^oC in all combustion cases.

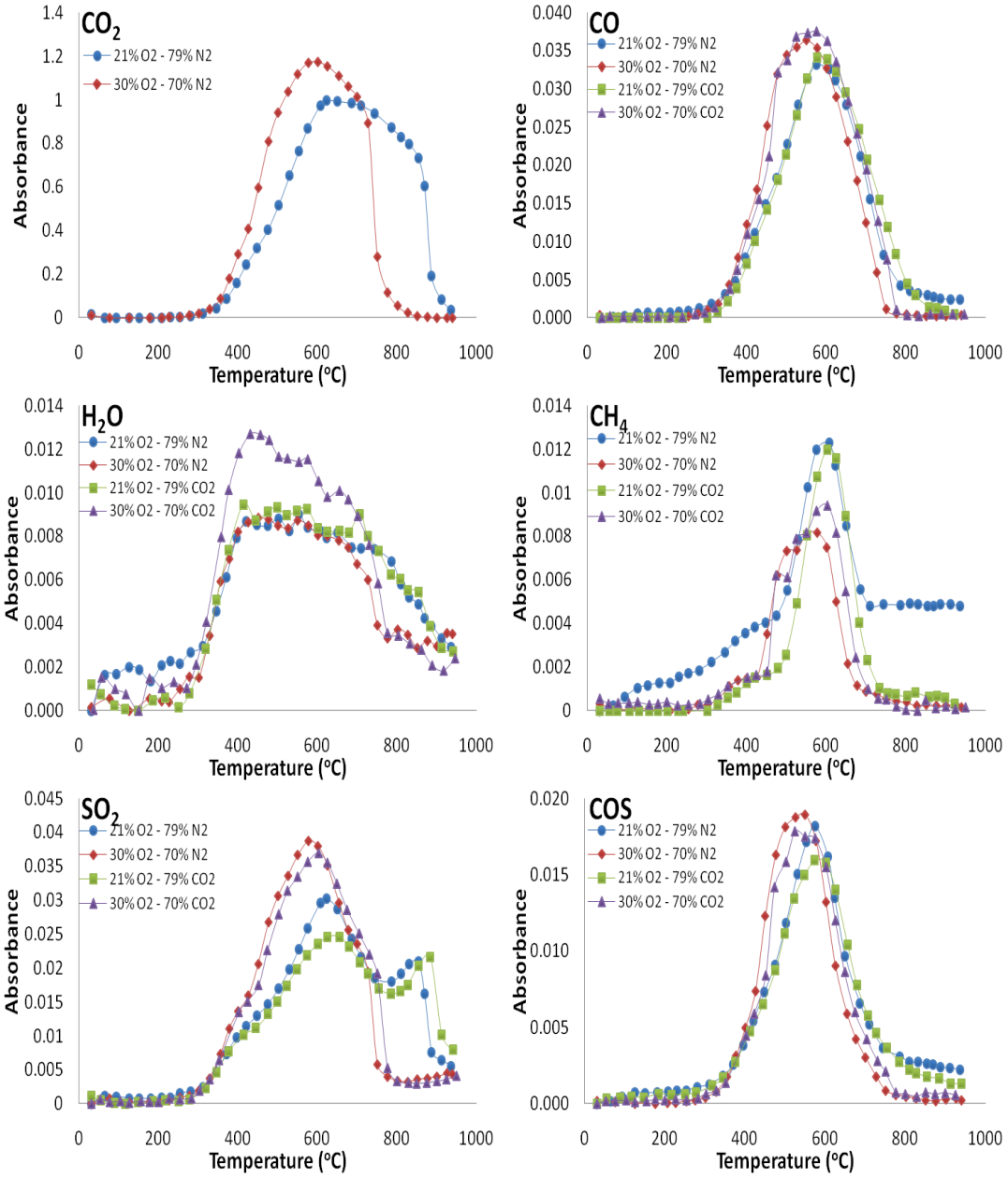

Figure 4.8: Formation profiles of evolved gases during combustion tests of petcoke

4.4 Lignite I

Lignite I is characterized by its low calorific value, high ash content and high total sulphur content.

4.4.1 Pyrolysis of Lignite I

TGA and DTG profiles of pyrolysis tests of lignite I are shown in Figure 4.9.

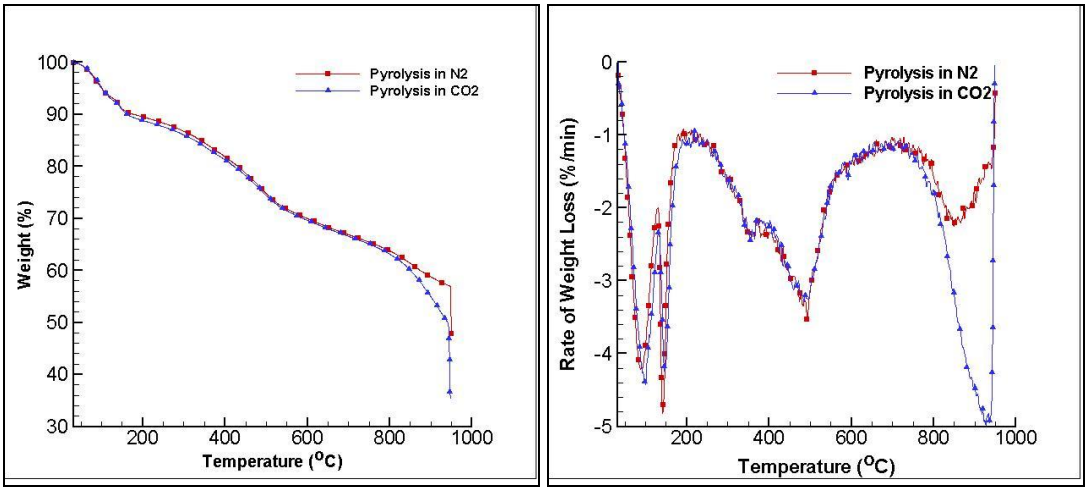

Figure 4.9: TGA and DTG profiles of lignite I in N_2 and CO_2 atmospheres

As can be seen from figures, pyrolysis behaviour of lignite samples in N_2 and CO_2 atmosphere is observed to be very similar up to around 720°C, which indicates that CO_2 behaves as an inert atmosphere until a certain temperature. After moisture release in the first 200°C temperature zone, pyrolysis continues with the release of volatile matter content in the range of 200-750°C. In CO_2 atmosphere, the maximum weight loss rate is found to be slightly lower with higher corresponding temperature (T_{max}) than the ones in nitrogen atmosphere, which could be due to

the effect of higher heat capacity of CO_2. The major difference in pyrolysis of lignite I samples in these two different atmospheres is observed after 720°C with the separation of TGA profiles. In 700-950°C temperature range, additional peaks are displayed in both DTG profiles. In nitrogen atmosphere, a small peak appearing after 700°C is attributed to partial burning of combustible matter at high temperatures by using inherent oxygen (almost 10 % in lignite I) in lignite sample. This is also confirmed with the FTIR results, which show a significant increase in CO_2 formation after 700°C. On the other hand, the sharp peak observed in DTG profile of pyrolysis in CO_2 environment can be attributed to char-CO_2 gasification reaction as also confirmed by higher total weight loss in CO_2 atmosphere as shown in Table 4.5.

Table 4.5: Pyrolysis Characteristics of Lignite I

	Pyrolysis in N_2	**Pyrolysis in CO_2**
T_{in} (°C)	230.8	216.7
$T_{max.-1}$ (°C)	482.9	481.0
$T_{max.-2}$ (°C)	859.8	924.0
T_b (°C)	-	-
$(dm/dt)_{max.-1}$ (%/min)	3.6	3.16
$(dm/dt)_{max.-2}$ (%/min)	1.9	4.8
T_{ig} (°C)	-	-
Weight loss up to 950°C (%)	41.0	50.3

Formation profiles of evolved gases including CO_2, CO, H_2O, CH_4, SO_2 and COS during pyrolysis in N_2 and CO_2 environments are shown in Figure 4.10. In nitrogen environment, CO_2 release starts after 150°C and continues up to 550°C. Additional peak appears in CO_2 and CO formation curves due to burning of combustible matter

in N_2 environment after 750^{o}C as explained in previous section. In the case of pyrolysis in CO_2 environment, significant amount of CO is evolved from char – CO_2 gasification reaction. Formation of CO in CO_2 environment is found to be the major contributor to the evolved gases with its highest absorbance intensity at high temperature zone. Evolution of CO continues with a distinctive increase after 600^{o}C in CO_2 environment. On the other hand, in N_2 environment, negligible amount of CO is formed due to partial burning of combustible matter. In both environments, H_2O is identified in the first 200^{o}C due to moisture release and in the temperature range of 400-600^{o}C as a consequence of coal oxidation reactions. Methane release starts at 300^{o}C and continues up to the end of the pyrolysis tests with a maximum release around 500^{o}C, in both environments. Similar trends are observed in evolution of CH_4 during devolatilization. In pyrolysis of high sulphur content lignite, SO_2 and COS release are noted. Similar SO_2 formation profiles are obtained in both environments in the temperature range of 250 – 625^{o}C, with two main peaks. Similar trends indicate that SO_2 formation does not depend on the pyrolysis environment. COS formation is observed to increase significantly with the initiation of gasification reaction in CO_2 environment. Higher CO concentration in pyrolysis environment leads to the formation of COS in CO_2 atmosphere, in contrast to N_2 atmosphere.

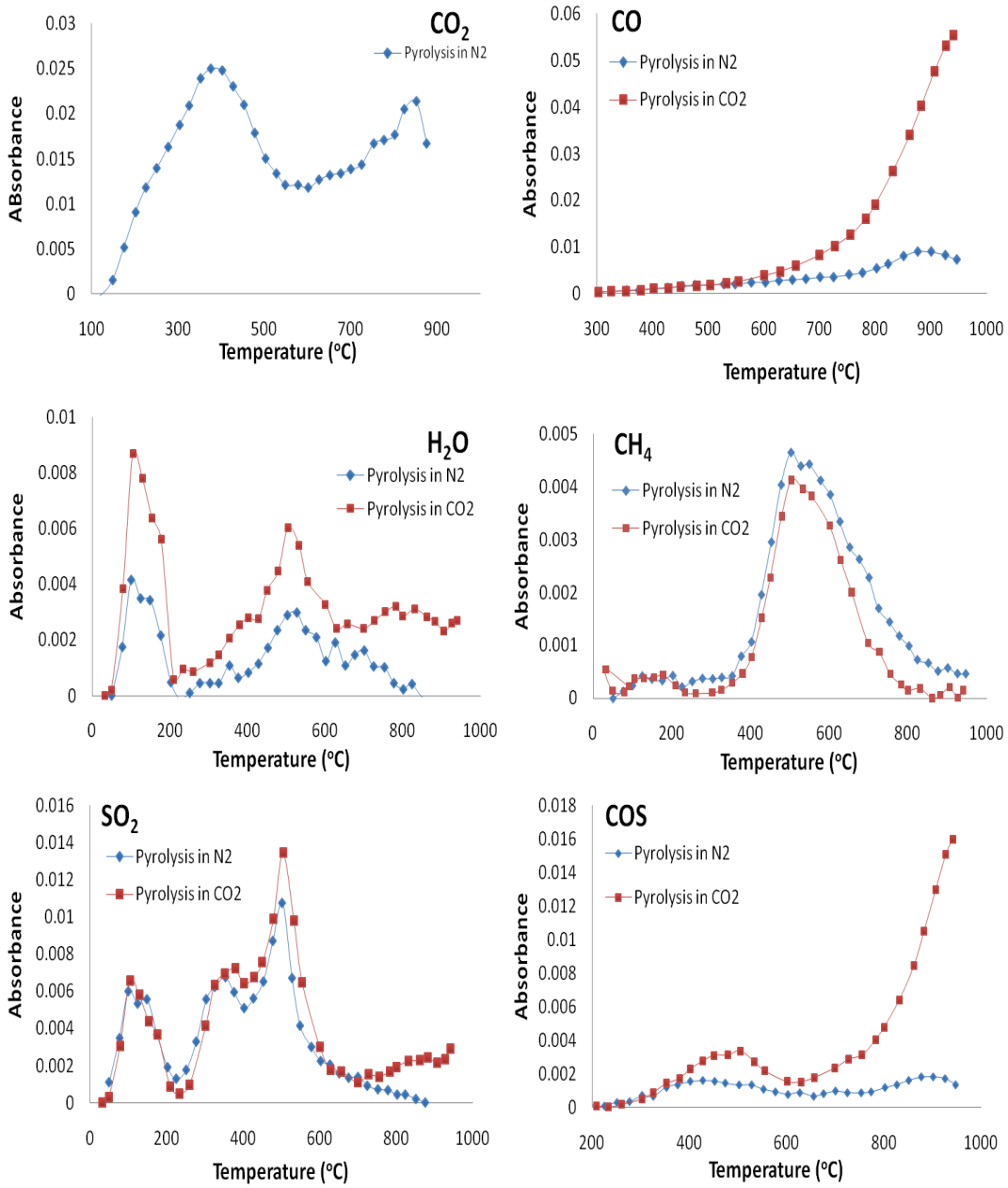

Figure 4.10: Formation profiles of evolved gases during pyrolysis tests of lignite I

4.4.2 Combustion of Lignite I

Figure 4.11 compares TGA and DTG profiles of lignite I under different combustion environments.

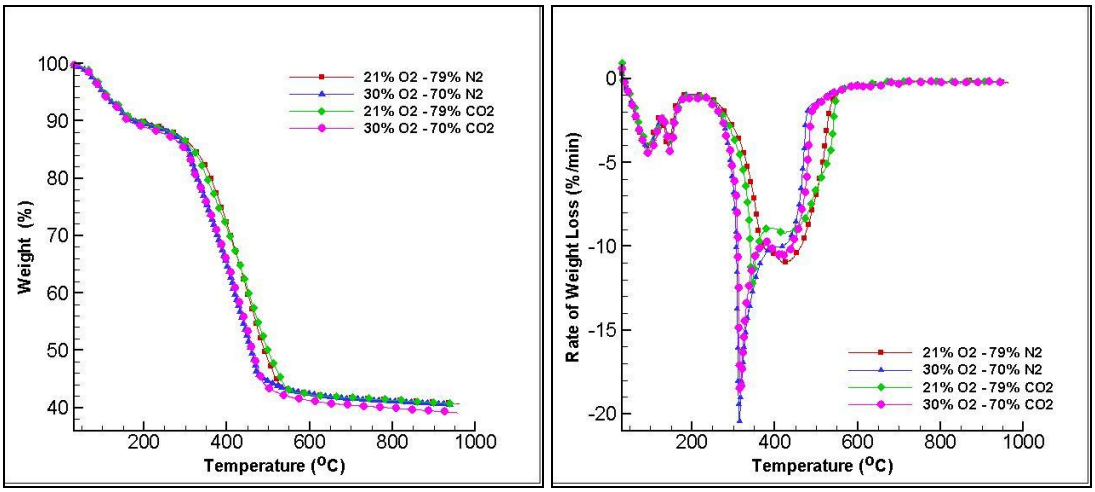

Figure 4.11: TGA and DTG profiles of lignite I in different combustion atmospheres

Comparison of TGA curves in Figure 4.11 indicates that the effect of oxygen concentration is more significant than that of the diluting gas (N_2 or CO_2) on the combustion profiles. While combustion in O_2/N_2 and O_2/CO_2 mixtures with identical oxygen concentrations results in only slight differences in combustion characteristics of lignite, elevated oxygen levels in combustion environment leads to shift in weight loss curves to lower temperatures. First step of the weight loss accounts for the moisture release in the first 200^{o}C temperature range and the corresponding weight loss due to moisture release is found approximately 10 % for all cases. The second step represents the weight loss due to devolatilization and char burning. Total weight loss of samples is found to be almost the same in all combustion cases.

First peak within 200^{o}C and the second peak within the temperature range 225-600^{o}C represent moisture release and devolatilization and char burning, respectively in the DTG profiles of the lignite I samples. In air firing case, devolatilization and char burning steps are not discretely separated; however, the shoulder around 370^{o}C can be attributed to volatile release. In oxy-fuel case the DTG profile of the lignite sample differs from the air-firing case with a small peak indicating the volatile matter release and a shoulder in 370-570^{o}C temperature interval indicating char burning which takes place within the same temperature interval in both cases. In oxygen-enriched conditions (30 % O_2 – 70 % N_2 and 30 % O_2 – 70 % CO_2) the DTG profiles are similar with distinct volatile release peaks and characteristic temperatures as shown in Table 4.6.

Table 4.6: Combustion Characteristics of Lignite I

	21 % O_2-79 % N_2	**30 % O_2-70 % N_2**	**21 % O_2-79 % CO_2**	**30 % O_2-70 % CO_2**
T_{in} (^{o}C)	224.0	226.1	225.8	202.8
$T_{max.-1}$ (^{o}C)	-	314.5	347.1	317.2
$T_{max.-2}$ (^{o}C)	426.2	-	-	-
T_b (^{o}C)	546.8	530.0	550.0	535.6
$(dm/dt)_{max.-1}$ (%/min)	-	20.5	12.3	19.0
$(dm/dt)_{max.-2}$ (%/min)	11.0	-	-	-
T_{ig} (^{o}C)	297.1	265.3	308.8	264.1
Weight loss up to 950^{o}C (%)	59.2	59.3	59. 6	61.2

The similarity in DTG profiles obtained at the same oxygen concentration levels but with different diluting gas environments is an expected result. In TGA technique

combustion temperature of the sample is controlled by electrical heating and sample temperature is not affected by combustion environment. Therefore, different heat capacities of diluting gases in combustion environment has no significant effect on combustion in contrast to practical tests as also confirmed in other studies [29, 33, 36]. Slightly higher burnout temperature in the CO_2 environment is indicative of slightly delayed combustion. Effect of higher oxygen concentration on the combustion process is investigated with the tests under 30 % O_2 – 70 % N_2 and 30 % O_2 – 70 % CO_2 environments. Similar trends in the early stage of the process (up to 250^oC) in both environments reveal that initiation of the combustion process is not affected by oxygen concentration level. However, at higher temperatures, more significant differences are displayed in DTG curves. In oxygen-enriched conditions, weight loss steps including volatile matter release and char burning are separately displayed in the DTG profile. In oxygen-enriched conditions, a sharper peak that is observed in 250 –400^oC temperature interval with a weight loss of 24 %, is attributed to volatile matter release since weight loss value is in accordance with the one determined in pyrolysis conditions. Sharper peak is observed to continue with a distinctive shoulder up to 500^oC as represented in Figure 4.11. In some studies, it was demonstrated that the force of the fusion layer around solid particles is reduced by the presence of oxygen [60, 62]. This situation also results in faster release of volatiles depending on the nature of solid particles and experimental conditions. High volatile matter content of lignite and the ease with which it is released, result in the formation of a sharper preliminary peak previously observed in low rank coals [14]. The shoulder following the peak is considered to account for weight loss due to burning of char in the sample. Increase in the oxygen concentration causes a shift of the burning profile to the lower temperature zone. Effect of oxygen concentration on characteristic temperatures is very clear. Characteristic temperatures including T_{ig}, T_{max} and T_b are found to be lower in oxygen-enriched conditions. Moreover, at higher O_2 concentrations complete combustion is achieved at lower temperatures and shorter times.

Figure 4.12 displays formation profiles of gases evolved in different combustion environments. The major contributor to the evolved gases is found to be CO_2 with its higher absorbance intensity as also observed in combustion of other fuels. The formation profile of CO_2 in oxygen-enriched air atmosphere shifts to lower temperature zone as elevated oxygen levels lead to faster burning and earlier release of CO_2. CO formation profiles display similar trends in identical oxygen concentration levels while increase in oxygen level results in lower peak temperature. H_2O formation profiles show that moisture is released first in all combustion environments with further release in the temperature range of 200^oC to 550^oC. Methane evolution mainly takes place in the temperature range of 250-550^oC. In oxygen-enriched conditions, maximum release is observed around 350^oC, which corresponds to the peak in DTG profile of volatile matter. In the case of sulphur containing gases, SO_2 and COS appear in the FTIR spectra. Trend of SO_2 evolution in FTIR spectra are found to be in accordance with the DTG curves. SO_2 release starts around 200^oC and displays different formation profiles depending on the combustion environment. Maximum release takes place at about 500^oC in air- and oxy-firing cases and 350^oC in oxygen-enriched firing conditions. COS formation is observed in all combustion tests in the temperature range of 200-550^oC with sharper peaks in oxygen-enriched conditions.

