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Pyrolysis and Gasification Characteristics of High Ash Indian and Turkish Coals

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Abstract

Pyrolysis and gasification studies of Indian and Turkish high ash coal samples have been performed using coupled TGA-MS method. Coal samples were heated in the TGA apparatus in an argon, steam, CO₂ and blended mixtures of CO₂ and steam in a temperature range from 25-1250°C with heating rates from 35 to 1000 K/min. Gas evolution measurements is performed using the mass spectrometry system. During the devolatilisation stage (350-700°C), the maximum mass loss has observed in which O₂, CO₂, CO, H₂ and small amount of hydrocarbon compounds are released. Char gasification is mainly influenced by operating conditions such as heating rate and reaction temperature and also the char production method, its physical structure and size and chemical composition of the char. The steam and CO₂ gasification rates of the chars are carried out at the temperatures of 850, 900, 950, and 1000°C. Three kinetic models are applied to describe the char conversion rates: volumetric model, grain model, and random pore model. The activation energy of Indian coal-char is varying from 122 to 177 kJ mol⁻¹ under steam gasification and from 130 to 214 kJ mol⁻¹ for CO₂ gasification. The activation energy for char-steam gasification is 156-173 kJ/mol, whereas in the steam blended with CO₂ gasification, it ranges between 162 and 196 kJ/mol for 3 mm particles. Similar trends are observed for the Arrhenius constant values for both sized particles.

Keywords: gasification, high ash coal, thermogravimetry, mass spectrometry, syngas production, kinetic models, clean coal technologies

1. Introduction

With the recent emphasis on clean coal technologies, numerous studies have been performed on coal gasification. Coal is a very complex heterogeneous material consisting of organic and

inorganic materials. Coal is mainly formed from partially decomposed and metamorphosed plant materials. Its formation has occurred over long time periods, and differences in plant materials and in their extent of decay influence the components present in coals. Description of coal components is part of the science of petrography [1]. Several efforts have been made to categorize the coals, and to relate coal properties to their behaviour in coal conversion processes.

Lignite, the lowest rank coal, has high moisture content, relatively more ash and a low heating value when compared with the other types of high rank coals. In spite of their high ash content, these coals have been widely used for the generation of power and industrial steam in India and Turkey. The use of indigenous coals is encouraged in both countries for energy supply security and to insure fuel price stability. In addition, clean coal technologies are also encouraged, especially to reduce the carbon footprint of coal based electricity generation but also to reduce all harmful emissions.

At present, coal accounts for more than 50% of total primary commercial energy supply in India and shares for about 58.3% of total electricity generation. Coal is expected to continue a key energy source for India, for at least the next 30–40 years as India has a significant amount of domestic coal reserves (relative to other fossil fuels) and a large installed-capacity for coal-based electricity production. This situation is also very similar in Turkey, and also for example in Greece. Hence, strong R&D and demonstration efforts are developed to improve the global sustainability of using high-ash content coals for electricity generation in such countries. The present method of using high-ash coals is mostly through direct combustion processes. This method is not only inefficient, but also is associated with high levels of pollution. With the intention of solve these problems and increase the coal usage, many countries in the world are supporting research and development of clean coal technologies. It is crucial for new coal technologies to reach the market in an appropriate time, with less impact on environment, and also at a competitive cost.

1.1. Gasification

Greenhouse gas (GHG) emissions from thermal power plants based on fossil fuel combustion are considered as one of the main source for global climate change [2]. A number of developing technologies towards carbon capture and sequestration are currently under progress; including pre- and post-combustion capture and oxy-fuel combustion [3]. Coal gasification has much contemporary importance because of the fact that it is considered as the technology for the future in terms of efficiency and cleaner environment. Gasification converts heated solid fuels (coal or biomass or other organic materials) using only partial oxidant concentration (compared to that for full conversion or combustion) Therefore, the generated gas after this partial conversion or oxidation has a very low level of CO₂ and a large proportion of H₂ and CO, with smaller concentrations of hydrocarbons. This gas is called synthetic gas (or syn-gas) and can be combusted in a gas turbine or gas engine or in a burner. It can also be used as a feedstock for the production of various chemicals including liquid fuels through catalytic chemical processes.

An Integrated Gasification Combined Cycle (IGCC) has higher overall efficiency than a direct combustion process and the volume flow of the gas that needs to be cleaned is also reduced. In fluidized bed gasifiers, the coal enters the top of the gasifier, whereas the fluidizing gases (oxidant, steam, recycled gas) enter at the bottom for complete mixing with the coal particles and to ensure an isothermal operation. During coal gasification, particles become smaller and lighter and could be entrained in the product gas. Hence, the fluidizing gas flow rate must be sufficient enough to fluidize and gasify the coal particles for minimizing the particle entrainment. In entrained flow gasifiers, finely ground coal particles are injected together with the oxidant (steam and oxygen) and can either flow upward or downward through the gasifier. The residence time of the coal in these gasifiers is in the order of seconds and they should be operated at high temperatures to achieve high carbon conversion rates. The selection of a gasification process to produce syngas for energy generation or chemical production depends on numerous factors governed by the feedstock nature, plant requirements and environmental regulations. The main factors include coal and ash properties. Steam and air, or pure oxygen and even CO₂ can be used for feedstock gasification. Syngas composition also strongly depends on the gasifier, oxidant, coal types and operating conditions. Commercial gasifiers are typically optimized to enhance the gasification of a particular coal; however, most gasifiers have considerable flexibility towards different coal types. The main reactions occurring during coal gasification process are summarized in **Table 1**.

1.2. Thermogravimetry and mass spectrometry

In general, coal conversion technologies and virtually all end uses of coal are mainly based on the application of heat. The structural changes of coal particles upon heating influences all features of coal based technologies. During thermal decomposition of coal when heated towards higher temperature, it undergoes a variety of physical and chemical changes at which occurs. Hence, thermal decomposition of coal has been investigated under many aspects [4–7].

Reaction	Equation	Enthalpy
Combustion	$C + O_2 \rightarrow CO_2$	$\Delta H = -405.9 \text{ kJ/mol}$
	$C + 0.5 O_2 \rightarrow CO + H_2$	$\Delta H = -123 \text{ kJ/mol}$
Steam gasification	$C + H_2O \rightarrow CO + H_2$	$\Delta H = 118.9 \text{ kJ/mol}$
Hydrogasification	$C + 2H_2 \rightarrow CH_4$	$\Delta H = -87.4 \text{ kJ/mol}$
Boudouard reaction	$C + CO_2 \rightarrow 2CO$	$\Delta H = 159.7 \text{ kJ/mol}$
Water-gas-shift	$CO + H_2O \rightarrow CO_2 + H_2$	$\Delta H = -40.9 \text{ kJ/mol}$
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$	$\Delta H = -206.3 \text{ kJ/mol}$

Table 1. Main reactions occurring during coal gasification process [4].

Thermal analysis is mainly applied to evaluate the thermodynamic properties which are required to establish the behavior of materials which has undergone various heating and cooling rates, in inert, reduction or oxidation atmospheres or under different gas temperatures and pressures. Thermal analysis encompasses a cluster of techniques wherein a physical property of a substance is estimated under controlled temperature program. The thermogravimetric analysis (TGA) of coal is a well-known technique to understand the change in the structural features of coal during combustions [8–12].

Thermogravimetry coupled with mass spectrometry (TG-MS) is a well-recognized technique in the pyrolysis research of solid fuels. It can deliver real-time and elaborate information on the weight loss and gas release features as a function of temperature [9–15]. MS method is used to identify the gaseous species released from the sample, according to their molecular mass. All coals release volatile matters when heated. The quantities evolved depend upon coal rank, the heating rate, the temperature to which the coal is heated and the operating pressure. The chemical composition of coal has a strong influence on its combustibility.

The application of non-isothermal pyrolysis associated with released gas analysis delivers a qualitative data of the pyrolysis characteristics of coal [16]. Pyrolysis is a substantial intermediate stage over the major coal conversion process stages, such as combustion, gasification, carbonization and liquefaction. This method is considered as simple and effective method for removing sulfur from coal [17–23] as well. Mahajan et al. [24] reported the DSC results for 12 coals using various ranks in the helium ambience at 5.6 MPa and temperature up to 580°C with a heating rate of 10°C min⁻¹. The major conclusion is that the thermal effects during pyrolysis of coals ranks from anthracite to bituminous were endothermic. Exothermic heats were detected only in the case of sub-bituminous coals or lignites. Whereas, the net thermal effect was found to be strongly rank dependent. Morris [25] performed the pyrolysis experiments in the temperature range from ambient to 900°C for various particle sizes, and established an empirical correlation's for the evolution rates of carbon monoxide, hydrogen, and methane as a function of particle size and process temperature. Nali et al. [26] have conducted the pyrolysis coupled with gas chromatography and mass spectrometry investigation on lignite which is originated from Poland and USA. Seo et al. [27] have reported the coal pyrolysis features using thermo-gravimetric analysis and gas release measurements of the evolved species for Chinese coals in non-isothermal conditions at different heating rates.

