

HIGH ASH INDIAN AND TURKISH COAL PYROLYSIS AND GASIFICATION STUDIES IN VARIOUS AMBIENCES

K. Jayaraman*, E. Bonifaci**, N. Merlo[‡] and I. Gökalp[†]

*Corresponding author: jayaraman_mit@yahoo.com

*Postdoc fellow, ICARE-CNRS, France

**Research engineer, ICARE-CNRS, France

[‡]PhD student, ICARE-CNRS, France

[†]Director, ICARE-CNRS, France

Abstract

High ash content coals from India and Turk have been investigated in this study. A coupled thermal analyzer and mass spectrometer system is used for the thermal characterization of the coal samples and the identification of the volatiles evolved during the heating of the samples. Coal samples are heated in the TGA apparatus in argon, air, oxygen or steam in various gaseous mixture combinations at a temperature range of 25-1250°C with heating rates of 35 and 45 K/min. The experiments were performed to study the pyrolysis and gasification kinetics of typical Indian and Turkish high ash coals. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were performed to measure weight changes and rates of weight loss used for calculating the kinetic parameters. The activation energy (E_a) is calculated from the experimental results by using an Arrhenius-type kinetic model. The maximum mass loss has occurs during the devolatilisation stage (350-700°C) of the coals, where mainly O₂, CO₂, CO, H₂ and a small amount of CH₄ are released in argon ambience. Coal particles start to react with decomposed steam and produce CO₂, CO, and H₂ gases above 800 °C. The exothermic reactions are completed at about 950°C for all gasifying media. TGA results contribute to enhance the knowledge on high ash coal thermal characterization and gasification and, therefore, to establish the optimum operational conditions for syngas production from high ash content coals.

Keywords : High ash coal, coal pyrolysis, thermal and mass spectrometric analysis, coal gasification, syngas production

1. Introduction

Coal gasification is considered as an effective way for clean use of coal. Coal conversion via gasification is significantly considered to the world's primary energy supply and global electricity production [1]. Coal is also playing an increasingly important role in the production of liquid fuels and chemicals [2], and is the fastest growing energy resource in the world with the 826 billion tons of proven reserves [3] expected to last for up to 200 years compared to about 65 years and 40 years for natural gas and crude oil respectively [4]. However, the increase in coal utilization results to the growing environmental concern due to greenhouse gas (GHG) emissions. Carbon dioxide is the major greenhouse gas and carbon dioxide emissions from coal-fired power plants are very high, accounting for 40% of total global emissions [5]. The greenhouse gas emissions from fossil fuel-fired power generation can be reduced by achieving the efficiency improvements, gasification process, switching to lower carbon fuels, and CO₂ capture and storage (CCS) [6]. There are several options for capture and storage of CO₂ from coal combustion and gasification.

The thermogravimetric analysis (TG) is a method to research the physical or chemical reaction rate of material, which could be used in isothermal and non-isothermal condition. This is a useful technique employed in coal research, since any information about the rate of weight loss either in an oxidant or inert atmosphere when temperature increases is a subject of main concern [7-9]. Binay et al [10] have thermal characterization of two coal samples from India using XRD, FT-IR, and TGA analysis. They have observed in the thermogravimetric study in the low-temperature region from 80 to 110 °C where dehydration is expected and the other mainly in the 300-650 °C region, where maximum loss of volatile materials occurs due to primary and secondary volatilizations. Combustion characteristics of a fuel before it is used in energy production can be determined by using thermo-analytical techniques such as TG, DTG, DTA, DSC and TMA which cover a wide range of applications in research, development and economic assessment of fuels. They have been used in a wide variety of areas related to proximate analysis, coal reactivity, and heat effects associated with coal pyrolysis, combustion and heat of hydrogenation [11]. However, coal is a very heterogeneous material and the temperature ranges of the various stages of decomposition overlap each other. These phenomena have led to the coupling of TG with other analytical techniques, which include chemical features. Consequently, the gases evolved can be assigned to the detected weight losses so that chemical information is correlated with the thermal event [12, 13].

