



Exploring pyrolysis characteristics of bituminous coal: a combined modelling and experimental investigation with TG-IR

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Abstract: This research investigates the pyrolysis characteristics of Barapukurian bituminous coal from Bangladesh. The aim is to address the escalating energy demand and mitigate reliance on rapidly depleting natural gas reserves. A thermogravimetry analyser (TGA) combined with infrared spectroscopy (IR) was employed to carry out the study. Kinetic parameters are derived from a two-stage kinetic model, followed by the validation against experimental data. The release of functional groups and the evolution of gas species were identified from IR. Results demonstrate the sensitivity of coal devolatilisation to operating conditions such as sample mass, particle size, and heating rate. The weight loss profile and its first-order derivatives reveal the multi-stage nature of the pyrolysis process, with most of the mass loss occurring during the rapid pyrolysis stage. The average activation energy determined from the kinetic model is 145.7 kJ/mol. The IR spectrum obtained from the study can be categorised into five main groups: OH, group stretching, CH group stretching, oxygen-containing stretching, C=C stretching, and absorption of inorganic metals.

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1. Introduction

Pyrolysis as the first step of gasification is a rapid spontaneous process of releasing volatile organic constituents from solid fuels (Porada et al., 2017). During pyrolysis, the release of volatile matter including tar and char varies with the physicochemical properties of coal and operating conditions (Yu et al., 2007). The extent of the pyrolysis process is heavily reliant on the operating temperature and is considered complete when char gasification initiates (Łabojko et al., 2012). However, in a large system with the presence of variable particle sizes, there is always an overlap between the pyrolysis and gasification reactions.

The operating conditions affecting the pyrolysis product also include pressure, heating rate, particle size, and reactor types (Urych, 2014). During pyrolysis, coal particles fragment due to the breaking of weak bonds between aromatic clusters and thermal shock (Fernando, 2014). The devolatilised part is known as light gas and tar.

Coal pyrolysis generally starts at a temperature of around 350 °C, releasing mainly CO, H₂, CO₂, CH₄, and C₂H₆ (Farrokh et al., 2017). The gas yield during pyrolysis is the results of the decomposition of functional groups and structural components, and partial gasification of the nascent char (Joanne et al., 2016). Increasing pyrolysis temperature increases the yield of CO and H₂ while decreasing the yield

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of CO₂, CH₄, and C₂H₆. The formation of CH₄ is due to the decomposition of methyl and methylene bridge groups at lower and higher temperatures, respectively. Whereas, CO is produced by the cracking of heterocyclic oxygen groups. Furthermore, the temperature of pyrolysis affects the reactivity of solid char. If coal is pyrolysed at a low temperature, the microporous surface area of char becomes small, resulting in a lower active site for gasification and thus lower reactivity (Tremel et al., 2012).

Besides, the heating rate plays a crucial role in pyrolysis. While there are contrasting views in the literature regarding the effect of heating rate on volatile release, most of the studies reported that increasing heating rates, increase the volatile release substantially (Griffin et al., 1993; Yu et al., 2007). Griffin et al., 1993 (Griffin et al., 1993) reported that increasing the heating rate from 10 K/s to 20,000 K/s resulted in an increased volatile yield by 52% at a temperature of 800 °C using particle size of 106-125 µm. Higher heating rates result in the loss of fixed carbon, robust fragmentation of coal particles, change in char structure, and elimination of secondary reactions (Berkowitz, 1979).

Berkowitz (1979) reported that the devolatilisation rate increases almost linearly with increasing heating rate. Likewise, Liu et al. (2014) studied the effect of heating rates using particle size between 14.7-52.7 µm and a maximum temperature of 1000 °C. The results showed that increasing the heating rate increases the product gases, although the changes are insignificant while using the two higher heating rates of 30 and 35 °C/min. Anthony (1974) compared the effect of heating rates on pyrolysis using bituminous and lignite coals. The study used the heating rates of 12.5 and 167 °C/min with a particle size of 75 µm and a peak temperature of 1000 °C. The results revealed that the variation in the final volatile yield is insignificant to the heating rate.

Concerning the effect of particle size, Badzioch and Hawksley, 1970 (Badzioch and Hawksley, 1970) reported that there was no significant effect of particle size on the devolatilisation characteristics of coal. The study was conducted with a mean particle size of 40, 50, and 60 µm. Anthony (1974) found that increasing particle size decreases the volatile yield slightly while experimenting using particle size of 53-1000 µm. Liu et al. (2014) studied the effect of particle size on volatile yield and found that decreasing particle size increases the yield of pyrolysis gases. However, no apparent trend concerning particle size

was noticed. Some other studies (Gavalas, 1982; Suuberg, 1978) in contrast, reported that increasing particle size increases the volatile yield. The higher volatile release from larger particles was claimed to be the result of secondary reactions (Yu et al., 2007).

In this current investigation, the effect of operating conditions on the pyrolysis behaviour of coal is characterised using the TG-IR technique (Song et al., 2017; Zangaro et al., 2019). Besides, kinetic modelling was carried out for the kinetic and diffusion regime of pyrolysis, known as two-stage kinetic modelling (Song et al., 2017). To understand its pyrolysis behaviour as a necessary precursor to eventual gasification, Bangladeshi Barapukurian bituminous coal has been used in this study as a first-ever pyrolysis study.

The current study is divided into four major sections. Firstly, analysing the effect of operating conditions on the devolatilisation behaviour of coal using the thermogravimetric infrared spectroscopy (TG-IR) technique. Secondly, developing a two-stage kinetic model and to determine the effect of heating rates on kinetic parameters. Thirdly, analysing the infrared spectroscopy (IR) spectrum to determine the release of functional groups and volatile gases under various heating rates. The result of this study is intended to generate information useful to design pyrolysis and gasification processes using this coal.

2. Experimental

2.1 Sample preparation

The coal studied in this study was collected from Barapukuria Coal Mining Company Limited (BCMCL), Dinajpur, Bangladesh. The raw coal was grounded and sieved to a particle size of 20-38 µm, 53-75 µm, and 90-106 µm to test the effect of particle size on devolatilisation. These particle sizes were chosen in line with the particle size employed for the commercial entrained flow gasifier. The prepared samples were stored in a sealed container at room temperature in a dry condition. Additionally, prior to conducting the experiments for the gasification study, the samples underwent overnight oven-drying to eliminate any residual moisture, following the standard practice.

