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STUDIES ON CO_2 GASIFICATION REACTIVITY OF HIGH ASH INDIAN COAL

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ABSTRACT

Coal is a prime energy source in India and will continue to play its role for coming several decades. However, our indigenous coal suffers from high ash content and present coal based conventional power generation technologies have several drawbacks such as, lower efficiency, environmental loading and damages thereof. Herein the importance of gasification lies because coal gasification is a mean to utilize coal more efficiently meeting stringent environment controlled parameters. Studies on coal gasification reactivity is essential to design and to select suitable gasifier matching with coal properties. Presently, systematic reactivity data on high ash Indian coals is limited. Considering this limited gasification data of high ash Indian coals, present study investiges CO_2 gasification of high ash Indian coal-char samples (preapred at 900 and 1000 ^{0}C) in the temperature range of 900 – 1000 ^{0}C and discusses the effect of coal properties and operating conditions on gasification reactivity.

Keywords: Coal gasification, High ash Indian coal, Gasification reactivity.

1. INTRODUCTION

Future energy demand – supply chain is mainly coal dependent due to gradual depletion of oil and natural gas sources. India is 4th largest coal producer country in the world with its 286 billion ton of coal reserve. India meets around 53% of its primary energy demand from coal and about 70% of electricity generation is coal based [1]. Therefore, coal is a prime energy source in India and will continue to play its role for coming several decades. However, our indigenous coal suffers from high ash content and present coal based conventional power generation technologies have several drawbacks such as, lower efficiency, environmental loading and damages thereof. Therefore, utilization of coal through environment friendly techniques has become a major challenge throughout the world and Clean Coal Technology (CCT) is essential to reduce CO_2 emission to atmosphere. CCT coupled with Carbon Capture and sequestration (CCS) is capable to emerge as ultimate Zero Emission Technology. Herein the importance of gasification lies because coal gasification is a mean to utilize coal more efficiently meeting stringent environment controlled parameters.

Considering the high ash content of Indian coals and environmental pollution, fluidized bed gasification technology is most suitable in Indian scenario. Fluidized bed gasifiers are genarlly operated at temperature around 1000 ^{0}C [2]. Therefore, to design fluidized bed gasifiers for high ash Indian coals, gasification reactivity data should be available for the temperature range around 1000 ^{0}C. Presently, systematic reactivity data on high ash Indian coals is limited. Considering this limited gasification data of high ash Indian coals, present study investiges CO_2 gasification of high ash Indian coal-char samples using thermogravimetric analysis (TGA). Char samples are preapred at 900 and 1000 ^{0}C and CO_2 gasification experiments have been conducted in the temperature range of 900 – 1000 ^{0}C which are closed to the conditions of fluidized bed gasifiers. Present paper also discusses the effect of coal properties and operating conditions on gasification reactivity

2. EXPERIMENTAL

2.1 SELECTION OF COAL SAMPLE

For the present study, one high ash coal sample from Mahanadi Coal Field Limited, India (MCL) has been chosen.

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Table 1 shows the proximate analysis of coal sample and Table 2 shows the ultimate analysis, i.e., weight percentage of Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S), and Oxygen (O). For all the experiments sample sizes have been kept < 212 µm. Proximate and ultimate analyses have been done following Indian standard, IS: 1350 series [3, 4].

Table 1: Proximate analysis of coal sample (air dried basis)

Sample	Moisture (M, wt%)	Ash (A, wt%)	Volatile Matter (VM, wt%)	Fixed carbon (FC, wt%)
Coal	6.5	41.3	24.5	27.7

Table 2: Ultimate analysis of coal sample on dry ash free basis (daf)

Sample	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O (wt%) (by difference)
Coal	71.17	5.42	1.65	1.05	20.71

2.2 CHAR PREPARATION

Fluidized bed gasifier is most suitable for high ash coals. Therefore, to design fluidized bed gasifiers for high ash Indian coals, gasification reactivity data should be available for the temperature range around 1000 ^{0}C. Presently, systematic gasification reactivity and kinetics data on high ash Indian coals is limited. Considering this limited gasification kinetics data of high ash Indian coals, char samples have been prepared at 900 (char 900) and 1000 ^{0}C(char 1000) for the present investigation.

