

Reactivity and kinetic study of high ash Indian coal and biomass blends

In the present study, char samples of two biomasses and their blends with high ash Indian coal were prepared at 900°C and then gasified in the temperature range of 850°C to 1000°C in CO₂ atmosphere using thermogravimetric analyzer (TGA). It is observed that the char gasification reactivity of coal-biomass blend is lesser in comparison with the gasification reactivity of pure biomass. The effect of gasification temperature on reactivity as well as comparison between gasification of two pure biomasses and their blends with coal have been studied. The activation energy of biomass and their blends has also been discussed in this paper. The gasification reactivity and kinetic data developed from thermogravimetric analysis study may be useful for modelling and designing of suitable gasifier as per the available feedstocks.

Key words: CO₂ gasification reactivity; kinetic; high ash India coal; biomass.

1. Introduction

Energy is one of the major inputs for the economic development of any country. In case of the developing countries, the energy sector assumes a critical importance in view of the ever-increasing energy needs and requires huge investments to meet them. The reserves for oil, natural gas and coal in India as on 31.03.14 are 762.74 million tonnes (mt), 1427.15 billion cubic meters (BCM), 301.05 billion tonnes, respectively (Energy Statistics Report, 2015).

Presently fossil fuels are depleting at a very fast rate due to their increasing demand. Their utilizations through conventional processes affect environment in the forms of NO_x, SO_x and greenhouse gases (GHG) which result into environmental pollution and global warming. So, there is a renewed interest on innovative ways to convert the existing reserves with improved technologies that may lead to a lower

impact on environment and gasification is one of the options to this problem. Gasification is defined as the reaction of solid fuels with air, oxygen, steam, carbon dioxide, or a mixture of these gases at a temperature exceeding 700°C, to yield a gaseous product suitable for use either as a source of energy or as a raw material for the synthesis of chemicals, liquid fuels or other gaseous fuels (Collet, 2006).

It is true that Indian coal suffers from high ash content and hampers smooth functioning of the gasifier causing problems such as agglomeration, clinkering, tar formation etc. (Datta et al, 2015). So, for making coal available for a longer period of time and solving operational problems in gasifier, biomass can be mixed with coal or lignite in different proportions (Filomena et al, 2003). Throughout Indian landmass there is a production of 500 mt of biomass every year, out of which 120 to 150 mt is surplus. This surplus amount of biomass can be used for energy production which has a potential of producing 18,000 MW of electricity (MNRE report). So, the blending of biomass with coal in different proportions and using it in gasifier (co-gasification) is a sustainable mode of energy generation which can help to cope up with rising energy demand as well as lower down GHG emissions.

Co-gasification is meant to utilize coal more efficiently meeting stringent environment controlled parameters. It is an important clean coal technology (CCT) which when coupled with carbon capture and sequestration (CCS) is capable to emerge as ultimate zero emission technology. In spite of having such a huge potential, neither this energy source has been utilized properly nor has proper research been done in this field. There is no systematic data available for the design of suitable gasifiers for the generation of power through this source. Biomass has higher volatile matter and reactivity as well as lower ash and sulphur content than coal. Therefore, blending high ash Indian coal with biomass and wastes could be attractive from economical, environmental and social points of view in order to make use of possible synergistic effects via the production of fuel gas (Pan et al, 2000). Biomass and coal are considered as potential feedstocks for the supply of syngas (CO and H₂) used in the synthesis of

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liquid fuels by gasification. It has the advantage that it yields higher energy syngas, reduced emissions, especially hazardous pollutants, lower gross power output, but higher thermal efficiency. This effect is due to coal and biomass sharing synergistic relationship when used together. It would be highly beneficial to take existing gasification plants that use coal as fuel, IGCC plants in particular, and supplement them with biomass feedstock. In areas especially where lots of biomass waste is produced, this becomes a good economic endeavour, considering the close proximity of supply and the cheap costs (Henry et al, 2011).

The objective of the present work is to investigate the CO₂ gasification kinetics and reactivity of chars prepared from two different types of biomasses (press mud and rice husk) and their blends with high ash Indian coal (10% biomass and 90% coal). Each char sample was prepared at 900°C. The chars so obtained were gasified at 850°C, 900°C, 950°C and 1000°C and there gasification reactivity and kinetics have been studied with the help of TGA in CO₂ atmosphere. The data obtained through this experimental study can be used for mathematical modelling so as to design and develop gasifier with higher efficiency according to the raw material that will be used as a feedstock in it.