Kök [14] performed differential scanning calorimetry (DSC) and thermogravimetry (TG/DTG) experiments for 17 coal samples which were from the Thrace basin of Turkey. Reaction intervals, peak and burnout temperatures of the coal samples were determined. Two different kinetic methods known as, Arrhenius and Coats-Redfern, were used to analyze the kinetic data. It was observed that the reaction intervals of the coal samples studies varied between 265 and 500 °C depending on the properties. It was also observed that the activation energies of the samples were varied in the range of 54-92 kJ/mol.

Varol et al [15] have found that the volatile matter content of the coal increases, the ignition temperature decreases and the maximum combustion rate is reached at lower temperatures. For the more reactive coals the maximum combustion rate is reached at lower temperatures. The use of non-isothermal pyrolysis with associated evolved gas analysis provides a qualitative explanation of the pyrolysis behaviour of coal [16]. Pyrolysis is an important intermediate stage of all major coal utilization processes, such as combustion, gasification, carbonization and liquefaction. It is also a simple and effective method to remove sulfur from coal [17-21].

Arenillas et al [22] have performed the optimization of TG-MS coupling and the development of a normalisation procedure allowed a semiquantitative comparison between different pyrolysis species from various rank coals. Nali et al [12] have done the pyrolysis, gas chromatography and mass spectrometry studies on lignite originated from Poland and USA. Seo et al [23] have studied the coal pyrolysis by thermo-gravimetric analysis (TGA) and concentration measurements of the evolved species for Chinese coals under non-isothermal conditions at various heating rates. They have found that the kinetic parameters (activation energy and pre-exponential factor) of devolatilization during weight loss were represented as 130 kJ/mol and $3.19 \times 10^7 \text{ min}^{-1}$, respectively.

Coal gasification is one of the important coal utilization process to the clean coal technologies development. The solid coal is converted into gaseous fuel used to power a turbine and other energy applications. With gasification, power station generation efficiencies can be improved from 35%, using coal combustion, to between 45% and 55% [24]. The emissions of CO₂ into the atmosphere can also be reduced. During gasification, the organic and inorganic matter undergoes various chemical and physical transformations. Campoy et al [25] have demonstrated that the addition of steam in the gasification process can lead to

higher H₂ yield and the appropriate combination of temperature and steam leads to higher CO and H₂ yields, heating value, carbon conversion and gasification efficiency.

The high ash coal has been widely used for the generation of power and industrial steam in India, Turkey and Greece. Coal is likely to remain a key energy source for these countries, for at least the next 306 40 years as a significant amount of domestic coal reserves (relative to other fossil fuels) and a large installed-capacity for coal-based electricity production. The project Optimash is executed to explore the possibility of high ash coal gasification using different methodology in which France, Netherland, Turkey and India are participated.

The gasification of high ash coals needs the systematic identification about the formation and evolution of H₂, CO, and CO₂ during heating process. Also, it is necessary to understand pyrolysis mechanism of coals in order to increase conversion of coal to oils and gases, especially to increase H₂ during coal pyrolysis. The use of non-isothermal pyrolysis with associated evolved gas analysis provides a qualitative explanation of the pyrolysis and gasification behaviour of coal. Hence, coal is pyrolyzed and gasified on a differential thermal analyzer and gas detection using mass spectrometry to deeply understand thermochemical reaction during coal pyrolysis and combustion reaction in this paper.