These char samples have been prepared using Thermogravimetric analyzer STA 449 F3 Jupiter, Netzsch, Germany in Argon (Ar) atmosphere keeping Ar flow constant at 50 ml/min through out the char preparation. Approximately 500 mg of coal sample has been taken in Alumina sample container. Then temperature has been raised at the rate of 10 ^{0}C/min in Ar flow upto the desired temperature. Then at that temperature, sample is kept for 30 min. It has been found that during char preparation from coal sample, complete removal of volataile matter has occurred at 900 and 1000 ^{0}C in 30 minutes. For carying out various gasification experiments and char characterization, same experiment has been repeated to get sufficient amount of samples. Details of STA 449 F3 Jupiter system has been discussed later.

2.3 SURFACE AREA MEASUREMENT

Tristar 3000 surface area analyzer (Micromeritics, USA) measures the N_2 surface area of the samples using Brunauer-Emmett-Teller (BET) equation.

The adsorbate gas is nitrogen (N_2) of purity 99.999%) and isotherm is measured at the boiling temperature of liquid nitrogen, i.e., at -196 ^{0}C. Five points of the isotherm are taken in the relative pressure range of 0.05 to 0 .3. Straight lines are obtained and the correlation coefficients for all the measurements are greater than 0.99. From the slope and intercept of straight line, surface area is calculated. Before conducting experiments, surface of the coal sample is cleaned by flowing nitrogen gas at 150 ^{0}C for 3 hours in a separate unit.

CO_2 surface area has been measured by same instrument using Dubinin-Radushkevich (D-R) equation. Here, the adsorbate gas is carbon dioxide (CO_2) of 99.999% purity and isotherm has been measure at 0 ^{0}C maintained by ice bath. Isotherm has been drawn in the relative pressure range of 0.0001 to 0.03. Straight line has been obtained and surface area value has been determined. Before conducting experiments, surface of the coal sample is also cleaned by flowing nitrogen gas at 150 ^{0}C for 3 hours in a separate unit. Table 3 shows the surface areas of coal and char samples.

Table 3: Surface areas of coal and char samples

Sample	N_2 surface area (m^2/g)	CO_2 surface area (m^2/g)
Coal	16.92	103.60
Char 900	24.67	246.38
Char 1000	18.19	200.01

2.4 THERMOGRAVIMETRIC ANALYSIS (TGA)

Isothermal thermogravimetric analysis (TGA) has been carried out to conduct the gasification experiments in CO_2 atmosphere using Netzsch STA 449 F3 Jupiter thermal analyzer. TGA is widely used for gasification reactivity due to its simplicity and accurate measurements [5 – 7]. 50 mg of char sample is taken for each experiment in the alumina crucible. Ultra pure dried Ar and CO_2 of purity 99.999% are chosen as inert and gasifying agents.

Gasification experiments have been conducted isothermally at 900, 950 and 1000 ^{0}C and CO_2 partial pressure of 0.1 MPa. First the sample is heated in inert atmosphere (Ar) at the rate of 10 ^{0}C/min up to the desired temperature. Then Ar flow has been changed to CO_2 flow and gasification experiment is conducted at that temperature for one and half hours. The flow rate of Ar and CO_2 is kept at 50 cc / min. The thermogravimetric analyzer is calibrated and repeatability of the instrument has been checked by several experiments taking calcium oxalate as reference sample. Blank run is carried out under the same experimental conditions and to minimize the Buoyancy effect each experiment is corrected with the blank run. S-type thermo couple has been used to measure the reaction temperature with accuracy level of ± 1 ^{0}C.

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3. RESULTS AND DISCUSSION

3.1 Comparison of N_2 and CO_2 surface area

Table 3 clearly reflects that CO_2 surface area values of coal and char samples are higher than those of N_2 surface areas. Mahajan [8], Ng et al [9], Chan et al [10]], Parkash & Chakrabartty [11] also reported that CO_2 surface areas of coal and char samples are higher than their N_2 surface areas.

CO_2 isotherms, usually measured at 0 or 25 ^{0}C, are capable in determining coal micropore volumes and micropore surface areas as CO_2 gas can access the finest porosity at these temperatures. Whereas, N_2 gas at -196 ^{0}C is generally not considered to have access to the finest microporosity of coal. This is called activated diffusion phenomenon.

3.2 Variation of surface area with char preparation temperature

Table 3 also reflects that surface areas (both CO_2 and N_2 surface areas) of char samples are higher than those of raw coal sample. These results also show that char sample which is prepared at 900 ^{0}C has higher surface area values than char sample prepared at 1000 ^{0}C. It means surface area decreases as the char preparation temperature increases. These results are consistent with the observations of other researchers also [12 – 13].

