Chapter-6

Beneficiation of Coal Using Choline Chloride and Urea-Based Deep Eutectic Solvent

6.1 Introduction

Finding high-quality coal with low ash content is one of the major problems for industries nowadays due to the high demand for coal in thermal power plants and blast furnaces all over the world (Bhoi et al., 2016; Heidrich et al., 2013). In India, the primary energy source comes from burning coal, which contributesabout 60–70% of the nation's energy requirements(Behera and Nandi, 2021). Coals are heterogeneous, complex materials consisting of organic compounds in the form of aliphatic and aromatic hydrocarbons (Ütnü et al., 2020; Zhang et al., 2018b). The occurrences of these aliphatic and aromatic hydrocarbons in coal vary with the different ranks of the coal. Coal with a high ash content, a low sulfur level, and a high mineral matter content has low strength and calorific value, resulting in enormous amounts of waste in thermal power plants. Rising demand for coke in the iron industry results in the conversion of non-coking coal to coke (Rahman et al., 2017; Rawat and Yadav, 2020). Solubility and swelling are significant for coal processing for coke ovens and iron smelting plants. The interaction of the solvent with the coal and its effects on solubility and swelling provides essential insights into coal's physical and chemical properties. Hence, it is essential to investigate the interaction of coal with the solvent and its effect on coal structures. Non-coking coals, comprise oxygen-carrying functional groups such as alcoholic, carboxylic, hydroxyl, and phenolic, and they are polar(Rahman et al., 2017; Zhang et al., 2015; Zhang et al., 2018b).The presence of these groups highly influences the physicochemical properties of coal, and they also

affect processes such as combustion and pyrolysis. These oxygen-carrying functional groups also play a significant part in lowering the carbon content and subsequently reducing their gross calorific value. These oxygen-containing functional groups can be reduced by dissolving coal in an appropriate solvent. Non-polar solvents like pyridine, toluene, and tetra-cyanoethylene are mostly used for the reduction, purification, and separation of these functional groups from coal (Bhoi et al., 2016; Mathews et al., 2015; Zhang et al., 2016). The nature of these groups is non-polar, which reduces their ability to disintegrate and swell the particles of coal constituents and creates problems for the hydrogenolysis and hydrogenation of coal particles. As the hydrogenolysis and hydrogenation processes require highly fragmented particles for coal liquefaction, various solvents frequently used for beneficiation are toxic and are not considered green solvents. Hence, it is essential to search for an alternative green solvent have characteristics such as cheap with improved efficiency to reduce phenolic, hydroxyl, and other oxygen-containing groups.

The swelling behavior of coal samples through an appropriate solvent is a familiar method to provide clues about the interaction of coal with the solvent (Bhoi et al., 2016). Nowadays, swelling experiments with green solvents have drawn more attention than the traditional toxic solvent. Ionic liquids are a new class of green solvents that are mainly used to study the swelling nature of coal (Bhoi et al., 2014; Xiao et al., 2019).Ionic liquids are combinations of organic anions and cations having a melting point of less than 100 °C. They arethermally and chemically stable with a low vapor pressure(Malolan et al., 2021; Wang et al., 2012). The ionic liquid can efficiently break the hydrogen bonding within the coal structures. Various researchers reported the interaction behavior of ionic liquid with coal samples. Painter et al. (2010) have reported the comparison between ionic liquid and other conventional

