Chapter - 5

5.1. Summary

The present work was essentially motivated by the need to address the biomass as a reliable renewable energy resource to fulfill mankind's need ranging from liquid biofuels to chemicals and other products usually derived from a modern petroleum refinery. However, successful implementation of any process for biomass conversion to fuels and chemicals primarily depends upon the availability of low cost, good quality feedstock. In this regard, the present study makes an effort to investigate the prospect of potential utilization of two bio-waste viz. MFSC and PGSC, and one microalgae species *S. dimorphus* for pyrolytic valorization into products. Pyrolytic conversion offers a great promise for producing liquid as well as solid fuels for the generation of heat and energy, and value added chemicals. Physicochemical properties of biomass and their thermal degradation profile were investigated by using a thermogravimetric analyzer (TGA). Pyrolysis kinetics of biomass samples were studied by TGA analyzer in relation to heating rate and temperature using three iso-conversional model free methods. Kinetic models were implemented for calculating activation energy and frequency factor of degradation reaction. Further, the biomass samples were subjected for pyrolysis experiment in a fixed-bed tubular reactor for a certain range of temperature and heating rate under an inert atmosphere. The effect of pyrolysis temperature and heating rate on product yield was predicted by a simulation technique named Response surface methodology (RSM) based on Central composite design (CCD) matrix which was again verified experimentally. Since, the biooil has some undesirable fuel properties such as low heating value, corrosiveness, high viscosity etc. An attempt on improvement of biooil properties was carried out by using a separation technique named liquid column chromatography. Further, the biooil and their sub-fractions obtained after chromatographic separation were analyzed for different physical and chemical properties by using different chromatographic and spectroscopic technique such as FT-IR, ^{1}H NMR and GC/MS.

Finally, the solid co-product of pyrolysis process i.e. biochar obtained at different temperatures were also investigated for different physical and chemical properties in order to estimate their suitability for fuel. The prospect of utilization of solid biochar as an adsorbent was also a part of the present investigation.

From the present investigation, following conclusions could be drawn:

5.2. Conclusions

1. Moisture contents of both the seed covers viz. MFSC (3.50 wt.%) and PGSC (3.50 wt.%), and dried microalgae species *S. dimorphus* samples were found to be low which indicated their suitability as feedstocks for energy production by thermochemical conversion.
2. Thermogravimetric analysis (TGA) showed the degradation profile of the raw materials around 300 ºC onwards, which helped to determine the pyrolysis temperature range. Using thermogravimetric data, kinetic study of the biomass samples were carried out. Three model free methods, such as Friedman, FWO and KAS were tested to estimate the activation energy and frequency factor of active pyrolysis zone for all three biomass samples. These three kinetic models were found to fit with the experimental data well with no major differences.
3. It was evident that the activation energy values obtained by the Friedman method were little lower than the values of activation energies obtained by the FWO and KAS methods. These differences could be due to the approximation of the temperature integral that was used in the derivations of the relations that ground the FWO and KAS methods and because of this fact the FWO and KAS methods involve a systematic error in E_a which is not the case in the Friedman method. Thus, the activation energies obtained as a function of the conversion from the Friedman method are more reliable than those obtained from the FWO and KAS methods.
4. Optimization of liquid product yield was carried out by using a statistical tool known as Response surface methodology (RSM) base on central composite design (CCD) matrix. RSM analysis suggested that for both PGSC and MFSC biomass the maximum yield of biooil could be obtained at a temperature of 550 ºC with a heating rate of 40 ºC/min and for *S. dimorphus* the maximum yield of biooil could be obtained at a temperature of 500 ºC with a heating rate of 40 ºC/min. Based on RSM analysis the pyrolysis experiments for all the samples were carried out with a temperature increment of 40 ºC/min to the final temperature in a fixed bed tubular reactor.