There are two competing effects that affect porosity and surface area during heat treatment of coal at higher temperature in inert atmosphere. These are i) removal of volatiles and tars at high temperature which leave a larger pore volume due to unblocking of closed pores and generation of new pores resulting in the increase of porosity and surface area. ii) Thermal annealing and structural reorganization of the carbon matrix at further higher pyrolysis temperature lead to closing of pore mouths and pore coalescence which result in reducing of surface area and porosity.

3.3 Char gasification reactivity

Gasification reactivity at 900, 950 and 1000 ^{0}C of char samples prepared at 900 and 1000 ^{0}C have been studied thermogravimetrically in CO_2 partial pressure of 0.1 MPa. Comparison of gasification reactivity of different char samples gasified at different temperatures has been carried out by determining reactivity index (R).

Values of reactivity index, R under different operating conditions for all the char samples have been depicted in Table 4. Greater the R of a particular char under definite condition, higher is its reactivity. R is generally used to compare reactivity of different coals and is defined as

$$R = 0.5/ \tau_{0.5} \qquad (1)$$

Where, $\tau_{0.5}$ represents the time required to reach 50% carbon conversion [14 – 18]. This definition has been applied here to compare gasification reactivity of different char samples under different gasification conditions.

R values have been calculated from $\tau_{0.5}$ which has been derived from fractional conversion, x versus time, t relationship of each experiment. In general, the curves of x versus t show a similar shape, irrespective of char type and experimental conditions. The curve is almost a straight line up to fractional conversion, x of 0.75.This is supported by other researchers also [7, 17, 19].

Coal-char gasification reactivity is a complex function of coal rank, coal properties, char preparation conditions and operating parameters during gasification. In the present study, as heating rate (10 ^{0}C/min) and residence time (30 min) during char preparation remain same for all the char samples, variation of reactivity of different char samples have been discussed with the variation of i) char preparation temperature, ii) gasification temperature and vi) surface area of char samples.

Table 4: Reactivity indices (R) of char samples

Sample	Char preparation Temperature (^{0}C)	Gasification Temperature (^{0}C)	Reactivity index, R (min^{-1})
Char 900	900	900	0.0143
		950	0.0238
		1000	0.0357
Char 1000	1000	900	0.01
		950	0.0172
		1000	0.0278

3.3.1 Effect of char preparation temperature on gasification reactivity

The Table 4 clearly shows that reactivity decreases with the increase in char preparation temperature. As for example, when char samples gasified at 950 ^{0}C in CO_2 partial pressure of 0.1 MPa, R values decrease from 0.0238 to 0.0172 min^{-1} as heat treatment temperature increases from 900 to 1000 ^{0}C. Such trend has been observed for all the experiments in the temperature range of 900 – 1000 ^{0}C.

Figure 1 clearly demonstrates that char gasification reactivity decreases with increasing char preparation temperature. This trend of decreasing reactivity with increasing pyrolysis temperature is well established in literature.

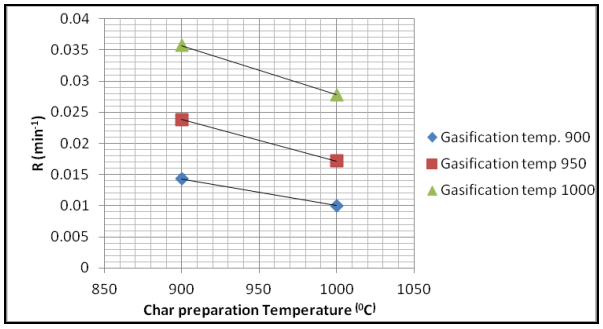

Figure 1: Variation of gasification reactivity with char preparation temperature.

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Van Heek and Miihlen [20], Khan [21], Fermoso et al [6], Naredi and Pisupati [14] and others [18] reported that gasification reactivity of char decreases with increasing heat treatment temperature. High heat treatment temperature removes heteroatoms which are considered to generate active sites on coal surfaces. Char deactivation with increasing pyrolysis temperature also happens due to the realignment of coal layer planes leading to graphite-like structure. It is also reported that catalytic metals such as Ca, K and Na lose their activity by sintering, formation of stable aluminosilicates or through vaporization [22] with the increasing heat treatment temperature. Moreover, surface area plays very important role in reactivity. Table 3 clearly shows that both N_2 and CO_2 surface areas decrease with increasing char preparation temperatures and decrease in reactivity with high heat treatment is also caused by decreasing surface area [18] which has been discussed in details later. Therefore, in the present study lower reactivity of high–temperature char is attributed to i) lower active sites available on coal surfaces due to the rearrangement of carbon structure, ii) lower available surface area and iii) lower catalytic effect.

