Devolatilisation Characteristics of Coal and Biomass with Respect to Temperature and Heating Rate for HIsarna Alternative Ironmaking Process

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HIGHLIGHTS

- **Devolatilisation behaviours of different carbon sources investigated for HIsarna alternative ironmaking process.**
- **Maximum peaks of evolved gases from VTF-QMS corresponded well to DTG curves.**
- **The kinetic parameters for coal and biomass samples were determined.**
- **Biomass pre-treatment temperature suggested to produce chars with similar properties to coal injected in HIsarna.**

Abstract: HIsarna process offers a novel low CO_2 emission alternative to the blast furnace for primary iron production. This new smelting ironmaking technology is flexible in raw material usage such as the substitution of biomass for coal as a reductant. Reduction is conducted through multiple mechanisms within the smelting vessel including gaseous reaction products from thermal decomposition of volatile matters reacting directly with iron oxide containing slags and injected iron ore. In this study, four coals with notable differences in volatile matter content along with two biomass samples sourced from wood and grass origins were investigated for the selection of suitable fuel mix. Thermogravimetric analysis (TGA) was used to measure the weight loss of the

carbonaceous materials and a vertical tube furnace coupled with a quadrupole mass spectrometer (VTF-QMS) was employed for off-gas analysis during the devolatilisation. During TGA tests the samples were heated under a 99.9999 % argon atmosphere to 1500 °C at three different heating rates to investigate the kinetics of thermal decomposition for these materials. Through use of the Kissinger– Akahira–Sonuse model an average activation energy was determined as a function of the conversion degree. The furnace experiments were carried out under a 99.999% Ar atmosphere to a peak temperature of 1500 °C, at a heating rate of 10 °C/min. The wt% of reducing gases e.g. H_2, CO, and hydrocarbons, and the temperature required for these gases to evolve was notably different for each materials, but the respective maximum peaks of evolution of these gases corresponded well to the maximum rate of mass loss. Furthermore, the off-gas analysis reveals torrefied grass contains large amount of water and carbon dioxide which will be released at very low temperature, therefore pre-treatment to the temperature of ~400 °C is necessary to produce chars with similar properties to coal injected in HIsarna.

Keywords:

HIsarna technology

Biomass

Coal

Heating rate

Devolatilisation

Kinetic analysis

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1. Introduction

Coal is the most widely used fossil fuel in the world, and it continues to dominate the energy supply and the demand is still set to grow, particularly in developing countries despite international environmental agreements. Stringent environmental legislations such as the compulsory target of 80-95% carbon dioxide (CO_2) emissions reduction by 2050 compared to the 1990 baseline, have forced all industries into innovation and transformation [1]. Ironmaking is an energy intensive process accounting for 4-7% of global CO_2 emissions alone [2]. With the strict environmental legislation and recent signing of the Paris agreement, steel manufacturers are under continually increasing pressure to reduce CO_2 emissions further to near net zero levels. Despite substantial improvements concerning environmental performance, around a 50% reduction in CO_2 emissions since 1990, it is believed a true step change in steel manufacturing technology is required. Current technologies consisting of sintering, coke making and blast furnace (BF) ironmaking contribute to approximately 90% of the CO_2 output from a blast furnace ironmaking-basic oxygen steelmaking integrate steel plant [2]. Therefore significant efforts are now being funnelled into alternative ironmaking technologies which promise the possibility to remove the necessity of coke making, sintering and ultimately BF ironmaking. Several alternative ironmaking processes have been commercialised or are under development, for example, commercially proven processes (COREX and FINEX), ITmk3 process, coal-based or gas-based HYL process, coal-based MXCOL or gas-based MIDREX, fluidised bed technologies (Cicored and circofer) and HIsarna technology [1, 4].

HIsarna technology is an alternative ironmaking process, which was developed under the European Ultra-Low CO_2 steelmaking (ULCOS) research programme since 2004. The potential economic benefits of low OPEX and CAPEX, its flexibility in raw materials (including scraps and wastes) and fuels, the environmental benefits of significant reduction in CO_2 and other greenhouse gases and its suitability for brownfield investment make the HIsarna process a prospective front runner as an

alternative to conventional BF. HIsarna represents a new route of smelting reduction, which has been developed by combining two known technologies of the Cyclone Converter Furnace (CCF) and the Smelting Reduction Vessel (SRV) [3, 4]. HIsarna has the ability to use a wider range of raw materials and fuels in comparison to the conventional BF ironmaking. HIsarna uses fine ores and thermal coals, and eliminate the sintering/agglomeration and coke plants, which consequently reduces the CO_2 emissions by up to 20% without carbon capture and storage (CCS) and potentially 80% with CCS [3, 5]. Partially substituting coking coal with thermal coal (pulverised coal injection), renewable biomass and natural gas in the conventional BF has been achieved but the requirement for burden support in the BF has set limitations on the use of these alternative fuels. However, HIsarna does not require burden support, therefore, it has great potential to fully substitute current coking coal with other fuels including biomass, while maintaining process efficiency and productivity [3].

The HIsarna process begins with iron ore (and fluxing materials) and oxygen being pneumatically injected into the CCF and hitting the wall of the CCF, where SRV off-gases are burning, as a result, iron ore is pre-reduced by 10-20% and becomes partially molten. The partially reduced ore then drips down along the wall under gravity at the temperature of approximately 1450 °C into the SRV where the metal bath temperature is between 1400-1500 °C. Thermal coal is injected into the SRV liquid metal which partly dissolves, adding carbon into the liquid metal to replenish that used in the smelting reaction steps of the process [3, 5]. The smelting reactions are shown in equations (1) to (3), (1) is an overall FeO reduction by carbon dissolved in the metal or solid char and (2) and (3) are intermediate/alternative steps [6].

$$FeO_{(l)} + [Fe–C_{(l)} \,/\, C_{(s)}] \rightarrow Fe_{(l)} + CO_{(g)} \quad (1)$$

$$CO_{(g)} + FeO_{(l)} \rightarrow Fe_{(l)} + CO_{2\,(g)} \quad (2)$$

$$CO_{2\,(g)} + C_{(s)} \rightarrow 2CO_{(g)} \quad (3)$$

Replacement of coal with a carbon-neutral biomass in ironmaking offers great potential to reduce reliance on non-renewable carbon sources in this major contributor to carbon dioxide emissions from the steel industry. However, to maintain HIsarna's performance while substituting coal, carbonisation of raw biomass is necessary to increase fixed carbon (C_{fix}) content and remove moisture, oxygen and part of the volatile components, since existence of these components decrease the energy content [7]. Different thermochemical conversion technologies can be used for pre-treatment of the raw biomass to obtain chars with suitable properties for HIsarna. The pre-treatment conditions as well as the type of raw biomass determine the chemical, physical, and mechanical properties of the chars, which are necessary properties to produce chars which qualities most closely resembles the thermal coal currently used in the HIsarna process to maintain process efficiency and enable the technological shift in raw material use [5].

Once being injected into the smelting reduction vessel, the carbonaceous materials go through complex reactions, two of which are devolatilisation and burning out of the carbon. Devolatilisation happens first, and it continues to influence the solid carbon particles to the point when it is burnout [8]. The gaseous products evolved during the heating process are light hydrocarbons (mainly CH_4 and C_2H_6) which may crack into C and H_2 or react with the environment to form CO and H_2 or a mixture of H_2, H_2O, CO, and CO_2, the balance of which will change the reducing environment and control other parameters such as ignition, temperature and flame stability in the post combustion zone. As such devolatilisation of carbonaceous materials used in HIsarna technology is a key phenomenon which needs to be considered to achieve high efficiency [9]. While volatile matter is released the char structure goes through significant changes e.g. particle break-up, softening and swelling, which is strongly dependant on the chemical properties and reaction conditions such as heating rate, temperature and pressure [8].

Biomass devolatilisation usually involves the thermal decomposition of three components namely hemicellulose, cellulose, and lignin [10]. The process of decomposition for these components proceeds in three stages: moisture desorption, active decay and passive decay. Moisture desorption

occurs at temperature < 150 °C. This is followed by active decay in which most of the volatile matter is released at temperature between 200-500 °C, during this stage decomposition of hemicellulose and cellulose takes place. Decomposition of lignin starts in active decay and continues to passive decay at a very slow rate through the full temperature range of treatment [11]. Coal devolatilisation proceeds through a similar thermal degradation process, starting with moisture desorption at temperature < 150 °C and then degradation mobile and immobile phases occur at the temperatures between 150-600 °C. This results in the formation of the aliphatic and aromatic tar components and a number of light gases (e.g. H_2O, CO, CH_4 and CO_2). The final stage of thermal coal decomposition is the breakup of heterocyclic compounds at temperature higher than 600 °C [12].

The literature contains studies on coal and biomass pyrolysis by using TGA [13-15], fixed-bed reactors [16-18] and fluidized-bed reactors [19, 20]. TGA is the most common technique used to study thermal decomposition and kinetic analysis of coal and biomass. Combining this equipment with different analytic techniques, e.g. Fourier transform infrared spectrometry (FTIR) [21-24], gas chromatography (GC) [25] and mass spectrometry (MS) [26-32] is quite common. Using these techniques the gaseous products evolved during heat treatment can be investigated simultaneously or afterwards to establish the mechanism for coal and biomass decomposition. TG-MS technique has been applied because of its main advantage of being the on-line monitoring of evolving gases, which can be used simultaneously with TG equipment to monitor the gas atmosphere during sample decomposition. The effect of important parameters such as particle size, heating rate, holding time and gas atmosphere have been studied using TGA. In addition there are numerous studies which used simultaneous thermal/gas analysis to analyse evolved gases.

Much of the pyrolysis work done on gas evolution analysis has focused on determining the effect of coal rank on the off-gas generated during thermal processing. Chinese coals with different grades and different H/C atomic ratios have been studied using simultaneous gas analysis under an inert atmosphere [26-28], and it was found that thermal decomposition and gas evaluation behaviour of coals are strongly dependent on temperature and the coal rank. This method has also been used to

study the effect of temperature and time [29] with regards to devolatilisation kinetics for different types of biomass and coal/biomass blends [30, 31]. These researchers found that devolatilisation of biomass is dependent on chemical properties including ash and volatile contents, temperature and thermal treatment time. Additionally the off-gas of chitin biomass with various molecular structures in an inert atmosphere was studied to determine the influence of zeolite catalysts on the utilization of chitin biomass [32].

Although extensive research has been carried out on the devolatilisation behaviours for a number of different coal and biomass, the research and development for the carbonaceous materials (coal and biomass) for HIsarna technology is scarce, and also there is very limited information on direct comparison between coal and biomass in term of devolatilisation. Much of the research done on devolatilisation or gas evolution focused on the pyrolysis of coals and biomass using simultaneous TGA-MS carried out with small sample size between (10-20) mg. Despite all the advantages of simultaneously measurement such as real time analysis, qualitative and quantitative analysis but small sample size may mean high level of uncertainty in the off-gas analysis due to side reactions. An increase in the sample size in TGA can cause a temperature distribution problem and on the other hand, TGA may struggle to handle heavy tar products if sample size increased. In this study a high temperature vertical tube furnace coupled with a mass spectrometer is utilised to reliably study larger samples with regards to their devolatilisation characteristics with an aim of attaining a more accurate representation of gaseous product evolution from each sample under novel alternative ironmaking technologies. This research aims to enable the selection of suitable fuel mix for the HIsarna alternative ironmaking process.

2. Materials and methods

2.1. Sample preparation

Four coals and two biomass samples were tested in this study. Their proximate and ultimate analysis are listed in Table 1. The four coal samples contain different levels of volatile matter (VM) from low

(8.63%, Coal C) to medium (16.00% Coal B and 22.18% Coal A) and high (36.00%, Coal D), while the two biomass samples are charcoal CC with 12.10% VM (a wood based pre-treated biomass) and torrefied grass TG with 63.60% VM (a grass-based torrefied material provided by OrangeGreen BV through Tata steel). Coal A and charcoal CC have already been used in HIsarna process during the pilot plant trials and torrefied grass TG is another renewable source which may be considered for future trials. The samples were dried at 80 °C for 12 hours to ensure the removal of the free moisture and then crushed into small particles with the size range from 90 to 300 μm. The coal samples selected have different sulphur and ash contents that directly affect their reaction performance at high temperatures while biomass samples are generally much lower in sulphur and lower in ash contents.

Table 1. Proximate and ultimate values of the carbonaceous materials used in this study

	Coal A	Coal B	Coal C	Coal D	Charcoal CC	Torrefied Grass TG
Proximate Analysis wt% (db)						
Moisture/ % (ad)	8.87	7.11	1.24	1.30	4.56	4.40
Volatile Matter	22.18	16.00	8.63	33.00	12.10	63.60
Ash	8.80	10.00	4.41	7.20	1.80	4.40
Fixed Carbon (by difference)	69.02	74.00	86.96	59.80	86.10	32.00
Ultimate Analysis wt% (db)						
Carbon	81.91	83.60	86.97	80.30	89.4	57.60
Hydrogen	4.27	3.93	3.43	5.09	3.11	5.60
Nitrogen	2.19	1.07	1.20	1.50	0.57	0.29

Sulphur	0.24	0.78	0.86	0.89	0.06	0.09
Oxygen by (difference)	2.59	0.62	3.13	5.02	5.06	32.02

db - on a dry basis; ad - on an air dried.

2.2. Thermogravimetric analysis

The mass loss due to devolatilisation under non-isothermal conditions was determined by using thermogravimetric analysis (TGA) with a NETZSCH STA 449 instrument that has an analytical balance sensitivity of ± 0.01 mg. A 20 mg ± 0.01 sample was placed in an alumina crucible (height 4 mm x diameter 6.8 mm). The alumina crucible with test sample was placed on a platinum stage, which has a thermocouple located directly underneath to provide real temperature of the sample tested. All the samples were heated in a high impurity (99.9999%) argon atmosphere at the flow rate of 50 ml/min. The mass loss due to volatile matter evolving was recorded from ambient temperature to 1500 °C, at the heating rates of 10, 20 and 30 °C min^{-1} respectively. To ensure the reliability and reproducibility of the tests, preliminary tests have been carried out to define experimental conditions, and the test for the same sample has been repeated three times to produce concordant results.

2.3. VTF-QMS gas analysis

The gas analysis during devolatilisation was carried out using a Carbolite-Gero high temperature vertical tube furnace with a recrystallized alumina tube (VTF-1700/50, internal diameter 88 mm x length 1000 mm) shown in Figure 1. The furnace was coupled with a Hiden HPR 20 Quadrupole Mass Spectrometer (QMS) to monitor gaseous products evolving from the samples. The VTF-QMS combination allowed an increase in the sample weight to produce more representative volatile measurements of the bulk material and reduce measurement uncertainties. The samples were heated to 1500 °C in a high purity (99.999%) argon atmosphere at the heating rate of 10 °C/min while the furnace exhaust was connected to the QMS through a heated capillary (150 ^{o}C) to monitor gaseous products evolving from the samples and ensure no condensations occurred before the

ionization chamber. Each sample was weighed to be approximately 1.0 g and placed in an alumina crucible on the alumina pedestal and lifted to the hot zone of the vertical tube furnace (VTF). The tube was sealed, vacuumed using a standard rotary pump and then back filled with argon gas at a flow rate of 300 ml min^{-1} that carried gaseous products to the mass spectrometer (QMS). The argon concentration was measured to be 99.7% before the furnace heating cycle started. The QMS was set to measure readings of the following gases evolving from devolatilisation: N_2, O_2, CO, CO_2, Ar, H_2O, H_2, CH_4 and C_2H_6. After the desired temperature was reached, the furnace cooled down at 5 °C/min to room temperature in Ar atmosphere. Then the samples were taken out to weigh and analyse.