2.2 Apparatus and operating procedure

The pyrolysis experiment of this study was conducted in a Perkin Elmer STA 8000, which is coupled with an infrared spectrometer (IR). This instrument is a combination of a

thermogravimetric analyser (TGA) and an IR, which simultaneously provides weight loss profile and evolution of gases species in terms of IR spectrums of the functional groups. During pyrolysis, the released volatile matter from TGA was automatically transferred to the IR cell via a transfer line.

Prior to conducting the experiments with a range of heating rates (10, 20, 50, and 100 °C/min), the variation in devolatilisation using different sample weights and particle sizes was checked. A sample weight of 10-17.5 mg was loaded into the Al₂O₃ sample pan to assess the effect of sample mass and decide the final mass for kinetic analysis. The sample was heated to the desired temperature (i.e. 1000 °C) using a particular heating rate under a pure N₂ flow rate of 120 ml/min, where the temperature was held for one minute and then cooled to room temperature. Data obtained from each experiment were blank-corrected to negate any buoyancy and drift effects.

The proximate analysis of the coal was conducted using Australian Standard: AS1038.1, while the ultimate analysis was conducted using ISO 29541 standard. The proximate and ultimate analyses data of the coal sample is presented in Table 1. Minerals present in the coal ash were analysed with X-ray fluorescence (XRF) using Australian standard AS1038.14.3. The mineral composition of ash is shown in Table 2.

3. Pyrolysis characteristics of Barapukurian Coal

3.1 Effect of sample mass on the pyrolysis behaviour of coal

Figure 1 shows the effect of sample mass on devolatilisation behaviour of coal through mass loss during pyrolysis using particle size of 20-38 µm and a maximum temperature of 900 °C. The result shows that the decomposition of Barapukurian is completed in a single stage, but the mass loss profile can be divided into two distinct zones slow pyrolysis and rapid pyrolysis. The slow pyrolysis starts at a temperature of around 200 °C, and last until around 350 °C. The pyrolysis between 350 and 650 °C can be considered as the rapid pyrolysis zone, where the majority of the mass is lost with a range between 25-30% depending on the sample mass. The maximum derivative of the thermogravimetric (DTG) peak was observed at a temperature of 430 °C.

A study conducted using Shenfu bituminous coal showed that the maximum DTG peak is obtained at a temperature of 740 °C using a heating rate of 30 °C/min (Li et al., 2015). In contrast, other studies (Arenillas et al., 2001; Folgueras et al., 2005) conducted using bituminous coal showed that the rapid pyrolysis completes between 350 and 650 °C with the highest DTG peak at around 665 °C, which is similar to the current finding. Similarly, the pyrolysis behaviour of three different bituminous coals was studied,

Table 1: Proximate and ultimate analyses of Barapukurian coal and char using different particle sizes.

Particle size (µm)	Proximate analysis (wt.%)				Ultimate analysis (wt.%, dry)					Heating value (MJ/kg, d.b.)
	Moisture (wt.%, air dry)	Volatile matter	Fixed carbon	Ash	C	H	N	S	O	
20-38	3.1	30.4	56.0	11.6	74.2	4.6	1.5	0.5	7.6	30.3
53-75	3.0	30.5	55.0	11.5	73.0	4.8	1.6	0.5	8.6	
90-106	2.6	31.7	54.6	11.1	72.4	5.0	1.7	0.5	9.3	

Table 2: Ash mineral matter of Barapukurian bituminous coal.

Mineral matter	(Wt.%)	Mineral matter	(Wt.%)
SiO ₂	51.68	Mn ₃ O ₄	0.04
Al ₂ O ₃	40.23	P ₂ O ₅	0.61
Fe ₂ O ₃	2.74	SO ₃	0.18
CaO	0.59	BaO	0.05
MgO	0.27	SrO	0.09
Na ₂ O	0.07	ZnO	0.01
K ₂ O	0.63	V ₂ O ₅	0.07
TiO ₂	2.74		

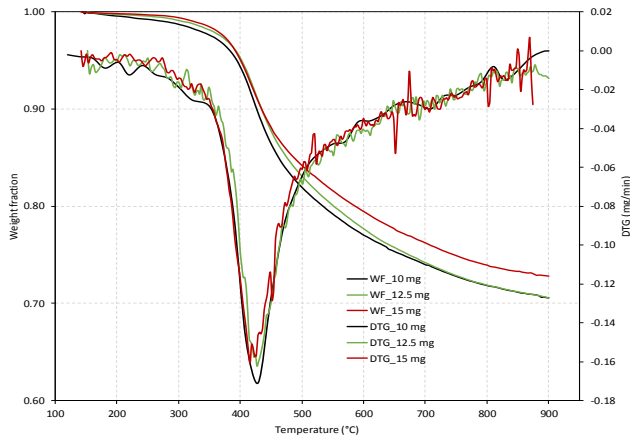


Fig. 1: Effect of sample mass on devolatilisation of coal using a heating rate of 10 °C/min, a peak temperature of 900 °C and the particle size of 20-38 μm .

and found that the pyrolysis process was completed in a single stage between the temperature range of 400 – 650°C (Alonso et al., 1999). Also, the maximum DTG peaks were determined within the temperature between 400 - 650 °C. A study (Arenillas et al., 1999) conducted using bituminous coals with different volatile content showed that the pyrolysis process started between the temperature of 218 and 344 °C, whereas the maximum mass loss was observed at a temperature between 470 and 550 °C (Arenillas et al., 1999). It was observed that the starting temperature of decomposition and the temperature of maximum mass loss were lower for the coal with higher volatile content.

As observed from Figure 1, decreasing sample mass increases the volatile decomposition, although the difference in the two lower sample masses is negligible. According to proximate analysis, the current coal sample contains 30.4% volatile, which is almost lost when using a sample mass of 10 and 12.5 mg at a temperature of 900 °C. In the case of lower sample mass, the penetration of carrier gas (N_2) was comparatively easier, and thus the release of volatile organic matter was faster.

