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Feasibility studies on cleaning of high sulfur coals by using ionic liquids

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Abstract Coal has been used as an energy resource around the world, primarily for the generation of electricity. The cleaning of coal by removing its unwanted sulfur and mineral matter components is utmost essential before their gainful utilizations. The ionic liquids (ILs) are considered as non-toxic solvents for using in different industrial processes. The effect of two ILs namely, 1-*n*-butyl, 3-methylimidazolium tetrafluoro borate (IL1) and 1-*n*-butyl, 3-methylimidazolium chloride (IL2) in oxidative de-sulfurization and de-ashing of two industrially important high sulfur coal samples from Meghalaya (India) is discussed in this paper. The maximum removal of total sulfur, pyritic sulfur, sulfate sulfur and organic sulfur are observed to be 37.36 %, 62.50 %, 83.33 % and 31.63 % respectively during this oxidative process. The quantitative diffuse reflectance Fourier transform-infrared spectroscopy analysis supports the formation of sulfoxides (S=O) and sulfones ($-SO_2$) and their subsequent removal during the oxidation of the coals in presence of ILs. The X-ray fluorescence combined with near edge X-ray absorption fine structure and scanning electron microscopic studies reveal the removal of mineral matters (ash yields) from the coal samples. The thermogravimetric analysis of the raw and clean coals indicates their high combustion efficiencies and suitability for using in thermal plants. The method is partially green and the ILs could be recovered and reused in the process.

Keywords High sulfur coals · De-sulfurization of coal · Indian coals · Ionic liquids · De-ashing

1 Introduction

Coal has been used as the major source for electricity generation in many parts of the world including India. India is the third largest coal producing country in the world and 'Coal India Ltd.' is one of the world's largest coal mining companies (Stracher and Taylor 2004). There are over 861 billion tonnes of proven coal reserves worldwide, which is enough to last for around 100 years at current rates of production. However, cleaner approaches are vital for gainful and sustainable utilizations of coals. Coal naturally contains sulfur and mineral matters (ash yield). Sulfur in coal is generally grouped into inorganic and organic forms. The high sulfur coals create environmental problems to the community and thus, minimization of sulfur and mineral matters from coals is very much essential before their various types of utilizations. The acid mine drainage (AMD) is also caused by the oxidation of pyritic sulfur in coals (Baruah et al. 2006). The performance of a coal-based power plant is also influenced by many coal properties. The mineral matters and sulfur contents of any coal have most impact on the boiler performance. The presence of mineral matter (ash contents) can cause ash deposition and erosion damage to the boiler tube. The acid dew point of flue gas is also determined by the sulfur content of the coal. Higher coal sulfur level may promote air heater corrosion (Juniper and Pohl 1997). In steel making industry, the sulfur content of coke, sediments

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on the iron crystal surface make steel more brittle and decrease its plasticity property (Ehsani 2006). In recent years, chemical desulfurization of coals has attracted much attention due to the gradual reduction of the statutory sulfur contents. A large number of chemicals have been used to remove the sulfur and mineral matters from coals (Yaman et al. 1954; Mazumdar et al. 1989; Sain et al. 1991; Demirbas and Balat 2004; Komintarachat and Trakarnpruk 2006; Baruah and Khare 2007; Ahmed et al. 2008; Zhang et al. 2009; Campos-Martin et al. 2010; Silva et al. 2011). The most common industrial process of catalytic hydro-desulfurization (HDS) needs hydrogen with additional high investments and operation cost (Schmitz et al. 2004). On the other hand, the chemicals used during the desulfurization processes also have been creating environmental hazards to the communities as well as surroundings. As a consequence, chemists are exposed to a large number of lethal chemicals during their working. Thus, the chemical desulfurization process must be compatible to the environmental restriction as well as to the chemists. So, suitable and environment friendly chemical desulfurization method is urgently needed for the coal processing plants. In the last few decades, there emerged a new class of green solvents known as "Ionic Liquid" (IL) (Rogers and Seddon 2003). They are composed of cation and anion, non-volatile, excellent solubility, great thermal/chemical stability and non-flammability and environmental friendliness. The ILs have been used potentially in different sectors including nuclear applications to the petroleum industry. The ILs have also been reported for direct extraction of S-compounds (extractive desulfurization, EDS) from liquid fuels (Bosmann et al. 2001; Esser et al. 2004; Zhao et al. 2005; He et al. 2008; Holbrey et al. 2008; Kendra-Krolik et al. 2011).