Jayaraman et al. have produced char particles from Indian [28] and Turkish high ash coal [29] using a high speed thermogravimetry system (NETZSCH STA 429 thermal analyzer with platinum furnace) at the heating rates of 40, 100, 500, 800 and 1000 K/min in argon ambience. After pyrolysis, chars were cooled to ambient temperature in argon ambience and used for further gasification studies. A separate water vapor (steam) generator is attached with the TGA system. Steam generator and its transfer lines are preserved at 180 and 150°C respectively. The produced char particles are heated with a heating rate of 40 K/min under argon ambience up to 850°C and further gasified in steam, CO₂ and blended (steam+ CO₂) ambience under various partial pressure conditions. The gasification experiments have been repeated

for 900, 950 and 1000°C. Argon is used as carrier gas for steam. In the gasification tests, the mass of the char samples are maintained around 15 mg. The TGA system records the weight loss from a highly sensitive analytical balance and it has the resolution of 10⁻³ mg. The sample temperatures are measured using thermocouples which were connected at the bottom section of the crucible, which holds accurately underneath the sample layer. The experimental setup used for the gasification studies was presented in detail elsewhere [13–16, 28–31]. The ultimate and proximate analyses results of the investigated high ash Indian and Turkish coals are given in Table 2.

1.3. Coal pyrolysis and gasification under low heating rates

The experiments are performed in argon and steam (WV – water vapor) ambience to estimate the thermal decomposition of the coals. It can be seen from the TG-DTG curves that the Turkish and Indian coals are pyrolysed in the temperature range from 300 to 750°C, presented in Figures 1 and 2. The gaseous species evolution as a result of decomposition of the coal sample was concurrently monitored by mass spectrometry during the TG tests. The mass spectra of the evolved gases during pyrolysis and gasification are depicted in Figures 3 and 4 for the Turkish and Indian coals respectively. A comparison of the evolution of the main species produced during thermal decomposition shows a relationship between volatile matter content and the species emissions. Wilson [32] has reported that the steam decomposition and coal gasification commence from 800°C. At temperatures below 350–400°C, different processes take place prior to primary pyrolysis, i.e. disruption of hydrogen bonds, vaporization and transport of the non-covalently bonded molecular phase [33].

Figures 1 and 3 show a first mass loss peak around 300°C corresponding to the elimination of moisture. The second peak, in which the major weight loss observed in the range of 350 to 700°C which is mainly due to the primary devolatilisation, during which carbon, hydrogen and oxygen compounds are evolved (Figures 3 and 4). The primary carbonization initially starts at 350°C in which the release of carbon dioxide and hydrogen has noticed. When the temperature is increased, methane and other lower aliphatics are also released together with carbon monoxide, hydrogen and alkyl aromatics. From the DTG curves of Turkish and Indian coal decomposition, it is concluded that the rate of devolatilization varies with coal type. The major devolatilization process is completed at around 550°C. Whereas, the secondary devolatilization of the coal is occurred over the

Coal type	Proximate analysis				Ultimate analysis				Heating value, MJ/kg
	Moisture	Ash	Volatile matter	Fixed carbon	C	H	N	S	
Indian coal	2.95	45.85	25.62	25.52	39.43	2.52	0.97	0.45	15.23
Turkish coal	11.15	32.33	36.4	21.7	54.34	3.74	1.57	3.74	10.81

Table 2. Proximate and ultimate analyses of Indian and Turkish high ash coal (as received).

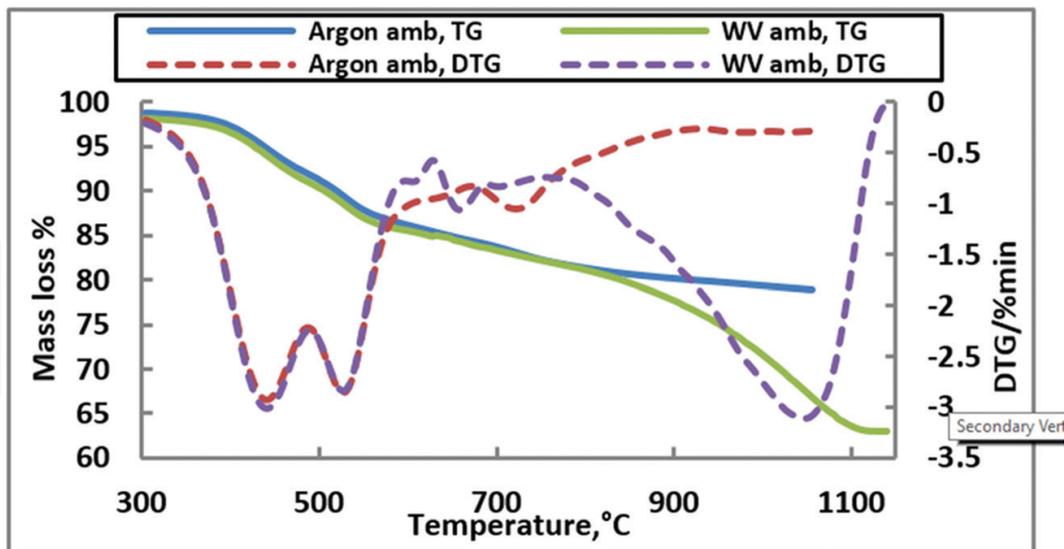


Figure 1. TGA curves of Turkish coal [14].

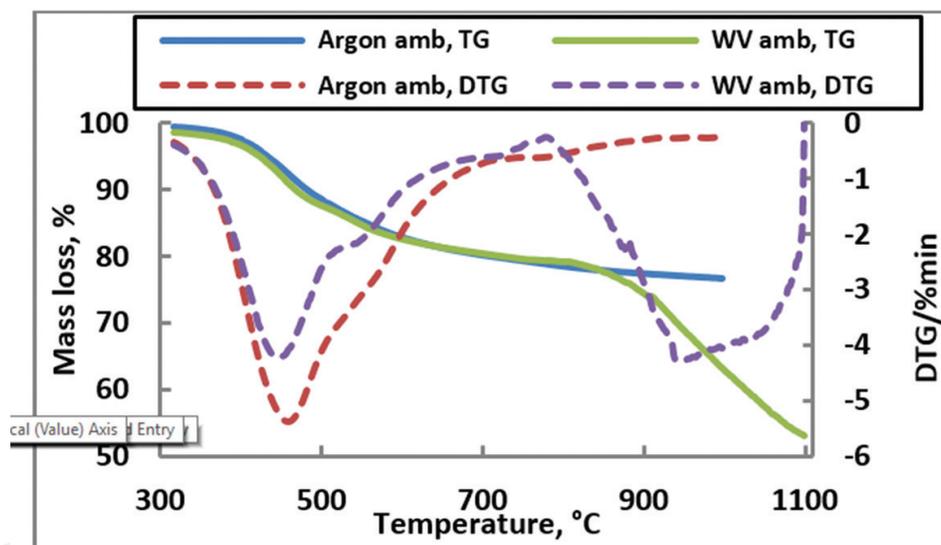


Figure 2. TGA curves of Indian coal [14].

temperature range from 600 to 800°C, produces CO , CO_2 , H_2O , H_2 and CH_4 as the major products. The maxima in the DTG curve corresponds to maximum gas release rates. H_2 peaks were detected at the temperature range from 500 to 750°C. The H_2 evolved is, in fact, only a part of the hydrogen present due to the higher volatile matter content in the coal. It can be seen in **Figures 2** and **4** that the formation of CH_4 starts at temperatures higher than 450°C. In general, CO_2 is formed from aliphatic and aromatic carboxyl and carboxylate groups at low temperatures from these high ash coals. Thus thermal decomposition is a compound process which involves coal devolatilization and pyrolysis. The gasification process is also a major complex and several competing processes impact to the thermal decomposition curves (**Figure 5**).

