ABSTRACT

As rapid industrialization and population growth drive up energy demands, the world community is turning its focus towards exploring alternative energy sources to combat environmental pollution. In recent years, there has been an increasing emphasis on generating energy from alternative sources like solar, wind, biomass, etc., in order to tackle various socio-economic problems such as energy shortages caused by an uneven distribution of resources and the insufficiency resulting from excessive use of fossil fuels. Biomass energy exhibits greater promise as a conventional fuel compared to other sources due to its increased abundance, feasibility, sustainability, and versatility.

Globally, biomass holds the rank of the fourth-leading primary energy source. The successful migration from petroleum to biomass-based energy requires the development and implementation of different conversion technologies. Among these technologies, thermo-chemical conversion technology like pyrolysis and gasification are highly efficient in processing a broad range of biomass feedstocks. These processes employ high temperatures to transform various components of biomass into favorable products. Among different thermochemical conversion methods, pyrolysis is the best for making biofuel (bio-oil, gas, and char), owing to its high adaptability and applicability. Bio-oil represents a renewable fuel having elevated energy density along with the advantages of transportability and storage. Biochar, a pyrolytic solid fuel, serves various purposes such as adsorption, dye removal, soil quality improvement, and catalysts. Various biomass feedstocks, including different woody forest materials and byproducts, herbaceous plant biomass, industrial residual waste, algal resources, non-native vegetation, and agricultural by-products, have already undergone pyrolysis.

Among the various biomass feedstocks, invasive plant species available in different regions are considered a threat to the biodiversity of that particular area. Adverse consequences such as damage to agricultural ecosystems, disruption of natural ecosystems, and changes in the survival of different species due to competition or predation are associated with its rapid spread into ecosystems. These unwanted species can be managed by using thermochemical conversion processes like pyrolysis, which can yield diverse products from a wide array of

biomass feedstocks. Many researchers have already conducted pyrolysis on various invasive weed species, including *Ageratum conyzoides*, *Prosopis juliflora*, *Sachharum ravanae*, *Parthenium*, algae, and various aquatic biomasses like duckweed, *Ipomea carnea*, and water hyacinth, among others. However, a vast array of underutilized weedy plants exists, holding immense potential as biofuel feedstocks if their viability is carefully assessed. *Tithonia diversifolia* (TD) or Mexican sunflower, is such an invasive weed species often seen in neglected farmlands, vacant lots, roadside areas, field margins, riverbanks, etc.

The objectives of the present study are (a) To evaluate physicochemical properties of *T. diversifolia* biomass for its suitability in a pyrolyric conversion process; (b) To investigate the effect of operating conditions on the pyrolysis of *T. diversifolia*; (c) To compare the artificial neural network (ANN) and response surface methodology (RSM) for evaluation of the predictive capability of bio-oil yield; (d) To investigate the kinetics, reaction mechanism, and thermodynamics of *T. diversifolia* pyrolysis; and (e) To determine the effect of catalysts on the pyrolytic conversion of biomass by elucidating the kinetics, thermodynamics, and mechanisms of the catalytic pyrolysis process..

The present thesis mainly consisting of five chapters viz., Introduction, Review of literature, Materials and methods, Results and discussion and finally Conclusions and Future prospects.

The introduction chapter (1st Chapter) deals with the need for renewable energy and importance of biomass as a source of renewable energy. A discussion on the generation of biowaste and its management with special emphasis on weed biowaste has been also included. In this backdrop, pyrolytic valorization of biomass and different products of pyrolysis is discussed briefly. The chapter also includes a brief idea about modelling and optimization of pyrolysis process as well as the importance of kinetics and thermodynamic study in biomass pyrolysis.

In the literature review chapter (2nd Chapter), different types of waste biomass feedstock used in pyrolysis process and different parameters that affect the non-catalytic as well as catalytic pyrolysis process are discussed. It is observed from the study that pyrolysis process can utilize almost all types of biomass feedstock to produce end products. However the product distribution and quality of bio-oil varies depending upon the type of feedstock and the pyrolysis reaction process parameters. The influencing parameter include temperature, rate of biomass heating, vapour residence time and biomass composition, particle size, sweeping gas flow rates, etc. Many studies have examined the effect of these operating factors on pyrolysis using various biomass samples via conventional methods. Specifically, they explore how certain parameters influence the product yield while keeping the other process parameters constant. However, this classical approach has some limitations, such as the lack of integration of the interaction effect between the process parameters and the large number of experiments. In addition to that, the classical way is a time-consuming and expensive approach to achieving optimal conditions. Hence, to overcome these limitations, mathematical modeling is considered an important tool for gathering knowledge on the significance of the factors affecting pyrolyser performance. Response surface methodology (RSM) and artificial neural network (ANN) are often employed techniques for modeling and optimizing process parameters. Both of these options possess several benefits and drawbacks. A few researchers have studied the modelling and optimization of biomass pyrolysis process for bio-oil and biochar production using RSM techniques. However, literature on utilization of ANN modelling in biomass pyrolysis is very less. Also, state of art review of pyrolysis of lignocellulosic biomass including different weed species have been discussed. Although biomass pyrolytic liquid holds promise as an energy source and commodity chemical feedstock, it poses challenges as a low-grade fuel due to properties like corrosiveness, high density, acidity, high oxygen content, high water content, and instability that make it unsuitable as a direct fuel source. Advanced technologies (e.g., hydrogenation, catalytic pyrolysis, catalytic cracking, emulsification) are essential to reduce oxygen content in bio-oil and enhance its quality. In recent times, catalytic pyrolysis has gained attention for improving bio-oil quality through several reactions like cracking, decarbonylation, decarboxylation, and deoxygenation. The catalytic pyrolysis is operable at atmospheric pressure and hence cost-effective; it catalytically improves the kinetics, reduces tar formation, and increases product yields. Zeolites, among various catalysts, stand out due to their abundance, cost-effectiveness, and tunability. Over the past three decades, zeolites, particularly ZSM-5, have proven to be preeminent catalysts, efficiently converting carbohydrates into aromatics and olefins, influencing oxygen reduction in pyrolytic vapors, and enhancing the carbon-to-oxygen ratio. Research conducted on applications of these catalysts in biomass pyrolysis have been discussed here. Kinetic parameters (such as activation energy, and pre-exponential factor) and thermodynamic parameters obtained from various methods aid in optimizing biofuel production processes as well as in determining the nature of the pyrolysis process in terms of energy requirements and energy balance. A discussion on the kinetics, reaction mechanism, and thermodynamics studies of biomass pyrolysis and catalytic pyrolysis have been discussed. The chapter also includes justification of present investigation followed by the research objectives defined for the current investigation.

