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CO_2 Gasification Reactivity and Kinetics Studies of Raw Coal, Super Clean Coal and Residual Coals obtained after Organo-refining (Solvent Extraction)

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Abstract

Gasification of coal is important for the generation of H_2. This is also good for Integrated Gasification Combined Cycle (IGCC) power generation which can be easily and relatively cheaply combined with CO2 concentration, storage and utilization systems. Solvent extraction of coal in organic solvents results in the production of super clean coal, mostly having less than 1% ash. The present paper reports the effect of solvent extraction (organo-refining) of Samla coal by using an industrial solvent, such as N-methyl-2-pyrrolidone (NMP), a coal derived solvent, such as, anthracene oil (AO) and a petroleum derived solvent, i.e. cetene (CE), on the CO_2 gasification of coal. Different solvents had different effects on the CO_2 gasification of super clean coal (SCC) or of residual coal (RC) obtained after the organo-refining of coals in different solvents. The CO_2 gasification reactivity of raw coal as well as of solvent treated coals was found to increase with increase in the temperature of the gasification from 900 to 1100°C. The treatment of coal with solvents has been found to affect the CO_2 gasification reactivity. Super clean coals obtained from the organo-refining in the cetene and NMP showed good CO_2 gasification reactivity. Residual coals obtained from the organo-refining in NMP and CE also showed good CO_2 gasification reactivity. Kinetics studies have revealed that the activation energies of CO_2 gasification reactions are reduced as a result of organo-refining of coal in different solvents. While organo-refining of coals in NMP and if possible in CE as well may help in obviating some of the major engineering problems in IGCC power generation, this integration may not be economically attractive at present. Future IGCC power generation may involve the use of CO_2 and O_2 as the gasifying medium.

Keywords: CO_2 gasification reactivity; organo-refining; NMP; anthracene oil; cetene; mineral matter; kinetics; IGCC power generation

1. Introduction

With declining reserves of oil and long-term rising prices (above US $ 30/barrel earlier), the dependence on coal as a major source of energy has increased. Direct use of coal leads to environmental pollution, including the emission of CO_2, a greenhouse gas. Gasification of coal is a clean coal technology. Gasification technology is an effective way to utilize the CO_2, a greenhouse gas, and obtain a cleaner fuel. Oxyfuel combustion of coal would produce a concentrated stream of CO_2 for use in the gasifier. In fact, CO_2 gasification would produce only one product: CO. Prins and Plasinki [1] have found that coal gasification was more effective than combustion for greener energy utilization, because the coal gasification reaction reduces 9% of the internal energy exchange. CO_2 may also be used to gasify coal and generate CO, which may be used to generate H_2 through a chemical shift reaction or microbial shift reaction, a cleaner fuel of the future, which may be used in fuel cells for power generation. Allothermic gasification reactors may be used for the CO_2 gasification of coal, where heat may be supplied by molten iron baths (of steel plants), solar energy, plasma reactors or by incineration of industrial or domestic waste or landfill gas etc.

Coal is currently a major fuel for power generation. About 39% of world power generation is based on coal. It is also used in steel plants, cement industries, and in some other industries to supply heat, byproduct coal tar chemicals, fertilizer etc. With declining reserves of oil and natural gas, it is envisaged that the incentives for refining coal, like crude oil, to covert the coal to an ultra low ash fuel having less than 1% ash or even to almost zero ash, would increase. Coal is more abundant than oil and gas. There are advantages of gasifying an ultra low ash super clean coal (U-SCC) [2], solvent extracted (or organo-refined) residual coals (RC) [3] or of original raw coal [4–6].

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2. Pros and cons of IGCC power generation and possible future role of CO_2 gasification and organo-refining

IGCC power generation and gasification of coal are one of the leading clean coal technologies, opening the way for utilizing coal without damaging the environment [7, 8]. Advantages of IGCC power generation technology are: higher efficiency (>45%), low water consumption, low emissions of NO_x, SO_x, CO_2, etc. generation of less residue, ability to use biomass, plastics, petcoke etc., prospects of polygeneration. Above all, its ability to be integrated with CO_2 concentration and storage at a lower cost. Next generation IGCC plants with CO_2 capture technology would be expected to have higher thermal efficiency and to keep costs down, as they may use CO_2 and O_2 instead of N_2 and O_2 for gasifying the coal. However, there are still problems in the process itself, which challenge its immediate commercial use either for IGCC power generation or for H_2 production for fuel cells in addition to this being a costly technology [9]. These include down time due to coal ash handling, problems due to coal slurry feeding, corrosion problems, gasifying problems, There are problems due to slag deposits, ceramic candle failure, fly ash deposition to mention a few etc. [10]. Moreover, there are problems of As, Se, cyanates in the wastewater [11]. Therefore the availability of gasifiers is a problem in IGCC based power plants besides, of course, the relative costs. Since coal is a contaminated organic mass, major problems are caused by the inorganic mineral matter i.e. ash. The use of U-SCC may obviate some of these problems, as the toxic mineral metals are removed or reduced through this process [8, 12, 13]. Similarly, the use of RCs may boost gasifier performance by enhancing the reactivities. The use of U-SCC for gasification would be free of several major engineering problems caused by the presence of ash in coal. Thus, this may increase the suitable clean feedstock for the IGCC power generation process, where its use may increase the availability of gasifiers in IGCC power generation without major engineering problems leading to down time, as is experienced at present due to the presence of ash in the coals. However, further studies in this direction are required.

Coal has a descendant in the form of biomass, which is a renewable (greener) resource. Most of the coal conversion technologies already developed can be readily adapted for use on biomass. This also includes the gasification of biomass for IGCC power generation.The use of about 15 % biomass in an IGCC power plant was tried. The residual coals may also be gasified along with biomass. Cogasification of lignite, biomass and petcoke in a bubbling fluidized bed has been studied by observing the synergism in the cogasification of lignite and biomass (Sharma, D.K., Ling, H and Gohla, M. Unpublished work). The effect of different gasifying atmospheres such as CO_2, steam, air, and air and steam was studied.

Gasification of U-SCC would go some way to solving the problems of hot gas clean up [14, 15] and catalyst recovery etc. Advanced IGCC systems would be developed based on the gasification of U-SCC at lower temperatures, preferably below 1,000–1,100°C. There is scope for adding catalysts to increase the gasification reactivity at low temperatures [2, 16, 17]. The low temperature catalytic gasification of hyper coal, an ultra low ash coal that may be almost ash free, and low sulfur coal has been reported [2, 18–21]. The authors have shown that hyper coal, an ashless coal, could be a potential hydrocarbon resource for H_2 and synthesis gas production at low temperature by catalytic steam gasification process [2]. The gasification characteristics of hyper coal were found to be four times better than those of raw coal when the K_2CO_3 catalyzed gasification was carried out to produce hydrogen and synthesis gas. Gersten and Zondlo [3] reported that the residual coal obtained after extraction with N-methyl-2-pyrrolidone (NMP) has higher CO_2 gasification reactivity than that of raw coal. The super clean coal obtained from organo-refining may also be used as a feedstock to obtain liquid fuels through Fischer Tropsch synthesis or oxo synthesis. However, it may be stated that the use of organo-refining technology may have the advantage from the environmental and efficiency point of view, but this may further increase the cost of IGCC power generation. Unless the cost of organo-refining is brought down or oil and gas reserves reduce to a trickle, this technology may not become economically attractive. Studies in this direction were extended by enhancing the NMP extraction of coals by using catalytic amounts of ethylenediamine in NMP [22, 23].

Irfan et al. [24] reviewed the literature on the CO_2 gasification of coal, where CO_2has been used as a diluent. These authors reported the effect of different parameters including kinetics studies on the CO_2 gasification of coal. Huo et al. [25] reported that the CO_2 gasification reactivity of biomass char was higher than that of coke and coal char. Pore diffusion was also found to play a role. Kandasamy and Gokalp [26] recently reported the effect of the char generation method on steam, CO_2 and blended mixture gasification of high ash Turkish coals using TGA apparatus.

Yang et al. [27] studied the CO_2 gasification reactivity of high ash Nanlong coal (39.06% ash) and reported that gasification reactivity increased with the increase in gasification temperature. Particle size had no effect on the reactivity. The activation energy of CO_2 gasification was found to be 137 kJ/mol and with O_2/H_2O gasifications it was 81 kJ/mol. The CO_2 gasification reactivity was found to be lower than that in O_2, H_2O atmosphere. The carbon conversion, cold gas efficiency and product heating value also increased with the increase in gasification temperature. The ash content was found to affect gasification reactivity and the catalytic effect of coal mineral matter in the gasification was observed when using acid washed coals for the gasification. Kopyscinski et al. [28] reported the K_2CO_3 catalyzed CO_2 gasification of ash free coal.