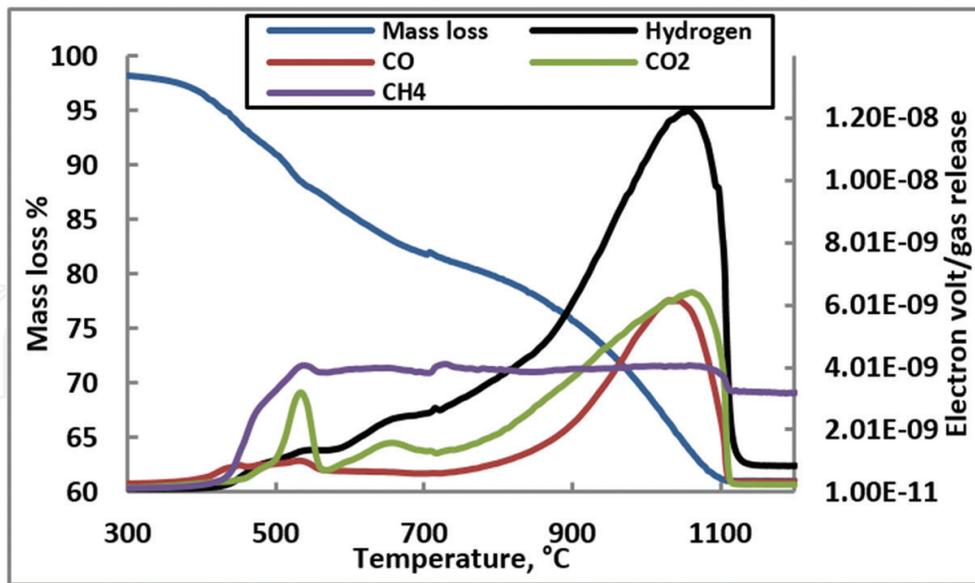


Figure 3. Mass spectrum analysis (gas detection).

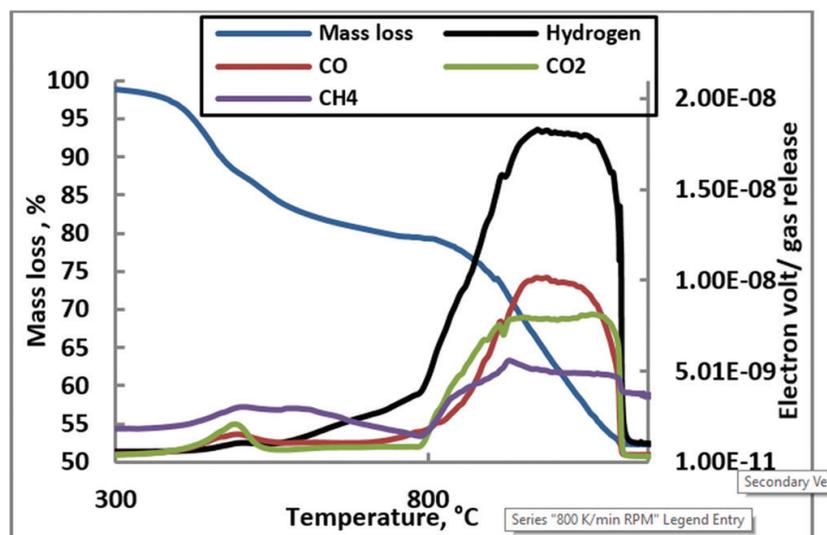


Figure 4. Mass spectrum analysis (gas Turkish coal samples at water vapor detection) of Indian coal samples at water vapor ambience [14].

1.4. Coal-char production under high heating rates

The TG experimental results, obtained as mass loss versus time data, are converted according to conversion level (X) versus time profiles (on ash-free basis).

$$X = \frac{m_o - m}{m_o - m_{ash}} \quad (1)$$

$$R = -\frac{dW}{dt} \frac{1}{m_o - m_{ash}}$$

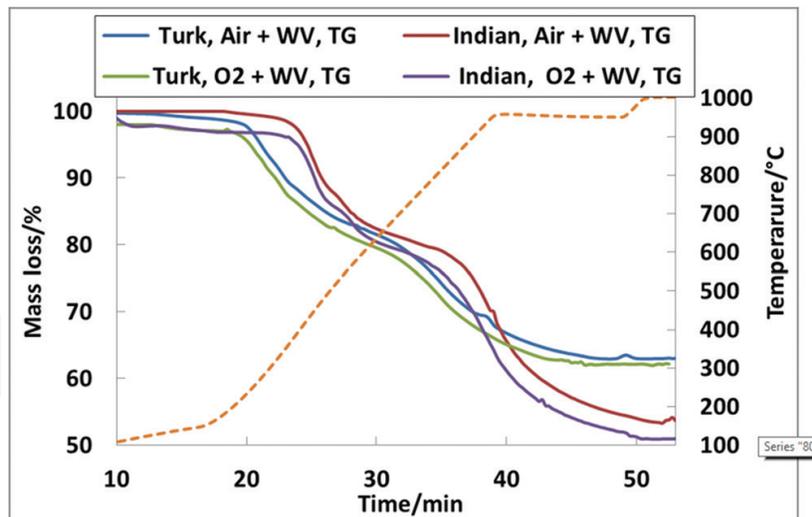


Figure 5. Comparison of TGA curves at blended gases of Turkish and Indian coal samples [14].

where m is the instantaneous mass of the sample, m_0 is the initial mass, and m_{ash} is the residual mass, and R is the reaction rate at time t . The apparent reaction rate is computed as a differential of the conversion degree versus time, denoted as $\frac{dX}{dt}$. The calculations from Eq. (1) are obtained and its validity is based on the assumption that reactions of mineral matter with steam and CO_2 is not occurred during gasification.

The half-life $t_{0.5}$ [34] was used as a reactivity index in order to describe the gasification reactivity of coal chars for quantitative comparison. $t_{0.5}$ denotes the time required for 50% conversion of the carbon in chars.

Pyrolysis tests of Indian and Turkish coal samples are carried out using the high heating rate thermogravimetric system at the heating rates of 40, 100, 500, 800, and 1000 K/min in an argon ambience for different particle sizes. **Figure 6a** illustrates the curves of Indian coal mass conversion level and temperature versus time during pyrolysis. The particle temperature is preserved constant for 5 minutes once it attains the value of 1000°C to make assure the completeness of the pyrolysis process. As anticipated, the mass loss curves reveals that the devolatilisation (or char generation) essentially depends on the heating rate. For example @ 1000 K/min, the total devolatilisation occurs in 1 minute compared to more than 10 min at 100 K/min. Pyrolysis studies of Turkish coal samples are performed using high heating rate thermogravimetric analysis with the heating rates of 100 K/min, 500 K/min and 800 K/min in argon ambience, as shown in **Figure 6b**.

As the heating rate increases, the pyrolysis process is observed independent of particle sizes and the rate of volatilization is almost constant in the initial stage, illustrated in **Figure 6c** and **d**. It can be observed that 800 μm particles exhibit the maximum DTG value of 80%, compared to the 50% value for 3 mm particles. It is noticed that the effect of particle size is not influential at low heating rates. Whereas, the DTG_{max} variation is significant at 1000 K/min, in which it is raised by 20% when the particle sizes are reduced from 900 to 60 μm . Owing to the variation in the ash and volatile content of the Turkish coals, larger particles have comparatively