The coal resources of India are available in older Gondowana formation of Peninsular India and younger to tertiary formation of North-eastern region (NER). The NER of India has a large reservoir of high sulfur (2 %–8 %) coals with sub-bituminous in rank (Saikia et al. 2014). The majority of sulfur functionalities of these coals were found to be in the organic forms (75 %–90 %), which are retardant to remove chemically (Baruah and Khare 2007). There are five types of organic sulfur functionalities found in these NER coals including aliphatic or aromatic thiols, aliphatic or mixed sulfides, aliphatic or aromatic disulfides, heterocyclic compounds of thiophenic and thioketonic types, etc., (Barooah and Baruah 1996); moreover, the NER coals are characterized by low ash and high caking index, suitable for use in cement plant and metallurgy as coking coal. But, these coals cannot be gainfully utilized because of their high sulfur contents as mentioned above.

We present here a partially green chemical beneficiation method for de-sulfurization and de-ashing of high sulfur low grade NER coals from Meghalaya (North-east India) by using ILs as non-toxic solvents in a mild reaction conditions with no need of hydrogen, pressure and reactor. The prime objective of this study is also to see the outcome of the oxidative desulfurization (ODS) process with those high sulfur coals in presence of the ILs. The ODS process includes oxidation of sulfur compounds followed by their extraction in solvents. The use of green solvents like ILs in this present coal cleaning process for high sulfur coals makes the process partially green and efficient. The process may also be considered in clean coal technology.

2 Materials and methods

The chemicals (Sigma-Aldrich and Merck) used were: hydrogen peroxide (30 %), formic acid (85 %), 1-*n*-butyl,3-methylimidazolium tetrafluoro borate (IL1) and 1-*n*-butyl,3-methylimidazolium chloride (IL2). The representative high sulfur coal samples (SCF and B) were collected from two different collieries of Bapung coalfield (N 27°13′–27°23′; E 95°35′–96°00′), Meghalaya (India) and ground to −0.211 mm sizes for other analyses by suing standard method (ASTM 2010). The areas under investigation is covered by the Barail group of rocks consist coarse sandstone, shale, minor coal lenses and carbonaceous shale. The coal seams are associated with the Lakadong Sandstone of Shella Formation of Jaintia group (Eocene) includes three persistent coal seams ranging from 1–3 m in thickness along with inter-seam sandstone and shale (Ahmed and Rahim 1996).

The proximate analysis and sulfur analysis were carried out in Proximate Analyser (TGA701, Leco) and Sulfur Analyser (LECO, 144DR) respectively by using standard method (ASTM 1991). The forms of sulfur were determined by following the standard method (ASTM 2005). The percent of organic sulfur was calculated by difference. The gross calorific values (GCV) were also determined in Bomb calorimeter (Model: Leco, USA) by using standard methods (ASTM 2013).

2.1 Quantitative diffuse reflectance FT-IR spectroscopic analysis of coals

Diffuse reflectance Fourier transform infrared (FT-IR) spectra of the coal samples were recorded using FT-IR instrument (System-2000, Perkin–Elmer Inc.) in the range of 500–1500 cm^{-1}. The samples (about 6–7 mg) were accurately weighed on single pan electronic balance (Model: SI-234, Denver Instrument) and thoroughly mixed with spectroscopic grade KBr powder (about 200 mg) in an agate mortar. Pure ground KBr was used to obtain the reflectance spectrum by taking 64 numbers of scan having

resolution 4.0 cm^{-1}. The FTIR spectra were processed using the software Spectrum V-3.02 (Version 3.02.01, Perkin–Elmer) in absorbance mode. At first the base line was corrected and was brought to the 0.0 reading. The spectra were normalized to 1 mg of the samples by dividing it with the amount of the sample taken for recording the drift spectra to compare the absorbance at 563 cm^{-1}.

2.2 Thermal (TG–DTG), XRF and SEM analysis of coals

Thermogravimetry (TG) and their first derivative thermogravimetric (DTG) spectra were recorded in the thermal analyzer (Model: TGA701, LECO) with heating rate of 10 °C/min in presence of oxygen environment. The combustion performance index (S) and energy of activation (Ea) were calculated by using the methods as reported elsewhere (Sonibare et al. 2005; Qing et al. 2011).