2. Experimentation

2.1 SELECTION OF COAL AND BIOMASS

In the present study a coal sample and two biomass samples have been selected. The selected coal sample has high ash content. The biomass selected here is press-mud and rice husk. Tables 1 and 2 show the proximate and ultimate analyses of the samples. These tests were conducted following Indian Standard IS:1350 series (Saha et al, 2013; Gangavatib et al, 2005).

2.2 CHAR PREPARATION

The char samples of pure biomass and desired blends have been prepared in thermogravimetric analyser (Netzsch STA 449 F3 Jupiter) at 900°C by keeping the sample in nitrogen environment where the flow rate of nitrogen was

kept constant at 100 ml/min. In this process, initially 50mg sample (pure or blends) was taken in alumina crucible and temperature of the furnace was increased from room temperature to the desired temperature i.e. 900°C at a steady rate of 10°C/min. At this temperature the sample was kept for a period of 1 hour so as to complete the removal of volatile matter and thus char was formed.

2.3 SURFACE AREA ANALYSIS

Surface area can be measured by two methods: N₂ adsorption method using BET (Brunauer Emmett Teller) equation (N₂ surface area) and CO₂ adsorption method using DR (Dubinin-Radushkevich) equation (CO₂ surface area). In the present study, both types of surface areas were found out with the help of surface area analyser (Tristar 3000, Micromeritics, USA). Before analysis in both the cases, the surfaces of the samples were cleaned by flowing nitrogen through the sample at 150°C for 3 hours.

For BET surface area, 99.999% pure N₂ gas was used as the adsorbate gas and the isotherm was measured at boiling point of nitrogen i.e. -196°C which was maintained by the help of liquid nitrogen. Isotherm was drawn in the relative pressure range of 0.05 to 0.3. Using these points a straight line was drawn where the correlation coefficient of all the measurements were greater than 0.99. From the slope and intercept of this straight line the surface area of the sample was calculated.

For CO₂ surface area, 99.999% pure CO₂ gas was used as the adsorbate gas and the isotherm was measured at 0°C which was maintained by the help of ice-water bath. Isotherm was drawn in the relative pressure range of 0.0001 to 0.3 and surface area was calculated as mentioned above. The N₂ and CO₂ surface area of the given samples are presented in Table 3.

2.4. THERMOGRAVIMETRIC ANALYSIS (TGA)

Gasification experiments were carried out in CO₂ atmosphere using isothermal thermogravimetric analysis (TGA) process. It was carried out in Netzsch STA 449 F3 Jupiter thermogravimetric analyser. TGA was used due to its simplicity and accuracy (Saha et al, 2012; Irfan et al, 2011; Fermose et al, 2010). The instrument was calibrated and its repeatability and accuracy was checked taking

TABLE 1: PROXIMATE ANALYSIS OF COAL AND BIOMASS SAMPLES

Sample	Moisture (M, weight %)	Volatile matter (VM, weight %)	Ash (A, weight %)	Fixed carbon (FC, weight %)
Coal	6.5	24.5	41.3	27.7
Rice husk	9.1	64.7	12.6	15.7
Press mud	10.67	57.12	19.25	12.96

TABLE 2: ULTIMATE ANALYSIS ON DRY ASH FREE (DAF) BASIS OF COAL AND BIOMASS SAMPLES

Sample	Carbon (C, weight %)	Hydrogen (H, weight %)	Oxygen (O, weight %) (by difference)	Nitrogen (N, weight %)	Sulphur (S, weight %)
Coal	71.17	5.42	20.71	1.65	1.05
Rice husk	45.20	5.80	47.60	1.02	0.21
Press mud	41.30	5	24.90	1.10	2.80

TABLE 3: SURFACE AREA OF COAL, BIOMASS AND CHAR SAMPLES

Sample	N ₂ surface area (BET) (in m ² /g)	CO ₂ surface area (DR) (in m ² /g)
Coal	16.92	103.60
Rice husk	1.30	100.07
Press mud	1.58	60.55
Coal (char at 900°C)	24.67	246.38
Rice husk (char at 900°C)	384.04	435.05
Press mud (char at 900°C)	235.52	348.47

calcium oxalate as the reference sample. It has S-type thermocouple fitted inside it which measures reaction temperature with accuracy of $\pm 1^{\circ}\text{C}$ temperature. Blank runs were performed under the similar conditions of gasification experiments and each gasification experiment was corrected with the blank run to minimise the buoyancy effect. In the present study, 99.999% pure CO₂ gas was used as the gasifying agent. The sample was first passed through the char making procedure mentioned in 2.2 and then this char was gasified. The gasification experiments were conducted at four different temperatures such as 850°C, 900°C, 950°C and 1000°C in CO₂ atmosphere where the flow rate was maintained at 100 ml/min. The data obtained from these reactions were analysed further for reactivity and kinetic study.

