ABSTRACT

The thesis focuses on the Coal and Ionic Liquid (ILs) interaction involving both theoretical as well as experimental studies. The initial theoretical study focuses on the RexFF reactive force field (ReaxFF) simulations for the pyrolytic and combustive phenomena of untreated coal. Thereafter potential combination of IL and coal were quantified with liquid phase activity coefficients using the Continuum Solvation Model namely COSMO-RS (COnductor like Screening MOdel for Real Solvents). The acquired combinations were then dissolved with coal samples to gain physical and chemical insights in the beneficiated coal. This includes both proximate and ultimate analysis along with other pertinent physical properties such as swelling ratio and extract yield.

Chapter 1 includes a brief introduction and a literature review on combustion and pyrolysis of raw and pretreated coal. It includes an extensive search on the dispersion and dissolution studies on Indian coal. The phenomena of fragmentation and swelling of coal using various conventional as well as green solvents are then demonstrated from literature. It also discusses the importance of computational studies for the selection of appropriate solvents toward coal beneficiation technology.

The first step was to analyse the detailed structural and kinetic insights involving the coal pyrolysis and combustion. This was performed using RexFF reactive force field MD simulation studies. Chapter 2 discusses the combustion and pyrolysis analysis of three different ranks of coals (anthracite, bituminous and lignite) using ReaxFF simulations. A detailed reaction mechanism along with the numerous intermediates evolved during the course of the reaction is explained. A part of this chapter is devoted to the combustion and pyrolysis study of brown coal. To examine the pyrolysis/combustion process and initiation mechanism of brown coal, a fuel lean (ϕ=2), fuel rich (ϕ=0.5), and stoichiometric (ϕ=1) condition were used in this chapter. The temperature used was kept higher (2000-4000 K) as per experimentally reported condition so as to enable chemical reaction within a computationally affordable time. Furthermore, the combustion of other ranks of coal was also studied in the same conditions namely fuel rich, fuel lean, and stoichiometric. Some important common intermediates such as formaldehyde (HCHO) generated during the simulation reaction was found to agree well with the experimental kinetic

data reported in the literature. Regardless of the rank of coal, the gases CO and CO_2 were found to be predominant in nature. The formation rate of CO and CO_2 were found to be higher for lignite coal which agreed with the experimental trend as reported in the literature. In a similar manner, the fraction of CO and CO_2 was found to be higher in pyrolysis process. Further, a large number of principal intermediates such as methane, ethane, and ethylene were also generated for low to high rank (lignite, bituminous, and anthracite) coal. The pyrolysis and combustion processes were seen to be affected by temperature (2000-4000 K), primarily with respect to the formation of various intermediates (methane, ethane, and ethylene).

Chapter 3 discusses the computational methodology based on Continuum Solvation Model (CSM) such as COSMO-RS model for the potential cation + anion or IL selection. The study was initiated with *ab-initio* calculations on IL and pseudo coal using both Density Functional Theory (DFT) and COSMO-RS model. Taking the process economics and the nature of ionic liquids into account, 18 ILs having cations: imidazolium, pyridinium, pyrrolidinium, phosphonium, and ammonium were selected from the *Sigma-Aldrich Catalogue*. A three-tier approach comprising of HOMO (Higher Occupied Molecular Orbital)-LUMO (Lower Unoccupied Molecular Orbital) energies, quantum descriptors (Electronegativity, Electrophilicity, Global hardness, Global softness); and Infinite Dilution Activity Coefficient (IDAC) by COSMO-RS model were selected to study the simultaneous interaction of coal and IL. Initially, the model was benchmarked qualitatively using the data available in the literature for coal and conventional solvents such as pyridine and N-Methylpyrrolidone (NMP). Thereafter, Gibb's Free Energy of solvation and Solid-Liquid Equilibria (SLE) predictions were performed for these 18 ILs. The IL showing the highest solubility was chosen as a potential solvent which possess the maximum ability to disrupt the hydrogen bonding of coal molecules. 1-butyl-1-methylpyrrolidinium methyl carbonate [BMPYR][CH_3CO_3] and 1-methyl-3-propylimidazolium methyl carbonate [MPIM][CH_3CO_3] were the recommended IL's on the basis of HOMO-LUMO band energy gap. A similar trend for IL-coal interactions were followed up and confirmed by the quantum descriptors and IDAC predictions.

