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Evaluation of CO_2 gasification kinetics for low-rank Indian coals and biomass fuels

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Abstract Gasification of solid fuels such as coals, lignite and biomasses has been studied using isothermal and non-isothermal thermogravimetric analysis (TG) with CO_2 as gasifying agent. Non-isothermal TG of three Indian coals (two bituminous and one sub-bituminous coal), one lignite and two biomass fuels (Casuarina and empty fruit bunches) at a constant heating rate of 20 °C min^{-1} in the temperature range from 25 to 1200 °C showed a clear separation of DTG peaks associated with pyrolysis and CO_2 gasification. Based on these studies, isothermal TG experiments were conducted in the temperature range from 900 to 1100 °C for coals and from 800 to 1000 °C for biomass fuels. These results show that the CO_2 gasification rate follows coal rank for the three coals and the lignite. The two biomasses have significantly higher reactivities than the three coals. The higher reactivity of one coal is attributed to the presence of calcium-containing minerals in its inorganic matter. The kinetic parameters for each fuel were extracted from the isothermal TG results using the volumetric reaction model for the coals and a zeroth-order model for biomass fuels. Biomass and lignite are found to have a much higher reactivity index and much lower conversion time than the three coals under identical conditions.

Keywords CO_2 gasification · Low-rank fuels · Thermogravimetric analysis · Reactivity · Kinetics

List of symbols

w_0	Initial mass of the sample
w_t	Instantaneous mass of the sample
w_f	Final mass of the sample
x	Fractional conversion of solid
r	Reactivity or rate of reaction
W	Mass of the sample
R_s	Reactivity index
t	Instantaneous time during conversion
$\tau_{0.5}$	Time required to reach 50 % conversion
k	Arrhenius rate constant
E	Activation energy
A	Pre-exponential factor
k_{VM}	Rate constant from volumetric model
k_{GM}	Rate constant from grain model
k_{RPM}	Rate constant from random pore model
Ψ	Structure parameter
x_{max}	Conversion at maximum reactivity

Introduction

Combustion of coal has been the mainstay of power generation for several decades but is facing severe challenges because of environmental concerns. Apart from NO_x and SO_x gases, particulate emissions have become a major issue in terms of dust pollution in a number of large cities in several parts of the world, which may be attributed to the burning of low-grade coals having high amount of ash. In recent years, the emission of CO_2 has also been added to

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the list of negatives of coal combustion. Against this background, coal gasification has emerged as a cleaner and more effective way of producing gaseous fuel from coal and biomass fuels, thus paving the way for clean power generation from these fuels. While sulphur and its compounds can be removed in fluidized bed gasifiers, gaseous fuels can be burned in ultra low NO_x burners to mitigate its emission problem, advanced CO_2 capture techniques such as oxyfuel combustion and chemical looping combustion can be readily incorporated in conventional gas-fired power plants [1–3]. The use of renewable fuels such as energy crops and biomass from forest and agricultural activities is also gaining importance for a variety of reasons. Firstly, they replace fossil fuels and therefore gain an advantage in terms of net CO_2 emissions and global warming. Secondly, they are often by-products of other activities, and their disposal for power generation adds to the economic benefit and waste disposal concerns of the primary product. Finally, co-firing of biofuels with conventional low-rank fuels can have beneficial effects in terms of increased reactivity and NO_x reduction. For example, the fuel from palm oil residue, often referred to as empty fruit bunch (EFB), is a major source of energy in terms of oil production and power generation in countries such as Malaysia, China and India [4–8]. Similarly, Casuarina equisetifolia is a fast-growing tree and is widely used in South East Asia as construction material. Its leaves and small twigs can be a source of renewable fuel. However, these fuels are radically different from conventional (fossil) fuels in terms of morphology and chemical structure of the organic and the inorganic matter and may cause severe fouling and slagging problems if they are fired directly in a combustor [9–11]. Gasification of these fuels can therefore be an optimal way to generate syngas, which can serve as a fuel for power generation or as a raw material for further conversion to useful chemicals [12]. Gasification of these low-grade fuels thus acquires new importance and provides the motivation for the present work. There is considerable research work on second-generation biofuels [13] where the emphasis is on extraction of liquid fuels from woody crops, agricultural residues and other lignocellulosic sources. These are outside the purview of the present work which is more focused towards power generation applications through combustion of solid or gasified fuels.

Gasification is an endothermic process, and a good understanding of the kinetics of devolatilization and char reactivity is important to ensure complete conversion of the fuel. During gasification, the fuel is partially combusted with oxygen to generate the thermal energy required for pyrolysis and char gasification by steam or CO_2. The product gas consisting a mixture of carbon monoxide, hydrogen and carbon dioxide has a high calorific value and can be directly used in high efficiency, combined cycle power plants or can replace solid fuels in heat or combined heat and power applications and can also be used in the production of liquid fuels and chemicals [12]. After purification to remove sulphur impurities, it can be used as a fuel in solid oxide fuel cells [14, 15] or can be used for generation of hydrogen through catalytic reforming. The process of gasification of a solid fuel begins with a rapid devolatilization leaving a char residue composed of carbon and ash. The gasification of char is a rate-controlling step in a gasifier as the rate of reaction is much slower than that of pyrolysis and has a strong effect on the overall performance of the gasifier. During the gasification of char, a number of physico-chemical transformations of the fuel occur which influence profoundly the primary and secondary reaction mechanisms that occur and transport of reactants and products to and from the reaction sites [16, 17]. A detailed understanding of char reactivity and reaction kinetics is essential for the modelling and design of gasifiers.

There is considerable literature on coal gasification (see e.g. [16, 18–21] and to a lesser extent on low-rank fuels and biomasses [22–26]. Some of the principal factors affecting char gasification are the temperature, pressure, composition of the atmosphere surrounding the char particles as well as the morphology and nature of the fuel itself. Thermogravimetric analysis (TG) of solid fuels is a widely used technique to study the kinetics and reactivity of gasification under standardized laboratory conditions and has recently been used to analyse the thermal decomposition of biomass and blends [8, 10, 23, 24, 27, 28]. Here, the mass loss of only a small fuel or char sample, prepared under standardized conditions, is monitored under well-defined environmental and thermal conditions. The kinetics of the overall gasification reaction and the reactivity of the fuel are then evaluated using a number of kinetic models and reactivity indices [18, 29]. The objective of the present study is to use non-isothermal and isothermal TG techniques to characterize the char gasification of five low-grade indigenous solid fuels available in India. Details of the study and the results obtained are discussed below.