3.2 Effect of particle size on pyrolysis behaviour of the coal

Figure 2 shows the effect of particle size on devolatilisation of coal using the maximum temperature of 900 °C. It can be seen that the rate of devolatilisation and the variation concerning particle size is negligible within the slow pyrolysis zone. However, at a temperature over 430 °C, the rate of volatile release and the variation in mass loss

among different particle sizes were different. Decreasing particle size from 90-106 to 53-75 μm did not show any change in the final volatile release. However, further decreasing the particle size to 20-38 μm , decreased the volatile release by 2%, which might be due to the lower volatile content in the sample.

Contradicting results have been found in the literature regarding the effect of particle size on devolatilisation. For example, Anthony, 1974 (Anthony, 1974) and Demirbas, 2004 (Demirbas, 2004) found that increasing particle size decreases the decomposition and thus the volatile yield. However, other studies (Gavalas, 1982; Suuberg, 1978) reported that increasing particle size increases the volatile yield. The current results indicate that decreasing particle size beyond a specific range affects devolatilisation behaviour. Decreasing particle size increases the microporous surface area, and thereby the heat and mass transfer (Badzioch and Hawksley, 1970). However, decreasing particle size below a critical range may retard the volatile decomposition due to lower hold-up residence time, elimination of secondary reactions, and increased adsorption effect (Liu et al., 2014).

3.3 Effect of heating rate on pyrolysis behaviour of coal

Figure 3 shows the effect of heating rates using the maximum temperature of 1000 °C and particle sizes of 53-75 μm . Overall, it can be seen that increasing the heating rate decreases the rate of devolatilisation, and thus increases the residual mass of char. Also, the temperature of maximum mass loss increases almost linearly with

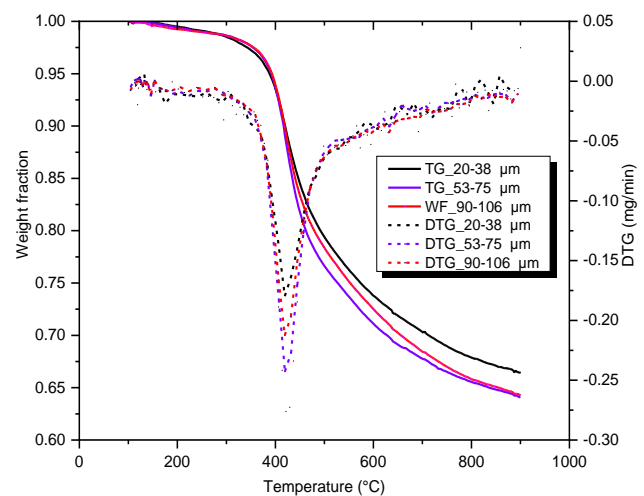


Fig. 2: Effect of particle size on weight fraction and DTG profile using a heating rate of 10 °C/min and a maximum temperature of 900 °C.

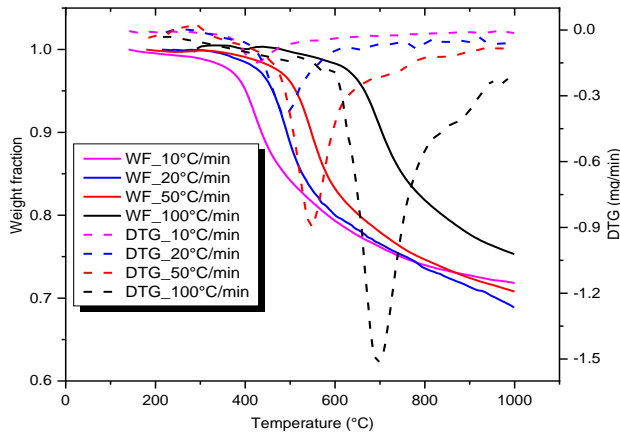


Fig. 3: Effect of heating rates on weight fraction and DTG curves using peak temperature of 1000 °C and the particle size of 53-75 μm .

increasing heating rate (Arenillas et al., 2001). Similar findings were observed in several studies (Li et al., 2015; Mehrabian et al., 2012) using bituminous coal and biomass at different heating rates. A higher heating rate results in the time available to a particle for the pyrolysis to be shorter, which leads to an incomplete volatile release.

Furthermore, in the thermogravimetric study, increasing the heating rate increases the difference between the programmed and actual sample temperature (Mehrabian et al., 2012). As observed in the current study, although the programmed maximum temperature was 1000 °C under all heating rates, the actual sample temperature was far below. The final sample temperature was recorded to be 772, 935, 978, and 987 °C using the heating rate of 100, 50, 20, and 10 °C/min. The current finding confirms other studies conducted in the literature (Li et al., 2015; Mehrabian et al., 2012), though those studies did not quantify the thermal lag.

4. Modelling approach

Depending on the properties of coal, two key steps occur while heating coal from room temperature to the desired maximum pyrolysis temperature. In the first step, the water vapour present in the coal is released after reaching a temperature of around 105 °C. In the second step of pyrolysis, volatile matter including CO, H₂, CO₂, CH₄, C₂H₆, and tar are driven off, leaving char as a solid product (Farrokh et al., 2017). This study considered coal pyrolysis to be a first-order reaction (Güldoğan et al., 1999). Mathematically, the decomposition rates due to thermal degradation can be expressed as Eq. (1) (Farrokh et al., 2017):

$$\frac{dx}{dt} = k(1-x) \quad (1)$$

where x is the degree of devolatilisation at a particular temperature, t is the time, and k is the reaction rate constant. The degree of devolatilisation at a specific temperature T can be calculated as $x = (m_i - m_f) / (m_i - m_f)$, where m represents the mass of the sample and subscripts i and f denote the initial and final conditions. The devolatilisation rate in pyrolysis can be written according to the Arrhenius equation as Eq. (2):

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

where A is the pre-exponential factor in min^{-1} ; E_a is the activation energy in kJ/mol; R is the universal gas constant in kJ/(mol.K), and T is the pyrolysis temperature in K. Inserting Eq. (2) into Eq. (1) gives.

$$\frac{dx}{dt} = A \exp\left(\frac{E_a}{RT}\right)(1-x) \quad (3)$$

During the thermogravimetric experiments, the pyrolysis temperature increases linearly with time, depending on the heating rates, which can be expressed as Eq. (4).