Once the potential IL was chosen, a validation was performed by the wet beneficiation technique using the Ionic Liquids as obtained in chapter 3. Chapter 4 hence comprises experimental studies on the dissolution and dispersion of coal with the potential cation and anion combination. The interaction between five different ionic liquids and four Indian coals from the mineral-rich eastern part of the country were carried out to identify its dissolution and swelling characteristics. Five ILs consisting of different cations namely: 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6], tributylmethylammonium methyl sulfate [TMA][$MeSO_4$], 1-butyl-1-methylpyrrolidinium methyl carbonate [BMPYR][CH_3CO_3], 1-butyl-4-methylpyridinium tetrafluoroborate [BMPY][BF_4], and tributylmethylphosponium methyl sulfate [MTBP][$MeSO_4$] were selected from Chapter 3 screening studies. Morphological studies of coal both before and after heating were carried out to determine the extent of swelling and fragmentation of coal particles. Using Fourier Transfer Infrared Spectroscopy (FTIR), the functional groups of ILs in untreated and ILs pretreated coal were identified. An overall 47.6, 55.6, and 68.1% reduction in the peak area of a hydroxyl group (phenolic and free hydroxyl radical) was observed for the ILs [BMIM][PF_6], [BMPY][BF_4], and [BMPYR][CH_3CO_3] in bituminous coal respectively. From the proximate analysis, the increase in fixed carbon content (on a weight basis) was found to be 1/3rd as compared to the raw coal. Among the ILs studied, [BMPYR][CH_3CO_3] was found to have a highest swelling ratio of 1.5. Following a similar trend, the morphological studies also concluded that the IL [BMPYR][CH_3CO_3] was the most effective in disintegrating the coal particles to micrometer size. The IL gave a total yield extraction of 27.41% (on *dry-ash-free* basis) for coal 2 (bituminous) and 35.13% (on *dry-ash-free* basis) for coal 4 (lignite).

The penultimate step was to observe the performance of mixed solvent namely IL and Pyridine. Chapter 5 focuses on the interaction of coal with three different ionic liquids (ILs) and a mixed solvent (IL + conventional solvent) for analysing the oxidizing effect on Indian Coal. The IL's used in Chapter 5 were 1-butyl-1-methylpyrrolidinium methyl carbonate [BMPYR][CH_3CO_3], 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF_6], and 1-butyl-4-methylpyridinium tetrafluoroborate [BMPY][BF_4]. They were subsequently used for dissolution studies in coal samples. The Thermogravimetric Analysis (TGA) results show that the mass loss was less for [BMPYR][CH_3CO_3] pre-treated coal as compared to coal treated with [BMPY][BF_4] and [BMIM][PF_6]. Hence the IL [BMPYR][CH_3CO_3] has the largest ability to fractionate the more active oxygen-containing functional groups present in the coal molecules. Mass loss of mixed solvent ([BMPYR][CH_3CO_3] + pyridine) treated coal was also less as compared to IL-pretreated coal. A kinetic study was also conducted using a first order, non-

isothermal kinetic method to investigate the insight into the coal structure. From the TGA scan, activation energy (E_a) and pre-exponential factor (A) were calculated. The thermal degradation study confirmed a high thermal stability (~630 ºC) for both mixed solvent and IL pre-treated coal when compared to raw coal (450 ºC). Further, the activation energy of IL pre-treated coal was also less when compared to the untreated coal.