2. Experimental details

A NETZSCH STA 429 thermal analyser combined with a quadrupole QMG 511 mass spectrometer and steam generator were used to perform investigations on a coal in various atmospheres with the flow rates of 6 g/hr of steam, 2 ml/min of air, 2 ml/min (gasification-process) and 50 ml/min (combustion-process) of oxygen and 20 ml/min of argon. Heating rates are varied from 35 deg/min to 45 deg/min. The excitation energy in the mass spectrometer was 1100 eV. The experiments were performed at a heating rate of 35 deg/min upto 1150 °C and in some cases two isothermal sections retained at 950 and 1000 C. The size of the coal samples are around 0.5 to 0.8 mm. Mass spectrometric analyses is used to measure the gas evolution during thermal analysis. The TGóMS runs were carried out in a dynamic gas atmosphere. The output of the TGA system was connected to the mass spectrometer through a heated line. The balance adapter, the transfer line, and the MS gas cell can be heated until 250 °C, thus avoiding the condensation of the less volatile compounds. Steam generator and steam transfer line are maintained at 180 °C and 150 °C respectively. On the other hand, the low volumes in the thermo balance microfurnace, transfer line, and gas measurement cell permit low carrier gas flow rates to be used and allow for good detection of the gases evolved in the pyrolysis, combustion and gasification process. Online gas analyses were performed for the detection of combustion gases fed to mass spectrometer, and experimental data were stored as a function of time. The ultimate and proximate analysis of the Indian and Turkish coal is given in table 1.

Kinetic analysis

Arrhenius method

In Arrhenius method [14], the measured rate of mass loss accounts for gross changes in the system, the reaction model assumes that the oxidation rate of mass loss of the total sample is dependent only on the rate constant, the mass of sample remaining (W) and the temperature.
 $dW/dt = k W^n$

The temperature dependence of k is expressed by the following Arrhenius equation:

$$k = A_r \exp(-E/RT)$$

Assuming first-order kinetics,

$$dW/dt = A_r \exp(-E/RT)W$$

$$[(dW/dt)1/W] = A_r \exp(-E/RT)$$

taking the logarithm of both sides,

$$\log [(dW/dt)1/W] = \log A_r \delta E/2.303 RT$$

where dW/dt is the rate of mass change, E is the activation energy, T is the temperature, A_r is Arrhenius constant and n is the reaction order. When $\log [(dW/dt)1/W]$ is plotted vs. $1/T$, a straight line is obtained which will have a slope equal to $E/2.303R$ and from the intercept the Arrhenius constant can be estimated.

Table 1. Proximate analysis, ultimate analysis and heating values of the coal samples.

	Turkish coal		Indian coal
Proximate Analysis			
	Unit	As Received	As Received
Moisture	%	11.15	2.95
Ash	%	49.23	45.85
V.M	%	24.60	25.62
Fixed Carbon	%	15.02	25.58
TOTAL	%	100	100
Ultimate Analysis			
Moisture	%	11.15	2.95
Ash	%	49.23	45.85
C	%	32.60	36.18
H	%	2.23	2.52
N	%	0.99	0.97
O	%	7.16	10.78
S	%		0.45
TOTAL	%		100
Heating Value			
LCV	kcal/kg	2405	3486
HCV	kcal/kg	2584	3642

3. Results and Discussions

a) Thermal decomposition

The experiments are carried out in the argon and water ambience to evaluate the thermal decomposition of the coal. The TG-DTG curves of the Turkish and Indian coals indicate that pyrolysis of coals occurs in the temperature range from 300 to 750 °C, presented in Figure 1 and 4. The evolution of gaseous species and products as a result of decomposition of the coal sample was simultaneously monitored by mass spectrometry during the TG experiment. The mass spectra of the gases evolved during pyrolysis and gasification are illustrated in Fig. 2 and 3 of the Turkish coal respectively. Figure 5 shows the mass spectra of the evolution gases at argon and water vapour ambience of Indian coal. The spectra were detected at increasing times, and the corresponding temperatures at which the spectra were recorded are denoted on the spectra. As can be seen from the Figures 1 and 3, the mass loss is noticed in Turkish coal due to the elimination of moisture in the temperature below 300 °C. A comparison of the evolution of the main species produced during thermal decomposition showed a relationship between volatile matter content and the species emission.