$$T = T_0 + \beta t \quad (4)$$

where T_0 is the initial temperature and β is the heating rate. Differentiating Eq. (4) with respect to temperature gives

$$\frac{dt}{dT} = \frac{1}{\beta} \quad (5)$$

Now, substituting Eq. 5 into Eq. 3 gives

$$\frac{dx}{dT} = \frac{1}{\beta} A \exp\left(\frac{E_a}{RT}\right)(1-x) \quad (6)$$

For two-stage kinetic modelling, the equations to determine kinetic parameters in the kinetic and diffusion regimes can be expressed by rearranging Eq. (6) in the following forms (Urych, 2014): The kinetic regime can be equated as:

$$-\ln(1-x_k) = \frac{A_k RT^2}{\beta E} e^{-E/RT} \quad (7)$$

Rearranging Eq. (7),

$$x_k = 1 - e^{-\frac{(A_k RT^2) e^{-E/RT}}{\beta E}} \quad (8)$$

On the other hand, in the case of the diffusion regime, the activation energy is very low, and for the simplification assuming the activation energy $E \cong 0$ (Urych, 2014). Hence, Eq. (6) can be written as:

$$-\ln(1-x_D) = \frac{A_D}{\beta} (T - T_{D,i}) \tag{9}$$

Rearranging Eq. (9),

$$x_D = 1 - e^{-\frac{A_D * (T - T_{D,i})}{\beta}} \tag{10}$$

Subscripts k and D in Eqs. (8) and (10) represent the kinetic and diffusion regimes, respectively.

Figure 4 shows the kinetic and diffusion regime for the pyrolysis experiments using different heating rates. It is clear that as the heating rate increases, the kinetic regime moves to a higher temperature. In the kinetic regime, a non-linear mass loss with temperature occurs at the beginning of the pyrolysis process. In contrast, the mass loss in the diffusion regime is almost linear.

4.1 Analysis of kinetic parameters

The activation energy and pre-exponential factor were determined from the slope and intercept of the straight line in Figure 4, respectively. The kinetic data were calculated, ignoring the initial and final one percent of the devolatilisation as they often associate some experimental errors.

The average activation energy from the current pyrolysis study is determined to be 145.7 kJ/mol. The variation in activation energy in the kinetic regime between the heating rate of 10 and 100 °C/min was determined to be 18 kJ/mol. The difference in activation energy in the kinetic regime increases slightly with increasing heating rate. However, the difference is higher between the two highest heating rates used in this study. Similar findings are also reported in the literature using bituminous coal (Li et al., 2015). Conversely, some studies (Arenillas et al., 2001; Kirtania and Bhattacharya, 2013) found nearly similar

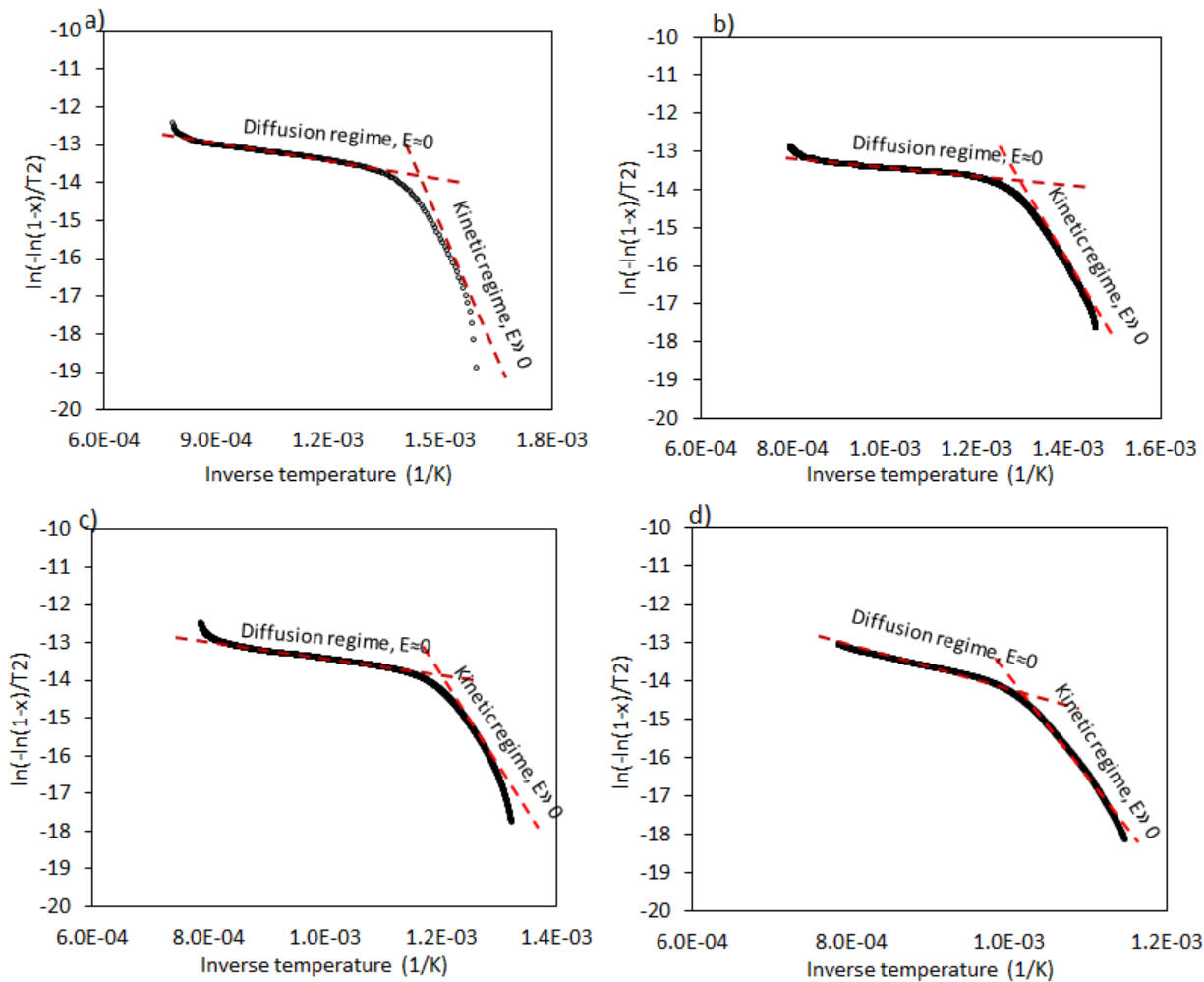


Fig. 4: Determination of kinetic and diffusion regimes using various heating rates (K/min): a) 10, b) 20, c) 50, and d) 100.

activation energy under different heating rates. Ideally, the dependence of activation energy on heating rate varies with rapid pyrolysis temperature, which depends on the properties of coal and other operating conditions (Arenillas et al., 2001).