In the present work, the aim was to study the CO_2 gasification of Samla coal, a low sulfur bituminous coal, (13.4% ash content), up to 1100°C in thermogravimetric analysis (TGA) apparatus. Several researchers have used TGA for studies relating to the gasification of coals [25, 26, 28–30].

Table 1: Analysis of Samla coal

Proximate Analysis (% air dried basis)	
Moisture	1.5
Ash	13.4
Volatile Matter	36.5
Fixed carbon	48.6
Ultimate Analysis (% on dry mineral matter free basis)	
C	73.8
H	5.2
N	2.2
S	0.9
O (by difference)	17.9
Atomic H/C ratio	0.84
Atomic O/C ratio	0.18
Vitrinite contents, %	24.3
Liptinite contents, %	51.9
Innertinite contents, %	23.8

Samla coal was also subjected to solvent extraction, i.e., organo-refining using N-methyl-2-pyrrolidone (NMP) an industrial solvent used by petroleum, polymer and other industries, anthracene oil (AO) (a coal derived solvent) and cetene (CE) a petroleum/ coal-derived solvent) at ambient pressure conditions under milder conditions for 2 to 24 h [12]. Solvent action during organo-refining would disrupt the active surface area of coal and would change the chemical composition of coal. Therefore, it was of interest to study the effect of organo-refining on the gasification of coal. The super clean coal (SCC) obtained and the residual coal (RC) so obtained after organo-refining were used for the studies on gasification. Kinetic studies were carried out under isothermal as well as nonisothermal conditions. Kinetic studies would help in design, operation and trouble shooting in coal gasification process plants and may help improve the availability of large scale coal gasifiers. In fact, as mentioned above, next generation IGCC plants may have turbine derived CO_2 and O_2 as the gasifying medium for improving the efficiency and for reducing the unburnt carbon (char). Therefore studies relating to CO_2 gasification are important. The effect of organo-refining of coal by different solvents on the CO_2 gasification of coal was investigated by studying the kinetics and reactivity of super clean coals (solvent extracts) and of the residual coals obtained after the organo-refining of coals.

3. Experimental

Samla coal, a noncoking bituminous coal was procured from the Raniganj coal fields. The coal was dried and crushed to -60 to $+120$ BSS mesh size. The analysis of the coal is shown in Table 1.

The coal (5 g) was put in a round bottomed flask fitted with a water cooled reflux condenser containing about 85 ml of the solvent, i.e., NMP /AO or CE. The mixture was refluxed for 2 h at the boiling point of the solvent under ambient pressure conditions and cooled and filtered to recover the residual by washing with a solvent. The super clean coal was recovered after concentrating the filterate by distillation and then precipitating the same by adding anti-solvents, i.e., petroleum ether or water etc. [12].

The TGA studies of dried raw coal or RC or SCC were carried out using a Perkin Elmer TGA instrument, by using 8–10 mg of sample in a flowing CO_2 atmosphere at a flow rate of 30 ml/min by using 40 K/min as the heating rate. The residual coal and the used mostly had a particle size of -60 to $+120$ BSS mesh size (about 75%) and -120 to $+200$ size BSS mesh size (about 25%). The experiments were conducted under both isothermal and nonisothermal conditions separately.

The calorific values were recorded using a Bomb calorimeter. The ^{1}HNMR and ^{13}CNMR spectra of SCCs were recorded using DMSO (d6) and pyridine (d5) as solvents, using TMS as the internal standard and using the Jeol JNM FX-100 (100 MHz) spectrometer.

GPC was performed by using polystyrene as standards, using a Waters ALC-201 HPLC instrument.

4. Results and Discussion

As part of the larger program of the authors' research group on studies relating to organo-refining of coal, different Indian coals and lignites were subjected to solvent extraction using the following solvents: hexane, heptane, toluene, methanol, ethanol, butanol, glycerol, acetone, chloroform, ethyl acetate, decalin, tetralin, dodecanol, cetene, cetanol, creosote oil, acetic acid, THF, dioxane, morpholine, ethylenediamine (EDA), monoethanolamine, diethanolamine, triethanolamine, DMSO, aniline, triethylamine, dimethylformamide, N-methyl-2-pyrrolidone (NMP), NMP containing small amount of EDA, NMP-CS_2, sulfolane, anthracene oil (AO), different long chain olefins, cetene (CE), liquid paraffin (LP), pyridine, quinoline, furfural, carbazole, phenanthrene, β-naphthol etc. under reflux conditions at atmospheric pressure [12, 22, 31, 32].

The extraction of Samla coal in the solvents such as NMP (15.2%), AO (11%) and CE (35%) was found after 2 h and the extraction was found to give premium grade coal, i.e., super clean coal mostly having less than 1% ash, i.e., about 0.38% in the NMP extract, i.e., / SCC-NMP (Table 2). The extraction yield was found to increase beyond 20–30% after 24 h extraction time [12]. The super clean coal may be used for premium purposes, including liquefaction or gasification. About 95% of the solvent may be recovered and recycled. The organo-refining process may enable the production of almost zero ash premium grade aromatic- heterocyclic comounds containing fuel. The process may become more interesting in future from an economic viewpoint when oil reserves become much lower.

Studies have been directed towards the kinetics of CO_2 gasification of raw coal, RC and SCC. CO_2 gasification reactions are slower than steam gasification reactions [27, 33]. The water forming H-bonds are weaker than the double bonds present in the CO_2 molecules. The following reactions may take place during the gasification of coal and the ΔH^o_{298} [34].

$$C_{\sim 90-120-240}H_{\sim 6-9-20}O_xS_yN_z + O_2$$
$$+H_2O \xrightarrow{\Delta} C_nH_m + \text{other products}$$

Table 2: Elemental analysis (on % daf basis) and % ash analysis of the original/raw Samla Coal and its super clean coals (SCCs) and residual coals (RCs)

	C, %	H, %	N, %	S, %	O (by difference)	Ash, %	Atomic C/H	Atomic C/O
Original raw / Samla Coal	71.9	3.9	2.2	0.50	21.54	13.4	1.54	7.90
NMP Extract (SCC-NMP)	70.4	4.3	3.0	0.05	22.25	0.38	1.36	4.17
NMP Extracted residue(RC-NMP)	80.4	6.0	1.8	0.40	11.40	18.27	1.21	9.40
AO Extract(SCC-AO)	77.4	4.6	1.2	0.05	16.75	0.75	1.39	6.16
AO Extracted residue (RC-AO)	77.1	3.5	2.7	0.40	16.30	17.99	1.81	6.30
CE Extract (SCC-CE)	74.1	4.2	0.80	0.03	20.87	0.84	1.47	4.73
CE Extract Residue(RC-CE)	75.2	3.9	3.60	0.40	16.90	22.44	1.60	5.93

$$C_nH_m \xrightarrow{\Delta} nC + mH$$

$$C + \frac{1}{2}O_2 \rightarrow CO \qquad \Delta H = +202.4\,kJ/mol$$

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -405.9\,kJ/mol$$

$$C + CO_2 \rightarrow 2CO \qquad \Delta H = +159.7\,kJ/mol$$

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H = +118.9\,kJ/mol$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H = -40.9\,kJ/mol$$

$$C + 2H_2 \rightarrow 2CH_4 \qquad \Delta H = -87.4\,kJ/mol$$

Since the CO_2 gasification reaction is a slow reaction, this could be a rate controlling reaction in the gasification of coal. Earlier studies of the authors' research group have described the catalyzed and non-catalyzed gasification of coals and chars [4–6, 17]. Coal is not a simple carbon but consists of macromolecules having $C_{\sim 90-120-240}H_{\sim 6-9-20}O_xN_yS_z$ (tentatively) heterogeneous polymers. These macromolecules contain 2-5 condensed ring polyaromatic ring structures along with naphthenic (hydroaromatic)-aliphatic-N-heterocyclic-O-heterocyclic-S-heterocyclic structural units, side chains, cross-linkages etc. Gasification of such macromolecules is a very complex phenomenon. In earlier papers the kinetics of steam gasification, boosting the gasification reactivity by organo-refining and steam pyrolysis and modeling of gasification reactions were reported [4–6]. The effect of organo-refining (solvent extraction) and organo-refining followed by steam pyrolysis seems to have been reported for the first time by the research group of the author [4–6, 17].

In the present work, organo-refining of Samla coal was performed by using AO, NMP and CE as solvents. AO peptizes the coal and extracts the organic matter from coal by following the like-dissolves-like principle, whereas NMP is an amphoteric solvent – this acts both as electron donor as well as electron acceptor having a lone pair of electrons. This disrupts intermolecular forces in coal. During NMP extraction the columbic forces of interaction between coal and NMP are involved. CE is a reactive solvent that alkylates (i.e. cetylates) the coal, (inorganic mineral matter of coal acts as catalysts), reducing the stacking between the adjacent polyaromatic lamellas resulting in enhanced extraction [12].