3.3.2 Effect of gasification temperature on reactivity

Table 4 clearly indicates that CO_2 gasification reactivity increases with increasing gasification temperature. As for example, R value of char 900 increases from 0.0143 to 0.0357 min^{-1} when gasification temperature increases from 900 to 1000 ^{0}C at 0.1 MPa partial pressure of CO_2. Same trend has been noticed in case of char 1000 also.

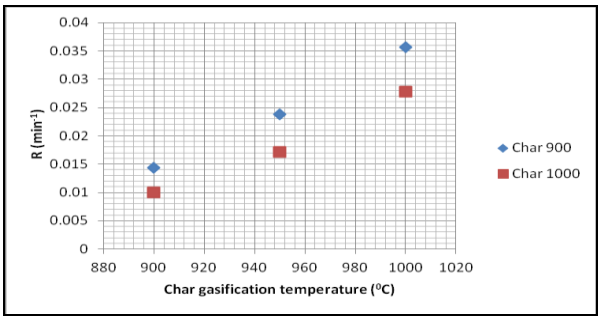

Figure 2: Variation of reactivity with gasification temperature.

This increase in gasification reactivity with temperature can be explained from the endothermic nature of C – CO_2 reaction and is agreeably consistent with the findings of various workers [23 – 24]. Figures 2 clearly illustrates that the reactivity increases with the increasing gasification temperature.

3.3.3 Effect of char surface area on gasification reactivity

In the present study, importance of pore structure of char has been studied from the influence of surface area on char gasification reactivity.

Coal contains random orientation of large number of pores ranging from micropores (pore diameter < 2 nm) to macropores (pore diameter > 50 nm). Both big (macro- and mesopores) and small (micropores) pores are important in coal gasification. Macro- and mesopores act as channels for reaching the reacting gas to the active sites in the micropores where gasification reaction takes place [25]. Product gas also diffuses out through the porous structure of solid.

Therefore, considering the role played by micro-, meso- and macropores in gasification reaction, in the present study, both N_2 and CO_2 surface areas of all the chars have been determined. N_2 surface area measures meso- and macropores, whereas CO_2 surface area gives a picture of microporous area. Values of N_2 surface area and CO_2 surface area of char samples prepared at two different temperatures, presented in Table 3 and reactivity indices, R of all the char samples gasified at different conditions, depicted in Table 4, show the effect of surface area on gasification reactivity. These results clearly indicate that CO_2 gasification reactivity decreases with decreasing surface area of char samples at different experimental conditions irrespective of gasification temperature. All the results establish the proportionality of CO_2 gasification reactivity of chars with their surface area values.

These results are in accord with the findings of other researchers reported in literature [6, 18, 26]. Wu et al [18] concluded that surface area is one of the main factors which affect the gasification reactivity of carbonaceous materials. If the N_2 surface area is less, gasification reactivity is lower. Chin et al [27] and Adschiri et al [28] also found the proportionality between reaction rate and surface area. Ng et al [9] reported good correlation between reactivity and surface area of Canadian coal derived chars both from N_2 and CO_2 adsorption isotherms. Fermoso et al [6] also reported a linear correlation between reactivity indices and micropore surface areas. Arenillas et al.[29] also reported decrease in reactivity of char samples prepared at different temperatures with the decrease in surface area and porosity. Sınagˇ et al [26] found proportionality between CO_2 gasification reactivity of lignite char and their specific surface area.. Feng and Bhatia [25] reported the participation of pores of all ranges (micro-, meso- and macropores) in CO_2 gasification.

4. CONCLUSIONS

From the above discussion it may be concluded that in the present investigation i) gasification reactivity decreases with the increasing char preparation temperature due to the structural rearrangement at higher pyrolysis temperature. ii) Gasification reactivity increases with increasing gasification temperature. iii) It has been observed for the present investigation that the surface area (both N_2 and CO_2) plays important role in gasification reaction, reactivity increases with increasing both N_2 and CO_2 surface areas.

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These gasification results for the high ash Indian coals may be utilized for designing and selecting suitable gasifier in Indian context.

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NOMENCLATURE

Symbol		
R	Reactivity index	(min^{-1})
$\tau_{0.5}$	Time required to achieve 50% conversion	(min)

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