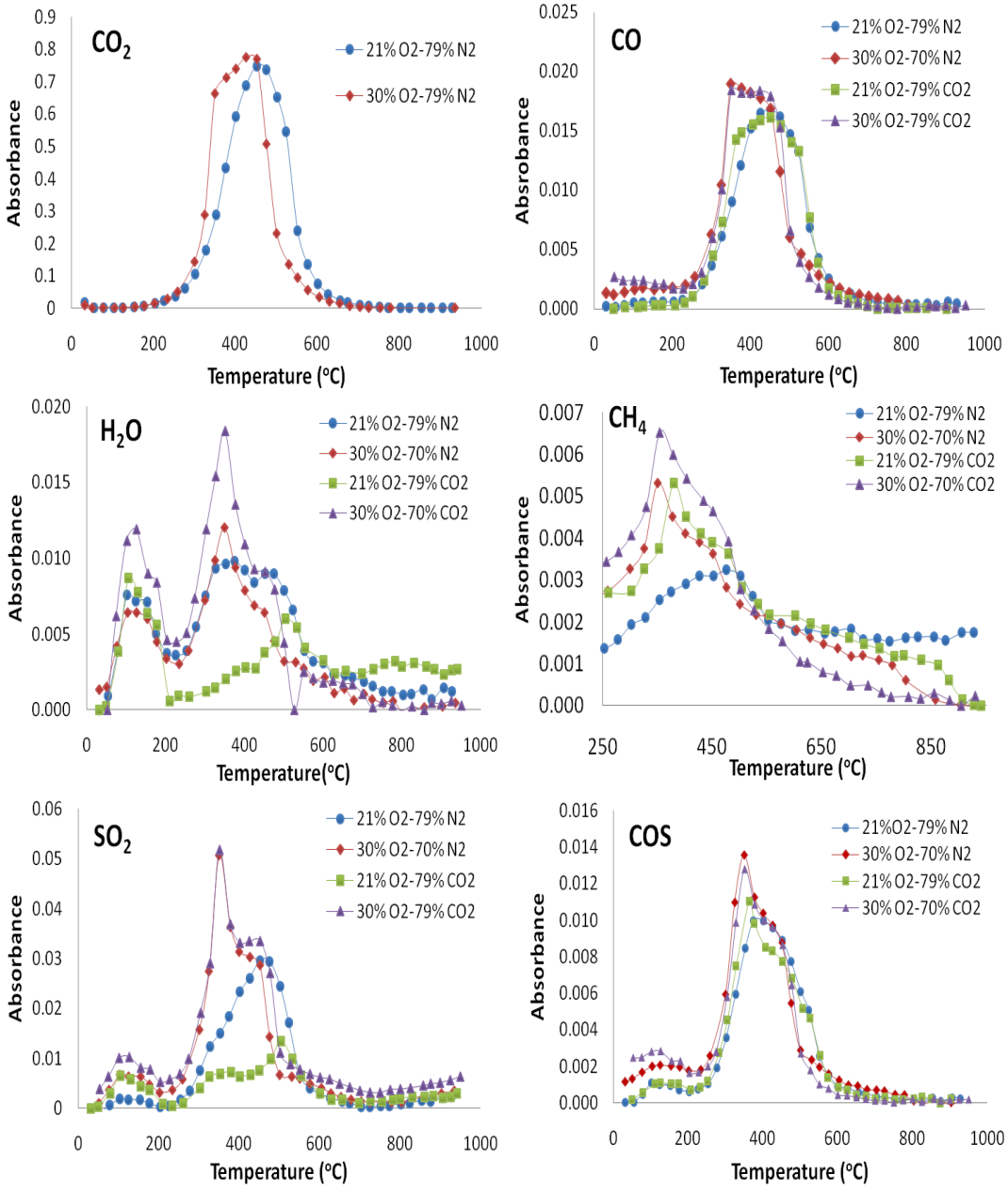

Figure 4.12: Formation profiles of evolved gases during combustion tests of lignite I

4.5 Lignite II

Lignite II is mainly characterized by its high moisture content, low calorific value and high CaO content in its ash.

4.5.1 Pyrolysis of Lignite II

TGA and DTG profiles of pyrolysis tests under are N_2 and CO_2 atmospheres are shown in Figure 4.13. The pyrolysis characteristics of lignite II determined from these profiles are summarized in Table 4.7.

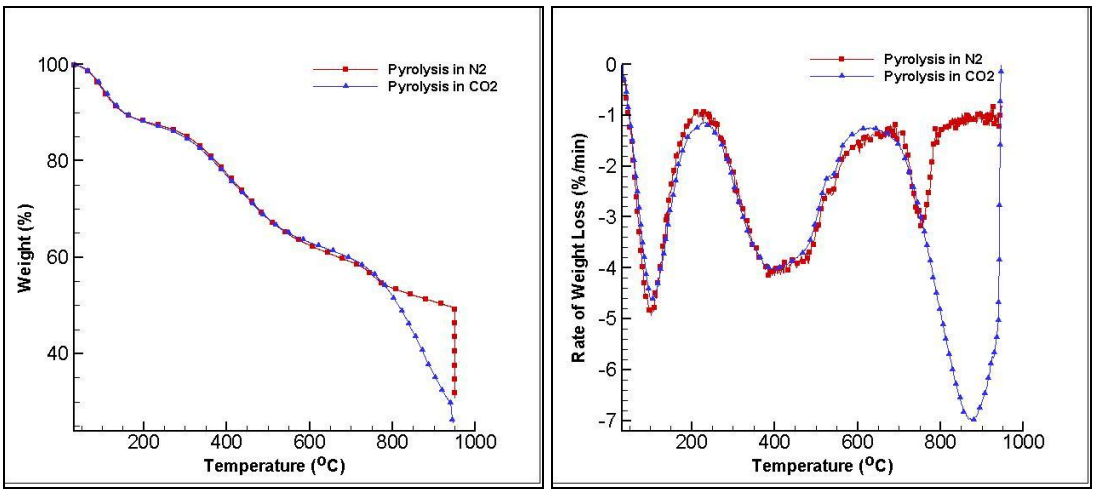

Figure 4.13: TGA and DTG profiles of lignite II in N_2 and CO_2 atmospheres

Pyrolysis results of lignite II samples show that weight loss profiles are almost the same up to a temperature of 720°C in N_2 and CO_2 environments, indicating that CO_2 behaves as an inert gas in this temperature range as also observed in pyrolysis of other fuels. After moisture release in the first 200°C temperature zone, pyrolysis continues with the release of volatile matter content in the range of 200-750°C. In

700-950^{o}C temperature range, additional peaks are displayed in pyrolysis profiles. A small peak appears after 700^{o}C which is attributed to calcite decomposition in N_2 atmosphere. The sharp peak observed in CO_2 environment is considered to be due to char-CO_2 gasification reaction.

Table 4.7: Pyrolysis Characteristics of Lignite II

	Pyrolysis in N_2	**Pyrolysis in CO_2**
T_{in} (^{o}C)	241.6	232.6
$T_{max.-1}$ (^{o}C)	400.0	398.3
$T_{max.-2}$ (^{o}C)	757.0	878.6
$(dm/dt)_{max.-1}$ (%/min)	4.1	4.0
$(dm/dt)_{max.-2}$ (%/min)	3.1	7.0
Weight loss up to 950^{o}C (%)	50.2	70.2

Formation profiles of the evolved gases during pyrolysis tests are represented in Figure 4.14. CO formation initiates at around 200^{o}C and takes place during the entire devolatilization process with two main peaks at 400^{o}C and 800^{o}C in N_2 environment. The peak displayed at 800^{o}C demonstrates the release of CO_2 due to calcite decomposition reactions. Significant increase is observed in CO and COS formation after 700^{o}C in CO_2 environment because of char-CO_2 gasification reactions. Sharp peaks in the first 200^{o}C temperature zone in H_2O formation profiles represent water vapour release from high moisture content lignite II. Similar trends are displayed in methane evolution which takes place between 300-800^{o}C in both environments. SO_2 formation is observed to reach its maximum value at 600^{o}C and takes place during the entire devolatilization process.

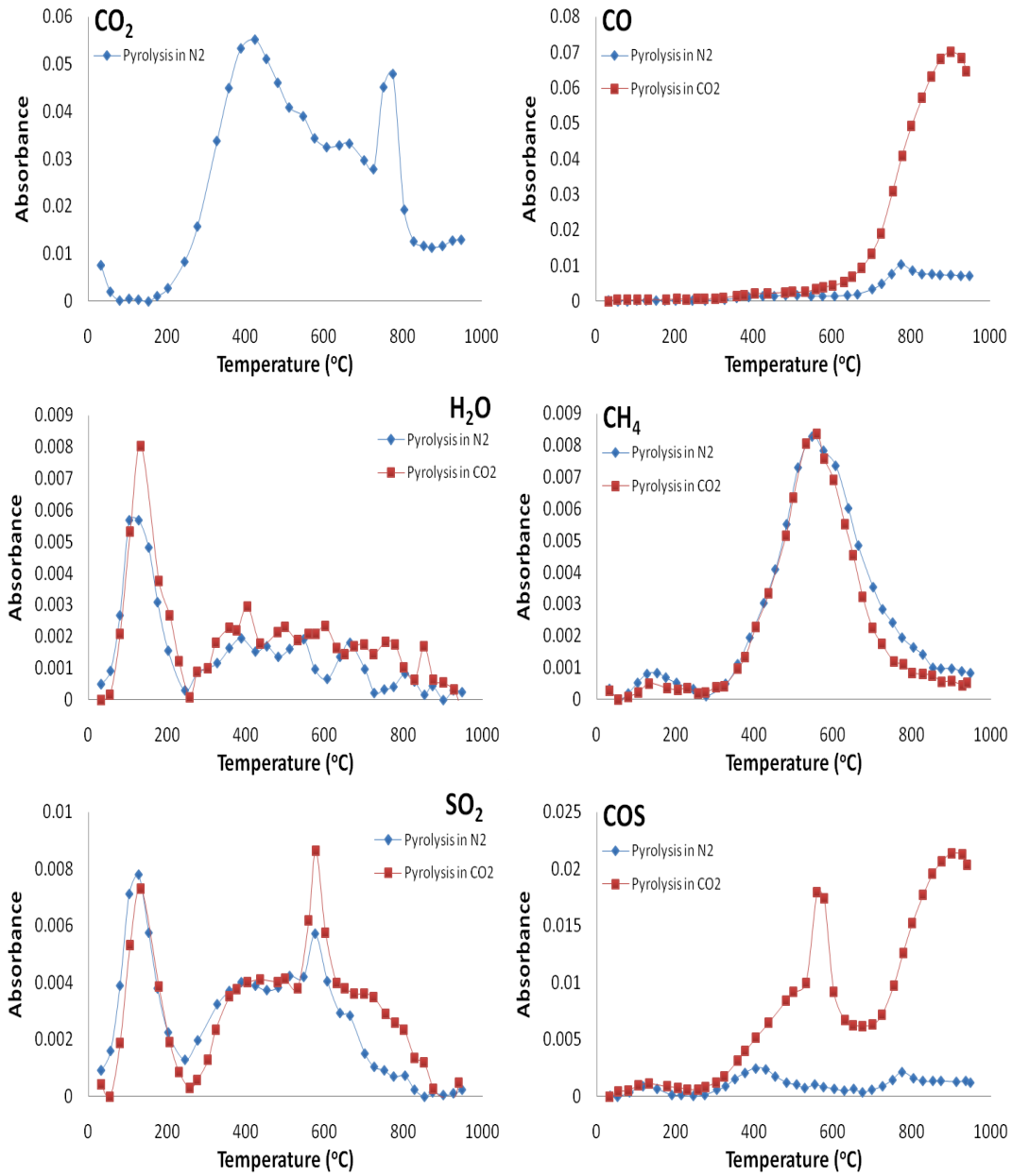

Figure 4.14: Formation profiles of evolved gases during pyrolysis tests of lignite II

4.5.2 Combustion of Lignite II

Figure 4.15 compares TGA and DTG profiles of lignite II in different combustion atmospheres. Combustion characteristics of lignite II is represented in Table 4.8.

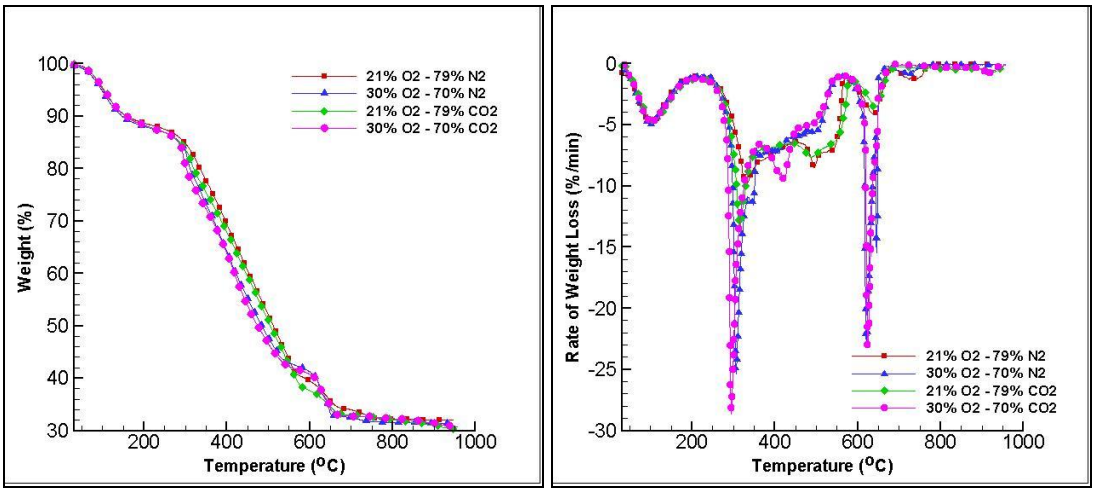

Figure 4.15: TGA and DTG profiles of lignite II in different combustion atmospheres

Comparison of TGA curves reveals that similar behaviours are observed in weight loss profiles in identical oxygen concentration conditions. In oxygen-enriched conditions TGA profiles shift to slightly lower temperatures as higher oxygen levels leads to easier and faster burning. Effect of oxygen concentration on combustion is more clearly displayed in DTG curves in Figure 4.15. Four different peaks are represented in the DTG profiles of lignite II samples. First peaks within 200^{o}C represent moisture release whereas other peaks within the temperature range 225-600^{o}C show devolatilization and char burning steps respectively, for all cases. High volatile matter content of lignite and the ease with its release result in the formation of two distinctive peaks in DTG profiles, representing devolatilization and char burning steps, which is widely observed in low rank coals.

The last peak is considered to account for calcite decomposition. Replacing N_2 by CO_2 in combustion environment causes slight delay, lower maximum rate of weight loss in char combustion zone and higher burnout temperature (Table 4.8) in combustion of lignite II. As O_2 concentration increases, profiles shift to lower temperatures, peak and burnout temperatures decrease, weight loss rate increases and complete combustion is achieved at lower temperatures and shorter times.

Table 4.8: Combustion Characteristics of Lignite II

	21 % O_2-79 % N_2	**30 % O_2- 70 % N_2**	**21 % O_2-79 % CO_2**	**30 % O_2-70 % CO_2**
T_{in} (^oC)	217.3	218.2	219.8	223.7
$T_{max.-1}$ (^oC)	330.9	306.2	315.3	294.8
$T_{max.-2}$ (^oC)	495.5	374.6	488.0	424.0
$T_{max.-3}$ (^oC)	639.6	621.5	644.0	623.6
T_b (^oC)	668.9	652.7	671.0	664.0
$(dm/dt)_{max.-1}$ (%/min)	9.8	25.5	13.4	28.7
$(dm/dt)_{max.-2}$ (%/min)	8.6	11.5	7.7	9.4
$(dm/dt)_{max.-3}$ (%/min)	4.2	22.9	3.5	23.0
T_{ig} (^oC)	284.5	256.6	262.7	263.3
Weight loss up to 950^oC (%)	67.9	68.5	69.8	69.2

Figure 4.16 compares evolution trends of the gases identified in combustion tests of lignite II. Three main steps are displayed in CO_2 formation profiles in O_2/N_2 mixtures, which correspond to CO_2 release due to volatile matter release, char burning and calcite decomposition. Different CO evolution profiles are observed in

all combustion cases. CO evolution takes place between 200-600^{o}C and 600-800^{o}C in two stages. Methane gas is identified in the temperature range of 300-600^{o}C and similar trends are obtained in its formation profiles when oxygen concentration is identical in combustion environment. Two peaks are represented in SO_2 profiles in all conditions. However, additional peaks are observed at around 650^{o}C in oxygen-enrcihed conditions. Certain amount of COS is evolved bewteen 300-600^{o}C in all combustion conditions.

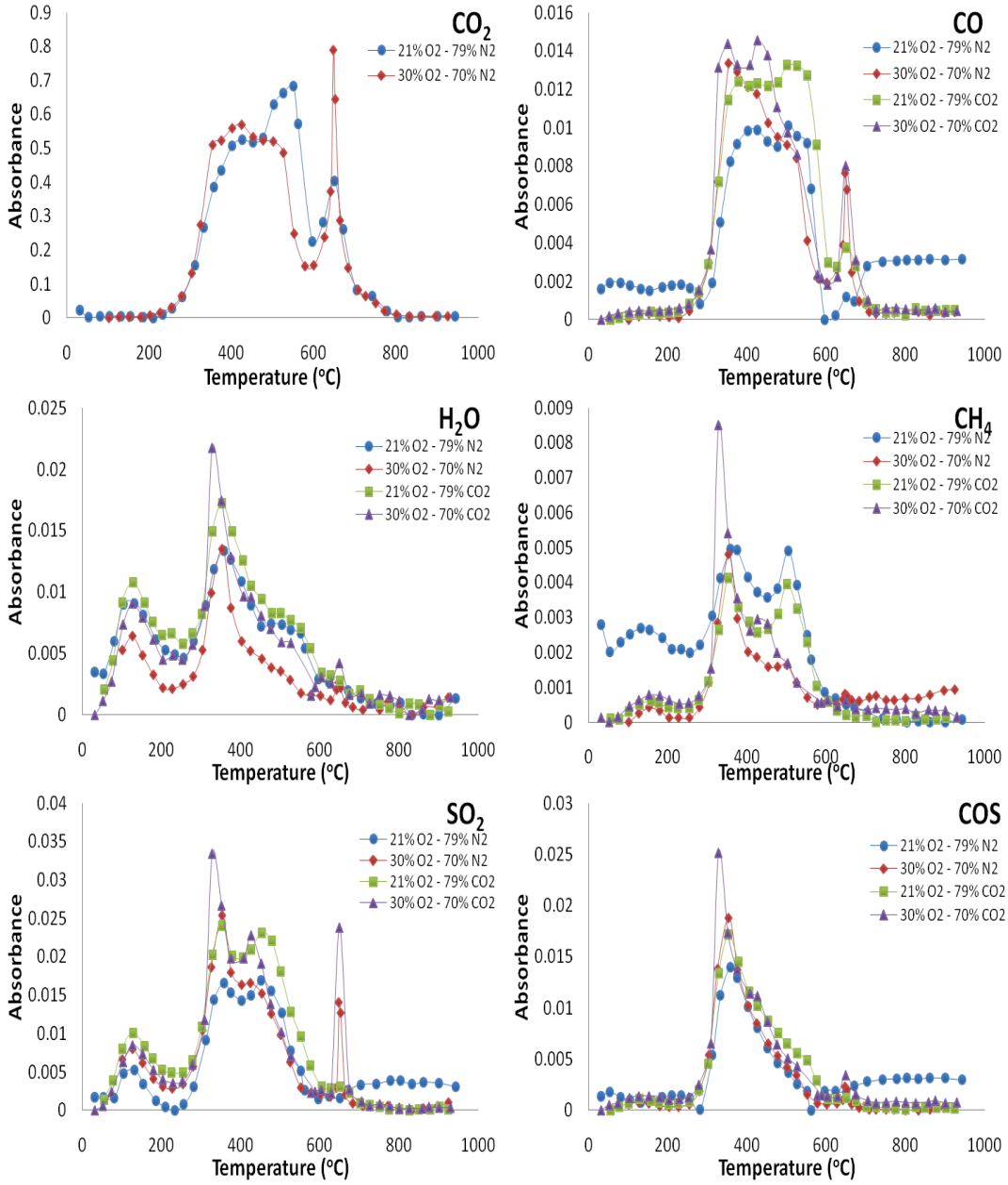

Figure 4.16: Formation profiles of evolved gases during combustion tests of lignite II

4.6 Olive Residue

Olive residue is the remaining part of olive after milling and extraction of the olive oil, which is a specific type of biomass from olive oil production process. It contains significant amount of oxygen and volatile matter, low moisture and ash content.

4.6.1 Pyrolysis of Olive Residue

TGA and DTG curves obtained in pyrolysis tests of olive residue are shown in Figure 4.17.

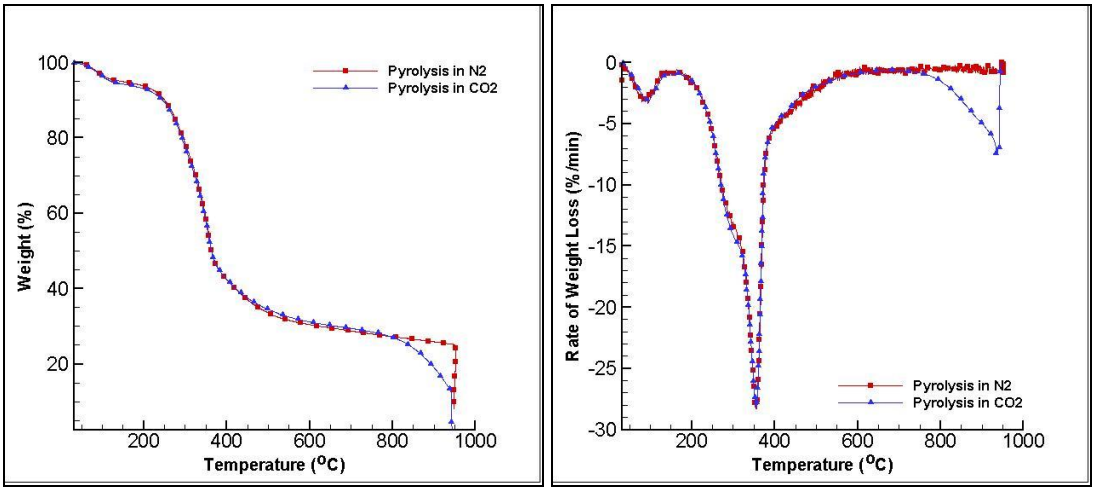

Figure 4.17: TGA and DTG profiles of olive residue in N_2 and CO_2 atmospheres

As can also be seen from Figure 4.17 and Table 4.9, pyrolysis of olive residue starts at around 180°C and continues with a shoulder at around 250°C representing decomposition of hemicellulose and a peak at around 350°C accounting for the decomposition of cellulose. Above 400°C, the weight loss continues at a slower rate, which corresponds to the slow degradation of lignin. Lignite, on the other hand, starts devolatilization at a slightly higher temperature (220°C) and weight loss

continues with a peak around 500°C. Two main weight loss steps are displayed in DTG profiles in nitrogen atmosphere while an additional weight loss step appears after 700°C in CO_2 environment. First weight loss step within 25-200°C temperature range demonstrates moisture release and the second weight loss step within 200-600°C is due to volatile matter release in both atmospheres. Additional peak after 700°C seen in DTG curve under CO_2 atmosphere is considered to be due to CO_2 – char gasification reaction.

Table 4.9: Pyrolysis Characteristics of Olive Residue

	Pyrolysis in N_2	**Pyrolysis in CO_2**
T_{in} (°C)	183.1	175.6
$T_{max.-1}$ (°C)	355.5	354.9
$T_{max.-2}$ (°C)	-	934.4
$(dm/dt)_{max.-1}$ (%/min)	28.4	28.3
$(dm/dt)_{max.-2}$ (%/min)	-	7.5
Total weight loss up to 950°C (%)	75.0	87.0

Formation profiles of the evolved gases during pyrolysis tests of olive residue are reported in Figure 4.18 . CO_2 formation initiates at around 200°C and continues up to 600°C. CO formation primarily identified at 400°C; however, significant increase is observed in high temperature zone due to gasification reaction in CO_2 environment. Water vapour is evolved between mainly at around 400°C in the temperature range of 200-600°C after moisture release. Two main peaks are displayed in the formation profile of methane at around 300°C and 600°C. SO_2 formation reaches to its maximum value at 400°C and similar evolution trends are observed in both pyrolysis environments. COS formation takes place in a relation with CO formation and is observed to increase after 800°C in CO_2 environment due to the effect of gasification.