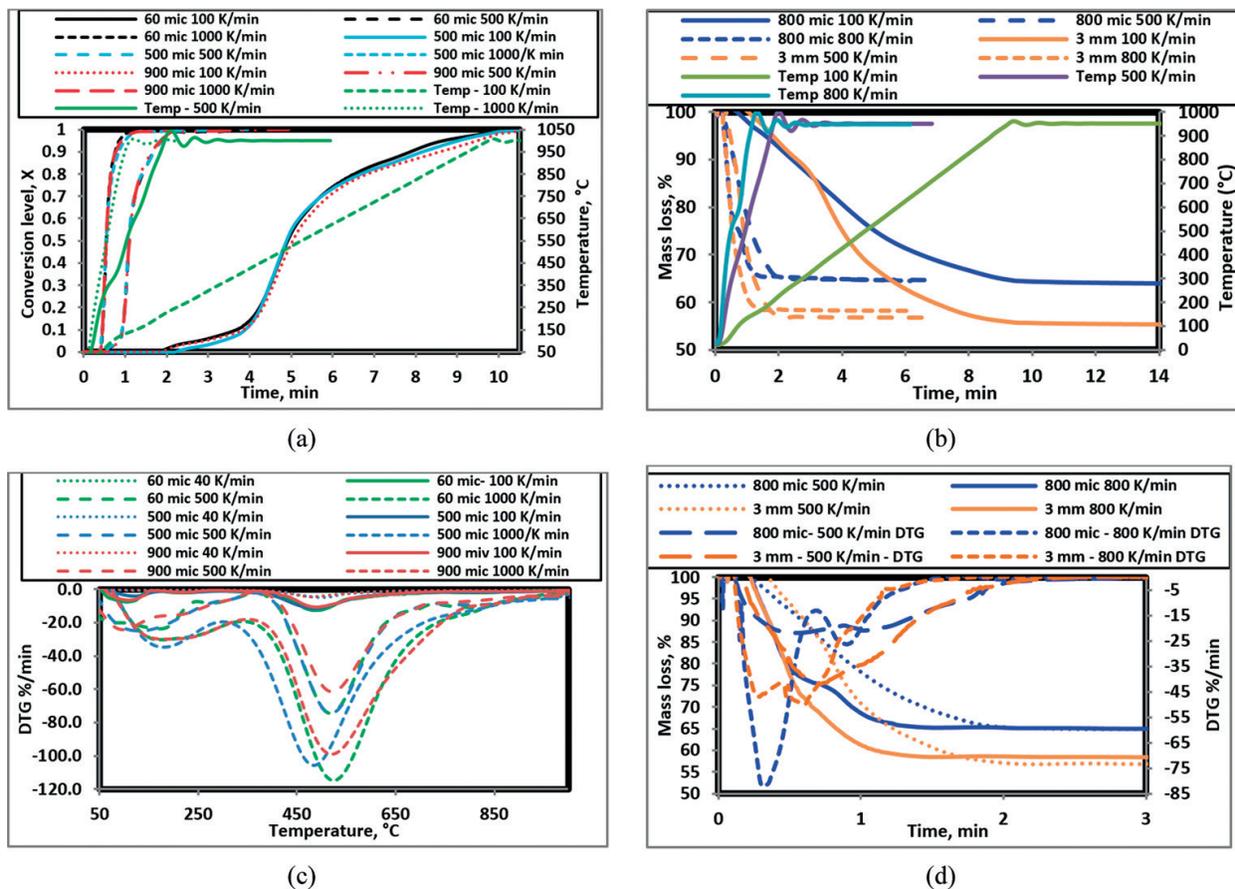


Figure 6. Char generation from Indian and Turkish coal in argon ambience. (a) Indian coal [34] (b) Turkish coal [36], (c) DTG – Indian coal [34], (d) DTG – Turkish coal [55].

higher content of residual char-mass, therefore, the DTG is quite low for 900 μm particles. This aspect can be elucidated by the fact that large particles exhibit more resistance to volatiles escape, in that way the secondary reactions rate increased and as a result of carbon deposition [37]. It can be seen that 800 μm particles shows the maximum DTG value of 80% when compared to the 50% value for 3 mm particles. Owing to the variations in the ash and volatile content of the different particle sizes, smaller particles exhibit relatively higher char mass. The effects of particle size can be directly related to heat and mass transfer effects and limitations.

The DTG results show that the maximum thermal degradation (DTG_{max}) of coal particles are shifted towards higher temperature as the heating rate increased. This is caused by differences in heat transfer and kinetic rates, thereby delaying sample decomposition [35, 37–39]. Hence, the heating rate mainly influences the primary pyrolysis stage of the coal, while the maximum weight loss rate and the corresponding temperature increases with heating rate. In addition to that, the primary pyrolysis is occurred over the temperature range from 300 to 600°C, whereas the secondary pyrolysis started at the temperature from 600 to 800°C at 40 K/min, represents almost agreed well with the results reported by Zhang et al. [30]. With increase in the heating rate, the primary pyrolysis stage of coal is prolonged up to 700°C and subsequently the secondary pyrolysis stage exhibited up to 900°C for 1000 K/min. These

features emphasize that the occurrences of thermal lag increases along with the pyrolysis of heating rate of the coal, similar to the results reported in the literatures [28, 35, 37–39].

1.5. Coal-char characterization studies

The char particles produced from Indian coal are characterized using ultimate and proximate analyses; their surface features were determined by Scanning Electron Microscopy. The ultimate and proximate analyses of the 60 μm (mic- micron) and 900 μm chars produced at 40 K/min are given in **Table 3**. It is noted that 900 μm char particles displayed rather additional ash and have lower heating value as compared to 60 μm char. The char structural properties resulting from different heating rates are investigated using BET analyses. The surface area analysis (BET) depicted that the char particles generated from higher heating rates show higher surface area as illustrated in **Table 4**. The surface area of the char particles is almost doubled when the heating/production rate is raised from 40 k/min to 800 K/min. The BET surface analysis results is well agreed to other studies in which the char particles are produced at low heating rates [40, 41]. Lua et al. [42] also investigated that the growth of pores during initial pyrolysis is mainly due to the higher volatile matter release rate. Chars produced from high heating rate have already their pores open and exhibits high surface area [43, 44], while the chars prepared from low heating rate possess a less-developed reactive surface and a narrower porous network, as presented in the SEM images (**Figure 7**) and confirmed by BET surface area analysis [35, 37]. Hence, the heating rate affects the coal devolatilisation rate, thereby it also influences the pore structure of the generated char particles and the probability of participation of active sites located in micropores.

1.6. Coal – char steam and CO₂ gasification

1.6.1. Effect of char heating rate

The pyrolysis heating rate of char has a marked influence on the gasification reactivity of the char. This study is to investigate the pathways for char-CO₂ (Boudouard reaction: $\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$) and its gasification rate [35]. **Figures 8–10** present the char conversion level of 900 μm char particles in steam and CO₂ gasification which are produced with different pyrolysis rates. The gasification process is conducted under isothermal regimes over the temperature of 900, 950 and 1000°C which are almost identical to the operating conditions of fluidized bed gasifiers. These outcome affirms that the chars produced at high heating rates exhibit better gasification rates

Proximate analysis				Ultimate analysis (dry basis)				Heating value
Particle size	Moisture	Ash (dry basis)	V.M (dry basis)	C	H	N	S	HCV
	%	%	%	%	%	%	%	MJ/kg
60 μm	2.44	64.4	2.33	36.6	0.39	0.75	0.59	12.01
900 μm	2.25	72.2	2.62	28.3	0.34	0.44	0.5	9.71

Table 3. Proximate and ultimate analysis of the Indian char produced at 40 K/min.

S.no	Heating rate of the char production, K/min	Surface area (BET), m ² /g
1	40	24
2	100	28
3	500	35
4	800	66

Table 4. Surface area of the 60 μm char particles produced at different heating rates.

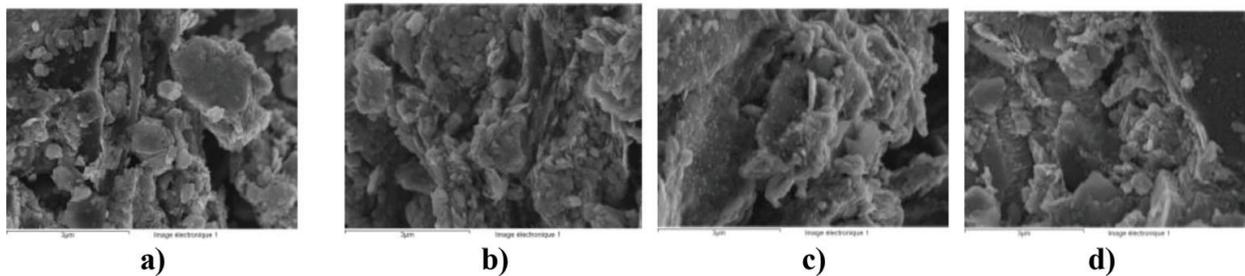


Figure 7. SEM images of Indian coal-char particles produced at various heating rates [35] (a) 40, (b) 100, (c) 500, (d) 800°C/min.

in all the cases over the three tested temperatures, also reported by other studies [34, 35, 45]. Wu et al. [46] and Chen et al. [47] have reported that the coal-char produced from fast pyrolysis show high gasification reactivity mainly because of the variation in the external surface area. Some authors [44, 46] also reported a identical behaviour from the coal-char and biomass-char gasification [10, 48, 49]. Wu et al. [46] also highlighted that surface area is among one of the main factors which majorly influence the gasification reactivity of carbonaceous materials. In general, the coal structure comprises randomly oriented large number of pores which is ranging from

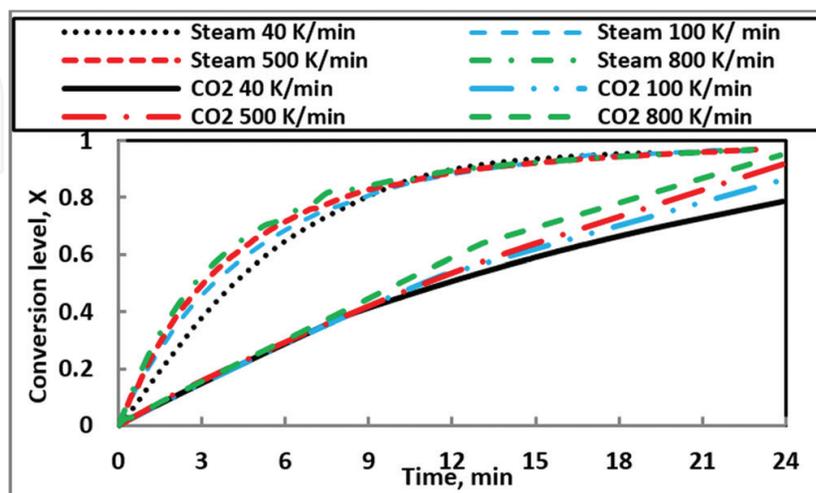


Figure 8. Comparison of Indian coal-char.

