High ash coal pyrolysis and gasification studies in argon, steam and air ambience for syngas production

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Abstract

Pyrolysis and gasification studies of Indian and Turkish high ash coal samples have been carried out using simultaneous TGA-MS method. Coal samples were heated in the TGA apparatus in argon (20 ml/min), air and oxygen (2 ml/min) and steam in various gaseous mixture combinations at a temperature range of 25-1250°C with heating rates of 35 and 45 K/min. Thermogravimetry (TG) and derivative thermogravimetry (DTG) were performed to measure the weight changes and rates of weight loss used for calculation of the kinetic parameters. Gas evolution measurements have been done using the mass spectrometry instrument. The activation energy (Ea) is calculated from the experimental results by using an Arrhenius-type kinetic model. During the devolatilisation stage (350-700°C) of the coals, the maximum mass loss has occurred during which mainly O_2, CO_2, CO, H_2 and a small amount of CH_4 released in argon ambience. Thermogravimetric analyses (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, clean coal gasification, syngas production

1. Introduction

With the recent reemphasis on coal as an important source of energy, numerous studies have appeared on the acceleration of coal gasification and the improvement of combustion efficiency. Coal is a very complex heterogeneous material mainly consists of organic and inorganic matters. It may also be considered as a combustible rock of variable compositions and often called the fuel of industrialization. Thus, coal conversion technologies and virtually all end uses of coal require the application of heat. The structural changes upon heating which accordingly influences all aspects of coal base technology. Coal undergoes variety of physical and chemical changes when heated to a temperature at which thermal decomposition occurs. Thus the thermal decomposition of coal has been the subject of many investigations 1-4. All coals release volatile matter when heated. The quantities evolved depend upon coal rank, the heating rate, the ultimate temperature to which the coal is heated, and to the system pressure. The chemical composition of coal has a strong influence on its combustibility and burnability. Thermal analysis is used to establish thermodynamic properties which are essential for understanding the behavior of material under different heating and cooling rates, under inert, reduction or oxidation atmosphere or under different gas pressures. Thermal analysis comprises a group of techniques in which a physical property of a substance is measured in a controlled temperature program. The thermogravimetric study of coal is a well-known method for understanding the change in structural features of coal during combustions 5-7. Binay et al [8] 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 300–570 °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 [9].

Kastanaki and Vamvuka 10 studied the combustion behavior and kinetics of four biomass chars, lignite and a hard coal char and their blends. Kinetic evaluation was performed using a power law model. Reaction kinetic parameters were obtained by modeling the combustion of biomass and coal chars as a single reaction, with the exception of lignite and olive kernel chars, the combustion of which was modeled by two partial reactions.

Kök [11] 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 studied were varied between 265 and 500 ℃ depending on the properties. It was also observed that

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the activation energies of the samples were varied in the range of 54–92 kJ/mol.

Varol et al [12] 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.

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% [13]. The emissions of CO2 into the atmosphere can also be reduced. During gasification, the organic and inorganic matter undergoes various chemical and physical transformations.

With the purpose of maximise the gasification efficiency of coal, it is essential to understand the mechanism for the chemical and physical transformation. These processes will assist in the reduction of carbon emissions in the process especially when gasifying low rank coals. Coal gasification is becoming an attractive alternative for power generation since it offers higher efficiency and improved environmental performance than conventional pulverised fuel technology carried out in combustion boilers 14. The volume of gas produced from gasification is much less compared to that obtained from combustion systems. The reduced volume of gas will require smaller equipment for CO_2 capture and hence results in lower cost and lower emission 15.

Arenillas et al 16 have performed the Optimisation 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 17 have done the pyrolysis, gas chromatography and mass spectrometry studies on lignite originated from Poland and USA. Seo et al 18 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 3.19E+07 min−1, respectively.