The molecular weights of AO, NMP and CE extracts were found to be 68453, 66908 and 57353 g/mol respectively, as determined by the GPC studies [12]. The aromaticity $f_a(C)$ i.e. carbon aromaticity of AO, NMP and CE extracts were observed to be 56.3, 61.4%, 57.3% and 50.4% respectively (Table 3 and 4) [12].

The detailed GPC, FTIR, UV, ^{1}HNMR, ^{13}CNMR spectral studies of these extracts and the fractions obtained by the Saturate-Aromatics-Resins-Asphaltenes-Asphaltols (SARA) separations, helped reveal the organic chemical structure of coal [12] after characterization of these extracts and putting the information together to construct the tentative structures of extracts and of coal therefrom. The salient features of the characterization of SCCs obtained after the extraction of Samla coal with NMP mainly are summarized herein. The proportion of carbon and hydrogen is shown in Table 3. The notable features are the types of carbon atoms in coal which could react with CO_2 during gasification. Most reactive would be aliphatic carbons, i.e., C_{al} which were at their maximum in the CE extract, i.e., SCC-CE (49.6% as expected (due to cetylation of coal reactions), followed by the AO extract, i.e., SCC-AO (43.7%) and by SCC-NMP (38.6%). Quaternary carbons (C_q) would be mostly the last to react and these were at their maximum in SCC-NMP (35%) followed by SCC-AO (34%) and at their minimum in SCC-CE (26%), as expected. Aromatic carbons attached to the hydrogen, i.e., C_H were at their minimum in SCC-AO and maximum in SCC-CE, as expected. The details of the characterization are also given later on in the text, to draw inferences on their possible relations with the reactivity of coals or solvent treated coals.

The calorific values of the Samla coal, its SCCs and RCs were studied. They were found to be at their maximum in SCC-CE (9125 kcal/kg), as expected, due to the possible reaction of coal with some of the cetene molecules resulting in the cetylation of coal. The calorific value of SCC-NMP was the lowest (7906 kcal/kg) amongst SCCs. Raw Samla coal had the calorific value (CV) of 6393 kcal/kg . RCs had a lower CV than raw coal, here RC-AO had the maximum CV (5722 kcal/kg) and RC-NMP had the minimum (5110 kcal/kg) and RC-CE had the intermediate value of 5613 kcal/kg. Table 4 shows the % C, H, N, S, O, ash contents in raw Samla coal and its extracts and residual coals in different solvents such as NMP, AO and CE. SCCs were found to contain almost zero mineral content, as low as 0.42% (0.38% ash) in SCC-NMP, 0.83% (0.75% ash) in SCC-AO and 0.93% (0.84%) in SCC-CE (Table 2). However, RCs as expected contained higher ash content than the raw

Table 3: Proportion of Carbons and Hydrogens from ^{13}CNMR and ^{1}H NMR Spectra of Coal Extracts in DMSO (d_6) and Pyridine (d_5)

Sample		$F_a(C)= C_{Ar}/C$	$F_a(C)^*=$ FC/C, %	$F_a(H)= H_{Ar}/H$	C_q/C_{Ar}	C_H/C_{Ar}	C_{OH}/C_{Ar}	H_α/H_{Al}	H_β/H_{Al}	H_r/H_{Al}	H_{OH}/H_{Al}	H_F/H_{Al}
NMP Extract (SCC-NMP)	Samla Coal	0.614	0.50	0.240	0.350	0.470	0.180	0.123	0.130	0.000	0.382	0.125
AO Extract (SCC-AO)	Samla Coal	0.563	0.74	0.301	0.340	0.460	0.200	0.144	0.067	0.042	0.380	0.066
CE Extract (SCC-CE)	Samla Coal	0.504	1.02	0.212	0.260	0.620	0.120	0.104	0.189	0.136	0.254	0.105

C—total carbon, C_{Ar}—aromatic carbon, C_H—hydrogen attached to aromatic carbon, C_q—quaternary carbon, C_{OH}—hydroxyl group attached to carbon, H—total hydrogen, H_{Ar}—aromatic hydrogen, H_α—hydrogen α—to aromatic ring, H_β—hydrogen β—to aromatic ring, H_r—hydrogen and onwards to aromatic ring, H_{OH}—phenolic hydrogen, H_F—hydrogen present in the bridge carbon, * F_a(C) calculated as reported by van Krevelen on the basis of data described in chapter 6 section 3.2

Table 4: Proportion of Carbons and Hydrogens from ^{13}CNMR and ^{1}H NMR Spectra of Coal Extracts in DMSO (d_6) and Pyridine (d_5)

Sample		Percentage Carbon		Percentage Hydrogen						
		(C_{Ar}/C)	(C_{Al}/C)	H_{Ar}/H	H_{Al}/H	H_{Ar}/C_{Ar}	H_{Al}/C_{Al}	H_{OH}/C_{OH}	H_β/H_α	H_r/H_α
NMP Extract (SCC-NMP)	Samla Coal	61.4	38.6	24.0	76.0	0.391	1.967	2.122	1.057	0.000
AO Extract (SCC-AO)	Samla Coal	56.43	43.7	30.1	69.9	0.535	1.599	1.90	0.465	0.292
CE Extract (SCC-CE)	Samla Coal	50.4	49.6	21.2	78.8	0.520	1.589	2.12	1.82	1.308

C—total carbon, C_{Ar}—aromatic carbon, C_{Al}—aliphatic carbon, C_q—quaternary carbon, C_{OH}—hydroxyl group attached to carbon, H—total hydrogen, H_{Ar}—aromatic hydrogen, H_α—hydrogen α—to aromatic ring, H_β—hydrogen β—to aromatic ring, H_r—hydrogen and onwards to aromatic ring, H_{OH}—phenolic hydrogen, H_{Al}—aliphatic hydrogen

Samla coal (OSC).

5. Kinetic studies of CO_2 gasification

Kinetic studies of steam as well as CO_2 gasification of coals and chars have been studied by several researchers in the past [35–44]. There is hardly any consensus on the order of the reaction or on activation energies. Most of the research work was also performed under high pressure. Several researchers assumed the gasification reaction to be a first order reaction for the simplicity of studies. Here the CO_2 gasification of coal is studied under ambient pressure conditions.

5.1. Isothermal Kinetic Studies

The following simple equation was assumed:

$$\text{Coal} + CO_2 \rightarrow \text{Ash} + CO$$

$$\frac{dx}{dt} = k\left(1 - \frac{x}{x_e}\right)$$

where: x—fractional weight loss at a time 't', x_e—equilibrium value of x, k—rate constant, values of x and x_e were taken from the TGA graphs [12].

The activation energy of CO_2 gasification of original or raw Samla coal (OSC) was found to be 103.97 kJ/mol. The activation energy (AE) of CO_2 gasification of NMP extract, i.e., of the super clean coal (SCC) or SCC-NMP and the residual coal obtained after NMP extraction (RC-NMP) were found to be 25.5 and 105.8 kJ/mol respectively. The SCC-NMP and RC-NMP samples were found to be powdery and free flowing, reactive and thus were fit for fluidized bed gasification or entrained bed gasification.

These studies showed that the CO_2 gasification reaction was mostly diffusion controlled. The calculated activation energies of original raw Samla coal, NMP extract (SCC-NMP) and RC-NMP of CO_2 gasification was higher than those of pyrolysis and combustion reactions of Samla coal [12]. Some of the pyrolysis and combustion reactions also take place during the gasification of coals in general. It was reported by Osafune and Marsh [44] that the activation energy [AE] of CO_2 gasification of char was in the 174.1 to 194.1 kJ/mol range. However, Shufen and Ruizberg [45] reported the same to be 148.5 kJ/mol. Ye et al. [46] reported AE of CO_2 gasification of coal as 90.8 kJ/mol. Kajitani et al. [39] reported the order of gasification as 0.73, 0.86 or 0.49 etc. and AE as 163. kJ/mol. The reaction was reported to be diffusion controlled. AE for the CO_2 gasification of petroleum coke was reported to be 196.6 kJ/mol [47].

Here, the values of AE found for the CO_2 gasification of raw coal and RC-NMP were found to be near those reported earlier by other researchers. It was also reported that gasification rates in TGA are same as in gasification reactors [33, 39]. AE for SCC-NMP was found to be low, which can be explained by the fact that SCC is the reactive organic component extracted from the coal.