The high energy X-ray fluorescence (XRF) measurements of coal samples before and after the treatment were obtained from the Canadian Light Source [Saskatchewanin the Soft X-ray micro-characterization Beamline (SXRMB)]. The Si(111) crystals were used for XRF measurements with photon energy set at 8350 eV. The powder sample was mounted using double-sided, conducting carbon tape, and loaded into a vacuum chamber (base pressure of 1×10^{-8} torr). The scanning electron microscopic (SEM) images were recorded in SEM (Model: JSM-6360 JEOL).

2.3 Removal of sulfur components and mineral matters (ash yield)

Thirty grams of coal sample were refluxed with a mixture of 13.2 mL of 20 % formic acid and 75 mL of 20 % H_2O_2 for 1 h. Then, the oxidized coal samples were filtered and washed with water until the pH of the filtrate became neutral. In another two separate experiments, 30 g coal samples (0.211 mm in size) were oxidized with the mixtures of 13.2 mL of 20 % formic acid and 75 mL of 20 % H_2O_2 in the same reflux conditions for 1 h in presence of the IL1 and IL2 (0.5 g for each) respectively. The coal-IL mixtures were centrifuged and the recovered coal residues were washed with hot distilled water until neutral and oven dried for 1 h. The filtrates obtained were kept for the recovery and further use of the ILs. The oven dried oxidized coal samples were used for subsequent analysis.

The filtrates obtained in the above step were centrifuged with absolute alcohol to separate out any impurities from the mixtures. Absolute alcohol was separated by traditional evaporation and then, the filtrates were mixed with 1 % $BaCl_2$ solution followed by CCl_4 (about 50 mL) to precipitate out dissolved sulfur functionalities. White colored substances were formed upon slight heating at about 60 °C due to the precipitation of inorganic and organic sulfur compounds, which were removed from coals during oxidation. The white precipitates were then filtered through Whatmann-42 filter paper. The final filtrate containing ILs became colorless. After boiling off the CCl_4, the filtrates could be used for another desulfurization experiments with slight decrease in activity.

3 Results and discussion

3.1 Physico-chemical characteristics of coals

The physico-chemical properties of the raw and oxidized coal samples are shown in Table 1. It demonstrates that the SCF and B coals are high sulfur and high ash in nature. Moreover, the majority of sulfur is organically bound in the coal samples (up to 79.0 %). The geochemical studies of sulfur in coals provide valuable information regarding the sources of sulfur and processes of sulfur incorporation into coals which helps in the study of the depositional environments and formation history of coals (Chou 2012). The major part of inorganic sulphur in these coals consists of pyrite (FeS_2), which is usually in particulate, to agglomerated forms (Baruah et al. 2006). The high sulphur content in the Northeast Indian coals resulted from the increased availability of sulphate ions in sea water coupled with the activity of anaerobic bacteria. The presence of high organic sulfur in northeast Indian coals suggests the marine influence as sulfur compounds are quickly formed by oxidation in marine environment. The oceanic sulfate sources have high sulfate reduction rates and during the coal formation, these sulfates are incorporated to the matrix of the coal molecule giving high organic sulfur groups. The geochemistry of the high sulphur Northeast Indian coals are reported elsewhere (Nayak et al. 2009; Saikia et al. 2014).

3.2 Removal of sulfur and mineral matter (ash yield)

As observed, the oxidation these coal samples (B and SCF) in ILs (IL1 and IL2), the pyritic, organic and sulfate sulfur contents have been significantly removed. On oxidation, the maximum removal of total sulfur and mineral matters (ash yield) of the coal samples are found to be 37.36 % and 13.89 % respectively. However, the pyritic, sulfate and organic sulfur are significantly removed by 62.50 %, 83.33 % and 31.63 % respectively during the process. Moreover, the fuel values (i.e., GCV) are also found to be increased after the beneficiation process (Table 1). The Fig. 1 shows the effectiveness of the process in removal of the mineral matters (ash yield) and sulfur components from

Table 1 Physico-chemical analysis of the raw and beneficiated coal samples (as received, %wt)

