INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
SHORT ABSTRACT OF THESIS

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SHORT ABSTRACT

Biomass has the potential to replace a large fraction of fossil fuels as feedstocks and thus capable to cater the energy, chemicals and materials requirement of mankind. In order to convert biomass into valuable products within a biorefinery approach, several processes must be applied. Fast pyrolysis, a thermo-chemical process, for liquid production is of particular interest as liquid can be stored and transported and then subsequently used for energy and chemicals production. Bio-oil is main product of fast pyrolysis but it can't be used directly for practical applications due to high oxygen content and low pH values. But at the same time, high concentration of oxygen containing compounds make bio-oil a good raw material for the isolation of valuable chemicals which are attractive in the commercial sense.

This thesis focusses on the extraction of bio-chemicals such as acetic acid, acetol and furfural from bio-oil due to its large composition in bio-oil. Accurate experimental liquid-liquid equilibria (LLE) data and reliable thermodynamic models are basic requirements for the development of optimum process design. In this thesis, these have been achieved through multicomponent Liquid-liquid Equilibria measurements and subsequent validation through multiscale strategies i.e. Excess Gibbs free energy models (NRTL/UNIQUAC), Perturbed-Chain Statistical Associating Fluid Theory (PC -SAFT) and Monte Carlo Simulation.

Solubility of bio-chemicals in aqueous phase in terms of intermolecular interaction energy using supermolecule approach was theoretically investigated. It was found that the computed interaction energy of the chosen molecules in water predicts the correct trend of the experimentally reported solubility parameters of the corresponding molecules. Thus, this approach can be used for computing the trend of distribution coefficients when experimental data are not available. Localized Molecular Orbital-Energy Decomposition Analysis (LMO -EDA) partitioned the interaction energy into its chemical origins (e.g. electrostatics, exchange-repulsion, polarization and charge transfer)

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which helped us in understanding the nature of interactions and this can be used to develop force fields for molecular simulations.

By experimental LLE measurement, ionic liquid, [BMIM][Tf2N], was found to be the best solvent for the extraction of acetic acid, furfural and acetol from aqueous solution. Liquid-liquid equilibria data for multicomponent systems were correlated by the UNIQUAC and NRTL models. The binary interaction parameters were estimated using the Cuckoo Search (CS) algorithm. CS algorithm satisfactorily predicted the LLE with high accuracy. The performance of the cuckoo search algorithm was further compared against genetic algorithm and particle swarm optimization algorithm. The comparison showed a higher efficiency for the CS algorithm in solving global optimization problems.

PC-SAFT EoS correctly predicted the LLE behaviour of polar and associating biochemical LLE ternary systems based on pure component and binary system data only. Prediction was better in mixtures where all the components were associating in nature compared to mixtures consisting of polar components. Gibbs Ensemble Monte Carlo molecular simulations in isobaric-isothermal (NPT) ensemble with Transferable Potentials for Phase Equilibria (United-Atom) and TIP4P force fields agreed favorably with the experimental data for all the systems over the entire composition range.

Reactive molecular dynamics (ReaxFF MD) simulations gave insights in understanding the reaction mechanism and product distribution for the combustion for oxygenated fuel.

In Summary, the thesis aims to study extraction based separation processes with the help of quantum chemical calculations, molecular simulations (Monte Carlo and ReaxFF MD), theoretical approaches (PC-SAFT EoS), optimization and experiments. The outcome of this research work will enhance the basic understanding of the extraction based processes.

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