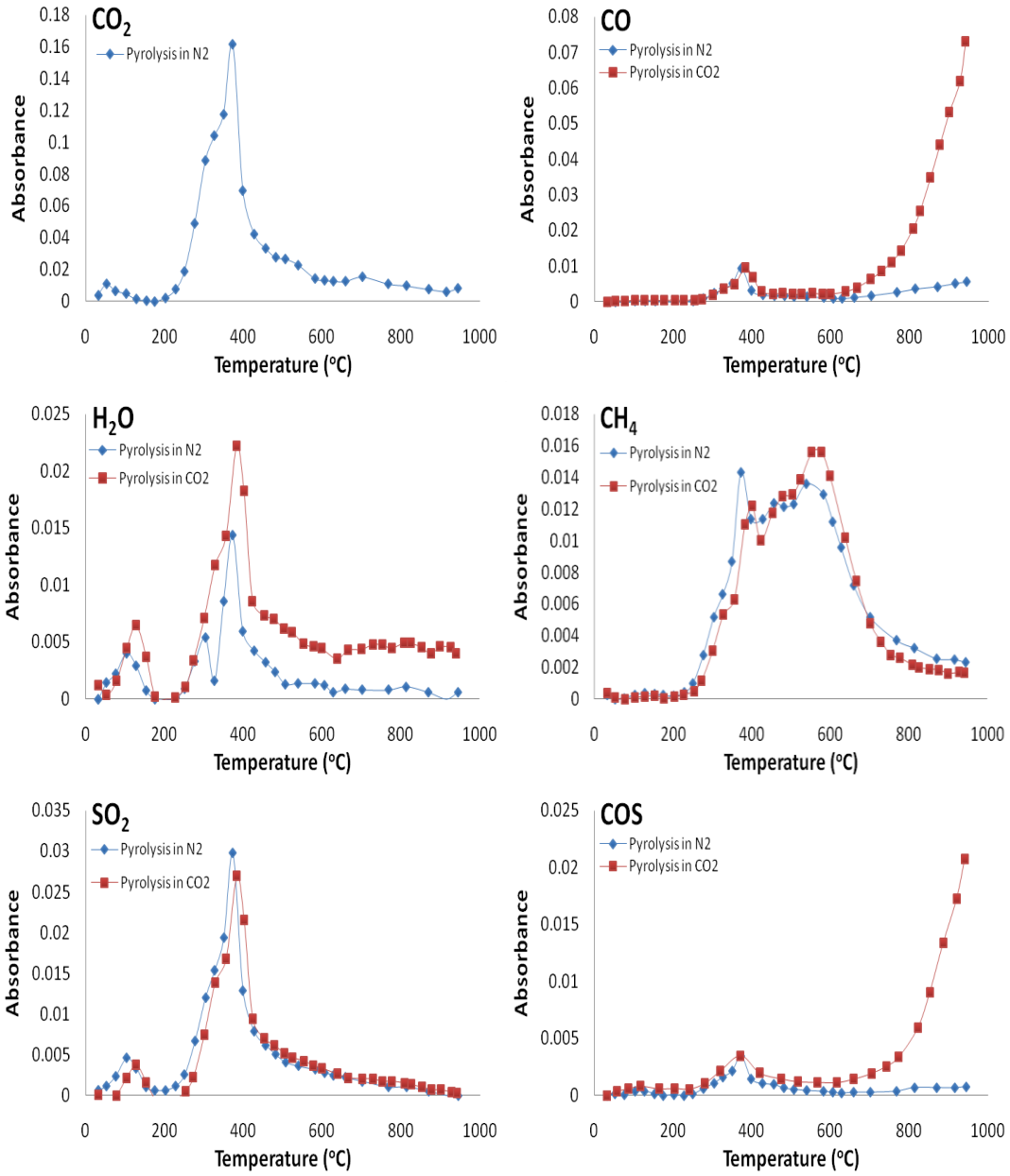

Figure 4.18: Formation profiles of evolved gases during pyrolysis tests of olive residue

4.6.2 Combustion of Olive Residue

Figure 4.19 compares TGA and DTG profiles of olive residue under different combustion environments.

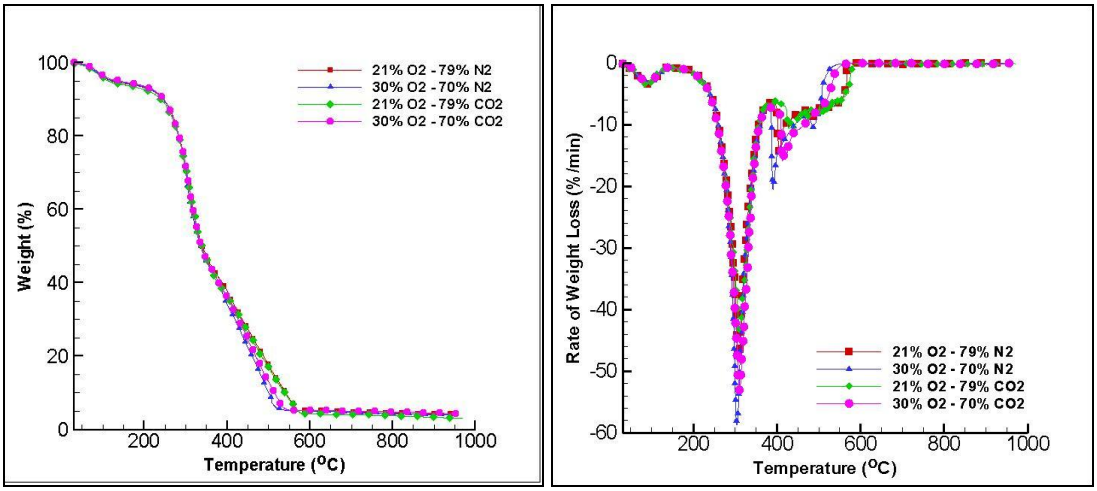

Figure 4.19: TGA and DTG profiles of olive residue in different combustion atmospheres

In the case of olive residue, thermal and oxidative degradation takes place in two stages in all combustion environments. In the first stage the main weight loss occurs within the temperature range 180-360°C. This region corresponds to devolatilization of hemicellulose and cellulose components and their subsequent ignition. The second stage weight loss is associated with char combustion within the temperature range 360-600°C. These findings are in agreement with those in the open literature [11, 63-65]

Table 4.10 displays combustion characteristics of olive residue. As can be seen from the table initial temperature of olive residue is not affected by combustion environment and is around 180°C in all combustion environments. Moreover, similar to initial decomposition temperature, main peak of volatile matter release

appears at around 310°C in all combustion environments. Rate of weight loss, on the other hand, is observed to vary with combustion environment. Increase in oxygen concentration results in higher maximum weight loss rates irrespective of the combustion environment while presence of CO_2 as diluting gas in combustion environment leads to decrease in peak height due to its higher heat capacity. Elevated oxygen level leads to a shift in char combustion peak to lower temperature zone with increase in its weight loss rate. However, higher char combustion peak and burnout temperatures in oxy-fuel conditions are indicative of delayed combustion due to the existence of CO_2 in the combustion environment.

Table 4.10: Combustion Characteristics of Olive Residue

	21 % O_2-79 % N_2	**30 % O_2-70 % N_2**	**21 % O_2-79 % CO_2**	**30 % O_2-70 % CO_2**
T_{in} (°C)	183.9	186.9	174.6	179.8
$T_{max.-1}$ (°C)	308.9	304.3	309.7	311.2
$T_{max.-2}$ (°C)	405.3	390.9	435.8	413.2
T_b (°C)	567.7	526.6	579.9	544.3
$(dm/dt)_{max.-1}$ (%/min)	48.4	58.9	43.7	53.2
$(dm/dt)_{max.-2}$ (%/min)	14.4	20.5	10.6	15.9
T_{ig} (°C)	258.8	258.5	229.5	264.1
Weight loss up to 950 (%)	95.6	95.8	96.9	95.7

FTIR analysis results of the combustion tests are shown in Figure 4.20. Two main steps are displayed in the formation profiles of CO_2 gas, representing the volatile matter and char combustion steps, respectively. CO and H_2O formation take place in the temperature range of 200-600°C. Similar trends are observed in the formation

of these gases in all combustion environments. Methane evolution profile displays two stages; one around 300^{o}C and the other 450^{o}C, under all combustion conditions. SO_2 and COS formation take place during entire combustion process with a maximum release at around 300^{o}C and their formation profile display similar trends in all cases.

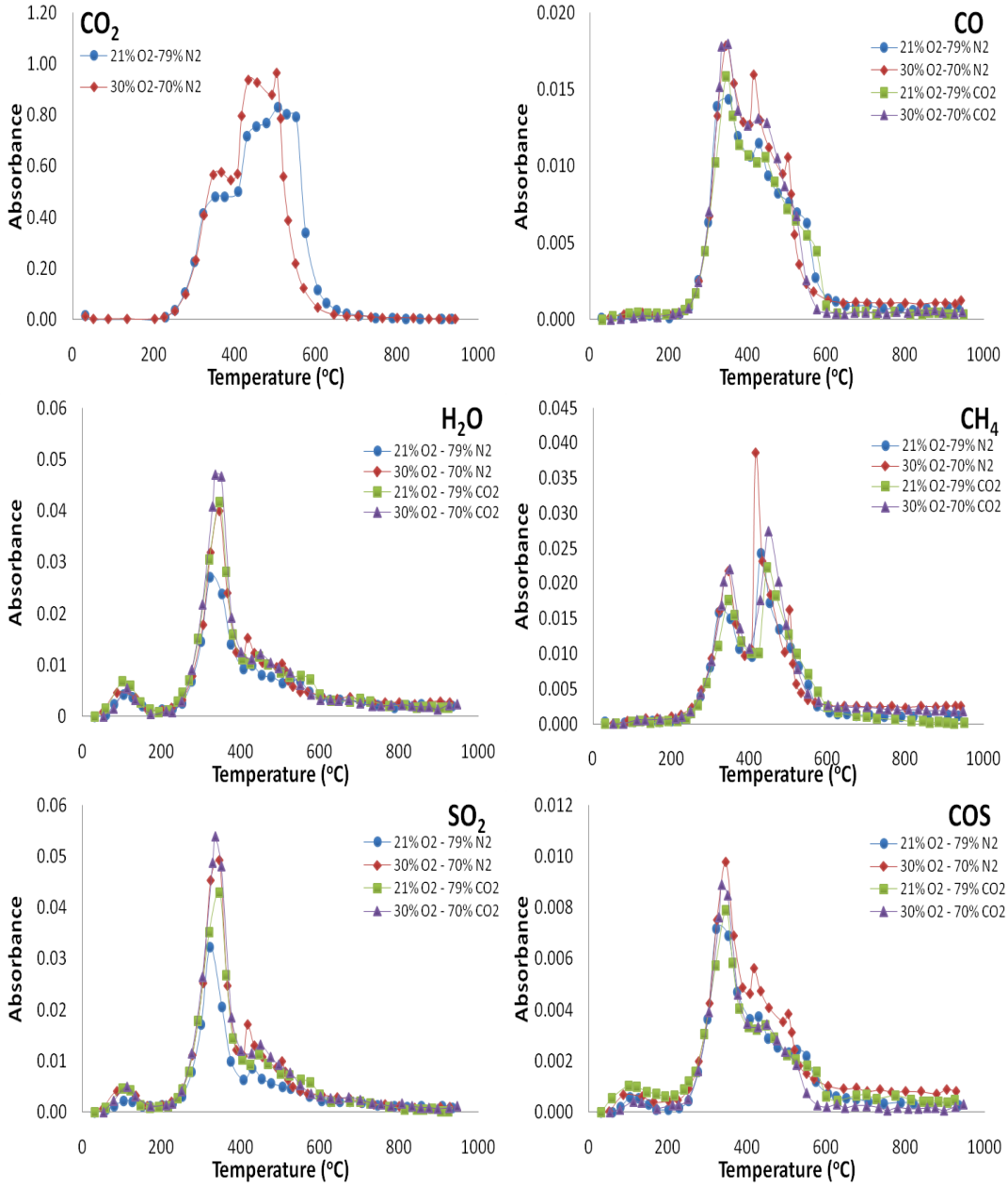

Figure 4.20: Formation profiles of evolved gases during combustion tests of olive residue

4.7 Imported Coal – Petroleum Coke – Lignite I Blend (Blend I)

Blend I was prepared by mixing high rank imported coal, low rank lignite I and petcoke in the proportion of 60:30:10.

4.7.1 Pyrolysis of Blend I

Pyrolysis profiles of the blend samples in N_2 and CO_2 conditions are shown in Figure 4.21. The pyrolysis characteristics of the blend and its parent fuels are summarized in Table 4.11.

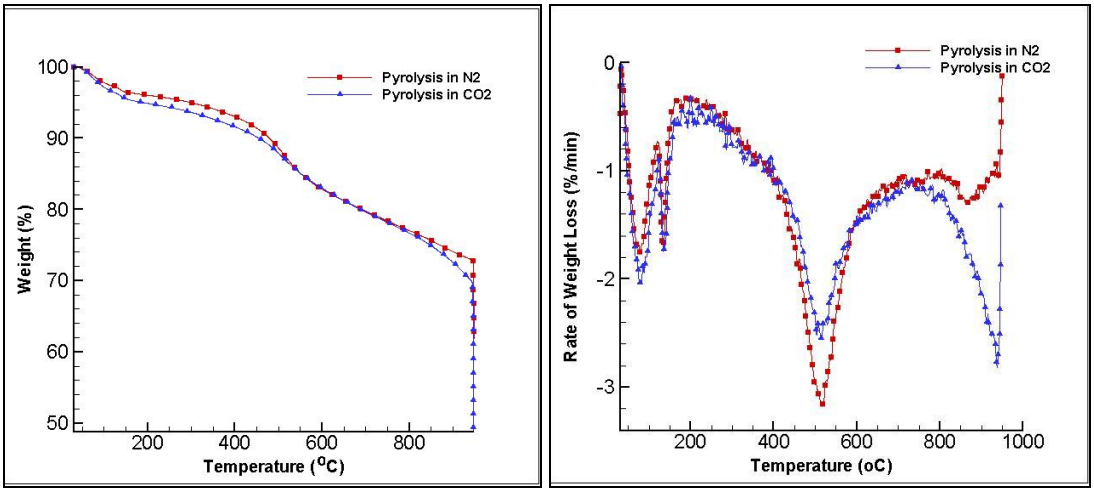

Figure 4.21: TGA and DTG profiles of Blend I in N_2 and CO_2 atmospheres

Two main weight loss steps are displayed in weight loss profiles of blend I in nitrogen atmosphere while further weight loss step appears after 700°C in CO_2 environment. Moisture is released within 25-200°C temperature range in both conditions. Second weight loss step represents devolatilization within 200-600°C. Similar trends are obtained in both pyrolysis tests, however, in CO_2 atmosphere, the weight loss rate is found to be lower than the one in N_2 atmosphere which is due to the effect of higher heat capacity of CO_2 (Table 4.11). Additional peak after 700°C

seen in DTG curve under CO_2 atmosphere is considered to be due to CO_2 – char gasification reaction.

Table 4.11: Pyrolysis characteristics of blend I and its parent fuels

		T_{in}	T_{max}	$(dm/dt)_{max}$	Weight loss up to 950°C
Imported Coal	**Pyrolysis in N_2**	465.2	517.0	2.0	21.1
	Pyrolysis in CO_2	463.9	528.4	2.0	23.2
Petcoke	**Pyrolysis in N_2**	514.9	582.3	1.4	14.4
	Pyrolysis in CO_2	570.9	638.7	1.3	17.0
Lignite I	**Pyrolysis in N_2**	230.8	482.9	3.6	41.0
	Pyrolysis in CO_2	216.7	481.0	3.16	50.3
Blend Exp.	**Pyrolysis in N_2**	389.6	512.5	3.1	27.1
	Pyrolysis in CO_2	392.3	512.1	2.4	30.0
Blend Theo.	**Pyrolysis in N_2**	405.4	500.1	2.1	26.5
	Pyrolysis in CO_2	409.2	532.2	2.0	30.3

Pyrolysis behaviours of blend I and its parent fuels under N_2 and CO_2 environments and the theoretical pyrolysis behaviour of the blend calculated by using additive rule are compared in Figure 4.22.

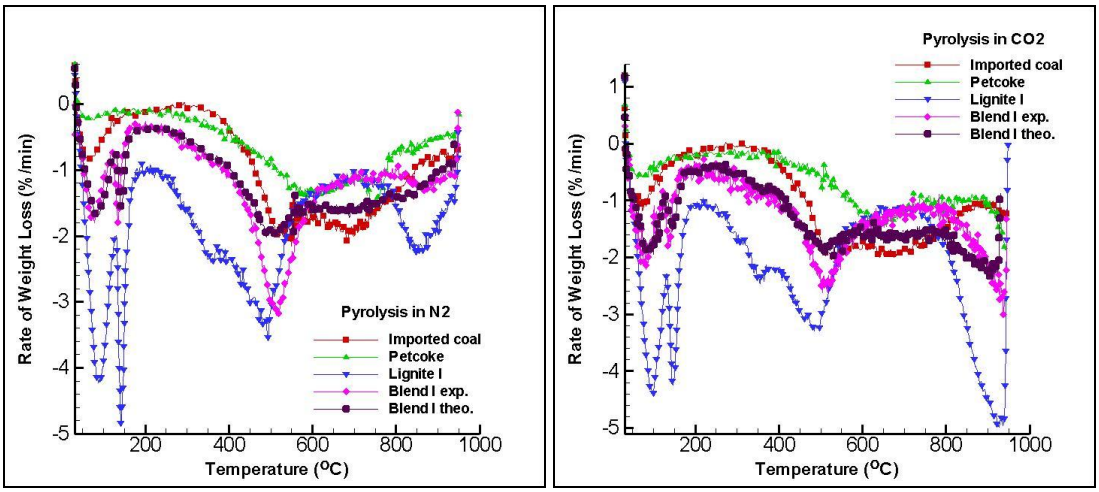

Figure 4.22: Pyrolysis profiles of blend I and its parent fuels in N_2 and CO_2 environments

As can be seen in Figure 4.22 lignite I 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 I reveals close resemblance with lignite I as lignite dominates pyrolysis behaviour of the blend with its significantly higher volatile matter content. Pyrolysis behaviour of blend I shows that peak height decreases and the peak position shifts to higher temperatures with the addition of imported coal and petcoke. Theoretical blend I 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. This is considered to be due to interactions (synergy) between parent fuels during pyrolysis process [49, 54, 66].

The evolution profiles of the gaseous species including CO_2, CO, H_2O, CH_4, SO_2 and COS, from the pyrolysis of blend I in nitrogen and carbon dioxide are shown in

Figure 4.23. In the formation profile of CO_2, three peaks are displayed at around 400, 550 and 750^oC during pyrolysis in N_2 atmosphere. The first peak represents CO_2 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 CO_2 release as a consequence of calcite decomposition of petcoke component at high temperature zone. In both environments, H_2O is identified in the first 200^oC due to moisture release. Methane formation takes place between 400-800^oC. Certain amount of SO_2 is also formed as a result of the high sulphur content of lignite and petcoke in the blend at around 350^oC and 500^oC with similar trends in both pyrolysis conditions. After 700^oC, distinctive increase is observed in CO and COS formation profiles in CO_2 atmosphere due to CO_2 – char gasification reaction.

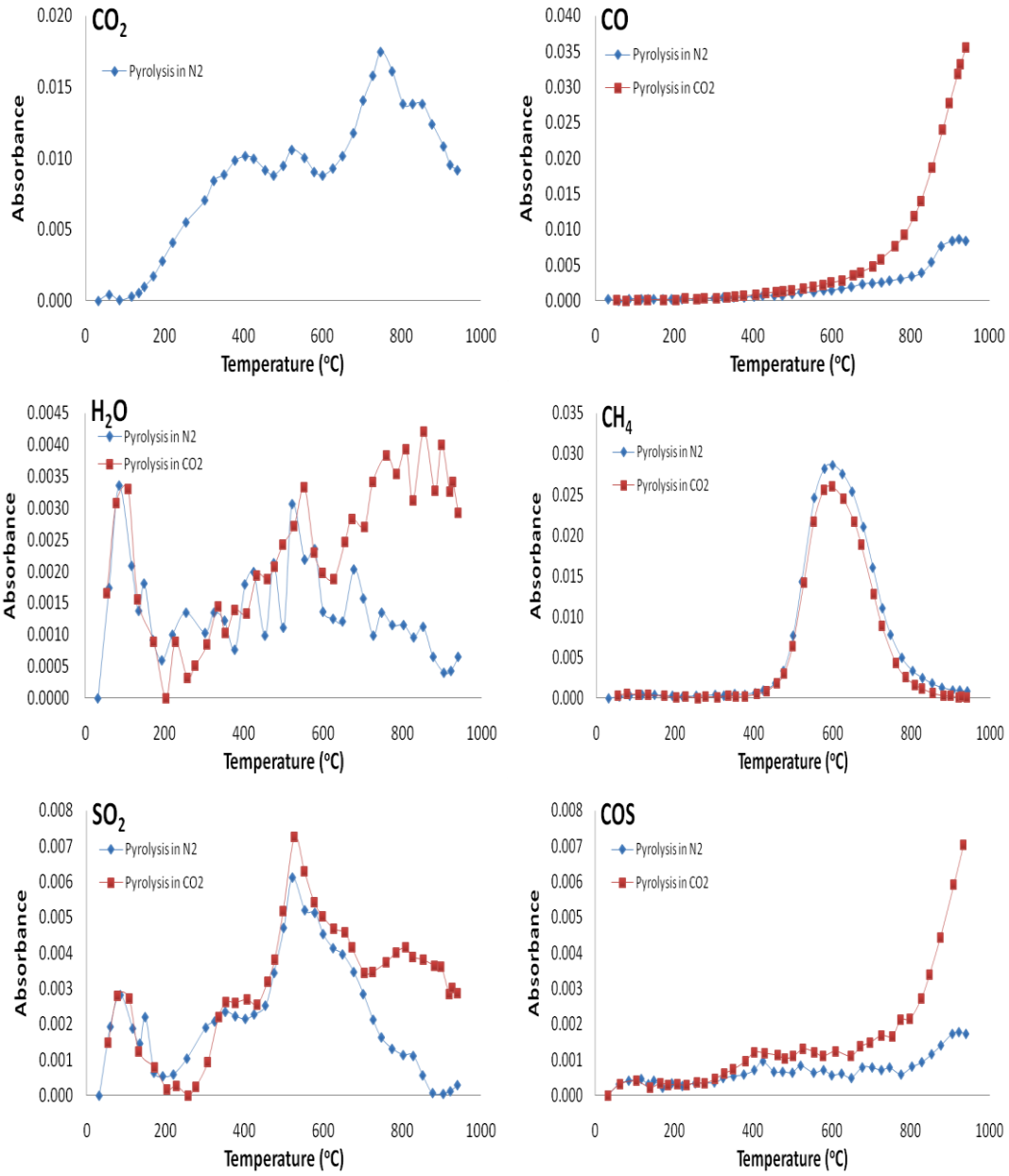

Figure 4.23: Formation profiles of evolved gases during pyrolysis tests of blend I

4.7.2 Combustion of Blend I

Combustion profiles of the imported coal-petcoke-lignite I blend in different combustion environments are given in Figure 4.24. Combustion characteristics of the fuel samples are summarized in Table 4.12.