5.2. Nonisothermal Kinetic Studies

TGA provides a semiquantitative understanding of gasification reactions under well controlled conditions. The use of fine coal particles and small sample sizes avoids the phenomenon related to transport problems to the minimum possible [35]. Thus, the validity of kinetic analysis of primary CO_2 gasification and devolatilization reactions is greatly increased. The advantages of investigating reaction kinetics in non-isothermal (i.e. dynamic) mode are as follows [48]: (I) considerably less experimental data are required than in the isothermal methods; (II) kinetics can be studied over the entire temperature range in a continuous manner, (III) same sample is used throughout and it undergoes reaction in being raised to the temperature of interest, (e.g., above

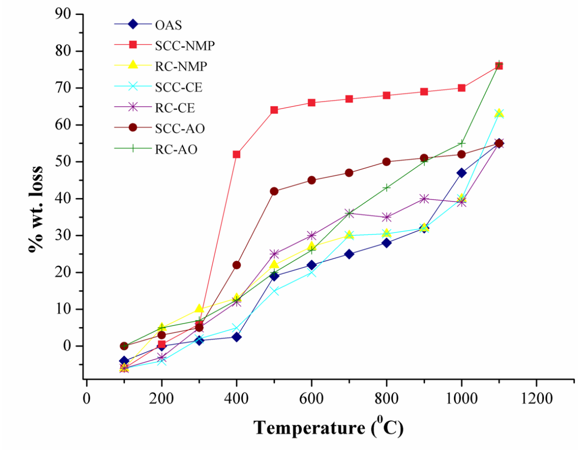

Figure 1: Thermograms of carbon dioxide gasification of raw Samla Coal, its super clean coals (SCCs) and residual coals (RCs)

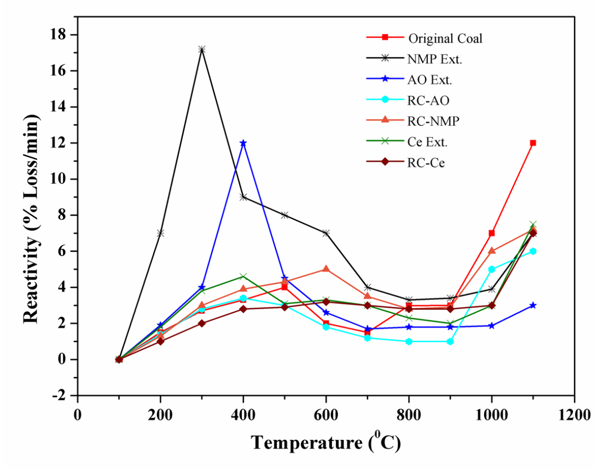

Figure 2: Differential thermogavimetric (DTG) analysis of the CO_2 gasification reactivities of raw Samla Coal, its super clean coals (SCCs) and residual coals (RCs)

600–800°C) for CO_2 gasification of coals, where the Bouduard reaction mostly takes place. Here, the Coats and Redfern kinetic model was used for the nonisothermal kinetic analysis of CO_2 gasification of coal (under ambient pressure conditions) [49–52]. Fig. 1 shows the thermograms of CO_2 gasification of raw Samla coal, SCCs and RCs.

6. CO_2 gasification reactivity of Samla coal and SCC and RC obtained after organo-refining at lower temperature through differential thermogravimetric (DTG) studies

Since the Bouduard reaction takes place mostly above 600°C, the DTG graphs showed reactivity peaks for the gasification reactions (Fig. 2) [12]. Table 5 shows the results of the CO_2 gasification reactivities of original Samla coal (OSC), the NMP extract of OSC, i.e., SCC in NMP (SCC-NMP), residual coal obtained after NMP extraction (RC-NMP), AO extract of OSC, i.e., SCC in AO (SCC-AO), residual coal obtained after AO-extraction (RC-AO), cetene extract of OSC, i.e., SCC in CE (SCC-CE) and the residual coal obtained after CE extraction (RC-CE). It can be seen that the CO_2 gasification reactivity peaks (% weight loss/min.) at lower temperatures, i.e., 600 and 800°C, are higher for SCC-NMP than for OSC. The same effect was observed for RC-NMP. In fact, SCC-CE and RC-CE also showed higher reactivities at lower temperature (600°C) than those of OSC. The order of reactivities (based on the reactivities (% weight loss/min.) at lower temperatures i.e., 600°C) was found to be as follows: SCC-NMP>RC-NMP>SCC-CE≥RC-CE>RC-AO≥OSC>SCC-AO (Table 5).

Table 5: Reactivities of Samla coal and products in CO_2 gasification at different temperatures

	Reactivities, % loss/min.			
	600°C	900°C	1000°C	1100°C
Orig. Samla Coal (OSC)	2.5	2.5	7	12
SCC-NMP (Ext)	7	2.5	5	6
RC-NMP	5	2.5	7	7.5
SCC-AO (Ext)	2	1.5	1.5	3
RC-AO	2.5	2.5	5	6
SCC-CE (Ext)	3.5	2.5	3.5	8
RC-CE	3.5	2.5	2.8	7

The reasons for this are discussed in detail later in this paper. SCCs also showed higher reactivities (min^{-1}) for CO_2 gasification at lower temperatures, except for SCC-AO (Table 5).

7. Effect of temperature on the CO_2 gasification of coal

Gasification reactivity depends upon the active surface area, pore structures, volatile matter, mineral matter and composition of coals. The action of different solvents may alter some of these factors and thus this may effect the gasification reactivity of coal.

It was found that the CO_2 gasification reactivity (% weight loss / min) of raw coal and the super clean coal (SCCs) by solvent extraction (organo-refining) and the residual (solvent treated) coals ((RCs) in different solvents increased with the increase in gasification temperature from 900°C to 1,100°C (Table 5). The CO_2 gasification reactivity was found to have the following trends at 1000°C: RC-NMP = OSC>SCC-NMP = RC-AO>SCC-CE>RC-CE>SCC-AO. This showed that RC-NMP had good reactivity at 1,000°C . Even SCC-NMP showed good reactivity at this temperature.

The CO_2 gasification reactivity of raw coal at 1,100°C (final temperature) was found to be at its maximum and more than that of solvent treated coals (Table 5). This may be due to the catalytic effect of the mineral matter (MM) present in the coal, as was also reported by Yang et al. recently [27]. Of the solvent treated coals, cetene (CE) treated coals, i.e., SCCs obtained from organo-refining in CE, i.e., SCC-CE as well as the residual coal obtained from the CE extraction, i.e., RC-CE showed good CO_2 gasification reactivity (% weight loss/min) at 1100°C (Table 5). This could be due to the cetylation of coals, which rendered the coals reactive by increasing the distance between the polyaromatic lamellas of coals. The extraction yield of Samla coal in CE was also good (35%).

RCs obtained from NMP extraction, i.e., RC-NMP also showed good CO_2 gasification reactivity at 1,100°C (Table 5). However, these had lower reactivity than raw coal at 1100°C. SCC obtained after NMP extraction of coal, i.e., the SCC-NMP coal, showed moderate reactivity at 1,100°C though this had shown good reactivity at a lower temperature, which may be attributed to the presence of high volatile matter contents of almost 65% in SCC-NMP (Table 5 and 6). SCC and RC obtained after AO extraction would lead to the reconstruction and reconfiguration of the coal structure after extraction, i.e., SCC-AO and RC-AO had the lowest CO_2 gasification reactivities ((% weight loss/min) at 1,100°C (Table 5). The trend of CO_2 gasification reactivity at 1,100°C was as follows: OSC>SCC-CE>RC-NMP>RC-CE>SCC-NMP = RC-AO>SCC-AO. In fact, AO extraction did not show good effects on the CO_2 gasification reactivity of coals. This showed that AO extraction had disrupted the structure or composition of coal in such a way that it renders coal less reactive at 1,100°C (Table 5), though this had shown good reactivity at a lower temperature. AO extraction results in the peptization of the coal structure and AO components get into coal to disrupt its coal structure after the reaction, which results in a reduction of its reactivity.

8. Reactivity of coals based on the half specific rates

Several researchers [26–29, 40] have shown that the gasification reactivity can be represented by the following formula:

$$R_{CO_2} = \frac{0.5}{\tau_{0.5}}(\text{min}^{-1})$$

where $\tau_{0.5}$ is the time for the 50% reaction of carbon.

Table 6 shows the results of R_{CO_2} of OSC, SCCs and RCs. The extraction of coal with different solvents such as NMP, AO and CE resulted in affecting the CO_2 gasification reactivity of treated Samla coal extracts as well as of residual coals. Table 6 shows the results of the values of the half reaction specific rate i.e., R_{CO_2} of the CO_2 gasification of raw coal and solvent treated coals in min^{-1} . The trend of the R_{CO_2} reactivities (min^{-1}) was as follows: SCC-NMP>SCC-CE>RC-CE>RC-AO>OSC>SCC-AO>RC-NMP. The cetene extraction was found to be a beneficial treatment for enhancing the R_{CO_2} of CO_2 gasification of coals, i.e., for the SCC-CE and RC-CE coals. The reason for this was explained earlier. SCC-NMP was found to show the maximum R_{CO_2} (Table 6), but RC-NMP showed moderate reactivity. RC-AO showed good R_{CO_2}, but SCC-AO showed poor R_{CO_2} (in min^{-1}) (Table 6). These results of CO_2 gasification reactivity did not match with those of the CO_2 gasification reactivity at 1100°C. Fan et al. [29] reported that R_{CO_2} can properly reflect the gasification reactivity of the early and middle periods, but not that at the final stage. Therefore, gasification at the final period (i.e., at 1100°C in the present case) is important for enhancing the coal utilization efficiency in a fixed bed gasifier and the R_{CO_2} is not suitable for describing the coal gasification in a fixed bed gasifier. Therefore, average gasification reactivity at the final temperature, i.e., here at 1100°C, should be considered for studying the effect of organo-refining in different solvents on the CO_2 gasification of coals.

