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G. Aranda Almansa **(ECN)**
A.J. Grootjes **(ECN)**
C.M. van der Meijden **(ECN)**
A. van der Drift **(ECN)**
D.F. Gupta **(RTIC)**
R.R. Sonde **(RTIC)**
S. Poojari **(RTIC)**
C.B. Mitra **(RTIC)**

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[a] Energy Research Centre of The Netherlands (ECN), Unit Biomass & Energy Efficiency, P.O. Box 1, 1755 ZG Petten, The Netherlands
[b] Research, Technology and Innovation Center (RTIC), Thermax Ltd., Pune 411019, India

A B S T R A C T

The use of domestic high-ash coal reserves contributes to the security of energy supply, and therefore high-ash coal is expected to remain as a key energy source in several countries (e.g., India, Turkey) for at least the next 30–40 years. However, the use of high-ash coals for energy production (currently performed mainly via combustion processes) poses a number of technical and economic challenges, e.g., low efficiency and environmental issues. Gasification is an attractive option, since it allows a more efficient, more environmentally friendly conversion of the coal. In particular, integrated gasification combined cycle (IGCC) offers high efficiency, reduced emissions and potential for the implementation of CO_2 capture.

With the aim of optimising the design and operation of high-ash coal fluidised-bed gasification processes, this paper studies the effect of temperature and partial pressure on the conversion and reactivity of coke from an Indian high-ash coal under CO_2 and steam gasification conditions using thermogravimetric analysis. Moreover, additional steam gasification tests have been carried out in order to determine the conversion rate under realistic fluidised-bed gasification conditions (e.g., coal ash as bed material, coal particle size, heating rate, bed hydrodynamics, gasification atmosphere), thus taking into account the effect of mass and heat transfer phenomena.

Results of isothermal TGA tests have shown that coke reactivity increases at higher temperatures and/or partial pressures of gasifying agent. The experimental data have been fitted to two conversion models (shrinking core and volumetric). The determination of kinetic parameters (reaction order b, pre-exponential factor A and activation energy E_a) has been carried out at three conversion levels: $X = 0.2$, $X = 0.5$, and $X = 0.8$. In the case of CO_2 gasification, the reaction order b ranges between 0.2 and 0.8, although at temperatures of 850–900 °C, the reaction order has a value around 0.6. In the case of steam gasification, the reaction order ranges between 0 and 1.1, and increases with reaction temperature.

Fluidised-bed steam gasification tests have shown that approximately 23–27% of the carbon contained in the coal (~40–45% of the overall coal, considering also hydrogen and oxygen released in the gas) is quickly converted during the devolatilisation stage. Between 12 and 22% of the carbon contained in the remaining coke is converted to gas within the first 25 min of steam gasification. Finally, 55–80% of the carbon in the coke remaining after steam gasification is converted during the first 25 min of oxidation with air. Conversion of the high-ash coal is favoured at higher steam partial pressures and/or higher gasification temperatures. The conversion rate under fluidised-bed conditions is significantly lower than that obtained in TGA tests at similar temperature and steam partial pressure values. Differences in coal particle size, heating rate during devolatilisation, inhibition issues, and other fluid-dynamic effects influence the reactivity of the produced coke as well as the heat and mass transport rates. The overall effect of these phenomena is a shift in reaction regime. Operation under realistic FB conditions has an equivalent effect to a decrease in the gasification temperature under TGA conditions.

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1. Introduction

Coal will continue to play a key role in the world's energy scenario, not only for power generation, but also for the production of fuels (e.g., coal-to-SNG) and chemicals. Globally, coal resources have been estimated at over 861 billion tonnes. Coal meets around 30.3% of the global primary energy needs and generates 42% of the world's electricity [1]. Around 45% of the world's coal is either high-moisture or high-ash. Due to their contribution to the security of energy supply, high-ash coals are currently used for power generation in several countries (India, China, Turkey, Czech Republic, Poland, South Africa, Romania) [2]. In addition, high-ash coal is expected to remain as a key energy source in several countries (e.g., India, Turkey) for at least the next 30–40 years due to the availability of large domestic reserves and the installed-capacity for electricity production [3]. However, the use of high-ash coals for

Table 1
Review of literature studies on kinetics of coal gasification.

Authors	Fuel	Reactant atmosphere, temperature, pressure	Research objective	Coke production	Equipment for kinetic determination	Results plot	Model fitting/kinetic mechanism	Notes
Engelbrecht et al., 2012 [30]	High-ash South African coals (New Vaal, Grootegeluk).	O_2-enriched air and steam 875–975 °C	Fluidised-bed gasifier modelling.	Fluidised-bed.	Fluidised-bed gasifier pilot plant	Carbon conversion vs. temperature/residence time.	CeSFaMB[a] model.	Conversion increases with coal reactivity, temperature and residence time.
Everson et al., 2006 [29]	South Africa high-ash coals.	CO_2, H_2O, 1073–1223 K, atmospheric pressure.	Determination of kinetics for model development.	Heating rate at 20 K/min in N_2, and soak at 973 K for 60 min.	TGA	Conversion vs. time.	Shrinking core model, Langmuir–Hinshelwood equation.	47 wt.% and 67 wt.% ash in coal chars with large amount of kaolinite and quartz. Inhibition of CO and H_2 on the reactions with CO_2 and H_2O. Variation of the internal porosity and internal surface area of the particles during gasification is not important (low porosity of carbon). The reactions (CO_2 in presence of CO or H_2O in presence of H_2) proceed on separate sites.
Huang et al., 2010 [31]	Lignite coal.	H_2O, CO_2, (CO, H_2), 1123–1223 K, atmospheric pressure.	Mechanism of char gasification with CO_2 and H_2O in presence of CO and H_2	Fluidised-bed reactor: heating rate 1000 °C/s. Residual coke held at 840 °C for 20 min in N_2.	TGA	Carbon conversion vs. time.	Langmuir–Hinshelwood equation.	Inhibition effects of H_2 and CO. C–H_2O and C–CO_2 reactions proceed on separate active sites.
Hüttinger, 1988 [32]	Brown coal, sugar, PVC.	H_2O (H_2), 0.15–2 MPa, 850 °C	Influence of H_2 and diluent gases on H_2O gasification.	600 °C, holding time 2 h	Fixed-bed reactor	Carbon conversion vs. time and temperature, reactivity vs. pressure.	Two-site surface reaction mechanism.	Strong inhibition due to H_2 at all pressures. Increasing pressure enhances H_2 inhibition. Helium also inhibits H_2O gasification at high pressures.
Jayaraman et al., 2013 [3]	Indian and Turkish high-ash coals.	Argon, steam, air/O_2. 1 bar, 950–1150 °C	Determination of kinetic parameters.	Tests with coal samples (no previous coke production).	TGA–MS	Mass loss vs. time, mass loss vs. temperature.	First-order Arrhenius model.	C–H_2O starts at 800 °C. Steam + air/O_2 is an efficient gasifying agent for high-ash coal. Complete carbon conversion at 900–950 °C.
Katta and Keairns, 1981 [33]	Pittsburgh seam coke breeze.	H_2O, CO_2 10 bar 920–1040 °C	Determination of C–H_2O and C–CO_2 rates.	Fluidised-bed under N_2 atmosphere at >1040 °C	Fluidised-bed reactor	Reactivity vs. conversion pH_2/pH_2O vs. 1/reaction rate pCO/pCO_2 vs. 1/reaction rate.	Langmuir–Hinshelwood equation and Ergun's model.	Rate constant of C–H_2O reaction ~2.5–5 times higher than C–CO_2 reaction. Activation energies: 48.2 and 69 kcal/mol, respectively.
Kwon et al., 1988 [34]	4 coals of different rank (from lignite to semianthracite).	CO_2, atmospheric pressure, 700–900 °C, 0.3–1 atm CO_2 partial pressure.	Effect of coal rank, particle size, temperature and concentration of reactant gas.	Heating up in furnace to 900 °C under N_2 at 0.1 °C/s, and holding at 900 °C for 1 h.	TGA	Weight vs. time, weight rate vs. time, conversion vs. time, reactivity vs. C in parent coal.	Shrinking core model, Arrhenius equation.	Apparent order of reaction with respect to CO_2 = 1. Good fitting of shrinking core model. Reactivity decreases at higher coal rank.

Table 1 (continued)

Authors	Fuel	Reactant atmosphere, temperature, pressure	Research objective	Coke production	Equipment for kinetic determination	Results plot	Model fitting/kinetic mechanism	Notes
Liliedahl and Sjöström, 1997 [12]	Ptolemais (Greece) lignite char.	CO–CO$_2$–H$_2$O–Ar mixtures, 0.1 MPa, 750–850 °C.	Development of semi-empirical gasification kinetic model.	Coal only partly pyrolysed beforehand (methodology not reported).	TGA	Conversion vs. time, reactivity vs. time, reactivity vs. conversion.	Johnson model (comparison) and own developed model.	Suitability of different models to chars from coal, lignite, peat and biomass
Mahajan et al., 1978 [35]	16 US coals ranging in rank from anthracite to lignite.	Air (1 atm) at 405 °C, CO$_2$ (1 atm) at 900 °C, steam (0.022 atm) at 910 °C, and H$_2$ (27.2 atm) at 980 °C.	Correlation of char reactivity with time.	Heating in N$_2$ atmosphere at 10 °C/min to 1000 °C, 2 h holding time.	TGA	Conversion vs. time. Fractional conversion vs. normalised time.	Cubic model.	Wide variation of $\tau_{0.5}$[b] values with coal range. Catalytic activity of impurities.
Mühlen et al., 1985 [36]	German bituminous coal.	H$_2$O, CO$_2$, H$_2$ 1–70 bar, 800–1000 °C.	Development of kinetic formula for steam and CO$_2$ gasification.	Not reported.	TGA	Reactivity vs. pressure. Reactivity vs. conversion.	Modified Langmuir–Hinshelwood.	Inhibition of H$_2$ and CO on either steam or CO$_2$ gasification. Inhibition by CO is much greater than that by H$_2$.
Roberts and Harris, 2006 [37]	3 Australian bituminous coals	CO$_2$ (900 °C), H$_2$O (850 °C), 0.1–3 MPa	Incorporation of high–pressure gasification reactivity data.	Heating in ceramic containers at atmospheric pressure to 1100 °C at 10 °C/min under N$_2$, 3 h holding time.	TGA	Reactivity vs. pressure.	Langmuir–Hinshelwood model.	Langmuir–Hinshelwood is suitable for partial pressures up to 3 MPa.
Saha et al., 2013 [9]	Indian high-ash coal.	CO$_2$ 1 atm, 900–1000 °C	Effect of char preparation temperature.	TGA under Ar atmosphere at 900 °C and 1000 °C.	TGA	Reactivity (50% conversion) vs. temperature.	No data fitting.	Reactivity decreases with increasing char preparation temperature. Reactivity increases with increasing gasification temperatures.
Salatino et al., 1998 [25]	South-African coal.	O$_2$: 653–733 K, 0.21–1 bar partial pressure. CO$_2$: 1023–1173 K, 0.1–1 bar partial pressure.	Structural changes of coke upon gasification with O$_2$ or CO$_2$. Kinetic study.	Fluidised-bed, 1123 K, atmospheric pressure.	TGA	Reactivity vs. conversion.	n-th order Arrhenius model.	Much more extensive activation of micropores during gasification with CO$_2$ than with O$_2$. Structural rearrangements due to thermal annealing in high-T CO$_2$ gasification.
Song et al., 2010 [38]	6 low rank coal chars (lignite and bituminous).	H$_2$O 750–900 °C	Influence of steam partial pressure on char conversion, influence of coal type.	Heating up to 1173 K in quartz tube at 10 K/min under N$_2$ atmosphere, holding time 0.5 h.	TGA	Conversion vs. time.	Shrinking-core, volumetric reaction, and modified volumetric reaction model.	High temperature and high steam partial pressure increase gasification rate. Lignite coal chars have much higher reactivity than bituminous coal chars.
Tay et al., 2011 [23]	Victorian (Loy Yang) brown coal.	Air, 400 °C	Changes in char structure and reactivity.	Fluidised bed/fixed bed at 800 °C with steam/Ar, O$_2$/CO$_2$ and O$_2$/steam/CO$_2$.	TGA	Char yield vs. time. Specific reactivity vs. char conversion.	–	Steam has a drastic effect on structure and reactivity of char. Chars are consumed most rapidly in the O$_2$ + H$_2$O + CO$_2$ mixture. Additivity in char conversion: O$_2$, H$_2$O and CO$_2$ do not compete for the same active sites on the coal/char.
Zhang et al., 2010 [39]	Low-rank coal from Indonesia and coal-based activated carbon.	CO$_2$ 850 °C, 0.1 MPa	Effect of catalytic activity of calcium and potassium.	Heating up to 900 °C at 10 °C/s in infrared furnace, 1 min holding time under Ar atmosphere.	TGA	Reactivity vs. conversion.	Random pore model.	Enhanced reactivity by Ca for $X < 0.4$. Increase of reactivity with X for K-catalysed gasification.