5. For pyrolysis of MFSC and PGSC the selected temperature range was from 350–650 ºC, whereas for *S. dimorphus* the selected temperature range was from 300–600 ºC. Maximum biooil yields of 29.6 wt.% and 28.5 wt.% for MFSC and PGSC respectively were obtained at 550 ºC at a heating rate of 40 ºC/min. Similarly, for *S. dimorphus* the highest yield of biooil (39.6 wt.%) was obtained at a temperature of 500 ºC with a 40 ºC/min heating rate. It was observed from the experiment that thermal degradation biomass mainly occured within the temperature range of 500–550 ºC resulted in maximum decomposition of sample by producing more volatiles which in turn had major influences on the yield of liquid product. Experimentally, biooil yield were found to be 0.78 wt.%, 0.17 wt.% and 1.41 wt.% higher than the predicted values given by the RSM software for MFSC, PGSC and *S. dimorphus* respectively.
6. Effect of temperature and heating rate on the product yield was illustrated by the 3D response surface plots and contour plots as suggested by the simulation software. With increase in pyrolysis temperature, the liquid product yield was found to increase up to a temperature of 550 ºC for both MFSC and PGSC, and for *S. dimorphus* species the liquid product yield was found to increase up to 500 ºC and thereafter, the yields showed a decreasing trend on further rise in temperature. The char yield decreased and the gas product yield increased with increase in final pyrolysis temperature. Liquid product yield increased with an increase in heating rate whereas solid char yield was found to decrease at higher heating rate. Heating rate did not have any major influence on yields of gaseous product.
7. Biooil is a complex mixture of oxygenated compounds. Oxygenated compounds present in the biooil causes problem in storage and long-term stability of the oil. Among the various treatments, fractionation could be a viable process for removal of oxygenated compounds from the biooil. Using liquid column chromatography, biooil could be separated by fractionating it into individual chemical classes by using solvents of different polarity. Firstly the compounds were eluted by using a non-polar solvent, n-hexane which was further followed by toluene, ethyl-acetate and methanol. Non-polar solvent

was able to eluate the aliphatic compounds from the biooil whereas the polar solvents separated the value added chemicals from the biooil.

8. Characterization of the biooils and their respective sub-fractions were carried out by using different spectroscopic and chromatographic techniques. FTIR analysis showed the presence of various functional groups in the biooils and their corresponding sub-fractions, and the results were consistent with the findings of ^{1}H NMR and GCMS analysis. GCMS results showed that fractionation of biooils using n-hexane as eluent was composed of mainly aliphatic compounds. Mostly, three types of compounds were identified in n-hexane fractions: n-alkanes, alkenes and branched hydrocarbons.
9. Presence of higher amounts of inorganic constituents in biochar could play a significant role in soil fertility and crop production. Further, the C–sequestration potential of biochar is also noteworthy. Due to high basic nature, biochar could also be potentially used for correcting the soil acidity in the agricultural soils of north-east region of India.
10. Further, biochars were also characterized by using SEM, EDX, FTIR and XRD analysis. Surface morphology of the biochars was given by SEM analysis which confirmed the heterogeneous structure of the biochars. EDX analysis showed the presence of high percentage of carbon element in the biochar along with some other elements in trace amount. A comparison of FTIR spectrum of biochars obtained at different terminal temperatures, showed revealed a decrease in the intensity of functional groups with increase in terminal temperature. This indicated the stability of the aromatic and hetero-aromatic compounds and occurrence of a possible cyclisation within biochar produced at higher temperature. XRD analysis also revealed that the development of carbonized material increased with increase in terminal temperature of biochar.
11. Furthermore, a study was carried out to find the application of biochar in the field of waste water treatment technology. Biochar derived from MFSC, PGSC and *S. dimorphus* were found to be a potential sorbent towards the removal of heavy metal (Co-II) from aqueous solution. Both MFSC and PGSC

derived char showed ~ 25% removal efficiency whereas *S. dimorphus* derived char showed ~30% removal efficiency within 60 min.

Similarly, PGSC derived biochar showed good efficiency towards the removal of dye pollutants from the aqueous solution. The present study also investigated the removal efficiency of two cationic dyes: Methylene Blue (MB) and Rhodamine B (RB) by using PGSC biochar as an adsorbent. At 50 ppm concentration, for adsorption of MB, the optimum biochar requirement was 30g/L which showed 90% of dye adsorption capacity, and for adsorption of RB the optimum biochar requirement was 50g/L with 60% of dye adsorption capacity. Adsorption of RB by biochar however, followed Langmuir adsorption isotherm model with a regression coefficient (R^2) of 0.98 and an R_L value of 0.02. This observation suggested that adsorption of MB by biochar was a heterogeneous type of adsorption with the pores in the adsorbent and that the adsorption of RB on biochar is homogenous and in a monolayer fashion.

5.3. Future scope

Several areas of interest with significant research potential have been identified based on the work contained in the thesis. It is recommended that future research should be focused towards the following investigations:

- Extended studies on effects of other pyrolysis parameters like particle size, vapor residence time, sweep gas flow rate etc. Further, the up-gradation of biooil can be studied by using catalytic modification.
- Extended studies may be carried out in case of solid state kinetic analysis of raw biomass.
- Extended studies on adsorption behavior of activated carbon prepared from the biochars produced from PGSC, MFSC and *S. dimorphus*.