The proportion of coal mineral matter may undergo change as the organic matter is removed from the coal by the solvents and this may also undergo change at different temperatures during the gasification, especially at higher temperatures. Removal of organic matter through organo-refining, swelling by the solvent and then disruption of the physical constitution of coal on solvent removal results in change in the coal constitution and its reactivity towards CO_2 by exposing more mineral matter. Volatile matter or residual volatile matter, i.e., the volatile matter (remaining) in the residual coal, was related to CO_2 gasification reactivity in several cases, but not in every case (Table 6). Raw coal, SCC-CE, RC-CE, RC-NMP and RC-AO had good CO_2 gasification reactivity. SCC showed poor CO_2 gasification reactivity. The role of catalysts in the gasification of coal was reported by several researchers in the past [3, 16, 17].

Different solvents had different effects on the CO_2 gasification of super clean coal (SCC) or of residual coal (RC) obtained after the solvent extraction, i.e., organo-refining of coals. The CO_2 gasification reactivity of raw coal as well as of solvent treated coals was found to increase with the increase in the temperature of the gasification from 900 to 1100°C. Mineral matter in the raw coal appeared to have a catalytic effect on the gasification reaction. Catalytic effects on the gasification of coal were studied earlier [16, 17]. Gersten and Zondlo [3] reported that NMP extraction leads to enhanced CO_2 gasification reactivity of the residual coals. The authors attributed this to the complex combination of catalytic and surface area effects.

The CO_2 gasification reactivities of CE treated coals were found to be good. RC obtained after organo-refining by NMP showed good CO_2 gasification reactivity at 1100°C. The effect of organo-refining by AO was not good as in the DTG (weight loss/min) studies (Fig. 2).

The present studies revealed that different solvents have different effects on CO_2 gasification reactivity and the kinetics of treated coals. SCCs obtained after organo-refining with NMP and CE were found to show good reactivity (Table 5 and 6). However, AO extraction was found to reduce the reactivity of SCC-AO. RC NMP, SCC-CE and RC-CE may be good feedstocks for the CO_2 gasification of coal at 1,100°C and for gasification for IGCC power generation. As described earlier, the organo-refining of coal results in the removal or reduction of toxic microconstituents of coals [12, 13].

9. Effect of organo-refining on activation energy and order of CO_2 gasification of coal

The Coats and Redfern kinetic model was used for kinetic studies of the CO_2 gasification of sample coal or pretreated

Table 6: The half specific rates of CO_2 gasification reactivities R_{CO_2} of original and pre-extracted coals

	VM or RVM	Temp., °C	Time = T/40, min	R_{CO_2}, min^{-1}	R_{CO_2}, min^{-1}
Orig. Samla Coal(OSC)	48	1010	25.25	0.0198	1.98×10^{-2}
SCC-NMP (Ext)	65	400	10.00	0.0500	5.00×10^{-2}
RC-NMP	42	1030	25.75	0.0194	1.94×10^{-2}
SCC-AO (Ext)	35	1020	25.50	0.0196	1.96×10^{-2}
RC-AO	36	1000	25.00	0.0200	2.00×10^{-2}
SCC-CE (Ext)	57	920	23.00	0.2170	2.17×10^{-2}
RC-CE	50	920	23.00	0.2170	2.17×10^{-2}

OSC—original Samla coal, RVM—volatile matter of residual coal, SCC-NMP—SCC obtained from NMP extraction, SCC-AO—SCC obtained from AO extraction, SCC-CE—SCC obtained from CE extraction,
RC-NMP—residual coal obtained after NMP extraction, RC-AO—residual coal obtained after AO extraction, RC-CE—residual coal obtained after CE extraction, Ext—extract i.e. super clean coal (SCC), VM—volatile matter, RVM—residual volatile matter, Temp—temperature

coals under non-isothermal conditions:

$n = 1$

$$\ln\left[\frac{-\ln(1-x)}{T^2}\right] = \ln\left[\left(\frac{AR}{aE}\right)\left(1-\frac{2RT}{E}\right)-\frac{E}{RT}\right]$$

$n \neq 1$

$$\ln\left[\frac{1-(1-x)^{1-n}}{(1-n)T^2}\right] = \ln\left[\left(\frac{AR}{aE}\right)\left(1-\frac{2RT}{E}\right)-\frac{E}{RT}\right]$$

where: x—fractional weight loss of coal in CO_2, T—temperature, A—frequency factor, R—gas constant, a—Heating rate, E—activation energy of the gasification reaction.

Table 7 shows the results of the nonisothermal kinetics analysis, i.e., AE, order and frequency factor for OSC, SCC-NMP, RC-NMP, SCC-AO, RC-AO, SCC-CE and RC-CE. These represent however a formal reaction parameter [53]. Therefore caution is required before drawing generalized conclusions.

CO_2 gasification of OSC was found to show AE as 115.1 kJ/mol and order as 4. This showed that the CO_2 gasification reaction is a multi-molecular complex reaction. Coal macromolecules ($C_{\sim90-120-240}H_{\sim6-9-20}O_xN_yS_z$) thermally degrade to give a very large number of degraded products, as the free radical reactive moieties which undergo chain reaction with CO_2 at temperatures above 600°C. AE calculated for OSC under isothermal conditions was found to be in the same range.

The CO_2 gasification of SCC-NMP also displayed a higher order as 4 and low AE of 20.9 kJ/mol. AE calculated from the isothermal kinetic studies for SCC-NMP was also low. This showed that SCC-NMP was reactive towards CO_2 gasification, probably because of the high volatile matter component which makes it reactive enough at lower temperatures. This was also supported by the earlier observation on the reactivity of SCC-NMP by the DTG (weight loss/min) (Fig. 2) and $\tau_{0.5}$ studies i,e., R_{CO2} (Table 5 and 6). The reactions were found to be mass transfer controlled.

RC-NMP showed the order of reaction as 1 and the value of AE was found to be 39.7 kJ/mol. This value was much less than that of OSC, showing that NMP extraction was a beneficial pretreatment for the CO_2 gasification of coal. The same observation was made earlier for the steam gasification reactions [4–6]. NMP extraction removes and leaches out organic matter from the coal. This results in creating more macro-, meso- and micro- pores in coal particles. Even cracks, channels, fissures, worm hole types pores etc. may be created as coal first swells (swelling index in NMP = 2.3) and then after leaching it may be like peeling onions and then the coal particle collapses after the solvents are removed. This was also observed from the SEM [12] and porosity studies on the organo-refining of coal using NMP containing small amount of EDA [22]. The solvent diffusion mechanism changes from relaxation to Fickian, as reported by the author and his coworkers [12, 31]. NMP beneficially disrupts the structure of coal by breaking the non-covalent hydrogen bondings, London forces, van der Waals forces, charge-transfer, $\pi-\pi$ interactions. The dipole moment (μ) of NMP is 4.04 to 4.72 and dielectric constant is 32, showing that NMP is a polar and potent solvent. In NMP, both electron deficient ($\delta+$) center over N and electron surplus center ($\delta-$) over carbonyl O exists therefore, it possesses simultaneously, both electron acceptor and electron donor property (acidic and basic). NMP is a well known aromatic extraction solvent for vacuum residue, kerosene, lubricating oil and crude oil etc. During extraction of coal by NMP, the Coulombic forces of interaction of NMP and coal molecules might be involved [12]. It is reported that in coal, the partially negative charge residing groups such as >C = 0 and –OH interact with partially positive charge residing groups such as R, NH, etc. During extraction the Coulombic forces develop between electron deficient N of NMP and anions (from acidic functional groups in coal macromolecules) and electron surplus -C=0 group of NMP with cations or cabanions of coals and the coal molecules from the three-dimensional cross-linked gel structure of coal [12]. The trapped molecules can, thus, be easily extracted. NMP extraction would leach out organic matter from coal particles, some like peeling off layers of onions and others like eating away of organic matter from coal particles by an all round random diffusional attack of solvent. This would expose the mineral matter (MM) present in coal. MM may act as catalysts and promoters for gasification reactions [3]. Thus, NMP extraction results in increasing the active surface area in coal, even generating nascent active sites for the reaction. Several cross-linked structural units become thermally unstable and thus rendered volatilizable

Table 7: Results of nonisothermal kinetic studies of original and pre-extracted coal

Sample	Order of Reaction, n	Activation Energy, kJ/mol	Frequency Factor, s^{-1}
Original Samla Coal (OSC)	4	115.436	0.007553188
NMP Extract (SCC-NMP)	4	20.929	8.81869
Residual Coal (RC-NMP)	1	40.094	2.584842
Cetene Extract (SCC-CE)	2	21.903	0.001299
Residual Coal after Cetene ext (RC-CE)	3	32.230	0.00471
AO-Extract (SCC-AO)	4	57.741	29.678
Residual Coal After AO Extn. (RC-AO)	2	36.306	0.000220397

and reactive.