solvents. According to Hu et al**.** (2014)**,** and Sonibare et al. (2010), the ionic liquid can effectively reduce oxygen-carrying functional groups and hydrocarbons (Hu et al., 2014; Sonibare et al., 2010). Various other researchers also studied the effects of ionic liquids on coal functional groups. They reported that they could efficiently reduce the oxygen-containing functional groups responsible for lowering the spontaneous combustion of coal (Bhoi et al., 2014; Lei et al., 2013; Wang et al., 2012; Xiao et al., 2019). Hence, it can be said that ionic liquids have advantages and that there is a need for a solvent with properties like an ionic liquid but that is cheaper and easier to synthesize. Deep eutectic solvents (DES) are the best quality for this criterion. DES areprepared by combining salts, one of which is a hydrogen-bond donor (organic acid) and the other is a hydrogen-bond acceptor (ammonium salt) (Emami and Shayanfar, 2020; Malolan et al., 2021). DES arelow cost and has physicochemical properties similar to those of the ionic liquid, and can be used as a replacement for the ionic liquid. In this study, we have taken choline chloride as a hydrogen-bond donor, an ammonium salt that is easily obtained from biomass, decomposable, non-toxic, and low cost along withurea as a hydrogen-bond acceptor to synthesize DES. A simple mixing technique was used for mixing these two salts at a higher temperature, and a clean solution of DES was formed. Medium volatile bituminous, India*n* Permian coalfrom the Singrauli coalfields was taken for the study. This method also removes the problems associated with the purification of waste disposal.

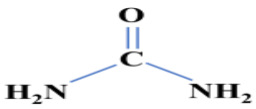
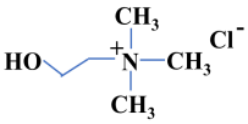
6.2 Experimental Study

6.2.1 Materials

The present study coded the samples as CS-1, CS-2, CS-3, CS-4, CS-5, and CS-6, respectively. Urea and choline chloride were purchased from Sigma-Aldrich and used

without further purification. The structures of the currently used solvents are given in Table 6.1**.** The ultimate and proximate data are given in Tables 6.3 and 6.4. This work reports the assessment of carbon content before and after coal treatment with deep eutectic solvents (DES; choline chloride, and urea) (Bhoi et al., 2016; Fatma and Banerjee, 2019).

Table 6.1. Structures of the DES used for coal treatment

Hydrogen-Bond Accepter (HA)	**Hydrogen-Bond Donor (HD)**
Urea	**Choline Chloride**
	

6.2.2 Methods

6.2.2.1 Synthesis of Deep Eutectic Solvent (DES)

For DES synthesis, the salts of choline chloride and urea were taken in 1:2 molar ratios. The salts were taken in a conical flask with a reflux condenser and heated at 80 °C with continuous stirring for 24 hours on a magnetic stirrer heating plate.

6.2.2.2 Preparation of Coal Samples

The collected coal samples (CS-1, CS-2, CS-3, CS-4, CS-5, and CS-6) were crushed and sieved using 200 mesh sizes and dried at 40 °C. Further, these samples were washed with the HCl (0.1 M) for 3 hours; then, they were washed with deionized water until we got a neutral pH. Then samples were put at 60 °C for 36 h in a vacuum oven. Vacuum dried samples were collected and further used for characterization.

6.2.2.3 Synthesis of DES Treated Coal Samples

To prepare DES-treated coal samples, 1.5 grams of coal sample were mixed with 3 ml of DES solution and placed in an oil bath at 100 °C for 4 hours. The collected solution has been cleaned with deionized water until it reaches neutral pH and kept in a vacuum oven (at 60 °C) for 36 hours, and used for characterization.

6.2.2.4 Measurement of Swelling Behavior of Coal Samples

The amount of swelling can be defined as the swelling index Q. It is taken as the ratio of final height (h_2), and the initial height of DES-treated coal samples (h_1) as given in equation (v) (Liu et al., 2015).

$$\boldsymbol{Q = \frac{h_1}{h_2}} \qquad \textbf{(v)}$$

For this measurement, the prepared coal samples were mixed with the DES solvent in 1.5 grams: 4.5 ml and kept back for centrifugation. This is the initial height of the sample and measured as h_1. After that, the samples have been put in the oil bath at 100°C for 5 hours and then left for 24 hours and again centrifugated. This is the final height h_2; the ratios of measured heights of samples are given in Table 6.2.