Coals	M	Ash	VM	FC	TS	PS	SS	OS	%PS removal	%SS removal	%OS removal	%TS removal	%Ash removal	GCV (kcal/kg)
SCF	4.07	25.9	31.8	38.3	4.47	0.80	0.12	3.6	–	–	–	–	–	6565.60
SCF Oxd	2.58	22.3	32	43.12	3.37	0.60	0.06	2.6	25.0	50.00	27.77	24.60	13.89	7155.00
SCF +IL1	2.10	23.5	33.3	41.10	3.25	0.55	0.04	2.6	31.25	66.66	26.11	37.36	9.26	7411.79
SCF + IL2	2.25	25.6	32.4	39.7	2.80	0.30	0.02	2.48	62.50	83.33	31.11	27.29	1.15	7780.60
B	4.30	17.8	33.7	44.0	3.47	1.08	0.67	1.77	–	–	–	–	–	6687.56
B Oxd	2.34	15.9	36.9	44.9	2.84	0.75	0.45	1.65	30.55	32.83	7.34	18.15	10.67	6812.08
B + IL1	4.72	15.5	33.7	46.08	2.71	0.98	0.52	1.21	9.25	22.38	31.63	21.90	12.92	7140.12
B + IL2	2.31	16.0	37.4	44.3	2.36	0.65	0.60	1.73	39.81	10.44	2.25	14.12	10.11	7213.40

M moisture, *VM* volatile matter, *FC* fixed carbon, *TS* total sulfur, *PS* pyritic sulfur, *SS* sulfate sulfur, *OS* organic sulfur

the two coal samples. It is observed that the present process of ODS is more effective for the SCF coal sample than that of B coal although they are from the same coalfield. Thus, the removal of sulfur including pyritic, sulfate and organic sulfur varies from one colliery to other in the same Bapung coalfield. It may be due to the difference in organic sulfur functional groups present in the coal structure. However, it needs geo-chemical study to understand these variations in the same coalfield. The oxidation in presence of ILs produces sulfone with other components of the product being controlled by factors such as reaction temperature and pH (Davalos et al. 1994). Some researcher found that S-removal in ODS does not linearly increases with H_2O_2

dosage in IL (Zhao et al. 2010). The results were reported that the sulfoxide functional groups decreases with coal rank, while the contents of thiophene increases (McCoy and Weiss 1954; Calkins 1994; Yperman et al. 1995; Maes et al. 1997). Thus, the stable thiophenes are formed from less stable organic sulfur compounds (thiols and sulfides) with increasing rank. On the other hand, coal of different ranks/types has a different distribution of organic-sulfur functionalities, which may affect the extent of desulfurization.

In the oxidative process, the acidic ILs decomposes H_2O_2 to form OH, which is strong oxidant for organic S-compounds present in the coals. The organic sulfur compounds were selectively oxidized into sulfone and sulfoxide in the IL phase. Generally, the divalent S-atom of the organic sulfur compounds undergoes the electrophilic addition of oxygen atom from the H_2O_2 to form sulfone during oxidation. The present Bronsted acidic ILs is water soluble and promotes catalytic reactions; hence in presence of hydrogen peroxide they will have more oxidizing effect. However, the strength and extent of coal oxidation may vary with the rank/type of coal and nature of ILs.