Materials and methods

Three coals of different rank from Godavari Khani, Bellampalli (both in the South Indian state of Andhra Pradesh) and Bilaspur (in the Central Indian state of Chhattisgarh) and one lignite from Neyveli (in the South Indian state of Tamil Nadu) of Indian origin mines and two biomasses, namely, palm oil residue called as, empty fruit bunch and Casuarina equisetifolia from locally available agrofields in South India, were used in the present study and are denoted based on their geographic region as GK, BM, BS, NL, EFB and CE, respectively. In order to ensure that the TG data would be under kinetic control, the coals and lignite were crushed and ground in jaw crusher and hammer mill, respectively, and were size-classified using a sieve shaker. Only particles in the size range of −106/+90 µm were used for TG. As the biomasses were in the form of grains, these were reduced to lower than 1 mm size for char preparation. After preparing chars in the muffle furnace, the size was further reduced to less than 100 µm to ensure that the reaction would be kinetically controlled. Estimated Thiele moduli for the particles indicated an effectiveness of close to 0.98 for all particles sizes.

Pre-characterization of the fuels was done using ASTM standard procedures for proximate analysis, ultimate analysis, calorific value and ash composition. The coal rank is classified as per ASTM D388-12 standard. Table 1 shows the proximate and ultimate analysis of the fuels, and Table 2 shows ash analysis of four (GK, BM, BS and EFB) fuels. One can see that the coals have high ash content, with the BS coal having nearly 48 % ash by mass and a very low calorific value of 11.73 MJ kg^{-1}. It has relatively low fixed carbon, is more oxygenated than the other coals and is classified as sub-bituminous B. The coal GK has the highest calorific value of 23 MJ kg^{-1} and is classified as high volatile A bituminous coal. The lignite has very little ash but has 51 % by mass of moisture (on an as-received basis) resulting in a low calorific value of 13.86 MJ kg^{-1}. However, the moisture content in the lignite was found to decrease significantly during sample preparation stage. The two biomasses have, as expected, low ash content and high volatile content. Both have higher calorific value than the Bilaspur coal. EFB has high sulphur content and will require flue gas cleaning if it is used for combustion or gasification. The ash composition, especially that of alkali metals, is important in terms of possible catalytic effect on gasification reactions [30–32]. Of the three coals, one coal (BM) has high CaO component compared with the other two. The two biomass fuels, as expected, have high amounts of alkali oxides.

Results and discussion

Sample characterization

Sample preparation for TG studies was performed as follows. TG studies were conducted with both raw fuels and chars, which were prepared using laboratory muffle furnace at a heating rate of 10 °C min^{-1}. One gram of the sample was taken into a silica crucible, and the top layer of the fuel was doused with five drops of benzene and a lid was placed on the crucible. The benzene, upon heating, would vaporize and help in maintaining a non-oxidizing environment in the crucible during the char preparation stage by preventing air ingress. The samples were exposed to 900 °C for 7 min as per ASTM standard. The resulting fine powder was used as char for TG experiments.

Non-isothermal and isothermal TG of the fuels and chars were carried out using TA Instruments SDT Q600 thermogravimetric analyzer. In non-isothermal TG, the fuel sample of mass of 8 to 9 mg was heated from 25 to 1200 °C at a heating rate of 20 °C min^{-1}. N_2 was used as the sweeping gas, and CO_2 was used as the gasifying agent. Isothermal experiments were performed in the temperature range of 900–1100 °C for coal chars and 800–1000 °C for biomass chars. For the Bellampalli coal and Neyveli lignite, isothermal TG data were obtained in the wider temperature range from 800 to 1100 °C. Preweighed sample of the fuel was placed in an alumina crucible inside the furnace and heated under inert

Table 1 Proximate and ultimate analysis of the fuels

Fuel	Proximate analysis/mass%				Ultimate analysis/mass%					GCV/MJ kg^{-1}	Classification by rank[c]
	M	VM	Ash	FC	C	H	N	S	O[b]		
Godavari Khani (GK)	4.00	29.25	28.17	38.58	53.68	3.834	1.52	0.561	8.23	23.02	High volatile A bituminous coal
Bellampalli (BM)	13.09	28.67	20.94	37.3	50.49	4.98	1.05	0.19	9.64	19.72	Sub-bituminous A
Bilaspur (BS)	5.50	28	47.75	18.75	31.03	2.599	1.34	0.583	11.198	11.73	Sub-bituminous B
Neyveli Lignite (NL)	51	26.75	1.37	20.88	38.78	3.296	0.92	0.857	3.78	13.86	Lignite B
Empty fruit bunch (EFB)[a]	6.53	71.4	6.57	15.5	66.77	7.3	0.89	4.66	7.28	15.51	Biomass
Casuarina (CE)[a]	12.2	66.16	4.88	16.76	45.51	5.58	1.79	–	–	17.82	Biomass

[a] Dry basis (mass %)

[b] By difference

[c] ASTM D388

Table 2 Ash analysis of the fuels

Fuel	Al_2O_3	SiO_2	Fe_2O_3	K_2O	MgO	CaO	Na_2O	P_2O_5	SO_3	TiO_2
GK	19.76	67.92	4.59	1.29	1.84	1.10	0.17	0.10	1.61	1.35
BM	19.24	71.08	0.69	0.54	1.28	3.40	0.16	0.04	1.96	1.38
BS	23.40	61.70	6.75	1.85	0.90	1.45	0.10	0.90	0.40	1.40
EFB	1.45	52.39	5.63	22.23	2.02	5.32	1.01	2.43	3.57	3.73

environment using nitrogen flow of 70 mL min^{-1} with a heating rate of 100 °C min^{-1}. The nitrogen flow rate was maintained constant throughout the measurement. After the isothermal temperature was reached, the isothermal gasification reaction with sample char was initiated by providing CO_2 at a flow rate of 30 mL min^{-1}. Mass remaining data were recorded by a highly sensitive analytical balance located in the casing of the TG apparatus. All experiments were carried out at atmospheric pressure. Results from these experiments, amounting to more than 50 TG runs, are discussed below.