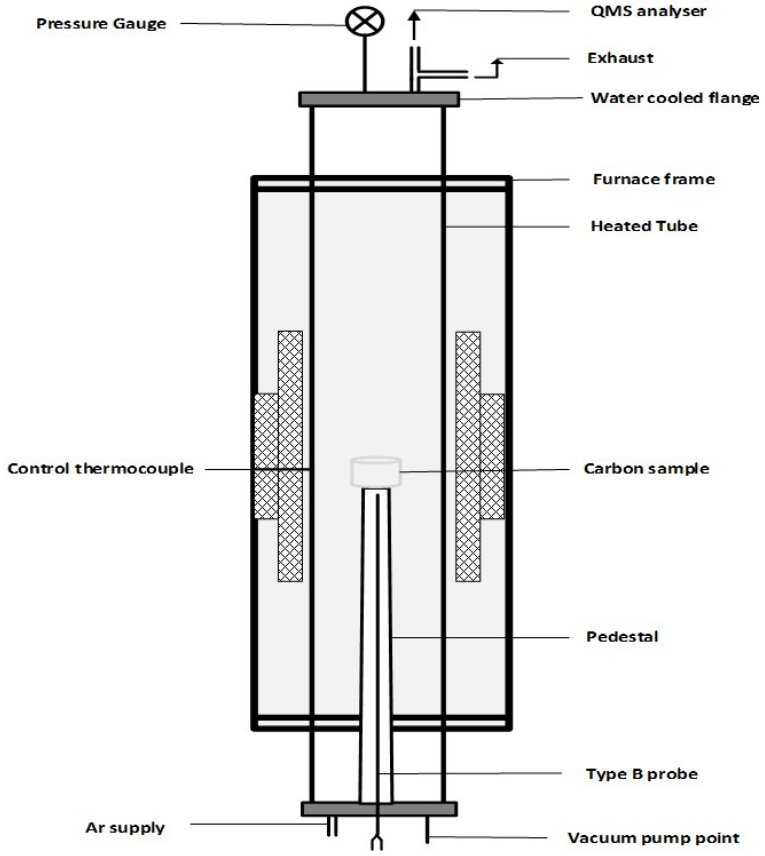


Figure 1. Vertical tube furnace (VTF) setup with a mass spectrometry for devolatilisation study. The quadrupole mass spectrometer (QMS) is connected to the gas sampling port.

3. Results and discussion

3.1. TG-DTG analysis

The weight loss curves and derivative thermogravimetric (DTG) curves produced from the TGA tests for the materials in Table 1, are shown in Figures 2a and 2b respectively. Figure 2a shows the weight loss due to devolatilisation of the samples at the heating rate of 10 °C/min under argon atmosphere.

Slow weight loss begins for all four coal samples at the temperature of ~100 °C and continues to ~180 °C, which is mainly associated with surface moisture loss. This is followed by rapid weight loss due to the release of organic volatile matter, and the starting temperature of the release of organic volatile matter depends on the volatile matter content of the coal sample. The weight loss curve starts at lower temperature for coals with higher volatile matter but all the curves stabilise at the temperature of around 650 °C regardless of the volatile matter contents. However, slow weight loss to the temperature of 1500 °C was still notable, this could be from decomposition of materials with a higher activation energy e.g. carbonyl and heterocyclic compounds, which subsequently leads to CO and H_2 formation [9].

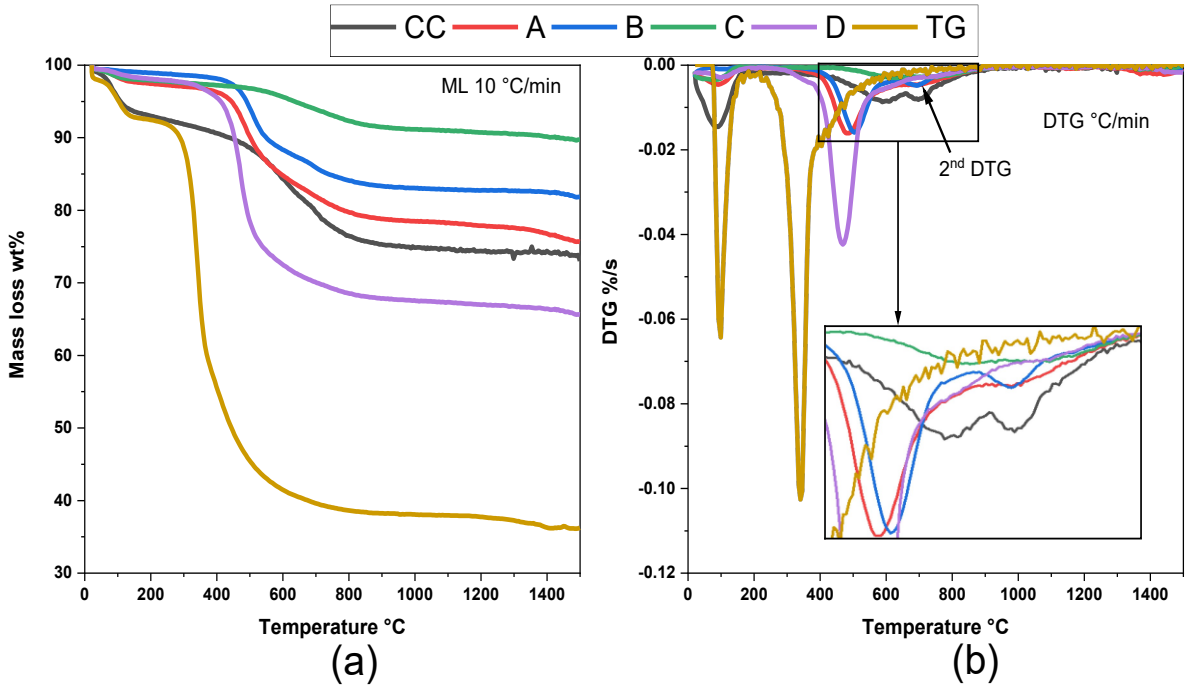


Figure 2. (a) Mass loss curves and (b) DTG curves of the carbonaceous materials tested in the high purity argon atmosphere at the heating rates of 10 °C/min from room temperature to 1500 °C.

These thermal decomposition results for coal samples can be explained with the reported mechanisms of coal devolatilisation [33], such as the devolatilisation process proposed by van Heek and Hodek (Figure 3) [12]. Coal decomposition starts with desorption of moisture and some light gasses at the temperatures of ~100 °C. On continued heating to ~250 °C the mobile phase degradation occurs which leads to tar formation, in particular the aliphatic tar component. Then at the temperatures of 300 °C and higher, degradation of the immobile phase occurs which results in formation of the aromatic tar components and a number of light gases (e.g. H_2O, CO, CH_4 and CO_2) as shown in Figure 3 [12], which is evidenced by the experimental results shown in Figure 4 (section 3.2). This is followed by decomposition of heterocyclic compounds at temperatures higher than 600 °C producing N_2, CO and H_2 gases.

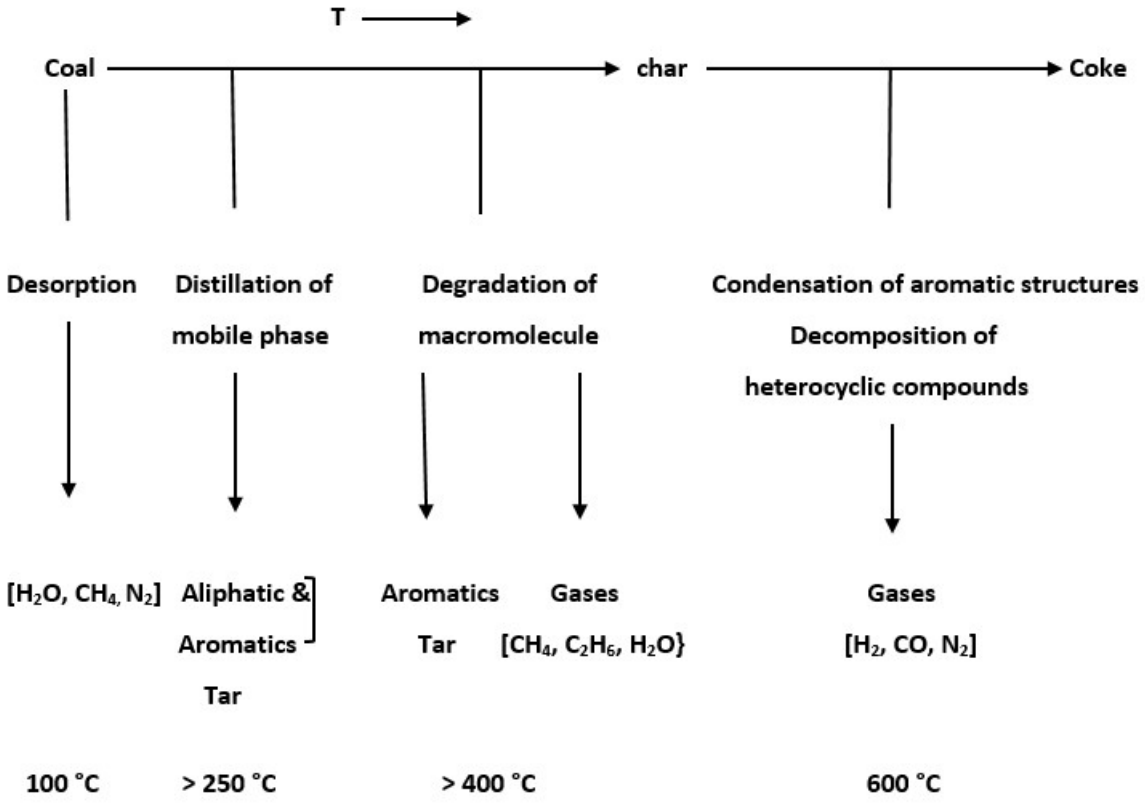


Figure 3. The main reactions occurring during the coal devolatilisation process [12]

As shown in Figure 2, decomposition behaviour of biomass samples are different from the four coals tested. The initial weight loss for both torrefied grass and charcoal starts at slightly lower temperatures of ~80 °C and continues steadily to the temperature of 200 °C. After this a sharp weight loss curve for torrefied grass occurs at temperatures from ~250 °C to 400 °C and the weight loss continues slowly to 1500 °C. However, the second step of weight loss for charcoal starts at much higher temperature of ~500 °C and continues to 1500 °C with a flatter weight loss curve that is because of the pre-treatment of the starting material. Decomposition of hemicellulose is expected to occur at the lower temperature range due to its random amorphous structure. The subsequent decomposition of cellulose and lignin follows at higher temperatures as the materials are more ordered and stronger bonded respectively. Biomass has a porous structure providing higher adsorption potential than thermal coal, which is likely to allow large amounts of moisture and carbon dioxide to be absorbed from the atmosphere. These absorbed components are weakly bonded and evolve at the very low temperatures [34]. Cellulose is the main component responsible for the second DTG peak, while lignin is the main component responsible for char formation. However thermal degradation of lignin can start at low temperature at a very slow rate and increases with the increase in temperature [35].

Figure 2b shows similar behaviour for coal samples, starting with the small peak at low temperature due to desorption followed by a large single peak due to devolatilisation. The exception for this is with coal B which has produced a clear secondary peak for devolatilisation, meaning coal B goes through extra phase of decomposition. However torrefied grass and charcoal both produced larger initial DTG peaks due to moisture loss followed by two devolatilisation peaks. There is one sharp peak which starts at the temperature of ~250 °C and the second peak which is partially superimposed on the late phase of the first peak for torrefied grass. This behaviour is linked to decomposition of cellulose and lignin respectively, while charcoal produces two peaks at much higher temperatures compared to torrefied grass which are from decomposition of lignin and agrees with other researchers' findings on similar materials [15, 35].

3.2. Comparison of devolatilisation behaviours for different carbonaceous materials

Various reactions occur simultaneously during devolatilisation upon heating, including break-up of chemical bonds, vaporisation, and condensation or recombination [22]. Using a quadrupole mass spectrometer (QMS) gaseous species evolved during heating process were measured continuously up to the temperature of 1500 °C. Figure 4 shows the mass loss due to devolatilisation measured in TGA tests against the normalized off-gas species measured in the VTF-QMS tests at the heating rate of 10 °C/min for the two biomass and four coal samples.

Similar behaviour has been observed for all the samples that gas species detected at low temperature of 100~200 °C were mainly H_2O, as the weight loss at low temperature is associated with the loss of surface moisture. However, at this low temperature range, the weight loss of the biomass samples was significantly higher than that of the coal samples measured, which is confirmed by the amount of these gases detected. Devolatilisation continued with increasing temperature, generating large amount of H_2O and CO_2 gas by biomass samples at temperature of >300 °C while none or very small amount of CO_2 from coal samples was measured but still significant amount of H_2O was produced. The amount of H_2O and CO_2 produced for torrefied grass during heating was much higher than charcoal, as charcoal has already been pre-treated. However, the amount of gas species generated by charcoal was still significantly higher than that from any of the coal samples tested at similar temperatures, which could be due to higher oxygen content in the charcoal, resulting in the oxidation of carbon and contributing to higher mass loss in charcoal.

The second region of weight loss is associated with the release of organic volatile matter, which started at similar temperatures for all the samples but the gas species generated were different. Both biomass samples started to generate H_2O and CO_2 at temperature > 300 °C, followed by the release of hydrocarbons at temperature > 400 °C, and H_2 and CO at > 500 °C. The peaks for gases generated in VTF-QMS tests spread over larger temperature range than those observed in TGA tests. This is caused by the gas mixing in the VTF and the time require for evolved gases travelling from the

300 sample location to the detection of mass spectrometer. This travelling distance in the VTF tube gives
301 rise to the comparatively consistent delay for all devolatilisation peaks compared to the TGA results.
302 All the four coal samples tested were found to produce H_2O, CO_2, CH_4, C_2H_6 and H_2 at temperatures >
303 500 °C which corresponds to the region of mass loss in the TGA test results. The H_2O released at
304 temperature >150 °C is associated with the release of inherent moisture which presents in the
305 pore/capillaries of the carbonaceous materials and H_2O produced from decomposition of organic
306 components. It is also known that some H_2O exist as part of the crystal structure of inorganic
307 minerals which can contribute to H_2O formation at higher temperatures [36].