3.3 X-ray diffraction analysis of coals

It is to be mentioned that the low removal of mineral matters (de-ashing) were observed during this process (Table 1). The similarities of the XRD profiles of the raw and treated coals also support the low removal of mineral matters (Figs. 2, 3). The associated minerals present in the raw and oxidized coals are also shown in Figs. 2 and 3. Meghalaya coals of the NER (India) are of Gondowana type, where the majority of mineral matters are present in the inertinite parts. It has higher density and hard to remove and hence cannot be separated by mild and conventional ash removal methods (Falcon and Ham 1988). However,
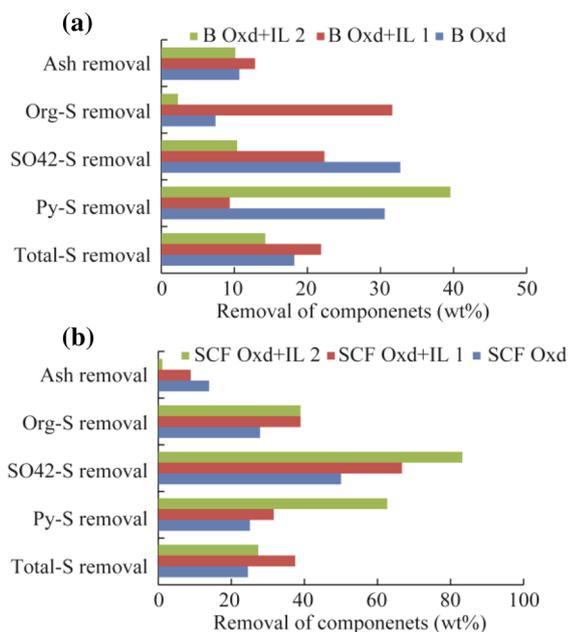
Fig. 1 Extent of removal of components during oxidation of coals with ILs
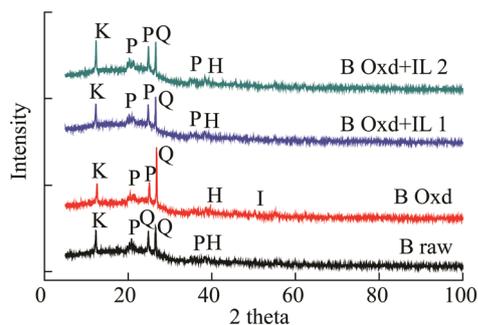
Fig. 2 X-ray diffractogram of raw and beneficiated B coal sample (*K* kaolinite, *P* pyrite, *Q* quartz, *H* hematite, *I* illite)
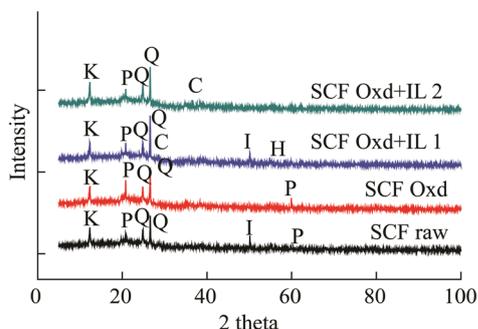
Fig. 3 X-ray diffractogram of raw and IL beneficiated SCF coal sample (*K* kaolinite, *P* pyrite, *Q* quartz, *C* calcite, *H* hematite, *I* illite)
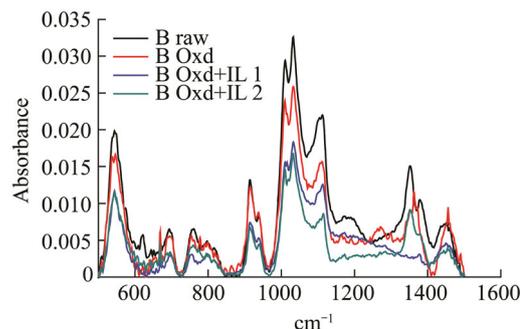
Fig. 4 FT-IR spectra of the raw and beneficiated coal samples (B) in IL1 and IL2
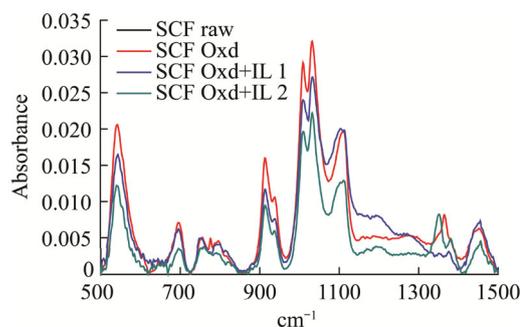
Fig. 5 FT-IR spectra of the raw and beneficiated coal samples (SCF) in IL1 and IL2

the pyrite of these coals is in the vitrinite part, which is removable easily after oxidation reactions.

3.4 Quantitative FT-IR spectroscopic analysis of sulfur transformation

The FT-IR spectra of the raw and oxidized coals are shown in Figs. 4 and 5 and it is observed that the amounts of sulfur functionalities are different in both the coals. The absorption bands in the region of 550 cm^{-1} are assigned to the stretching vibration of S–S bonds of sulfides and C–S bonds in primary and secondary thiols (Silverstein et al. 1987). The bands in the region of 1415–1380 and 1200–1185 cm^{-1} are observed due to the presence of organic sulfates. The stretching frequencies in the range of 1070–1030 cm^{-1} are due to the presence of sulfoxide in the coal samples. The bands in the range of 1050–1020 cm^{-1} are due to the formation of S=O in the oxidized coal samples (Silverstein et al. 1987; De Filippis and Scarsella 2003). However, these regions are also seen in the raw coal sample due to the presence of sulfate (–SO$_4$). The FT-IR spectra of the raw and oxidized coals were normalized and it is interestingly observed that the

absorbance of the sulfoxide, sulfones and sulfate groups were decreased appreciably during the total beneficiation process. Thus, the FT-IR analysis reveals that the sulfur has been converted to sulfoxide (S=O) and sulfone (−SO$_2$) on oxidation and subsequently removed by ILs. In this study, the extent of desulfurization differs due to the difference in sulfur contents in the coal samples.