Non-isothermal gasification

Typical results obtained in the non-isothermal gasification using CO_2 as the gasifying agent are shown in Fig. 1 for the six fuels. Here, the raw fuel samples were used for analysis, and the mass loss was therefore due to the release of inherent moisture, pyrolysis as well as fuel and char gasification. The TG and the derivative TG curves are given in Fig. 1a, b, respectively. From the mass fraction remaining at the end of the test at 1200 °C, one can readily observe the large amount of ash present in the coals and the rank dependence of the char gasification reaction in the six fuels. The pyrolysis and the char gasification reactions are distinctly separated in terms of temperature range in which they occur. The two biomass fuels show a double-hump variation characteristic of biomasses [23]. For EFB, the pyrolysis is nearly completed by 400 °C, while for Casuarina, significant mass loss occurs up to 550 °C. For the coals, pyrolysis was confined to the temperature range of 350–600 °C with a well-defined peak at around 475 °C. The lignite shows a nearly continuous variation over the entire temperature range although the pyrolysis and the gasification peaks are still clearly visible. Part of this may be attributed to the combined effect of variation of the inherent moisture within the fuel particle and the fairly high heating rate of 20 °C min^{-1} used in the non-isothermal TG study. In all the cases, significant char gasification is initiated at much higher temperatures compared with that of pyrolysis. For the biomasses, it begins around 750 °C and is completed by about 925 °C. For the lignite and the coals, both the initiation and the peaking temperature are much higher and they follow a clear rank dependence with a clear demarcation between the lignite, the two sub-bituminous coals and the bituminous coal. The characteristic temperatures at which the various processes occur are summarized in Table 3. One may note that the absolute values of these characteristics may depend on the heating rate, among other parameters. Similarly, the peak reactivities, i.e. the magnitude of the char gasification peak in the derivative TG curve (Fig. 1b), cannot be compared across the fuels because of the different amounts of fuel left for

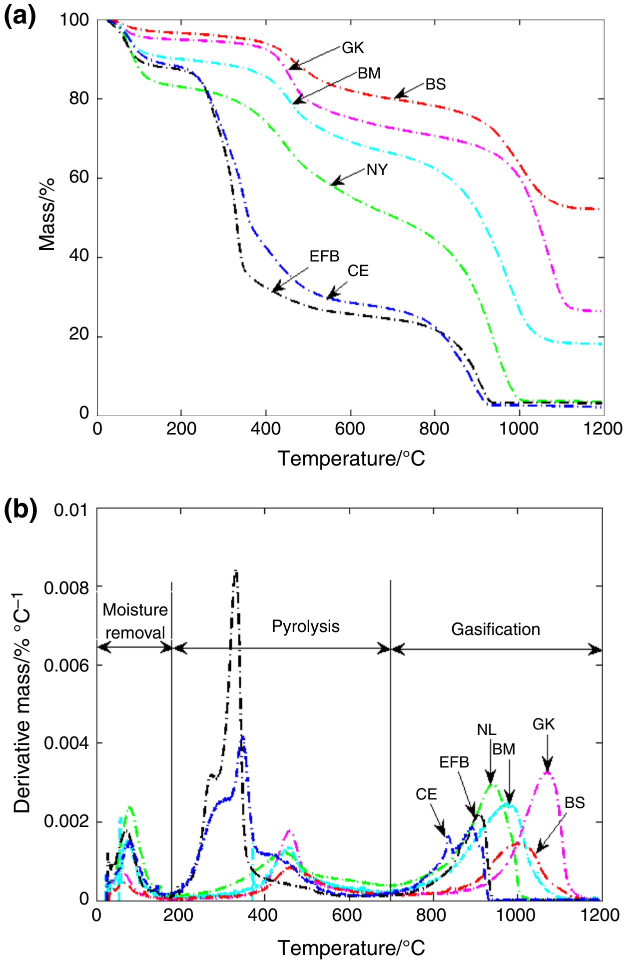

Fig. 1 **a** TG and **b** DTG curves for the six fuels obtained under non-isothermal conditions at a heating rate of 20 °C min^{-1}. *GK* Godavari Khani, *BM* Bellampalli, *BS* Bilaspur, *NL* Neyveli Lignite, *EFB* empty fruit bunch, *CE* Casuarina equisetifolia

Table 3 Characteristic parameters of non-isothermal TG analysis of the six chars

Fuel char	Pyrolysis			Gasification		
	Decomposition temperature range/°C	Peak temperature/°C	Max. mass loss rate/mg $°C^{-1}$	Reaction temperature range/°C	Peak temperature/°C	Maximum mass loss rate/mg $°C^{-1}$
GK	300–800	460	0.0177	800–1150	1075	0.0327
BM	300–700	456	0.0137	700–1110	980	0.0250
BS	300–800	461	0.0093	800–1150	1007	0.0144
NL	200–700	444	0.0121	700–1030	937	0.0296
EFB	170–700	331	0.0842	700–950	910	0.0223
CE	170–700	348	0.0418	700–930	891	0.0184

char gasification in the fuel. These should therefore be taken as indicative only of the temperature range in which these processes are active. It is interesting to note that BM char has a CO_2 gasification reaction profile which is similar to that of NL despite it being classified as a sub-bituminous coal. While the proximate analysis does not give any clue of its higher reactivity, the ultimate analysis shows that it has a higher hydrogen content relative to carbon compared with the other two coals and is more like that of the biomasses. The presence of higher amount of CaO in ash may also have enhanced the reactivity of the BM coal [32]. Petrographic analysis may throw further light on the behaviour of BM with respect to BS and GK.

From these non-isothermal TG data, one can infer that the CO_2 gasification temperature range for GK and BS coals is different from that of the lignite and biomasses. The devolatilization profiles are also different. These differences may have some significance in terms of gasifier design in case of co-firing. Another important aspect from the point of view of gasifiers is the rate of reaction with chars. In order to find the kinetics of char gasification reaction for these fuels, isothermal TG experiments have been conducted in the temperature range from 900–1100 °C for the coals in the range of 800–1000 °C for the lignite and biomasses. Since NL and BM are active over a wider range, these tests have been conducted over the temperature range from 800–1100 °C for these two fuels.