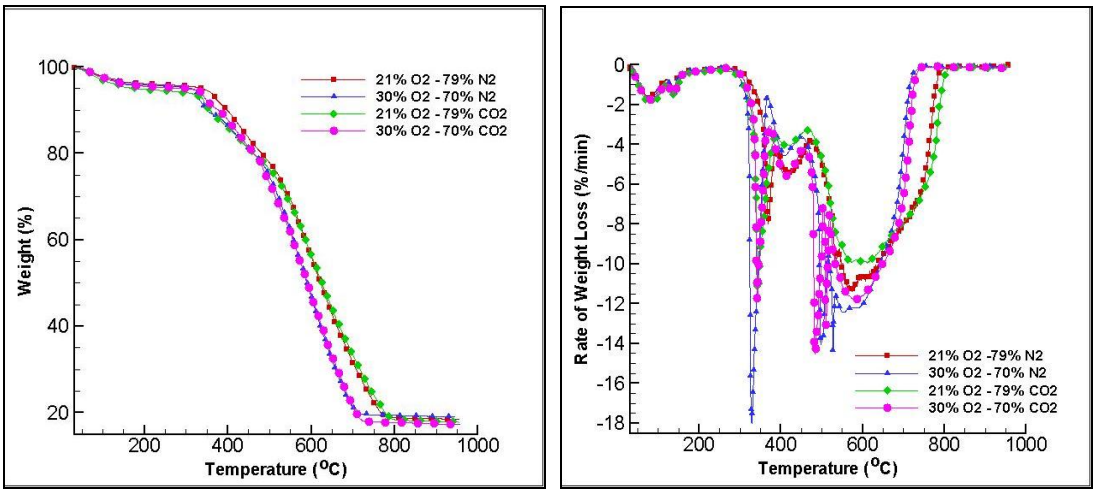

Figure 4.24: TGA and DTG profiles of blend I in different combustion atmospheres

In air and oxy-fuel cases, after moisture release in the first 200°C temperature zone, three weight loss steps are displayed in weight loss curves. The first two steps account for combustion of highly reactive lignite component in the temperature range of 300-450°C. In this interval, volatile matter and char combustion steps of lignite I 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, peak and burnout temperatures are higher in oxy-fuel conditions as higher heat capacity CO_2 leads to delay in combustion. The effect of oxygen concentration is found to be more significant than that of the diluting gas (N_2 or CO_2) on the combustion profiles. At elevated oxygen levels, weight loss rates increases 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 lignite between 400-700^{o}C. These additional peaks demonstrates burning of volatiles in imported coal and petcoke as volatile matter and char burning steps are separated due to the effect of oxygen concentration.

Table 4.12: Combustion characteristics of blend I and its parent fuels

		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 I	**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

Combustion profiles of imported coal, petcoke and lignite I and their blend with its theoretical behaviour under different combustion environments are shown in Figure 4.25.

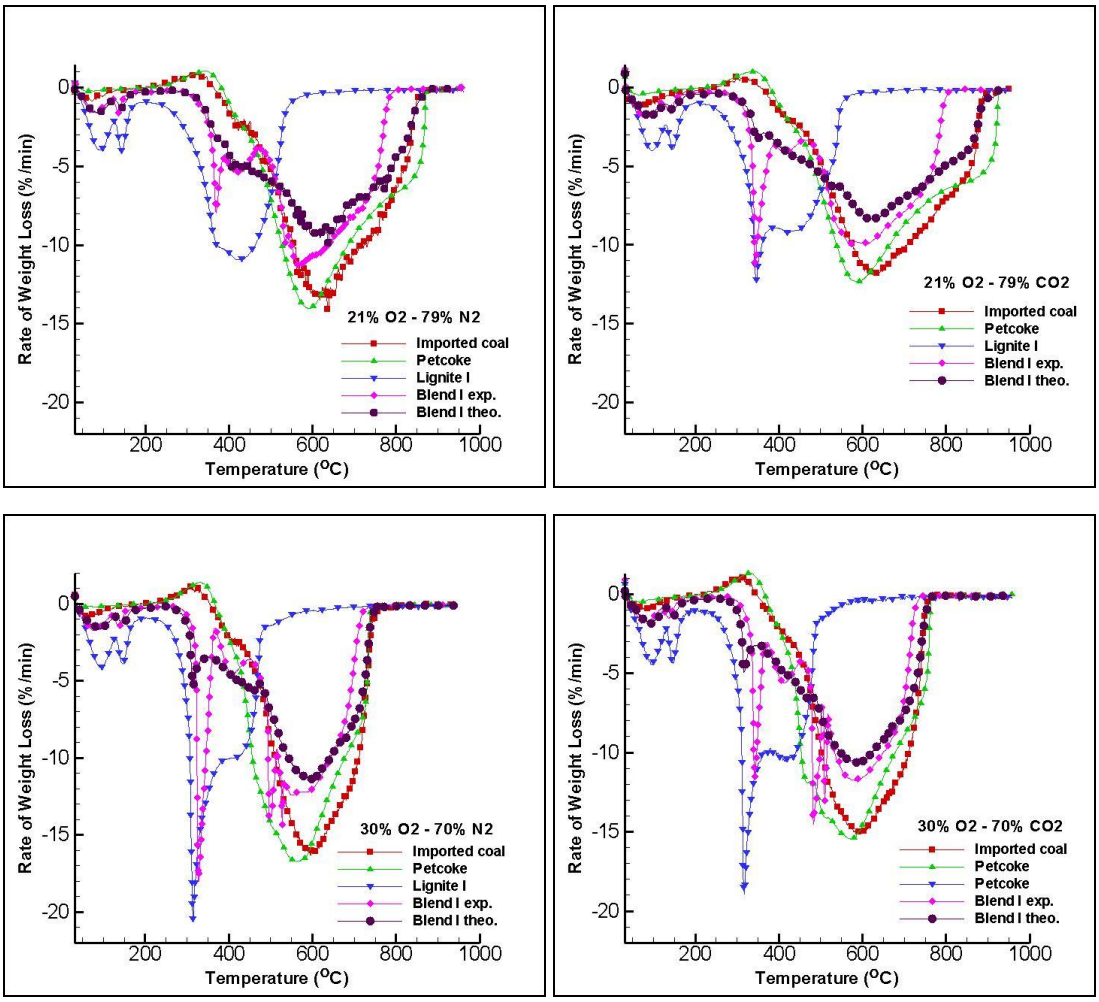

Figure 4.25: Combustion profiles of blend I and its parent fuels in different combustion environments

Theoretical and experimental combustion profiles of the blend 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 DTG curves in contrast to the expected behaviour. The positive effect of blending is observed at high 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 the indicative of interaction behaviour of the component coals during combustion in all cases.

The formation profiles of evolved gases during combustion of the blend I in different atmospheres are shown in Figure 4.26. The formation profile of CO_2 in oxygen-enriched air atmosphere shifts to lower temperature zone as elevated oxygen levels lead to faster burning and earlier release of CO_2. Two steps are observed in formation profiles of CO_2 gas due to burning of lignite and imported coal-petcoke, consecutively. CO formation takes place between 300-800^{o}C with a shoulder at around 375^{o}C. H_2O formation profiles show that moisture is released first in all combustion environments with further release in the temperature range of 200-800^{o}C. CH_4, SO_2 and COS gases evolve between 250-750^{o}C and reveal two stages in their evolution profiles. Mainly similar formation trends are observed for gases in all combustion cases.

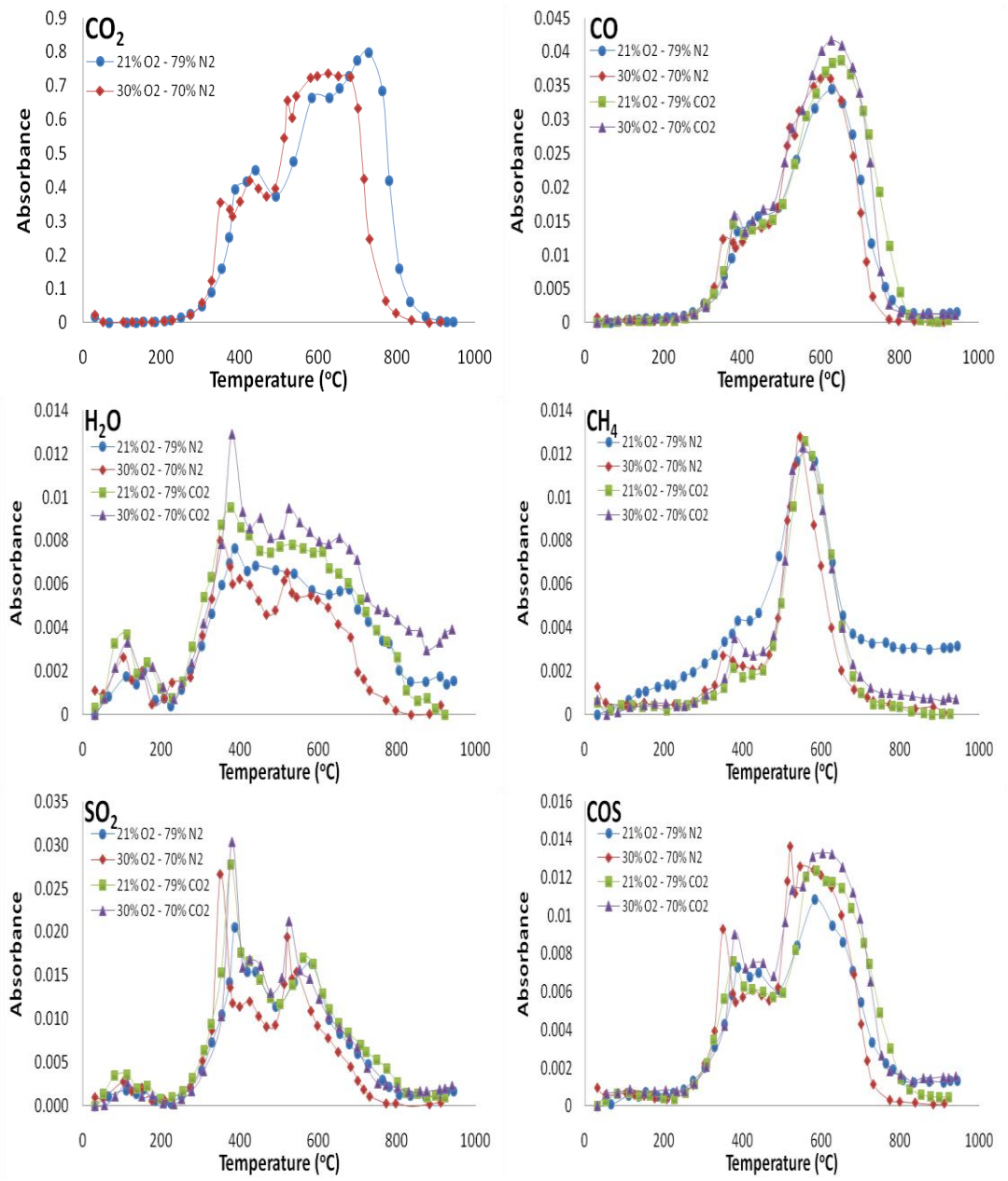

Figure 4.26: Formation profiles of evolved gases during combustion tests of blend I

4.8 Petroleum Coke – Lignite II Blend (Blend II)

Blend II was prepared by mixing lignite II with low calorific value, high ash and moisture contents with high calorific value, low ash and moisture content petcoke in the proportion of 70:30. Their pyrolysis and combustion characteristics in air and oxy-fuel conditions are described in the following sections.

4.8.1 Pyrolysis of Blend II

TGA and DTG profiles of pyrolysis tests are shown in Figure 4.27. The pyrolysis characteristics of the blend and its parent fuels are summarized in Table 4.13.

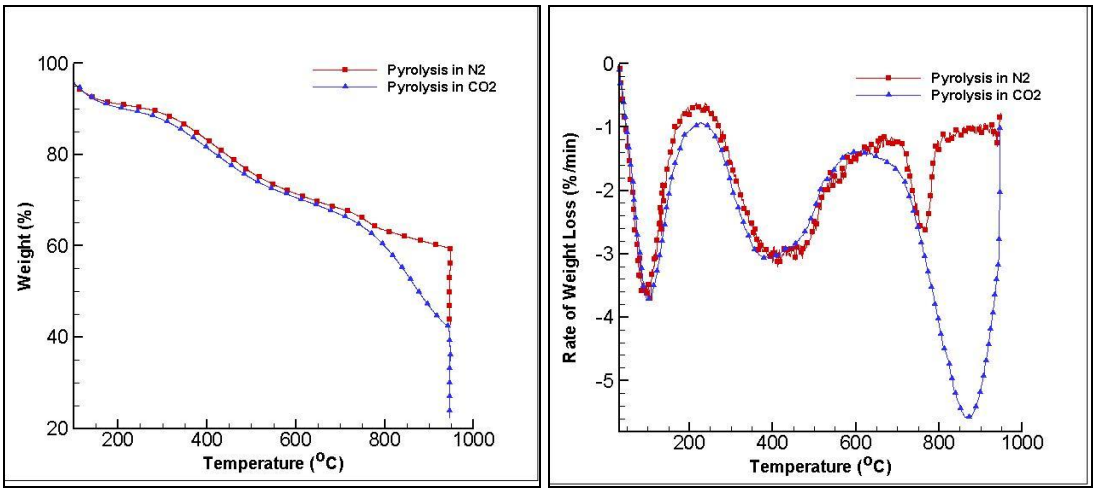

Figure 4.27: TGA and DTG profiles of blend II in N_2 and CO_2 atmospheres

Three main weight loss steps appear in weight loss profiles in both pyrolysis atmospheres. In DTG profiles of Figure 4.27, peaks appearing in the first 200°C temperature zone are attributed to moisture release while second main peak accounts for volatile matter release up to 650°C. Identical DTG trends up to 650°C indicates that CO_2 behaves as an inert atmosphere before high temperature zone.

However, at high temperature zone, weight loss profiles start to differ and additional weight loss steps are displayed. Additional peak after 700^{o}C in N_2 atmosphere is considered to be due to calcite decomposition of the parent fuels in the blend while in CO_2 atmosphere CO_2 – char gasification reaction leads to further weight loss.

Table 4.13: Pyrolysis characteristics of blend II and its parent fuels

		T_{in}	T_{max}	$(dm/dt)_{max}$	Weight loss up to 950°C
Lignite II	**Pyrolysis in N_2**	241.6	400.0	4.1	50.2
	Pyrolysis in CO_2	232.6	398.3	4.0	70.2
Petcoke	**Pyrolysis in N_2**	514.9	582.3	1.4	14.4
	Pyrolysis in CO_2	570.9	638.7	1.3	17.0
Blend Exp.	**Pyrolysis in N_2**	270.6	393.8	3.0	40.3
	Pyrolysis in CO_2	246.6	378.1	3.1	59.6
Blend Theo.	**Pyrolysis in N_2**	276.0	393.0	3.2	39.6
	Pyrolysis in CO_2	248.4	399.6	3.1	56.6

Pyrolysis behaviours of blend II and its parent fuels under N_2 and CO_2 environments are compared in Figure 4.28. The theoretical pyrolysis behaviour of the blend calculated by using additive rule is also displayed in the figure.

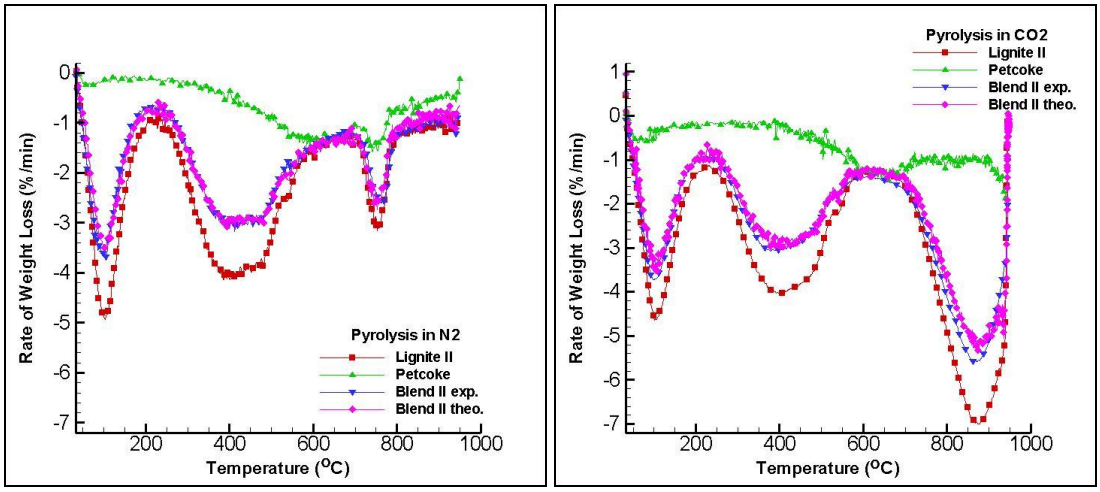

Figure 4.28: Pyrolysis profiles of blend II and its parent fuels in N_2 and CO_2 environments

As can be seen from Figure 4.28, lignite II devolatilizes at lower temperatures with higher weight loss rate due to its significantly high volatile matter content compared to petcoke. Overall comparison of DTG curves clearly indicate that pyrolysis behaviour of the blend II is dominated by lignite II as can also be observed with the similarity in their DTG profiles. Pyrolysis behaviour of blend II shows that peak height decreases and the peak position shifts to higher temperatures with the addition of petcoke.

Identical pyrolysis characteristics (Table 4.13) and overlap between the DTG curve of the blend itself (experimental) and the DTG curve found by additive rule (theoretical) of the two components of the blend (Figure 4.28) shows that there is no interaction (synergy) between lignite II and petcoke during pyrolysis in both conditions.

The evolution profiles of the gaseous species including CO_2, CO, H_2O, CH_4, SO_2 and COS, from the pyrolysis of blend II in nitrogen and carbon dioxide are shown in Figure 4.29. In the formation profile of CO_2, two peaks at around 400°C and 750°C are displayed between 200°C and 800°C which corresponds to the devolatilization temperature interval as represented in DTG curve of blend. These two peaks

account for CO_2 release due to devolatilization and calcite decomposition, respectively. Formation of CO_2 in N_2 environment is found to be the major contributor to the evolved gases with its highest absorbance intensity. In both environments, H_2O is identified in the first 200^oC due to moisture release. CH_4 and SO_2 formation take place during the entire devolatilization process. Certain amount of SO_2 is also formed as a consequence of the high sulphur content of petcoke in the blend at around 350^oC and 550^oC. CO and COS display different trends in CO_2 atmosphere due to CO_2 – char gasification reaction. After 700^oC, a distinctive increase is observed in the formation profile of CO with the initiation of the gasification reaction. Moreover, higher CO concentration leads to formation of COS which is formed by reaction of pyrite or sulphur formed during pyrite decomposition with CO.

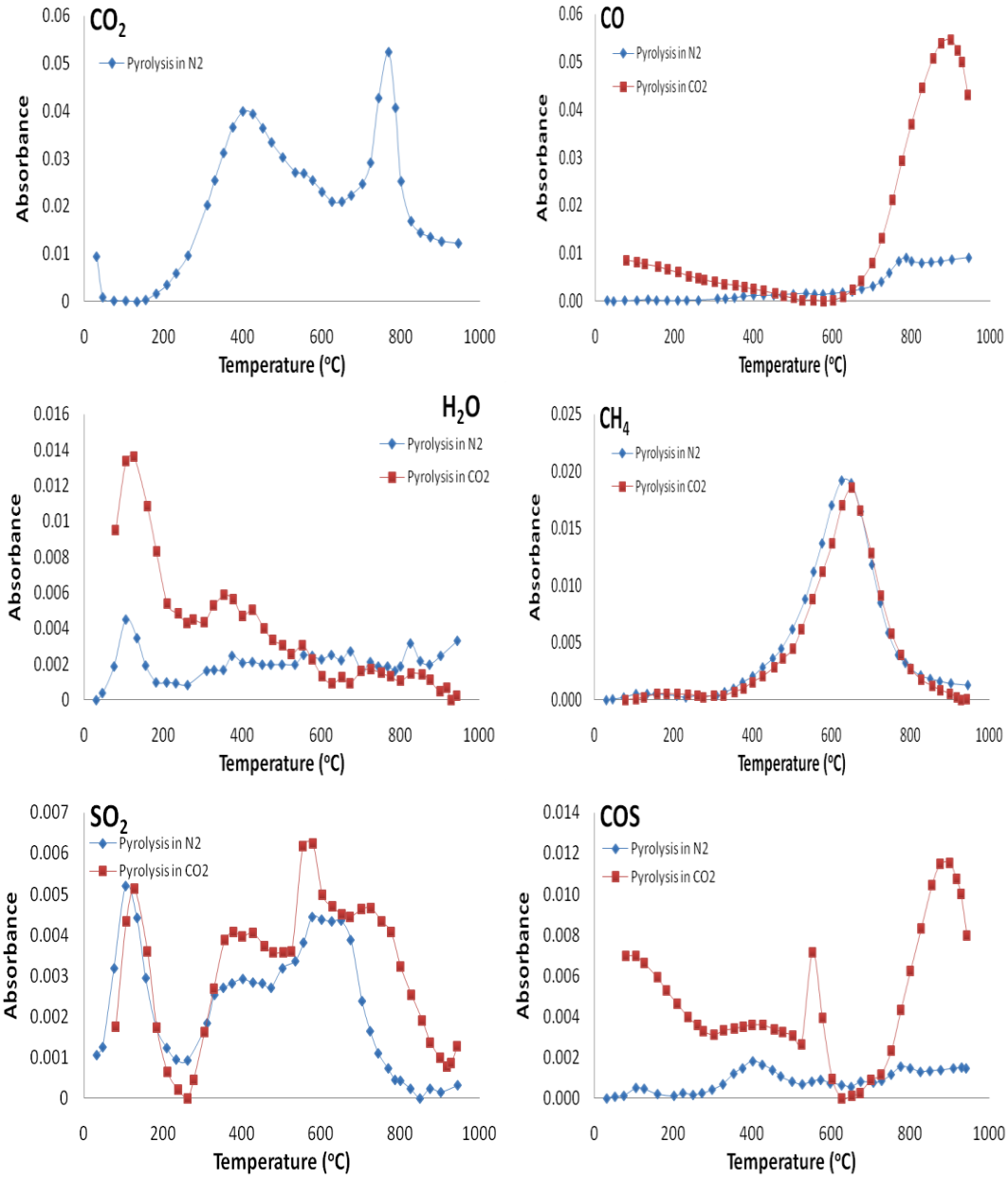

Figure 4.29: Formation profiles of evolved gases during pyrolysis tests of blend II

4.8.2 Combustion of Blend II

Combustion profiles of the lignite II-petcoke blend in different combustion environments are given in Figure 4.30.