Folgueras et al., 2005 (Folgueras et al., 2005) and Arenillas et al., 2001 (Arenillas et al., 2001) calculated the activation energy of 127 and 115 kJ/mol for bituminous coal. The lower activation energies from those studies were mainly due to the slower heating rate of < 65 °C/min being used. The pre-exponential factor was determined to be higher at higher heating rates, which is potentially due to the increased interparticle mass transfer and shifting of rapid pyrolysis at higher temperatures. In the kinetic region, rapid degradation and decomposition result in the formation of light gas and tar (Song et al., 2017). Therefore, these processes require higher activation energy for the fragmentation of heavy molecules. On the other hand, in the diffusion regime, the pyrolysis process is

slow, where some secondary decomposition, a slight release of light gas, and small fragmentation occur. Thus, the need for activation energy in this stage is very little.

4.2 Model validation

Figure 5 shows the modelled devolatilisation against experimental data in kinetic and diffusion regimes. The result shows a good match between the experimental and predicted devolatilisation profiles, especially in the kinetic regime. The discrepancy in the diffusion regime (high-temperature range) can be explained as the temperature limitation due to increased thermal lag between the sample and programmed temperature (Mehrabian et al., 2012).

4.3 Analysis of infrared spectroscopy (IR) data

Infrared spectroscopy (IR) was used to characterise the functional groups of the product gases under different heating rates, as shown in Figure 6. The IR absorbance

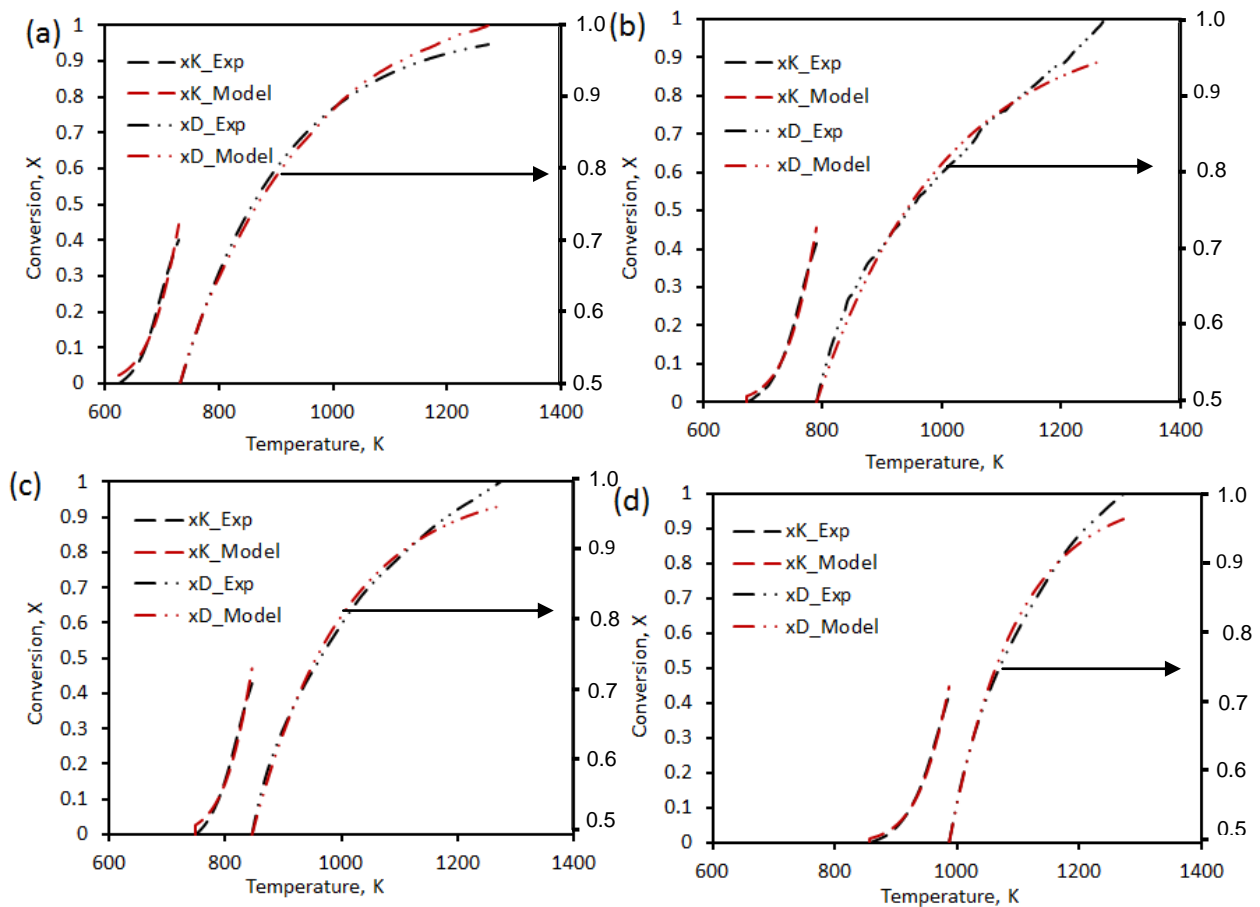


Fig. 5: Degree of conversion using the two-stage kinetic model with experimental validation using different heating rates: (K/min): a) 10, b) 20, c) 50, and d) 100.