Isothermal gasification

Typical mass remaining data from a TG test are shown in Fig. 2a which shows the mass remaining as a function of time for BM char during the test. The mass loss occurs in two distinct stages. During storage, the chars pick up a small amount of moisture and retain some of the volatiles during the char preparation in the muffle furnace. During the heating-up (non-isothermal) stage in nitrogen environment, some mass loss occurs due to moisture loss and pyrolysis. This is represented by the portion of mass loss curve between points *a* and *b* in Fig. 2a. Once the target temperature is reached for isothermal gasification, the gasifying agent, CO_2 in the present case, is introduced into the nitrogen stream. The Boudouard reaction which is then activated will lead to an accelerated phase of mass loss, which is represented by the curve portion between points *b* and *c* in Fig. 2a. The mass loss occurring in the isothermal stage between points *b* and *c* is used in the present study for kinetics study. Figure 2b shows the mass remaining expressed as a percentage of the initial mass for different isothermal temperatures. It can be seen that typically about 3–5 % of mass loss occurs due to moisture release at temperatures less than 200 °C during the rapid ramping up of the crucible temperature to the desired test temperature (of 1000 °C in this case). Another 5–10 % mass loss occurs gradually in the rest of the heating up to the test temperature (Fig. 2a). The rapid mass loss condition as soon as the reactive gas is introduced is clearly distinguished in all cases. Usually, this is followed by a phase of more gradual rate of loss (Fig. 2b). Taking this mass as the initial mass, char conversion can be defined as

$$x = \frac{w_0 - w_t}{w_0 - w_f} \tag{1}$$

where w_0 is the initial mass of the sample when the reaction initiated, w_t is the instantaneous mass of the sample and w_f is final mass of the sample, i.e. the mass of the ash. Figure 2c shows the variation of char conversion with time for the furnace-prepared BM char during isothermal runs at temperatures of 800, 850, 900, 950, 1000, 1050 and 1100 °C. One can see that the rate of conversion increases steadily as the temperature is increased.

The gasification reactivity can be calculated from the conversion plots as

$$r = -\frac{-1}{W_0}\frac{dW}{dt} = \frac{dx}{dt} = \frac{x_i - x_{i+1}}{t_{i+1} - t_i} \tag{2}$$

where dx/dt is obtained by numerical differentiation.

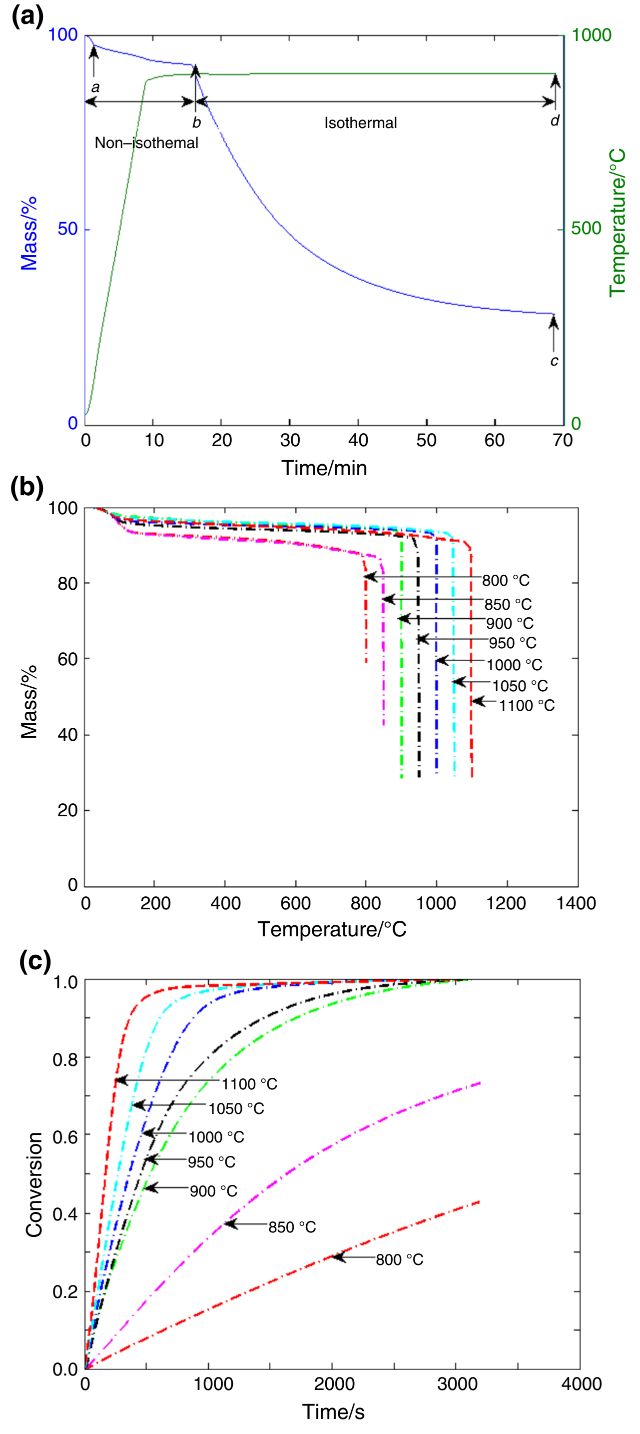

Fig. 2 **a** Temperature programme and mass loss during isothermal gasification of BM char. **b** Mass loss curves for BM char for different isothermal TG runs. **c** Effect of temperature on conversion for BM char under isothermal TG runs

A comparative plot of the conversion of the six fuels during an isothermal test at 1000 °C is given in Fig. 3a, and the corresponding reactivity plot is given in Fig. 3b. Note that this reactivity is different from that obtained in non-isothermal TG test where it represents the rate of mass loss with respect to temperature. One can see the significantly higher isothermal reactivity of the two biofuels compared with the coal chars. The maximum isothermal reactivity of the fuels at various temperatures is listed in Table 4. Their conversion plot (Fig. 3a) shows almost a linear variation with time compared to the more nonlinear variation of the coal chars. This may be attributed to the virtual absence of ash in the char (<5 % by mass) in the two biofuels while coal chars have ash content going up to 65 % by mass. Further analysis is presented below.