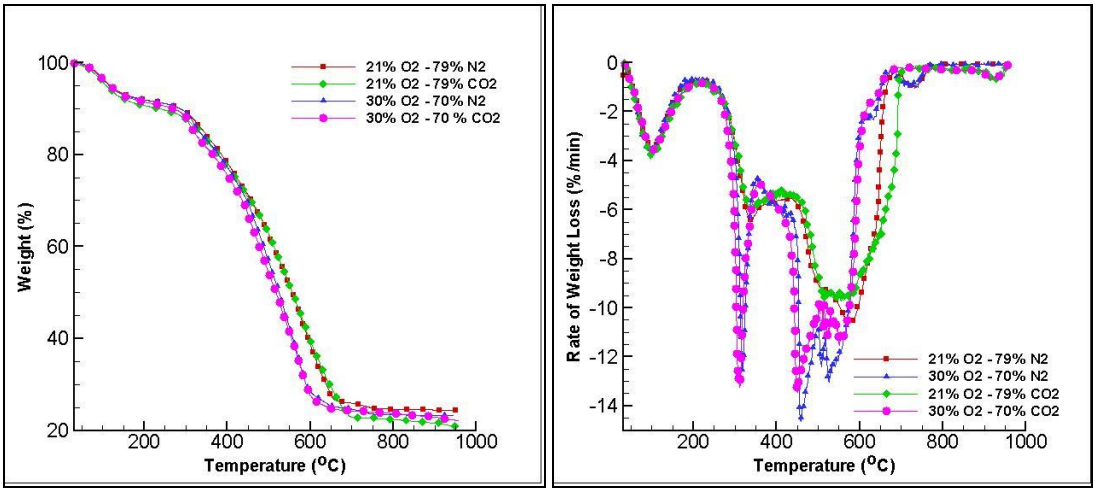

Figure 4.30: TGA and DTG profiles of blend II in different combustion atmospheres

In air and oxy-fuel cases, after moisture release in the first 200°C temperature zone, rate of weight loss curves continue with a shoulder at around 330°C, as also displayed in Table 4.14. The main peak between 400-650°C, is attributed to combustion of petcoke and lignite chars in both conditions. A small peak appears after 650°C in air case due to decomposition of calcite. However, this small peak is not observed in oxy-fuel conditions as calcite decomposition is prevented by CO_2. Similar trend in burning profiles with air and oxy-firing conditions is observed with less weight loss rate and higher burnout temperature in oxy-fuel conditions, which are indicative of the slight delay in combustion. The effect of oxygen concentration is found to be more significant than that of the diluting gas (N_2 or CO_2) on the combustion profiles. At elevated oxygen levels, more significant differences are

displayed in the DTG profiles of blend samples. Higher oxygen concentration in combustion environment leads to significant increase in weight loss rates and decrease in characteristic temperatures including T_{ig}, T_{max} and T_b. Moreover, in oxygen-enriched conditions, burning of lignite II and petcoke are discretely separated as displayed with two different steps in the main combustion peak of DTG profiles.

Table 4.14: Combustion characteristics of blend II and its parent fuels

		T_{in}	T_{max}			$(dm/dt)_{max}$			T_{ig}	T_b	Total weight loss up to 950°C
Lignite II	**21 % O_2 - 79 % N_2**	217.3	330.9	495.5	639.6	9.8	8.6	4.2	284.5	668.9	67.9
	30 % O_2 - 70 % N_2	218.2	306.2	374.6	621.5	25.5	11.5	22.9	256.6	652.7	68.5
	21 % O_2 - 79 % CO_2	219.8	315.3	488.0	644.0	13.4	7.7	3.5	262.7	671.0	69.8
	30 % O_2 - 70 % CO_2	223.7	294.8	424.0	623.6	28. 7	9.4	23.0	263.3	664.0	69.2
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
Blend Exp.	**21 % O_2 - 79 % N_2**	257.3	332.6	581.4	726.6	6.3	10.6	1.0	312.1	663.7	75.5
	30 % O_2 - 70 % N_2	257.6	317.5	450.5	525.3	12.5	14.6	13.1	303.4	652.7	76.8
	21 % O_2 - 79 % CO_2	246.1	334.0	575.4	-	5.8	9.6	-	311.9	694	79.3
	30 % O_2 - 70 % CO_2	248.8	310.9	448.6	551.4	13.3	13.4	11.5	304.7	650.3	77.0
Blend Theo.	**21 % O_2 - 79 % N_2**	261.0	332.0	540.0	635	6.6	8.3	6.6	302.2	866.0	76.3
	30 % O_2 - 70 % N_2	256.7	306.7	485.7	620.3	17.4	8.2	20.1	283.7	734.7	76.8
	21 % O_2 - 79 % CO_2	247.7	314.7	544.7	641.7	9.1	7.6	5.8	300.5	923.7	77.8
	30 % O_2 - 70 % CO_2	252.7	294.7	506.7	623.7	19.8	7.4	20.1	281.3	759.7	77.8

Combustion profiles of lignite II, petcoke and their blend with its theoretical behaviour under different combustion environments are shown in Figure 4.31.

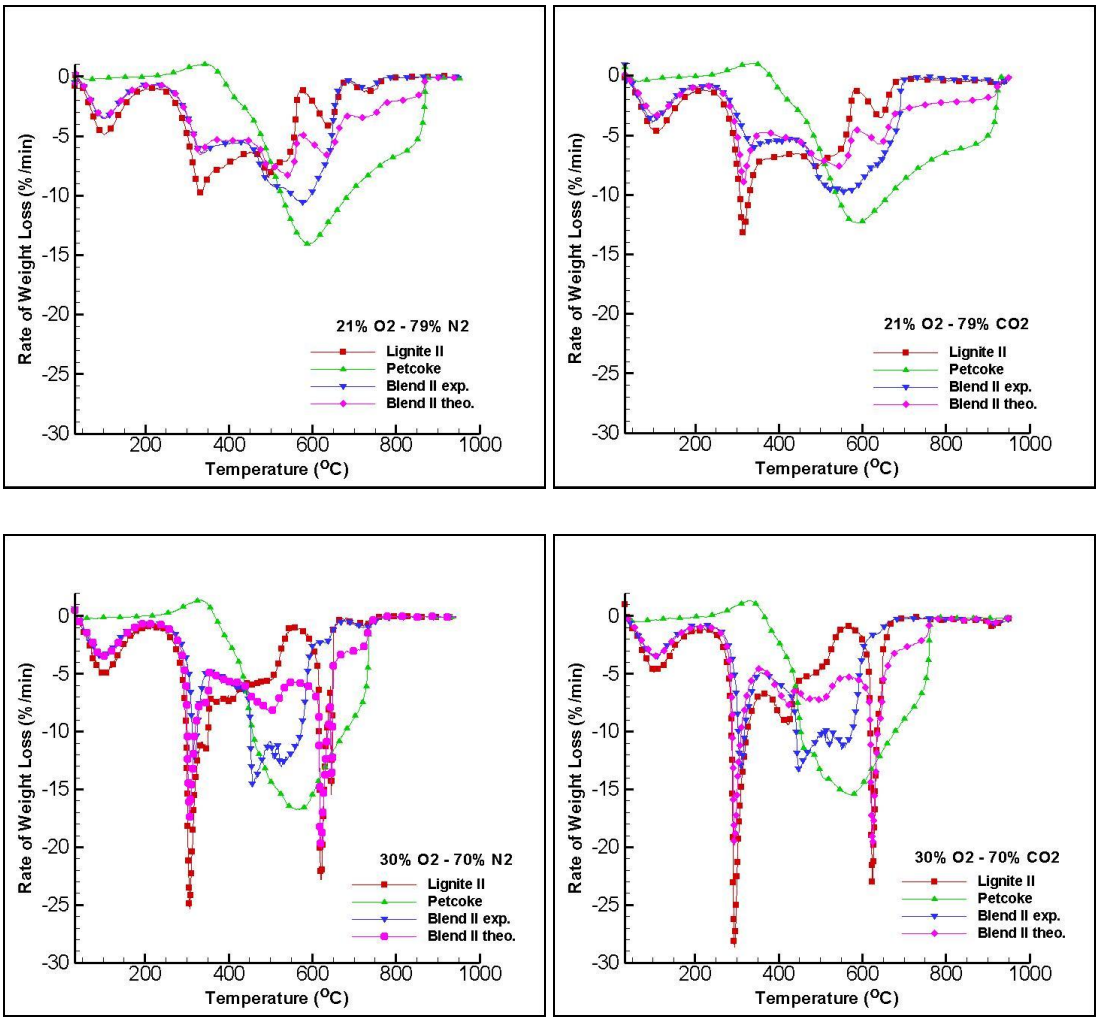

Figure 4.31: Combustion profiles of blend II and its parent fuels in different combustion environments

As can be seen from Figure 4.31, combustion profile of the blend lies between those of parent fuels in all combustion environments. Theoretical and experimental combustion profiles of the blend mainly display different trends, which may be due to synergistic interactions between lignite and petcoke in all combustion environments. Some deviations from expected behaviour are observed DTG curves and characteristic temperatures. Theoretical DTG curves of the blend samples

contain each weight loss step observed in individual DTG curves of lignite and petcoke. However, comparison of experimental and theoretical curves reveals that in experimental DTG curves, some peaks are observed to disappear. In all combustion conditions, weight loss rate of main peak in the temperature range of 250-650^{o}C is always higher than the expected behaviour which may indicate the positive effect of the blending. All these results point out that there is an interaction between component coals during combustion in all cases.

The formation profiles of evolved gases during combustion of the blend in different atmospheres are shown in Figure 4.32. The formation profile of CO_2 in oxygen-enriched air atmosphere shifts to lower temperature zone as elevated oxygen levels lead to faster burning and earlier release of CO_2. CO formation takes place between 300-700^{o}C with a shoulder at around 375^{o}C. H_2O formation profiles show that moisture is released first in all combustion environments with further release in the temperature range of 300-700^{o}C. CH_4, SO_2 and COS reveal two stages in their evolution profiles. Similar trends are observed for all gases in identical oxygen conditions.

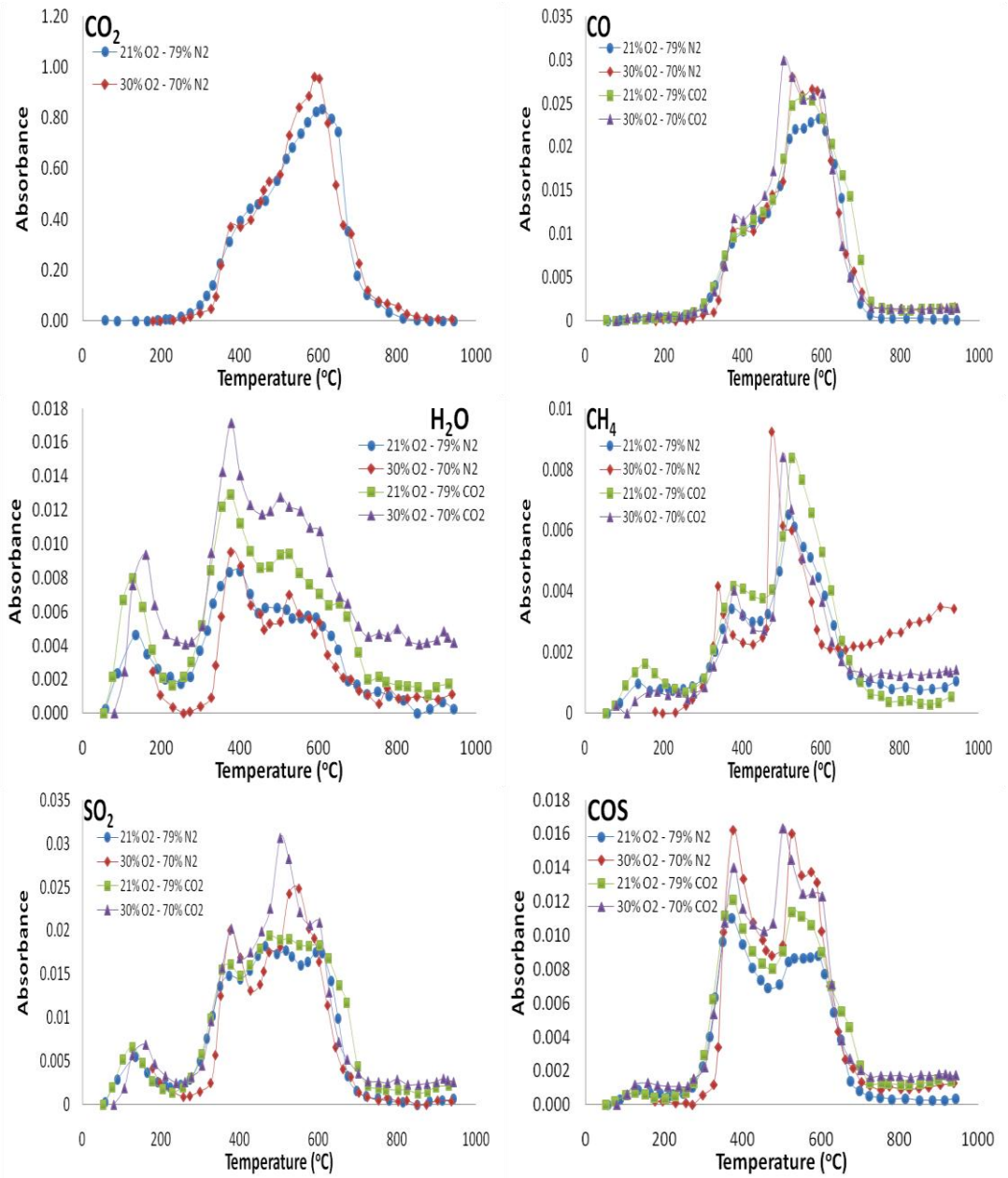

Figure 4.32: Formation profiles of evolved gases during combustion tests of blend II

4.9 Lignite I - Olive Residue Blend (Blend III)

In this section, pyrolysis and combustion behaviour of indigenous lignite, olive residue and their 50/50 wt % blend in air and oxy-fuel conditions is described.

4.9.1 Pyrolysis of Blend III

Pyrolysis tests are carried out under N_2 and CO_2 atmosphere which are the main diluting gases of air and oxy-fuel environments. TGA and DTG curves of lignite-olive residue blend are shown in Figure 4.33. The pyrolysis characteristics of the blend and its parent fuels for comparison are summarized in Table 4.15.

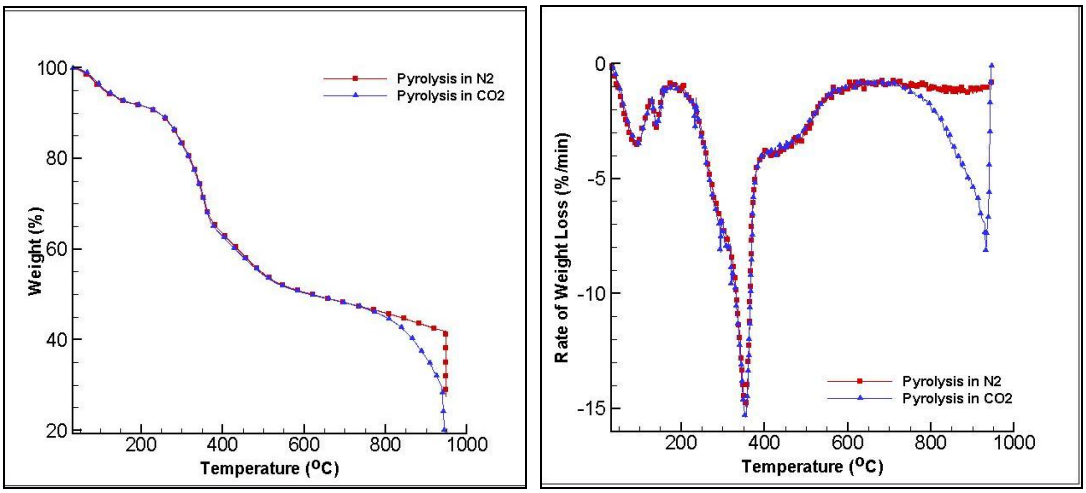

Figure 4.33: TGA and DTG profiles of blend III in N_2 and CO_2 atmospheres

Two main weight loss steps appear in weight loss profiles in nitrogen atmosphere while an additional weight loss step is observed after 700°C in CO_2 environment. First weight loss step within 25-200°C temperature range accounts for moisture release and the second weight loss step within 200-600°C corresponds to volatile matter release in both atmospheres. Identical DTG trends up to 700°C are obtained in both atmospheres in pyrolysis tests. This indicates that CO_2 behaves as an inert atmosphere before high temperature zone [34]. Additional peak after 700°C seen in DTG curve under CO_2 atmosphere is considered to be due to CO_2 – char gasification reaction.

Table 4.15: Pyrolysis characteristics of blend III and its parent fuels

		T_{in}	T_{max}	$(dm/dt)_{max}$	Weight loss up to 950°C
Lignite I	**Pyrolysis in N_2**	230.8	482.9	3.6	41.0
	Pyrolysis in CO_2	216.7	481.0	3.2	50.3
Olive Res.	**Pyrolysis in N_2**	183.1	355.5	28.4	75.0
	Pyrolysis in CO_2	175.6	354.9	28.3	87.0
Blend Exp.	**Pyrolysis in N_2**	196.0	355.6	15.0	57.9
	Pyrolysis in CO_2	187.8	354.4	15.5	74.1
Blend Theo.	**Pyrolysis in N_2**	184.7	355.3	15.4	58.9
	Pyrolysis in CO_2	189.9	354.9	15.4	68.9

Pyrolysis behaviours of lignite I and olive residue samples and their blend under N_2 and CO_2 environments are compared in Figure 4.34. The theoretical pyrolysis behaviour of blend is also included in DTG profiles of fuel samples in the figure.

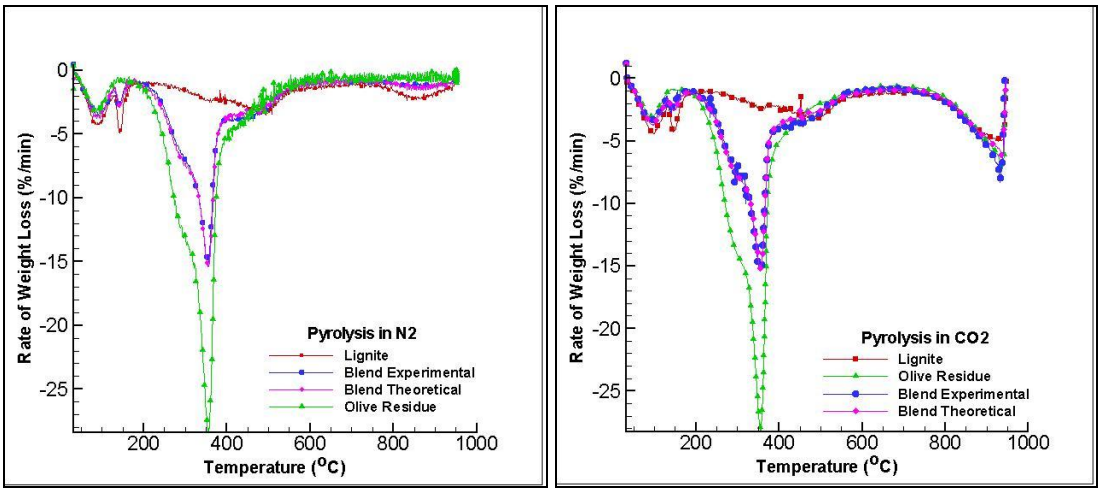

Figure 4.34: Pyrolysis profiles of blend III and its parent fuels in N_2 and CO_2 environments

Comparison between the DTG profiles of olive residue and lignite clearly shows that olive residue devolatilizes at lower temperatures than lignite. Lower resistance to heat even at lower temperatures displayed by olive residue is considered to be due to the weaker bonds between the macromolecular constituents of this biomass. Pyrolysis behaviour of lignite/olive residue (50/50 wt. %) blend shows that peak height increases and the peak position shifts to lower temperature with the addition of olive residue.

The overlap between the DTG curve of the blend itself (experimental) and the DTG curve found by additive rule (theoretical) of the two components of the blend reveals the absence of synergy between lignite and olive residue during pyrolysis.