6.2.2.5 Extraction yield (EY) of Coal Samples

To calculate the extraction yield, DES-treated coal samples were separated from the DES solution by centrifugation and followed by washing with deionized water. The residue was collected and kept for drying at 60 °C temperature for 24 hours in a vacuum oven.

$$\boldsymbol{Extract\ yield} = \frac{\text{mass of coal smaple} - \text{mass of residue}}{\text{mass of coal sample}} \times \mathbf{100} \qquad \text{(vi)}$$

For calculating the percentage extraction yield equation (vi) have been used

(Yue et al., 2021). The value of the extracted yield tabulated in Table 6.2.

6.2.2.6 Proximate and Ultimate Analysis of Coal Samples

The proximate analysis of the coal has been carried out to understand the percentage of fixed carbon before and after DES treatment. The ultimate and proximate analysis of the coal samples has been carried out with both raw coal samples and DES-treated coal samples. Ultimate analysis was carried out via Euro EA-3000 elemental analyzer, and proximate analysis was conducted according to ASTM D 3173-3187 standards(ASTM, 1989).The proximate and ultimate analysis have been tabulated in Tables 6.3 and 6.4. For the valuation of moisture and ash present in the samples, 1 gram of coal sample was taken in a crucible. The samples were kept at 105 °C for the 1 hour and the initial and final weight of the sample was measured after heat treatment. To estimate % ash contents, a muffle furnace manufactured by ISO-TECH (Varanasi-India) was used, and samples were kept at 750 °C for 3 hours. Further, to calculate the % volatile matter (VM), the furnace temperature was set at 925 °C for 7 minutes. In all the cases, the weight of coal samples before and after heat treatment has been recorded (ASTM D3173)(ASTM, 1989; Fatma and Banerjee, 2019).

Characterization:

To understand the effects of DES on coal samples, coal samples qualitative and quantitative characterization has been carried out. The Fourier Transform Infrared Spectroscopy (FTIR) technique gives information about the various functional groups present in the coal samples and the amount and reduction of oxygen-carrying functional groups after the DES treatment. For the FTIR measurement, the KBr pellet method has been adopted. The pellet of coal samples was formed by taking coal samples and KBr in a 100:1 ratio. The measurement was performed for the 500-4000

cm^{-1} range. Further, to analyze the peak area under the FTIR, the Origin software has been used.

6.3 Results and Discussion

6.3.1 Swelling Behavior of Coal with DES

In Table 6.2**,** the swelling behavior of six different coal samples with DES has been given. It was observed that the swelling of coal samples depends on the nature of the solvent and the rank of coal samples. Various researchers reported that swelling increases the porosity of the coal samples and makes them more dispersed (Bhoi et al., 2016; Liu et al., 2015). The DES solvent can break weaker non-covalent bonds of coal and form micropores. The increase in the porosity led to the dispersal of the coal molecules (Bhoi et al., 2016; Fatma and Banerjee, 2019).They described the treatment of coal with ionic liquid and mentioned the increase in swelling and porosity obtained in these coal samples. It can be seen that swelling lies in the range of 1.12 to 1.43, given in Table 6.2.

Table 6.2: Swelling ratios and extraction yields of different coals samples

Coal Samples	**CS-1**	**CS-2**	**CS- 3**	**CS- 4**	**CS- 5**	**CS- 6**
Ratio (Q) = (h_2) /(h_1)	1.12	1.41	1.43	1.27	1.37	1.32
Extract yield	12.60	20.60	23.30	28.30	26.60	22.00

6.3.2 Extraction Yield of Coal in DES

The calculated extraction yield of the different coal samples has been estimated according to equation (vi), and the respective values are given in Table 6.2. The DES[ChCl][Urea] has a high change in density, which may lead to good interaction with the coal particle. This causes a high extraction yield of coal with DES and obtains 28.30 % for CS-4. These are higher than the values reported by Bhoi et al.

(2016). They have reported the maximum extraction yield of 27.41 % with [ChCl][Urea].