Kinetic analysis

Many gasification models have been proposed to study the solid fuels gasification reaction with CO_2 as the reactant gas; these include the volumetric or homogeneous model [20, 27], the grain model [26] and the random pore model [28]. In all these cases, the rate of conversion of the char is expressed as being linearly proportional to a function of the fraction of the fuel yet to be converted, thus showing an effective order with respect to the solid reactant (there is a reaction order dependence on the concentration of the gas phase reactant; since all the present experiments have been conducted with at a fixed CO_2 partial pressure of 0.3 bar, the rest of the 0.7 bar being nitrogen, the order of the gas phase reaction cannot be determined from the present data). The apparent reaction rate is expressed as

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(T)f(x) \tag{3}$$

where k is a temperature-dependent rate constant and $f(x)$ describes the functional dependence on the remaining char which includes the amount of char left, and in some indirect way on the amount of ash left and on the morphology of pores through which the reactant has to diffuse and which also creates the surface area or sites available for the reaction to occur. Of the two functional parameters, the rate constant is invariably represented in terms of an Arrhenius type of expression:

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{4}$$

Here, A and E are pre-exponential factor and activation energy, respectively, R is the gas constant and T is the absolute temperature. The form of $f(x)$ varies depending on the model:

$$f(x) = (1-x) \quad \text{in the volumetric model} \tag{5a}$$

$$= (1-x)^{2/3} \quad \text{in the grain model} \tag{5b}$$

$$= (1-x)\sqrt{1-\psi\ln(1-x)} \quad \text{in the random pore model} \tag{5c}$$

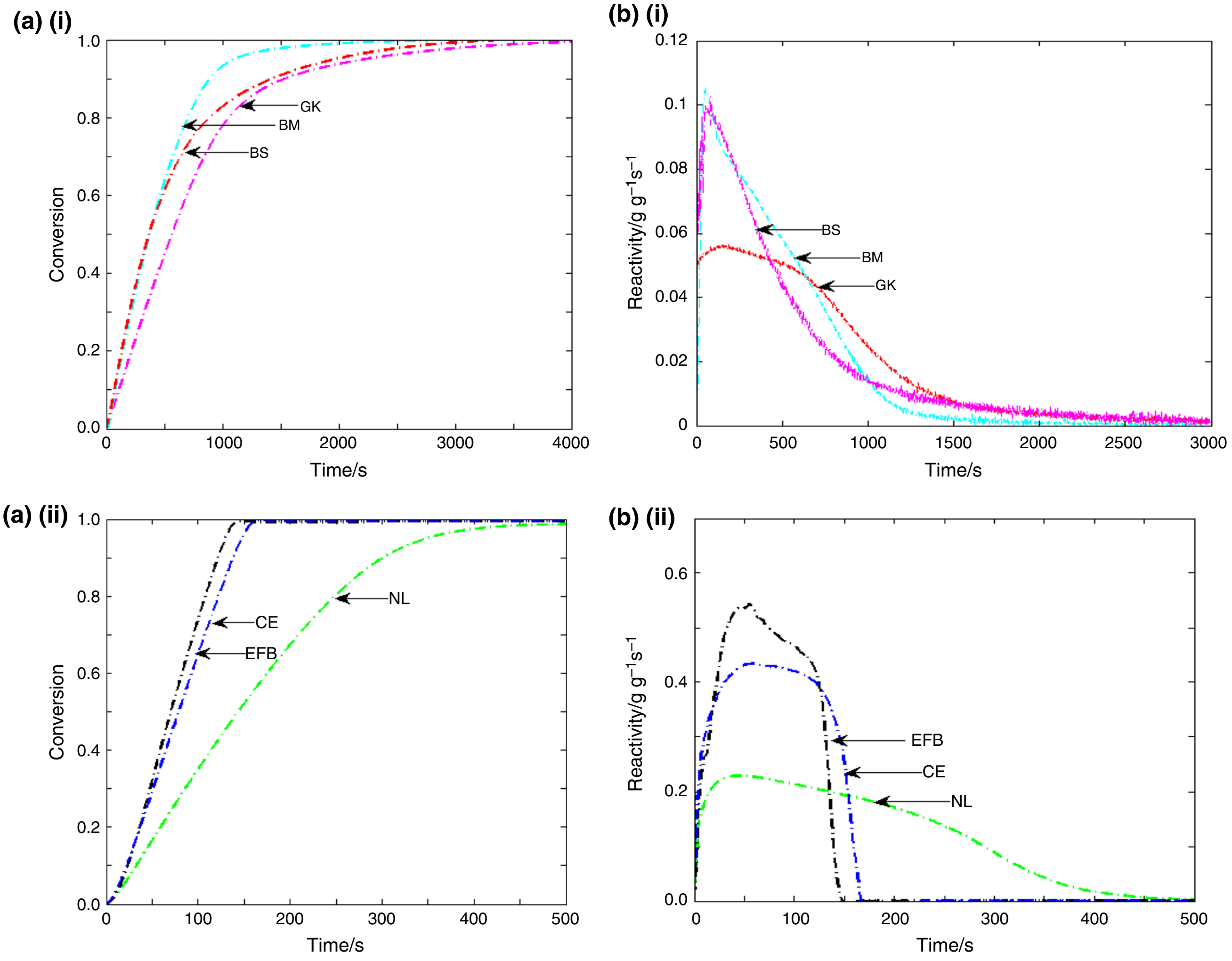

Fig. 3 Effect of char source on **a** conversion and **b** reactivity at 1000 °C

Table 4 Maximum isothermal reactivity of the fuels at different temperatures

Temperature/°C	Maximum isothermal reactivity/s^{-1}					
	GK	BM	BS	NL	EFB	CE
800	–	0.020	–	0.014	0.071	0.051
850	–	0.023	–	0.042	0.145	0.121
900	0.092	0.080	0.025	0.088	0.249	0.279
950	0.069	0.094	0.064	0.183	0.309	0.312
1000	0.054	0.107	0.092	0.229	0.543	0.434
1050	0.112	0.120	0.173	0.383	–	–
1100	0.217	0.196	0.261	0.389	–	–

Thus, the volumetric model and the grain model are parameter free as far as the function $f(x)$ is concerned. The random pore model requires the evaluation of the structural parameter, defined as $\psi = 4\pi L(1-\varepsilon)/S^2$, where L is the pore length, ε is the porosity and S is the surface area. The structural parameter needs to be determined empirically and may change dynamically as the reaction progresses. It is usual in the literature [16, 28, 33] to use an initial estimate (i.e. of the yet to be gasified char) through BET surface area analysis. Since these data were not available for all the fuels, in the present study, an estimated value of the structural parameter was obtained from the measured maximum reactivity information, as suggested in [34]:

$$\psi = 2/\{2\ln(1-x_{\max})+1\} \tag{6}$$

For the fuels in question, the above expression gave values of Ψ of between 2 and 4, which agree in order of magnitude with the values of between 1.25 and 1.5 reported by Saravanan et al. [35] for high ash Indian chars.