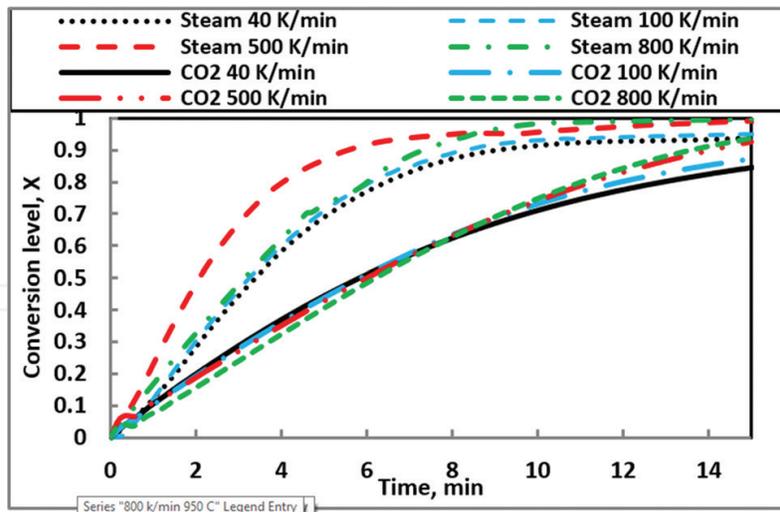


Figure 9. Comparison of Indian coal-char gasification rate produced at various heating conversion rate produced at various heating at rate at steam and CO₂ ambience with the coal rate at steam and CO₂ ambience with the size of 900 micron at 950°C coal size of 900 micron at 1000°C.

micropores (pore diameter < 2 nm) to macropores (pore diameter > 50 nm). The coal is subjected to structural modifications during the pyrolysis process owing due to the phenomena for instance pore enlargement, coalescence or blocking [50]. Heating rate of the coal have an effect on devolatilisation rate, hence these also impact the pore structure of the produced char particles. The participation probability of active sites towards gasification positioned in micropores is relatively higher from high heating rate chars. Both large (macro-and mesopores) and micropores pores are important in coal gasification [51]. These features have to be ascribed between the two contending effects which are regarded with char structure evolution throughout the reaction course: Initial pore growth in the early stages which are subsequently followed by gradual collapse of the pore structure that is mainly because of the coalescence of neighboring pores as gasification further advanced. The reacting gas enters into the macro-and mesopores

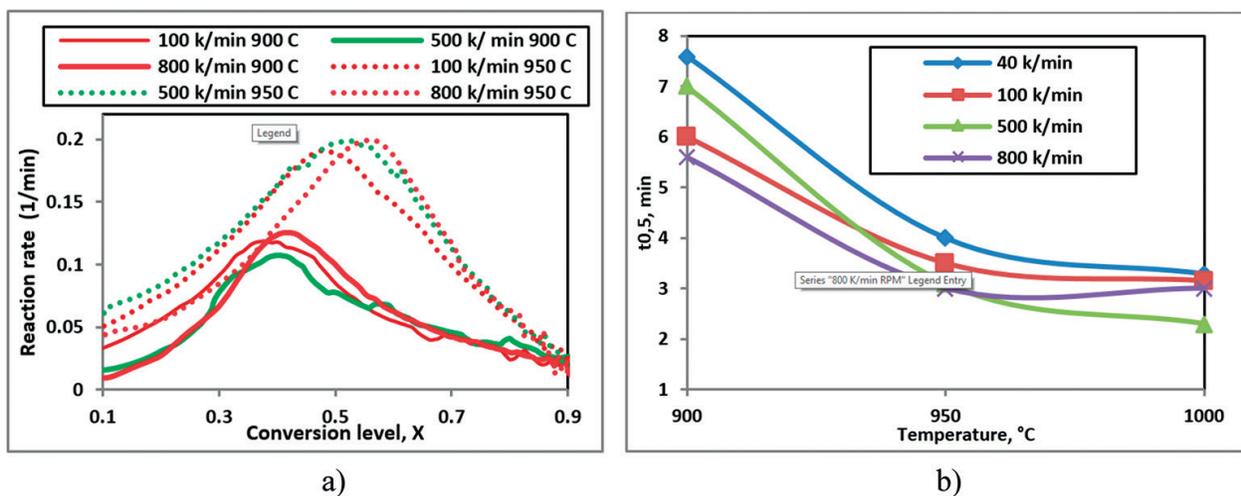


Figure 10. Gasification reactivity of 900 μm Indian coal-char in steam ambience. (a) Reaction rate vs. carbon conversion, (b) time required for 50% conversion level.

which are act as channels to the active sites in the micropores in which the char gasification reaction occurred. The diffusion of product gas occurred through the porous structure of the solid which pave the way to variations arises in the number of carbon-active sites accessible for the gasifying agents. These effects are significant at later stages with CO₂ gasification at high temperatures which is mainly observed beyond the conversion level of 0.4. Initially, the reaction rate is increased with different heating rate of char and passes through a maximum in the conversion range of about 30–70% as illustrated in **Figure 10a**. The half-life of each char have lessen effect as gasification temperature increases and this effect of gasification temperature on $t_{0.5}$ is relatively small above the gasification temperature of 950°C as represented in **Figure 10b**, whereas the heating rate effect exists. These type of trends are also noticed to the particle size of 60 and 500 μm in CO₂ gasification [35].

1.6.2. Effect of gas temperature and gasification agent

It can be noticed that the rate of a reaction influenced by the reaction temperature which emphasize the reaction rate will be higher at high temperature. Besides, the gasification time also reduces and also the influence of the gasification reactions towards higher particle temperature subsequently it increases the char conversion rate, mainly based on the higher activation energies from these reaction temperature, as expected. **Figures 8 and 9** illustrated the steam ambience outcome which depict that the conversion degree steeply rises from starting of the reaction until it reaches the conversion degree of approximately 0.65, 0.85, and 0.95 for the temperatures of 900, 950, 1000°C respectively [35]. Afterwards, very slow reaction is observed and approach towards plateau until complete conversion. The initial steep increment in the conversion degree can be directly related with the rapid evolution of the surface area, which is continued upto collapsing of all the pores. As the reaction surface is reduced, accordingly the gasification rate is also decreasing. These results are in accordance with the findings of other studies [52, 53]. For the same oxidant to coal ratio of the corresponding gasification agents, the gasification rate of steam is about two to three times faster than CO₂ at lower temperature ranges up to conversion level of 0.5. Whereas, gasification rate also increases along with the gasification temperature which is well agreed with the reported studies [44, 46, 47, 54].

1.6.3. Effect of particle size on CO₂ gasification

The particle size effect on Indian coal-char conversion is illustrated in **Figure 11**. During the starting stage of gasification, similar conversion rates are observed, as the time continues, the gasification rate variation diversified among the sizes of the particles. The complete gasification of the 60 μm particles are occurred within 20 min, against with larger particles. As expected, higher gasification rates are noticed with smaller particles, the main features like diffusion restrictions and heat transfer limitations cannot be ignored while considering the high ash coal, over the temperature and sizes of coals tested [35]. As noted earlier [48, 54–57], the reduction in coal particle size, the TG and the DTG curves move into lower temperature regions, and burning rate increment of coal is seen so time for burnout is reduced. Owing to the fact that the more specific area available with the smaller pulverized coal particles influences the