6.3.3 Proximate, Ultimate, and GCV Analysis

Tables 6.3 and 6.4 present the proximate, ultimate analysis, and GCV of the raw coal and DES-treated coal samples. The amount of ash present in raw coal samples is high, which gets reduced after treatment with the DES. With this, it can also be observed that the fixed carbon contents of the DSE treated coal samples have increased compared to the raw coal samples. This increase in fixed carbon is 4.5% for the treated coal samples. The percentage of VM in the DES-treated coal samples also shows a decrease.

Table 6.3. Proximate analysis of raw and DES-treated coal, wt%, (ad)

Sample No.	**Moisture (%)**	**VM (%)**	**Ash (%)**	**FC (%)**	**GCV**(kcal/kg)
CS-1	8.1	30.4	26.2	36.0	3243
CS-1+DES	6.5	28.3	24.3	38.1	3589
CS-2	6.0	32.8	10.3	51.2	5954
CS-2+DES	4.2	31.3	8.41	52.3	6253
CS-3	5.6	32.6	18.1	44.4	5902
CS-3+DES	3.8	30.7	16.2	45.8	6210
CS-4	8.3	27.3	26.6	39.0	3295
CS-4+DES	6.6	25.6	23.9	41.1	3458
CS-5	10.3	25.2	23.4	42.0	3693
CS-5+DES	8.2	23.1	21.2	43.9	3980
CS-6	6.3	31.8	11.7	52.0	5901
CS-6+DES	4.6	29.4	9.4	54.3	6239

Table 6.4: Ultimate analysis of raw coal and DES treated coal **,** wt%(daf)					
Sample No.	**Nitrogen (%)**	**Carbon (%)**	**Hydrogen (%)**	**Oxygen (%)**	**Sulfur (%)**
CS-1	1.32	33.7	3.71	13.1	0.92
CS-1+DES	1.89	35.7	4.62	11.9	ND*
CS-2	1.34	54.8	4.43	12.5	0.08
CS-2+DES	1.63	56.3	6.22	10.7	ND
CS-3	1.72	66.2	4.84	17.1	0.55
CS-3+DES	1.47	67.1	6.75	15.3	ND
CS-4	1.19	31.6	3.83	21.0	0.92
CS-4+DES	1.96	33.4	5.17	19.6	ND
CS-5	1.18	33.4	2.91	17.4	0.73
CS-5+DES	1.48	35.8	3.56	15.8	ND
CS-6	1.94	62.5	4.74	18.3	0.60
CS-6+DES	1.27	64.1	6.83	15.9	ND

*Not Detected

The percentage increase in GCV of treated coal is used to compare raw coal and treated coal.There is also a 4.7% increase in the gross calorific value of the DSE-treated samples. This increase in calorific value might be due to a decrease in ash yield and other hydrocarbons containing phenolic and hydroxyl groups after treatment. These analyses also correspond with the FTIR measurements. After DES treatment, a considerable reduction of oxygen-containing functional groups and an increment of carbon-containing functional groups have been observed. The result shows that the DES treatment of coal helps in utilizing low-grade coal. Hence, it can be said that this method is helpful for low-grade coal to increase its calorific values by increasing fixed carbon and reducing ash. Moreover, the reduction of ash contained might be helpful for the environment and fly ash management which is emitted during combustion (Basu et al., 2009; Behera et al., 2018)

6.3.4 FTIR Spectra of Raw and Treated CS

Figure 6.1 (a-f) represents the FTIR spectra of untreated and treated coal samples with DSE [ChCl] [Urea]. FTIR study gives information about the effect of DSE on raw coal samples by observing the effect of DES on the associated hydroxyl, alcoholic, phenolic, and carboxylic groups. It can be observed that there are several organic functional groups present in raw and treated coal samples (Behera et al., 2020; Hu et al., 2014; Nag et al., 2011; Zhang et al., 2015). All the characteristic vibrations, which are primarily present in coal, are tabulated in the Table 6.5.