The conversion data in the range from 0 to 90 % for the BM char at each temperature have been plotted in Fig. 4a in the form of the volumetric model. One can see that there

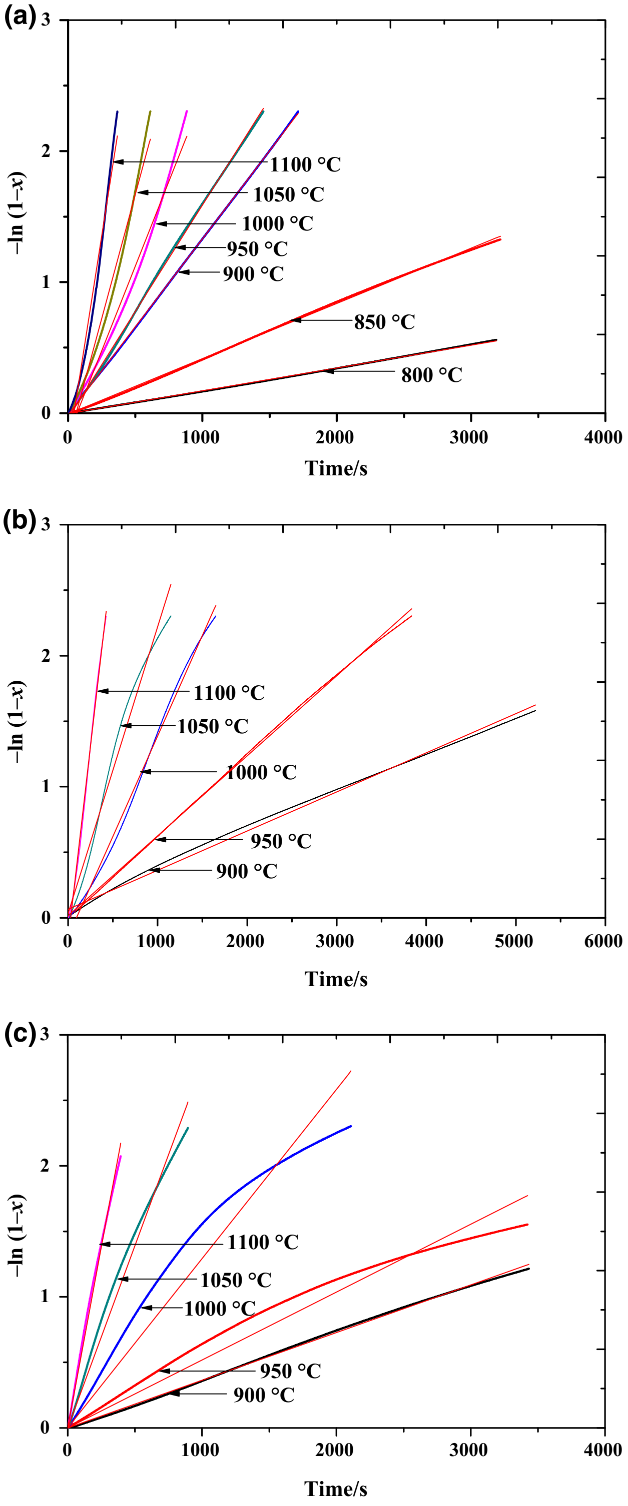

Fig. 4 CO_2 gasification data redrawn in the form of volumetric model for **a** BM, **b** GK and **c** BS chars

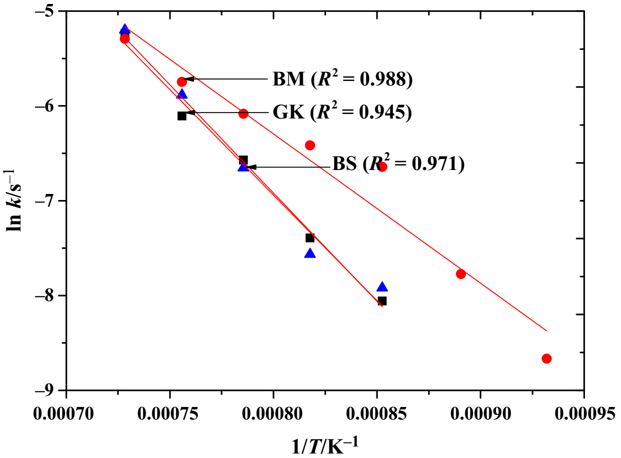

Fig. 5 Linear fits for coal chars using the volumetric model

is a fair degree of linearity with respect to time at each temperature and that, as the temperature increases, the slope increases indicating a higher value of the rate constant (see Eq. 5a). Figure 4b, c shows the corresponding figures for GK and BS chars. The value of the rate constant at each temperature is obtained for each fuel and is plotted against $1/T$ in Fig. 5. One can see that a linear fit is obtained in each, though with different slopes, which is to be expected. From these, the Arrhenius parameters (Eq. 4) have been obtained for these three coal chars and are listed in Table 5. Figure 6 shows a comparison of the predicted and the measured conversion plots for the three coal chars using these kinetic data. Good agreement is found between the data and the predictions over the temperature range considered. It is therefore concluded that the three Indian coal char reactivities with CO_2 are sufficiently slow and their porosity sufficiently high, that uniform gas diffusion within the entire particle occurs quickly and that the reaction proceeds over the entire volume of the particle in a homogeneous manner.

Biomass fuels, which are in the very early stages of coalification compared with the three coals, can be very different from coals. As mentioned above (see Table 2), the inorganic matter in biomass contains significant amounts of alkali compounds which are known to be catalytic in CO_2 gasification reactions [30, 32]. Also, the BET surface area of biomass chars is much higher than of coals. For example, Lee et al. [36] have reported a surface area of $\sim 600\ m^2\ g^{-1}$, while Saravanan [37] reported BET surface areas of the order of 30 to 60 $m^2\ g^{-1}$ for high ash Indian coal chars and 280 $m^2\ g^{-1}$ for lignite char. Therefore, one may expect a different functional relationship between conversion and time for the biomass fuels. Indeed, examination of reactivity data for the two biomass fuels plotted separately in Fig. 3b(ii) shows that in this case the reactivity exhibits a three-stage response: a rapid increase initially, followed by a fairly flat/plateau region followed by a precipitous decrease. The first stage of initial increase can