Wilson [26] has observed that the steam decomposition and coal gasification commenced from 800 °C, presented in the figs 1 and 4. The thermal decomposition characteristics of the coal are same when the coal is heated until 800 °C at argon and as well as at water vapour ambience.

At temperatures below 350 - 400 °C, different processes take place prior to primary pyrolysis, i.e. disruption of hydrogen bonds, vaporisation and transport of the non-covalently bonded molecular phase [27]. The second peak, where essential weight loss occurs in the range of 350 to 700 °C is related to primary devolatilisation, during which carbon, hydrogen and oxygen compounds are released (figs 2 and 4). At 350 °C, the primary carbonisation starts initially with the release of carbon dioxide and hydrogen. Along with the increase in temperature, methane and other lower aliphatics are evolved together with hydrogen, carbon monoxide and alkyl aromatics. When comparing the DTG curves of Turkish and Indian coal decomposition, the rate of devolatilization decreases with increasing coal rank when compare the figs 1 and 4.

The DTG rate is comparatively higher for Turkish coals, due to high ash present in the coal. This rapid devolatilization essentially complete at 550 °C. Secondary devolatilization of coal, occurring largely in the 600-900 °C ranges, produces CO, CO₂, H₂O, H₂ and CH₄ as the major products. The maxima in the DTG curve corresponds to the maximum gas release when compare the figures 1-4. Also fractional loss of oxygen is very high in lignites and low-rank coals.

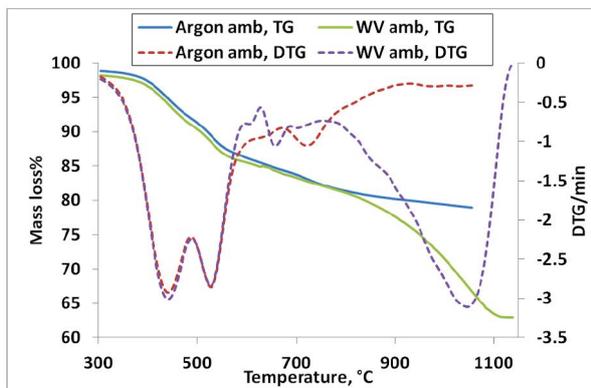


Figure 1. TGA curves of Turkish coal samples

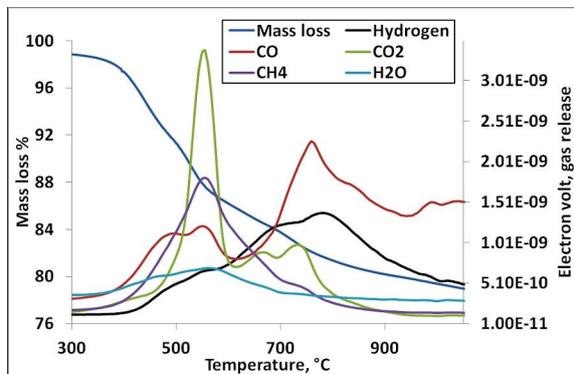


Figure 2. Mass spectrum analysis (gas detection) of Turkish coal samples at argon ambience

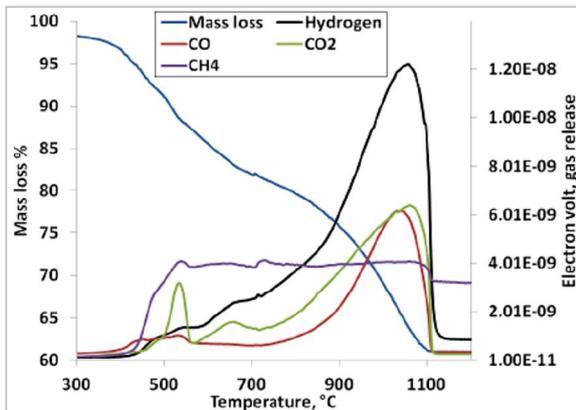


Figure 3. Mass spectrum analysis (gas detection) of Turkish coal samples at water vapour ambience