Table 6.5. FTIR spectra of characteristic vibrations and functional groups present in coal

Number of Band	Position of Vibrational Band (cm^{-1})	Presence of functional groups/minerals
1.	776-730	Aromatic (-CH) group
2.	770-794	Si-O Symmetric, Quartz
3.	915	Aromatic group (-CH)
4.	1080	Quartz
5.	1030-1070	Stretching of Silicates(Si-O), asymmetric stretching vibration of Si-O-Si, vibrations of -C-O, and -C-O-R groups
6.	1380	Symmetric deformation of $-CH_2$
7.	1435	Aliphatic bending vibration of $-CH_2$ and $-CH_3$
8.	1585-1695	Aromatic (-C=C) carbonyl/carboxyl groups
9.	2848-2863	Aliphatic $-CH_3$ symmetric stretching vibration
10.	2919-2975	Aliphatic $-CH_2$ and $-CH_3$ asymmetric stretching vibration
11.	3080-3037	C-H stretching vibration
12.	3600-3200	Stretching vibration of -OH groups
13.	3625-3700	Illite / Muscovite /Kaolinite

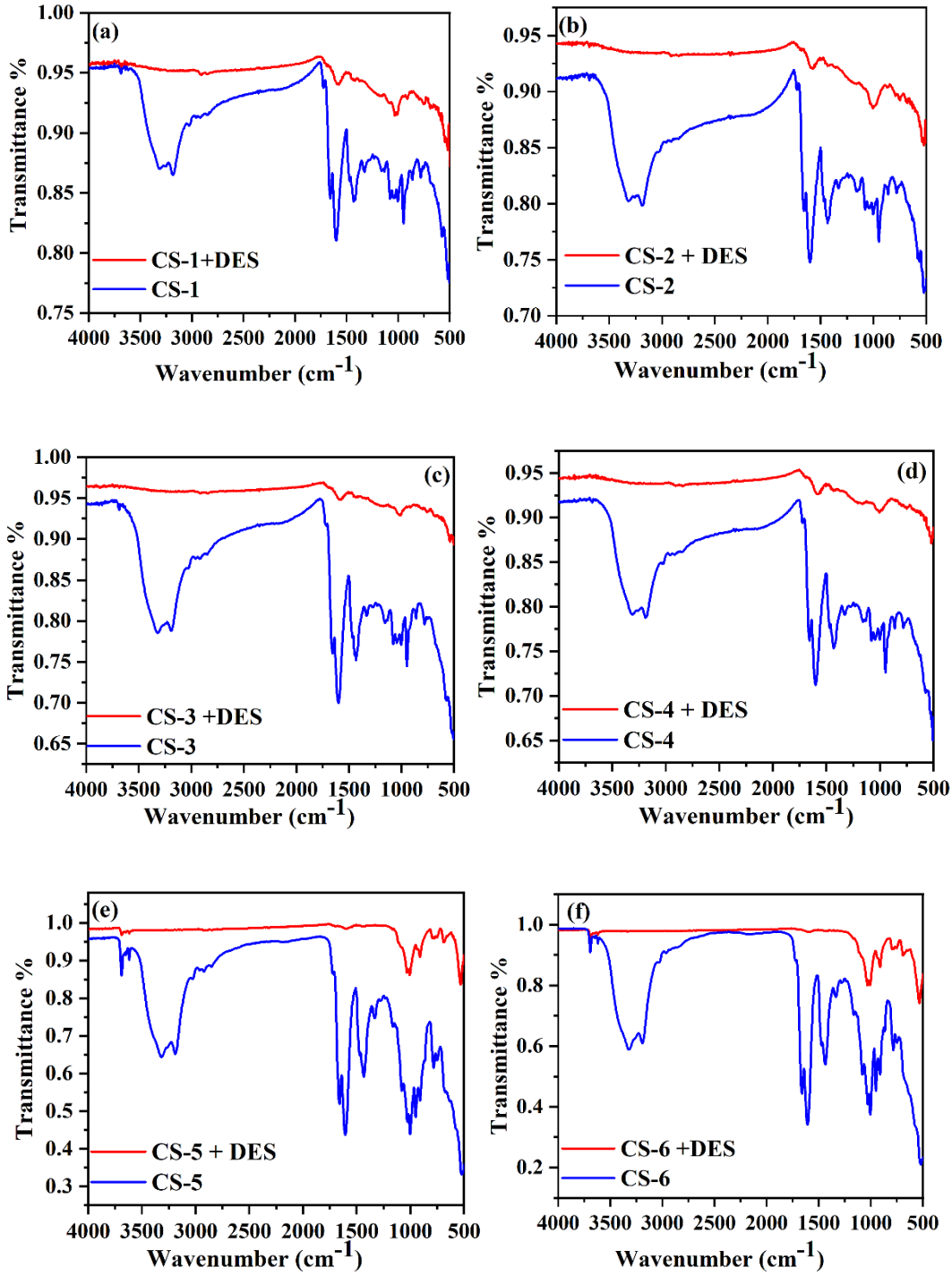


Figure 6. 1 (a-f). FTIR spectra of **(a)** Raw CS-1 and DES-treated CS-1,**(b)** Raw CS-2 and DES-treated CS-2,**(c)** Raw CS-3 and DES-treated CS-3,**(d)** Raw CS-4 and DES-treated CS-4, **(e)** Raw CS-5 and DES -treated CS-5, and **(f)** Raw CS-6 and DES-treated CS-6, respectively.