The evolution profiles of the gaseous species including CO_2, CO, H_2O, CH_4, SO_2 and COS, from the pyrolysis of olive residue-lignite blend in nitrogen and carbon dioxide are shown in Figure 4.35. In the formation profile of CO_2, a peak at around 350°C is displayed between 200°C and 600°C which corresponds to the devolatilization temperature interval as represented in DTG curve of blend. Formation of CO_2 in N_2 environment is found to be the major contributor to the evolved gases with its highest absorbance intensity. The high yield of CO_2 during the pyrolysis of blend is

considered to be due to high oxygen contents of olive residue and lignite [49]. In both environments, H_2O is identified in the first 200^oC due to moisture release. In the temperature range of 200-700^oC, further H_2O release is observed probably from condensation of phenols as also confirmed in the literature. Methane formation takes place during the entire devolatilization process. Certain amount of SO_2 is also formed as a consequence of the high sulphur content of lignite in the blend at around 350^oC and 500^oC. Formation profiles of H_2O, CH_4 and SO_2 are not affected by pyrolysis environment and display identical evolution trends in both N_2 and CO_2 environments. However, CO and COS display different trends in CO_2 atmosphere due to CO_2 – char gasification reaction. After 700^oC, a distinctive increase is observed in the formation profile of CO with the initiation of the gasification reaction. Moreover, higher CO concentration leads to formation of COS which may be caused by pyrite (FeS_2) – CO gas solid reaction.

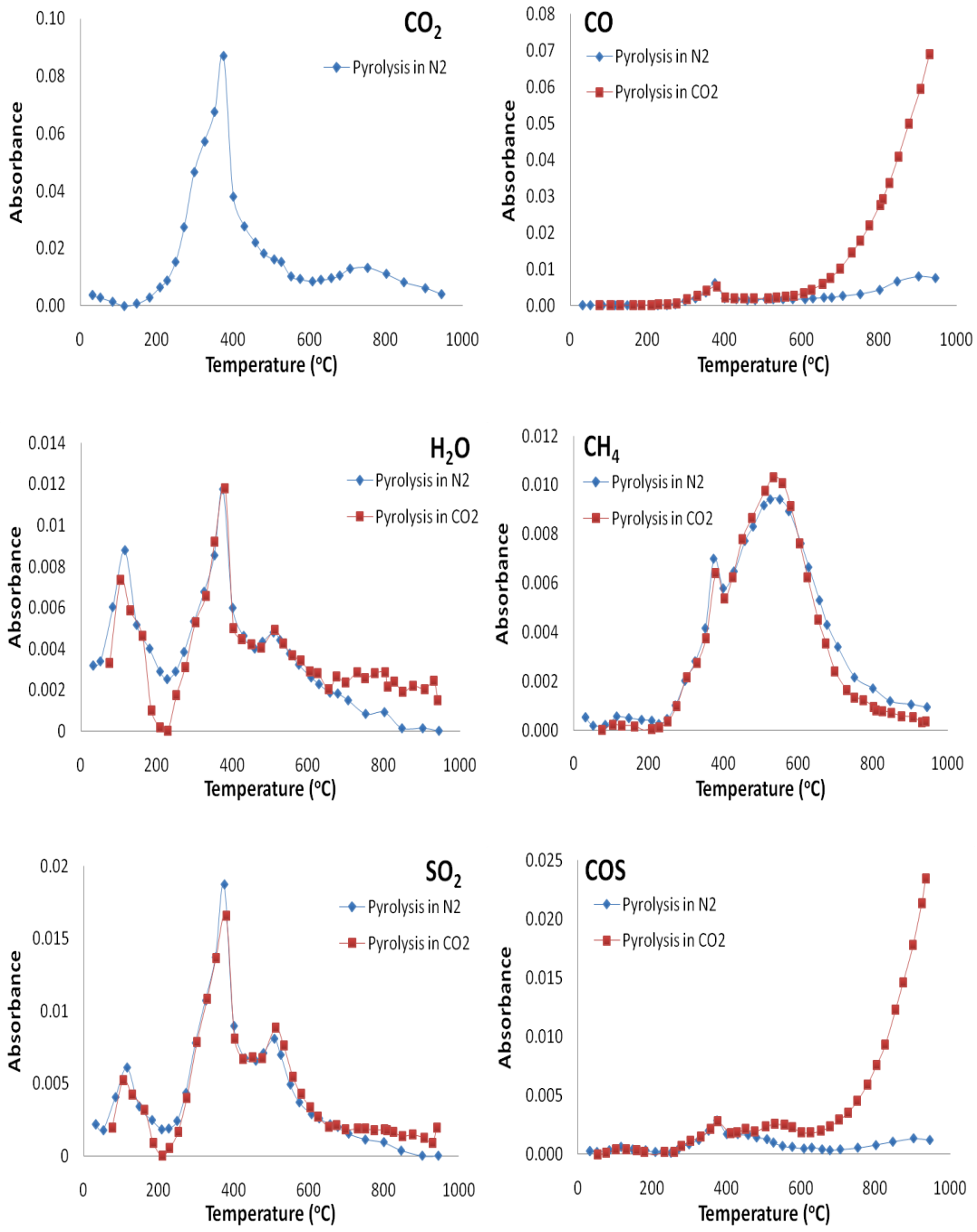

Figure 4.35: Formation profiles of evolved gases during pyrolysis tests of blend III

4.9.2 Combustion of Blend III

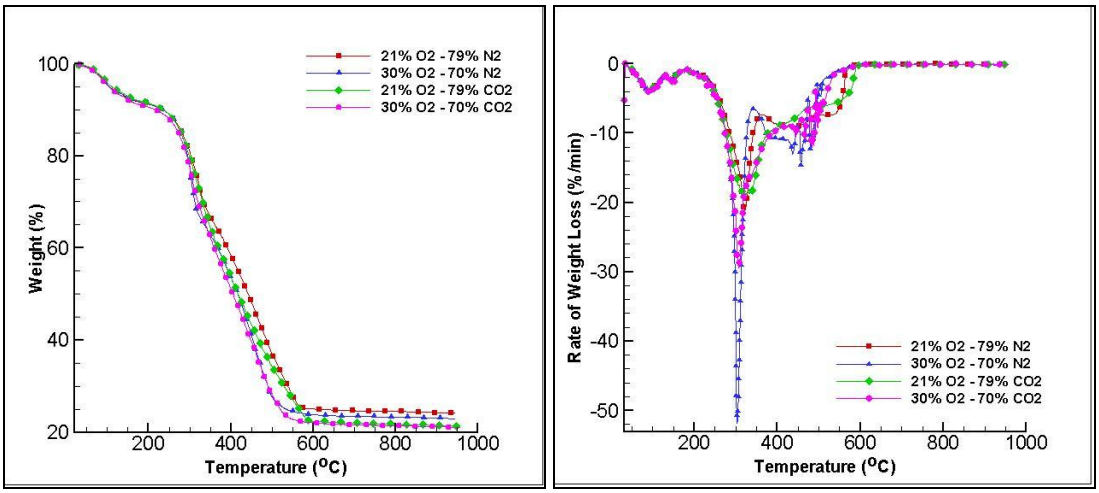

Figure 4.36: TGA and DTG profiles of blend III in different combustion environments

Combustion profiles of the olive residue/lignite blend in different combustion environments are compared in Figure 4.36. In air-firing case three weight loss steps are displayed in the DTG curve of the blend. The main peak between 200-360°C is attributed to release of volatiles in olive residue and their burning. The second step represented with a shoulder at around 430°C is considered to be due to burning of biomass char and volatile matter of lignite whereas the last stage is mostly due to combustion of lignite char after 500°C. Similar trend in burning profiles with air- and oxy-firing conditions is observed with less loss rate and higher burnout temperature in oxy-fuel conditions which are indicative of the delay in combustion. The effect of oxygen concentration is found to be more significant than that of the diluting gas (N_2 or CO_2) on the combustion profiles. As can be seen from Table 4.16, at elevated oxygen levels characteristic temperatures including T_{ig}, T_{max} and T_b are found to be lower, complete combustion is achieved at lower temperatures and shorter times.

Table 4.16: Combustion characteristics of blend III and its parent fuels

		T_{in}	T_{max}		$(dm/dt)_{max}$		T_{ig}	T_b	Total weight loss up to 950°C
Lignite I	**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
Olive Res.	**21 % O_2 - 79 % N_2**	183.9	308.9	405.3	48.4	14.4	258.8	567.7	95.6
	30 % O_2 - 70 % N_2	186.9	304.3	390.9	58.9	20.5	258.5	526.6	95.8
	21 % O_2 - 79 % CO_2	174.6	309.7	435.8	43.7	10.5	229.5	579.9	96.9
	30 % O_2 - 70 % CO_2	179.8	311.2	413.2	53.2	15.9	264.1	544.3	95.7
Blend Exp.	**21 % O_2 - 79 % N_2**	188.8	321.3	-	21.2	-	267.4	567.8	75.7
	30 % O_2 - 70 % N_2	187.7	303.5	-	52.0	-	263.5	544.2	77.0
	21 % O_2 - 79 % CO_2	183.0	323.5	-	18.8	-	239.2	587.2	79.0
	30 % O_2 - 70 % CO_2	180.8	306.7	-	29.4	-	264.0	553.7	79.2
Blend Theo.	**21 % O_2 - 79 % N_2**	186.9	309.7	405.9	25.8	12.5	260.8	567.0	77.5
	30 % O_2 - 70 % N_2	185.2	311.2	391.2	34.1	15.3	256.2	527.2	77.7
	21 % O_2 - 79 % CO_2	188.8	309.8	438.8	23.9	10.2	231.9	576.8	78.1
	30 % O_2 - 70 % CO_2	188.5	315.5	413.5	33.9	13.2	235.9	543.5	78.3

Combustion behaviours of lignite I and olive residue samples and their blend including theoretical curves under different combustion environments are compared in Figure 4.37.

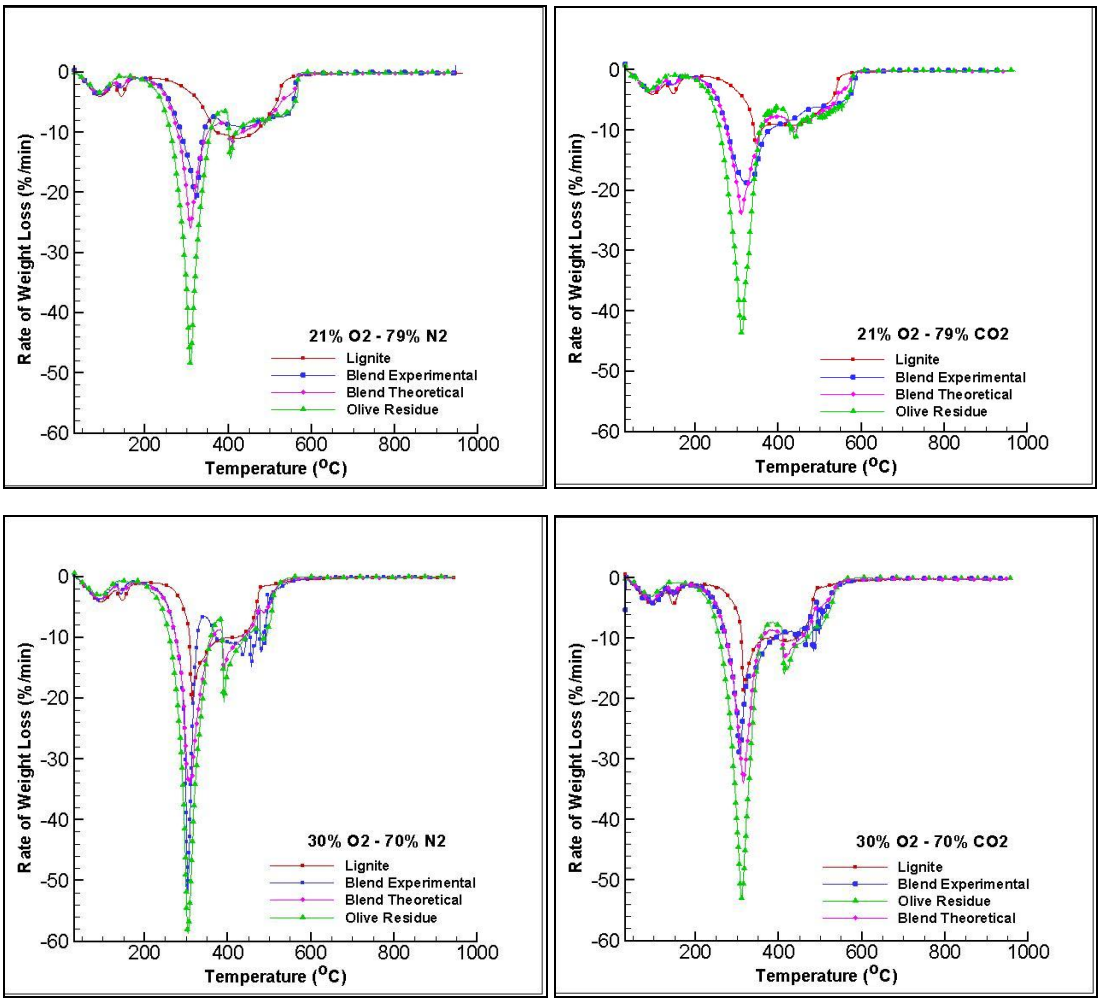

Figure 4.37: Combustion profiles of blend III and its parent fuels in different combustion environments

As can be seen from Figure 4.37, combustion profile of the blend lies between those of parent fuels in all combustion environments. Theoretical and experimental combustion profiles of the blend mainly display similar trend with slight deviations, which may be due to synergistic interactions between olive residue – lignite. Some

deviations from expected behaviour are observed in T_{max} and $(dm/dt)_{max}$ values in volatile matter decomposition stage. In air, oxy-fuel and oxygen-enriched conditions maximum weight loss rate is found lower in experimental conditions than the calculated ones. In oxygen-enriched air combustion conditions, on the other hand, weight loss is observed faster than expected which may indicate the positive effect of the blending. Another point that indicates the synergistic behaviours is the disappearance of the peak at around 400^{o}C in the experimental profile. Moreover, theoretical and experimental results differ in characteristic temperatures such as ignition and burnout temperatures, which reflect the interaction behaviour of component fuels.

The formation profiles of evolved gases during combustion of the blend in different atmospheres are shown in Figure 4.38. The formation profile of CO_2 in oxygen-enriched air atmosphere shifts to lower temperature zone as elevated oxygen levels lead to faster burning and earlier release of CO_2. H_2O formation profiles show that moisture is released first in all combustion environments with further release in the temperature range of 200-500^{o}C. Also sulphur containing gases, SO_2 and COS reveal two stages in their evolution profiles in air firing conditions, whereas one stage formation is observed in oxy-fuel conditions. This can be due to effect of high CO_2 concentration under oxy-fuel conditions.

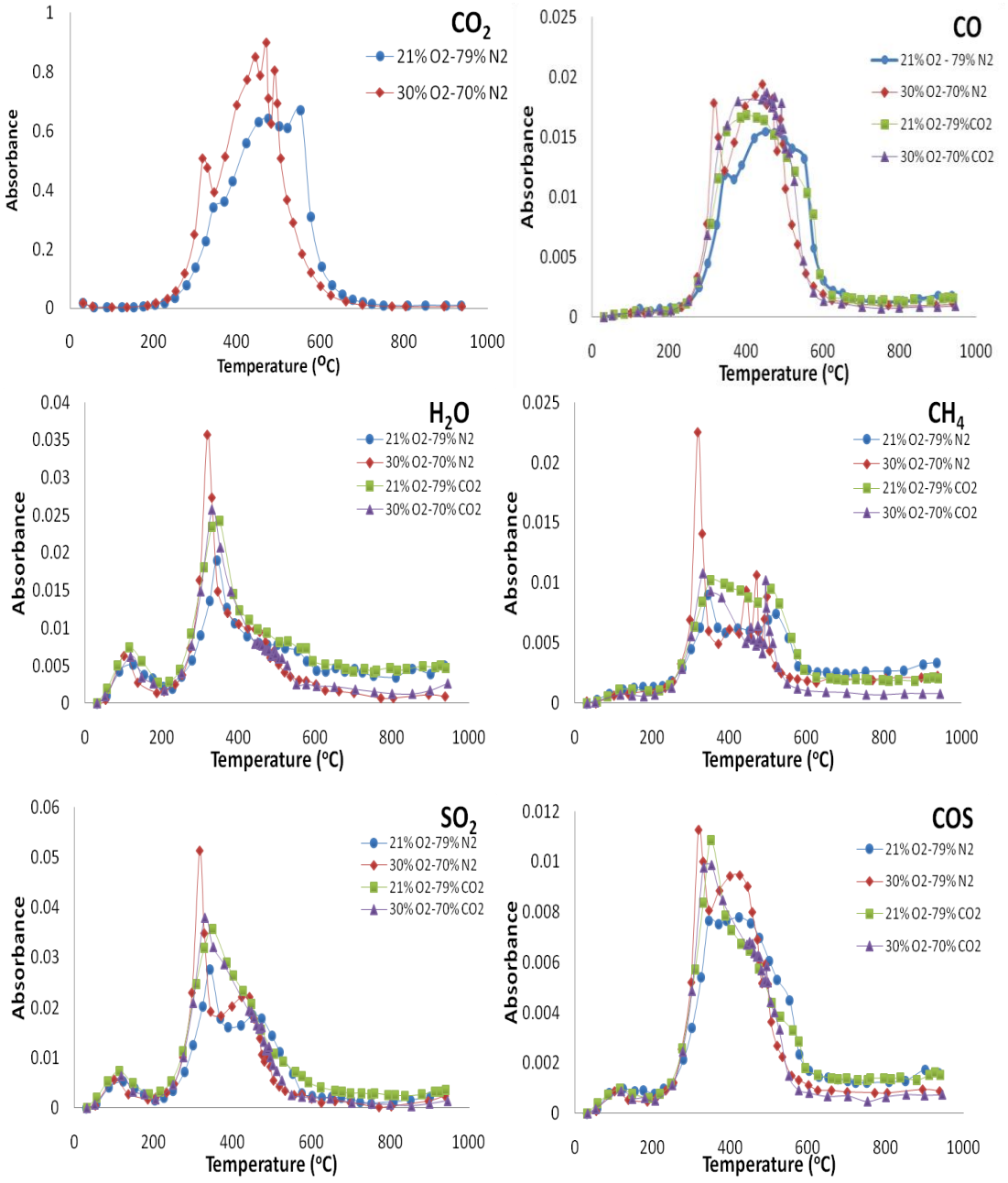

Figure 4.38: Formation profiles of evolved gases during combustion tests of blend III

CHAPTER 5

CONCLUSIONS

5.1 General

Pyrolysis and combustion characteristics of different fuels; imported coal, petroleum coke, two kinds of indigenous lignite, olive residue and their blends with various proportions is investigated in air and oxy-fuel conditions by using a combined TGA-FTIR system. The following conclusions were reached under the observations of this study:

- Pyrolysis tests were carried out in nitrogen and carbon dioxide environments which are the main diluting gases of air and oxy-fuel environment, respectively. Pyrolysis tests under N_2 and CO_2 environments reveal that fuel samples display similar behaviour up to 700^{o}C regardless of the diluting gas. However, DTG profiles are observed to differ in high temperature zone due to char-CO_2 gasification reaction in CO_2 atmosphere. Moreover, distinctive increase in CO and COS is identified from FTIR formation profiles due to gasification reaction.

- Combustion experiments were carried out in four different atmospheres; air, oxygen-enriched air environment (30 % O_2 – 70 % N_2), oxy-fuel environment (21 % O_2 – 79 % CO_2) and oxygen-enriched oxy-fuel environment (30 % O_2 – 70 % CO_2). Combustion behaviour of fuels and their blends in air and oxy-

fuel conditions show that burning process is slightly delayed in oxy-fuel conditions compared to air conditions at the same oxygen levels. However, as oxygen concentration increases, weight loss profiles shift to lower temperatures, rate of weight loss increases and complete combustion is achieved at lower temperatures.

- Pyrolysis and combustion behaviour of three different fuel blends were investigated. Pyrolysis tests reveal that there is no interaction between parent fuels during pyrolysis of petcoke-lignite and lignite-olive residue blend under both N_2 and CO_2 environments as theoretical and experimental behaviours of the samples overlap. However in pyrolysis of imported coal-petcoke-lignite blend and all combustion tests of these three blends deviations from expected behavior which are indicative of synergistic interactions are observed. Therefore it can be concluded that it is not possible to predict blends behaviour from that of the parent fuels.

- During pyrolysis and combustion tests gaseous products CO_2, CO, H_2O, CH_4, SO_2 and COS in flue gas were identified and analyzed by using FTIR. In pyrolysis tests, significant amount of CO due to char – CO_2 gasification reaction and consecutively COS is evolved in CO_2 atmosphere in all fuels. No general consensus has been obtained in combustion tests as formation profiles displayed different trends in each case.

In conclusion, the current results add to previous literature data on pyrolysis and combustion behaviour of different rank fuels and their blends in air and oxy-fuel conditions, some of which such as; petcoke, indigenous lignite, olive residue have not been studied to date. Moreover, these results provide basic information about retrofit applications to existing coal-fired power plants or alternatively be used in designs of new coal-fired power plants with near zero emissions.

5.2 Suggestions for Future Work

Based on the experience gained in the present study, the following recommendations for future extension of the work are suggested:

- Pyrolysis and combustion behaviour of different types of energy sources including various coals, biomass or municipal solid wastes can be investigated in similar conditions.
- Pilot scale combustion tests of the fuels investigated in the present study can be carried out in fluidized bed combustion systems under oxygen enriched air and oxy-fuel conditions.
- Mathematical models of fluidized bed combustion systems under oxygen enriched air and oxy-firing conditions can be developed.

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APPENDIX A

Pilot Scale Carbon Capture and Storage Projects

In this section, Tables A.1 and A.2 shows large and pilot scale carbon capture and storage projects in worldwide, respectively. In these tables, names of projects, leader companies, fuel types, size, capturing type, start up time and location are summarized.