3. Results and discussion

3.1. COMPARISON OF N₂ AND CO₂ SURFACE AREA

From the surface area data given in Table 3 it can be clearly seen that CO₂ surface area of the samples are greater

than the N₂ surface area of the samples. This type of result is observed due to activated diffusion phenomenon. As the N₂ surface areas of samples were measured at -196°C , at such low temperature the adsorbate gas could not access the small microporosity of coal and there by less surface area was recorded. Where as in the case of CO₂ surface area, the measurement was carried at 0°C and the adsorbate gas had access to finest micropore volumes and micropore surface area of the sample and as a result the surface area is greater than the other case. This phenomenon has been also observed, recorded and published by Saha et al (2013), (Mahajan, 1991; Ng et al 1988; Chan et al 1999; Parkash and Chakrabarty, 1986).

3.2 CO-GASIFICATION REACTIVITY STUDY

In the present study, two types of samples were analysed with the help of TGA for the reactivity and kinetic study. The first was pure sample of biomass i.e. rice husk and press mud, where as the second type was a 10% blend of these biomass with selected coal. The reactivity and kinetic data for all the samples are given in Table 4. In reactivity analysis, basically the reactivity index (R) of the sample at a given temperature was determined. The greater the reactivity index, greater is the reactivity of a substance. The reactivity index can be defined as

$$R = 0.5/T_{1/2} \text{ min}^{-1}$$

Where

R = Reactivity index and its unit is min^{-1} .

$T_{1/2}$ = Time required to achieve 50% conversion.

TABLE 4: REACTIVITY AND KINETIC DATA OF PURE BIOMASS AND COAL-BIOMASS BLEND SAMPLES

Sample	Char preparation temperature (°C)	Gasification temperature (°C)	Half life period $T_{1/2}$ (min)	Reactivity R (min^{-1})	Rate constant (k)	Activation energy (KJ/mole)
Pure rice husk (RH)	900	850	94/93	0.0053	0.0022	204.67
		900	38	0.0132	0.0055	
		950	16.12/16.5	0.0310	0.0134	
		1000	8.19/8.2	0.0611	0.0288	
C90RH10	900	850	111.5	0.0045	0.0018	169.86
		900	43.8/43.5	0.0128	0.004	
		950	20.5	0.0253	0.0085	
		1000	11.4	0.0495	0.0151	
Pure press mud (PM)	900	850	27.4	0.0182	0.008	167.72
		900	10.2	0.0490	0.0232	
		950	4.39	0.1139	0.039	
		1000	3.56/3.4	0.1404	0.0699	
C90PM10	900	850	192	0.0026	0.001	221.81
		900	70	0.0071	0.003	
		950	25.6/25.5	0.0195	0.0082	
		1000	13.5	0.037	0.0159	

So, from the analysis of the experimental data the followings points were observed –

- i. Effect of gasification temperature on reactivity.
- ii. Comparison between reactivities of pure biomass to that of coal-biomass blends.

3.2.1 Effect of gasification temperature on reactivity

From the Table 4 it is found that the reactivity of the samples increases as the gasification temperature increases. As for example, gasification reactivity of pure rice husk increases from $0.005319 \text{ min}^{-1}$ to 0.06105 min^{-1} as the gasification temperature increases from 850°C to 1000°C . The same trend has been observed by all the other samples. This behaviour of the samples is explained from the endothermic nature of C-CO₂ reactions and this is consistent with the findings of various researchers (Ye et al, 1998; Everson et al, 2008). This can be more clearly understood by the Figs.1 and 2.

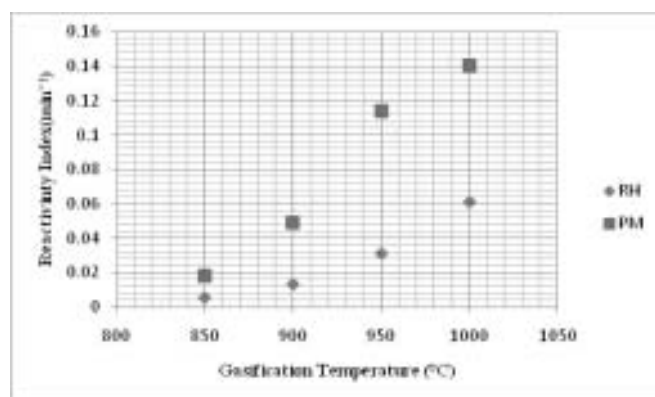


Fig.1 Reactivity index and gasification temperature of pure samples of rice husk and press mud