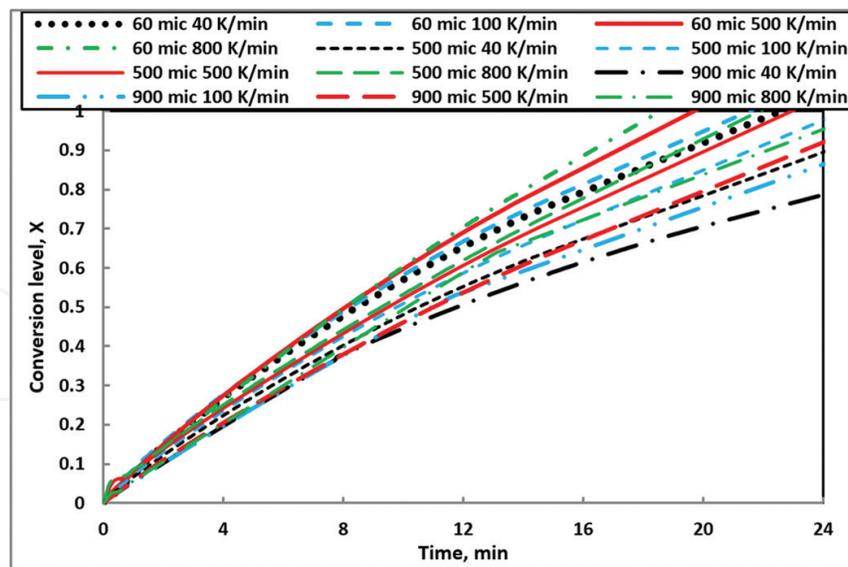
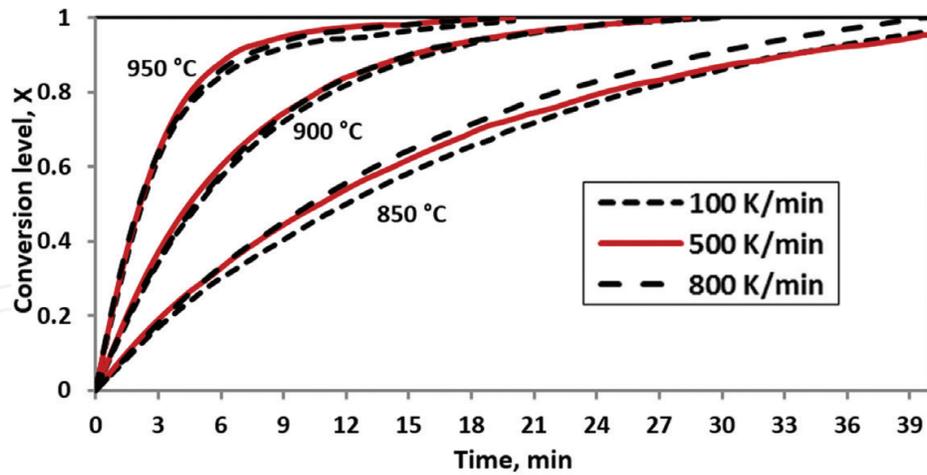


Figure 11. Comparison of Indian coal-char conversion produced at various heating rate at CO_2 ambience of different coal sizes at 950°C .

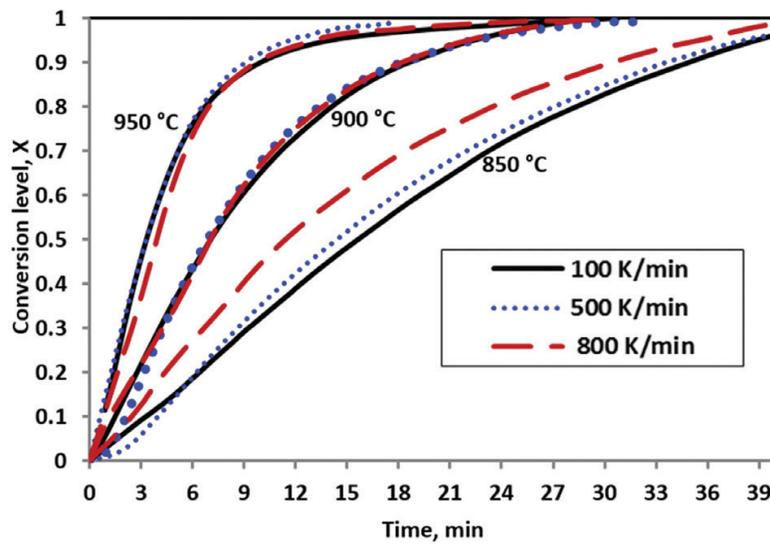
gasification rate over the larger ones, also smaller particles are favorable to the development and ignition of the coal particles. This again affirms that the finer pulverized coal particles are enabling towards gasification performance improvement.

1.6.4. Effect of partial pressure of steam and CO_2 on gasification

The gasification experiments of $800\ \mu\text{m}$ Turkish coal-char are performed under isothermal conditions at the temperatures of 850 , 900 and 950°C at (i) steam partial pressure of 0.9 ; (ii) steam partial pressure of 0.75 ; (iii) CO_2 partial pressure of 0.7 and (iv) blended ambience with steam partial pressure of 0.6 and CO_2 partial pressure of 0.2 , as illustrated in **Figures 12** and **13**. The char gasification in steam with the partial pressure of 0.75 proceeded slowest whereas gasification of char proceeded fastest with higher concentration of H_2O when the char is produced under low heating rates. On the other hand, the partial pressure and temperature effects on $800\ \mu\text{m}$ char conversion during the gasification in H_2O are weaker when the char particles were produced at higher heating rates [36]. **Figure 13a** shows that an increase in the pyrolysis heating rate and also of the gasification temperature increases the gasification reaction rate under CO_2 ambience. **Figure 13b** illustrates the effect of the blended ambience on gasification rate. Investigations concerning the reactions of H_2O and CO_2 with high ash chars during gasification are quite limited. According to reported results [29, 43, 47, 58–64], possibility of two surface reaction mechanisms to be emerged. First approach claims that $\text{C}-\text{H}_2\text{O}$ and $\text{C}-\text{CO}_2$ reactions takes place in common active sites, whereas the another approach asserts that the reaction of CO_2 and steam happen in separate active sites. The researchers [59, 65] also indicated that the overall carbon-conversion rate in the presence of CO_2 and steam/ H_2O might be relatively more when compared to the sum of single ambience char reactivities, which is otherwise considered that during the mixed atmosphere gasification, there is a possibility of



a)



b)

Figure 12. Comparison of Turkish coal-char gasification rate of 800 micron in steam at various partial pressure (a) steam partial pressure – 0.9 (b) steam partial pressure – 0.75.

synergetic phenomenon between the gases. In addition to that, even though the reactions are occurred on separate active sites [59, 65], an active cooperation between the gases is for seen for better accessibility to the reactive surfaces, which implies that one reactant may support to improve the char reactivity regarding to the second gas by the way of either creating additional porosity or by retenting the catalytic mineral species inside the char. **Figure 13** presents the conversion degrees versus time plots. The conversion degree graphs comparison has shown for steam-CO₂-char gasification at corresponding temperatures, the effect of the pyrolysis heating rate on mixed gasification is examined. While comparing the pyrolysis heating rate impact on the gasification time in single atmospheres, only slight differences are observed with blended ambience imparted. It can be seen that some decrement in the reaction rate for the blended ambience at the lowest gasification temperature (850°C). At higher gasification temperatures, this effect almost disappears. Thus also

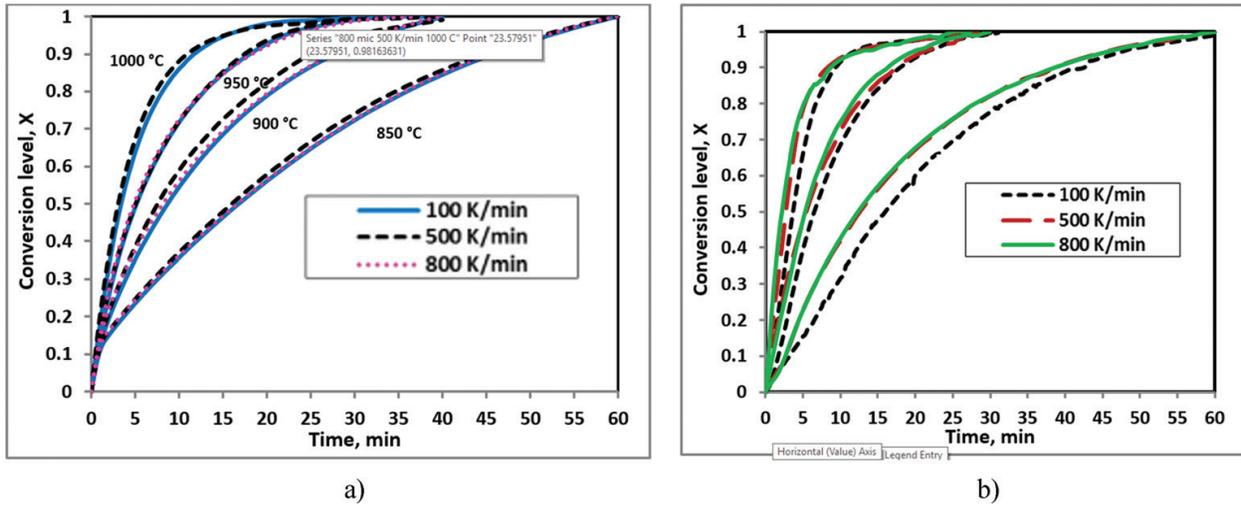


Figure 13. Comparison of Turkish coal-char gasification rate of 800 micron in CO₂ and steam + CO₂ blended ambience. (a) CO₂ ambience, (b) steam +CO₂ blended ambience.

reported from various studies [43, 44, 47, 59, 66] these results indicate that the introduction of CO₂ would not inhibit the steam-char gasification reactions, at least at high gasification temperatures, and do not compete for reactive sites.