Table 6.6 Peak area of characteristic transmittance peaks of different coal samples

Classification of Peak Structure	**Aromatic Hydrocarbon Groups**			**Aliphatic Hydrocarbon Groups**				**Oxygen Containing Functional Group**		
Peak position (cm-1)	**756**	**914**	**1692**	**1327**	**1432**	**2838**	**2911**	**1025**	**1104**	**3309**
Associated Functional Groups	**- CH**	**- CH**	**- C=C**	**-CH (methyl)**	**-CH (methylene and methoxy)**	**-CH (Methyl-CH_2)**	**-CH (Methyl-CH_3)**	**-C-O-H**	**- C=O**	**-OH (hydrogen bonded hydroxyl)**
CS-1	0.65	4.09	7.92	1.76	10.06	0.51	0.31	2.7	2.76	36.9
CS-1+ DES	4.46	0.46	3.28	0.18	0.83	2.24	2.37	11.9	0.55	9.32
CS-2	0.06	3.10	6.05	1.38	8.03	0.01	0.04	2.01	1.07	26.8
CS-2+DES	2.77	11.8	1.64	0.36	1.11	0.79	0.56	18.3	1.40	13.0
CS-3	0.87	2.8	9.13	0.32	8.76	0.04	0.25	2.14	1.31	32.7
CS-3+ DES	1.75	1.74	0.97	1.79	3.42	0.73	1.05	11.2	2.51	14.2
CS-4	0.58	3.85	11.1	0.37	8.41	0.61	0.54	2.85	1.08	33.2
CS-4+DES	4.97	0.49	1.65	2.04	1.55	1.13	0.83	4.69	1.13	13.7
CS- 5	1.79	4.63	9.08	1.08	7.19	0.17	0.11	4.63	1.48	27.9
CS-5+ DES	4.71	14.7	3.19	0.83	0.98	0.29	0.35	20.12	8.12	4.04
CS-6	1.63	1.58	9.97	0.78	8.39	0.16	0.13	5.77	4.68	26.1
CS-6+ DES	4.52	11.7	0.48	0.02	0.25	0.03	0.04	22.6	8.36	3.92