[a] Comprehensive simulator of fluidised and moving beds.
[b] $\tau_{0.5}$: time at which 50% conversion of the coke is achieved.

power production, which is currently performed mainly via subcritical combustion processes, results often in inefficient operation of the power plants. Moreover, the emission of fly-ash in power plants as well as the ash disposal constitutes an ecological and environmental challenge [4].
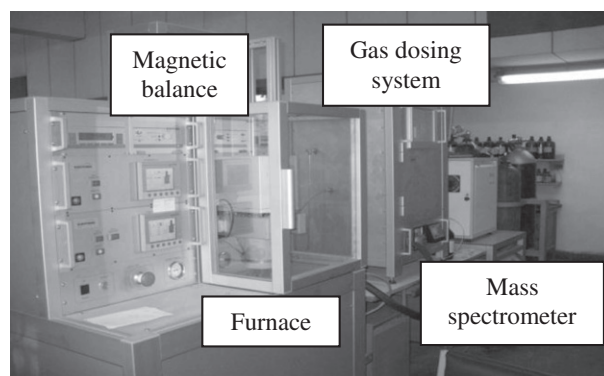
India is a good example of the status of high-ash coal. India's vast coal resources (58.6 billion tonnes of proven hard coal reserves, i.e., 7% of global reserves [5]) contribute to a large share of its energy supply (42% of the primary energy in 2008) as well as to the security of energy supply [6]. However, the coal-based electricity sector in India faces up to several challenges, which include the low efficiency of thermal plants [5]. The low average efficiencies of Indian coal-fired power plants (27.6% LHV [7]) are partly due to the widespread use of high-ash coals in subcritical cycles as well as to the use of coal-fired plants for peak load electricity production, among other factors [8]. Only 13% of the Indian coal resources is of coking quality; the remainder is high-ash steam coal [5], with typically 40 wt.% ash and a low calorific value (~3600 kcal/kg), which is difficult to wash below 30% ash to make it suitable for power generation [7]. Since it is expected that coal will remain the dominant energy source for India in the short and medium term, it is necessary to improve the efficiency of electricity generation from coal to exploit the extensive domestic high-ash coal resources while reducing emissions [5]. For this, several strategies have been proposed: enhancement of the efficiency of the existing power plants, improvement of coal beneficiation processes (decrease of combustibles loss in the rejects, ash disposal, reduction of energy- and water consumption), and development of clean coal technologies such as

Table 2
Thermochemical properties of Indian high-ash coal.

Moisture (wt.%, as received)		3.9
Ultimate analysis (wt.%, dry basis)	C	31.9
	H	2.4
	N	0.86
	S	0.56
	O	11.2
Proximate analysis (wt.%, dry basis)	Volatile matter	21.2
	Ash 550 °C	54
	Fixed carbon[a]	24.8
Lower heating value (MJ/kg, dry basis)		11.98
ICP analysis (mg/kg, dry basis)	Al	67020
	As	<3.4
	B	12.6
	Ba	272
	Ca	4282
	Cd	0.27
	Cl	17
	Co	6.92
	Cr	56.4
	Cu	21.9
	F	276
	Fe	24085
	K	8341
	Li	52.2
	Mg	2515
	Mn	259
	Mo	<2.10
	Na	369
	Ni	27.4
	P	1369
	Pb	19.0
	Sb	<8
	Se	<3.40
	Si	150629
	Sn	<2
	Sr	82.3
	Ti	4382
	V	60.0
	W	<3.0
	Zn	32.5

[a] By difference.

supercritical and ultra-supercritical combustion cycles and integrated gasification combined cycles (IGCC).

IGCC technology is an attractive option for the use of high-ash coals for power production, since it offers high efficiency, reduced emissions, and potential for the implementation of CO_2 capture and sequestration (CCS) techniques. Nevertheless, in order to make use of domestic high-ash coals, the IGCC technology has to be adapted to the specific quality of the fuel [5], and costs and reliability issues have to be addressed [2]. High-ash coal requires the use of fluidised-bed gasifiers rather than the well-established entrained-flow gasifiers used for low-ash coals, since heating and melting of the ash lead to an increased oxygen consumption in entrained-flow gasifiers [5,9].

The conversion of a coal particle to producer gas includes a number of stages, namely drying and devolatilisation of the coal particle, and gasification of the remaining coke. Since the coke gasification stage is the controlling step of the overall conversion process, coke reactivity is an important issue for the design, modelling and optimisation of processes, equipment and control systems [10]. The conversion of a coke particle to gas is the result of the interaction of several physical and chemical processes, mainly the mass transfer of the gaseous reactants and products through the particle pores, and the intrinsic kinetics of the reaction [10]. The reaction rate depends on the temperature and concentrations of the reactants, as well as on the coke properties (particle size, mineral content, porosity, pretreatment conditions) [11–14]. The presence of catalysts in the inorganic fraction of the coke plays an extremely important role [11,15].

The reactions between porous solids and gases take place mainly in active sites on the solid surface. Active sites are surface irregularities where the resulting valence forces induce the transfer of electrons, thus creating a bond between solid and gas. Active sites include dislocations or edge atoms, inorganic impurities and (O–, H–) heteroaromatic functional groups [13,16]. The reactions occur sequentially with the following stages: (1) chemical adsorption of the reaction gas on the free active carbon sites; (2) carbon/gasifying agent reaction; and (3) desorption of the product gases [17]. In this process, both the relative position

Fig. 1. HP–TGA–MS facility.

Table 3
Conversion vs. time and reactivity vs. conversion according to the volumetric and the shrinking core models.

	$X(t)$	$R(X)$
Volumetric model (VM)	$X(t) = 1 - e^{-\Omega t}$ (4)	$R(X) = \Omega$ (6)
Shrinking core model (SCM)	$X(t) = 1 - (1 - \Psi t)^3$ (5)	$R(X) = 3\Psi(1-X)^{1/3}$ (7)

Table 4
Operating conditions of fluidised-bed gasification tests.

| Test	Stage	T (°C)	$\dot{m}_f$ (kg/h)	$\dot{V}_{N_2}$ (NL/min)	$\dot{V}_{air}$ (NL/min)	$\dot{m}_{steam}$ (kg/h)	$\dot{V}_{Ar}$ (NL/min)	U_{mf} (cm/s)[b]	U/U_{mf}	N_2/steam (vol.%/vol.%)
1	DEV	850	~1[a]	19	0	0	1	6.4	4.2	100/0
	SG		0	9.7	0	0.27	1	6.5	3.3	65/35
	OXID		0	0	19	0	0	6.0	4.5	–
2	DEV	850	~1[a]	19	0	0	1	6.4	4.2	100/0
	SG		0	29	0	0.27	1	6.4	7.6	85/15
	OXID		0	0	19	0	0	6.0	4.5	–
3	DEV	920	~1[a]	19	0	0	1	6.1	4.9	100/0
	SG		0	9.7	0	0.27	1	6.1	3.8	65/35
	OXID		0	0	19	0	0	5.7	5.2	–

[a] Feeding for 30 min.
[b] Calculation is based on the properties of the bed material (1500 kg/m^3 density, 0.5 mm average particle diameter), and temperature and composition of the reaction atmosphere.
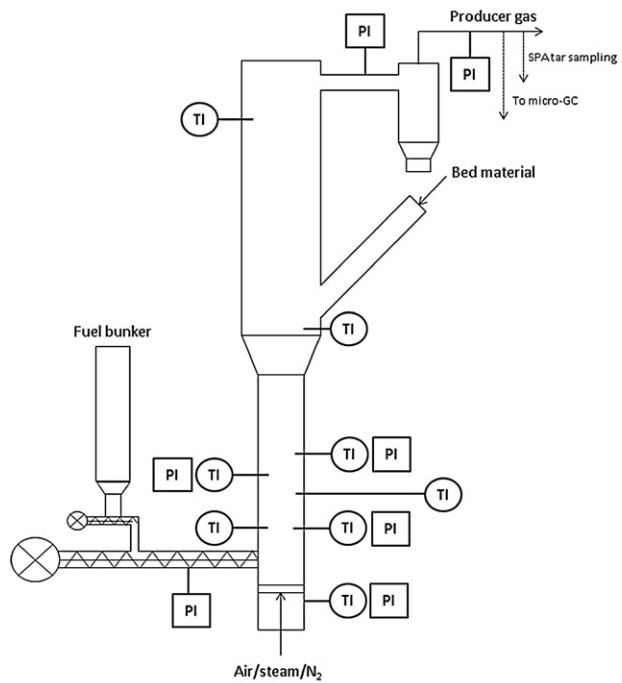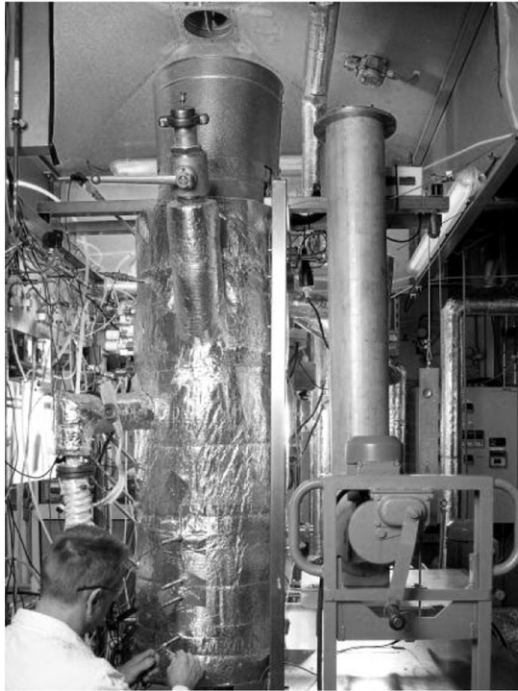
Fig. 2. Fluidised-bed gasifier.