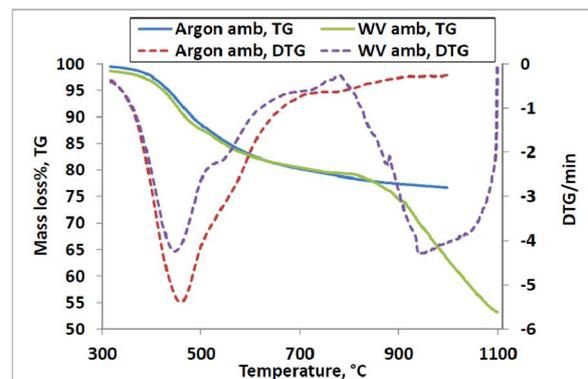
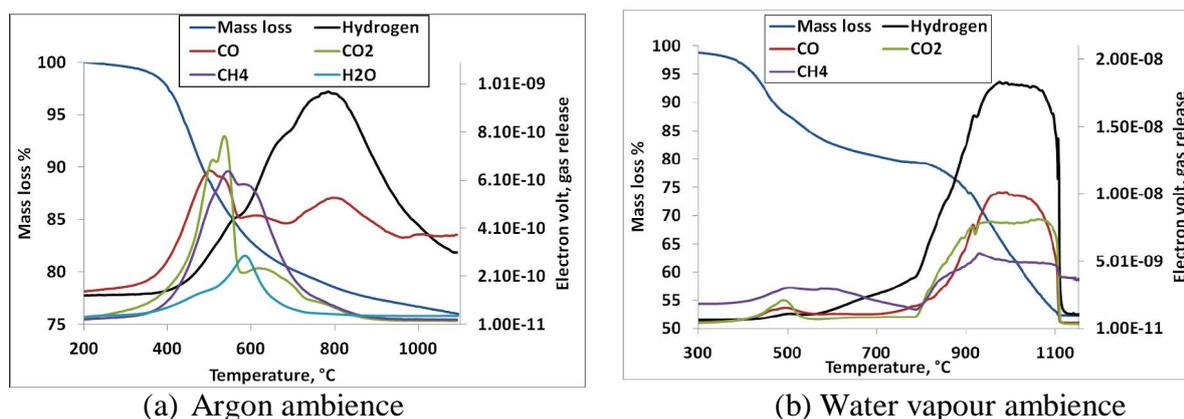


Figure 4. TGA curves of Indian coal samples



(a) Argon ambience (b) Water vapour ambience
Figure 5. Mass spectrum analysis (gas detection) of Indian coal samples

The H₂ peaks were detected in the thermal decomposition at the temperature range of 500 to 750 °C. The H₂ evolved is, in fact, only a part of the hydrogen present due to the higher volatile matter content in the coal. The evolution of CH₄ with temperature for the high ash coals is presented. It can be seen in the figures 2 and 5(a) that the formation of CH₄ starts at temperatures higher than 450°C. It can be seen that the higher the volatile matter content, the more groups are likely to produce CH₄ during pyrolysis processes. In the case of high ash coals, CO₂ is formed from aliphatic and aromatic carboxyl and carboxylate groups at low temperatures. Thus decomposition is a complex process that involves coal devolatilization and pyrolysis.