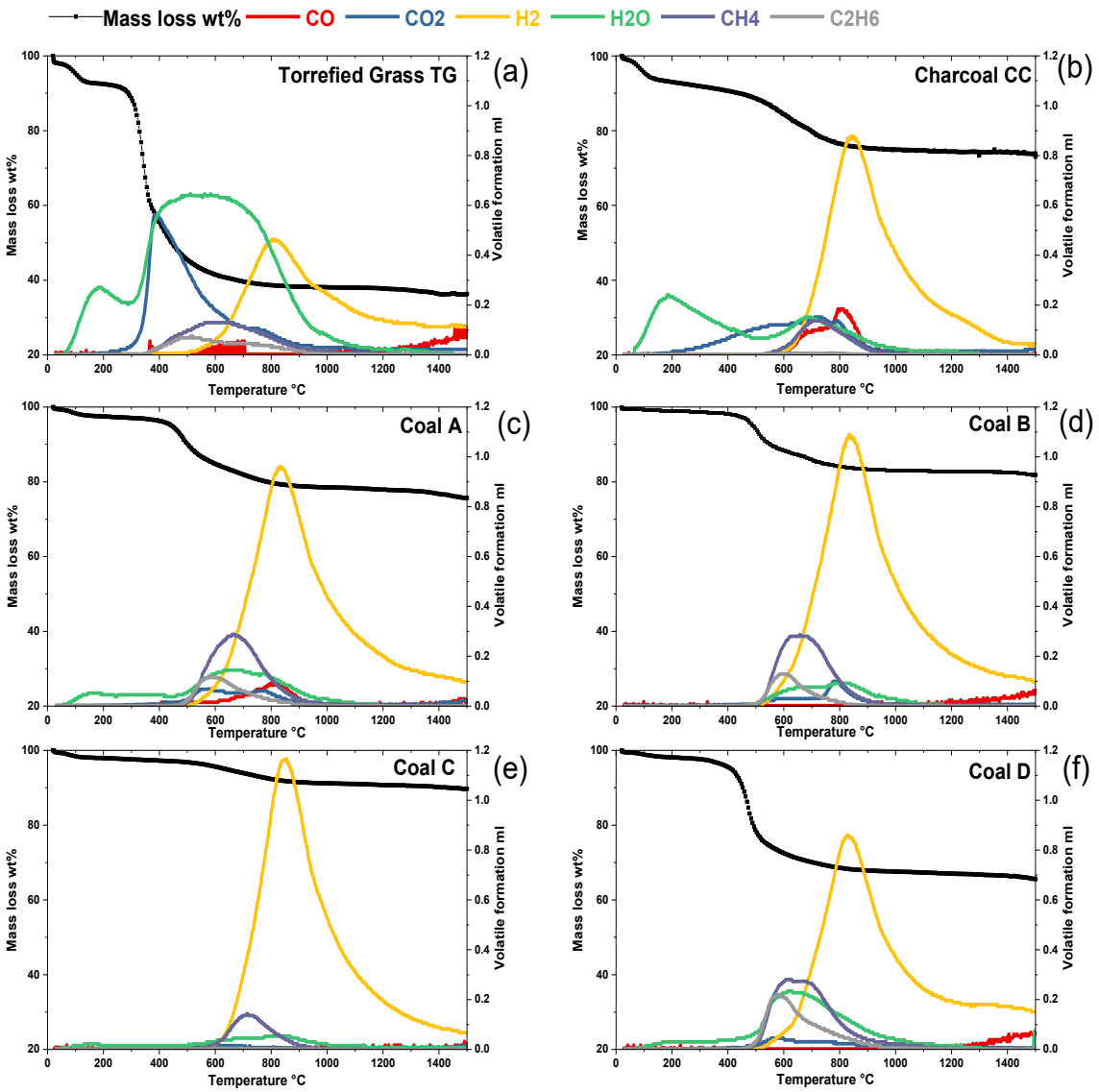


Figure 4. VTF-QMS for normalised gas species (CO, CO_2, H_2, H_2O, CH_4, and C_2H_6) evolved against TGA mass loss during heating at the heating rate of 10 °C/min under argon atmosphere for (a) Torrefied grass (TG); (b) charcoal (CC), (c) coal A; (d) coal B; (e) coal C; (f) coal D.

The gas products evolved during the heating process are plotted in Figure 5, and some common phenomena can be observed for the biomass and coal samples. As it can be seen that both charcoal and torrified grass samples produced larger amounts of H_2O at low temperature (100 to 200 ˚C) than that of all coal samples. Each sample produced a peak for H_2O and CO_2 gas during the heating within the temperature range of 300 - 800 °C, but the peak for both biomass samples was significantly

larger than those for the four coal samples. The sharp H_2O and CO_2 peaks for torrefied grass at the temperature of 300-400 °C links well with the second sharp DTG peak for torrefied grass (shown in Figure 2b) and presents the case that this is due to the release of H_2O and CO_2 from decomposition of hemicellulose and cellulose at that temperature. Charcoal produced a flatter but wide peak of H_2O and CO_2 which may be as a result of the sample already being pre-treated to similar temperatures during the charcoal formation. Previous studies linked the amount and the temperature required for the gas species to be produced to the chemical structure of the biomass component used for the investigation [37]. Hemicellulose is higher in carboxyl content which results in higher CO_2 yield, while cellulose contains carbonyl and carboxyl species which results in CO and CO_2 product yield, and Lignin releases much more H_2 and CH_4 from cracking of aromatic rings and methoxyl [15, 37].

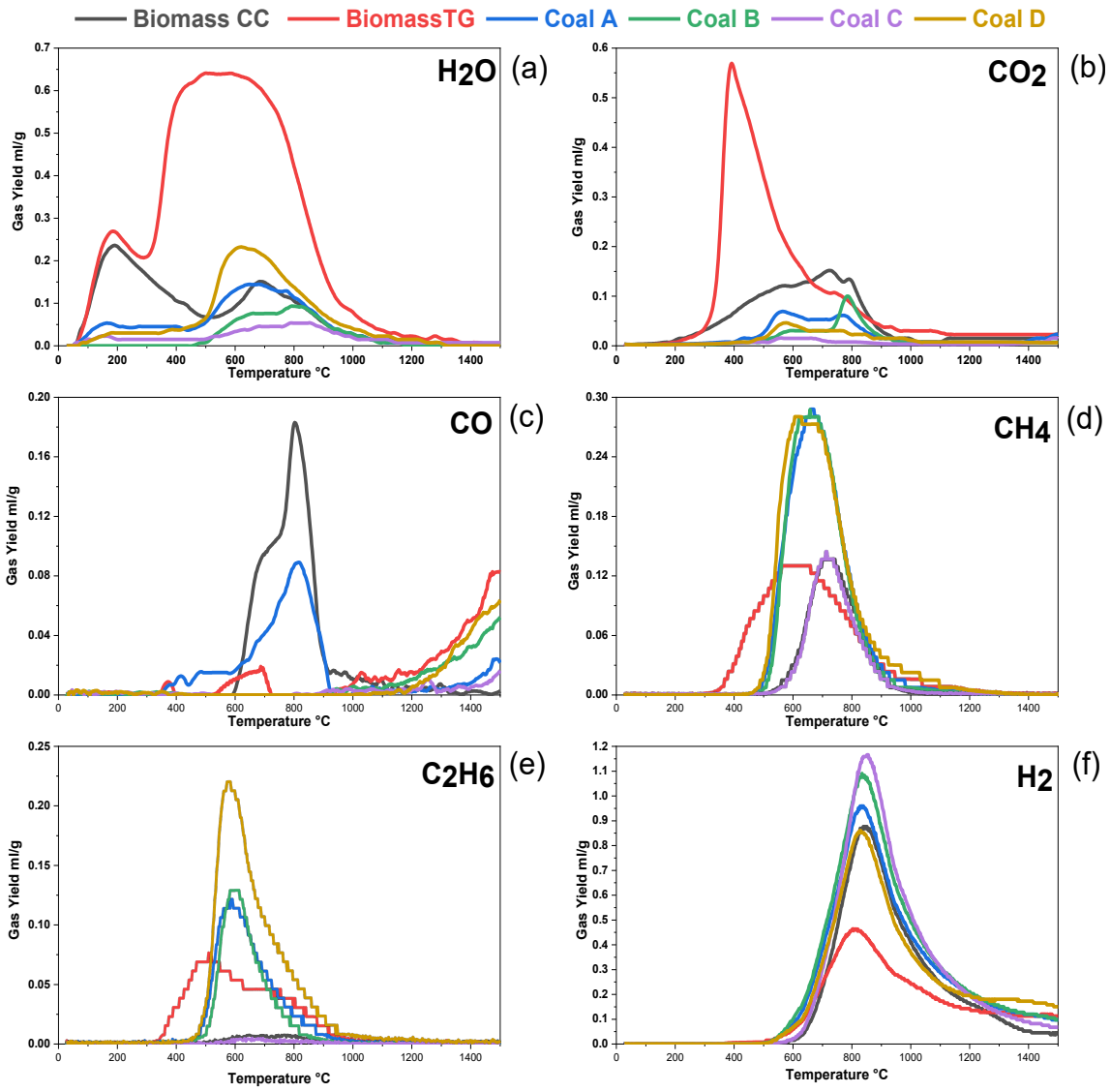


Figure 5. An off-gas analysis of (a) H_2O; (b) CO_2; (c) CO; (d) CH4; (e) C_2H_6; and (f) H_2 evolved during VTF-QMS experiments.

Torrefied grass was the only material which started to produce CH_4 and C_2H_6 at the temperatures under 400 °C, while all the other samples produced these gases at the temperature > 500 °C. Finally H_2 and CO formation happened in the higher temperature range which is linked to reactions that take place at higher activation energy [8, 38]. In addition, the thermal cracking of hydrocarbons is possible at temperature > 600 °C. The formation of CO and H_2 at high temperature is also linked to CH_4 reaction with CO_2 to form CO and H_2 [39]. Also hydrocarbons evolved at higher temperatures

may react with H_2O to form H_2 and some CO [30, 40] through the reaction schemes presented in equations (4) and (5).

$$CO_{2\,(g)} + CH_{4\,(g)} \rightarrow 2CO_{\,(g)} + 2H_{2\,(g)} \quad (4)$$

$$H_2O_{\,(g)} + CH_{4\,(g)} \rightarrow CO_{\,(g)} + 3H_{2\,(g)} \quad (5)$$

4. Kinetic analysis

4.1. The Kissinger–Akahira–Sunose method

The devolatilisation for carbonaceous materials is a complex process as several reactions occur during thermal decomposition, which includes carbonizing and gas evolution simultaneously during the heating process. For a better understanding of the devolatilisation process, many researchers studied thermal decomposition of carbonaceous materials using TGA technique (which is the most common technique) to measure the weight loss for kinetic analysis. The kinetic parameter obtain are used to understand the complexity of the reaction and in modelling devolatilisation process to predict the mass and energy balances. The devolatilisation mechanism can be described as following: [22]

Raw carbonaceous materials ⟶ Volatile + Char

The devolatilisation conversion and apparent rate of reaction is calculated through equation (6):

$$\frac{dx}{dt} = \boldsymbol{k}(\boldsymbol{T})\boldsymbol{f}(\boldsymbol{x}) \quad (6)$$

The temperature dependent reaction rate constant ***k (T)*** can be expressed by equation (7):

$$\boldsymbol{k}(\boldsymbol{T}) = \boldsymbol{A}\, \boldsymbol{e}^{\left(\frac{E_x}{RT}\right)} \quad (7)$$

By combining equations (6) and (7) the overall reaction conversion rate can be expressed by equation (8):

$$\frac{dx}{dt} = \boldsymbol{A}\, \boldsymbol{e}^{\left(\frac{E_x}{RT}\right)} \boldsymbol{f}(\boldsymbol{x}) \quad (8)$$

where x, $\frac{dx}{dt}$, A, E_x, R, T and $f(x)$ denote the devolatilisation conversion degree, reaction conversion rate, pre-exponential factor, activation energy, universal gas constant, temperature and reaction function respectively.

The devolatilisation conversion degree(x) is defined by equation (9):

$$x = \frac{mi - mt}{mi - mf} \tag{9}$$

where mi is the initial weight of the sample, mt is the instant weight of the sample at time t, and mf is the final weight of the sample after the reaction.

The experiments are carried out using non-isothermal heating with a constant linear heating rate, β :

$$\beta_i = \frac{dT}{dt} \tag{10}$$

where i represents the given heating rate being considered.

The following equation for reaction conversion rate can be obtained by equations (8) and (10):

$$\frac{dx}{dT} = \frac{A}{\beta} e^{\left(\frac{E_x}{RT}\right)} f(x) \tag{11}$$

Equation (12) can be obtained by integrating equation (11) to represent the cumulative reaction rate:

$$\mathbf{g(x) = \int_0^x (f(x))^{-1} = \frac{A}{\beta} \int_0^T e^{\left(\frac{E_x}{RT}\right)} dT} \tag{12}$$

where $g(x) = \int_0^x (f(x))^{-1}$ is the integral form of the reaction model [32]. There are several integral methods available which can be used to accurately estimate kinetic parameter. Among them Kissinger–Akahira–Sunose (KAS) model is used by many researchers as a proven model, since the kinetic parameters of a solid state reaction can be obtained without knowing the reaction mechanism and also it is known to have high accuracy in estimating kinetic parameter [10, 31]. The apparent activation energy (E_x) obtained by plotting natural logarithm of heating rate over

temperature square at a given value of conversion $\boldsymbol{In}(\frac{\boldsymbol{\beta i}}{\boldsymbol{T_{xi}}^2})$ versus $\frac{\mathbf{1000}}{\boldsymbol{T_{xi}}}$, which is represented by a linear equation (13) for the KAS model for a given value of conversion, $\boldsymbol{x}$, where the gradient is equal to $-\frac{\boldsymbol{E_x}}{\boldsymbol{R}}$ [41].

$$\mathbf{In}(\frac{\mathbf{\beta i}}{\mathbf{Txi^2}}) = \mathbf{l\,n}\left(\frac{\mathbf{Ax\,Rx}}{\mathbf{E_x gx)}}\right) - \frac{\mathbf{E_x}}{\mathbf{RT_{xi}}} \quad (13)$$

4.2. Kinetic analysis

The results obtained from the TGA tests at three heating rates (10, 20, and 30 °C/min) are inputted to a calculation according to the KAS method in order to calculate the activation energy ($\mathbf{E}_a$) [10]. As can be seen from off-gas analysis plots in Figure 5, at the temperature of < 200 °C the weight loss is mostly related to surface moisture, with the devolatilisation process related to reducing gases beginning at > 200 °C and then proceeding rapidly to 900 °C. So the devolatilisation conversion degree (x) was calculated according to equation (9) for weight loss in the temperature range of 200-900 °C for all carbonaceous materials tested. Figure 6 shows the devolatilisation conversion degree(x) for torrefied grass (TG) as a function of temperature in TGA tests at the heating rates of 10, 20, and 30 °C/min.