of the carbon atoms in the carbonaceous matrix and stereoeffects (i.e., need for the right orientation of the gaseous reactants molecules) are important factors.
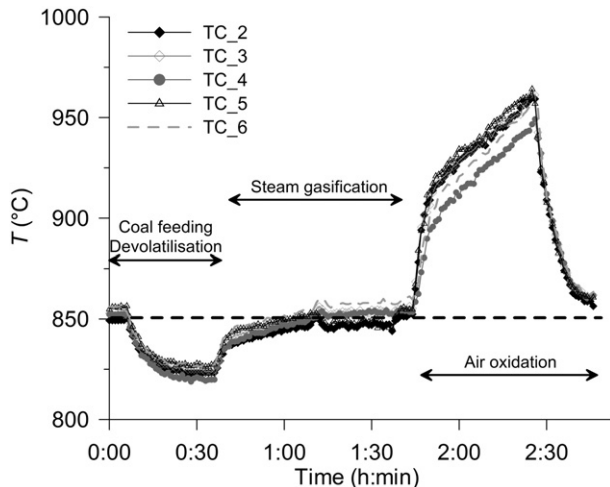
Fig. 3. Bed temperature profile during fluidised-bed test 1.

Reactivity is a property of a solid fuel defined as its capacity for chemical reaction, and it is expressed as the reaction rate under specific conditions of temperature, pressure and gasifying agent [18]. There are several types of facilities for the determination of the reactivity of a fuel, e.g., thermogravimetric analysis (TGA), fixed/fluidised bed reactors, entrained flow/drop-tube reactors, and wire mesh reactors. [11,13,19, 20]. The gasification rate is defined as the change in carbon mass along time, and can be expressed by the burn-off factor (conversion degree), X, or through reactivity r or R [3,10,14,18,21]:

$$X(t) = 1 - \frac{m(t)}{m(t = 0)} \tag{1}$$

$$r = \frac{dX(t)}{dt} \tag{2}$$

$$R = -\frac{1}{m}\frac{dm}{dt} = \frac{1}{1-X}\frac{dX}{dt} \tag{3}$$

$m(t)$ being the coke mass in instant t, and $m(t = 0)$ is the initial mass of coke. Eq. (2) expresses the reaction rate r with respect to the initial coke mass (overall reactivity), whereas (Eq. (3)) refers to the remaining coke mass at the time t (instantaneous reactivity). The reactivity can be expressed as a combination of two terms: a kinetic term, which takes
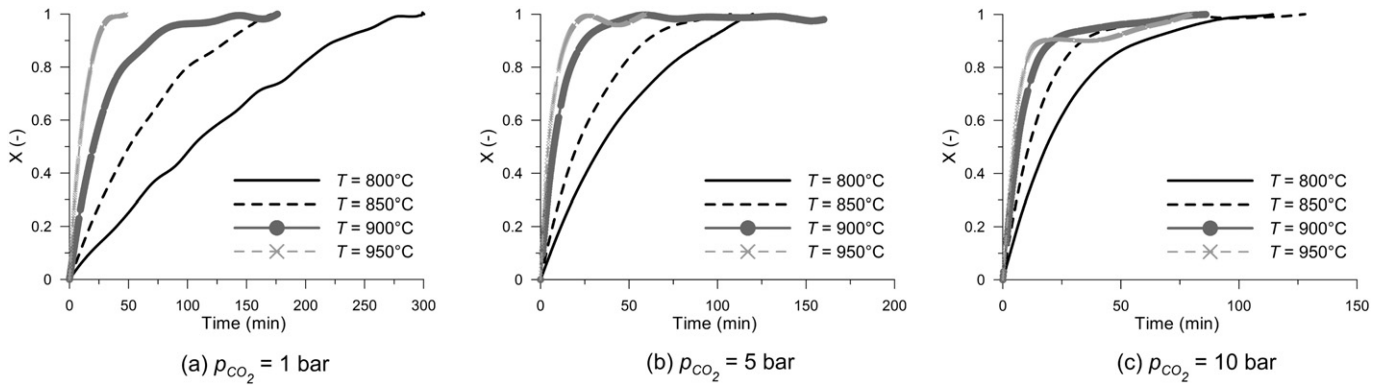
Fig. 4. Conversion vs. time of coke from Indian high-ash coal under CO_2 gasification conditions.

into account the temperature and partial pressure of the reactants; and a structural term, which describes the available internal surface, the active sites, and the evolution of the pore structure [10].

The reactivity of a coke produced from a specific fuel depends on a number of factors [10,12,13,15,16,18,21–25]:

– Chemical composition of the fuel (volatile matter and fixed bed carbon content, oxygen/hydrogen content), related to active sites.
– Structure of the material (particle size, porosity, specific surface area, pore size distribution), which influences the accessibility of the gaseous reactants into the particle.
– Thermal history of the fuel (i.e., conditions under which the coke is produced): pressure, temperature and heating rate during devolatilisation, reaction atmosphere, conversion degree.
– Catalytic effect of elements present in the fuel ash, particularly

alkaline and alkaline-earth. The effect of these elements is related to factors such as the carbon/catalyst ratio (loading), and the degree of dispersion in the carbonaceous matrix, which in turn influence the accessibility of the reactant gases to the active sites.

Coal/coke undergoes drastic changes in its structure and reactivity during the devolatilisation and gasification stages [13,16]. Associated to the release of volatiles and the consumption of the remaining coke, several phenomena can take place, which include melting and fusion of the solid matrix, shrinking or swelling, fragmentation, formation of vesicles, holes and bubbles, development of the microporosity due to the opening of closed pores and of the macroporosity due to the coalescence of small pores, and crystal growing. Moreover, heteroaromatic (H–, O–, N–, S–) groups (thus, the edge atoms and dislocations
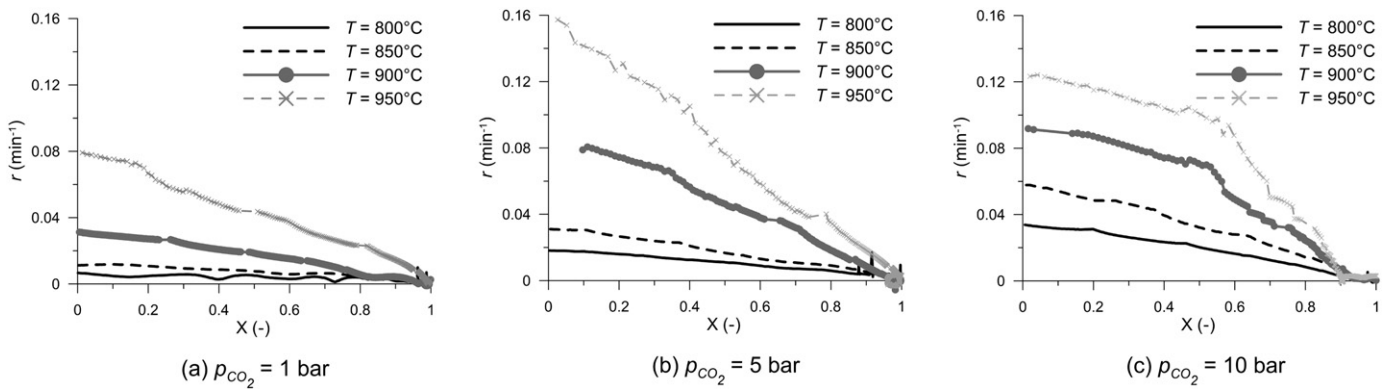

Fig. 5. Overall conversion rate r vs. conversion of coke from Indian high-ash coal under CO_2 gasification conditions.
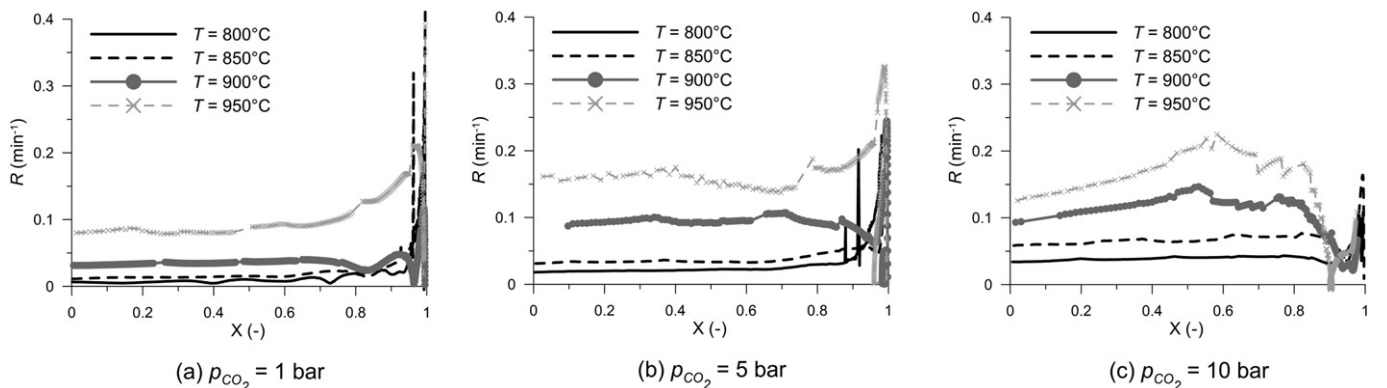

Fig. 6. Instantaneous reactivity R vs. conversion of coke from Indian high-ash coal under CO_2 gasification conditions.

Table 5
Parameters Ω (volumetric model) and ψ (shrinking core model) for modelling of CO_2 gasification of coke from Indian high-ash coal as a function of temperature and pressure.