b) Combustion tests

Combustion tests of the high ash coals were carried out in oxygen-enriched (75% O₂ and 25% argon) ambient conditions. The characteristic temperatures and parameters of T_{ig} (onset, ignition temperature), T_{pmax} (the temperature corresponding to the peak of the derivative thermogravimetric - DTG curve), T_b (burn out temperature) and |(dm/dt)_{2max}| were investigated to explore the effects of the coal samples. Fig. 6 shows the temporal weight losses and DTG of the Turkish and Indian coal at oxygen ambience which can be considered as combustion related conditions. In the case of Turkish coal, some weight loss observed at 120 °C due to its moisture content. The weight loss starts above 320 °C, and the ignition temperature is 360 °C which is slightly higher with the reported values of Wang et al [28] of high ash coals. This may be due to the thermal and size effect of the particle. Devolatilisation and oxidation is followed by the fixed carbon combustion occurred in a continuous manner. The order of reactivity of coal is assessed primarily on the peak temperature T_{pmax} [31], the higher this temperature, the less reactive the coal. Coals with greater weight loss rates at lower temperatures are easier to ignite and burn. Profiles which extend into very high temperature ranges indicate slow burning coals, for which longer combustion times are required for complete combustion. The burn out temperature of the Turkish coal is around 675 °C, and for the Indian coal is around 875 °C, but the T_{pmax} and |(dm/dt)_{2max}| is almost identical for both the origin coals. The higher value of the burn out temperature of the coals is due to the higher heating rate of the samples. There is variation in the residual mass of the burn out samples which is due to the ash content variation in the coal samples.

c) Coal gasification

The reactivity of coals towards oxidizing gases is an important property in connection with their uses such as combustion, gasification and carbonization. There are many properties that govern the reactivities of coals, and which also contribute to the heterogeneity of coals, for example, carbon content, mineral matter (both quantity and composition), particle size and

porosity. The gasification process is exceedingly complex and many competing processes contribute to the thermal analysis curves. In this study, the coal sample was subjected to dynamic heating rate until 1150 °C at the presence of steam and in the water vapour blended air/water ambience kept isothermal conditions of 950 °C for 10 minutes and heated until 1000 °C, illustrated in Fig 9. As it might be examined, on raising the temperature, combustion of the sample occurred with a related mass loss. Once the fuel content of the coal was consumed, the mass corresponding to the ashes stayed constant. Burning characteristics obtained from a TGA analyzer may be a good guide in order to compare the reactivity and combustibility of the fuels which will be used in combustors. On-line mass spectra recordings of the combustion cum gasification of coal indicated the oxidation of carbonaceous and hydrogen content of the coal and release of some hydrocarbons due to pyrolysis reactions that occurred during combustion of the coal. The weight loss versus time curves showed two sequential zones, as in the coal exposed to heating environment. The evolution of different volatile products could provide information on the chemical reactions occurring during thermal decomposition. The first zone of weight loss, temperatures below 700 °C and conversion up to 20%, is the pyrolysis (decomposition) stage, whose characteristics were not affected by the presence of argon or steam environment. The residual mass of the burn out samples at water vapour ambience infers that the complete burn out of the coal samples occurred at 950 °C when compare the Figs 6 and 9.

The gasification process started above 800 °C at steam ambience which was exhibited by Wilson [26]. The combustion and gasification process of the coal started at around 700 °C for Turkish coal and around 750 °C for Indian coal at water vapour and air/oxygen blended medium. The TG-DTG curves of Turkish coal indicate that the mass loss starts at lower temperature which may be the difference in the mineral matter and carbon contents as shown in Table 1. Maxima in the intensities of the gas evolution are always accompanied by maxima in the weight loss when compare the Figs 7, 8 and 9. The maximum mass loss occurred at around 950 °C for Indian coal and 900 °C for Turkish coal. The complete burn out of both the coal sample occurs at 950 °C to keep isothermal conditions for longer time. The mass loss is preserved even if the temperature is increased to 1000 °C. This clearly demonstrates that the high ash coal gasification can be carried out at around 950 °C using the blended gaseous steam and air/mixtures with efficient carbon conversion. The major gaseous evolved from the coal gasification is CO, H₂, CH₄ and CO₂ which is shown in Figs 8a and 8b. This ensures that combustion cum gasification (partial oxidation) process occurred in the described gas flow rates. There is slight shift in the ignition temperature of the coal at steam and oxygen environment when compared to steam and air ambience. This may be due to the higher reactivity potential of steam and oxygen mixtures.