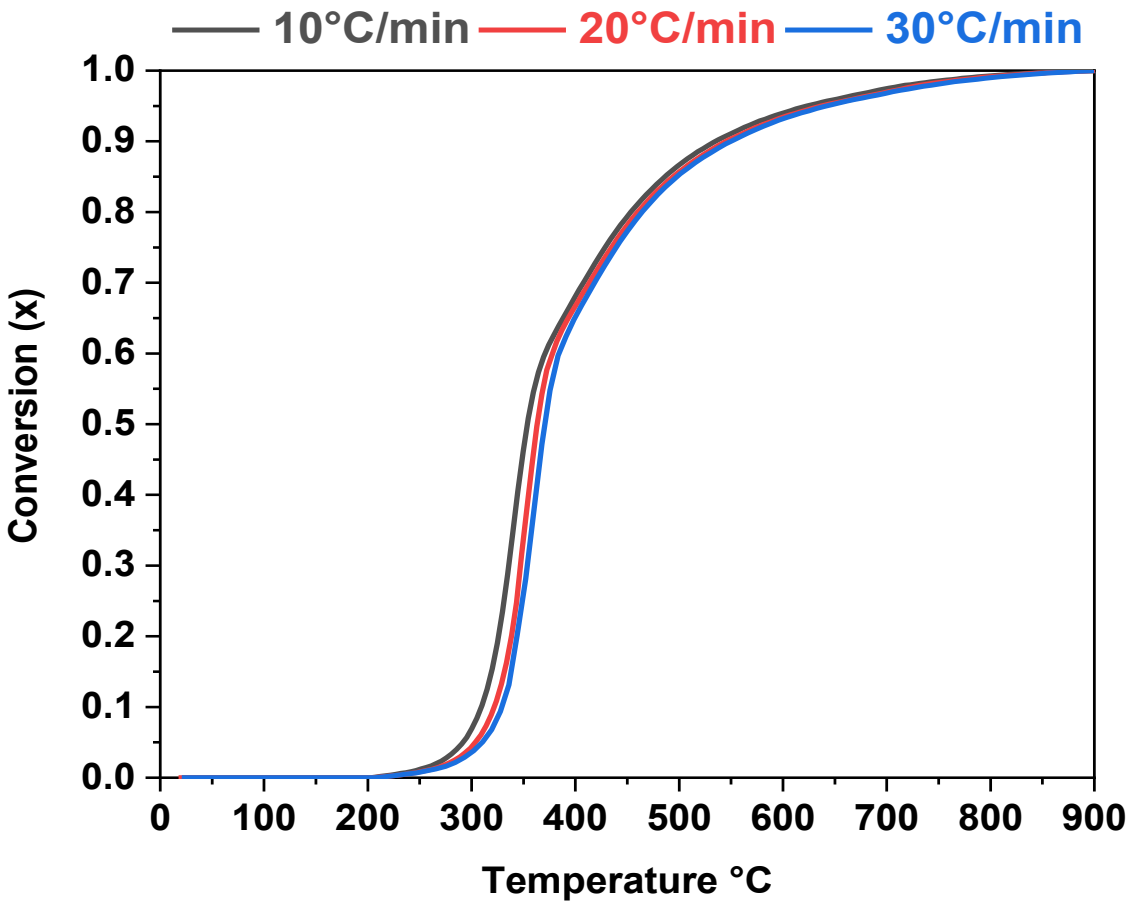
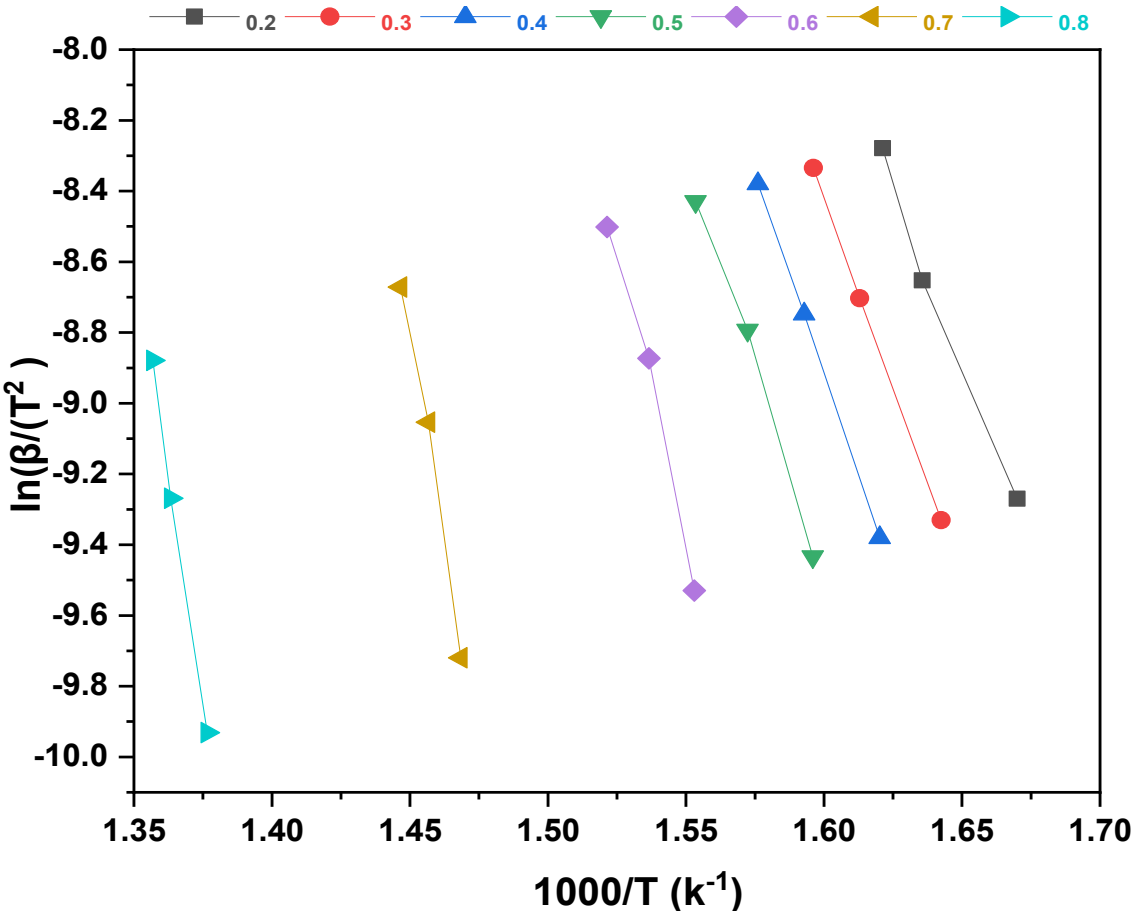


Figure 6. Extent of conversion curves for the devolatilisation process of torrefied grass (TG) as a function of temperature in TGA tests at different heating rates.

The apparent activation energy from a plot of $In(\frac{\beta i}{T_{xi}^2})$ versus $\frac{1000}{T_{xi}}$, for a given value of conversion (x) in the range of 0.2 to 0.8 is shown in Figure 7 for torrefied grass (TG). The average activation energy is calculated from the gradient equal to $-\frac{E_x}{R}$ and the correlation coefficients. R^2 values corresponding to the linear lines of best fit were in the range of 0.91 to 1.00 [33] showing good agreement.



404

405 *Figure 7. KAS plot of torrefied grass (TG) for different values of conversion to calculate the activation*

406 *energy at different heating rates.*

407 Table 2 contains the calculated variables for all carbonaceous materials tested in this study. It is

408 seen that the apparent activation energy was not the same for all conversion degrees, which

409 confirms the occurrence of different reactions at different temperatures during the experiment.

410 Charcoal has quite high and stable $\mathbf{E}_{\alpha}$ values throughout, and the value does not change a lot with

411 the change in conversion degree probably because of the effects of pre-treatment on this material.

412 Torrefied grass behaved differently, starting with a low $\mathbf{E}_{\alpha}$ value at a low conversion degree and

413 increasing linearly with an increase of conversion. This may correspond to low $\mathbf{E}_{\alpha}$ values for

414 decomposition of the remaining hemicellulose and cellulose but higher $\mathbf{E}_{\alpha}$ values for lignin

415 decomposition. Coal A shows a similar behaviour to charcoal with quite stable high $\mathbf{E}_{\alpha}$ values, while

416 coal B which contains medium volatile matter content has low stable $\mathbf{E}_{\alpha}$ values. Coal C has low $\mathbf{E}_{\alpha}$

value at low conversion degree and increases linearly with an increase in conversion. Coal D starts with low $\mathbf{E_a}$ value at low conversion degree and increases linearly with an increase in conversion degrees up to 0.6 conversion, and then there is a significant increase in the values at conversion degrees of 0.7 and 0.8. This behaviour may be influenced by error in the method since the difference for conversion degrees at different heating rates are not very large, which is seen in Figure 6.

Table 2. Activation energy Ea values in kJ/mol obtained for different carbon sources by using KAS, R^2 corresponding to linear fittings

	CC		TG		A		B		C		D	
Conversion (x)	E_a	R^2	E_a	R^2	E_a	R^2	E_a	R^2	E_a	R^2	E_a	R^2
0.2	201	0.99	165	0.99	215	1.00	183	0.96	77	0.95	192	0.99
0.3	224	1.00	179	1.00	246	1.00	194	0.97	120	0.93	242	0.99
0.4	293	1.00	189	1.00	247	1.00	197	0.97	154	0.93	278	1.00
0.5	313	1.00	198	0.99	268	1.00	193	0.96	185	0.95	311	1.00
0.6	341	1.00	271	0.98	304	1.00	180	0.91	219	0.94	390	0.99
0.7	366	1.00	400	0.99	294	1.00	169	0.92	264	0.95	650	0.98
0.8	294	1.00	440	1.00	323	1.00	173	0.95	335	0.95	1897	95.00
Average E_a	290		263		271		184		194		566	

These kinetic models assume the same reactions occurring at a specific conversion degree for different materials but as it can be observed from Figure 4 that multiple reactions take place at different temperatures. Therefore it is difficult to make accurate comparison between different carbon materials. This means the reaction mechanism can change during the devolatilisation process, therefore $\mathbf{E_a}$ is dependent on conversion and the average value of $\mathbf{E_a}$ can be estimated as a function of conversion. Kinetic analysis showed charcoal, torrefied grass and coal A (already injected

in HIsarna trials) have similar average activation energy values (290, 263 and 271 kJ/mol respectively). Since decomposition of the carbon materials consists of multiple chemical reactions, the $\mathbf{E}_{\boldsymbol{a}}$ value may change depending on the reactions taking place at specific conversion degree. It can be noticed in Figure 8 that the value of $\mathbf{E}_{\boldsymbol{a}}$ increases with an increase in conversion.

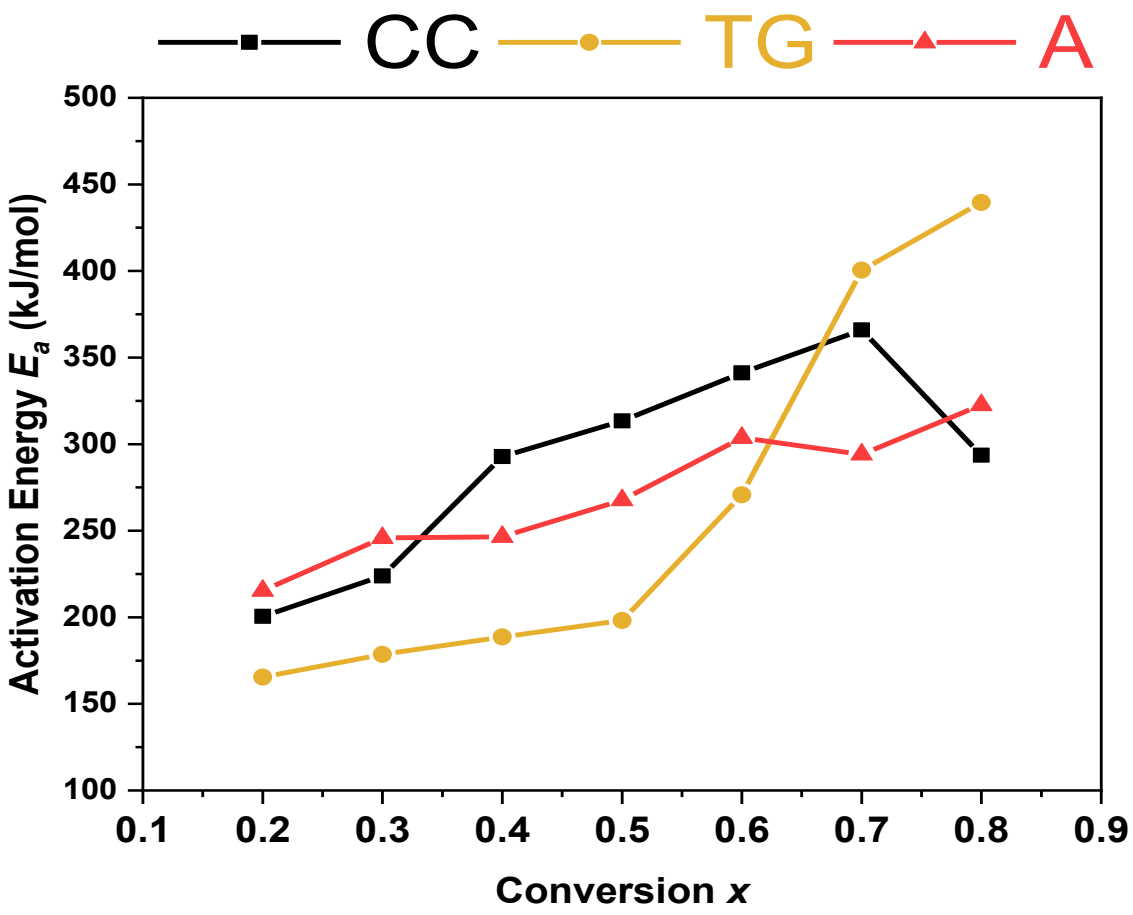


Figure 8. Activation energy Ea as a function of the conversion degree for charcoal (CC), torrefied gas (TG) and Coal A.

The increase in $\boldsymbol{E}_{\boldsymbol{a}}$ for torrefied grass is notably larger. This is because at low conversion levels very large amounts of weakly bonded components evolved e.g. H_2O and CO_2 shown in Figure 4 (a), therefore less energy is required for them to be removed. Charcoal starts with lower $\boldsymbol{E}_{\boldsymbol{a}}$ at conversion degrees of 0.2 and 0.3 compared to coal A, but coal A has lower *Ea* at conversion degree of 0.4 - 0.7. As can be seen in Figures 4 (b) and (c) charcoal produces larger amount of CO_2 at low temperature where coal A produces more of the other volatiles e.g. CH_4, C_2H_6 and H_2 at lower

443 temperature which confirms the differences in the E_a values. Based on off-gas analysis and kinetic
444 values charcoal with current properties is the more likely source of biomass which can replace
445 thermal coal in HIsarna technology, however material handling and pre-treatment may need to be
446 re-considered to optimise its use in the process.

447 **5. Comparison of carbonaceous materials for HIsarna process**

448 The results of this study indicate that different reactions take place during specific conversion
449 degree for different carbon materials, therefore devolatilisation is affected by the material
450 properties which in turn is linked to volatile mater content. There has been similarities in
451 devolatilisation behaviour (such as devolatilisation temperature), which is essential for smelting
452 reduction vessel in HIsarna process. Biomass samples produced significantly larger amount of H_2O
453 and CO_2 at low temperatures, however, coal samples produce more CH_4, C_2H_6 and H_2.

454 Despite the pre-treatment of biomass charcoal samples, this study showed that there is still
455 significant weight loss (release of H_2O) at low temperatures because H_2O is absorbed from
456 atmosphere due to their porous structure of the charcoal. Torrefied grass releases a large amount of
457 H_2O and CO_2 at the temperature between 300-400 °C due to its high oxygen potential. These gases
458 and H_2O releasing at lower temperatures can cause temperature drop in the HIsarna furnace which
459 needs heat compensation and due to high O_2 level much more carbon material may be needed. To
460 avoid these problems and utilise torrefied grass efficiently, a pre-treatment at the temperature of up
461 to 400 °C in inert atmosphere is necessary to reduce the oxygen content and produce bio-chars with
462 similar chemical properties to thermal coal currently used in HIsarna. To complete this process heat
463 sources from other parts of the steel plant can be utilized to keep the “green” credentials of
464 biomass, the gasses and tars released in the pre-treatment process can be used to generate heat
465 and power for HIsarna process.

466 Because of the porous structure of biomass carbon sources (e.g. charcoal), material handling needs
467 to be different to avoid H_2O absorption from atmosphere which is evidence in the test results. It may

need to consider pre-heating biomass to the temperature of ~200 °C before injection to remove all H_2O and other oxide impurities from biomass surface to maintain HIsarna process efficiency. Further studies may be required to investigate the effect of H_2O content in carbonaceous materials on HIsarna process such as materials handling and heat balance.

6. Conclusions

In order to enable the selection of suitable fuel mix in the novel HIsarna ironmaking process, four coals with notable differences in volatile matter content along with two biomass samples sourced from wood and grass origins were investigated in this study. The following conclusions can be obtained.

- The wt% of reducing gases e.g. H_2, CO, and hydrocarbons, and the temperature required for these gases to evolve was notably different for all the carbonaceous materials tested in this study, but the respective maximum peaks of evolution of these gases corresponded well to the maximum rate of mass loss.
- The off-gas analysis reveals torrefied grass contains large amount of water and carbon dioxide which will be released at very low temperature, therefore pre-treatment to the temperature of ~400 °C is necessary to produce chars with similar properties to coal injected in HIsarna.
- The change of reactivation energy E_a as a function of conversion degree is determined, which is linked to different reactions at different temperatures.
- Materials handling needs to be different for biomass (compared to thermal coal) to avoid H_2O absorption.

Acknowledgement

DK would like to thank Tata Steel Nederland Technology BV for providing PhD scholarship (Reference Number: COL1421/GIPS03241) to carry out this research. ZL would like to appreciate the funding from EPSRC under the grant number EP/N011368/1. The authors appreciate Tata Steel HIsarna team for fruitful discussions and providing samples. DK also would like to thank Dr. Ian Moore at Material

Processing Institute for providing coal C and coal D samples, and Tata Steel IJmuiden would like to acknowledge OrangeGreen BV for providing the torrefied grass sample.