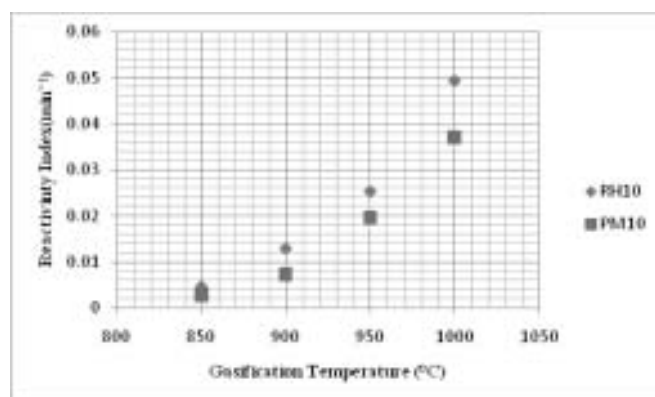


Fig.2 Reactivity index and gasification temperature of 10% blended samples of rice husk and press mud with coal

3.2.2. Comparison between reactivities of pure biomass to that of coal-biomass blends

During the comparison of the reactivity of pure biomass with each other it is found that reactivity of press mud is greater than the reactivity of pure rice husk. This can be seen

from the Fig.1, at all the gasifying temperatures the reactivity of the press mud is greater than that of rice husk. But in case of coal-biomass blend it is noticed that the reactivity of coal-rice husk blend is higher than that of the coal-press mud blend. This behaviour of the two types of blends can be clearly seen from the Fig.2. This interesting observation may be due to the catalytic effect of alkali and alkaline earth metal present in press mud ash. Press mud ash contains significant amount of Ca (21-30%) and K (2.5-4%) (Saleh-e-In et al, 2012). On the other hand, rice husk is a silica rich biomass containing 90-98% silica in its ash (Omatola and Onojah, 2009). But when press mud is blended with coal, its mineral matter reacts with the mineral matter of coal and catalytic activity is deactivated which results in to reduce coal-press mud blend reactivity.

3.3 CO-GASIFICATION KINETIC STUDY

Gasification kinetics are generally studied with some kinetic models and various reserachers have utilized mostly homogeneous model (HM), shrinking core model (SCM) and random pore model (RPM). Considering the simplicity and efficiency to describe experimental data, shrinking core model (SCM) has been utilized for the present investigation.

Shrinking core model has been described in details in elsewhere (Saha, PhD). Rate expression and its linearised form are $dx/dt = k_s (1 - x)^{2/3}$ and $1 - (1 - x)^{1/3} = k_s t$, respectively, if the reaction is chemically controlled. Here, x is the conversion and k_s is the rate constant. $1 - (1 - x)^{1/3}$ has been plotted against time, t for all the experiments. Rate constant, k_s , has been obtained by this model from the slope of the plot of $1 - (1 - x)^{1/3}$ versus t and depicted in Table 4.

When partial pressure of reactant remains constant during gasification reaction, rate constant, K_s , can be represented by Arrhenius equation as

$$K_s = A \exp (-E/RT)$$

where A , R , E and T are the pre-exponential factor (min^{-1}), universal gas constant ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$), activation energy (kJ/mol) and absolute temperature, respectively.

In the present investigation, $\ln k_s$ has been plotted against $1/T$ and activation energy, E has been derived from the slope of the straight line. E values obtained by shrinking core model have been depicted in Table 4.

This table clearly reflects that rate constant follows the same order as reactivity index. Activation energy of pure press mud is lower than that of pure rice husk. As the reactivity of coal-rice husk blend is higher than that of coal-press mud blend, activation energy of coal-rice husk co-gasification is lower than that of coal-press mud co-gasification.

4. Conclusions

CO₂ gasification reactivity and kinetics of pure rice husk, press mud and their blends with high ash Indian coal (10%

rice husk or press mud and 90 % coal) have been studied in the temperature range of 850^oC to 1000^oC using TGA. The kinetic study is carried out by using shrinking core model. It can be concluded that the reactivity increases with the increase in temperature in pure or blended form. The reactivity of coal-rice husk blend is more than the coal press mud blend. This is due to the presence of higher concentration of alkaline earth metal in press mud as compared to rice husk. Activation energy of pure press mud is lower than that of pure rice husk. But activation energy of coal-rice husk co-gasification is lower than that of coal-press mud co-gasification. The reactivity and kinetic data obtained from TGA can be utilized for modelling and design of suitable gasifier.

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