Table 5 Rate constants and kinetics parameters of fuels

Temperature/°C	Rate constant/s^{-1} for char of					
	GK	BM	BS	NL	EFB	CE
800	–	0.00017	–	0.00022	0.00099	0.00060
850	–	0.00042	–	0.00060	0.00206	0.00184
900	0.00032	0.00130	0.00036	0.00100	0.00346	0.00447
950	0.00062	0.00163	0.00052	0.00274	0.00427	0.00431
1000	0.00140	0.00228	0.00129	0.00315	0.00725	0.00640
1050	0.00223	0.00319	0.00278	0.00412	–	–
1100	0.00531	0.00503	0.00552	0.00465	–	–
Kinetic parameters						
E/kJ mol^{-1}	185.04	130.92	189.83	126.59	107.68	129.27
A/s^{-1}	5.23E+04	5.46E+02	8.47E+04	4.30E+02	1.91E+02	1.60E+03
Conversion time/min (for 90 % at 1000 °C)	29	17	28	5	2	2

be attributed to the phase where some delay occurs in the diffusion of the reactant gas (CO_2) through the carrier gas (nitrogen) to reach the reaction site. The second phase is where much of the conversion happens; this phase is marked by a fairly constant reactivity over the entire variation of the conversion. This is reflected by a linear variation of conversion with time as shown in Fig. 7 for conversions up to 90 % or greater. The third phase is where the conversion rate is influenced perhaps by a thin ash layer and occurs only for conversions in excess of 90 % (as can be seen in Fig. 7). Thus, the reactivity data for the biomass fuels can be interpreted as showing a rate of reaction which does not depend on the extent of conversion. This may imply diffusion-controlled reaction; however, in the present case, the reaction rate clearly depends on the temperature, indicating that there is kinetic control over the reaction. The lignite char exhibited a trend which is a mixture of the coal-like and biomass-like variation. On the whole, like in the biomass char, the reactivity does not change greatly with conversion over a large range. Given the small amount of ash in these fuels, it is clear that pore diffusion or diffusion through ash layer was not contributing to the reaction rate.

In view of these observations, for these fuels, a zeroth-order model has been sought with respect to amount of char unconverted, i.e.

$$dx/dt = k(T) \tag{7}$$

was used to describe the kinetics. Since the char gasification was occurring at lower temperatures for these fuels (see Fig. 1) compared with coal chars, isothermal TG test was done in the temperature range from 800 to 1000 °C in temperature increments of 50 °C. For the lignite, data were also collected at 1050 and 1100 °C. The conversion curves obtained for these are shown in Fig. 7a for EFB, Fig. 7b for CE and Fig. 7c for NL. Figure 8 shows the dependence of the rate constant on the temperature for these three fuels. From these data, the kinetic constants, in the form of the pre-exponential factor and the activation energy, have been extracted and are listed in Table 5. These have been used to predict the conversion plots at various temperatures. These are shown in dotted lines in Fig. 7. One can see that the temperature effect on the reaction rate is captured rather well using the fitted values of A and E in the zeroth-order model.

Conversion time is a measure of relative reactivity of the fuels, and it includes the effect of both A and E. Conversion time calculated at 1000 °C for 90 % conversion using kinetic information derived from rate expression shows that the conversion time is high for high ash coal and low for biomass fuels, as follows: EFB < CE < NL < BM < GK < BS. Another way of classifying the reactivity of a wide range of fuels is the reactivity index [26], given by the following equation:

$$R_s = \frac{0.5}{\tau_{0.5}} \tag{7}$$

where $\tau_{0.5}$ is the time required for carbon conversion of 50 %. This reactivity index is useful for low gasification temperatures where the conversion may not reach 90 % or higher. Using the conversion data for the fuel chars, the reactivity index has been calculated at various temperatures for 50 % conversion and is listed in Table 6. As expected, the reactivity index increases with temperature and decreases with increase in rank of the coal. The two biomass fuels exhibit high reactivity.

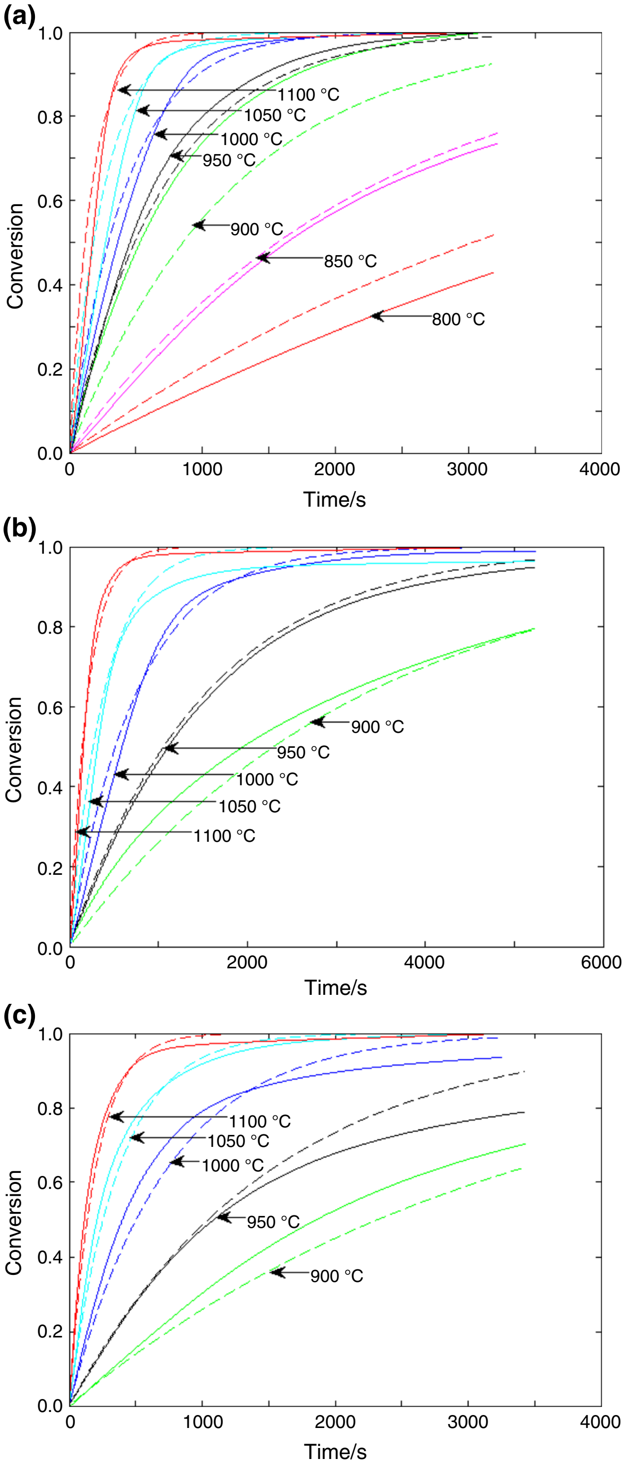

Fig. 6 Experimental (*solid line*) versus predicted (*dashed line*) conversion plots for **a** BM, **b** GK and **c** BS chars