d) Kinetic analysis

The non-isothermal kinetic study of mass loss during a gasification and combustion process is extremely complex, because of the presence of numerous components and their parallel and consecutive reactions. The activation energy (E) of the high ash coal is determined for low temperature thermal decomposition and high temperature combustion and gasification processes using the Arrhenius method (Fig 10) and the results are given in Table 2. A regression analysis with the least square method was used to determine the best straight line. Activation energy calculated at thermal decomposition stage of the Indian and Turkish coal is in the range of 72 to 77 kJ/mol, in the combustion and gasification stage, Turkish coal exhibit relatively low values when compared to Indian coals. The obtained activation energies of Turkish coal were in consistency with the values calculated by Kok [14]. The activation of the coal particles are varied from 30 to 32 kJ/mol for the Turkish and Indian coals which is in

consistency with the reported range of values by Ming-gao et al [29] for coal combustion under various oxygen concentrations and temperatures.

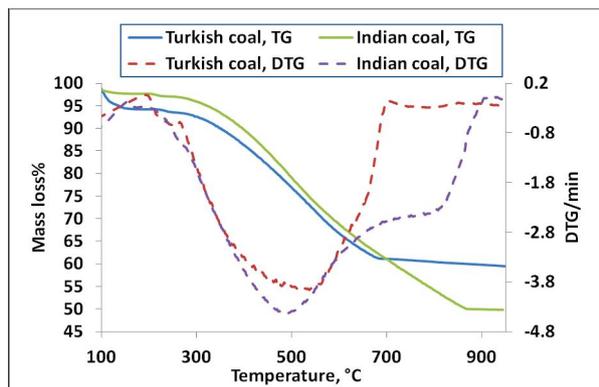


Figure 6. TGA curves at oxygen ambience

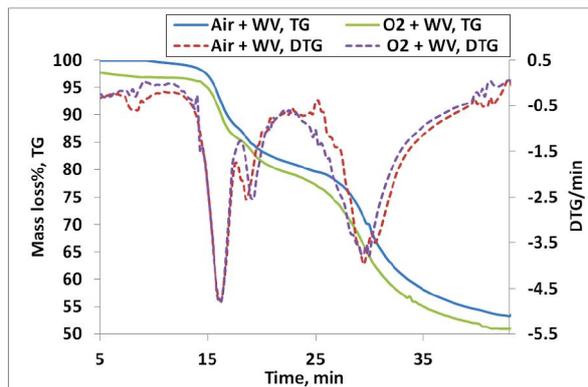
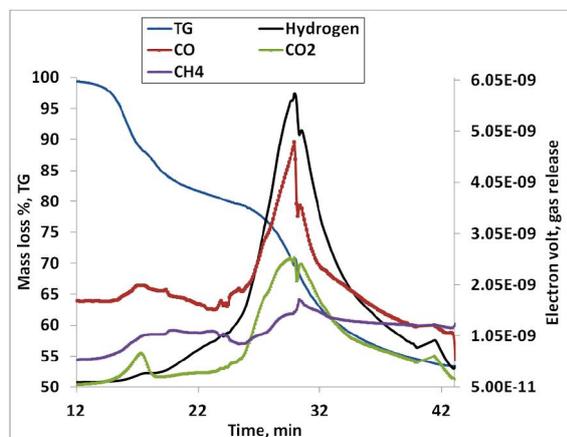
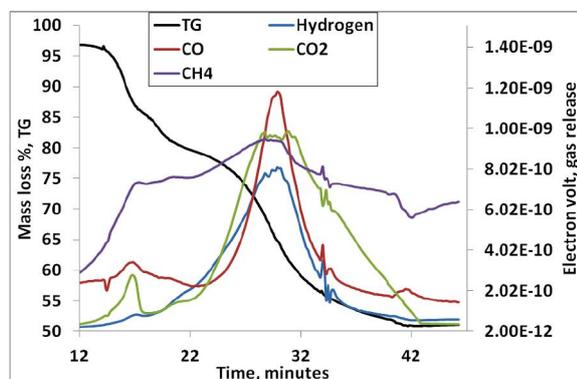