6.3.4.1 Oxygen-containing Functional Groups:

FTIR characterization revealed the presence of functional groups. Functional groups are given by the position of the FTIR spectral peaks (Arenillas et al., 2004). Therefore, the peak area has been calculated using the Gaussian function peak processing method to analyze and compare treated and untreated coal samples for the quantitative analysis. This method can be used to quantify oxygen-carrying functional groups such as - OH (hydrogen-bonded phenols and alcohol). Hydroxyl group vibrations are present in the 3600–3200 cm^{-1} range in FTIR spectra (Chen et al., 2012). Figure 6. 1 (a-f) displays a characteristic transmittance peak for all (with and without DES treatment) coal samples, and the peak area corresponding to these vibrations are given in the Table 6.6**.** The hydrogen-bonded phenolic and alcoholic group vibrations are at 3309 cm^{-1} with this transmittance peak near 1025 $cm^{-1}$and 1104 cm^{-1}correspond to phenolic C-O-H and carboxylic C=O vibrational band (Wang

et al., 2012). The intensities and area of these peaks are used to quantify carboxylic and phenolic groups that appear in the untreated and treated coal samples. It can be seen from Figure 6.1 that the transmittance peak has a large peak area for the untreated coal samples, but it gets reduced after DSE treatment. The trend is observed in all the treated DES coal samples. Hence, DES treatment influences the presence of various functional groups in the coal samples. The decrease in the peak area of hydrogen-bonded alcoholic groups (-OH) is evident in Figure 6. 1 (a-f)**.** Hence, DES can reduce the effect of many oxygen-carrying functional groups. From FTIR, it has been observed that hydrogen-bonded phenols and alcohols which are present at 3304 cm^{-1} are reduced by up to 72%, 52 %, 57.%, 51.0%, 86.% % and 85 % for CS-1, CS-2, CS-3, CS-4, CS-5, and CS-6, respectively, after treatment. A similar type of reduction is also reported by the Fatma and Banerjee, (2019); and Yue et al., (2021).Further, the transmittance peak of carboxylic at 1108 cm^{-1} and for phenolic -C-OH is at 1025 cm^{-1} (Yue et al., 2021).The positions of their functional groups are unaffected by the treatment of DES. Hence, the DES does not influence the position of functional groups, but a reduction in peak intensity has been noted. Hence, both these peaks, taken for the quantification study of carboxylic and phenolic groups, appear in both coal samples. It is observed that the area of treated carboxylic groups (C=O) at 1108 cm^{-1} was higher than the raw coal samples except for CS-1. The increment in C=O group (1108 cm^{-1}peak) for CS- 2 is 30 %, CS- 3 is 47 %, CS-4 is 4%, CS- is 64 %, and CS- 6 is 61 % but for CS- 1 peak reduced to 80 %. Similarly, for the phenolic -C-O-H transmittance peak at 1025 cm^{-1}, the corresponding value is elevated for the treated coal sample compared to the raw samples. The increment is 77% CS-1, 89 % CS- 2, 80 % CS- 3, 82 % CS- 4, 77 % CS-5, and 74 % CS- 6, respectively. Hence, DES is not able to reduce the phenolic groups in coal. The

overall effect of the DES on the raw coal for the hydroxyl groups is concluded in Table 6.6. Bhoi et al. (2016) also reported the increment after treatment of coal with DES [ChCl][Urea].

6.3.4.2 Aliphatic Hydrocarbon Groups

However, the estimation of aliphatic hydrocarbon groups is not very significant, but it can be considered for extracting long-chain paraffin or olefin in the solution phases(Fatma and Banerjee, 2019). As we know, functional groups cannot be directly obtained through the shape and position of the FTIR spectra. However, peak intensity and area can be used for the quantitative analysis of the groups. The transmittance peaks at 2838 cm^{-1} and 2911 cm^{-1} correspond to stretching vibrations of-CH_3 of aliphatic groups and symmetric stretch vibrations of methyl (-CH_3) groups. However, the vibrational peaks at 1327 cm^{-1} and 1432 cm^{-1} correspond to the symmetric vibrations of the aliphatic methoxy group and asymmetric-CH_3 groups, respectively (Ibarra et al., 1996; Smook, 2007; Yue et al., 2021). From Table 6.6 and Figure 6. 1 (a-f), the reduction in these vibrational peaks after treatment of DES is less compared to the -OH (hydroxyl groups). For the CS-1, a qualitative reduction in peak 1329 cm^{-1} is CS-2 has an 89.6%, CS-2 has a 73.3%, CS-2 has a 23.2%, and CS-6 has a 74.6%. In contrast, in CS-3 and 4, the increment was up to 82 % and 81 %, respectively, for the peak of 1329 cm^{-1}. Similarly, the reduction is high for the asymmetric -CH_3 aliphatic transmittance peaks (1432 cm^{-1}), almost 97 % compared to raw coal samples. This might be because the integration of coal with DES eventually breaks a portion of the C-H bonds with other bonds. With this, a huge increment of approximately 90% observed for the symmetric stretching of -CH_3 at 2911 $cm^{-1}$and the aliphatic methyl (-CH_3) group at 2838 cm^{-1}. Hence, there is an increment in the CH_3 and CH_2 groups for all the coal samples after DES