3.5 X-ray fluorescence analysis on mineral matter (ash yield) removal

The XRF combined with the NEXAFS analysis of the raw and beneficiated (oxidized) coal samples are depicted in Fig. 6. The excitation energy has been chosen just above potassium. All XRF spectra were normalized to the same intensity at the excitation energy (scattered X-rays), so it is easy to say that the current beneficiation process converts the sulfur functionalities to sulfones and sulfoxide (Fig. 6f). The XRF could be useful in showing: (a) the change in sulfur intensity due to oxidation; (b) change in inorganic composition, particularly in for oxidation followed by IL extractions (Fig. 6c–f); (c) the B sample has more sulfur than SCF sample, which is in agreement with
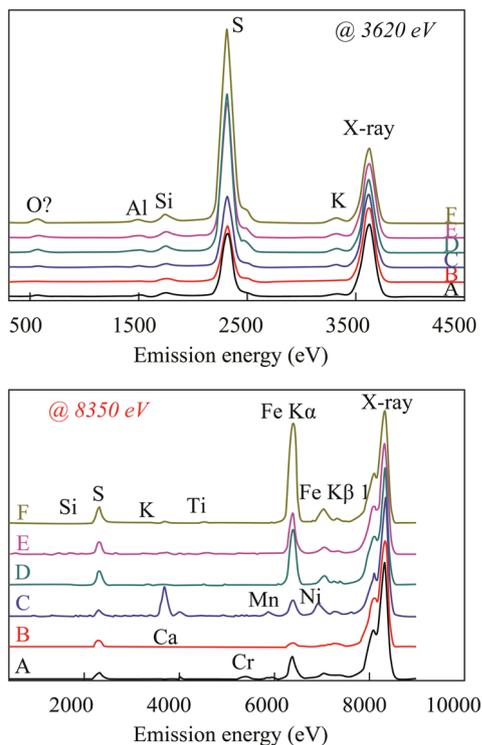
Fig. 6 XRF Spectra of the raw and beneficiated coal samples at two different eV (*A* SCF raw, *B* SCF Oxd, *C* B raw, *D* B Oxd, *E* B Oxd + IL1, *F* B Oxd + IL2)

the chemical analysis. It has also a lot more Ca, Mn and Ni along with pyrite and sulfate as seen in the XAFS; (d) for SCF coal: most of the inorganic species have been removed/reduced after the treatment indicating the maximum removal of ash (13.09 %); (e) for both the coals, it seems that sulfur peak has increased after the treatment, which could be due to the conversion of sulfur forms to inorganic sulfur, such as Fe_2S and $FeSO_4$, as seen in the increase of the Fe intensity. In addition, the ILs treatment of B coal removed most of other inorganic species such as Ca, Mn and Ni.

3.6 SEM analysis of raw and beneficiated coal samples

The effect of H_2O_2, HCOOH and ILs on the microstructure of the coals is displayed in Fig. 7, which compares the changes in morphologies of the raw and beneficiated coal samples. The SEM micrographs of the beneficiated coal samples (Fig. 7d–h) reveal the occurrence of leaching of the coals during oxidation. The appearance of small hollow pits on their surface might be due to the disappearance of pyritic, sulfate and mineral matters from the coal samples on oxidation. A few small and large particles (in Fig. 7d–g) are found

to be dispersed in the beneficiated coals. Thus, the changes in the SEM morphologies support the present beneficiation process through removal of sulfur components and mineral matters from the coal samples (Ishak and Ismail 2004).