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Devolatilisation Characteristics of Coal and Biomass with Respect to Temperature and Heating Rate for HIsarna Alternative Ironmaking Process

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HIGHLIGHTS

- **Devolatilisation behaviours of different carbon sources investigated for HIsarna alternative ironmaking process.**
- **Maximum peaks of evolved gases from VTF-QMS corresponded well to DTG curves.**
- **The kinetic parameters for coal and biomass samples were determined.**
- **Biomass pre-treatment temperature suggested to produce chars with similar properties to coal injected in HIsarna.**

Abstract: HIsarna process offers a novel low CO_2 emission alternative to the blast furnace for primary iron production. This new smelting ironmaking technology is flexible in raw material usage such as the substitution of biomass for coal as a reductant. Reduction is conducted through multiple mechanisms within the smelting vessel including gaseous reaction products from thermal decomposition of volatile matters reacting directly with iron oxide containing slags and injected iron ore. In this study, four coals with notable differences in volatile matter content along with two biomass samples sourced from wood and grass origins were investigated for the selection of suitable fuel mix. Thermogravimetric analysis (TGA) was used to measure the weight loss of the

carbonaceous materials and a vertical tube furnace coupled with a quadrupole mass spectrometer (VTF-QMS) was employed for off-gas analysis during the devolatilisation. During TGA tests the samples were heated under a 99.9999 % argon atmosphere to 1500 °C at three different heating rates to investigate the kinetics of thermal decomposition for these materials. Through use of the Kissinger– Akahira–Sonuse model an average activation energy was determined as a function of the conversion degree. The furnace experiments were carried out under a 99.999% Ar atmosphere to a peak temperature of 1500 °C, at a heating rate of 10 °C/min. The wt% of reducing gases e.g. H_2, CO, and hydrocarbons, and the temperature required for these gases to evolve was notably different for each materials, but the respective maximum peaks of evolution of these gases corresponded well to the maximum rate of mass loss. Furthermore, the off-gas analysis reveals torrefied grass contains large amount of water and carbon dioxide which will be released at very low temperature, therefore pre-treatment to the temperature of ~400 °C is necessary to produce chars with similar properties to coal injected in HIsarna.

Keywords:

HIsarna technology

Biomass

Coal

Heating rate

Devolatilisation

Kinetic analysis

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1. Introduction

Coal is the most widely used fossil fuel in the world, and it continues to dominate the energy supply and the demand is still set to grow, particularly in developing countries despite international environmental agreements. Stringent environmental legislations such as the compulsory target of 80-95% carbon dioxide (CO_2) emissions reduction by 2050 compared to the 1990 baseline, have forced all industries into innovation and transformation [1]. Ironmaking is an energy intensive process accounting for 4-7% of global CO_2 emissions alone [2]. With the strict environmental legislation and recent signing of the Paris agreement, steel manufacturers are under continually increasing pressure to reduce CO_2 emissions further to near net zero levels. Despite substantial improvements concerning environmental performance, around a 50% reduction in CO_2 emissions since 1990, it is believed a true step change in steel manufacturing technology is required. Current technologies consisting of sintering, coke making and blast furnace (BF) ironmaking contribute to approximately 90% of the CO_2 output from a blast furnace ironmaking-basic oxygen steelmaking integrate steel plant [2]. Therefore significant efforts are now being funnelled into alternative ironmaking technologies which promise the possibility to remove the necessity of coke making, sintering and ultimately BF ironmaking. Several alternative ironmaking processes have been commercialised or are under development, for example, commercially proven processes (COREX and FINEX), ITmk3 process, coal-based or gas-based HYL process, coal-based MXCOL or gas-based MIDREX, fluidised bed technologies (Cicored and circofer) and HIsarna technology [1, 4].

HIsarna technology is an alternative ironmaking process, which was developed under the European Ultra-Low CO_2 steelmaking (ULCOS) research programme since 2004. The potential economic benefits of low OPEX and CAPEX, its flexibility in raw materials (including scraps and wastes) and fuels, the environmental benefits of significant reduction in CO_2 and other greenhouse gases and its suitability for brownfield investment make the HIsarna process a prospective front runner as an

alternative to conventional BF. HIsarna represents a new route of smelting reduction, which has been developed by combining two known technologies of the Cyclone Converter Furnace (CCF) and the Smelting Reduction Vessel (SRV) [3, 4]. HIsarna has the ability to use a wider range of raw materials and fuels in comparison to the conventional BF ironmaking. HIsarna uses fine ores and thermal coals, and eliminate the sintering/agglomeration and coke plants, which consequently reduces the CO_2 emissions by up to 20% without carbon capture and storage (CCS) and potentially 80% with CCS [3, 5]. Partially substituting coking coal with thermal coal (pulverised coal injection), renewable biomass and natural gas in the conventional BF has been achieved but the requirement for burden support in the BF has set limitations on the use of these alternative fuels. However, HIsarna does not require burden support, therefore, it has great potential to fully substitute current coking coal with other fuels including biomass, while maintaining process efficiency and productivity [3].

The HIsarna process begins with iron ore (and fluxing materials) and oxygen being pneumatically injected into the CCF and hitting the wall of the CCF, where SRV off-gases are burning, as a result, iron ore is pre-reduced by 10-20% and becomes partially molten. The partially reduced ore then drips down along the wall under gravity at the temperature of approximately 1450 °C into the SRV where the metal bath temperature is between 1400-1500 °C. Thermal coal is injected into the SRV liquid metal which partly dissolves, adding carbon into the liquid metal to replenish that used in the smelting reaction steps of the process [3, 5]. The smelting reactions are shown in equations (1) to (3), (1) is an overall FeO reduction by carbon dissolved in the metal or solid char and (2) and (3) are intermediate/alternative steps [6].

$$FeO_{(l)} + [Fe{-}C_{(l)} \,/\, C_{(s)}] \rightarrow Fe_{(l)} + CO_{(g)} \qquad (1)$$

$$CO_{(g)} + FeO_{(l)} \rightarrow Fe_{(l)} + CO_{2\,(g)} \qquad (2)$$

$$CO_{2\,(g)} + C_{(s)} \rightarrow 2CO_{(g)} \qquad (3)$$

Replacement of coal with a carbon-neutral biomass in ironmaking offers great potential to reduce reliance on non-renewable carbon sources in this major contributor to carbon dioxide emissions from the steel industry. However, to maintain HIsarna's performance while substituting coal, carbonisation of raw biomass is necessary to increase fixed carbon (C_{fix}) content and remove moisture, oxygen and part of the volatile components, since existence of these components decrease the energy content [7]. Different thermochemical conversion technologies can be used for pre-treatment of the raw biomass to obtain chars with suitable properties for HIsarna. The pre-treatment conditions as well as the type of raw biomass determine the chemical, physical, and mechanical properties of the chars, which are necessary properties to produce chars which qualities most closely resembles the thermal coal currently used in the HIsarna process to maintain process efficiency and enable the technological shift in raw material use [5].

Once being injected into the smelting reduction vessel, the carbonaceous materials go through complex reactions, two of which are devolatilisation and burning out of the carbon. Devolatilisation happens first, and it continues to influence the solid carbon particles to the point when it is burnout [8]. The gaseous products evolved during the heating process are light hydrocarbons (mainly CH_4 and C_2H_6) which may crack into C and H_2 or react with the environment to form CO and H_2 or a mixture of H_2, H_2O, CO, and CO_2, the balance of which will change the reducing environment and control other parameters such as ignition, temperature and flame stability in the post combustion zone. As such devolatilisation of carbonaceous materials used in HIsarna technology is a key phenomenon which needs to be considered to achieve high efficiency [9]. While volatile matter is released the char structure goes through significant changes e.g. particle break-up, softening and swelling, which is strongly dependant on the chemical properties and reaction conditions such as heating rate, temperature and pressure [8].

Biomass devolatilisation usually involves the thermal decomposition of three components namely hemicellulose, cellulose, and lignin [10]. The process of decomposition for these components proceeds in three stages: moisture desorption, active decay and passive decay. Moisture desorption

occurs at temperature < 150 °C. This is followed by active decay in which most of the volatile matter is released at temperature between 200-500 °C, during this stage decomposition of hemicellulose and cellulose takes place. Decomposition of lignin starts in active decay and continues to passive decay at a very slow rate through the full temperature range of treatment [11]. Coal devolatilisation proceeds through a similar thermal degradation process, starting with moisture desorption at temperature < 150 °C and then degradation mobile and immobile phases occur at the temperatures between 150-600 °C. This results in the formation of the aliphatic and aromatic tar components and a number of light gases (e.g. H_2O, CO, CH_4 and CO_2). The final stage of thermal coal decomposition is the breakup of heterocyclic compounds at temperature higher than 600 °C [12].

The literature contains studies on coal and biomass pyrolysis by using TGA [13-15], fixed-bed reactors [16-18] and fluidized-bed reactors [19, 20]. TGA is the most common technique used to study thermal decomposition and kinetic analysis of coal and biomass. Combining this equipment with different analytic techniques, e.g. Fourier transform infrared spectrometry (FTIR) [21-24], gas chromatography (GC) [25] and mass spectrometry (MS) [26-32] is quite common. Using these techniques the gaseous products evolved during heat treatment can be investigated simultaneously or afterwards to establish the mechanism for coal and biomass decomposition. TG-MS technique has been applied because of its main advantage of being the on-line monitoring of evolving gases, which can be used simultaneously with TG equipment to monitor the gas atmosphere during sample decomposition. The effect of important parameters such as particle size, heating rate, holding time and gas atmosphere have been studied using TGA. In addition there are numerous studies which used simultaneous thermal/gas analysis to analyse evolved gases.

Much of the pyrolysis work done on gas evolution analysis has focused on determining the effect of coal rank on the off-gas generated during thermal processing. Chinese coals with different grades and different H/C atomic ratios have been studied using simultaneous gas analysis under an inert atmosphere [26-28], and it was found that thermal decomposition and gas evaluation behaviour of coals are strongly dependent on temperature and the coal rank. This method has also been used to

148 study the effect of temperature and time [29] with regards to devolatilisation kinetics for different
149 types of biomass and coal/biomass blends [30, 31]. These researchers found that devolatilisation of
150 biomass is dependent on chemical properties including ash and volatile contents, temperature and
151 thermal treatment time. Additionally the off-gas of chitin biomass with various molecular structures
152 in an inert atmosphere was studied to determine the influence of zeolite catalysts on the utilization
153 of chitin biomass [32].

154 Although extensive research has been carried out on the devolatilisation behaviours for a number of
155 different coal and biomass, the research and development for the carbonaceous materials (coal and
156 biomass) for HIsarna technology is scarce, and also there is very limited information on direct
157 comparison between coal and biomass in term of devolatilisation. Much of the research done on
158 devolatilisation or gas evolution focused on the pyrolysis of coals and biomass using simultaneous
159 TGA-MS carried out with small sample size between (10-20) mg. Despite all the advantages of
160 simultaneously measurement such as real time analysis, qualitative and quantitative analysis but
161 small sample size may mean high level of uncertainty in the off-gas analysis due to side reactions. An
162 increase in the sample size in TGA can cause a temperature distribution problem and on the other
163 hand, TGA may struggle to handle heavy tar products if sample size increased. In this study a high
164 temperature vertical tube furnace coupled with a mass spectrometer is utilised to reliably study
165 larger samples with regards to their devolatilisation characteristics with an aim of attaining a more
166 accurate representation of gaseous product evolution from each sample under novel alternative
167 ironmaking technologies. This research aims to enable the selection of suitable fuel mix for the
168 HIsarna alternative ironmaking process.

169 **2. Materials and methods**

170 **2.1. Sample preparation**

171 Four coals and two biomass samples were tested in this study. Their proximate and ultimate analysis
172 are listed in Table 1. The four coal samples contain different levels of volatile matter (VM) from low

(8.63%, Coal C) to medium (16.00% Coal B and 22.18% Coal A) and high (36.00%, Coal D), while the two biomass samples are charcoal CC with 12.10% VM (a wood based pre-treated biomass) and torrefied grass TG with 63.60% VM (a grass-based torrefied material provided by OrangeGreen BV through Tata steel). Coal A and charcoal CC have already been used in HIsarna process during the pilot plant trials and torrefied grass TG is another renewable source which may be considered for future trials. The samples were dried at 80 °C for 12 hours to ensure the removal of the free moisture and then crushed into small particles with the size range from 90 to 300 µm. The coal samples selected have different sulphur and ash contents that directly affect their reaction performance at high temperatures while biomass samples are generally much lower in sulphur and lower in ash contents.

Table 1. Proximate and ultimate values of the carbonaceous materials used in this study

	Coal A	Coal B	Coal C	Coal D	Charcoal CC	Torrefied Grass TG
Proximate Analysis wt% (db)						
Moisture/ % (ad)	8.87	7.11	1.24	1.30	4.56	4.40
Volatile Matter	22.18	16.00	8.63	33.00	12.10	63.60
Ash	8.80	10.00	4.41	7.20	1.80	4.40
Fixed Carbon (by difference)	69.02	74.00	86.96	59.80	86.10	32.00
Ultimate Analysis wt% (db)						
Carbon	81.91	83.60	86.97	80.30	89.4	57.60
Hydrogen	4.27	3.93	3.43	5.09	3.11	5.60
Nitrogen	2.19	1.07	1.20	1.50	0.57	0.29

Sulphur	0.24	0.78	0.86	0.89	0.06	0.09
Oxygen by (difference)	2.59	0.62	3.13	5.02	5.06	32.02

db - on a dry basis; ad - on an air dried.

2.2. Thermogravimetric analysis

The mass loss due to devolatilisation under non-isothermal conditions was determined by using thermogravimetric analysis (TGA) with a NETZSCH STA 449 instrument that has an analytical balance sensitivity of ± 0.01 mg. A 20 mg ± 0.01 sample was placed in an alumina crucible (height 4 mm x diameter 6.8 mm). The alumina crucible with test sample was placed on a platinum stage, which has a thermocouple located directly underneath to provide real temperature of the sample tested. All the samples were heated in a high impurity (99.9999%) argon atmosphere at the flow rate of 50 ml/min. The mass loss due to volatile matter evolving was recorded from ambient temperature to 1500 °C, at the heating rates of 10, 20 and 30 °C min^{-1} respectively. To ensure the reliability and reproducibility of the tests, preliminary tests have been carried out to define experimental conditions, and the test for the same sample has been repeated three times to produce concordant results.

2.3. VTF-QMS gas analysis

The gas analysis during devolatilisation was carried out using a Carbolite-Gero high temperature vertical tube furnace with a recrystallized alumina tube (VTF-1700/50, internal diameter 88 mm x length 1000 mm) shown in Figure 1. The furnace was coupled with a Hiden HPR 20 Quadrupole Mass Spectrometer (QMS) to monitor gaseous products evolving from the samples. The VTF-QMS combination allowed an increase in the sample weight to produce more representative volatile measurements of the bulk material and reduce measurement uncertainties. The samples were heated to 1500 °C in a high purity (99.999%) argon atmosphere at the heating rate of 10 °C/min while the furnace exhaust was connected to the QMS through a heated capillary (150 ^{o}C) to monitor gaseous products evolving from the samples and ensure no condensations occurred before the

ionization chamber. Each sample was weighed to be approximately 1.0 g and placed in an alumina crucible on the alumina pedestal and lifted to the hot zone of the vertical tube furnace (VTF). The tube was sealed, vacuumed using a standard rotary pump and then back filled with argon gas at a flow rate of 300 ml min^{-1} that carried gaseous products to the mass spectrometer (QMS). The argon concentration was measured to be 99.7% before the furnace heating cycle started. The QMS was set to measure readings of the following gases evolving from devolatilisation: N_2, O_2, CO, CO_2, Ar, H_2O, H_2, CH_4 and C_2H_6. After the desired temperature was reached, the furnace cooled down at 5 °C/min to room temperature in Ar atmosphere. Then the samples were taken out to weigh and analyse.