1.7. Coal-char gasification kinetics

Various models have been reported in the literature to evaluate the gasification reactions of coal-char steam and CO₂ ambience. Three models are considered in the kinetic analysis, in which the assumption of one-step reaction mechanism are chosen. The variation in the apparent reaction rate can be termed as follows:

$$\frac{dX}{dt} = k(T)f(X)$$

where k is the rate constant, temperature dependent, T and $f(X)$, explains the changes in the physical or chemical properties of the material as the gasification proceeds which corresponds to the selected n^{th} -order expressions. Based on the Arrhenius relationship, the kinetic constant as a function of temperature is derived,

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (2)$$

where E and A are the activation energy and the pre-exponential factor respectively, and T is the absolute temperature.

In the present study, three n^{th} -order models were applied to facilitate the reactivity description of the studied chars: the volumetric model (VM), the grain model (GM) and the random pore model (RPM). All models provide various expressions for the term $f(X)$ [35, 36].

The VM is considered as simplest model, in which the heterogeneous gas–solid reaction of coal gasification is converted into a homogeneous reaction using the assumption of uniform gas diffusion within the entire particle and char reaction over the all possible directions, together with outside and inside of the particle surface [67].

The reaction rate is represented based on the kinetic expression by equation.

$$\frac{dX}{dt} = k_{VM}(1 - X) \quad (3)$$

or in the integrated form by Eq. (2):

$$-\ln(1 - X) = k_{VM} t$$

The GM or shrinking core model, proposed by Szekely and Evans [68], in which the assumption of a porous particle that comprises of an assembly of uniform nonporous spherical grains and the occurrence of reaction as observed on the surface of these grains. The porous network is established using the space between the grains. The shrinking core behaviour is ascertained in each of these grains during the reaction stage. When the reaction proceeds gradually inside the particle, finally the ash layer retains. In chemical kinetics controlled regime, the expression for the overall reaction rate in these models is expressed as [67]:

$$\frac{dX}{dt} = k_{GM} (1 - X)^{2/3} \quad (4)$$

and in an integrated form by

$$3[1 - (1 - X)^{1/3}] = k_{GM} t \quad (5)$$

The RPM model considers the overlapping of pore surfaces, which reduces the area available for reaction [69]. The fundamental equation of this model follows:

$$\frac{dX}{dt} = k_{RPM} (1 - X) \sqrt{1 - \psi \ln(1 - X)} \quad (6)$$

The maximum reactivity can be able to predict from this model as the reaction proceeds, since it considers the competing effects of pore growth during the starting stages of gasification, and the pores collapse is observed owing to the coalescence of adjacent pores throughout the reaction. The main two parameters are considered in the RPM model, the reaction rate constant, k_{RPM} , and ψ , this parameter narrate the pore structure of the unreacted sample ($X = 0$). If, initial porosity, ϵ_0 surface area, S_0 and pore length, L_0 of the solid are identified this parameter is expressed as

$$\Psi = \frac{4 \pi \pi_0 (1 - \epsilon_0)}{S_0^2}$$

Moreover, the structural parameter is computed using the value of maximal conversion degree of the solid fuel, X_{\max} , for which the utmost reaction rate is noticed. The value of ψ can be evaluated based on the relation [53, 70]

$$\Psi = \frac{2}{2 \ln(1 - X_{\max}) + 1}$$

The rate constant is evaluated from the integrated form of relation (5) which provides

$$\frac{2}{\psi} (\sqrt{1 - \psi \ln(1 - X)} - 1) = k_{\text{RPM}} t$$

In order to evaluate the applicability of the chosen kinetic models and establish the kinetic behavior of the tested samples, experimental data is used to fit the models. At specific conversion level, the reactivity is calculated. To determine the kinetic parameters, reactivities at 10–50% of char conversion are frequently used; the latter is generally used in various similar investigations [35, 44]. In our investigation, the reaction rate is nearly stable until 50% conversion level as illustrated in **Figure 10a**, consequently, for calculating the kinetic parameters, this is considered as a reference. The reaction rate constants are determined using the slopes of the linearized relationships represented in the Eqs. (2), (3) and (5) depending on the test results of char conversion X , using the linear regression, for the VM, GM and RPM models respectively. Estimation of the rate constants are performed from the data for three temperatures. The kinetic parameters are evaluated using Arrhenius relationship, the reciprocal relationship between the logarithm of the rate constant and the absolute temperature ($1/T$) of the reaction arrived by each model at the studied temperature range is estimated.

1.8. Indian coals

The Arrhenius plots for the 900 μm chars are shown in **Figure 14**. Based on the slope and the intersection values, the activation energy E and the pre-exponential factor A were computed for the studied models. **Tables 5** and **6** show the summarized kinetic parameters (E and A) estimation from the test data for three models. A small inconsistency is noticed in model fitting for the char gasification rate at 100 K/min. Whereas, the other samples and models are found very satisfactory fits. As represented in **Figure 14**, observable changes in the slopes of the Arrhenius relations were noticed from 950 to 1000°C, affirms that temperature increment does shift the reactions from chemically controlled to diffusion controlled regimes. The slopes of the relationships calculated for the VM and the RPM models are an almost parallel line which indicates that almost similar activation energy values are calculated from these models. The activation energy of the steam gasification is varying from 129 to 177 kJmol^{-1} using GM model, and around 110 kJmol^{-1} using RPM model, and the reaction rate constants from 4×10^3 to $3 \times 10^6 \text{ min}^{-1}$ which are similar to values obtained in previous studies [33, 35, 36, 43, 44, 47, 64, 71]. It can be observed that the activation energy of VM model is always higher irrespective of the char generation method.

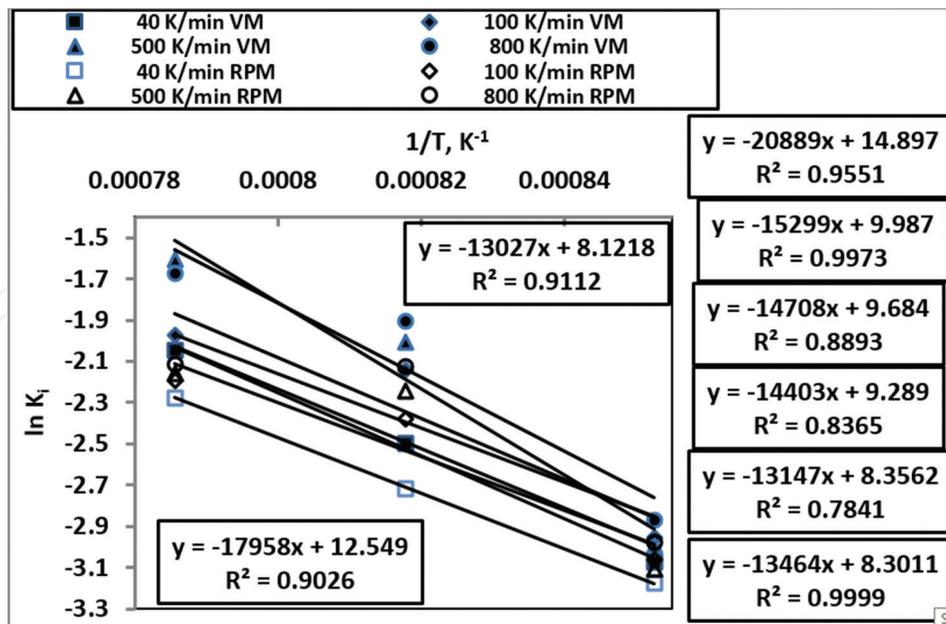


Figure 14. Arrhenius relationships of 900 μm char in steam ambience.