Table A.1: Large-Scale Power Plant Carbon Capture and Storage Projects

Large-scale Power Plant CCS Projects Worldwide							
USA							
Project Name	**Leader**	**Feedstock**	**Size MW**	**Capture Process**	**CO_2 Fate**	**Start-up**	**Location**
AEP Mountaineer	AEP	Coal	235	Post	Saline	2016	West Virginia
Taylorville	Tenaska	Coal	602	Pre	Saline	2012	Illinois
WA Parish	NRG Energy	Coal	60	Post	EOR	2013	Texas
TCEP	Summit Power	Coal	400	Pre	EOR	2014	Texas
Trailblazer	Tenaska	Coal	600	Post	EOR	2014	Texas
Kemper County	Southern	Coal	582	Pre	EOR	2014	Missisippi
HECA	HEI	Petcoke	390	Post	EOR	2014	California
FutureGen	FutureGen Alliance	Coal	200	Oxy	Saline	TBD	Illinois
Sweeny Gasification	ConocoPhilips	Coal	460	Pre	Saline & EOR	TBD	Texas
Antelope Valley	Basin Electric	Coal	120	Post	EOR	On Hold	North Dakota

Table A.1 Continued

Canada							
Project Name	**Leader**	**Feedstock**	**Size MW**	**Capture Process**	**CO_2 Fate**	**Start-up**	**Location**
Boundary Dam	SaskPower	Coal	100	Oxy	EOR	2015	Saskatchewan
Project Pioneer	TransAlta	Coal	450	Post	Saline &EOR	2015	Alberta
Bow City	BCPL	Coal	1000	Post	EOR	2014	Alberta
Belle Plaine	TransCanada	Petcoke	500	Pre	Undecided	Undecided	Saskatchewan
European Union							
Project Name	**Leader**	**Feedstock**	**Size MW**	**Capture Process**	**CO_2 Fate**	**Start-up**	**Location**
Belchatow	PGE	Coal	250-858	Post	Saline	2011-15	Poland
Ferrybridge	SSE	Coal	500	Post	Seq	2011-2012	UK
Longannet	Scottish Power	Coal	300	Post	EOR	2014	UK
Janschwalde	Vattenfall	Coal	250	Oxy	Saline	2015	Germany
Maasvlkte	E.ON	Coal	1100	Post	EGR	2015	Netherlands
Porto Tolle	ENEL	Coal	660	Post	Saline	2015	Italy
Compostilla	ENDESA	Coal	30-500	Oxy	Saline	2015	Spain
Goldenbergwerk	RWE	Coal	450	Pre	Saline	2015	Germany
Magnum	Nuon	Various	1200	Pre	EOR/ EGR	2015	Netherlands
Hatfield	Powerfuel	Coal	900	Pre	EOR	On hold	UK

Table A.1 Continued

Norway							
Project Name	**Leader**	**Feedstock**	**Size MW**	**Capture Process**	**CO_2 Fate**	**Start-up**	**Location**
Kårstø	Naturkraft	Gas	420	Post	Undecided	2011-2012	Norway
Husnes	Sargas	Coal	400	Post	EOR	2011	Norway
Mongstad	Statoil	Gas	350	Post	Saline	Waiting Funding	Norway
Rest of the World							
Project Name	**Leader**	**Feedstock**	**Size MW**	**Capture Process**	**CO_2 Fate**	**Start-up**	**Location**
GreenGen	GreenGen	Coal	250/800**	Pre	Saline	2010	China
NZEC	UK&China	Coal	460	Pre	EOR	2015	China
ZeroGen	ZeroGen	Coal	100	Pre	Saline	2012	Australia
UAE Project	Masdar	Gas	420	Pre	EOR	2015	UAE

Table A.2: Pilot Scale Power Plant Carbon Capture and Storage Projects

Pilot CCS Projects							
Project Name	**Leader**	**Feedstock**	**Size MW**	**Capture Process**	**CO_2 Fate**	**Start-up**	**Location**
Schwarze Pumpe	Vattenfall	Coal	30	Oxy	--	2008	Germany
ECO2 Berger	Powerspan	Coal	1	Post	Vented	2008	OH, USA
Pleasant Prarie	Alstom	Coal	5	Post	Vented	2008	WI, USA
AEP Mountaineer	AEP	Coal	30	Post	Saline	2009	WV, USA
Karlshamn	E.ON	Oil	5	Post	Vented	2009	Sweden
Shidongkou	Huaneng	Coal	0.1MT/Yr	Post	Commercial use	2009	China
Lacq	Total	Oil	35	Oxy	Depleated Gas	2010	France
Buggenum	Vattenfall	Coal	20	Post	Vented	2010	Netherlands
Brindisi	Enel &Eni	Coal	48	Post	EOR	2010	Italy
Kimberlina	Clean Energy Systems	Coal	50	Oxy	Saline	2011	CA, USA
Callide-A Oxy Fuel	CS Energy	Coal	30	Oxy	Saline	2011	Australia
Plant Barry	Southern Energy	Coal	25	Post	EOR	2011	AL, USA
Big Bend Station	Siemens	Coal	1	Post	Vented	2013	FL, USA
ZENG Risavika	CO2-Norway	Gas	50-70	Oxy	Undecided	Undecided	Norway
ZENG Worsham-Steed	CO2-Global	Gas	70	Oxy	EOR	Undecided	TX, USA

APPENDIX B

Published Paper

In this section, one of the papers that is published in Journal of Analytical and Applied Pyrolysis with doi:10.1016/j.jaap.2010.11.003, in the scope of this thesis study is given in Figure B.1.

Figure B.1: Published Paper

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Journal of Analytical and Applied Pyrolysis xxx (2010) xxx–xxx

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Combustion behaviour of Turkish lignite in O_2/N_2 and O_2/CO_2 mixtures by using TGA–FTIR

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ABSTRACT

The pyrolysis and combustion behaviour of a low calorific value Turkish lignite with high sulphur and ash content in air and oxy-fuel conditions were investigated by using non-isothermal thermo-gravimetric method (TGA) coupled with Fourier-transform infrared (FTIR) spectrometer. Pyrolysis tests were carried out in nitrogen and carbon dioxide environments which are the main diluting gases of air and oxy-fuel environment, respectively. Pyrolysis results show that weight loss profiles are almost the same up to a temperature of 720 °C in these two environments, indicating that CO_2 behaves as an inert gas in this temperature range. However, further weight loss takes place in CO_2 atmosphere at higher temperatures due to CO_2–char gasification reaction. Combustion experiments were carried out in four different atmospheres: air, oxygen-enriched air environment (30% O_2–70% N_2), oxy-fuel environment (21% O_2–79% CO_2) and oxygen-enriched oxy-fuel environment (30% O_2–70% CO_2). Combustion experiments reveal that replacing nitrogen in the gas mixture by the same concentration of CO_2 does not affect the combustion process significantly but only leads to slight delay in combustion. Overall comparison of derivative thermogravimetry (DTG) profiles shows that oxygen content in the combustion environment is the most effective parameter irrespective of the diluting gas. As O_2 concentration increases profiles shift through lower temperature zone, peak and burnout temperatures decrease, weight loss rate increases and complete combustion is achieved at lower temperatures and shorter times. During pyrolysis and combustion tests gaseous products CO_2, CO, H_2O, CH_4, SO_2 and COS in flue gas were identified and analyzed by using FTIR. Results indicate that higher CO and COS formation takes place during pyrolysis due to gasification reaction. Gaseous species evolution trends in combustion tests are found to be almost identical in oxygen enriched conditions independent of the diluting gas.

1. Introduction

Today, demand for electric power continues to increase due to population growth, technological and economical development. With 826 billion tones of proved coal reserves, coal combustion has an important role in energy production worldwide [1]. Growing concern about greenhouse gas emissions and their potential impact on climate change necessitate investigation of alternative technologies for reduction of CO_2 emissions from coal fired power plants. Conventional technologies for removing CO_2 from the stack gas in the existing coal fired power plants are expensive since CO_2 is diluted (typically about 14% by volume on a dry basis) [2]. The cost of gas separation can be reduced by increasing the concentration of CO_2 in the flue gas. Oxy-fuel combustion technology is suggested as one of the new promising technologies for capturing CO_2 from power plants. This technology is based on burning coal in a mixture of oxygen and recycled flue gas (RFG) leading to CO_2 concentrations greater than 95% in the exhaust gas. Recycled flue gas is used to control flame temperature and supply the volume of missing N_2. Oxy-fuel combustion technology for coal-fired power generation has been briefly described and reviewed in detail recently [3–5]. Oxy-fuel combustion is found to differ from air combustion in combustion characteristics such as burning stability, char burnout, gas temperature profiles and heat transfer due to differences in gas properties between CO_2 and N_2, the main diluting gases in oxy-fuel and air, respectively. Previous studies on oxy-fuel combustion mainly revealed that similar temperature profiles with air case are achieved at higher oxygen concentrations, around 30% in the combustion environment, as the higher heat capacity of CO_2 causes delay in combustion process [2–7].

Non-isothermal thermo-gravimetric analysis (TGA) technique is a rapid, inexpensive and simple method that has been widely used in studying the pyrolysis and combustion behaviour of coal and evaluating the relative burning properties of coal samples.

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Figure B.1 Continued

There exists a considerable number of studies carried out for the investigation of combustion behaviour high rank coals in oxy-fuel environment by TGA [8–13]. However, an investigation of oxy-fuel combustion characteristics of indigenous lignites by TGA–FTIR technique is not available to date. Therefore, pyrolysis and combustion behaviours of an indigenous lignite with low calorific value, high ash and sulphur contents are studied in air and oxy-fuel conditions by using a TGA–FTIR combined system.

2. Experimental

2.1. Sample

A typical low quality indigenous lignite from Çan town of Çanakkale province in Turkey was used in pyrolysis and combustion tests. Proximate analysis of the Çan lignite was performed by using LECO TGA-701. Ultimate analysis was carried out with LECO CHNS-932. Calorific values of the fuels are measured by using AC-500 bomb calorimeter. Analyses were performed according to ASTM standards. The Jeol JSM-6400 scanning electron microscope (SEM) configured with a Noran energy dispersive spectrometer (EDS) was utilised for determination of ash composition. Proximate, ultimate and ash analyses of Çan lignite together with its calorific value are briefly summarized in Table 1. As can be seen from the table, Çan lignite can be characterized by its low calorific value, high ash content (~25%) and high total sulphur content (~4%).

2.2. Experimental setup and method

In the present work TGA/DTG were used to determine pyrolysis and combustion characteristics of lignite samples. TGA system was coupled with FTIR spectrometer for determination of evolved gases during pyrolysis and combustion experiments. Fig. 1 shows a schematic diagram of the experimental setup consisting of Perkin Elmer Pyris STA 6000 thermo-gravimetric analyzer, Spectrum 1 FTIR spectrometer and a mass flow controller (MFC) for each gaseous species. TGA and FTIR were connected by a heated line with a temperature of 270 °C in order to prevent the condensation of gases. FTIR spectra were collected with 4 cm^{-1} resolution, in the range of 4000–700 cm^{-1} IR absorption band.

About 12 mg of coal sample with particle size less then 100 μm was held initially at room temperature for 1 min and then heated with a heating rate of 40 °C/min from room temperature up to 950 °C during each experiment. In pyrolysis tests, samples were held at 950 °C for an additional 60 min. The required combustion environments were formed by mixing two gases in the desired ratio by using two different mass flow controllers in order to regulate the flow rates of the gases. The total gas flow was set to 70 ml/min for pyrolysis and 45 ml/min for combustion experiments.

Table 1
Proximate, ultimate and ash analysis of Çan lignite.

Ultimate analysis (as received, % by wt.)		Proximate analysis (as received, % by wt.)	
C	37.31	Moisture	16.35
H	3.3	Ash	28.78
O	10.02	Volatile matter	29.79
N	0.91	Fixed carbon	25.08
$S_{Combustible}$	3.33		
Ash	28.78	LHV (MJ/kg)	9.89
Total moisture	16.35		
S_{Total}	3.49		

Ash analysis (% by wt.)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	TiO_2
43.13	18.2	15.78	7.63	0.48	2.0	0.63	11.08	1.07

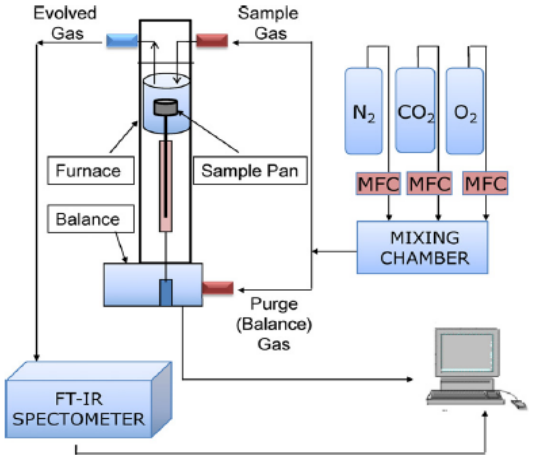

Fig. 1. Schematic diagram of the experimental setup.

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 lignite sample. The base case was considered as lignite combustion in air environment. In oxygen-enriched air case the sample is burned in 30% O_2–70% N_2 atmosphere. In oxy-fuel combustion tests, the volume of N_2 used in the base case was replaced with an equal volume of CO_2. In the last case, combustion of lignite sample was investigated in oxygen-enriched oxy-fuel environment, that is, in 30% O_2–70% CO_2 atmosphere.

TGA and DTG profiles obtained during pyrolysis and combustion experiments were used to determine some characteristic parameters such as initial decomposition temperature (T_{in}), peak temperature (T_{max}), ignition temperature (T_{ig}) and burnout temperature (T_b). T_{in} represents the initiation of weight loss and is defined as the temperature at which the rate of weight loss reaches 1%/min after initial moisture loss peak in DTG profile [22]. T_{max} is the point at which maximum reaction rate occurs. Different from initial decomposition temperature, ignition temperature T_{ig} is defined as the temperature at which coal starts burning. It is taken as the temperature at which the weight loss curves in the oxidation and pyrolysis experiments diverge [20]. The last characteristic temperature considered is burnout temperature which represents the temperature where sample oxidation is completed. It is taken as the point immediately before reaction ceases when the rate of weight loss is 1%/min [21].

A linear relation between spectral absorbance at a given wavenumber and concentration of gaseous components is given by Beer's Law. In this study, the points of absorbance at a certain wavenumber are plotted against temperature in order to obtain a formation profile for each evolved gas observed in the spectra during experiments. The IR wavenumbers of CO_2, CO, H_2O, CH_4, SO_2 and COS are 2360, 2112, 1540, 3016, 1340 and 2042 cm^{-1}, respectively. Formation profiles of NO_x related species such as NO and NO_2 are not reported due to overlap of their absorption bands with the characteristic absorption bands of water in the range of 3900–3500 and 1900–1350 cm^{-1}.

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Figure B.1 Continued

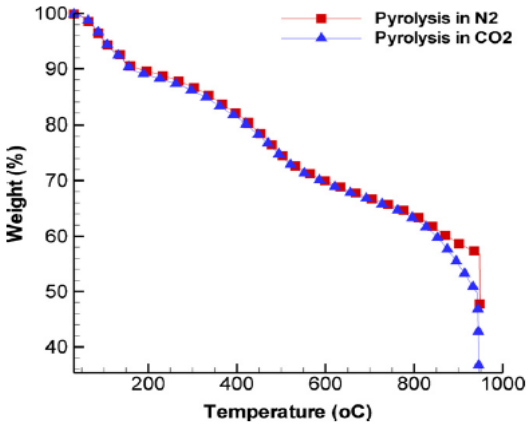

Fig. 2. TGA profile of Çan lignite during pyrolysis in N_2 and CO_2 atmospheres.

3. Results and discussion

3.1. Pyrolysis tests of lignite in CO_2 and N_2 environments

3.1.1. TGA/DTG results of pyrolysis tests

Pyrolysis as the preliminary process of coal combustion plays a crucial role in determining flame stability, ignition, and product distributions [14]. The possible impacts of different gases on pyrolysis process necessitate the investigation of devolatilization behaviour of coal in both N_2 and CO_2 environments. In nitrogen and carbon dioxide atmospheres, devolatilization of coals may differentiate in volatile composition, volatile yield and possible CO_2–char reaction at high temperature range. TGA and DTG profiles of pyrolysis tests are shown in Figs. 2 and 3, respectively.

As can be seen from figures, pyrolysis behaviour of lignite samples in N_2 and CO_2 atmosphere is observed to be very similar up to around 720 °C which indicates that CO_2 behaves as an inert atmosphere until a certain temperature. After moisture release in the first 200 °C temperature zone, pyrolysis continues with the release

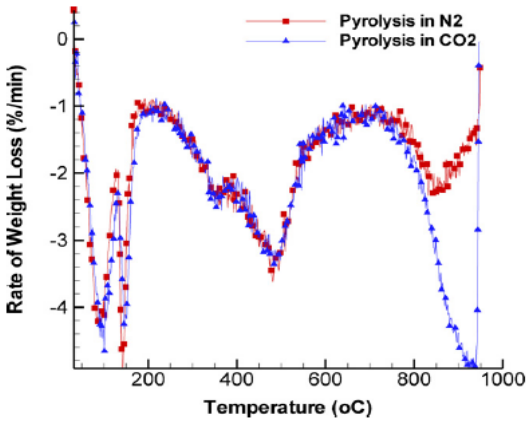

Fig. 3. DTG profile of Çan lignite during pyrolysis in N_2 and CO_2 atmospheres.

Table 2
Pyrolysis characteristics of Çan lignite in N_2 and CO_2.

	Pyrolysis in N_2	Pyrolysis in CO_2
T_{in} (°C)	230.8	216.7
T_{max} (°C)	482.9	481.0
$(dm/dt)_{max}$ (%/min)	3.6	3.2
Total weight loss up to 950 °C	41.0	50.3

of volatile matter content in the range of 200–750 °C. In 250–490 °C temperature interval, it is known that primary pyrolysis takes place which includes the release of larger fraction of volatiles, mainly light species and gases; CO_2, light aliphatic gases, CH_4 and H_2O. Tar and hydrocarbons evolve between 490 and 640 °C. During secondary pyrolysis additional gas formation such as CH_4, CO and H_2 from ring condensation is mainly observed [14,15]. In CO_2 atmosphere, the maximum weight loss rate is found to be slightly lower with higher corresponding temperature (T_{max}) than the ones in nitrogen atmosphere which could be due to the effect of higher heat capacity of CO_2. The major difference in pyrolysis of lignite samples in these two different atmospheres is observed after 720 °C with the separation of TGA profiles. In 700–950 °C temperature range, additional peaks are displayed in both DTG profiles as shown in Fig. 3. In nitrogen atmosphere, a small peak appearing after 700 °C is attributed to partial burning of combustible matter at high temperatures by using inherent oxygen (almost 10% in Çan lignite) in lignite sample. This is also confirmed with the FTIR results which show a significant increase in CO_2 formation after 700 °C as presented in Fig. 4. On the other hand, the sharp peak observed in DTG profile of pyrolysis in CO_2 environment can be attributed to char–CO_2 gasification reaction as also confirmed by higher total weight loss in CO_2 atmosphere as shown in Table 2 and by other studies [8,9,12].

3.1.2. FTIR results of pyrolysis tests

Formation profiles of evolved gases including CO_2, CO, H_2O, CH_4, SO_2 and COS during pyrolysis in N_2 and CO_2 environments are shown in Fig. 4. In both environments, H_2O is detected in the first 200 °C due to moisture release and also in the temperature range of 400–600 °C. In nitrogen environment, CO_2 release starts after 150 °C and continues up to 550 °C. Additional peak appears in CO_2 and CO formation curves due to burning of combustible matter in N_2 environment after 750 °C as explained in previous section. In the case of pyrolysis in CO_2 environment, significant amount of CO is evolved from char–CO_2 gasification reaction. Formation of CO in CO_2 environment is found to be the major contributor to the evolved gases with its highest absorbance intensity at high temperature zone. Evolution of CO continues with a distinctive increase after 600 °C in CO_2 environment. On the other hand, in N_2 environment, negligible amount of CO is formed due to partial burning of combustible matter. Methane release starts at 300 °C and continues till the end of the pyrolysis tests with a maximum release around 500 °C, in both environments. Similar trends are observed in evolution of CH_4 during devolatilization. In pyrolysis of high sulphur content lignite, SO_2 and COS release is noted. Similar SO_2 formation profiles are obtained in both environments in the temperature range of 250–625 °C, with two main peaks. Similar trends indicate that SO_2 formation does not depend on the pyrolysis environment. The other sulphur containing gas COS is formed by reaction of pyrite or sulphur formed during pyrite decomposition with CO [12,16]. COS formation is observed to increase significantly with the initiation of gasification reaction in CO_2 environment. Higher CO concentration in pyrolysis environment leads to the formation of COS in CO_2 atmosphere, in contrast to N_2 atmosphere.

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Figure B.1 Continued

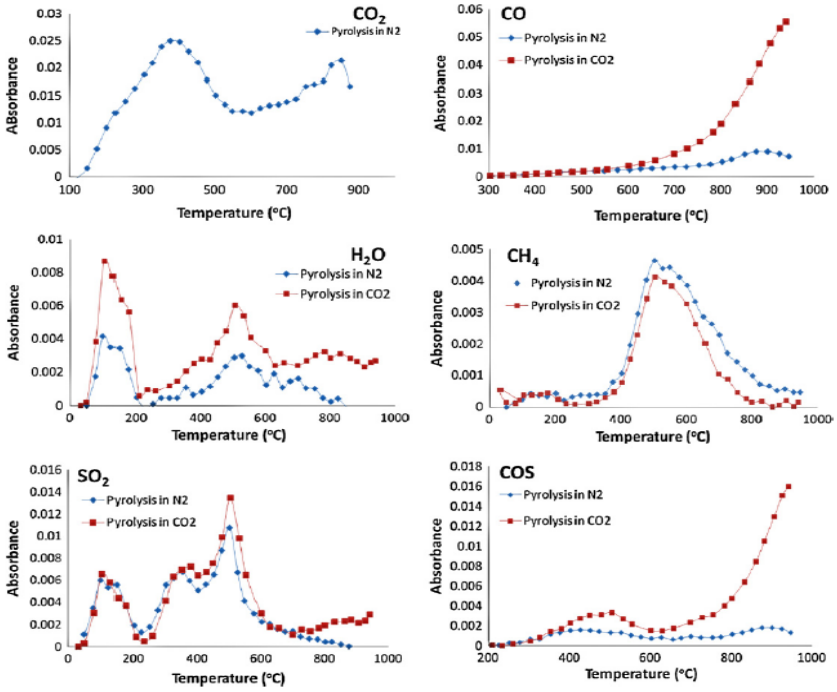

Fig. 4. Formation profiles of evolved gases during pyrolysis tests.

3.2. Combustion tests of lignite in O_2/N_2 and O_2/CO_2 environments

3.2.1. TGA/DTG results of combustion tests

Combustion tests of lignite were carried out in air, oxygen-enriched air (30% O_2–70% N_2), oxy-fuel environment (21% O_2–79% CO_2), and oxygen-enriched oxy-fuel environment (30% O_2–70% CO_2) and their TGA/DTG curves are shown in Figs. 5 and 6. Results obtained from combustion profiles show clear differences in the combustion characteristics as summarized in Table 3.