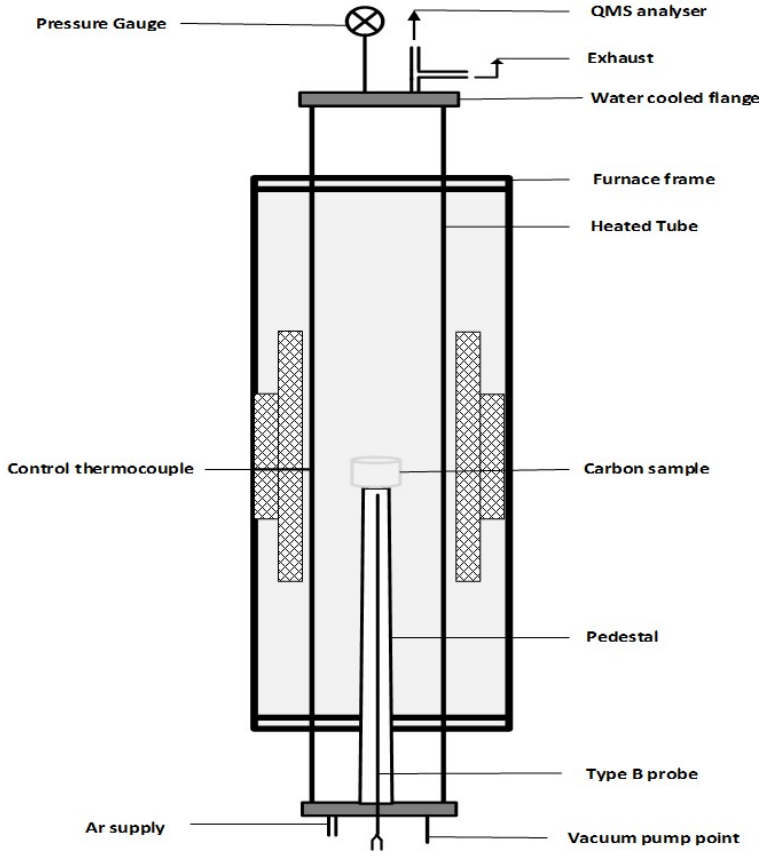


Figure 1. Vertical tube furnace (VTF) setup with a mass spectrometry for devolatilisation study. The quadrupole mass spectrometer (QMS) is connected to the gas sampling port.

3. Results and discussion

3.1. TG-DTG analysis

The weight loss curves and derivative thermogravimetric (DTG) curves produced from the TGA tests for the materials in Table 1, are shown in Figures 2a and 2b respectively. Figure 2a shows the weight loss due to devolatilisation of the samples at the heating rate of 10 °C/min under argon atmosphere.

Slow weight loss begins for all four coal samples at the temperature of ~100 °C and continues to ~180 °C, which is mainly associated with surface moisture loss. This is followed by rapid weight loss due to the release of organic volatile matter, and the starting temperature of the release of organic volatile matter depends on the volatile matter content of the coal sample. The weight loss curve starts at lower temperature for coals with higher volatile matter but all the curves stabilise at the temperature of around 650 °C regardless of the volatile matter contents. However, slow weight loss to the temperature of 1500 °C was still notable, this could be from decomposition of materials with a higher activation energy e.g. carbonyl and heterocyclic compounds, which subsequently leads to CO and H_2 formation [9].

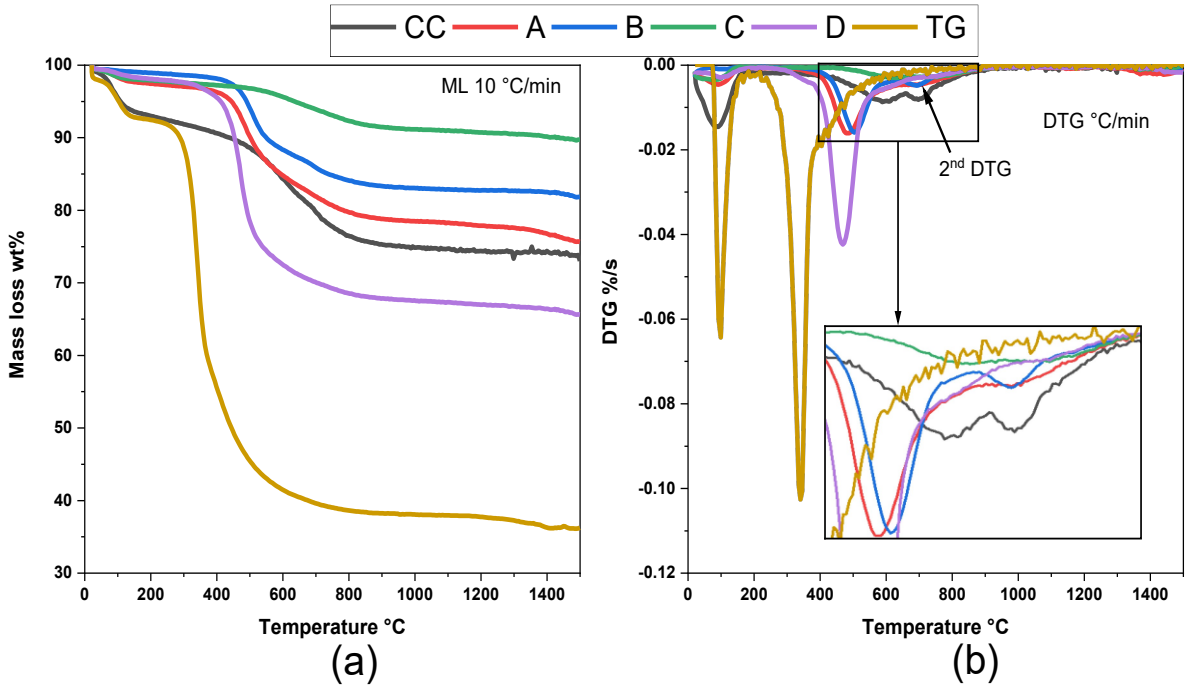


Figure 2. (a) Mass loss curves and (b) DTG curves of the carbonaceous materials tested in the high purity argon atmosphere at the heating rates of 10 °C/min from room temperature to 1500 °C.

These thermal decomposition results for coal samples can be explained with the reported mechanisms of coal devolatilisation [33], such as the devolatilisation process proposed by van Heek and Hodek (Figure 3) [12]. Coal decomposition starts with desorption of moisture and some light gasses at the temperatures of ~100 °C. On continued heating to ~250 °C the mobile phase degradation occurs which leads to tar formation, in particular the aliphatic tar component. Then at the temperatures of 300 °C and higher, degradation of the immobile phase occurs which results in formation of the aromatic tar components and a number of light gases (e.g. H_2O, CO, CH_4 and CO_2) as shown in Figure 3 [12], which is evidenced by the experimental results shown in Figure 4 (section 3.2). This is followed by decomposition of heterocyclic compounds at temperatures higher than 600 °C producing N_2, CO and H_2 gases.

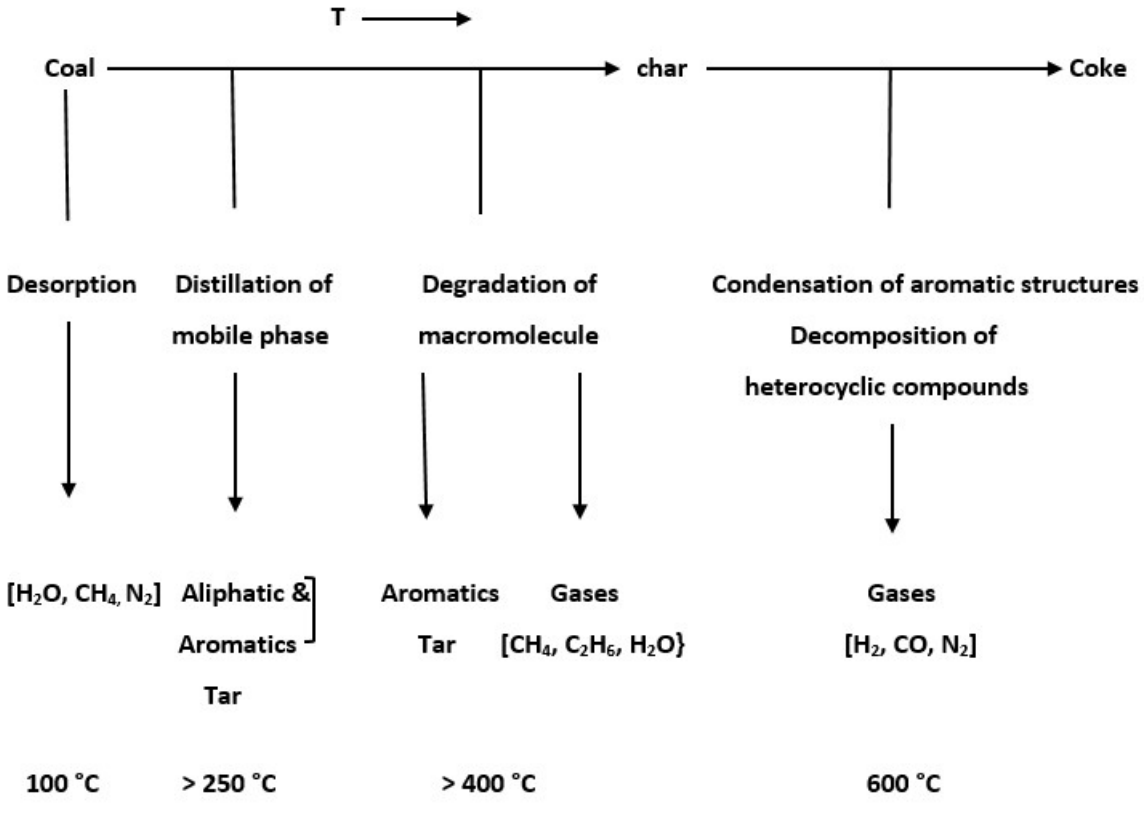


Figure 3. The main reactions occurring during the coal devolatilisation process [12]

As shown in Figure 2, decomposition behaviour of biomass samples are different from the four coals tested. The initial weight loss for both torrefied grass and charcoal starts at slightly lower temperatures of ~80 °C and continues steadily to the temperature of 200 °C. After this a sharp weight loss curve for torrefied grass occurs at temperatures from ~250 °C to 400 °C and the weight loss continues slowly to 1500 °C. However, the second step of weight loss for charcoal starts at much higher temperature of ~500 °C and continues to 1500 °C with a flatter weight loss curve that is because of the pre-treatment of the starting material. Decomposition of hemicellulose is expected to occur at the lower temperature range due to its random amorphous structure. The subsequent decomposition of cellulose and lignin follows at higher temperatures as the materials are more ordered and stronger bonded respectively. Biomass has a porous structure providing higher adsorption potential than thermal coal, which is likely to allow large amounts of moisture and carbon dioxide to be absorbed from the atmosphere. These absorbed components are weakly bonded and evolve at the very low temperatures [34]. Cellulose is the main component responsible for the second DTG peak, while lignin is the main component responsible for char formation. However thermal degradation of lignin can start at low temperature at a very slow rate and increases with the increase in temperature [35].

Figure 2b shows similar behaviour for coal samples, starting with the small peak at low temperature due to desorption followed by a large single peak due to devolatilisation. The exception for this is with coal B which has produced a clear secondary peak for devolatilisation, meaning coal B goes through extra phase of decomposition. However torrefied grass and charcoal both produced larger initial DTG peaks due to moisture loss followed by two devolatilisation peaks. There is one sharp peak which starts at the temperature of ~250 °C and the second peak which is partially superimposed on the late phase of the first peak for torrefied grass. This behaviour is linked to decomposition of cellulose and lignin respectively, while charcoal produces two peaks at much higher temperatures compared to torrefied grass which are from decomposition of lignin and agrees with other researchers' findings on similar materials [15, 35].

3.2. Comparison of devolatilisation behaviours for different carbonaceous materials

Various reactions occur simultaneously during devolatilisation upon heating, including break-up of chemical bonds, vaporisation, and condensation or recombination [22]. Using a quadrupole mass spectrometer (QMS) gaseous species evolved during heating process were measured continuously up to the temperature of 1500 °C. Figure 4 shows the mass loss due to devolatilisation measured in TGA tests against the normalized off-gas species measured in the VTF-QMS tests at the heating rate of 10 °C/min for the two biomass and four coal samples.

Similar behaviour has been observed for all the samples that gas species detected at low temperature of 100~200 °C were mainly H_2O, as the weight loss at low temperature is associated with the loss of surface moisture. However, at this low temperature range, the weight loss of the biomass samples was significantly higher than that of the coal samples measured, which is confirmed by the amount of these gases detected. Devolatilisation continued with increasing temperature, generating large amount of H_2O and CO_2 gas by biomass samples at temperature of >300 °C while none or very small amount of CO_2 from coal samples was measured but still significant amount of H_2O was produced. The amount of H_2O and CO_2 produced for torrefied grass during heating was much higher than charcoal, as charcoal has already been pre-treated. However, the amount of gas species generated by charcoal was still significantly higher than that from any of the coal samples tested at similar temperatures, which could be due to higher oxygen content in the charcoal, resulting in the oxidation of carbon and contributing to higher mass loss in charcoal.

The second region of weight loss is associated with the release of organic volatile matter, which started at similar temperatures for all the samples but the gas species generated were different. Both biomass samples started to generate H_2O and CO_2 at temperature > 300 °C, followed by the release of hydrocarbons at temperature > 400 °C, and H_2 and CO at > 500 °C. The peaks for gases generated in VTF-QMS tests spread over larger temperature range than those observed in TGA tests. This is caused by the gas mixing in the VTF and the time require for evolved gases travelling from the

300 sample location to the detection of mass spectrometer. This travelling distance in the VTF tube gives
301 rise to the comparatively consistent delay for all devolatilisation peaks compared to the TGA results.
302 All the four coal samples tested were found to produce H_2O, CO_2, CH_4, C_2H_6 and H_2 at temperatures >
303 500 °C which corresponds to the region of mass loss in the TGA test results. The H_2O released at
304 temperature >150 °C is associated with the release of inherent moisture which presents in the
305 pore/capillaries of the carbonaceous materials and H_2O produced from decomposition of organic
306 components. It is also known that some H_2O exist as part of the crystal structure of inorganic
307 minerals which can contribute to H_2O formation at higher temperatures [36].