The third chapter, titled "Materials and Methods", provides a detailed explanation of the research methodology used in this study. This chapter focuses on the specific procedures employed to conduct all the experiments in the current study. The experimental and characterization approaches used for analyzing the feedstocks and products, such as bio-oil, biochar, and catalyst, are reviewed.

The feedstock used in this investigation, *T. diversifolia* is a highly competitive invader, that can thrive in new habitats due to its ability for heat and drought tolerance, rapid growth, prolific seed production capacity, easy dispersibility by wind, water, and animals. Once established, it forms dense stands that can out-compete native vegetation, hindering the growth of local plant species and potentially impacting medicinal resources due to allelochemicals in its leaves.

The "Results and Discussion" has been divided into four sub-sections.

The first part of this chapter focuses on biomass characterization, encompassing physicochemical and biochemical analyses to check the potentiality for sustainable energy, as well as biomaterials and chemical production. It also delves into the effect of operating conditions on product distribution in biomass pyrolysis. Temperatures ranging from 400 to 600 ºC were used for performing pyrolysis under different operating conditions. The production of bio-oil was found to increase until temperatures reached 500 °C; after that, it began to decline upon further temperature increases. The best conditions for optimal bio-oil production of 30.16±0.09 wt.% were found at 500 ºC (temperature), 150 ml/min (nitrogen flow rate), 0.25-0.50 mm (particle size), and 40 ºC/min (heating rate). Furthermore, the bio-oil exhibited a calorific value of 25.84 MJ/kg, which was greater than the biomass feedstock (15.95 MJ/kg), and this enhancement could be attributed to the lower oxygen and higher carbon content of the bio-oil (31.49 and 57.75 wt%, respectively) than the original biomass feedstock (51.53 and

41.69 wt%, respectively). The physicochemical characterization of biochars was also performed to evaluate their potential as a fuel and for other applications.

This chapter compares artificial neural networks (ANN) and response surface methodology (RSM) to determine the bio-oil yield from biomass pyrolysis. A four-factor, five-level RSM-CCD and ANN-MLP network (LM training algorithm) with 14 neurons in the hidden layer was used to develop models. Both models were compared for their predictive abilities in the pyrolysis of biomass in the present study. Both models were statistically assessed by R^2, RMSE, SEP, MAE, and AAD. These parameters revealed that the ANN outperformed the RSM model in predicting bio-oil yield. Better accuracy, as well as 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, the ANN methodology can also satisfactorily model the pyrolysis process. 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.

The third part of the 'Results and Discussion' investigates the reaction kinetics, mechanisms, and thermodynamics of biomass pyrolysis. The assessments of thermo-kinetic and thermodynamic 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 (E_a) for Friedman, FWO, and KAS methods were 198.13, 196.15, and 195.54 kJ mol^{-1}, 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. 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 parameters provided useful information for designing a pyrolytic processing system using *Tithonia diversifolia* as a feedstock, and establishing this weed as a potential feedstock for bioenergy and biofuel generation. Sestak-Berggren combined kinetic model (CK model) results reveal that the single-step pyrolysis of biomass can be described by $f(\alpha) = (1-\alpha)^{1.1585}\alpha^{-3.02}[-\ln(1-\alpha)]^{0.80}$.The activation energies and

Arrhenius constants predicted from CK models are almost equal to the value predicted by isoconversional methods.

The fourth part explores the influence of catalysts on biomass pyrolysis, presenting the experimental results as well as their effect on kinetics, mechanisms, and thermodynamics. Different catalysts affect the product distribution of the pyrolysis process, and physicochemical characterization 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. The mean 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. Thermodynamic analysis also supports the catalytic enhancement of biomass devolatilization. This investigation offers valuable insights into ZSM-5 catalysts' pivotal role in thermo-chemical biomass conversion.

Along with these chapters, the thesis has the last chapter on 'Conclusions and Future prospects', which discusses the summary drawn out from all the respective experiments along with the prospects of the research.