Comparison of TGA curves in Fig. 5 indicates that the effect of oxygen concentration is more significant than that of the diluting gas (N_2 or CO_2) on the combustion profiles. While combustion in O_2/N_2 and O_2/CO_2 mixtures with identical oxygen concentrations results in only slight differences in combustion characteristics of lignite, elevated oxygen levels in combustion environment shift the weight loss curves to lower temperature zone. First step of the weight loss accounts for the moisture release in the first 200 °C temperature range and the corresponding weight loss due to moisture release is found approximately 10% for all cases. The second step represents the weight loss due to devolatilization and char burning. Total weight loss of samples is found to be almost the same in all combustion cases.

Fig. 6 demonstrates comparison between DTG curves of combustion in different atmospheres. First peak within 200 °C and the second peak within the temperature range 225–600 °C represent moisture release and devolatilization and char burning, respectively. In air firing case, devolatilization and char burning steps

Table 3
Combustion characteristics of Çan lignite in different atmospheres.

	21% O_2–79% N_2	30% O_2–70% N_2	21% O_2–79% CO_2	30% O_2–70% CO_2
T_{in} (°C)	224.0	226.1	225.8	202.8
T_{max} (°C)	426.2	314.5	347.1	317.2
T_{ig} (°C)	297.1	265.3	308.8	264.1
T_b (°C)	546.8	530.0	550.0	535.6
$(dm/dt)_{max}$ (%/min)	11.0	20.5	12.3	19.0
Total weight loss up to 950 °C	59.2	59.3	59.6	61.2

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Figure B.1 Continued

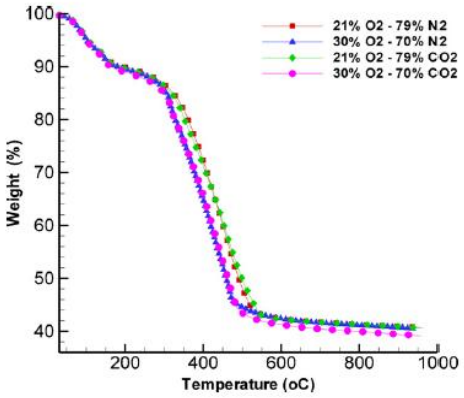

Fig. 5. TGA profile of Çan lignite in different combustion atmospheres.

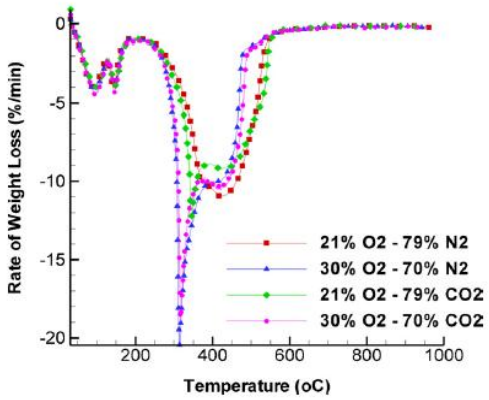

Fig. 6. DTG profile of Çan lignite in different combustion atmospheres.

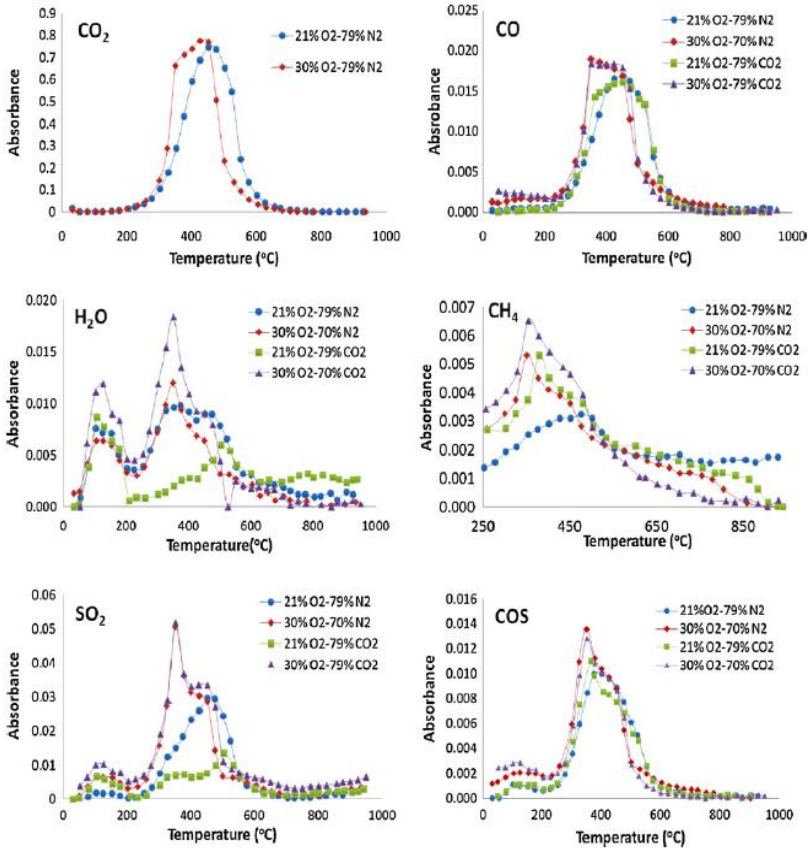

Fig. 7. Formation profiles of evolved gases during combustion tests.

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Figure B.1 Continued

are not discretely separated; however, the shoulder around 370 °C can be attributed to volatile release. In oxy-fuel case the DTG profile of the lignite sample differs from the air-firing case with a small peak indicating the volatile matter release and a shoulder in 370–570 °C temperature interval indicating char burning which takes place within the same temperature interval in both cases. In oxygen-enriched conditions (30% O_2–70% N_2 and 30% O_2–70% CO_2) the DTG profiles are similar with distinct volatile release peaks and characteristic temperatures as shown in Table 3. The similarity in DTG profiles obtained at the same oxygen concentration levels but with different diluting gas environments is an expected result. In TGA technique combustion temperature of the sample is controlled by electrical heating and sample temperature is not affected by combustion environment. Therefore, different heat capacities of diluting gases in combustion environment has no significant effect on combustion in contrast to practical tests as also confirmed in other studies [9,10,13]. Slightly higher burnout temperature in the CO_2 environment is indicative of slightly delayed combustion.

Effect of higher oxygen concentration on the combustion process is investigated with the tests under 30% O_2–70% N_2 and 30% O_2–70% CO_2 environments. Similar trends in the early stage of the process (up to 250 °C) in both environments reveal that initiation of the combustion process is not affected by oxygen concentration level. But at higher temperatures, more significant differences are displayed in DTG curves. In oxygen-enriched conditions, weight loss steps including volatile matter release and char burning are separately displayed in the DTG profile. In oxygen-enriched conditions a sharper peak that is observed in 250–400 °C temperature interval with a weight loss of 24%, is attributed to volatile matter release since weight loss value is in accordance with the one determined in pyrolysis conditions. Sharper peak is observed to continue with a distinctive shoulder up to 500 °C as represented in Fig. 6. In some studies it was demonstrated that the force of the fusion layer around solid particles is reduced by the presence of oxygen [17,18]. This situation also results in faster release of volatiles depending on the nature of solid particles and experimental conditions. High volatile matter content of lignite and the ease with which it is released, result in the formation of a sharper preliminary peak previously observed in low rank coals [19]. The shoulder following the peak is considered to account for weight loss due to burning of char in the sample. Increase in the oxygen concentration causes a shift of the burning profile to the lower temperature zone. Effect of oxygen concentration on characteristic temperatures is very clear. Characteristic temperatures including T_{ig}, T_{max} and T_b are found to be lower in oxygen-enriched conditions. Moreover at higher O_2 concentrations complete combustion is achieved at lower temperatures and shorter times.

3.2.2. FTIR results of combustion tests

Fig. 7 displays formation profiles of gases evolved in different combustion environments. Gaseous species evolved during combustion tests were found to be CO_2, CO, H_2O, CH_4, SO_2 and COS. As can be seen from the figure, the same specie evolves in different combustion environments.

H_2O formation profiles show that moisture is released first in all combustion environments with further release in the temperature range of 200 °C to 550 °C. The major contributor to the evolved gases is found to be CO_2 with its higher absorbance intensity. The formation profile of CO_2 in oxygen-enriched air atmosphere shifts to lower temperature zone as elevated oxygen levels lead to faster burning and earlier release of CO_2. CO formation profiles display similar trends in identical oxygen concentration levels while increase in oxygen level results in lower peak temperature. Methane evolution mainly takes place in the temperature range of 250–550 °C. In oxygen-enriched conditions, maximum release is observed around 350 °C which corresponds to the peak in DTG profile of volatile matter. In the case of sulphur containing gases, SO_2 and COS appear in the FTIR spectra. Trend of SO_2 evolution in FTIR spectra are found to be in accordance with the DTG curves. SO_2 release starts around 200 °C and displays different formation profiles depending on the combustion environment. Maximum release takes place at about 500 °C in air- and oxy-firing cases and 350 °C in oxygen-enriched firing conditions. COS formation is observed in all combustion tests in the temperature range of 200–550 °C with sharper peaks in oxygen-enriched conditions.

4. Conclusions

Pyrolysis and combustion characteristics of a typical indigenous lignite is investigated in air and oxy-fuel conditions by using a combined TGA–FTIR system. In pyrolysis tests, similar profiles are observed up to 720 °C in N_2 and CO_2 environments. However, at high temperature zone, further weight loss is observed due to CO_2–char gasification reaction in CO_2 atmosphere. Combustion tests were carried out in O_2/N_2 and O_2/CO_2 mixtures with oxygen concentrations of 21% and 30%. Results indicate that combustion in O_2/CO_2 environment is delayed to a small extent compared with that in O_2/N_2 environment at the same oxygen concentration. It is important to note that higher oxygen content in the combustion environment is the dominant factor affecting the combustion rather than the diluting gas. As oxygen concentration increases, DTG profiles shift to lower temperature zone, combustion rate increases and burnout time gets shorter. CO_2, CO, H_2O, CH_4, SO_2 and COS are clearly identified in the FTIR spectra. Significant amount of CO due to char–CO_2 gasification reaction and consecutively COS is evolved in CO_2 atmosphere. In combustion, formation profiles displayed similar trends in oxygen-enriched conditions regardless of diluting gas in combustion environment. The current results add to previous literature data pyrolysis and combustion behaviour of indigenous lignite in air and oxy-fuel conditions.

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Figure B.1 Continued

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APPENDIX C

FTIR Profiles of Imported Coal

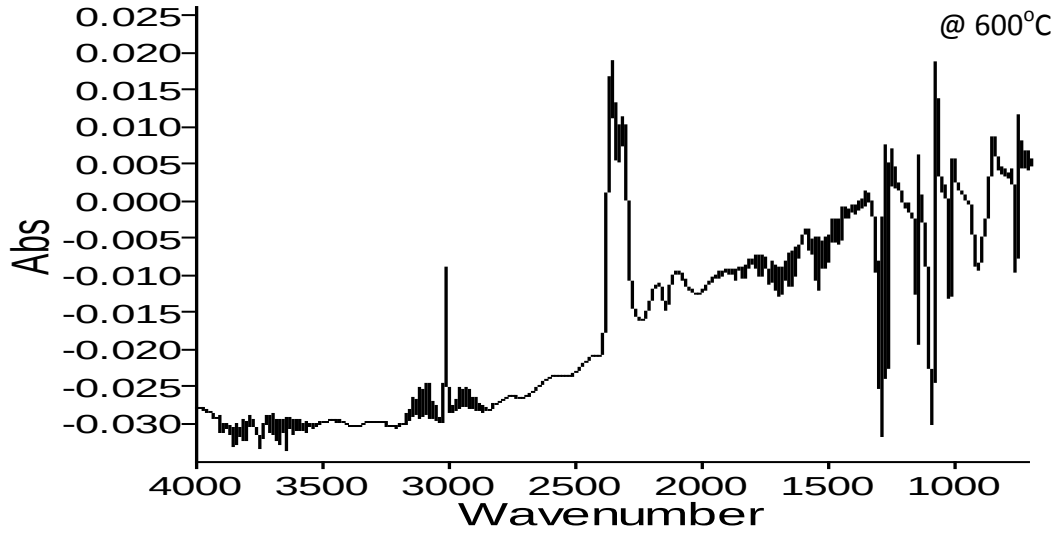

Figure C.1: FTIR profile of pyroylsis of imported coal in N_2 atmopshere.

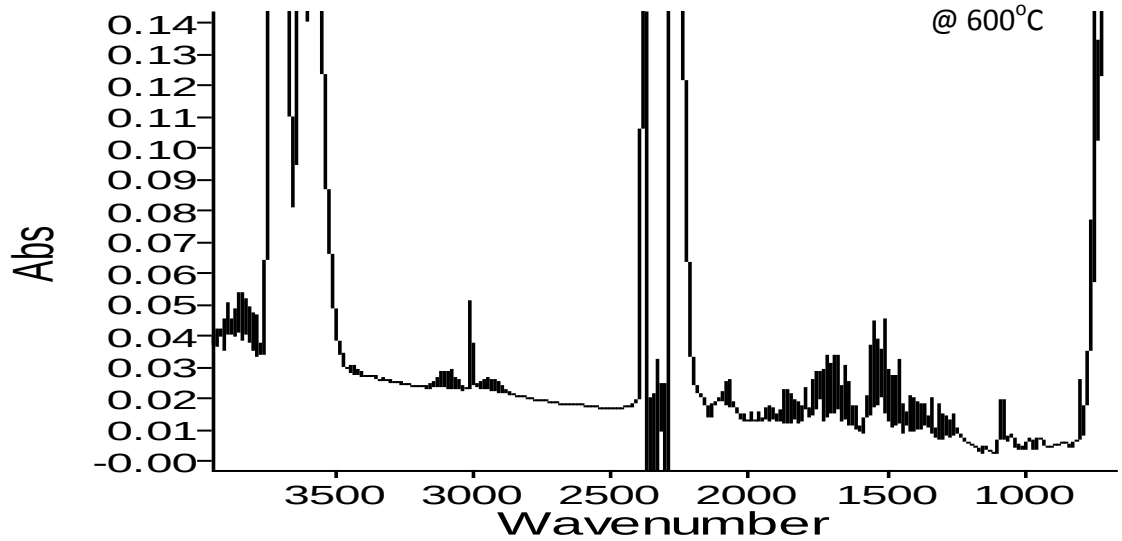

Figure C.2: FTIR profile of pyroylsis of imported coal in CO_2 atmopshere.

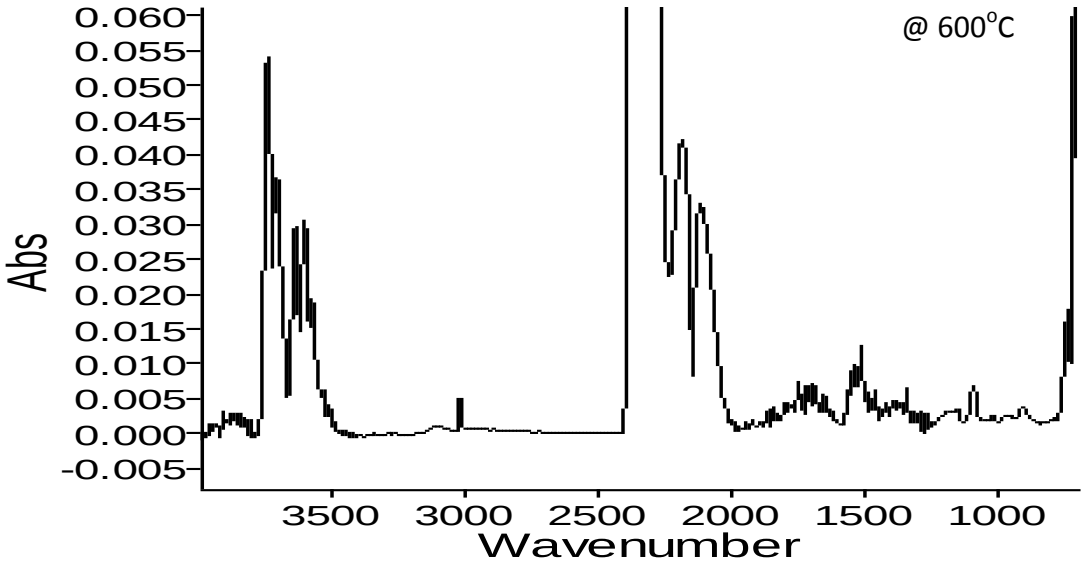

Figure C.3: FTIR profile of combustion of imported coal in 21% O_2 – 79% N_2 atmopshere.

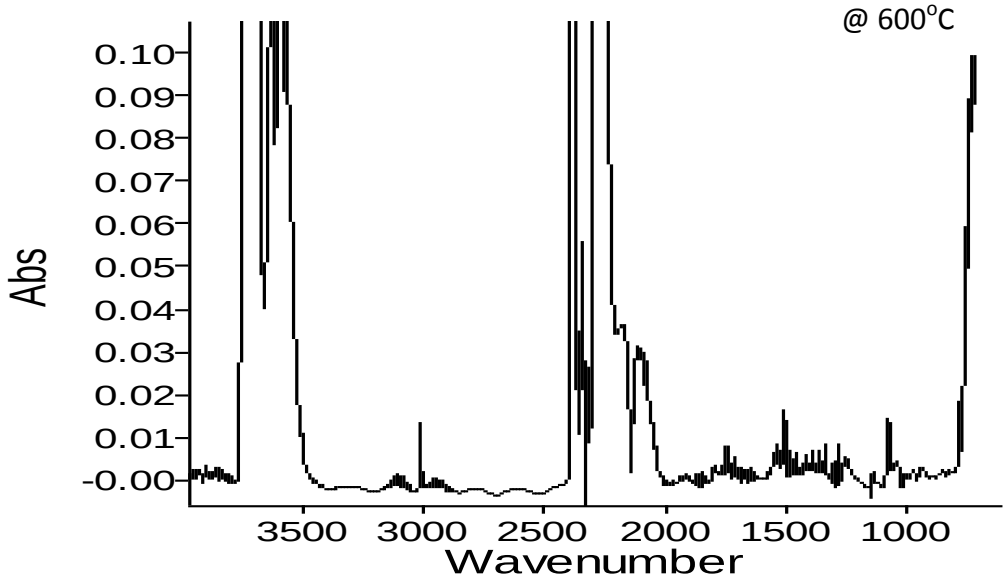

Figure C.4: FTIR profile of combustion of imported coal in 21% O_2 – 79% CO_2 atmopshere.

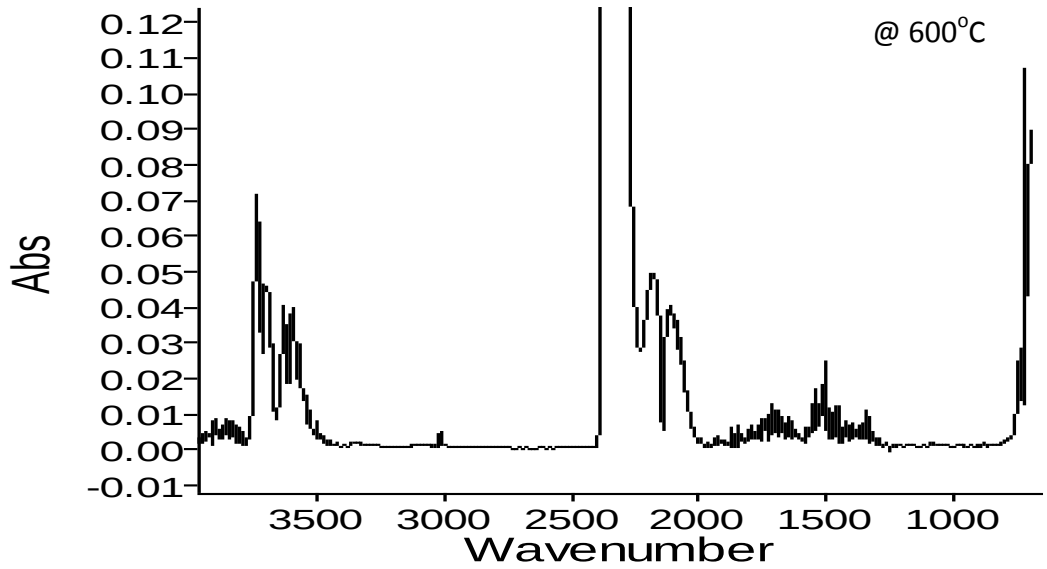

Figure C.5: FTIR profile of combustion of imported coal in 30% O_2 – 70% N_2 atmopshere.

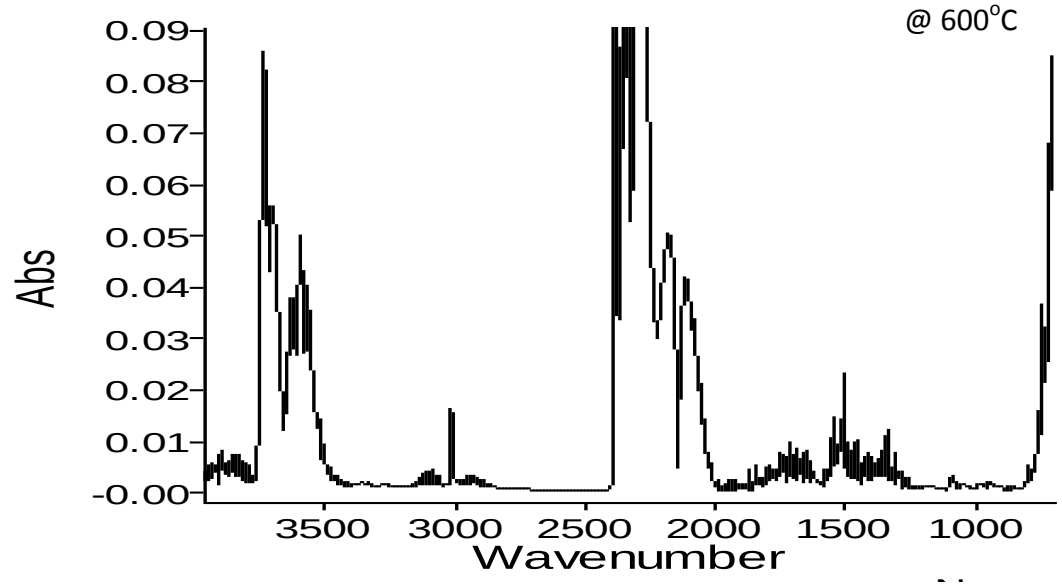

Figure C.6: FTIR profile of combustion of imported coal in 30% O_2 – 70% CO_2 atmopshere.