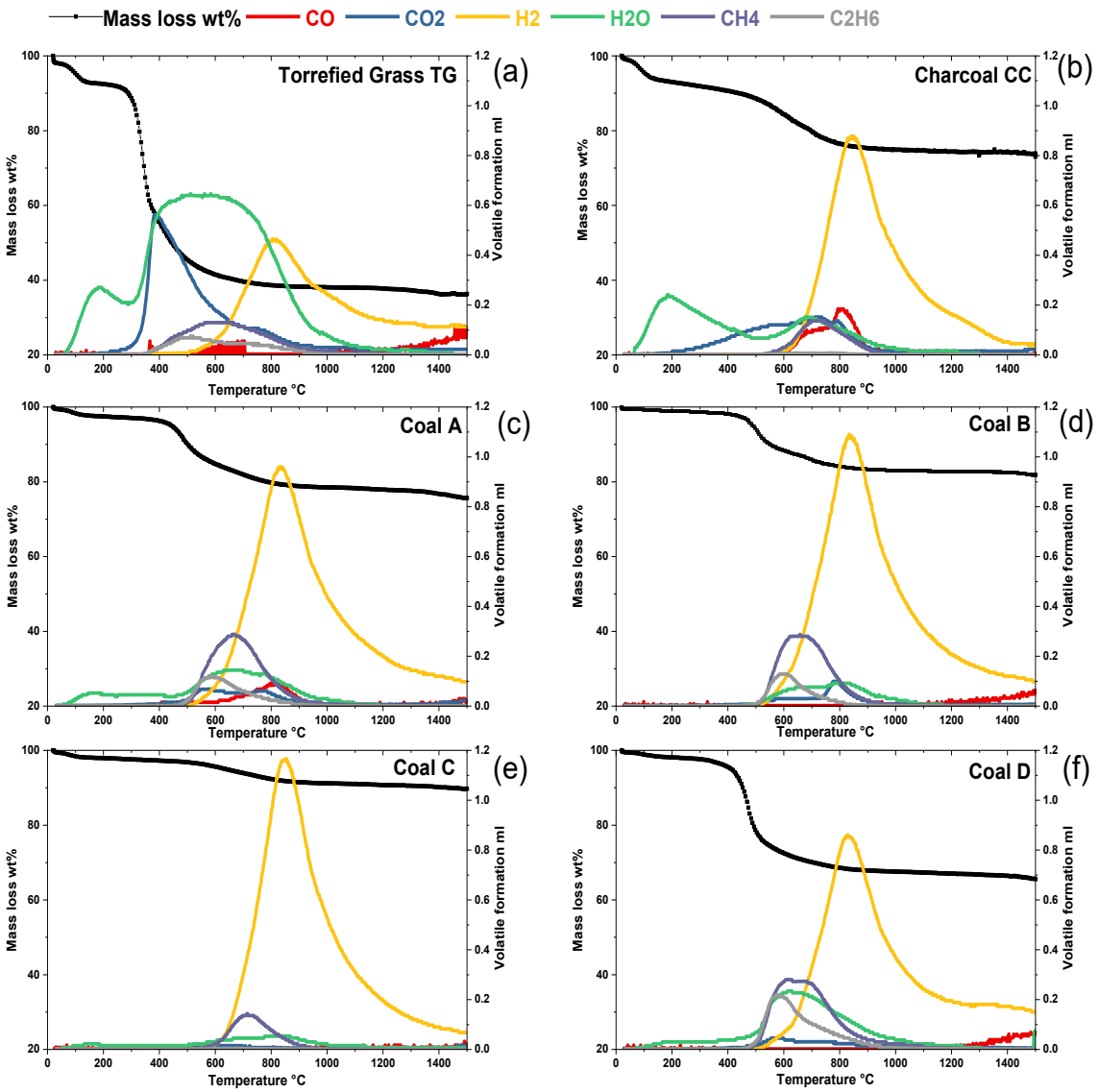


Figure 4. VTF-QMS for normalised gas species (CO, CO_2, H_2, H_2O, CH_4, and C_2H_6) evolved against TGA mass loss during heating at the heating rate of 10 °C/min under argon atmosphere for (a) Torrefied grass (TG); (b) charcoal (CC), (c) coal A; (d) coal B; (e) coal C; (f) coal D.

The gas products evolved during the heating process are plotted in Figure 5, and some common phenomena can be observed for the biomass and coal samples. As it can be seen that both charcoal and torrified grass samples produced larger amounts of H_2O at low temperature (100 to 200 ˚C) than that of all coal samples. Each sample produced a peak for H_2O and CO_2 gas during the heating within the temperature range of 300 - 800 °C, but the peak for both biomass samples was significantly

318 larger than those for the four coal samples. The sharp H_2O and CO_2 peaks for torrefied grass at the
319 temperature of 300-400 °C links well with the second sharp DTG peak for torrefied grass (shown in
320 Figure 2b) and presents the case that this is due to the release of H_2O and CO_2 from decomposition
321 of hemicellulose and cellulose at that temperature. Charcoal produced a flatter but wide peak of
322 H_2O and CO_2 which may be as a result of the sample already being pre-treated to similar
323 temperatures during the charcoal formation. Previous studies linked the amount and the
324 temperature required for the gas species to be produced to the chemical structure of the biomass
325 component used for the investigation [37]. Hemicellulose is higher in carboxyl content which results
326 in higher CO_2 yield, while cellulose contains carbonyl and carboxyl species which results in CO and
327 CO_2 product yield, and Lignin releases much more H_2 and CH_4 from cracking of aromatic rings and
328 methoxyl [15, 37].

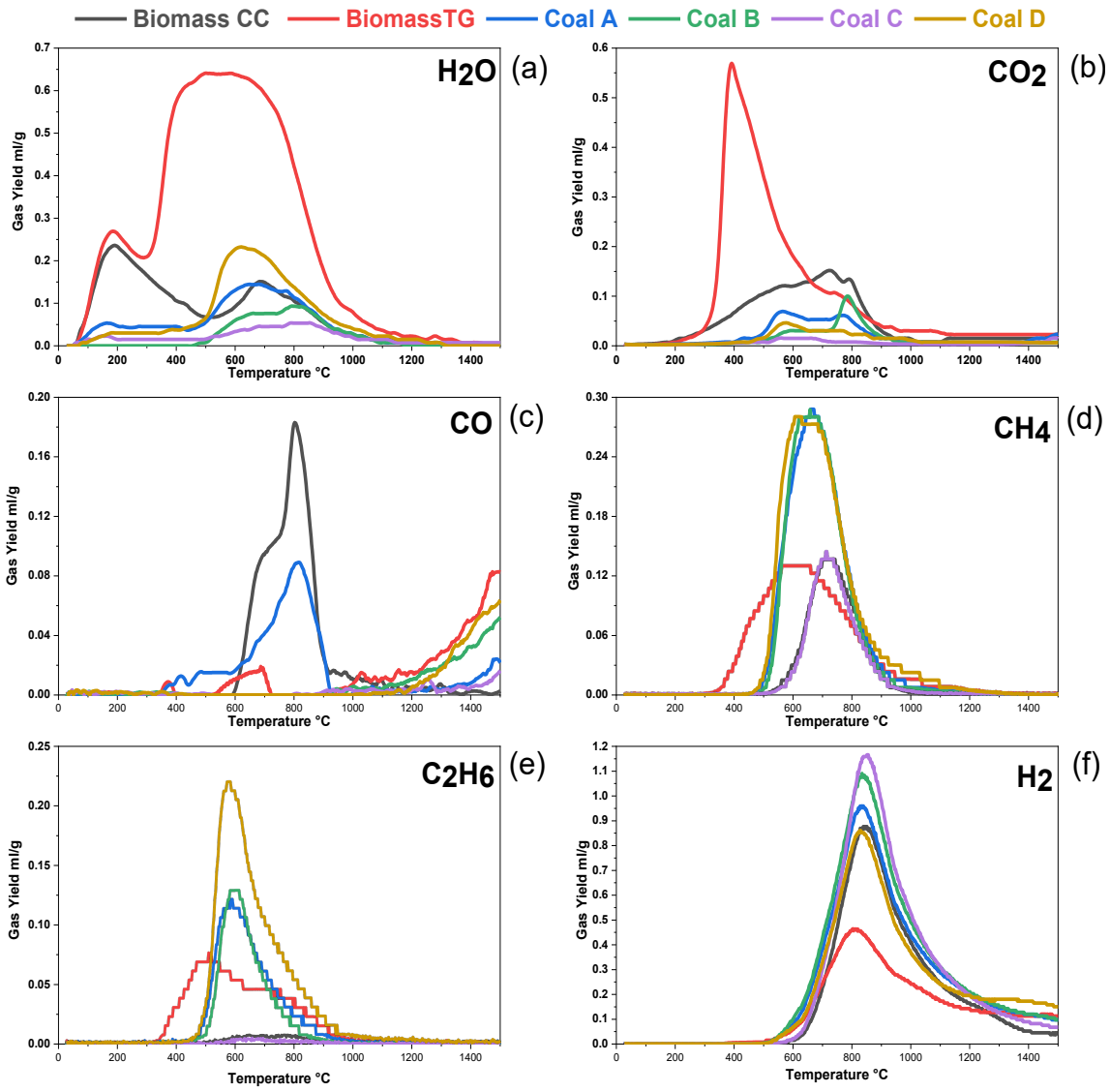


Figure 5. An off-gas analysis of (a) H_2O; (b) CO_2; (c) CO; (d) CH4; (e) C_2H_6; and (f) H_2 evolved during VTF-QMS experiments.

Torrefied grass was the only material which started to produce CH_4 and C_2H_6 at the temperatures under 400 °C, while all the other samples produced these gases at the temperature > 500 °C. Finally H_2 and CO formation happened in the higher temperature range which is linked to reactions that take place at higher activation energy [8, 38]. In addition, the thermal cracking of hydrocarbons is possible at temperature > 600 °C. The formation of CO and H_2 at high temperature is also linked to CH_4 reaction with CO_2 to form CO and H_2 [39]. Also hydrocarbons evolved at higher temperatures

may react with H_2O to form H_2 and some CO [30, 40] through the reaction schemes presented in equations (4) and (5).

$$CO_{2\,(g)} + CH_{4\,(g)} \rightarrow 2CO_{\,(g)} + 2H_{2\,(g)} \quad (4)$$

$$H_2O_{\,(g)} + CH_{4\,(g)} \rightarrow CO_{\,(g)} + 3H_{2\,(g)} \quad (5)$$

4. Kinetic analysis

4.1. The Kissinger–Akahira–Sunose method

The devolatilisation for carbonaceous materials is a complex process as several reactions occur during thermal decomposition, which includes carbonizing and gas evolution simultaneously during the heating process. For a better understanding of the devolatilisation process, many researchers studied thermal decomposition of carbonaceous materials using TGA technique (which is the most common technique) to measure the weight loss for kinetic analysis. The kinetic parameter obtain are used to understand the complexity of the reaction and in modelling devolatilisation process to predict the mass and energy balances. The devolatilisation mechanism can be described as following: [22]

Raw carbonaceous materials ⟶ Volatile + Char

The devolatilisation conversion and apparent rate of reaction is calculated through equation (6):

$$\frac{dx}{dt} = \boldsymbol{k(T)f(x)} \quad (6)$$

The temperature dependent reaction rate constant ***k (T)*** can be expressed by equation (7):

$$\boldsymbol{k(T) = A\, e^{\left(\frac{E_x}{RT}\right)}} \quad (7)$$

By combining equations (6) and (7) the overall reaction conversion rate can be expressed by equation (8):

$$\frac{dx}{dt} = \boldsymbol{A\, e^{\left(\frac{E_x}{RT}\right)} f(x)} \quad (8)$$

where x, $\frac{dx}{dt}$, A, E_x, R, T and $f(x)$ denote the devolatilisation conversion degree, reaction conversion rate, pre-exponential factor, activation energy, universal gas constant, temperature and reaction function respectively.

The devolatilisation conversion degree(x) is defined by equation (9):

$$x = \frac{mi - mt}{mi - mf} \tag{9}$$

where mi is the initial weight of the sample, mt is the instant weight of the sample at time t, and mf is the final weight of the sample after the reaction.

The experiments are carried out using non-isothermal heating with a constant linear heating rate, β :

$$\beta_i = \frac{dT}{dt} \tag{10}$$

where i represents the given heating rate being considered.

The following equation for reaction conversion rate can be obtained by equations (8) and (10):

$$\frac{dx}{dT} = \frac{A}{\beta} e^{\left(\frac{E_x}{RT}\right)} f(x) \tag{11}$$

Equation (12) can be obtained by integrating equation (11) to represent the cumulative reaction rate:

$$g(x) = \int_0^x (f(x))^{-1} = \frac{A}{\beta} \int_0^T e^{\left(\frac{E_x}{RT}\right)} dT \tag{12}$$

where $g(x) = \int_0^x (f(x))^{-1}$ is the integral form of the reaction model [32]. There are several integral methods available which can be used to accurately estimate kinetic parameter. Among them Kissinger–Akahira–Sunose (KAS) model is used by many researchers as a proven model, since the kinetic parameters of a solid state reaction can be obtained without knowing the reaction mechanism and also it is known to have high accuracy in estimating kinetic parameter [10, 31]. The apparent activation energy (E_x) obtained by plotting natural logarithm of heating rate over

temperature square at a given value of conversion $\boldsymbol{In}(\frac{\boldsymbol{\beta i}}{\boldsymbol{T_{xi}}^2})$ versus $\frac{\mathbf{1000}}{\boldsymbol{T_{xi}}}$, which is represented by a linear equation (13) for the KAS model for a given value of conversion, $\boldsymbol{x}$, where the gradient is equal to $-\frac{\boldsymbol{E_x}}{\boldsymbol{R}}$ [41].

$$\mathbf{In}(\frac{\mathbf{\beta i}}{\mathbf{Txi^2}}) = \mathbf{l\,n}\left(\frac{\mathbf{Ax\,Rx}}{\mathbf{E_x gx)}}\right) - \frac{\mathbf{E_x}}{\mathbf{RT_{xi}}} \quad (13)$$

4.2. Kinetic analysis

The results obtained from the TGA tests at three heating rates (10, 20, and 30 °C/min) are inputted to a calculation according to the KAS method in order to calculate the activation energy ($\mathbf{E}_a$) [10]. As can be seen from off-gas analysis plots in Figure 5, at the temperature of < 200 °C the weight loss is mostly related to surface moisture, with the devolatilisation process related to reducing gases beginning at > 200 °C and then proceeding rapidly to 900 °C. So the devolatilisation conversion degree (x) was calculated according to equation (9) for weight loss in the temperature range of 200-900 °C for all carbonaceous materials tested. Figure 6 shows the devolatilisation conversion degree(x) for torrefied grass (TG) as a function of temperature in TGA tests at the heating rates of 10, 20, and 30 °C/min.