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 30– 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 H_2, CO, and CO_2 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 H_2 during coal pyrolysis. For simultaneous thermal gas analysis, mass spectrometry (MS) is the most common techniques. It is used to identify the gaseous species emitted by a sample, according to their mass spectra. 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 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 TG–MS 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 ºC, thus avoiding the condensation of the less volatile compounds. Steam generator and steam transfer line are maintained at 180 ºC and 150 ºC 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 11, 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,

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

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 fuel 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 ºC, presented in Figure 1 and 3. 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 4 of the Turkish and Indian coal respectively. 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 ºC. 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 [19] has observed that the steam decomposition and coal gasification commenced from 800 ºC, presented in the figures 1-4. The thermal decomposition characteristics of the coal are same when the coal is heated until 800 ºC at argon and water vapour ambience.

At temperatures below 350 - 400 ºC, different processes take place prior to primary pyrolysis, i.e. disruption of hydrogen bonds, vaporisation and transport of the non-covalently bonded molecular phase [20].

The second peak, where essential weight loss occurs in the range of 350 to 700 ºC is related to primary devolatilisation, during which carbon, hydrogen and oxygen compounds are released (figs 2 and 4). At 350 ºC, 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. This rapid devolatilization essentially complete at 550 °C. Secondary devolatilization of coal, occurring largely in the 600–800 °C ranges, produces CO, CO_2, H_2O, H_2 and CH_4 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. 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 4 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) Coal gasification

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 ºC for 10 minutes and heated until 1000 ºC, illustrated in figures 5-9. 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.
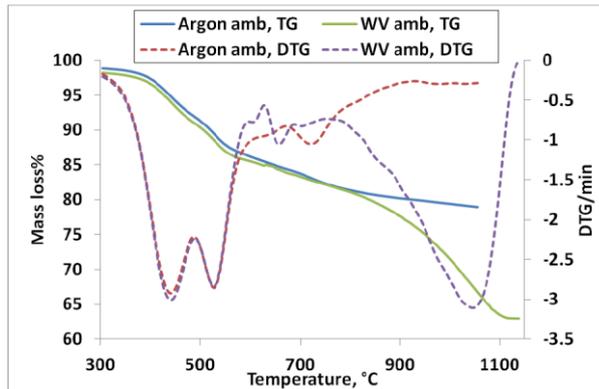
Fig. 1. TGA curves of Turkish coal samples
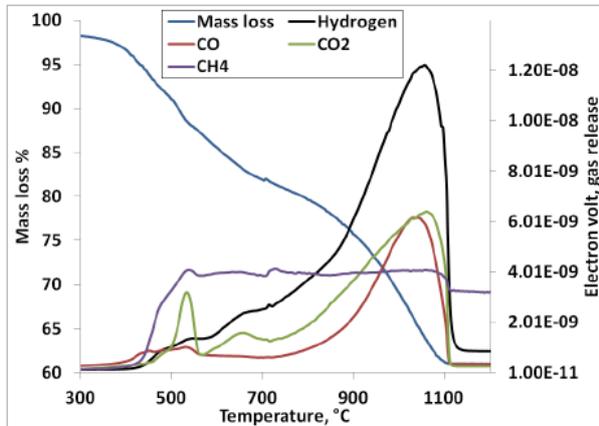
Fig. 2. Mass spectrum analysis (gas detection) of Turkish coal samples at water vapour ambience
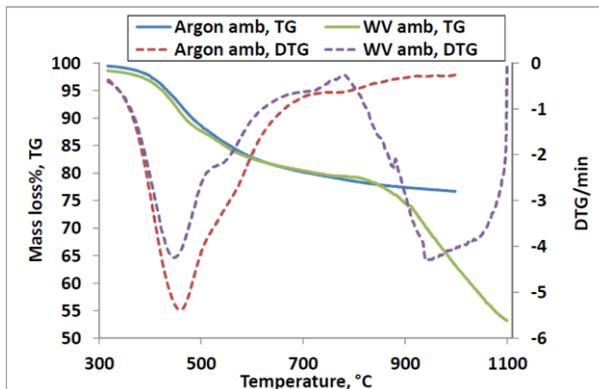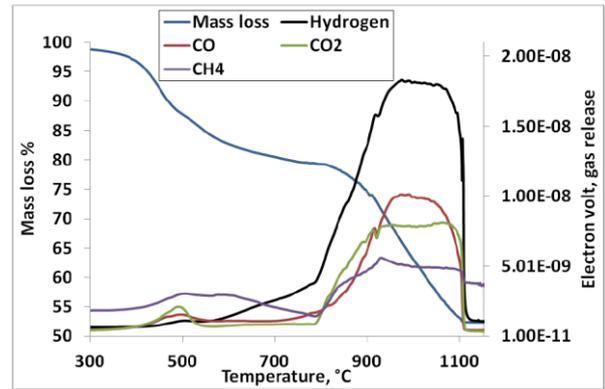