T (°C)	Ω (VM) (min^{-1})			ψ (SCM) (min^{-1})		
	$p_{CO_2} = 1$ bar	$p_{CO_2} = 5$ bar	$p_{CO_2} = 10$ bar	$p_{CO_2} = 1$ bar	$p_{CO_2} = 5$ bar	$p_{CO_2} = 10$ bar
800	0.0081	0.0228	0.0408	0.0021	0.0059	0.0095
850	0.0168	0.0447	0.0694	0.0041	0.0086	0.0156
900	0.0344	0.0962	0.1142	0.0087	0.022	0.0279
950	0.1235	0.16	0.178	0.0216	0.0343	0.0476

associated to active sites of the material) are progressively lost from the carbonaceous structure due to the release of volatiles during pyrolysis [16]. Depending on the pressure, temperature and residence time conditions, the carbonaceous structure undergoes reordenation via thermal annealing, thus increasing char aromaticity. Simultaneously, the mineral matter present in the coal/coke suffers modifications such as changes in chemical bonds and allotropic form, creation/disappearance/reaction/modifications of mineral phases, sintering, softening, and vaporisation [15,16,26–28], which in turn affect the catalytic activity of the inorganic elements. Since the structure of the solid fuel changes as the carbon atoms are being consumed, the reactivity and the porosity of the coke are interrelated in two ways: the internal structure influences the reaction rate, and the reaction conditions modify the internal structure [18].

Even though there is an extensive existing literature devoted to reactivity of char from coal and biomass [10,13,16,20,21], only a limited number of works specifically deal with high-ash coals (>40 wt.% ash) [3,9,29,30]. The main features of some selected works on kinetics of coal are summarised in Table 1, although there exist excellent reviews in literature, both for coal, e.g., [13,16,20,21], as well as for biomass chars [10]. Most of the works reported in Table 1 use thermogravimetric analysis, with coke prepared also under TGA conditions. With the aim of

designing and optimising the operating conditions of high-ash coal fluidised-bed gasification processes, this paper studies the conversion and reactivity of coke produced from an Indian high-ash coal under CO_2 and steam gasification conditions, determining the effect of the temperature and the partial pressure. Besides TGA tests performed under kinetic regime conditions for the determination of the intrinsic kinetics of CO_2 and steam gasification, additional steam gasification tests have been carried out under realistic fluidised-bed conditions (coal particle size, heating rates, reactant atmosphere, fluid-dynamics of bed material…) in order to determine the conversion rate of the Indian high-ash coal taking into account also the effect of mass and heat transfer phenomena.

2. Materials and methods

2.1. Coal feedstock

The feedstock used in this work is a sub-bituminous high-ash coal from the Indian region of Bilaspur. Table 2 summarises the thermo-chemical properties of the fuel. As can be seen, this coal contains 54 wt.% ash. The ash is mainly rich in silica (15.1 wt.% of the total feedstock), and alumina (6.7 wt.% of the feedstock), with minor amounts of potentially catalytic elements such as iron (2.4 wt.% feedstock), potassium (0.8 wt.% feedstock), and calcium (0.4 wt.% feedstock). The role of Ca, K, and Fe during CO_2 gasification of coal has been extensively discussed in literature [20,40]. On the contrary, Si and Al are claimed to suffocate char reactivity, i.e., they tend to suppress gasification reaction on the coke surface [41].

2.2. Equipment and methodology

2.2.1. CO_2 and steam gasification in TGA

Intrinsic kinetics of CO_2 and steam gasification of coke from Indian high-ash coal has been studied in a thermogravimetric analyser

Table 6
Valid range of conversion levels for model fitting of CO_2 gasification of Indian high-ash coal.

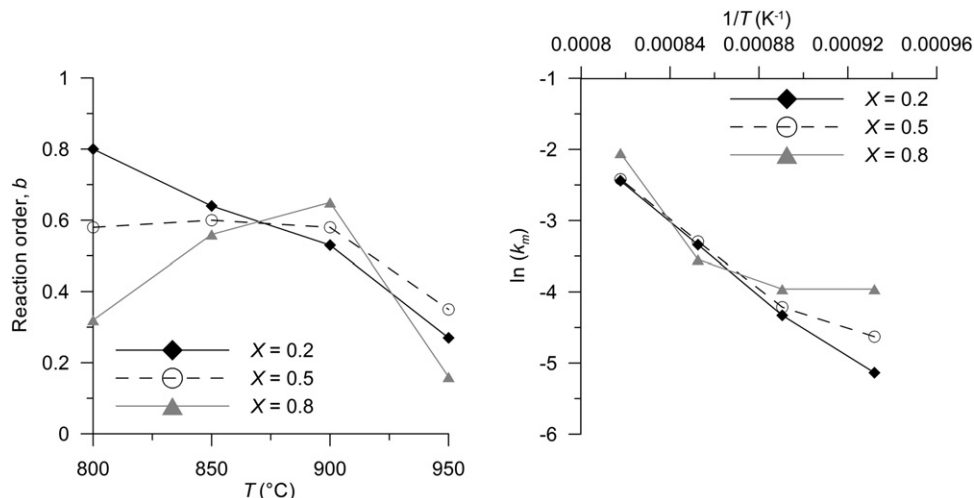|	T = 800 °C	T = 850 °C	T = 900 °C	T = 950 °C
$p_{CO_2} = 1$ bar	SCM: X ≤ 0.80	SCM: X ≤ 0.97	SCM: X ≤ 0.84	SCM: X ≤ 0.99
	VM: X ≤ 0.82	VM: X ≤ 0.89	VM: X ≤ 0.96	VM: X ≤ 0.99
$p_{CO_2} = 5$ bar	SCM: X ≤ 0.98	SCM: X ≤ 0.9	SCM: X ≤ 0.79	SCM: X ≤ 0.94
	VM: X ≤ 0.98	VM: X ≤ 0.9	VM: X ≤ 0.79	VM: X ≤ 0.94
$p_{CO_2} = 10$ bar	SCM: X ≤ 0.88	SCM: X ≤ 0.92	SCM: X ≤ 0.87	SCM: X ≤ 0.76
	VM: X ≤ 0.98	VM: X ≤ 0.92	VM: X ≤ 0.91	VM: X ≤ 0.73

Fig. 7. Reaction order b of CO_2 gasification of coke from Indian high-ash coal, and determination of pre-exponential factor and activation energy.

Table 7
Comparison of the reaction order b of CO_2 gasification obtained in this work with results from literature.

Reaction order b, this work	Reaction order b, literature
$b \sim 0.2$–0.8	Walker et al., Turkdogan et al., Turkdogan and Vinters, Dutta et al., Fuchs and Yavorski: reaction is ~1st order at pressures ≪atmospheric, but approaches 0th order at pressures above 1.52 MPa (reported in [20]).
	Kajitani et al.: $b = 0.79$ (reported in [20]).
	Everson et al.: $b = 0.5$ (reported in [20]).
	Ahn et al.: $b = 0.4$ (reported in [20]).
	Kajitani et al.: $b = 0.43$–0.56 (reported in [20]).
	Kasaoka et al.: $b = 0.45$–0.5 (reported in [20]).
	Lu and Do: $b = 0.53$ (reported in [20]).
	Mahajan and Walker: $b = 0.55$ (reported in [20]).
	Salatino et al.: $b = 0.74$ [25].
	Vamvuka et al.: $b = 0.4$–0.6 [22].
	Kwon et al.: $b = 1$ [34].

DynTHERM HP-TGA (Rubotherm, Germany) with mass spectrometer (Fig. 1). The analyser has a maximum pressure of 40 bar and maximum temperature of 1100 °C, with heating rates up to 50 K/min. Tests were carried out at different temperatures and pressures under isothermal mode. In the case of CO_2 gasification, experiments were carried out at 800–950 °C and 1–10 bar, being the CO_2 partial pressure equal to the total pressure. In the case of steam gasification, tests were performed at 800–900 °C and 0.2–0.7 bar steam partial pressure, being the total pressure equal to 5 bar. The mass of the coal samples was ~35–40 mg, with a particle size of 200–300 μm, in order to avoid mass transfer effects. Coke from coal was produced in the TGA under argon atmosphere at the same pressure and temperature as those of the respective isothermal CO_2/steam experiment. Then, the produced coke was depressurised and cooled down to 300 °C. For the gasification tests, the coke sample was firstly pressurised to the set value and then heated up at ~15 °C/min from 300 °C to the set temperature. Once the set conditions were reached, isothermal gasification of the coke sample under CO_2 or N_2/H_2O atmosphere took place until complete conversion of the coke.

The experimental TGA data were fitted to the volumetric and the shrinking core conversion models. These models have been selected because of mathematical simplicity and acceptable description of the behaviour of conversion with time [21]. The expressions of conversion X and instantaneous reactivity R of the selected models are summarised in Table 3 (Eqs. (4)–(7)).

The gasification rates of coke under CO_2 and steam atmospheres were assumed to follow a b-order Arrhenius model (Eq. (8)):

$$R_i(X) = \frac{1}{1-X}\frac{dX}{dt} = k_m p_i^{\,b} = A\ e^{\frac{-E_a}{RT}} p_i^{\,b} \tag{8}$$

where b is the reaction order, A is the pre-exponential factor (expressed in $bar^{-b}\ min^{-1}$), R is the universal constant of gases (8.314 J/mol K), T is the temperature in K, and E_a the activation energy in J/mol. Subindex i expresses CO_2 or H_2O gasification. The kinetic parameters have been determined for three conversion levels: $X = 0.2$, $X = 0.5$ (reference selected by most of the works in kinetics literature [10]), and $X = 0.8$.

Table 8
Pre-exponential factor and activation energy of CO_2 gasification of coke from Indian high-ash coal at different conversion levels.

	$X = 0.2$	$X = 0.5$	$X = 0.8$
A ($bar^{-b}\ min^{-1}$)	$2.27 \cdot 10^7$	$7.74 \cdot 10^5$	$1.83 \cdot 10^8$
E_a (kJ/mol)	197.55	163.72	216.34
Valid temperature range	800–950 °C	800–950 °C	850–950 °C

2.2.2. Steam gasification under fluidised-bed conditions

Additional experimental tests for the determination of the conversion of Indian high-ash coal under realistic operating conditions have been carried out in a lab-scale fluidised-bed gasifier (78 mm inner diameter, 102 mm freeboard diameter, 900 mm freeboard height, 1630 mm total height), shown in Fig. 2.

Even though the operating conditions of these tests are out of the kinetic regime, factors affecting large-scale fluidised-bed gasification (e.g., coal particle size, heating rate, bed fluid-dynamics, and gasification atmosphere) can be taken into account. Most importantly, the coke is produced under actual conditions of the application of interest. Therefore, these tests can provide valuable data to complement the TGA kinetic study of high-ash coal.

In order to reproduce realistic operating conditions, a mixture of standard bed material and Indian coal ash from previous gasification tests containing a large amount of coal ash was used as bed material. A batch of 765 g of bed material (1500 kg/m³ density) sieved to a fraction of 0.4–0.5 mm was introduced in the reactor prior to tests. This bed material is within the B group (sand-like) of the Geldart's classification of particles. Indian high-ash coal with a particle size of 0.7–2 mm was used as feedstock. Fuel conversion was evaluated during three different stages:

1. Devolatilisation of coal under inert atmosphere for coke production, DEV. During this stage, approximately 1 kg/h coal is fed into the reactor for 30 min under N_2 atmosphere. Devolatilisation is considered to be complete when evolved gases are no longer detected.
2. Gasification of the resulting coke for 25 min under N_2/steam atmosphere (and final flushing with N_2 for ~5 min), SG.
3. Oxidation of the remaining coke under air atmosphere, OXID.

