Chapter 8

Summary of thesis and scope for future work

This chapter aimed to summerize the results from various aspects of torrefaction of *Acacia nilotica*, pyrolysis of torrefied *Acacia nilotica*, application of biochar from pyrolysis of DAN and TAN towads removal of aqueous methylene blue and finally the scope and recommendation of future work. This chapter has been devided into two parts: (1) summary of thesis and (2) scope for future work.

8.1 Summary of thesis

The pyrolysis of torrefied biomass and comparative study for removal of methylene blue form aqueous solution using biochar from pyrolysis of DAN and TAN as an adsorbent has been performed. The following results can be drawn from present work:

- Fuel and flow characteristics of DAN have been improved after torrefaction and are closure to the properties of coal. The higher heating value (HHV) increased by 28.2 % when DAN was torrefied at 280 ℃ for 40 min.
- Torrefied DAN was found to be less hygroscopic as moisture reabsorbed was 6.61 % (TAN280-40, 120 h) as compared to 35.44 % (DAN, 120 h). Also, the contact angle of TAN280-40 (79.1°/77.5°) was close to 90° confirming the hydrophobic nature.
- The bulk density of torrefied DAN was suitable for use as briquette and co-firing with coal in thermal plants with HR value less than 1.29 and CCI less than about 23. There was significant decrease in volatile matter (57.4 %) with simultaneous increase in fixed carbon content (~4 times). Hence, less volatile matter and high fixed carbon make torrefied *Acacia nilotica* a better solid fuel.
- TGA results showed that devolatilization temperature shifted to higher value and residual char yield increases when torrefied *Acacia nilotica* was pyrolysed.
- ICP-MS analysis revealed that torrefied biomass enriched by important elements such as sodium (Na), potassium (K), calcium (Ca), magnesium (Mg) etc. making it suitable for soil amendment.

- Compositional analysis showed that at lower temperature during torrefaction, the relative cellulose content in the torrefied biomass (TAN-220) is higher than the DAN, while, it goes on decreasing on further increase in temperature. The higher cellulose content attributed to higher activation energy of TAN-220 than DAN.
- The average activation energy of torrefied biomass obtained at 280 ℃ (TAN-280) is 42.39% lower than the DAN. Slight difference between activation energy and enthalpy favors the formation of activated complex. Accordingly, bio-energy generation through pyrolysis can be positively attained. It was noticed that at lower conversion value ($\alpha \leq 0.5$) the diffusion mechanism was rate determining for DAN and TAN-220, however, for TAN-250 and TAN-280, the 2nd order random nucleation model is dominant for rate determination. At higher conversion ($\alpha \geq 0.5$), DAN and TAN-220 follow the 2nd order random nucleation and Avrami-Erofeev models, while, in case of TAN-250 and TAN-280, 3rd order random nucleation is dominant.
- A different set of parameters were obtained in case of optimum HHV and EY of TAN individually. The optimum value of temperature, retention time and heating rate to obtain maximum value of HHV and EY combined, were 252 ℃, 60 min, and 5 ℃/min, respectively.
- It was noted that the effect of temperature on torrefaction was significant, while effect of retention time and heating rate were minimal.
- The physical and chemical properties of DAN improved due to torrefaction. For example, MC, H/C ratio and O/C ratio decreased by 73.23, 52.94 and 46.22 %, respectively; whereas FC content and HHV increased by 75.54 and 18.62 %,

respectively. FR increased by 87.39 %; whereas, CI and VI decreased by 83.32 and 22.71 %, respectively. Flow properties such as angle of repose, HR, CCI and cohesion coefficient (C) decreased by 8.04, 6.20, 22.48, and 12.5 %, respectively. Bulk, tapped and particle densities of TAN252-60-5 were decreased by 16.4, 21.62 and 7.59 %, respectively.

- Torrefaction has greatly enhanced surface defects and reduced crystallinity of biomass as revealed by SEM-EDX and XRD analysis individually.
- Torrefaction improves many properties associated with DAN, while production of solid biofuels is the prime concern. Hence, pyrolysis of TAN-252-60-5 was carried out to obtain high-quality pyrolysis oil.
- The maximum yield of pyrolysis oil (33.59 wt %) was obtained at 507.04 ℃, retention time of 58.25 min, heating rate of 38.00 ℃/min, and sweeping gas flow rate of 40.52 mL/min. Analysis of variance confirmed that pyrolysis of torrefied biomass for maximum pyrolysis oil yield highly depended on temperature followed by heating rate, retention time, and sweeping gas flow rate, respectively.
- It was observed that pyrolysis oil obtained from TAN-252-60-5 was superior in terms of improved HHV, pH, and chemical composition and lower water content, etc. total aromatic carbon, carbonyl carbon, and primary alkyl carbon of pyrolysis oil from torrefied biomass increased by 40.28, 51.36, and 6.34 %, respectively, as compared to pyrolysis oil from DAN. The phenol derivative compounds are increased by 18.91 %. The HHV and pH of pyrolysis oil from torrefied biomass increased by 23.53, 42.15 %, respectively, while water content decreased by 34.37 % as compared to pyrolysis oil from DAN.

- The FTIR analysis showed the decrease in intensity and shifting of peaks which illustrates the adsorption of MB onto both biochar.
- The BET surface area of Biochar-DAN and Biochar-TAN was found to be 80.40 and 103.47 m^2/g, respectively, and both biochar can be classified as mesoporous material. The void pores and honey comb like structure of biochar was also revealed by SEM analysis.
- The maximum adsorption capacity for Biochar-TAN was 158.13 mg/g, while, for Biochar-DAN it was 85.68 mg/g. The higher adsorption capacity of Biochar-TAN towards MB removal was due to higher surface area, pore volume and surface complexation as compared to Biochar-DAN.
- The Sips isotherm model was best fitted to the experimental results for both biochar as compared to Langmuir, Freundlich and Temkin model. This showed that Langmuir model was followed at lower concentration, while, Freundlich model was followed at higher concentration of MB.
- The kinetic study for adsorption showed that the pseudo-second-order kinetic model best described the adsorption process of MB dye onto biochar revealing that diffusion through liquid film, adsorption at surface and intra-particle diffusion might be the rate-determining step during adsorption of MB.
- Additionally, mass transfer studies revealed that both film diffusion and intra-particle diffusion was the rate determining step. The thermodynamic study showed that adsorption of MB onto biochar was endothermic and spontaneous in nature.

- Further, it was found that four kind of interaction between MB dye and adsorbent were mainly responsible for adsorption process namely, electrostatic attraction, hydrogen bonding, ion exchange and surface complexation and π- π interaction.

8.2 Scope for future work

- Catalytic pyrolysis of torrefied biomass can further increase the yield and quality of pyrolysis oil
- Co-pyrolysis of torrefied biomass with other biomass, plastic and municipal solid waste can be possible route for energy generation from waste
- Torrefied biomass can be mixed with coal in thermal power plants to reduce harmful emissions
- In place of fixed bed reactor, fluidized bed reactor can increase the yield of pyrolysis oil due to better heat transfer
- Gasification of torrefied biomass can be used to increase the production of syngas
- Biochar from pyrolysis of torrefied biomass can be used to remove other dyes and heavy metal from waste water
- The efficacy of biochar from pyrolysis of torrefied biomass can be enhanced by chemical modification