RC-NMP would be thus rendered reactive. Even the residual volatile matter (RVM), i.e., the volatile matter remaining in RC , is still sufficiently high for this (Table 6). The C % of RC-NMP was found to be high (80.4%) (Table 2), thus this would offer more carbon for reaction with CO_2 (Table 2). The order of CO_2 gasification reaction for SCC-AO was also found to be 4, AE was higher (57.3 kJ/mol) than that of SCC-NMP. These reactions were found to be diffusion controlled.

RC-AO displayed an order of 2 and lesser AE (35.9 kJ/mol) than that of OSC, showing that AO extraction was a beneficial pretreatment for the CO_2 gasification of coals as well.

SCC-CE showed the CO_2 gasification reactions' order as 2 and a low AE (21.9 kJ/mol), as expected for the reactive extracts (obtained after cetylation of coal). Even the AE values for RC-CE were much lower (31.8 kJ/mol) than that of OSC. The order of reactions was found to be 3. This could also be attributed to the enhancement in the reactivity caused by cetylation of coal, which may lead to the reduction in the stacking of aromatic lamellas in coal to render these more extractable and reactive. Cetene extraction also results in an increase in the volatile matter in coal (Table 6). This also results in increasing the active surface area in coal [12].

These studies showed that both extracts as well as residual or pretreated coals were reactive towards CO_2 gasification reactions. The order of AE for different reacting coal samples studied is as follows: SCC-NMP<SCC-CE<RC-CE<RC-AO<RC-NMP<SCC-AO<OSC. These reactions were found to be mostly diffusion controlled.

The present studies have revealed that different solvents have a different effect on CO_2 gasification reactivity and the kinetics of treated coals. SCCs obtained after organo-refining with NMP and CE were found to have good reactivities (Table 5 and 6). However, AO extraction was found to reduce the reactivity of SCC-AO. SCC-NMP and SCC-CE may be good feed stocks for the CO_2 gasification of coals and for IGCC power generation. AEs for RC-NMP, RC-CE and RC-AO were also found to be lower (Table 7).

Tomaszewicz et al. [54] have reported that the calculated values of activation energy of coal char CO_2 gasification are in the range of 180–250 kJ/mole. Kopyrinski et al. [28] compared the K_2CO_3 catalyzed CO_2 gasification of ash-free coal, raw coal and uncatalyzed ash-free coal. The gasification reactivity of catalyzed coal was found to be 3 times faster than that of raw coal and 60 times faster than that of ash-free coal. AE for catalyzed ash free coal gasification (264 kJ/mol) was 100 kJ/mol larger than that for raw coal (133 kJ/mol) and uncatalyzed ash free coal (121 kJ/mol). The increase in AE was reported to be due to the energy required for the potassium transfer or caused by the pyrolysis process. The studies were carried out using TGA apparatus. Yang et al. [27] have reported AE for the CO_2 gasification of high ash coal as 137 kJ/mol. Presently observed values of AE for the solvent treated coals i.e., SCCs and RCs, were found to be low and these were also lower than that of the original raw coal. This showed that the treatment of coal with different solvents results in reducing their AE for the CO_2 gasification reactions of Samla coal. These reactions are controlled by diffusion rather than kinetics reactions.

10. Comparison of activation energy for CO_2 gasification of Samla coal with intermolecular bond energies

In order to study the cleavage of bond energies in coal during the CO_2 gasification reactions, AE of the same with the different bond energies in the coal structure were compared. The presently observed values of AE for the CO_2 gasification reaction were found to be low. The bond dissociation energies of C-C, C=C, C-H bonds are 349.4, 585.8 and 414.2 kJ/mol respectively. The observed C-C bond energies in biphenyl and benzyl phenyl ether are 279.1 and 217.1 kJ/mol. These are much higher than the observed AE values for the combustion, pyrolysis and gasification reactions [12]. The reason for this could be that coal macromolecules – due to their larger structural units having polyaromatic ring attachments through several interlinking aliphatic and other heteratomic linkages – degrade thermally to yield free radicals rather readily. The larger sizes render coal macromolecules thermodynamically less stable. Thus degradation of such larger molecules require relatively less energy

The C-C bond dissociation energy for the cleavage of C-C bonds between Ph_3C-CPh_3 is much lower (45.6 kJ/mol) than the normal C-C bond dissociation energy. Even C-C bond energies in diphenyl ethane are low. In fact, coal macromolecules – having several strains, cross-linkages, heteroatomic bondings, longer structural units including polyaromatic rings, alicyclic rings and longer aliphatic chains or side chains or side chains in these three dimensional cross-linked gel structures – undergo several free radical reactions on being thermally degraded and on reaction of these degraded free radical moieties with CO_2 above 600°C. The observed values of AE for the CO_2 gasification reactions are average values.

If the orders of reactivities based on the DTG and $^{\tau}0.5$ reactivity, i.e., RCO_2 studies and lower AE values are compared then it becomes clear that SCC-NMP, SCC-CE, RC-CE have good CO_2 gasification reactivity. The low CO_2 gasification reactivity of SCC-AO is also clear from these studies, though, RC-AO has still relatively higher gasification reactivity. The main reason for the lower reactivities of SCC-AO and even of RC-AO could be the low RVM in these samples. It seems that AO extraction of coal results in the reduction of volatile matter in coal and also reduction of active surface area in coal. NMP extraction results in increase in the volatile matter in SCC and it also leads to an increase in the active surface area in coals.

11. Relation of the characteristics of SCCs with Gasification reactivity

Table 2 and 3 show the results of characterization of the coal extracts, obtained in different solvents. The $f_a(C)$ and the proportion of other carbon and hydrogen were calculated from the ^{13}CNMR and ^{1}HNMR spectral analyses. Thus, Table 3 and 4 show the results of characterization of NMP-SCC, AO-SCC and CE-SCC. The extraction yields of Samla Coal in NMP, AO and CE were found to be 32.6, 32.4 and 53% after 24 h. Extraction yields varied between 11% in AO to 15.2% in NMP to 35% in CE after 2 h (Table 2). The C-aromaticity i.e. $f_a(C)$ of SCC-NMP was found to be the highest (61.4%) in comparison to that of other extracts as revealed by the ^{13}CNMR spectral studies (Table 3 and 4) [12]. Even the quaternary carbon atoms were found to be the highest in SCC-NMP. The aromatic hydrogen was also found to be low in SCC-NMP. In fact, NMP is known as a solvent used for the dearomatization of kerosene or lube oils. Thus, NMP can predominantly extract aromatic components from coal macromolecules. These carbon rich extracts, i.e., SCC-NMP having C_H/C_{Ar} ratio of 47%, would have higher reactivities with CO_2 to yield CO. Saturates-Aromatics-Resins-Asphaltene (SARA) separation / fractionation and characterization of different fractions also supported these results and these showed that extracts, i.e., SCCs, contained mainly resins (based on the SARA fractionation studies) [12]. No suitable correlation of the C, H, N, S, O (% elemental analysis), the atomic C/H ratio or of the atomic C/O ratio of RCs and SCCs could be found with the CO_2 gasification reactivity excepting that of RC-NMP as described before also (Table 2).The reason for this could be that the coal is a macromolecule – not a simple carbon – with a complex three dimensional gel network structure having fused polycyclic aromatic ring structural units linked to naphthenic, N, S, O-hetrocyclic and paraffinic units. Therefore its reaction with CO_2 during gasification would be complex and not a simple carbon and CO_2 reaction at high temperature.

12. Generalized observations on the CO_2 gasification reactivity of raw coal, SCCs and RCs

Overall analysis of all the results from the DTG (weight loss/min), R_{CO2} reactivity studies (min^{-1}) and from the Coats and Redfern modeling studies revealed the following general observations: Amongst SCCs, SCC-NMP and SCC-CE showed good reactivity after considering all the three reactivity studying parameters, i.e., reactivity from the TGA, R_{CO2} and the formal reaction parameters based on the Coats and Redfern nonisothermal model. Amongst the residual coals, the residual coals obtained from organo-refining in NMP and CE were found to be good feedstocks, though not always. In general, the organo-refining of coal in CE seemed to be good but the same in NMP may be considered as still more beneficial pretreatment for the CO_2 gasification of coal. From the extraction yield point of view at shorter times of 2 h these solvents seemed to better solvents. The research work from the authors' laboratory has shown that the shorter time (i.e., 2 h) extraction yield of Samla coal in NMP can be enhanced up to 31% by adding catalytic amounts of EDA (i.e., EDA : coal ratio of 1:1 by weight) as a co-solvent in the extraction of coals at lower reflux temperature than in pure NMP [22, 55]. Thus this extraction (organo-refining) system may also be a candidate for future studies for the gasification of SCCs and RCs of coals obtained from the organo-refining by NMP containing small amount of EDA in different gasifying media such as, the CO_2, steam, CO_2 + steam + O_2 and steam + O_2 and CO_2 + O_2 atmospheres.