Table 4 summarises the operating conditions of the fluidised-bed tests performed. Tests 1 and 2 are performed at the same bed temperature, but at a different steam partial pressure. Tests 1 and 3 are carried out at a the same steam partial pressure, but at different temperatures. Based on the average density and particle size of the bed material, the minimum fluidisation velocity was estimated as approximately 0.06 m/s. In Fig. 3 it is shown as an example the profile of bed temperatures throughout test 1. As can be observed, the temperature drops during the devolatilisation stage, keeps stable at the set temperature during the steam gasification stage, and increases during the final air oxidation step.

Conversion data have been derived from the evolved gas composition and mass/molar balances. Micro-GC analysis (H_2, Ar/O_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, benzene, toluene, H_2S, and COS) was used for the continuous measurement of the gas composition. Via a molar balance (with argon tracer gas in the devolatilisation and steam gasification stages, and with N_2 in the air oxidation stage), the molar and mass flow rates of the components of the producer and flue gas can be calculated. By integrating the mass of gases evolved during each stage, and subtracting it from the mass of fuel introduced into the reactor (calculated from the fuel mass flow rate, and the properties of the feedstock), the mass and composition of the coke produced at the end of the devolatilisation stage can be derived. This value is used as an input for the calculation of the carbon conversion during the steam gasification stage, obtained through the integration over time of the carbon contained in the producer gas. The mass of the remaining coke is in turn used as input for the calculation of the carbon conversion during the air oxidation stage.

3. Results and discussion

3.1. CO_2 gasification of coke from Indian high-ash coal under TGA conditions

Fig. 4 shows the results of conversion along time of coke from Indian high-ash coal at different pressures and temperatures. As can be observed, both temperature and pressure have a significant impact on
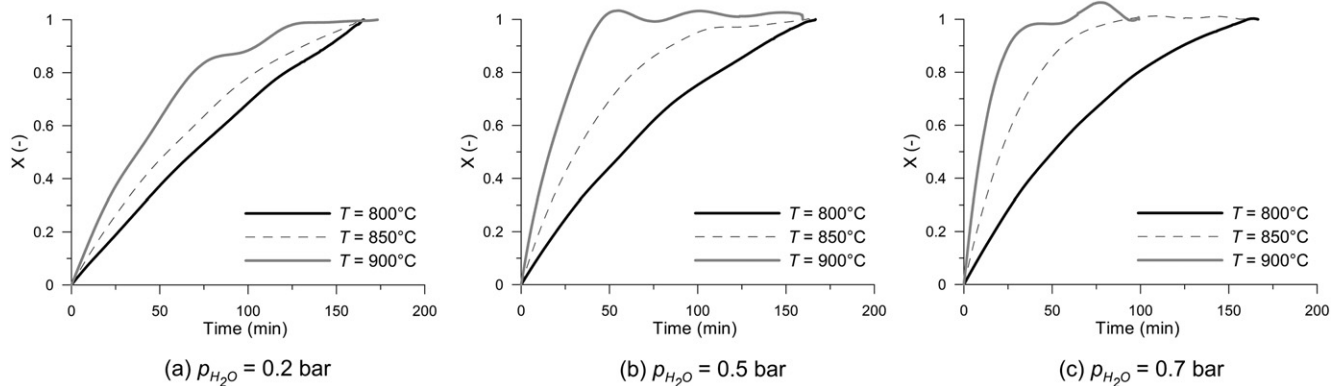
(a) p_{H_2O} = 0.2 bar (b) p_{H_2O} = 0.5 bar (c) p_{H_2O} = 0.7 bar

Fig. 8. Conversion vs. time of coke from Indian high-ash coal under steam gasification conditions.

the conversion of coke. The time required for a conversion of 50% of the coke at 850 °C is reduced from 50 min to 10 min when increasing pressure from 1 bar to 10 bar. Moreover, at 1 bar CO_2 pressure, the time required for 50% conversion of the coke is reduced from 104 min to 9 min when increasing temperature from 800 °C to 950 °C. These results are consistent with those reported in literature both for coal, peat and biomass char [17,20,26]. Char gasification is known to be very sensitive to temperature and to reactant partial pressure [17]. However, it must be taken into account that the coke used in each TGA test has been produced at different pressures and final temperatures during devolatilisation, and therefore its initial structure and reactivity is different [16]. In general, more severe thermal treatment conditions (higher temperatures, lower heating rates, longer residence times) are considered to negatively influence coke reactivity [10,13,16]. Even though the release of volatiles is enhanced at higher temperatures and heating rates, the remaining coke loses more active sites and can also undergo a reordenation in its structure via thermal annealing, thus becoming more aromatic and less reactive [10,13,16,25]. On the other hand, higher pressures hinder the release of volatiles out of the coal particle, thus increasing the residence time of the volatiles within the particle and favouring particle swelling, pore blockage, and polymerisation and graphitisation of the carbonaceous structure. This in turn leads to a decrease of coke reactivity [11]. The extent of the changes suffered by the inorganic matter (e.g., vaporisation, softening, sintering, changes in mineral phases…) is also affected by the thermal conditions during devolatilisation and gasification [26,27]. These changes in turn influence the catalytic activity of the inorganic elements during conversion.

In Fig. 5 it can be observed that the overall conversion rate r is progressively reduced as conversion proceeds. This can be due to the preferential consumption of the most reactive compounds of the material, which makes the coke structure increasingly graphitic and thus less reactive [10,41]. On top of that, there might be also a loss of catalytic

activity of the inorganic compounds present in the coke due to e.g., vaporisation of Na and K, migration, sintering and transformation of mineral phases [10,42], which affects the catalytic activity of the inorganic elements, thus adding up to the decrease in the coke reactivity. As can be also observed in Fig. 5, the values of the reaction rate increase in general at higher temperatures and/or CO_2 pressures, with the exception of data obtained at 950 °C and 10 bar, where the reaction rate is lower than at 5 bar. It is likely that the diffusion resistance of the reactant gas through the char sample (which becomes more important at high temperatures and pressures) is the responsible for the decrease in the reaction rate [38]. This suggests that the run performed at 10 bar and 950 °C might be out of kinetic regime conditions. On the other hand, the effect of the devolatilisation conditions (pressure, temperature) on the reactivity of the produced coke is a factor that also has to be taken into account. The behaviour of the inorganic matter (e.g., changes in mineral phases, softening, sintering, and vaporisation [26,27]) affects the evolution of the organic matter during the thermochemical conversion process, e.g., the softening or coalescence at the inlet of the pore particles can reduce the accessibility of the reactant gases. Under severe conditions, the modifications suffered by the inorganic elements can even lead to a loss of their catalytic activity due to changes in the loading (i.e., catalytic species/carbon ratio), the mineral phases, or the dispersion degree of the catalyst in the carbonaceous matrix (sintering, agglomeration) [26,42]. In this sense, a deep study of the extent of the catalytic activity of the inorganic matter of this high-ash coal when varying the operating conditions should be addressed in future work.

Fig. 6 displays the instantaneous reactivity R of the coke of Indian high-ash coal at different pressures and temperatures under CO_2 gasification. As can be seen, R keeps approximately stable throughout the conversion of the coke, except at very high conversion values. These stable trends might be the result of a balance between the formation and the consumption of active sites during the conversion. It might be also
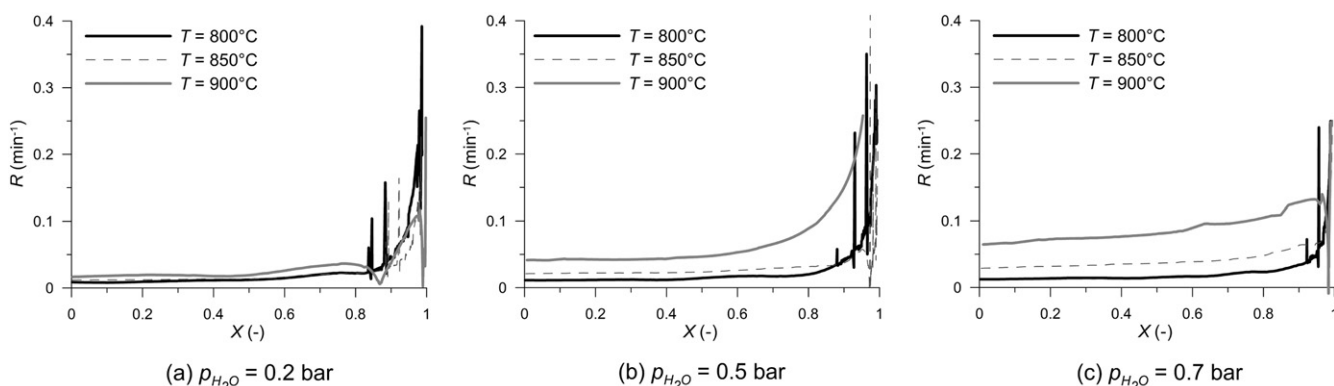

(a) p_{H_2O} = 0.2 bar (b) p_{H_2O} = 0.5 bar (c) p_{H_2O} = 0.7 bar

Fig. 9. Instantaneous reactivity R vs. conversion of coke from Indian high-ash coal under steam gasification conditions.

Table 9
Parameters Ω (volumetric model) and ψ (shrinking core model) for modelling of steam gasification of Indian high-ash coal as a function of temperature and pressure.

T (°C)	Ω (VM) (min^{-1})			ψ (SCM) (min^{-1})		
	$p_{H_2O} = 0.2$ bar	$p_{H_2O} = 0.5$ bar	$p_{H_2O} = 0.7$ bar	$p_{H_2O} = 0.2$ bar	$p_{H_2O} = 0.5$ bar	$p_{H_2O} = 0.7$ bar
800	0.0108	0.0147	0.0153	0.035	0.0039	0.0044
850	0.0142	0.0258	0.0375	0.042	0.0061	0.0094
900	0.0198	0.0473	0.0824	0.053	0.0138	0.0199

possible that the low porosity of the high-ash coke hinders the accessibility of gases, thus making the reactivity relatively insensitive to the conversion degree, as previously discussed in high-ash coal kinetic studies [29]. The steep increase of R when approaching complete conversion ($X \sim 1$) might be due to the collapse of the coke structure by percolation. At high pressures and temperatures (10 bar, 900–950 °C) a maximum can be observed at intermediate conversion levels ($X \sim 0.6$). The identification of a maximum in the reaction rate at intermediate burn-off degrees has been previously observed. During conversion, simultaneous processes occur in the coke structure: the opening of closed pores, the widening of open pores, and the development of pore interconnections [34]. When increasing both the number of pores and their average radius, the specific surface area of the coke also progressively increases with the conversion degree. However, the local specific surface area increases until reaching a critical level of porosity, beyond which the number of pores and the surface area start to decrease due to the fusion of adjacent pores [34]. However, these hypotheses should be further studied in future work by correlating the gasification rate with changes in the coke structure along conversion.