3.7 Thermal properties of the coals

The TG–DTG profiles of the raw and beneficiated coals mainly indicate four temperature ranges (Fig. 8). The DTG curve express the starting and closing temperatures of the decomposition and the sharp peak gives the point of decomposition of the coal samples. The residual moisture releases at temperatures range of 25–100 °C. In this stage, the rate of weight loss increases as observed in the TG–DTG curves (Fig. 8). It is observed that the volatile matters start to be released along with the reduction of H-bonding around 223 °C. The weight loss is also increased at this stage as revealed from the TG curve of the both coal samples. However, both the beneficiated coal samples (oxidized) show significant release in volatile matters at this stage temperature. In the third stage (at higher temperature around 400 °C), the fixed carbon in coals begins to oxidize (releasing CO and H_2) and the volatile matters are completely released and the weight loss has been sharply increased. The functional groups, like R–O–R, R–OH present in beneficiated coals facilitates greater decomposition at lower temperature that are released as CO and CO_2. However, the C–H bond present in the raw coal samples are difficult to break than the C–O bond present in the oxidized coal samples (Saikia et al. 2009). Thus, the burning temperatures of the beneficiated coals are reduced indicating their better combustion efficiency. At a temperature range of 500–600 °C, the decomposition of ash occurs e.g., kaolinite → metakaoline at 550–600 °C. The combustion performance index (*S*) of the raw (B and SCF) and beneficiated coal samples (oxidized) were also determined. It is observed that the beneficiated SCF coal samples have lesser combustion performance index than that of the raw coal samples (Table 2). However, the B coal samples shows higher combustion performance index than that of raw coal samples. Thus, the beneficiated B coal samples will have higher combustion activity in the thermal application at lower temperatures. The combustion performance indexes (*S*) along with the activation energies (*E*a) of the raw and beneficiated coal samples are listed in the Table 2, which shows significant variations with different types of the treatments. The activation energies (*E*a) of the beneficiated coals are also found to be generally lesser than the raw coals that decrease with the rise in their S values. However, the activation energies of the IL oxidized coals are found to be higher, which may be due to the increase in carbon contents during the oxidation. It is to be noted that the lower the ignition temperature the easier the
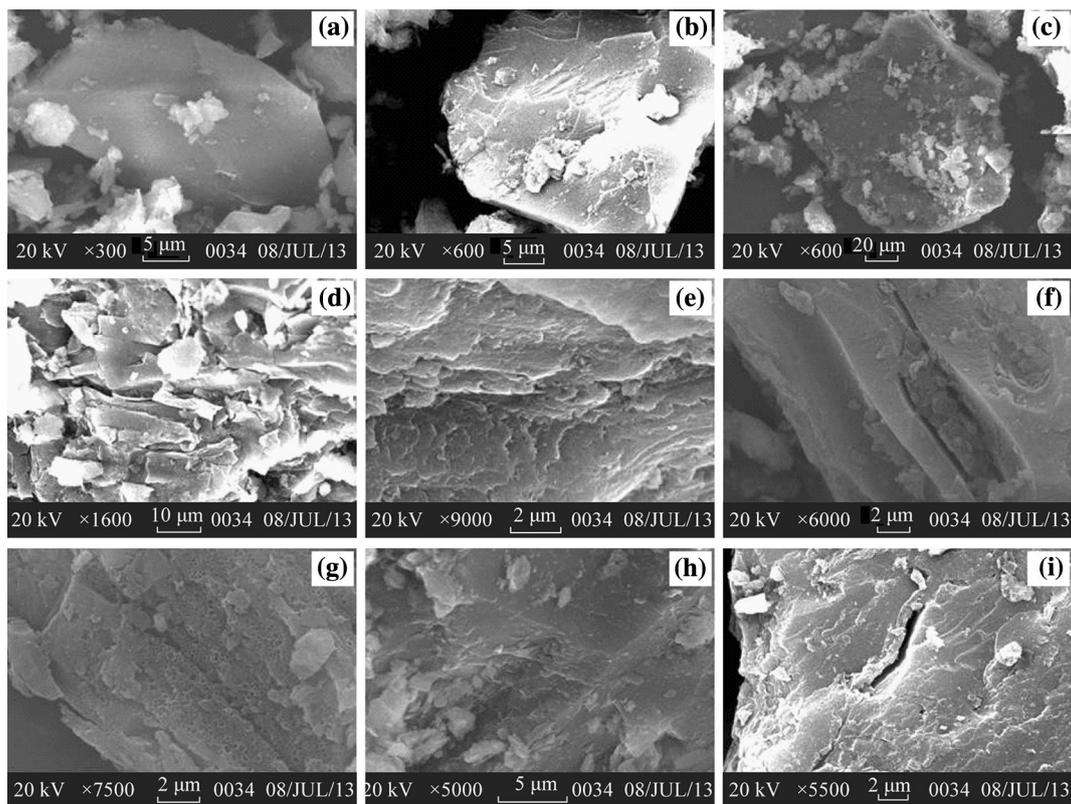
Fig. 7 SEM (SE) morphology of the raw and beneficiated coal samples (**a–c** raw coals; **d–i** IL-treated coals)
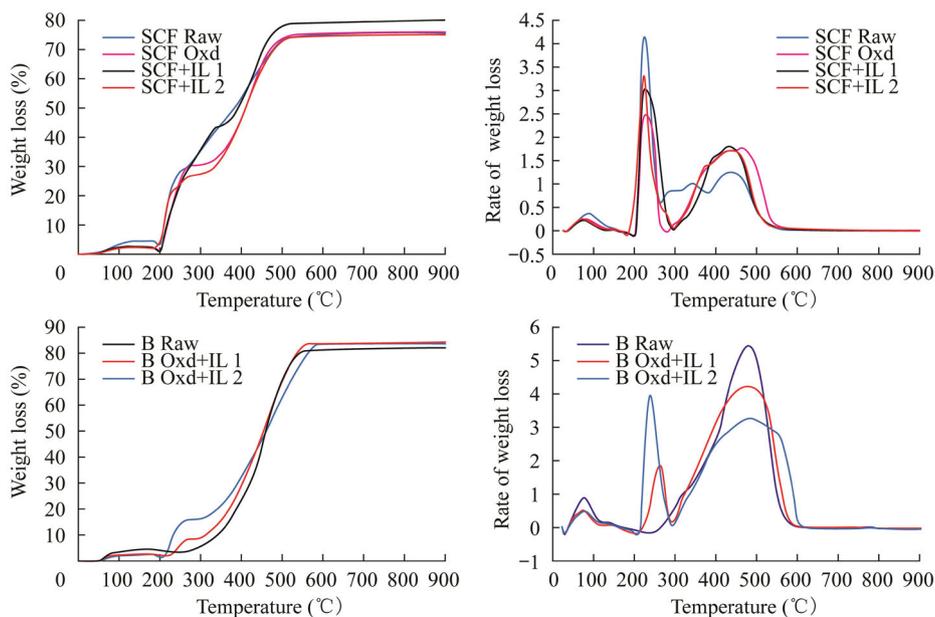
Fig. 8 TG–DTG of raw and beneficiated (B and SCF) coal samples