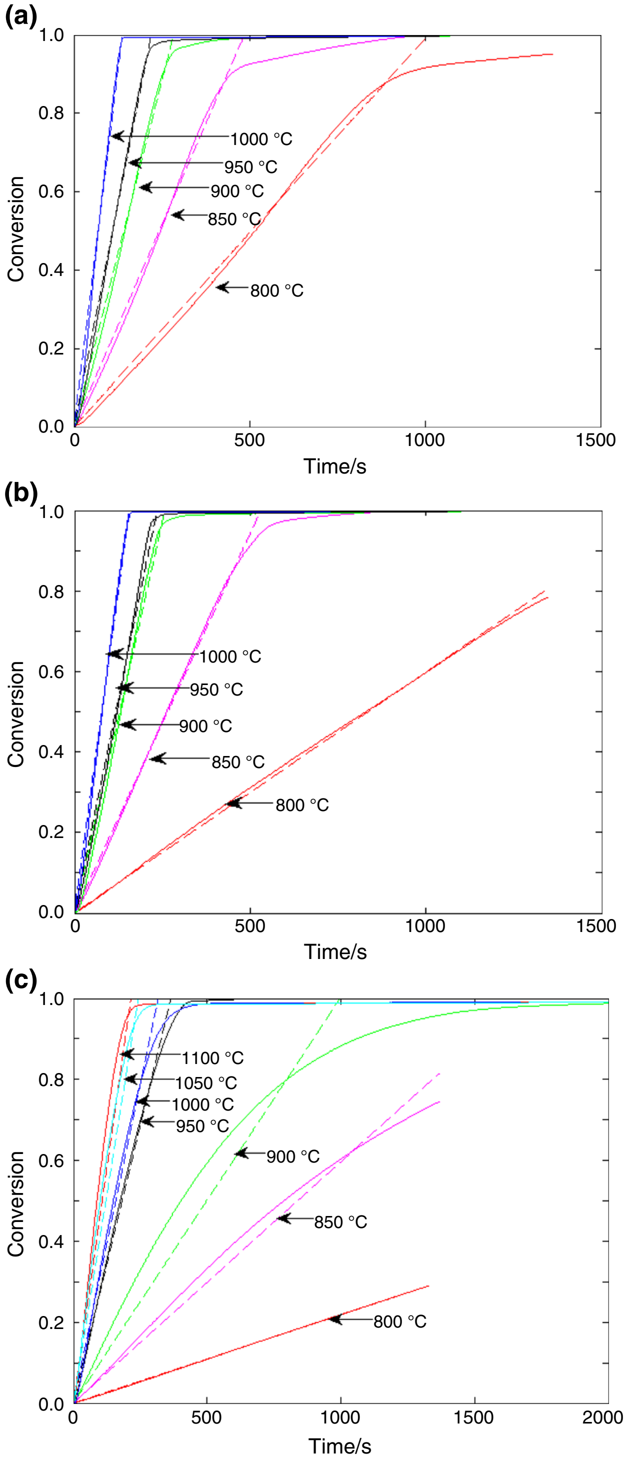

Fig. 7 Experimental (*solid line*) and predicted (*dashed line*) conversion plots for **a** EFB, **b** CE and **c** NL chars

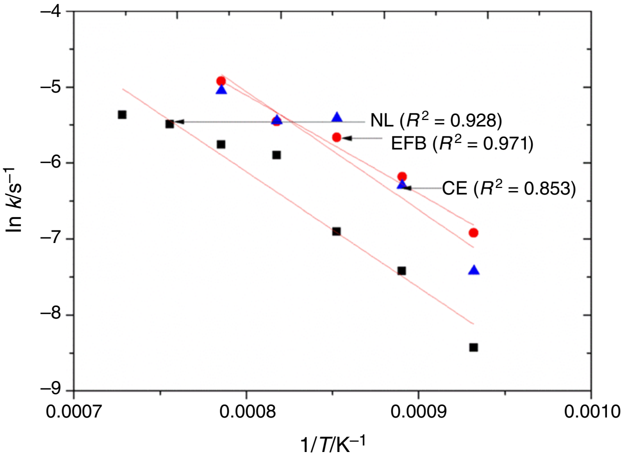

Fig. 8 Linear fits for EFB, CE and NL chars using the zeroth-order model

Table 6 Reactivity index obtained from conversion data for 50 % conversion of fuels at various temperatures

Temperature/°C	Reactivity index/h^{-1}					
	GK	BM	BS	NL	EFB	CE
800	–	0.57	–	1.36	3.49	2.17
850	–	1.10	–	2.28	7.29	6.67
900	0.92	3.36	0.97	4.48	12.41	13.04
950	1.62	4.16	1.65	10.11	16.22	14.75
1000	3.03	4.99	4.13	12.00	25.71	22.78
1050	5.66	6.55	8.57	16.51	–	–
1100	11.46	9.63	13.04	17.31	–	–

Conclusions

The gasification kinetics of the Boudouard reaction involving char and CO_2 have been studied using non-isothermal and isothermal TG of furnace-prepared chars of six fuels. The Arrhenius parameters, namely activation energy and pre-exponential factor for the char gasification, have been obtained by fitting literature models. It is found that a volumetric model fitted well for the coal chars, while a zeroth-order model with respect to char remaining fitted well for the lignite and the biomass fuel chars. The time required for 90 % char conversion at a temperature of 1000 °C has been calculated for the biomass fuels and is considerably less than that of the coal chars. The 90 % conversion time is high for high ash coal chars and low for biomass fuel chars, as follows: EFB < CE < NL < BM < GK < BS. Reactivity index based on 50 % conversion shows similar variation.

BS coal char shows high reactivity at temperatures of about 1000 °C which augurs well for its gasification using CO_2. Given the large amount of ash, this may be attributed to the catalytic nature of the high ash coal as one would have expected the ash layer resistance to decrease the reactivity. Similarly, BM exhibits a reactivity profile that is closer to that of NL and the biomasses than to that of the coals. These results demonstrate the usefulness and relevance of thermogravimetric analysis in evaluating gasification characteristics of fuels.

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