Table 5 summarises the parameters of the volumetric model and shrinking core model, obtained from the fitting of the experimental TGA data. Table 6 shows the valid range of X values for the application of each model. In general, the fitting was acceptable at low and medium conversion levels (up to $X \sim 73$–99% depending on temperature and pressure conditions), but is not reliable anymore at very high conversion levels.

The kinetic parameters of CO_2 gasification of coke from the Indian high-ash coal have been determined for three conversion levels. As an example, Fig. 7 displays the reaction order b as a function of conversion level and temperature, and the plot of ln (k_m) vs. $1/T$ for the determination of the activation energy and the pre-exponential factor. As can be seen, the reaction rate b ranges between 0.2 and 0.8, although it is approximately 0.5–0.6 for temperatures between 850 and 900 °C. Moreover, the effect of temperature on the reaction order varies depending on the conversion degree of the coke. For low conversion levels ($X = 0.2$), b decreases monotonically in the range of temperatures tested, whereas at very high conversion levels ($X = 0.8$), a maximum can be observed at 850–900 °C. At intermediate conversion levels ($X = 0.5$), the reaction order keeps constant at $b = 0.6$ between 800 and 900 °C, but decreases to 0.4 when further increasing temperature to 950 °C. The reaction order b represents the effect of the reactant partial pressure on the gasification rate, and therefore, changes in b imply that the accessibility of the reactant to the particle is affected both by temperature and burn-off degree. Probably, the initial reactivity of the coke (affected by the different conditions of temperature and pressure) also plays an important role. In this sense, future work should be devoted to correlate the coke structure with the gasification rate for the improvement of the understanding of the phenomena taking place. As can be checked in Table 7, the results of the reaction order obtained in this work are within the range reported in other works in literature.

Table 8 summarises the results of activation energy and pre-exponential factors determined at the different conversion degrees. At a conversion level of 50%, the activation energy of the CO_2 gasification reaction is approximately 164 kJ/mol. As can be observed, at very high conversion levels ($X = 0.8$), the fitting is less accurate and the validity range is limited to 850–950 °C. The values found in this work are of the same order as those found in literature [10,13,20,22,25,29,34].

3.2. Steam gasification of coke from Indian high-ash coal under TGA conditions

Fig. 8 shows the TGA results of conversion along time of coke from the Indian high-ash coal at different steam partial pressures and temperatures. It can be seen that the time required for a conversion of 50% of the coke at 850 °C is reduced from 54 min to 21 min when increasing the H_2O partial pressure from 0.2 bar to 0.7 bar. Moreover, at 0.2 bar steam partial pressure, the time required for 50% conversion of the coke is reduced from 69 min to 38 min when increasing temperature from 800 °C to 900 °C. These results are in agreement with those found in literature [46]. Similarly to what was discussed in Section 3.1, it must be taken into account that the initial reactivity of the coke used in the TGA runs differs due to the different devolatilisation conditions (temperature and pressure). On the other hand, when comparing the data from tests at 0.7 bar steam partial pressure (Fig. 8) and tests at 1 bar CO_2 pressure (Fig. 4), it can be noticed that the gasification rate of steam gasification is approximately twice as high as that of CO_2 gasification, in agreement with previous works [10,13–15,17,33,43].

Fig. 9 shows the instantaneous reactivity R of the coke of Indian high-ash coal at different partial pressures and temperatures under steam gasification. As expected, the instantaneous reaction rate increases with the temperature and/or the steam partial pressure. However, when comparing with Fig. 6, slightly different trends in the reaction rate when gasifying with CO_2 or steam can be observed. At $p_{CO_2} = 1$ bar and $T = 800$–900 °C (Fig. 6), R keeps approximately constant throughout the conversion range, and with values around 0.01–0.03 min^{-1}. On the contrary, at $p_{H_2O} = 0.7$ bar and $T = 800$–900 °C (Fig. 9), R increases slightly but monotonically with conversion, and the reaction rate shows higher values, $R \sim 0.01$–0.06 min^{-1}. Furthermore, the increase of reactivity along conversion becomes more significant at higher steam partial pressures and/or higher temperatures. Similar trends were found by Sekine et al. [41] in a study of the reactivity and structural changes of coke during steam gasification. This implies that both the changes suffered by the coke structure and reactivity are different depending on the gasifying agent used. In this sense, Tay et al. already identified the drastic effect of steam on the structure and reactivity of char [23]. Kühl et al. also observed different effects of CO_2 and steam on the pore structure and the specific surface area of different cokes [47]. Sekine et al. [41] stated that the ash morphology had a more significant effect on the gasification rate than the changes in the carbonaceous structure. Moreover, the mineral matter content influences each gasification reaction to a different extent [33].

Table 10
Valid range of conversion levels for model fitting of steam gasification of coke from Indian high-ash coal.

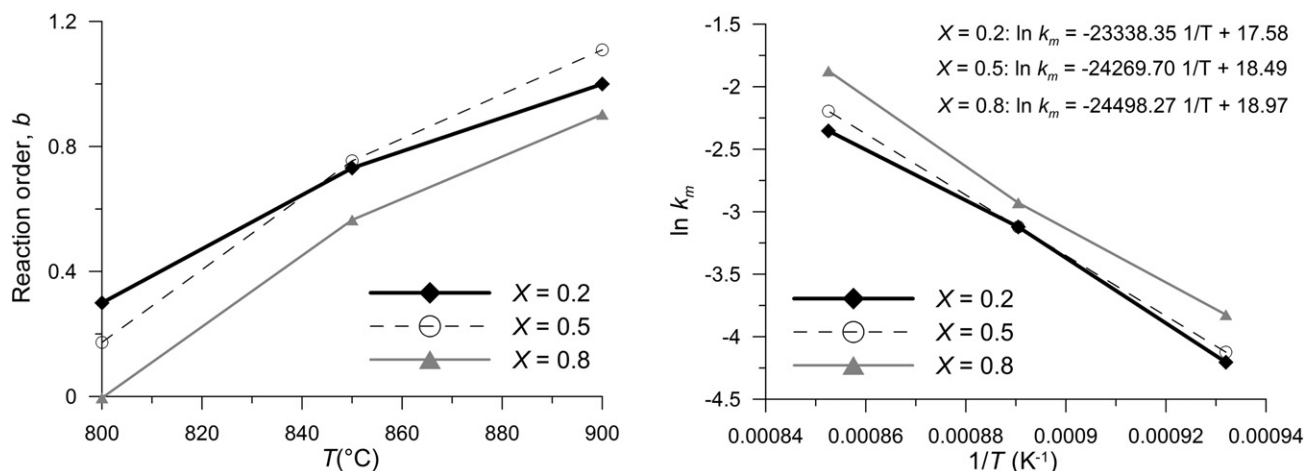|	$T = 800$ °C	$T = 850$ °C	$T = 900$ °C
$p_{H_2O} = 0.2$ bar	SCM: $X \leq 0.87$	SCM: $X \leq 0.91$	SCM: $X \leq 0.97$
	VM: $X \leq 0.64$	VM: $X \leq 0.83$	VM: $X \leq 0.77$
$p_{H_2O} = 0.5$ bar	SCM: $X \leq 0.95$	SCM: $X \leq 0.97$	SCM: $X \leq 0.99$
	VM: $X \leq 0.74$	VM: $X \leq 0.85$	VM: $X \leq 0.83$
$p_{H_2O} = 0.7$ bar	SCM: $X \leq 0.93$	SCM: $X \leq 0.9$	SCM: $X \leq 0.98$
	VM: $X \leq 0.69$	VM: $X \leq 0.74$	VM: $X \leq 0.78$

Fig. 10. Reaction order b of steam gasification of coke from Indian high-ash coal, and determination of pre-exponential factor and activation energy.

The experimental reactivity data have been fitted to the volumetric and the shrinking core models. The parameters Ω and ψ of the models determined for the steam gasification of coke from the Indian high-ash coal are summarised in Table 9. Table 10 displays the range of conversion levels for which the fitting to each conversion model is valid. As can be seen, the fitting is valid up to ~64–99% depending on the conditions of pressure and temperature. In general, the conversion models cannot be applied at very high conversion levels.

Fig. 10 shows the results of the calculated reaction order for the steam gasification of the coke. As can be seen, the reaction order ranges between 0 and 1.1, and increases with reaction temperature for all the conversion levels evaluated. This means that the reactivity is increasingly sensitive to the reactant partial pressure as the reaction temperature increases, this effect being somehow lessened at very high conversion levels ($X = 0.8$). This could be due to the loss of accessibility of the reactant gases to active sites, which is further hindered by the high ash content of the coke and the changes suffered by the inorganic matter towards complete conversion. On the other hand, it is worth observing the different trends in reaction order obtained in CO_2 gasification and steam gasification, which points again at the different changes in structure and reactivity undergone by the coke during gasification depending on the gasifying agent. Table 11 compares the reaction orders found in this work with others determined in other works of coal kinetics. Table 12 summarises the results of activation energy and pre-exponential factors determined at the different conversion levels. As can be seen, at 50% conversion, the activation energy of the steam gasification reaction is approximately 202 kJ/mol. The values determined in this work are of the same order as those found in literature [10,13,29,33].

3.3. Atmospheric steam gasification of Indian high-ash coal under fluidised-bed conditions

Fig. 11 firstly compares the concentration of the main compounds present in the evolved throughout tests 1 and 3, performed at 850 °C and 920 °C, respectively. The gas composition, measured from micro-GC analysis, is expressed in dry basis. As can be seen, the H_2 and CO content of the gas during the devolatilisation and steam gasification stages increases when operating at higher temperatures. Gaseous hydrocarbons C_xH_y (C_2H_4 being the most abundant) are only evolved during the devolatilisation stage. The presence of CO observed at the beginning of the air oxidation stage reveals that at first the remaining coke is gasified, but as the coke is consumed and thus the relative fuel/air mass ratio is decreased, the process turns progressively into combustion (CO is no longer present, and only CO_2 is detected by the micro-GC).

Fig. 12 shows the overall carbon conversion of the high-ash coal throughout the test, as well as the fuel conversion (i.e., the total volatile content released with respect to the initial dry, ash-free coal) during the devolatilisation stage. In all the tests it can be seen that conversion stabilises just after 30 min operation (corresponding to the time of continuous feeding of fuel into the reactor at 1 kg/h rate). Therefore, it can be assumed that devolatilisation can be considered almost an instantaneous process as compared to steam gasification. After devolatilisation, 37–45% of the coal is converted to gas.

Fig. 13 displays the carbon conversion of the Indian high-ash coal in each stage tested (devolatilisation, steam gasification, and air oxidation). In this case, carbon conversion refers to the carbon contained in the gas with respect to the carbon present in the coke at the beginning of each stage. As can be seen, coke from the high-ash coal shows 15–22% conversion after 25 min gasification. It can be also checked that, as expected, conversion is favoured at high steam partial pressures and/or higher temperatures. Higher temperatures also enhance the conversion of the coke during the air oxidation stage. Lastly, it is remarkable the significant higher rate of air oxidation with respect to steam gasification, in consistency with results from literature [14,15,17,43]. At 920 °C, ~22% carbon is converted after 25 min reaction under steam gasification conditions, whereas ~80% carbon is converted under air oxidation conditions in the same time.