treatment. There is a similar increments with DES treatment (Bhoi et al., 2016; Fatma and Banerjee, 2019).

6.3.4.3 Aromatic Hydrocarbon Groups:

The occurrence of aromatic structures in the coal samples can be represented by transmittance peaks of 1692 cm^{-1}, 914 cm^{-1}, and 756 cm^{-1}, respectively, given in Table 6.5(Hu et al., 2014; Rawat and Yadav, 2020; Saikia et al., 2009; Smook, 2007). Although reducing aromatic c structure is not important for the coal samples, reducing this group can reduce the GCV of the coal samples. Nevertheless, to understand the overall effect of DES on the raw coal sample, it is essential to detect the change in the peak area, intensity, and position of the transmittance peaks of aromatic structures. The aromatic ring (C=C) can be identified near 1692 cm^{-1}, and it can be seen that there is a reduction in the peak area after treatment with DES. It is 58 % for CS- 1, 72 % for CS- 2, 89 % for CS-3, 85 % for CS-4, 64% for CS-5, and 95.0% for CS-6, respectively. Similarly, for the aromatic structure (C-H) at 915 cm^{-1}, the spectral intensity decreases by 88% for CS-1, 62% for CS-3, and 87% for CS-4, respectively. Whereas it increased by 73, 71, and 86 percent for the CS-2, CS-5, and CS-6. In contrast, the presence of aromatic ring (C-H) vibrations at 780 cm^{-1} increases by 85% for CS-1, 97% for CS-2, 50% for CS-3, 88% for CS-4, 56% for CS-5, and 63% for CS-6 after DES treatment, respectively. As a result, an increase in these contents in the DSE treated coal sample implies an increase in the GCV of coal samples. Hence, DSE (choline chloride and urea) can be considered a suitable solvent for reducing hydroxyl and phenolic groups in the raw coal samples and increasing their gross calorific value. Hence, choline chloride urea-based DES is good for coal beneficiation.

6.4 Conclusion

This study reports the dissolution behavior of different coal samples with deep eutectic solvent (DES) prepared by choline chloride and urea. To understand and confirm the interaction effect of DES with coal, different characteristics such as ultimate, proximate analysis, swelling, and FTIR have been carried out. DES treatment increases the percent fixed carbon and GCV while decreasing the ash content. The swelling experiment has been carried out and shows an increase in swelling ratio of up to 1.41 with DES. This result signifies that the DES can disrupt the coal particles and might be able to reduce the oxygen-containing functional groups. FTIR confirms the presence of different oxygen-containing functional, phenolic, aromatic, and aliphatic hydrocarbon groups in the studied coal samples. Quantitative analysis of FTIR confirms DES treatment significantly reduces the oxygen-carrying functional groups by up to 80%, increases the aromatic hydrocarbon groups, and benefits the coal for use. However, DES treatment also reduces aliphatic hydrocarbon groups but cannot reduce phenolic groups. This limits the ability of DES.

Moreover, quantitative analysis, in this case, gives better results than the ionic liquid. With this, DES is a green solvent that is easy to synthesize, low cost, and useful for the increasing efficiency of coal. Hence, this method should be studied deeply to make it applicable for industrial use for coal beneficiation.