13. Chemistry of solvent extraction of coal and its effect on the CO_2 gasification of coal or treated coals

Studies on the particle size distribution of residual coals obtained after NMP, AO and CE extractions showed that the particle size reduces after the extraction [12]. This would lead to increase in the active surface area in RCs. RC-NMP showed the lowest reduction (26%) of particle size as compared to RC-AO (30%) and more than of RC-CE (23%). Yang et al. [27] have reported that particle size has no effect on the coal gasification reactivity. This showed the reason for RC-AO having higher gasification reactivity than OSC as this had a larger active surface area in comparison to OSC. The higher reactivity of RC-CE could be explained to be because of cetylation reaction (as also supported by FTIR spectral studies) resulting in an increase in the volatile matter contents in coals. SEM studies also showed that the action of solvents had altered the morphology of RCs [12]. SCCs were obtained after precipitation of extracts and these obviously had larger active surface areas excepting SCC-AO, which had undergone thermal treatment for a longer time (as AO is a eutectic mixture of different aromatic and heterocyclic compounds) during recovery of the extract; this resulted in its devolatilization to make its volatile matter leaner than other treated coal samples (SCCs, RCs and OSC). AO extract was also found to contain more (about 93%) colloidal matter against cetene extract (60%) and NMP extract (20%). AO extracts the coal by the like-dissolves-like principle and by thoroughly shaking up the coal particles and breaking up the intermolecular and intramolecular bonds randomly by peptization, recovering larger molecular weight (average weight 66,908 g/mol) coal lamellas. It seems that since AO is a viscous solvent, its recovery from extract (to recover SCC-AO) resulted in larger amounts of devolatilization (almost charring). The AO extract had a higher number average molecular weight (40533 g/mol) and had polymeric properties, as revealed by GPC studies. UV spectral studies of the AO extract also showed that it contained a higher percentage of asphaltenes than NMP and CE extracts. This could be the reason for the lower CO_2 gasification reactivities of SCC-AO and RC-AO.

The present studies show that NMP extract, i.e., SCC-NMP which has less than 1% ash (i.e., about 0.38% ash), shows good reactivity for CO_2 gasification at lower temperatures. NMP extraction or organo-refining is a beneficial pretreatment for the CO_2 gasification of coal, generating more active surface area and more volatile matter and exposing more MM in coal, which may act as catalysts and promoters. It is expected that – using SCC-NMP and RC-NMP – the reactivities of coal for gasification may be enhanced. Thus, these studies may help solve some of the problems plaguing coal gasification processes, IGCC power generation and generation of H_2, which may be used in fuel cells. SCC may be utilized for added value purposes such as obtaining carbon nanotubes [56], nanocomposites [51, 52], composites [51, 52] carbon materials, conducting polymers smart materials etc. [57].

The use of SCC or U-SCC may be made for low temperature gasification, i.e., below 700–1,000°C by using catalysts which may be easily recovered and thus may not be lost in reaction with the inorganic MM present in the raw coal [4–6, 8]. The CO_2 gasification of coal (or of biomass) may also be used for CO_2 sequestration in allothermic reactors where solar heating may be utilized in future.

14. Conclusions

Gasification of coal leads to the production of H_2 and the process has been used for IGCC power generation, a clean coal technology with higher efficiencies and lower emissions of CO_2. It is easier and relatively cheaper to integrate IGCC power generation systems with CO_2 concentration, sequestration and utilization. However, gasification of coal still suffers from several major engineering problems, mostly due to the ash present in the coals, which may reduce the availability of gasifiers in the commercial gasifiers. Organo-refining of coals by using industrial solvents such as NMP or by using CE, a petroleum derived solvent, renders the coal reactive for the CO_2 gasification. The use of AO extraction does not lead to much enhancement in the gasification reactivity of coal, though AO is a coal derived solvent. The CO_2 gasification reactivity of RC obtained after NMP and CE extraction is also high. The CO_2 gasification reactivity was found to increase with an increase in temperature. The mineral matter in the raw coal seemed to increase its CO_2 gasification reactivity at temperatures above 1,000°C. Different solvents had produced different effects on the CO_2 gasification of coal after organo-refining. The organo-refining of coals in different solvents resulted in reducing the activation energy of the CO_2 gasification reactions. The CO_2 gasification reactions of solvent treated coals were found to have low activation energies and the reactions were found to be mass transfer controlled rather than being kinetics controlled. Some of the reactions had even higher orders showing complex molecular reactions, as is expected from coal macromolecules, while kinetics modeling gives mostly the formal reaction parameters. The use of SCC or U-SCC, i.e., ultra-super clean coal obtained after the extraction of coals in NMP containing smaller amounts of EDA, may also be made for low temperature catalytic gasification, to conserve energy and catalyst used. However, the organo-refining technology is still not economically established and further work on this may be required to make it cost effective for integration with IGCC power generation systems. The CO_2 gasification of coal (or of biomass or of coal and biomass mixed feedstocks) may also be used for CO_2 sequestration. Future IGCC power generation systems may use CO_2, steam and O_2 gasifying medium for gasification with ashless coals. However, the processes to obtain ashless coals may have to be economically established by organo-refining or other techniques.

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References

[1] M. Prins, K. Ptasinski, Energy and exergy analyses of the oxidation and gasification of carbon, Energy 30 (7) (2005) 982–1002.

[2] A. Sharma, T. Takanohashi, K. Morishita, T. Takarada, I. Saito, Low temperature catalytic steam gasification of hypercoal to produce h 2 and synthesis gas, Fuel 87 (4) (2008) 491–497.

[3] J. A. Gerstner, J. W. Zondlo, Gasification kinetics of residual coal produced from solvent extraction with n-methylpyrrolidone, Fuel science & technology international 10 (3) (1992) 335–346.

[4] D. K. Sharma, S. K. Singh, S. K. Mathew, The steam gasification of coal under milder low temperature conditions—nonisothermal kinetics studies for reactor design, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 33 (2) (2010) 171–181. arXiv:http://dx.doi.org/10.1080/15567030902882935, doi:10.1080/15567030902882935.
URL `http://dx.doi.org/10.1080/15567030902882935`

[5] D. Sharma, Enhancing the steam gasification reactivity of coal by boosting the factors affecting the gasification reactions in the stepwise coal conversion, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 32 (18) (2010) 1727–1736.

[6] D. Sharma, Modeling the steam gasification reactions for reactor design, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects 33 (1) (2010) 57–71.

[7] Accessed on 22/02/2016. [link].
URL https://en.wikipedia.org/wiki/Integrated_gasification_combined_cycle

[8] D. K. Sharma, Cleaner coal technologies—concept of coal refineries for added value and efficient use of coal, Ind. Chem. Engr 50 (2008) 155–168.

[9] Accessed on 22/02/2016. [link].
URL https://www.usea.org/sites/default/files/082013_Recent%20operating%20experience%20and%20improvement%20of%20commercial%20IGCC_ccc222.pdf

[10] Accessed on 22/02/2016. [link].
URL http://www.nedo.go.jp/content/100580318.pdf

[11] Accessed on 22/02/2016. [link].
URL http://www.sourcewatch.org/index.php/Integrated_Gasification_Combined_Cycle_(IGCC)

[12] C. Giri, Studies on development of a process for solvent deashing of coal to obtain environmentally clean fuels and characterization of products, Ph.D. thesis, Indian Institute of Technology, Delhi, New Delhi, India (1995).

[13] S. Bhatia, Studies on bio-refining of fossil fuels (lignite,coal and petroleum oil), Ph.D. thesis, Indian Institute of Technology, Delhi, New Delhi, India (2007).

[14] S. Gangwal, R. Gupta, W. McMichael, Hot-gas cleanup—sulfur recovery technical, environmental, and economic issues, Heat recovery systems and CHP 15 (2) (1995) 205–214.

[15] N.-K. Park, D.-H. Lee, J. H. Jun, J. D. Lee, S. O. Ryu, T. J. Lee, J.-C. Kim, C. H. Chang, Two-stage desulfurization process for hot gas ultra cleanup in igcc, Fuel 85 (2) (2006) 227–234.

[16] E. Furimsky, Catalytic effect of mineral matter of high ash onakawana lignite on steam gasification, The Canadian Journal of Chemical Engineering 64 (2) (1986) 293–298.

[17] D. K. Sharma, N. K. Sandle, S. K. Singh, M. Venugopal, Solvolytic extraction and pyrolysis pretreatment for steam gasification of assam coal at atmospheric pressure, Journal of mines, metals and fuels 39 (3) (1991) 60–66.