1.9. Turkish coal

Tables 7 and 8 summarize the kinetic parameters (the activation energy, E and pre-exponential factor, A) estimated from the TG data using the models for 800 μm and 3 mm Turkish coal samples. The activation energies estimated by the three models in CO_2 ambience are in the range of 115–138 kJ mol^{-1} . These values are in accordance with the reported literature values [43, 44, 47, 53, 72] even for similar rank of coals. The activation energy of 3 mm particles varies from 156 to 173 kJmol^{-1} and 162 to 196 kJmol^{-1} in steam and blended ambience respectively. These values are in the range of 111–169 kJmol^{-1} for 800 μm particles. These values are in good agreement with the recently reported studies using different reactant concentration and origins of coal [35, 36, 43, 47, 73]. Also, the pre-exponential factors are in the range from 8.22×10^5 to 6.26×10^6 in steam ambience, 8.52×10^3 to 4.23×10^7 in blended ambience. These values are in accordance with those found in the literature [35, 43, 44, 47, 71]. Generally, the RPM model

Heating rate K/min	Activation energy values (kJ/mol)			A/min ⁻¹		
	VM	GM	RPM	VM	GM	RPM
40	127.19	129.87	111.93	2.1E + 04	2.5E + 04	4E + 03
100	122.28	129.50	108.3	1.6E + 04	2.8E + 04	1E + 04
500	173.67	177.57	119.7	2.9E + 06	3.7E + 06	3.3E + 03
800	149.30	144.36	109.3	2.8E + 05	1.5E + 05	4.2E + 03

Table 5. Kinetic parameters of the 900 μm Indian coal-char gasification in steam using VM, GM and RPM models [35].

Heating rate K/min	900 μm			500 μm			60 μm		
	VM	GM	RPM	VM	GM	RPM	VM	GM	RPM
40	214.45	192.	179.88	151.83	138	129.24	161	143.54	134.24
100	202.69	179.41	167.94	189.28	168	157	197	181.27	175.58
500	195.52	175.77	171	210	190	184	194.8	181.31	175.5
800	212	189	184	171.75	156.8	153	207.8	193.27	187.3

Table 6. Comparison of the activation energy values (kJ/mol) of Indian coal-char gasified at 900, 950 and 1000°C in CO₂ ambience.

exhibits relatively lower values of activation energy as comparing with other two models. The changes in the activation energy over the char heating rate are almost consistent regardless of the particle sizes considered in the blended ambience. Moreover, a significant observation from this study is that the gasification activation energy of 3 mm char is higher when compared to 800 μm char particles. This is mainly caused due to the better reactivity potential of 800 μm char owing to its higher specific surface area.

(a) CO₂ ambience									
Heating rate K/min	800 μm			3 mm					
	VM	GM	RPM	VM	GM	RPM			
CO ₂ ambience									
100		132.5	132.51	131.63	132.9	132.93	132.33		
500		115.71	115.63	115.26	130.85	130.66	130.32		
800		128.21	128.47	128.19	138.34	138.35	137.37		
(b) Steam and blended ambience [36]									
Heating rate	100 ml argon (steam – 0.8)			75 ml argon +25 ml CO ₂ (steam – 0.7 & CO ₂ – 0.1)			75 ml argon +50 ml CO ₂ (steam – 0.6 & CO ₂ – 0.2)		
	K/min	VM	GM	RPM	VM	GM	RPM	VM	GM
3 mm									
100	161.2	158.8	156.4	179.0	179.1	179.6	173.9	164.2	162.3
500	172.9	172.9	173.6	172.7	172.6	172.8	169.1	169.1	167.6
800	170.6	170.9	171.2	190.7	190.6	190.9	196.7	196.7	194.7
800 micron									
100	155.3	154.6	154.5	156.7	156.7	156.6	133.4	133.5	131.3
500	132.3	131.8	131.6	111.5	111.8	112.1	127.4	127.6	126.2
800	152.1	152.1	152.2	169.4	169.1	169.0	149.9	150.1	147.1

Table 7. Comparison of the activation energy values (kJ/mol) of 800 μm and 3 mm chars gasified at 850, 900 and 950°C under argon, CO₂ and steam ambience.

(a) 3 mm coal-chars									
Heating rate	100 ml argon (steam – 0.8)			75 ml argon +25 ml CO ₂ (steam – 0.7 & CO ₂ – 0.1)					
	VM	GM	RPM	VM	GM	RPM	VM	GM	RPM
100	1.6E + 06	1.2E + 06	8.2E + 05	1.0E + 07	9.6E + 06	8.8E + 06			
500	6.2E + 06	5.7E + 06	5.1E + 06	6.3E + 06	5.7E + 06	5.2E + 06			
800	4.9E + 06	4.6E + 06	4.2E + 06	4.2E + 07	3.7E + 07	3.3E + 07			
Heating rate	100 ml argon (steam – 0.8)			75 ml argon +25 ml CO ₂ (steam – 0.7 & CO ₂ – 0.1)			75 ml argon +50 ml CO ₂ (steam – 0.6 & CO ₂ – 0.2)		
	VM	GM	RPM	VM	GM	RPM	VM	GM	RPM
3 mm									
100	161.2	158.8	156.4	179.0	179.1	179.6	173.9	164.2	162.3
500	172.9	172.9	173.6	172.7	172.6	172.8	169.1	169.1	167.6
800	170.6	170.9	171.2	190.7	190.6	190.9	196.7	196.7	194.7
800 micron									
100	155.3	154.6	154.5	156.7	156.7	156.6	133.4	133.5	131.3
500	132.3	131.8	131.6	111.5	111.8	112.1	127.4	127.6	126.2
800	152.1	152.1	152.2	169.4	169.1	169.0	149.9	150.1	147.1
(b) 800 μm coal-chars									
Heating rate	100 argon			75 ml argon +25 ml CO ₂					
	VM	GM	RPM	VM	GM	RPM	VM	GM	RPM
100	6.9E + 05	5.4E + 05	4.8E + 05	8.1E + 05	7.6E + 05	6.5E + 05			
500	8.9E + 04	7.3E + 04	6.6E + 04	9.9E + 03	9.3E + 03	8.5E + 03			
800	5.6E + 05	4.8E + 05	4.4E + 05	3.2E + 06	2.9E + 06	2.5E + 06			

Table 8. Comparison of the pre-exponential factor (min⁻¹) of 800 μm and 3 mm chars gasified at 850, 900 and 950 °C in argon, CO₂ and steam ambience.

2. Conclusions

Pyrolysis and gasification studies of Indian and Turkish high ash coal samples have been carried out using coupled TGA-MS method. Coal samples were heated in the TGA apparatus in various gaseous mixture combinations at a temperature range of 25–1250°C under various heating rates. The mass loss data show that the devolatilisation is essentially influenced by the heating rate. Even at higher heating rates, particle sizes do not influence the pyrolysis process and the rate of volatilization is essentially constant. During thermal decomposition and devolatilization of coal, CO, CO₂, H₂ and CH₄ are the major gaseous products. The reaction of coal with steam starts around 800 °C. The complete carbon conversion takes place in the temperature range of 900–950 °C. The syngas production rate is maximum in these temperature limits. In order to study

char gasification, char particles are generated in argon ambience with various heating rates. Char gasification rates investigation in steam and CO₂ blended ambience shows that the pyrolysis heating rate (for char generation) has a considerable impact on the gasification reactivity of the char. Also smaller particles exhibit higher char-CO₂ and char-steam gasification rates. Increasing the temperature from 850 to 950°C leads to the reduction of the time required for 50% conversion by a ratio of more than fourfold. The chars generated under high heating rates present enhanced gasification rates which are mainly due to the alteration of the char pore structure and the accessibility of more active sites to initiate reactions with the gasification agent. The gasification rate of char-H₂O is mainly dependent on H₂O partial pressure, temperature and particle sizes. The maximum reaction rate is shifted to the higher conversion stage for chars produced with high heating rates. The introduction of CO₂ did not inhibit the steam-char gasification reactions and also did not compete for reactive sites. Steam and CO₂ react simultaneously on different active sites on the char surface. Kinetic parameters of the char particles were estimated using different kinetic models. The activation energy for steam gasification is 156–173 kJ/mol, whereas in the steam blended with CO₂ ambience they are between 162 and 196 kJ/mol for 3 mm Turkish coal-char particles. For the Indian coal, the reaction rate is chemically controlled in steam ambience at lower temperatures. The activation energy for steam gasification varies from 122 to 177 kJ mol⁻¹ for different sized char particles. The activation energies estimated by the GM model for the three particles are in the range of 138–193 kJ mol⁻¹. The RPM model predicted values in the range from 129 to 187 kJ mol⁻¹ for CO₂ gasification. The activation energies for char gasification essentially depend on the char generation method (pyrolysis heating rate) and on the particle size.

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