Fig. 14 compares the effect of the partial pressure of CO_2 and steam on the conversion of coke from Bilaspur coal at a fixed temperature of 900 °C (data from TGA tests). In the case of steam gasification, the results obtained in the fluidised bed (FB) experiment at 920 °C and a steam partial pressure of approximately 0.35 bar are compared with

Table 11

Comparison of the reaction order b of steam gasification obtained in this work with results from literature.

Reaction order b, this work	Reaction order b, literature
$b \sim 0$–1.1	Song et al.: $b \sim 0.16$–1.16 [38].
	Lee: $b \sim 0.96$ (reported in [38]).
	Chin et al.: $b \sim 0.87$ (reported in [38]).
	Shufen and Ruizhang: $b \sim 0.26$ (reported in [20]).

Table 12

Pre-exponential factor and activation energy of steam gasification of coke from Indian high-ash coal at different conversion levels.

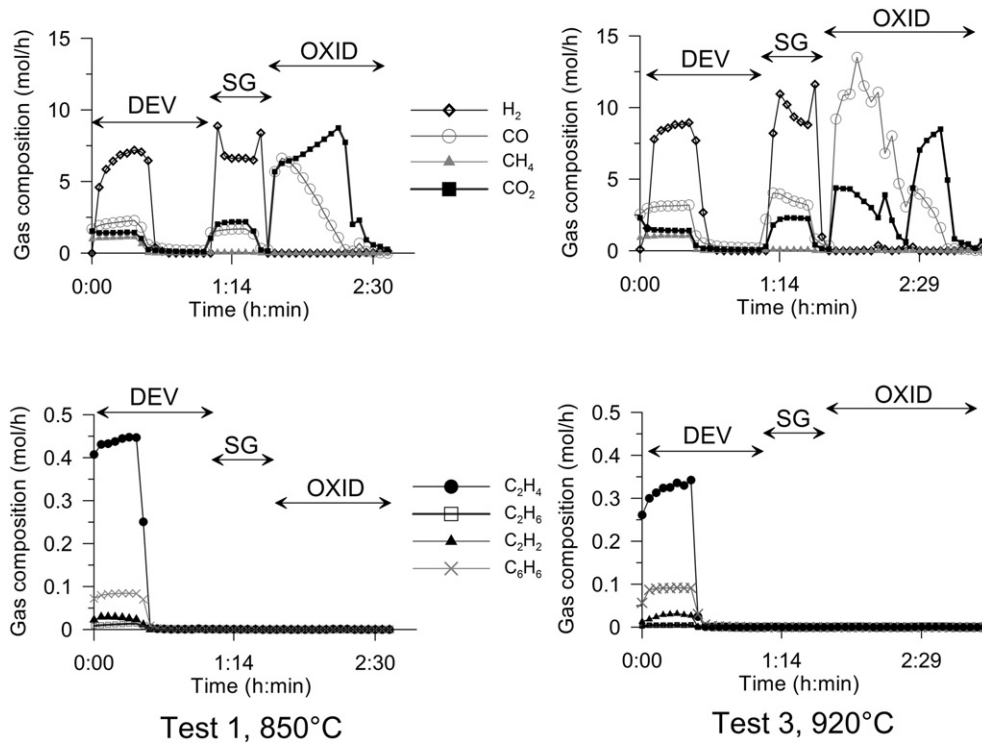|	$X = 0.2$	$X = 0.5$	$X = 0.8$
A (bar^{-b} min^{-1})	$4.33 \cdot 10^7$	$1.08 \cdot 10^8$	$1.73 \cdot 10^8$
E_a (kJ/mol)	194.03	201.78	203.68
Valid temperature range	800–900 °C	800–900 °C	800–900 °C

Fig. 11. Comparison of gas composition (dry basis) in tests 1 and 3.

the TGA data. Firstly, it can be seen that regardless of the gasifying agent used there is a saturation effect when increasing the partial pressure of reactant gas. For example, in the case of CO_2 gasification, the conversion rate increases significantly when increasing the CO_2 partial pressure from 1 to 5 bar, but the conversion rate levels off when further rising CO_2 partial pressure from 5 to 10 bar. Therefore, the effect of pressure on the gasification rate is more significant in the low pressure region, as has been previously reported both for CO_2 and H_2O gasification [20, 21,32,36,37]. On the other hand, in the case of steam gasification, it can be observed that the conversion under fluidised-bed conditions is significantly lower than that obtained in the TGA tests at similar temperature and steam partial pressures. It must be taken into account, however, that the selection of operating conditions typical of real large-scale fluidised-bed gasifiers imply that the conversion values obtained are out of the kinetic regime (as in the case of thermogravimetric analysis), also affecting the structure and reactivity of the produced

coke. The main differences, summarised in Table 13, refer to the properties of the coal (particularly with respect to the particle size), the heating rate during the devolatilisation stage (which dramatically affects the reactivity of the produced coke, and in turn affects the conversion rate during the gasification stage), inhibition effects due to differences in both reacting gas flow/coke mass ratio and superficial velocity of reactant gas, and other fluid-dynamic effects taking place during fluidised-bed operation which influence the heat and mass transport rates. As can be seen, all these processes are interrelated with each other in a complex way, and the overall effect is a shift in reaction regime from the kinetic region I (TGA) to the intermediate region II (FB). As previously reported, in industrial processes, where the particle size is often larger than 1 mm, the gasification reaction is also controlled by heat and mass transfer [17]. In particular, under fluidised-bed conditions, the fuel is claimed to be likely gasified in the intermediate regime [14]. Fig. 15 attempts to quantify the effect of
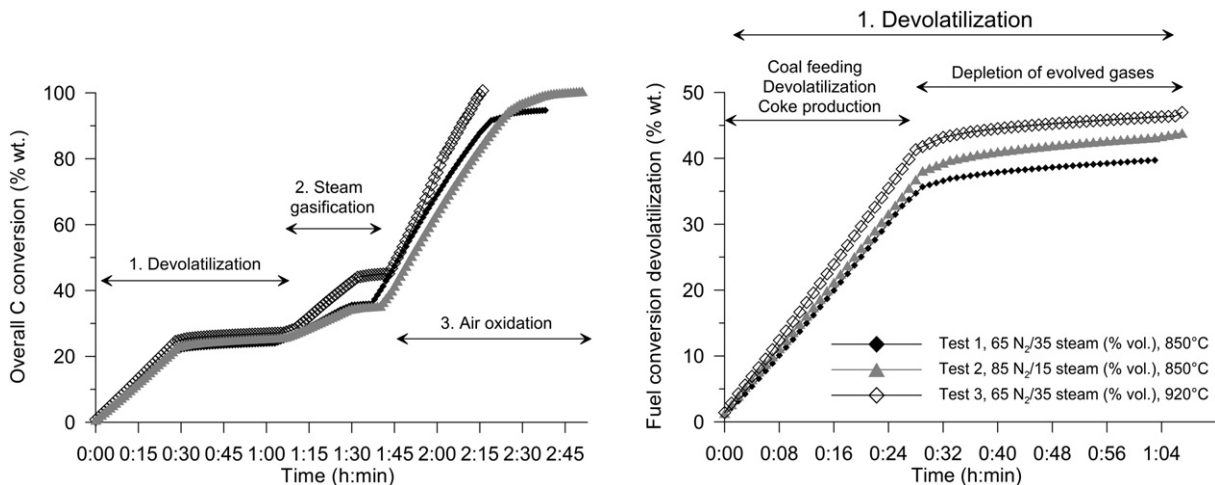

Fig. 12. Overall carbon conversion vs. time of Indian high-ash coal, and fuel conversion during devolatilisation stage.
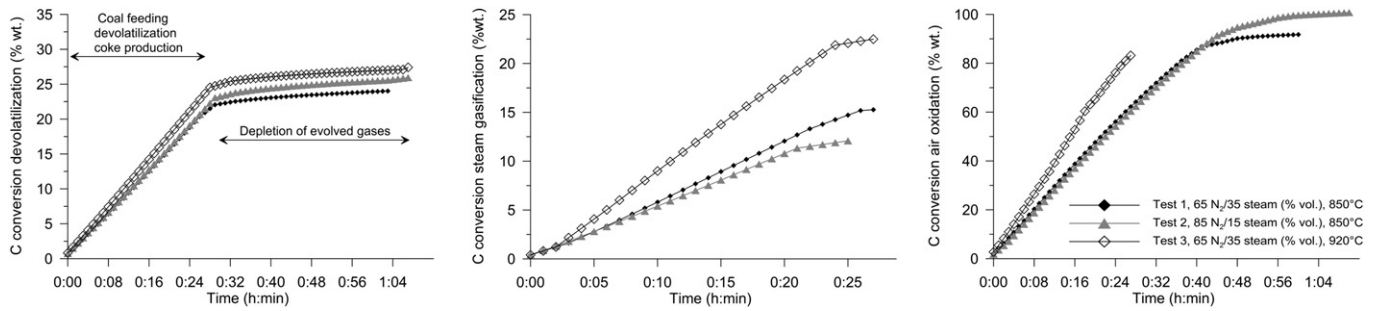
Fig. 13. Carbon conversion vs. time of Indian high-ash coal under devolatilisation, steam gasification, and air oxidation stages (referred to the carbon contained in the coke at the beginning of each stage).

operating under fluidised-bed compared to TGA conditions. For this, the parameter Ω of the volumetric model has been compared for the TGA tests (see Table 9) and the FB experiments (see Fig. 15 left). When extrapolating values, it can be seen that the operation under realistic FB conditions has an equivalent effect to a decrease in the gasification temperature when evaluating data from TGA. To sum up this section, the results from the TGA tests have provided the intrinsic kinetics of the coke, whereas the fluidised-bed experiments have complementary shed light on the actual behaviour of the high-ash coal under real large-scale fluidised-bed operation (i.e., coal properties, reactivity of the produced coke, fluid-dynamics of bed material).

4. Conclusions

In order to optimise the design of fluidised-bed gasification processes for the efficient use of high-ash coals for energy production, this paper studies the conversion and reactivity of an Indian high-ash coal under CO_2 and steam gasification conditions. Both isothermal TGA tests for the determination of the intrinsic kinetics and additional tests under realistic fluidised-bed (FB) gasification conditions have been carried out. The main findings are summarised below:

a) Gasification of coke from Indian high-ash coal in TGA:
  • Both the conversion and the reaction rate of the coke increase at higher temperatures and/or partial pressures of the gasifying agent.
  • The time required for a conversion of 50% of the coke at 850 °C under CO_2 gasification conditions is reduced from 50 min to 10 min when increasing pressure from 1 bar to 10 bar. Moreover, at 1 bar CO_2 pressure, the time required for 50% conversion of the coke is reduced from 104 min to 9 min when increasing temperature from 800 °C to 950 °C.