ignition of coal. The lower the burnout temperature, the shorter the burnout time of the coal, and the lower the combustible matter content of the ash. Thus, it is obvious that the initial ignition and burnout temperatures of coal samples not only vary with the reactants but also with the coal properties. The present partially green process can also be adopted for the development of value added products from coals.

Table 2 Combustion characteristics of coals

Coal samples	Ignition temperature (T_i)	Burnout temperature (T_h)	The combustion performance index ($S \times 10^{-7}$)	Activation energy (E_a; kJ/mol)
SCF	222.18	586.53	3.18	164.64
SCF Oxd	240.13	564.85	1.25	155.34
SCF + IL1	219.13	564.85	1.40	192.90
SCF + IL2	219.13	546.79	1.22	192.93
B	483.61	625.55	356.8	208.00
B Oxd	492.47	641.91	323.0	241.30
B Oxd + IL1	485.74	627.43	418.0	163.70
B Oxd + IL2	487.91	652.67	450.8	181.42

4 Conclusions

The ILs can be used for the beneficiation of high sulfur coals through removal all forms of sulfur including mineral matters. In the present process, ILs are able to reduce the pyritic, sulfate and organic sulfur by maximum of 62.50 %, 83.33 % and 31.63 % from Meghalya (India) coals. The FT-IR, XRF and SEM analyses support the beneficiation process through removal of sulfur components and mineral matters from the coal samples. The GCVs of the beneficiated coals are enhanced after oxidation in ILs. The process removed some of inorganic species such as Ca, Mn and Ni. The combustion performance indexes (S) and activation energies (E_a) indicate the suitability of the beneficiated coals for thermal applications. Moreover, the chemical process finds merits for industrial application as it could be carried out in mild conditions. In summary, the present green process of chemical desulfurization of coals with ILs is observed to substitute the use lethal chemicals in coal beneficiation.

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