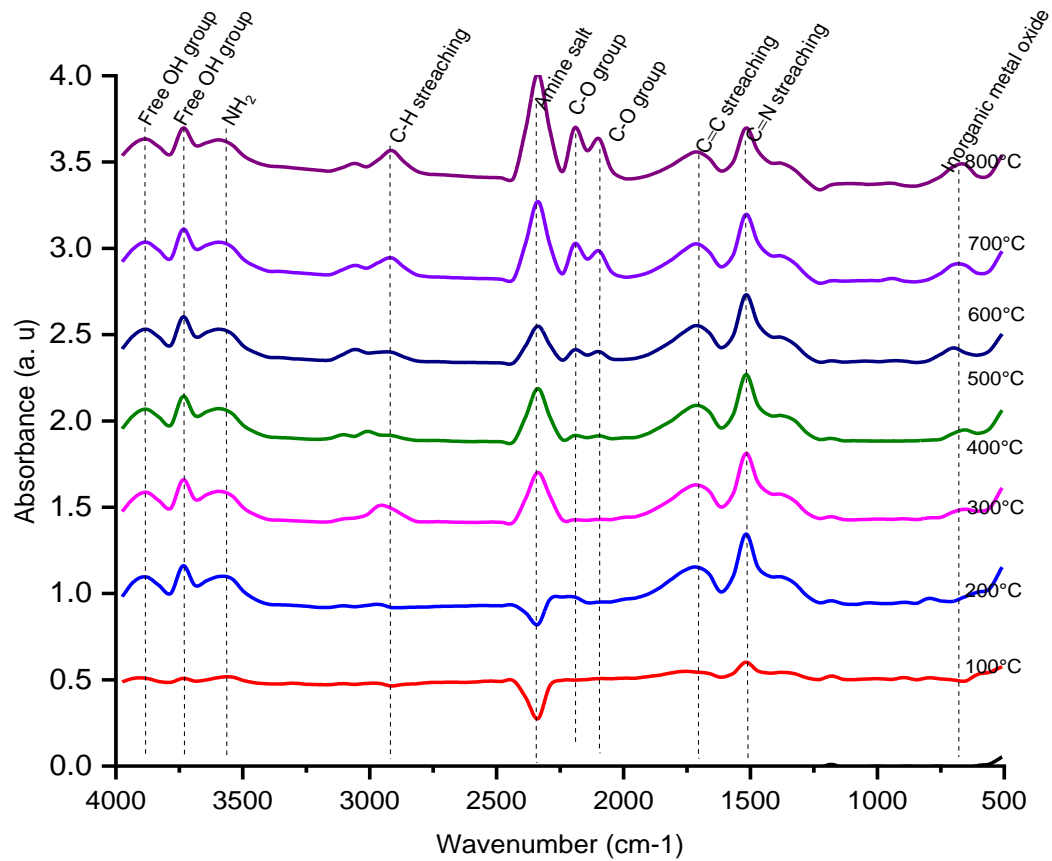


Fig. 6: a) Effect of temperatures and heating rates on absorbance during pyrolysis at a heating rate of 20 K/min

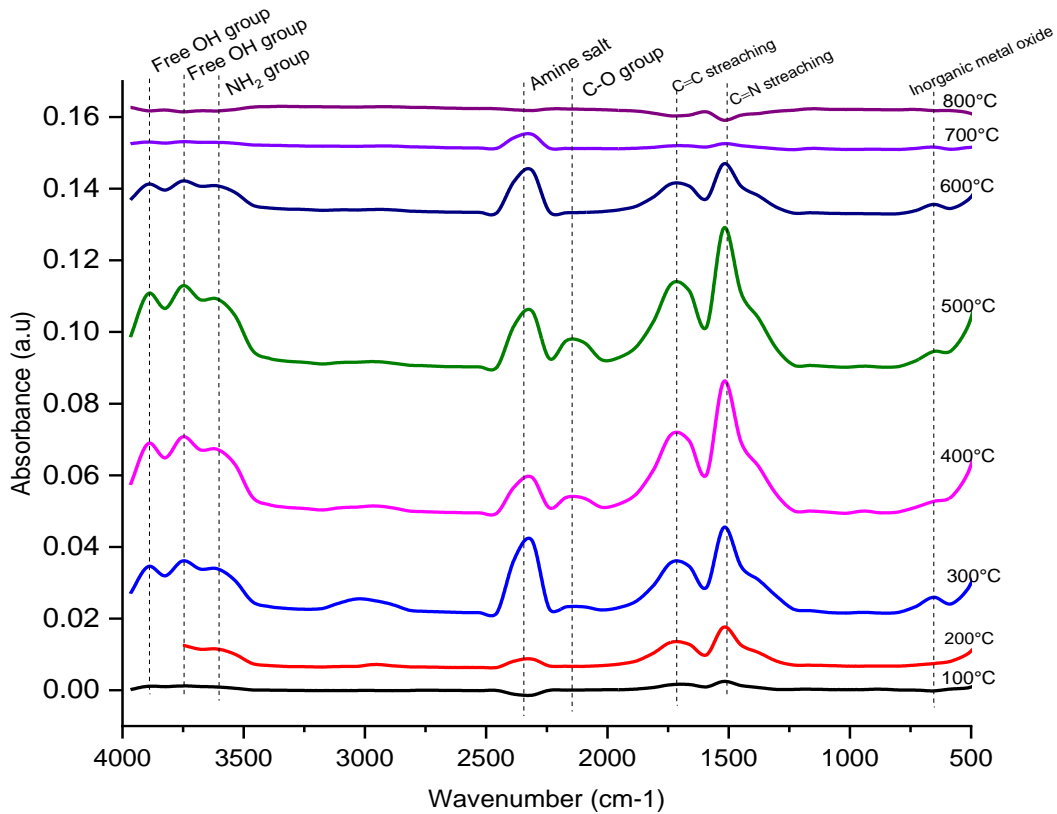


Fig. 6: b) Effect of temperatures and heating rates on absorbance during pyrolysis at a heating rate of 50 K/min