Figure 7. TGA curves at blended gases of Indian coal samples



(a) Turkish coal



(b) Indian coal

Figure 8. Mass spectrum analysis (gas detection) of coal samples at air and water vapour blended ambience

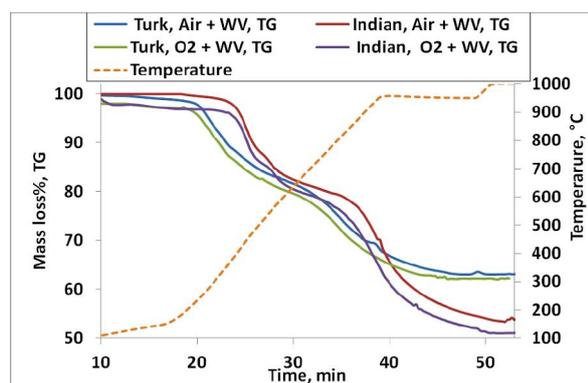


Figure 9. Comparison of TGA curves at blended gases of Turkish and Indian coal samples

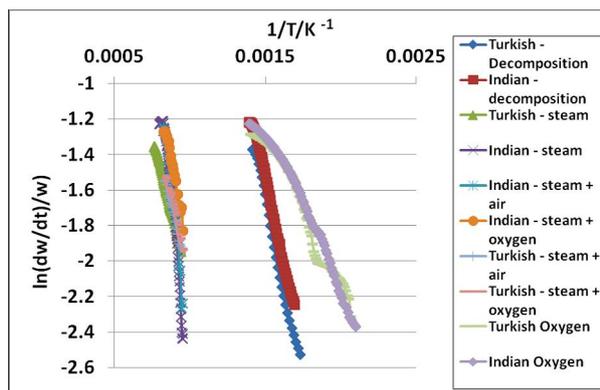


Figure 10. Activation energy calculation by Arrhenius method

Table 2. Kinetic parameters of coal samples at different atmospheres.

Origin of coal, and ambience	R ²	Slope	Activation Energy, kJ/mol
Turkish, argon	0.99	-4046	77.4
Turkish, steam	0.99	-3457	66.2
Turkish oxygen	0.96	-1613	30.8
Turkish, steam + air	0.98	-3365	64.4
Turkish, steam + oxygen	0.97	-3418	65.4
Indian, argon	0.99	-3808	72.9
Indian, steam	0.89	-7064	135.25
Indian oxygen	0.97	-1675	32
Indian, steam + air	0.95	-7706	147.5
Indian, steam + oxygen	0.97	-4437	84.9

4. Conclusions

The pyrolysis, combustion, and gasification behaviors of high ash Turkish and Indian coals were investigated by the coupled TGóMS method. The results indicate that the ignition temperature and the temperature of maximum mass loss rate are identical for both coals, but the burn out temperature of Indian coal occurs at higher temperatures. During thermal decomposition and devolatilization of the coal, CO, CO₂, H₂ and CH₄ are the major gaseous products. The gasification process of the coal starts around 700 °C for blended mixtures of water vapour, air and oxygen. The complete burn out of both coal samples occurs at 950 °C which indicates the optimum gasification temperature with higher carbon conversion rate and cold gas efficiencies for high ash coals. The activation energies are comparatively higher for the Indian coal under various reducing ambient conditions compared to values for the Turkish coals. The explanation of these differences is under investigation presently.

Acknowledgement

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