Chapter 5

Conclusions and Future Prospects

5.1. Summary

The present study makes an effort to investigate the prospect of the potential utilization of an invasive weed plant *T. diversifolia* for pyrolytic valorization into products. Pyrolytic conversion offers a great promise for producing liquid as well as solid fuels for generation of energy, and value-added chemicals. The physicochemical properties of biomass have been investigated using proximate and ultimate analysis, and their thermal degradation profile was investigated by using a thermogravimetric analyzer (TGA). Further, the biomass samples were subjected to pyrolysis in a fixed-bed tubular reactor for a certain range of temperatures, heating rate, particle size, and N_2 gas flow rate. The solid co-product of the pyrolysis process i.e. biochar obtained at different temperatures was also investigated for different physical and chemical properties in order to asses their suitability for fuel.

The effect of pyrolysis operation parameters on product yield was predicted by two different simulation techniques, viz. Response surface methodology (RSM) based on a Central composite design (CCD) matrix, and Artificial neural network (ANN). Both models were again verified experimentally and compared using statistical parameters.

On the basis of TGA data obtained, pyrolysis kinetics of biomass samples, as well as catalysts containing biomass, were studied at different heating rates using three iso-conversional model-free methods. Kinetic models were employed for calculating activation energy, frequency factor, and solid-state mechanism of degradation reaction.

Since, the bio-oil has some undesirable fuel properties such as low heating value, corrosiveness, high viscosity, etc., an attempt was made to improve the bio-oil properties by using catalysts such as ZSM-5 and metal-impregnated ZSM-5. The bio-oil obtained were analyzed for different physical and chemical properties by using different chromatographic and spectroscopic technique such as ^{1}H-NMR and GC/MS.

5.2 Conclusion

From the present investigation, the following conclusions could be drawn:

1. From the results, we can conclude that the investigation explored *T. diversifolia,* a prolific weed species of marginal economic importance, as an alternative energy source. The proximate and ultimate analysis of *T. diversifolia* indicates the

feedstock's suitability for the thermochemical conversion process. The low moisture content (6.26±0.21%), high volatile matter contents (70.25±0.36%), smaller ash content value (7.04±0.09 %) as well as lower nitrogen content (0.93%) indicate its suitability for the thermal processing such as combustion and pyrolysis.

2. Using the conventional or classical process optimization techniques, i.e. keeping one parameter constant while changing the other in the pyrolysis methods, the best conditions for optimal bio-oil production (30.16±0.09 wt.%) from *T.diversifolia* pyrolysis were found to be 500 ºC (temperature), 150 ml/min (nitrogen flow rate), 0.25-0.50 mm (particle size), and 40 ºC/min (heating rate).
3. The bio-oil exhibited a calorific value of 23.84 MJ/kg, which was greater than the biomass feedstock (15.95 MJ/kg), attributed to lower oxygen and higher carbon content of bio-oil (31.49 and 57.75 wt.%, respectively) than the original biomass feedstock (51.53 and 41.69 wt.%, respectively).
4. Physico-chemical characterization of the biochar obtained at different temperatures also reveals the potential of TD biochar as a fuel and for other applications.
5. For optimization of the process parameters for maximum liquid product yield and evaluation of the predictive capability of statistical models, two widely used techniques Response surface methodology (RSM) and Artificial neural network (ANN) have been used. Four-factor levels RSM-CCD and ANN-MLP network (LM training algorithm) with 14 neurons in hidden layer were used to develop models. Both models were statistically assessed by R^2, RMSE, SEP, MAE, and AAD. Based on these parameters it was found that the ANN was more efficient than the RSM model in predicting bio-oil yield. Better accuracy, as well as the generalization capability of ANN, was observed even after feeding some additional data. Thus, it can be established that even though RSM is the most widely used method for modeling biomass pyrolysis, ANN methodology can also satisfactorily model the pyrolysis process.
6. From the relative importance of process parameters, as calculated from the ANN model, it was observed that the pyrolysis temperature was the most significant factor for bio-oil yields followed by heating rate, nitrogen flow rate, and particle size. A similar finding was observed for the RSM model as well.
7. The assessments of thermokinetic parameters as well as the degradation model of TD pyrolysis affirm that it is a multistep thermal devolatilization process. The outcomes demonstrated that the average activation energies (Ea) for Friedman, FWO, and KAS

methods were 198.13, 196.15, and 195.54 kJ/mol, respectively. Further, the reaction chemistry of the main decomposition stage elucidated that the most probable pyrolysis kinetic model for devolatilization of the TD went through a set of order-based (F4, F3, and F2) and diffusion (D3) reactions, indicating the complex mechanism of the biomass pyrolysis.