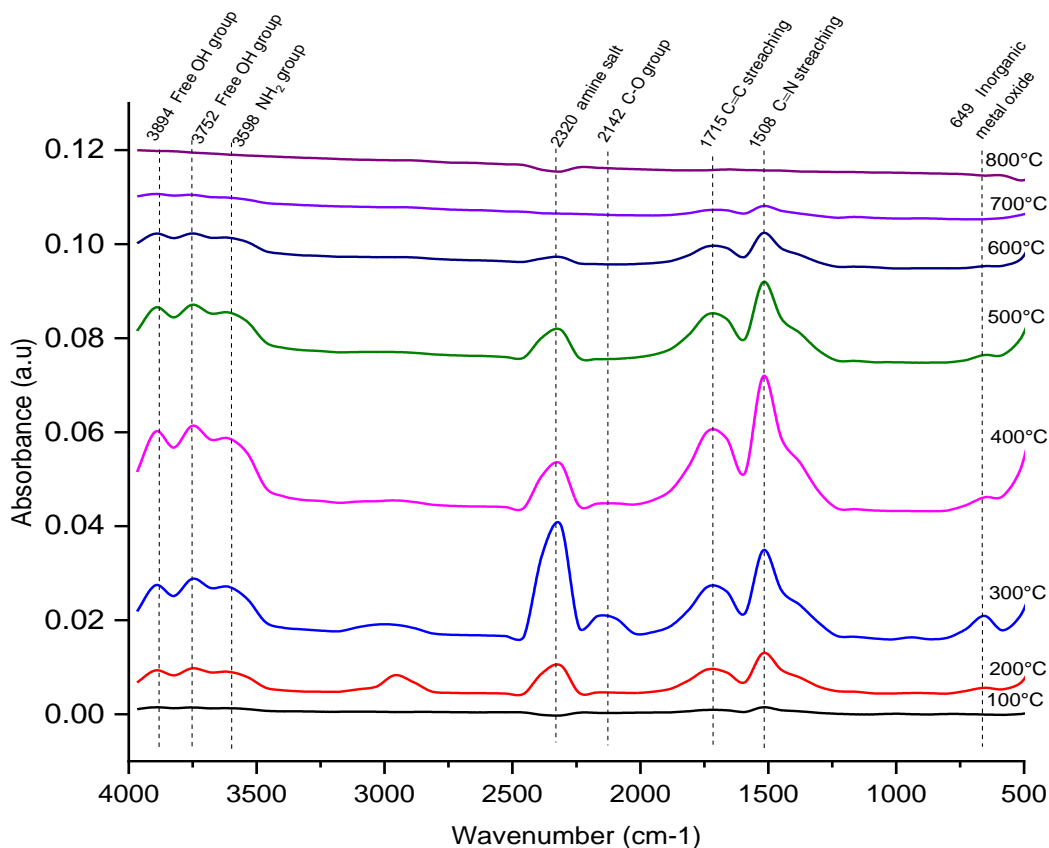


Fig. 6: c) Effect of temperatures and heating rates on absorbance during pyrolysis at a heating rate of 100 K/min.

distinct zones. The region between the wavenumber of 3400-4000: free OH group stretching vibration; 2400-2900: CH group stretching vibration; 2000-2400: oxygen-containing stretching vibration; 1500-1700: C=C stretching and finally 500-800: absorption of inorganic metals (Colthup, 2012; Xu et al., 2016). The absorption peaks located between 3400-4000 cm^{-1} and 1215-2090 cm^{-1} appeared due to the stretching vibration as a result of moisture present in the coal (Xu et al., 2016).

There was an overlapping among the peaks due to the moisture, C=C, and C=N stretching vibrations, especially in the region at 1500-1700 cm^{-1} (Xu et al., 2016). Furthermore, overlapping with the OH group in the upper band at around 3665 cm^{-1} was presumably due to the absorption of the NH_2 group (Colthup, 2012).

The peak observed in the region 2828-3175 cm^{-1} was due to the symmetric and asymmetric CH group stretching vibration (Song et al., 2017). Notably, the peak found at 2904 cm^{-1} was due to the absorption of aliphatic CH_2 stretching vibration. Few bands in the region 2050-2450 cm^{-1} were observed due to the absorption of carbonyl oxygen compounds (Colthup, 2012).

The integrated area ratio between 2800-3000 cm^{-1} to 1540 cm^{-1} as well as 3000-2800 cm^{-1} to 900-700 cm^{-1} were used to calculate the relative abundance between aliphatic and aromatic content (Guo et al., 1996). The relative abundance of the aliphatic group was found to be higher in the lower heating rate compared to the aromatic group. In contrast, the degree of condensation in the aromatic ring was similar for two lower heating rates but significantly lower at the higher heating rate of 100 $^\circ\text{C}/\text{min}$. The integrated area ratio between CH_2 and CH_3 was relatively higher at the lower heating rate of 20 $^\circ\text{C}/\text{min}$. However, the value calculated from the two higher heating rates were determined to be almost unity, which indicates that, the formation of CH_2 and CH_3 do not change beyond a specific heating rate.

A significant difference in absorption peaks in terms of position, strength, and spacing was observed due to the difference in heating rates. Although the peak positions from different heating rates are similar, the intensities and wideness are different. Also, the peak intensities were found to be varying with temperature. Some peaks, particularly in the wavenumbers of around 2750 and 3230 cm^{-1} disappeared from the spectrums of higher heating

rates. Also, some new peaks, along with a difference in shape and size, are observed with increasing heating rates. Hence, a variation in devolatilisation behaviour is observed using different heating rates and temperatures.

The evolution of gas species during pyrolysis is the result of the decomposition of various functional groups. The decomposition reactions are called dehydration, demethylation, and decarboxylation, which cause to remove OH, CH₃ COOH groups, respectively (Xu et al., 2016). The decomposition of functional groups results in the release of CO₂, CO and CH₄ during pyrolysis. In this study, these gas compositions were quantified by the normalised peak area identified between the regions 2250-2400, 2000-2250 and 2800-3175 cm⁻¹, respectively. The normalisation and peak area integrations were conducted with the algorithm provided in Origin 9.1 software. The evolution of gas species with respect to heating rates and temperatures are shown in Figure 7.

As seen, increasing the heating rate from 20 to 50 °C/min increased the evolution of gas species, which then decreased with further increasing the heating rate to 100 °C/min. Although, the total yield of gas species using 100 °C/min under the whole temperature range was well above the yield of 20 °C/min.

It is worth mentioning that the temperature range through which the yield of gas observed at 50 °C/min was larger than that of 100 °C/min. For example, the yield of CO and CO₂ using the heating rate of 100 °C /min was observed between the temperature of 200-500°C, which was between the temperature of 200-600 °C in the case of 50 °C/min. Also, using 20 °C /min, the gas species evolution started at a temperature of ~300 °C and was not completed even at a temperature of 800 °C.