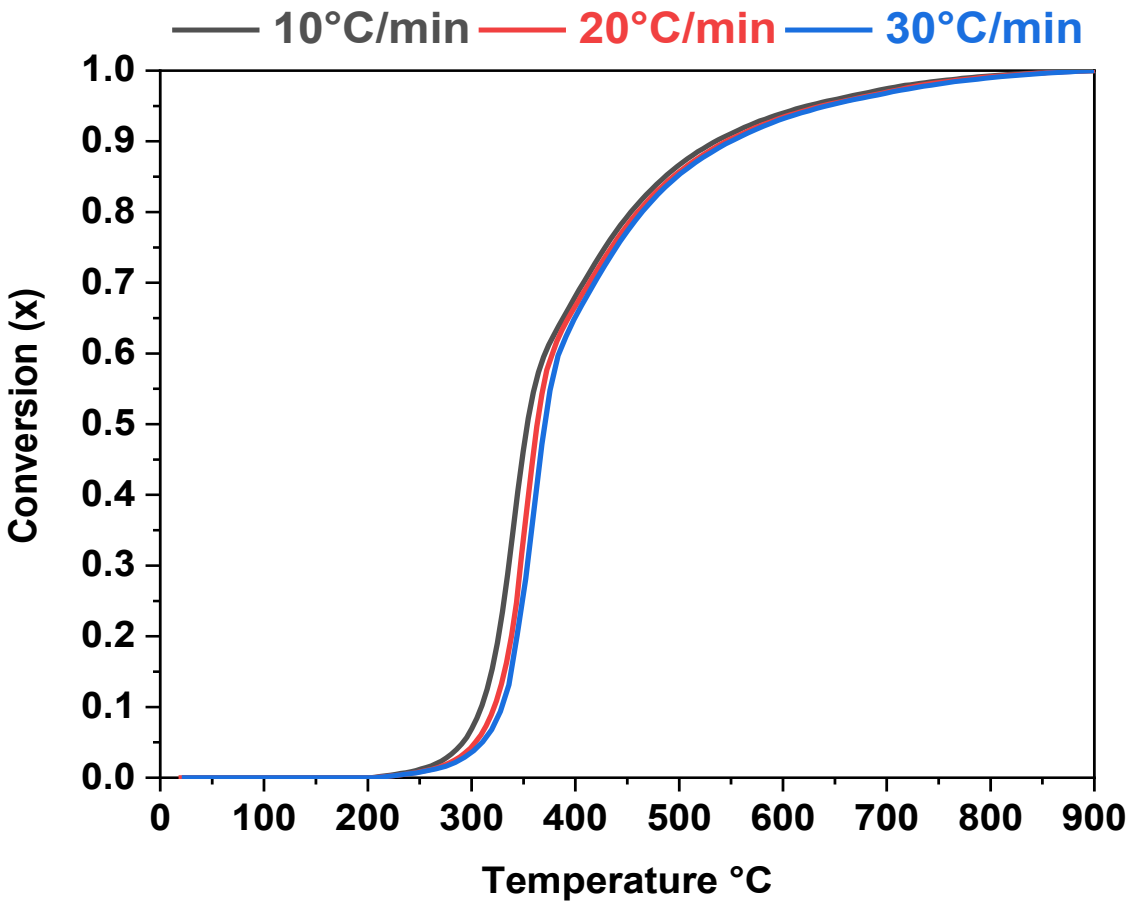
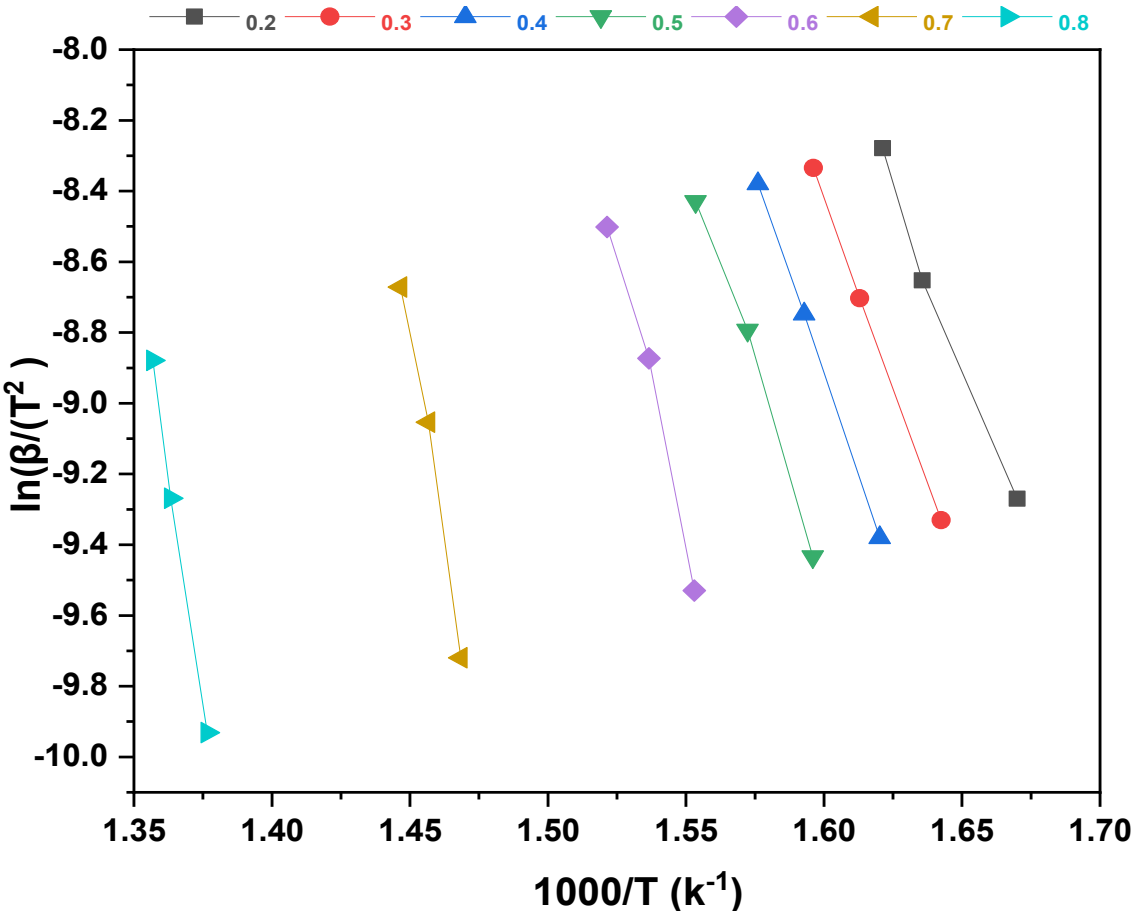


Figure 6. Extent of conversion curves for the devolatilisation process of torrefied grass (TG) as a function of temperature in TGA tests at different heating rates.

The apparent activation energy from a plot of $In(\frac{\beta i}{T_{xi}^2})$ versus $\frac{1000}{T_{xi}}$, for a given value of conversion (x) in the range of 0.2 to 0.8 is shown in Figure 7 for torrefied grass (TG). The average activation energy is calculated from the gradient equal to $-\frac{E_x}{R}$ and the correlation coefficients. R^2 values corresponding to the linear lines of best fit were in the range of 0.91 to 1.00 [33] showing good agreement.



404

405 *Figure 7. KAS plot of torrefied grass (TG) for different values of conversion to calculate the activation*

406 *energy at different heating rates.*

407 Table 2 contains the calculated variables for all carbonaceous materials tested in this study. It is

408 seen that the apparent activation energy was not the same for all conversion degrees, which

409 confirms the occurrence of different reactions at different temperatures during the experiment.

410 Charcoal has quite high and stable $\mathbf{E}_{\alpha}$ values throughout, and the value does not change a lot with

411 the change in conversion degree probably because of the effects of pre-treatment on this material.

412 Torrefied grass behaved differently, starting with a low $\mathbf{E}_{\alpha}$ value at a low conversion degree and

413 increasing linearly with an increase of conversion. This may correspond to low $\mathbf{E}_{\alpha}$ values for

414 decomposition of the remaining hemicellulose and cellulose but higher $\mathbf{E}_{\alpha}$ values for lignin

415 decomposition. Coal A shows a similar behaviour to charcoal with quite stable high $\mathbf{E}_{\alpha}$ values, while

416 coal B which contains medium volatile matter content has low stable $\mathbf{E}_{\alpha}$ values. Coal C has low $\mathbf{E}_{\alpha}$

value at low conversion degree and increases linearly with an increase in conversion. Coal D starts with low $\mathbf{E_a}$ value at low conversion degree and increases linearly with an increase in conversion degrees up to 0.6 conversion, and then there is a significant increase in the values at conversion degrees of 0.7 and 0.8. This behaviour may be influenced by error in the method since the difference for conversion degrees at different heating rates are not very large, which is seen in Figure 6.

Table 2. Activation energy Ea values in kJ/mol obtained for different carbon sources by using KAS, R^2 corresponding to linear fittings

	CC		TG		A		B		C		D	
Conversion (x)	E_a	R^2	E_a	R^2	E_a	R^2	E_a	R^2	E_a	R^2	E_a	R^2
0.2	201	0.99	165	0.99	215	1.00	183	0.96	77	0.95	192	0.99
0.3	224	1.00	179	1.00	246	1.00	194	0.97	120	0.93	242	0.99
0.4	293	1.00	189	1.00	247	1.00	197	0.97	154	0.93	278	1.00
0.5	313	1.00	198	0.99	268	1.00	193	0.96	185	0.95	311	1.00
0.6	341	1.00	271	0.98	304	1.00	180	0.91	219	0.94	390	0.99
0.7	366	1.00	400	0.99	294	1.00	169	0.92	264	0.95	650	0.98
0.8	294	1.00	440	1.00	323	1.00	173	0.95	335	0.95	1897	95.00
Average E_a	290		263		271		184		194		566	

These kinetic models assume the same reactions occurring at a specific conversion degree for different materials but as it can be observed from Figure 4 that multiple reactions take place at different temperatures. Therefore it is difficult to make accurate comparison between different carbon materials. This means the reaction mechanism can change during the devolatilisation process, therefore $\mathbf{E_a}$ is dependent on conversion and the average value of $\mathbf{E_a}$ can be estimated as a function of conversion. Kinetic analysis showed charcoal, torrefied grass and coal A (already injected

in HIsarna trials) have similar average activation energy values (290, 263 and 271 kJ/mol respectively). Since decomposition of the carbon materials consists of multiple chemical reactions, the $\mathbf{E}_{\boldsymbol{a}}$ value may change depending on the reactions taking place at specific conversion degree. It can be noticed in Figure 8 that the value of $\mathbf{E}_{\boldsymbol{a}}$ increases with an increase in conversion.

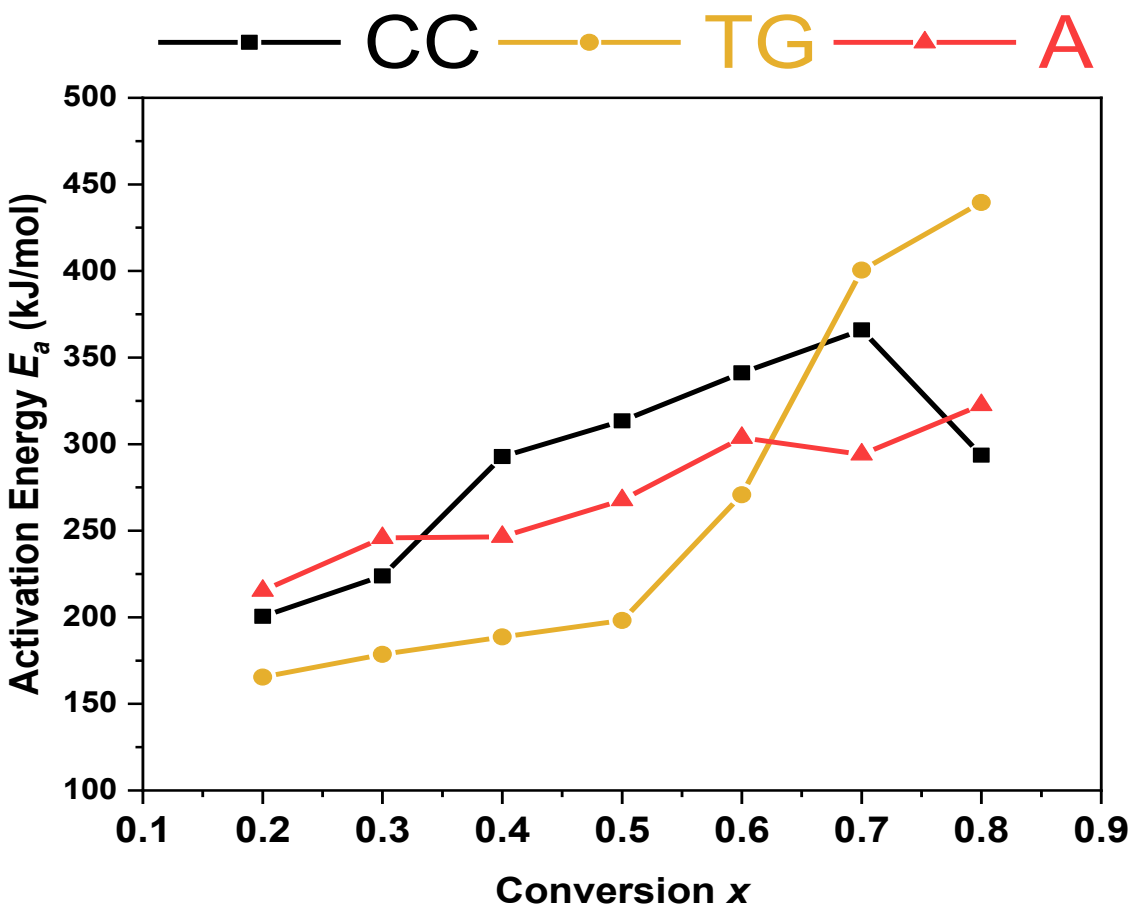


Figure 8. Activation energy Ea as a function of the conversion degree for charcoal (CC), torrefied gas (TG) and Coal A.

The increase in $\boldsymbol{E}_{\boldsymbol{a}}$ for torrefied grass is notably larger. This is because at low conversion levels very large amounts of weakly bonded components evolved e.g. H_2O and CO_2 shown in Figure 4 (a), therefore less energy is required for them to be removed. Charcoal starts with lower $\boldsymbol{E}_{\boldsymbol{a}}$ at conversion degrees of 0.2 and 0.3 compared to coal A, but coal A has lower *Ea* at conversion degree of 0.4 - 0.7. As can be seen in Figures 4 (b) and (c) charcoal produces larger amount of CO_2 at low temperature where coal A produces more of the other volatiles e.g. CH_4, C_2H_6 and H_2 at lower

temperature which confirms the differences in the E_a values. Based on off-gas analysis and kinetic values charcoal with current properties is the more likely source of biomass which can replace thermal coal in HIsarna technology, however material handling and pre-treatment may need to be re-considered to optimise its use in the process.

5. Comparison of carbonaceous materials for HIsarna process

The results of this study indicate that different reactions take place during specific conversion degree for different carbon materials, therefore devolatilisation is affected by the material properties which in turn is linked to volatile mater content. There has been similarities in devolatilisation behaviour (such as devolatilisation temperature), which is essential for smelting reduction vessel in HIsarna process. Biomass samples produced significantly larger amount of H_2O and CO_2 at low temperatures, however, coal samples produce more CH_4, C_2H_6 and H_2.

Despite the pre-treatment of biomass charcoal samples, this study showed that there is still significant weight loss (release of H_2O) at low temperatures because H_2O is absorbed from atmosphere due to their porous structure of the charcoal. Torrefied grass releases a large amount of H_2O and CO_2 at the temperature between 300-400 °C due to its high oxygen potential. These gases and H_2O releasing at lower temperatures can cause temperature drop in the HIsarna furnace which needs heat compensation and due to high O_2 level much more carbon material may be needed. To avoid these problems and utilise torrefied grass efficiently, a pre-treatment at the temperature of up to 400 °C in inert atmosphere is necessary to reduce the oxygen content and produce bio-chars with similar chemical properties to thermal coal currently used in HIsarna. To complete this process heat sources from other parts of the steel plant can be utilized to keep the “green” credentials of biomass, the gasses and tars released in the pre-treatment process can be used to generate heat and power for HIsarna process.

Because of the porous structure of biomass carbon sources (e.g. charcoal), material handling needs to be different to avoid H_2O absorption from atmosphere which is evidence in the test results. It may

need to consider pre-heating biomass to the temperature of ~200 °C before injection to remove all H_2O and other oxide impurities from biomass surface to maintain HIsarna process efficiency. Further studies may be required to investigate the effect of H_2O content in carbonaceous materials on HIsarna process such as materials handling and heat balance.

6. Conclusions

In order to enable the selection of suitable fuel mix in the novel HIsarna ironmaking process, four coals with notable differences in volatile matter content along with two biomass samples sourced from wood and grass origins were investigated in this study. The following conclusions can be obtained.

- The wt% of reducing gases e.g. H_2, CO, and hydrocarbons, and the temperature required for these gases to evolve was notably different for all the carbonaceous materials tested in this study, but the respective maximum peaks of evolution of these gases corresponded well to the maximum rate of mass loss.
- The off-gas analysis reveals torrefied grass contains large amount of water and carbon dioxide which will be released at very low temperature, therefore pre-treatment to the temperature of ~400 °C is necessary to produce chars with similar properties to coal injected in HIsarna.
- The change of reactivation energy E_a as a function of conversion degree is determined, which is linked to different reactions at different temperatures.
- Materials handling needs to be different for biomass (compared to thermal coal) to avoid H_2O absorption.

Acknowledgement

DK would like to thank Tata Steel Nederland Technology BV for providing PhD scholarship (Reference Number: COL1421/GIPS03241) to carry out this research. ZL would like to appreciate the funding from EPSRC under the grant number EP/N011368/1. The authors appreciate Tata Steel HIsarna team for fruitful discussions and providing samples. DK also would like to thank Dr. Ian Moore at Material

Processing Institute for providing coal C and coal D samples, and Tata Steel IJmuiden would like to acknowledge OrangeGreen BV for providing the torrefied grass sample.

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***Declaration of Interest Statement**

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

***Credit Author Statement**

CRediT author statement:

Darbaz Khasraw: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Resources, Writing - Original Draft, Writing - Review & Editing, Visualization, Supervision, Project administration **Stephen Spooner:** Conceptualization, Writing - Review & Editing, Supervision, **Hans Hage**: Conceptualization, Resources **Koen Meijer**: Conceptualization, Resources, Writing - Review & Editing, Supervision **Zushu Li:** Conceptualization, Validation, Writing - Review & Editing, Supervision, Project administration, Funding acquisition.

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