Fig. 3. TGA curves of Indian coal samples

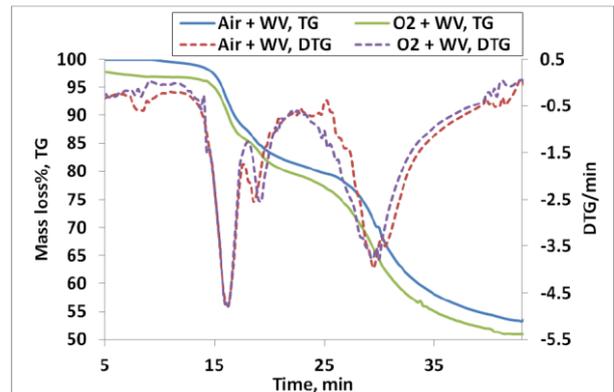Fig. 4. Mass spectrum analysis (gas detection) of Indian coal samples at water vapour ambience

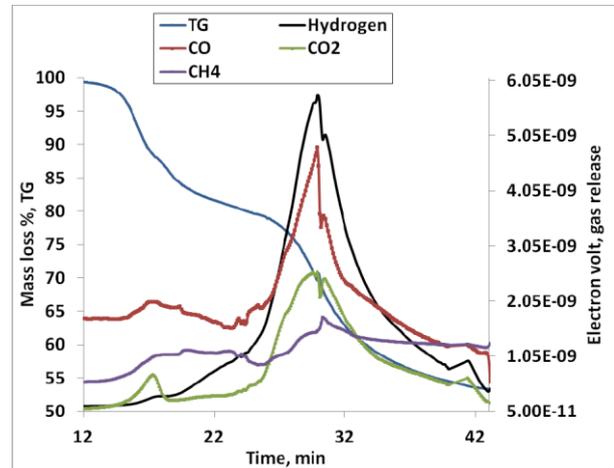Fig. 5. TGA curves at blended gases of Indian coal samples

Fig. 6. Mass spectrum analysis (gas detection) of Indian coal samples at air and water vapour blended ambience

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 ℃ and conversion up to 20%, is the pyrolysis (decomposition) stage, whose characteristics were not affected by the presence of oxygen or air or steam environment.
The gasification process started above 800 ℃ at steam environment which was demonstrated by Wilson 19. The combustion and gasification process started at

around 700 ºC 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 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 figures 5, 6 and 7. The maximum mass loss occurred at around 950 ºC for Indian coal and 900 ºC for Turkish coal. The complete burn out of both the coal sample occurs at 950 ºC to keep isothermal conditions for longer time. The mass loss is preserved even if the temperature is increased to 1000 ºC. This clearly demonstrates that the high ash coal gasification can be carried out at around 950 ºC using the blended gaseous steam and air/mixtures with efficient carbon conversion.