8. From the assessment of thermodynamic parameters, the appearance of both positive as well as negative entropy change values also supports the formation of complex products from the TD pyrolysis. The values of kinetic and thermodynamic parameters provided useful information for designing a pyrolytic processing system using *T. diversifolia* as feedstock, and establishing this weed as a potential feedstock for bioenergy and biofuel generation.
9. Catalysts affect the product distribution of the pyrolysis process, and physicochemical characterization such as NMR, and GCMS analyses of bio-oil reveal improved properties when catalysts are employed, including reduced O and greater C content, and higher calorific values. This study sheds light on the potential of catalytic pyrolysis of biomass as a convenient method for upgrading bio-oil quality
10. The average activation energy values for the non-catalytic pyrolysis were evaluated within 195.54-198.13 kJ/mol, while the catalytic pyrolysis processes involving HZSM-5 zeolite, Co/ZSM-5, and Ni/ZSM-5 were assessed in the range of 151.64-154.11 kJ/mol, 107.32-111.58 kJ/mol, and 105.42-109.75 kJ/mol, respectively, indicating that catalysts play a role in providing an alternative reaction pathway or reducing the activation energy required for specific reactions, making the overall pyrolysis process more energetically favorable.
11. Thermodynamic analysis also supports the catalytic enhancement of biomass devolatilization. The associative mechanism is often associated with catalytic reactions where the availability of a catalyst facilitates the creation of intermediates or activated complexes, leading to faster and more controlled reactions. For catalytic pyrolysis, negative ΔS and higher ΔG value compared to ΔH implies that a significant portion of the heat energy supplied to the system is in excess or surplus. Thus, the catalytic pyrolysis process becomes more exothermic, and less heat is absorbed than the non-catalytic pyrolysis process.

5.3 Potential Limitations

1. **Scale-up Challenges**: While the study provides valuable insights into the bench-scale pyrolysis of *Tithonia diversifolia*, scaling up the process to industrial levels may face challenges. Issues such as maintaining uniform heat and mass transfer, reactor design, and process optimization at larger scales could impact the efficiency and feasibility of the process.

2. **Catalyst Deactivation**: The use of ZSM-5 catalysts blended with biomass in the pyrolysis process introduces several limitations. Challenges such as fouling, coke formation, and the loss of active sites during pyrolysis can reduce catalytic effectiveness. These issues may necessitate frequent regeneration or replacement of the catalyst, increasing operational complexity and costs. Additionally, the blending process itself could affect the uniformity of catalytic activity, further impacting the efficiency of the pyrolysis process.

3. **Characterization of Bio-oil**: While this study includes detailed analyses of bio-oil properties using spectroscopic techniques like NMR and GC-MS, more advanced and comprehensive characterization could provide deeper insights. Techniques such as FTICR-MS (Fourier Transform Ion Cyclotron Resonance Mass Spectrometry), TG-FTIR etc. could help identify complex compounds and improve understanding of the bio-oil's potential applications.

4. **Economic Feasibility**: The economic viability of utilizing *Tithonia diversifolia* as a bioenergy feedstock requires further investigation. Factors such as feedstock collection and transportation, processing costs, catalyst expenses, and market competitiveness of the end-products need a detailed cost-benefit analysis to assess commercial scalability.

5. **Environmental Impact**: Although the study highlights the potential environmental benefits of utilizing an invasive weed, a comprehensive environmental impact assessment is needed. Factors such as greenhouse gas emissions, water and energy usage, and waste management during the pyrolysis process should be analyzed to evaluate the sustainability of the process fully.

5.4 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 focus on following investigations:

- On the basis of the properties of the char, extended studies on the application of char in various other fields such as soil amendment, as adsorbent, as catalysts need to be caried out.
- Ex situ up-gradation bio-oil using different catalysts may also be taken up as a future study. By doing both ex-situ and in situ up-gradation, the maximum conversion of bio-oil could be found and can be compared to its up-graded properties.
- The catalyst-to-biomass ratio could be optimized along with pyrolysis temperature both in in-situ and ex-situ conditions.
- Study of techno-economical analysis of catalytic pyrolysis of biomass is another area of future study on this area.
- Evaluation of the effect of different biomass catalyst ratios in product distribution as well as the quality of pyrolysis oil (bio-oil) may also be an area of future investigation.
- Utilization of bio-oil as a chemical feedstock for the production of high-value fuel and fine chemicals needs to be studied.
- The valorization of non-condensable gas produced during the pyrolysis process for other applications may also be explored.
- Evaluation of kinetic parameters and mechanisms of pseudo-components of biomass using Fraser-Suzuki deconvolution is an area for more detailed understanding of pyrolysis kinetic reaction mechanisms.