  • The time required for a conversion of 50% of the coke at 850 °C under steam gasification conditions is reduced from 54 min to 21 min when increasing H_2O partial pressure from 0.2 bar to 0.7 bar. Moreover, at 0.2 bar steam partial pressure, the time required for 50% conversion of the coke is reduced from 69 min to 38 min when increasing temperature from 800 °C to 900 °C. The gasification rate of steam gasification is approximately twice as high as that of CO_2 gasification.
  • The experimental TGA data have been fitted to the volumetric and the shrinking core conversion models. The fitting is valid up to ~73–99% (CO_2 gasification), and ~64–99% (steam gasification), depending on the conditions of pressure and temperature. In general, the conversion models cannot be applied at very high conversion levels.
  • Determination of kinetic parameters (reaction order b, pre-exponential factor A and activation energy E_a) has been carried out at three reference conversion levels: $X = 0.2$, $X = 0.5$, and $X = 0.8$. In the case of CO_2 gasification, the reaction order b ranges between 0.2 and 0.8, although at temperatures of 850–900 °C the reaction order has a value around 0.6. In the case of steam gasification, reaction order ranges between 0 and 1.1, and increases with reaction temperature. The activation energy of CO_2 gasification is 164–216 kJ/mol, whereas the activation energy for the steam gasification reaction ranges between 194 and 204 kJ/mol, depending on the conversion degree.

b) Steam gasification of Indian high-ash coal under fluidised-bed conditions:
  • Approximately 23–27% of the carbon contained in the coal (~40–45% of the overall coal, considering also hydrogen and oxygen released in the gas) is quickly converted during the devolatilisation
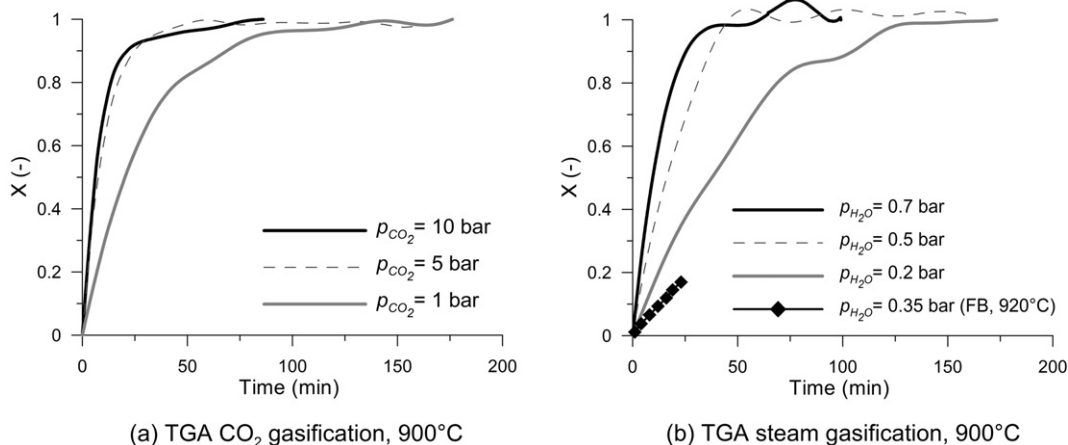

(a) TGA CO_2 gasification, 900°C　　　　　　(b) TGA steam gasification, 900°C

Fig. 14. Effect of CO_2 and steam partial pressure on the conversion of coke from Indian high-ash coal.

Table 13
Differences between fluidised bed and TGA operating conditions affecting coke reactivity and gasification rate.

Parameter	TGA tests	Fluidised bed tests	Influence/effect
Coal particle size, d_p	200–300 μm (35–40 mg sample).	0.75–2 mm (500 g batch).	Extent of drying and devolatilisation → coke structure → coke reactivity [44] (e.g., lower d_p → higher release of volatiles → more porous coke → higher coke reactivity). Gasification reactions: d_p → specific surface area → heat and mass transfer (intra-particle temperature gradient) → shift in reaction regime [14,17,45,46]. Influence on mixing/segregation issues in fluidised bed reactors (hydrodynamics) → mass and heat transfer [14,16] → shift in reaction regime.
Devolatilisation conditions (coke production)	p/T: 5 bar, 800–950 °C. 15 K/min heating rate. Intermediate cooling before gasification.	p/T: 1 bar, 850–920 °C. ~73 K/s heating rate[a] No intermediate cooling.	Temperature/pressure/residence time → rate of volatile release → changes in coke structure: size and density, development of surface area and pore structure, melting, swelling, pore blockage, bubble formation, graphitisation (thermal annealing), polymerisation, changes in mineral matter [10,11,13,16,21,24–28,42,47] → coke reactivity. Behaviour of inorganic matter (melting/sintering, changes in mineral phases, etc.) → catalytic activity of the inorganic compounds [10,15,26] → coke reactivity. Intermediate cooling → changes in coke structure (e.g., polymerisation, graphitisation) → coke reactivity.
Gasification atmosphere	CO_2 or N_2/H_2O[b]	N_2/H_2O + producer gas (CO, H_2, CO_2, CH_4...)[b]	Effect on coke structure (composition, pore structure, surface area) → coke reactivity [10,11,23–25,36,47]. Inhibition of C–H_2O reaction by H_2 and CO [10,15,21,26,29,30,32,36] → modification of reaction rate.
Bed fluid-dynamics	–	Velocity and size of bubbles, fraction of bubbles in the bed (voidage), fluidisation velocity, bed material properties, attrition, segregation, contact time distribution, elutriation [11,14].	Flow patterns of solids and gas → transport rates of heat and mass, degree of gas and solid mixing [14] → extent of devolatilisation [14] → coke structure → coke velocity. Flow patterns of solids and gas → attrition → coke structure [16] → coke reactivity. Flow patterns of solids and gas → transport rates of heat and mass, degree of gas and solid mixing [14] → shift in reaction regime. Interactions between bed material and coal ash [15] → catalytic activity of inorganic elements → reaction rate. Interactions between bed material and coal ash → agglomeration → heat and mass transfer rates → shift in reaction regime. Fluid-dynamics → mixing and segregation → mass and heat transfer rates → shift in reaction regime. Superficial velocity → local composition of reactant atmosphere → inhibition issues → changes in reaction rate.

[a] Estimation is based on 2000 W heating element operating at 10% power; N_2 and coal entering at 25 °C; reaction temperature 850 °C.
[b] In the TGA tests, the reactant flow is much higher than the coal sample. Thus, the reactant gas rapidly sweeps the evolved gases from the coal reactions, and the extent of inhibition by product gas is largely reduced compared to the fluidised bed conditions.

stage. Between 12 and 22% of the carbon contained in the remaining coke is converted to gas within the first 25 min of steam gasification. Finally, 55–80% of the carbon in the coke remaining after steam gasification is converted during the first 25 min of oxidation with air.

- Gasification conversion is favoured at higher steam partial pressures and/or higher temperatures.
- Carbon conversion is significantly higher under air oxidation than under steam gasification conditions. At 920 °C, ~23% carbon is
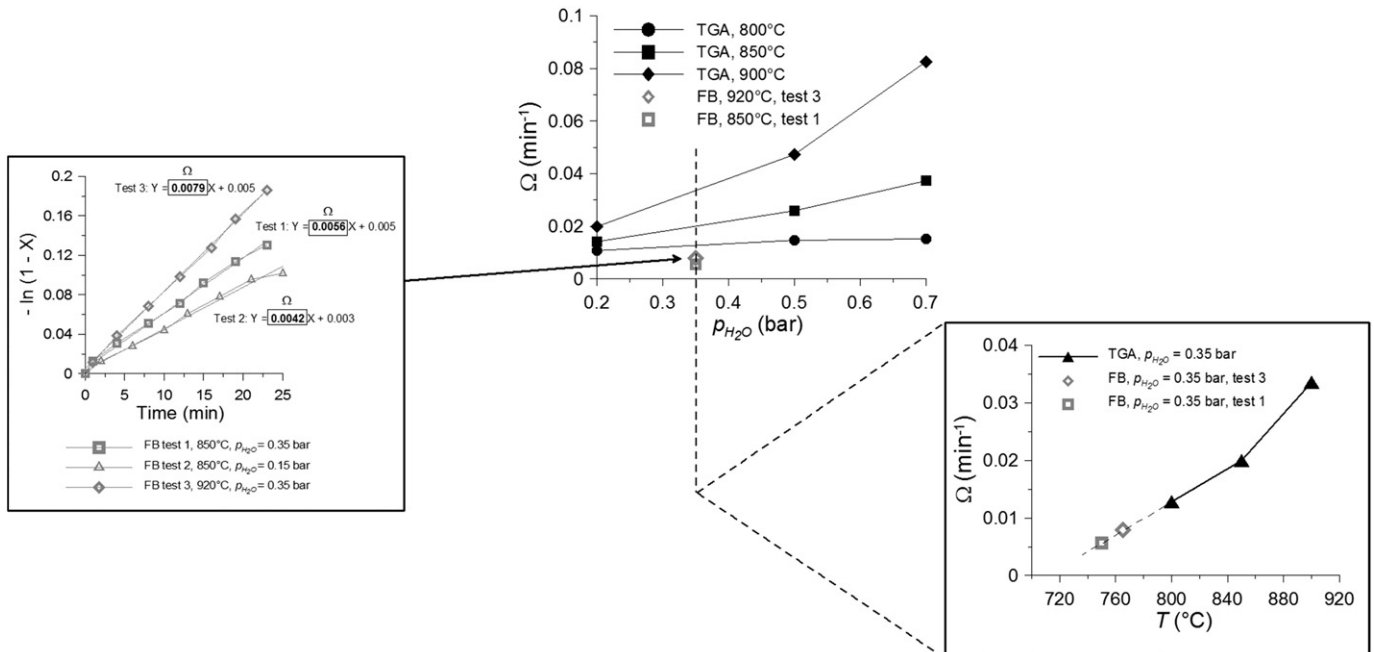
Fig. 15. Comparison of parameter Ω (volumetric model) for steam gasification in TGA and fluidised-bed.

converted after 25 min reaction under steam gasification conditions, whereas ~80% carbon is converted under air oxidation conditions in the same time.

- Conversion under realistic fluidised-bed conditions is significantly lower than that obtained in TGA tests at similar temperature and steam partial pressure values. Differences in the coal particle size, the heating rate during devolatilisation, inhibition issues, and other fluid-dynamic effects influence the reactivity of the produced coke as well as the heat and mass transport rates. The overall effect of these phenomena is a shift in reaction regime. Operation under realistic FB conditions has an equivalent effect to a decrease in the gasification temperature under TGA conditions.

Acknowledgements

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ECN

Westerduinweg 3	Postbus 1
1755 LE Petten	1755 LG Petten

T 088 515 4949
F 088 515 8338
info@ecn.nl
www.ecn.nl