[18] N. Okuyama, N. Komatsu, T. Shigehisa, T. Kaneko, S. Tsuruya, Hypercoal process to produce the ash-free coal, Fuel Processing Technology 85 (8) (2004) 947–967.

[19] T. Yoshida, T. Takanohashi, K. Sakanishi, I. Saito, M. Fujita, K. Mashimo, The effect of extraction condition on 'hypercoal'production (1)—under room-temperature filtration, Fuel 81 (11) (2002) 1463–1469.

[20] T. Takanohashi, T. Shishido, H. Kawashima, I. Saito, Characterisation of hypercoals from coals of various ranks, Fuel 87 (4) (2008) 592–598.

[21] R. Ashida, K. Nakgawa, M. Oga, H. Nakagawa, K. Miura, Fractionation of coal by use of high temperature solvent extraction technique and characterization of the fractions, Fuel 87 (4) (2008) 576–582.

[22] S. Pande, D. Sharma, Ethylenediamine-assisted solvent extraction of coal in n-methyl-2-pyrrolidone: Synergistic effect of ethylenediamine on extraction of coal in n-methyl-2-pyrrolidone, Energy & fuels 16 (1) (2002) 194–204.

[23] K. C. Vimal, P. Banerjee, D. Sharma, Process flow sheet for pretreatment of high ash coal to produce clean coal, uS Patent App. 14/344,210 (Sep. 4 2012).

[24] M. F. Irfan, M. R. Usman, K. Kusakabe, Coal gasification in co 2 atmosphere and its kinetics since 1948: a brief review, Energy 36 (1) (2011) 12–40.

[25] W. Huo, Z. Zhou, X. Chen, Z. Dai, G. Yu, Study on co 2 gasification reactivity and physical characteristics of biomass, petroleum coke and coal chars, Bioresource technology 159 (2014) 143–149.

[26] K. Jayaraman, I. Gokalp, Effect of char generation method on steam, CO2 and blended mixture gasification of high ash Turkish coals, Fuel 153 (2015) 320 – 327. doi:http://dx.doi.org/10.1016/j.fuel.2015.01.065.

[27] Z. Yang, L. Zhang, J. Peng, M. Guo, Gasification of inferior coal with high ash content under co2 and o2/h2o atmospheres, International Journal of Green Energy 12 (10) (2015) 1046–1053.

[28] J. Kopyscinski, R. Habibi, C. A. Mims, J. M. Hill, K2co3-catalyzed co2 gasification of ash-free coal: kinetic study, Energy & Fuels 27 (8) (2013) 4875–4883.

[29] D. Fan, Z. Zhu, Y. Na, Q. Lu, Thermogravimetric analysis of gasification reactivity of coal chars with steam and co2 at moderate temperatures, Journal of thermal analysis and calorimetry 113 (2) (2013) 599–607.

[30] S. Saha, G. Sahu, S. Dutta, P. Chavan, B. K. Sharma, T. Sharma, Studies on co$_2$ gasification activity of high ash indian coal, International Journal of Emerging Technology and Advanced Engineering 3 (3) (2013) 29–33.

[31] D. K. Sharma, S. K. Singh, Multisolvent successive extractive refining of coal, Energy sources 18 (1) (1996) 1–19.

[32] D. K. Sharma, S. Mishra, Successive extractive disintegration of coal under atmospheric pressure conditions, Energy and Fuels 3 (1989) 641–647.

[33] A. Molina, F. Mondragon, Reactivity of coal gasification with steam and co 2, Fuel 77 (15) (1998) 1831–1839.

[34] S. Lee, Handbook of Alternative Fuel Technologies, CRC Press, New York, 2007, Ch. Gasification of coal.

[35] B. Bayarsaikhan, J.-i. Hayashi, T. Shimada, C. Sathe, C.-Z. Li, A. Tsutsumi, T. Chiba, Kinetics of steam gasification of nascent char from rapid pyrolysis of a victorian brown coal, Fuel 84 (12) (2005) 1612–1621.

[36] J. Corella, J. M. Toledo, G. Molina, Steam gasification of coal at low-medium (600-800 c) temperature with simultaneous co2 capture in a bubbling fluidized bed at atmospheric pressure. 2. results and recommendations for scaling up, Industrial & Engineering Chemistry Research 47 (6) (2008) 1798–1811.

[37] D. Fung, S. D. Kim, Gasification kinetics of coals and wood, Korean Journal of Chemical Engineering 7 (2) (1990) 109–114.

[38] J. Johnson, Chemistry of Coal Utilization, Wiley - Interscience, N.Y., USA, 1981, Ch. Fundamentals of Gasification.

[39] S. Kajitani, S. Hara, H. Matsuda, Gasification rate analysis of coal char with a pressurized drop tube furnace, Fuel 81 (5) (2002) 539–546.

[40] K. Miura, K. Hashimoto, P. L. Silveston, Factors affecting the reactivity of coal chars during gasification, and indices representing reactivity, Fuel 68 (11) (1989) 1461–1475.

[41] G.-s. Liu, A. Tate, G. Bryant, T. Wall, Mathematical modeling of coal char reactivity with co2 at high pressures and temperatures, Fuel 79 (10) (2000) 1145–1154.

[42] R. C. Everson, H. W. Neomagus, H. Kasaini, D. Njapha, Reaction kinetics of pulverized coal-chars derived from inertinite-rich coal discards: gasification with carbon dioxide and steam, Fuel 85 (7) (2006) 1076–1082.

[43] K. H. Van Heek, H.-J. Mühlen, H. Jüntgen, Progress in the kinetics of coal and char gasification, Chemical engineering & technology 10 (1) (1987) 411–419.

[44] K. Osafune, H. Marsh, Gasification kinetics of coal chars in carbon dioxide, Fuel 67 (3) (1988) 384–388.

[45] L. Shufen, S. Ruizheng, Kinetic studies of a lignite char pressurized gasification with co 2, h 2 and steam, Fuel 73 (3) (1994) 413–416.

[46] D. Ye, J. Agnew, D. Zhang, Gasification of a south australian low-rank coal with carbon dioxide and steam: kinetics and reactivity studies, Fuel 77 (11) (1998) 1209–1219.

[47] J. H. Zou, Z. J. Zhou, F. C. Wang, W. Zhang, Z. H. Dai, H. F. Liu, Z. H. Yu, Modeling reaction kinetics of petroleum coke gasification with co 2, Chemical Engineering and Processing: Process Intensification 46 (7) (2007) 630–636.

[48] T. Lee, S. Beck, A new integral approximation formula for kinetic analysis of nonisothermal tga data, AIChE journal 30 (3) (1984) 517–519.

[49] M. Ahmaruzzaman, D. Sharma, Non-isothermal kinetic studies on co-processing of vacuum residue, plastics, coal and petrocrop, Journal of analytical and applied pyrolysis 73 (2) (2005) 263–275.

[50] M. Ahmaruzzaman, D. Sharma, Kinetic studies on cocracking of petroleum vacuum residue with thermoplastics and biomass (petrocrop), Petroleum Science and Technology 25 (7) (2007) 925–936.

[51] M. Ahmaruzzaman, D. Sharma, Characterization of liquid products from the co-cracking of ternary and quaternary mixture of petroleum vacuum residue, polypropylene, samla coal and calotropis procera, Fuel 87 (10) (2008) 1967–1973.

[52] M. Ahmaruzzaman, D. Sharma, Characterization of liquid products from the co-cracking petroleum vacuum residue with coal and biomass, Journal of Analytical and Applied Pyrolysis 81 (1) (2008) 37–

44.
[53] S. Porada, G. Czerski, T. Dziok, P. Grzywacz, D. Makowska, et al., Comparison of steam gasification kinetics of coal and its char, Przemysl Chemiczny 93 (12) (2014) 2059–2063.
[54] M. Tomaszewicz, G. Łabojko, G. Tomaszewicz, M. Kotyczka-Morańska, The kinetics of co2 gasification of coal chars, Journal of thermal analysis and calorimetry 113 (3) (2013) 1327–1335.
[55] S. Pande, D. Sharma, Studies of kinetics of diffusion of n-methyl-2-pyrrolidone (nmp), ethylenediamine (eda), and nmp+ eda (1: 1, vol/vol) mixed solvent system in chinakuri coal by solvent swelling techniques, Energy & fuels 15 (5) (2001) 1063–1068.
[56] R. B. Mathur, C. Lal, D. K. Sharma, Development of catalyst free carbon nanotubes from coal based material, Energy Sources, Part A 29 (2007) 21–27.
[57] V. Choudhary, A. Panwar, P. Garg, B. Singh, R. Mathur, et al., Effect of commercial and synthesized multiwalled carbon nanotubes on the electrical and thermal properties of polystyrene, in: Abstracts Of Papers Of The American Chemical Society, Vol. 242, American Chemical Society, 2011, pp. 1–4.