The major gaseous evolved from the coal gasification is CO, H_2, CH_4 and CO_2 (figs 6 and 7). 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.
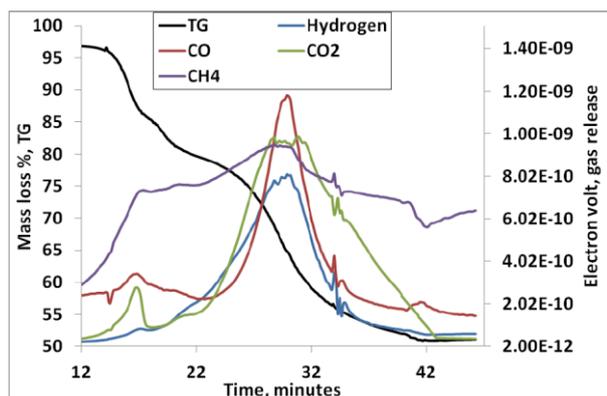
Fig. 7. Mass spectrum analysis (gas detection) of Indian coal samples at oxygen and water vapour blended ambience
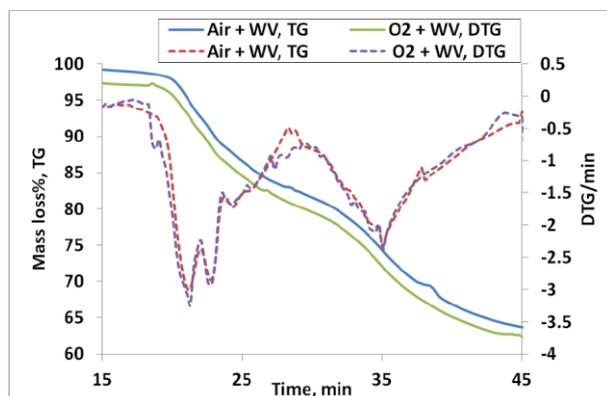
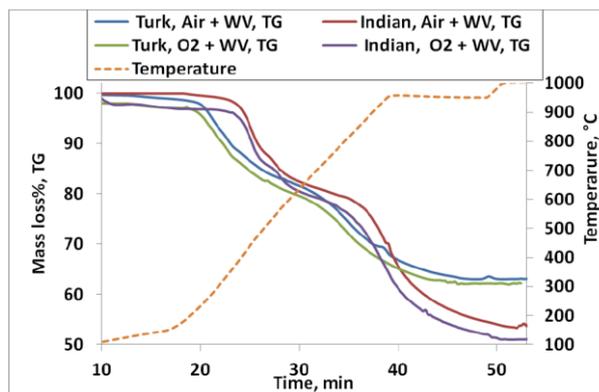Fig. 8. TGA curves at blended gases of Turkish coal

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

c) 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 11.

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

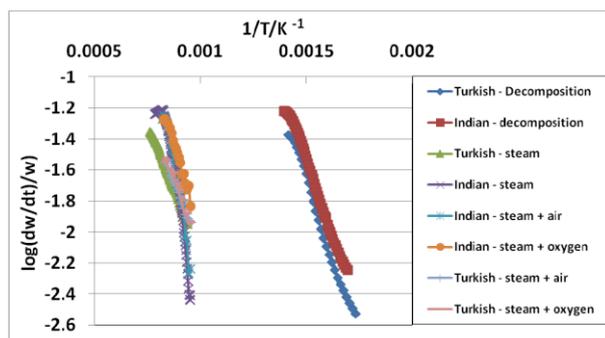| Origin of coal, and ambience	R^2	Slope	Activation Energy, kJ/mol
Turkish, argon	0.99	-4046	77.4
Turkish, steam	0.99	-3457	66.2
Turkish, steam + air	0.98	-3365	64.4
Turkish, steam + oxygen	0.97	-3418	65.4
Indian, argon	0.99	-3808	72.9
Indian, steam	0.89	-7064	135.25
Indian, steam + air	0.95	-7706	147.5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

Fig. 10. Activation energy calculation by Arrhenius method

4. Conclusions

In this study, TGA and MS were used along with the models under non-isothermal conditions to investigate the pyrolytic, combustion and gasification behavior of high ash Indian and Turkish coal at different ambiences. The following conclusions were drawn:

It seemed that during thermal decomposition and devolatilization of coal, CO, CO_2, H_2 and CH_4 are the major gaseous products. The reaction of coal with steam starts around 800 ºC in which partial oxidation process occurred. The blended mixture of steam and air/oxygen is an efficient gasifying agent for high ash coal gasification. The complete carbon conversion takes place in the temperature range of 900 to 950 º C. The syngas production rate is maximum in these temperature limits. The activation energy of Turkish and Indian is determined by using Arrhenius approach at various ambiences and the results are varied between 64 and 77 kJ mol $^{-1}$ for Turkish coal, 72 to 147 kJ mol $^{-1}$ for Indian coal.

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