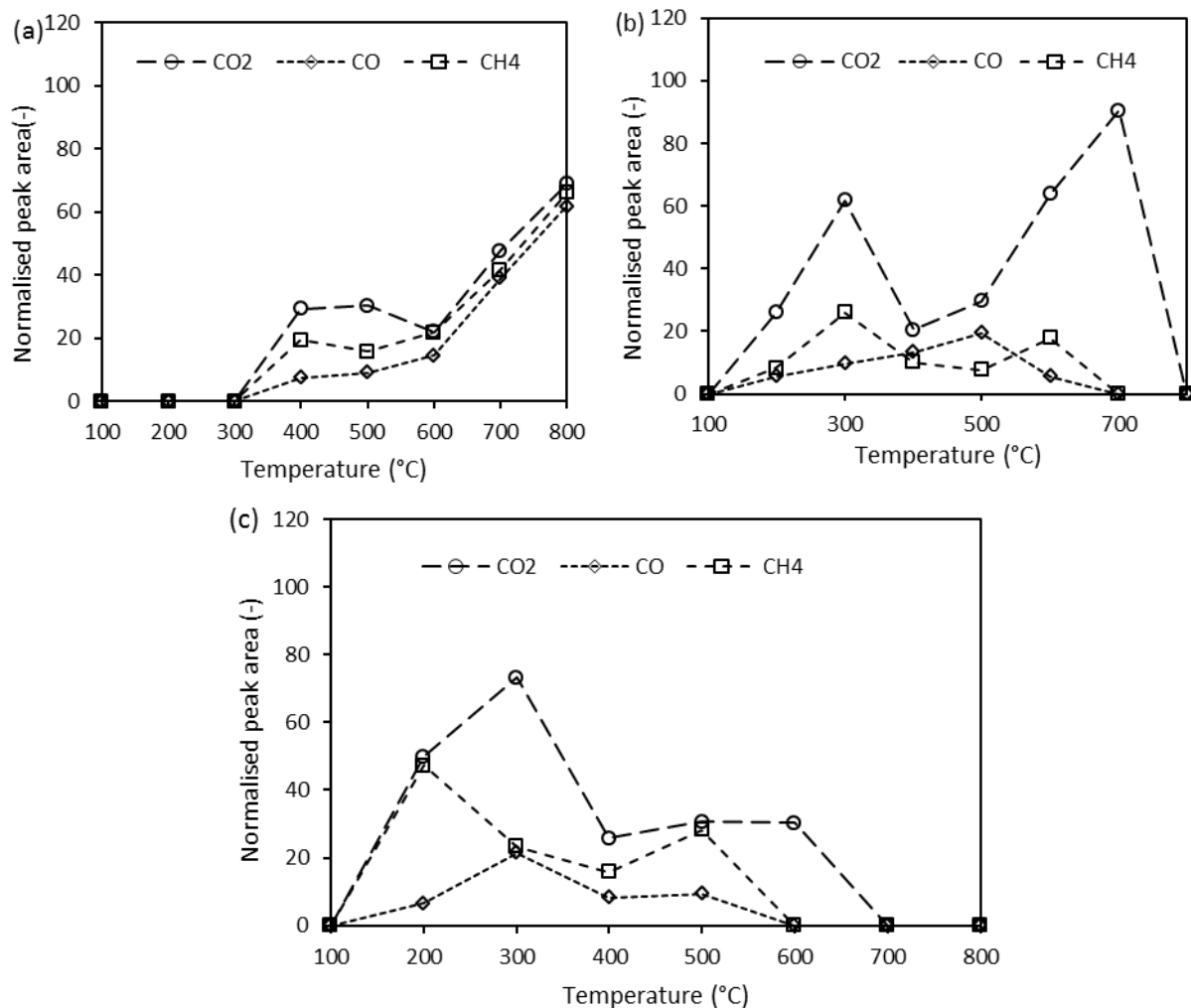


Fig. 7: Evolution of pyrolysis gas species with respect to temperature and heating rate: a) 20, b) 50, and c) 100 °C/min.

Likewise, in other species, the first appearance of CH₄ was observed at a temperature above 300 °C using the heating rate of 20 °C/min, which was increased gradually with increasing temperature of up to 800 °C (Song et al., 2017). The evolution of CH₄, using 50 and 100 °C/min, were started much earlier and ended up at a temperature of 700 °C and 600 °C, respectively without following any noticeable trend. Similar to CO₂ evolution, a fall-off trend for CH₄ between the temperature of 300-500 °C was identified. The formation of CH₄ was the decomposition of several functional groups such as the methoxy group, methylene carbons, a methyl ether bond, a long aliphatic chain, and aromatic heterocyclic structures (Liu et al., 2014; Song et al., 2017).

The overall yield throughout the temperature range shows that the yield of CH₄ decreases using the heating rate of 100 °C/min compared to that of 50 °C/min. In addition, the yield of CH₄ at 50 °C/min was significantly higher than that of 20 °C/min. The previous studies showed that increasing the heating rate increases the evolution of CH₄ considerably in the low heating rates of 10 and 20 °C/min (Liu et al., 2014). However, a minor difference in the initial stage and an overlapping in the latter stage between the heating rates of 30 and 35 °C/min were observed. The reason for the lower gas evolution at 100 °C/min might be attributed to the incomplete decomposition of functional groups due to shorter residence time. Therefore, it is important to adjust the peak temperature and isothermal residence time considering heating rates in the practical pyrolysis process.

5. Conclusion

In this investigation, the pyrolysis characteristics of Barapukurian bituminous coal were examined using the TG-IR method. The TG and DTG curves reveal a multi-step pyrolysis process encompassing moisture removal, slow pyrolysis, and rapid pyrolysis. The entire pyrolysis process can be delineated into two distinct regimes: kinetic and diffusion. Throughout pyrolysis, the release of OH, CH₃, and COOH functional groups led to the formation of CO, CO₂, and CH₄ gases. The features of IR peaks exhibited variations with different heating rates and temperatures. The evolution of gas species increased as the heating rate rose from 20 to 50 °C/min. However, a reduction in the yield of gas species was noted with a further increase in the heating rate to 100 °C/min, attributed to the elimination of secondary reactions and shorter residence

time. Therefore, in practical pyrolysis processes, adjusting peak temperature, heating rate, and, if necessary, isothermal residence time is crucial for achieving complete devolatilisation.

Disclosures

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