Pyrolysis of Agricultural and Industrial Waste Biomasses into Cleaner Fuels and Value Added Products

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by

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Chapter 10

Conclusions and Recommendations for Future Study

10. Conclusions and Recommendations for Future Study

This chapter summarizes the major conclusions of the present work and future scope of investigation.

10.1 Conclusions

Increasing environmental pollution and related global issues like climate change and global warming coupled with rising cost and finite availability of fossil fuels confined primarily in the politically unstable regions of the world have provided impetus to look for alternative, less polluting and sustainable energy resources. Various carbonaceous wastes such as agricultural residues, municipal solid waste and industrial wastes are being considered as almost carbon neutral and sustainable renewable energy resources. Out of these, lignocellulosic biomass from various sources is being considered as potential substitute for conventional fossil fuels (coal, gas and liquid petro-fuels). Their global availability and renewable nature makes them attractive over other renewable energy sources on several counts. In view of this global efforts are being made to use these as feedstock for producing cleaner fuels and other value added products through biochemical and/or thermo-chemical conversion routes. For a country like India their potential is enormous but still underutilized. In this work lingo-cellulosic biomasses such as wheat straw (WS), rice straw (RS), banana trunk (BT), rice husk (RH) arhar stalk (AS), sugar cane bagasse (SB), sugar cane leaves (SCL), peanut shell (PS) and paper mill waste (PMW) were used as the target biomasses. The thermogravimetric analyses of nine biomasses studied in this work showed more or less similar TGA curve profiles, but exhibited difference in the degradation temperature range and residual mass values. Degradation profile of all nine biomasses showed that the maximum weight loss was observed between temperature ranges 200 –500°C. The results demonstrate that each type of biomass has a specific degradation rate which depends on its cellulose, hemicellulose, and lignin contents. The FTIR spectra of all biomasses indicated the presence of alcoholic and phenolic groups, alkanes and alkenes and some aromatic molecules were present in all biomasses. During thermal degradation, maximum weight loss was recorded within the temperature range of 200–500°C in all cases.

Thermal degradation kinetics of sugar cane leaves has been investigated using TGA/DTA. The model-free methods are better than the regression analysis method in representing the thermal degradation kinetics. The Vyazovkin AIC model-free method has been found to be better compared to other models. The activation energy has been found to vary with conversion indicating the complex multi-step nature of the thermal degradation kinetics. For conversion values below 0.2 the thermal degradation process is controlled by the nucleation and growth mechanisms and the reaction follows between 1.04 and 1.41 order kinetics. The higher yield of liquid product was found to be 44.78wt% at temperature of 550^{o}C, heating rate 25^{o}C/min. bed height of 16cm and particle size in the range of 0.300-0.180mm. Product distribution demonstrated that the liquid yield was increases up to 550^{o}C and decreases after that on the other hand the gaseous products yield raises and bio-char yield reduces continuously with increase in temperature. It was noted that the liquid yield increases with heating rate and maximum at 25^{o}C/min thereafter decreased while biochar decreases continuously. The yield of liquid product was also increases with increases in bed height while decreases with increase in the range of particle size. Characterization of liquid product and their different properties indicated that it can be useful for fuel and various value added chemicals after necessary refining and up gradation. As a solid fuel and a precedent for activated carbon, biochar may also be used. It also assists in increasing crop production through the neutralization of soil acidity. The present study concludes that SCL is a strong potential source of renewable energy for pyrolysis; if all the pyrolysis products are used competently.

The banana trunk (or pseudo-stem) biomass is likely to be a reasonably good fuel. Its higher heating value (HHV) is 12.7 MJ/kg that is very close to that of the biomasses from other parts of banana including banana fruit peels (13.41 to 17.20MJ/kg). Pyrolysis of banana trunk takes place in four distinct sages that depend upon the heating rate with maximum weight loss occurring in the second stage. The activation energy increases with conversion (α) irrespective of the iso-conversional model used. The small difference between activation energy and change in enthalpy (≈ 5 kJ/mol) indicates feasibility of pyrolysis. The pyrolysis follows the nucleation, growth and phase boundary mechanism.

The thermo-chemical characteristics and pyrolytic behaviour of peanut shell indicate it to be good feedstock for energy and chemicals. The kinetic analysis of TGA/DTG-temperature data using six iso-conversional models indicate that the lowest average activation energy (186 kJ/mol) is obtained by the Vyazovkin model and maximum (226.97 kJ/mol) by the KAS model. The enthalpy change is found to be very close to the activation energy for all six models which indicating the feasibility of the pyrolysis for energy generation. The optimization of pyrolysis process using Box-Behenken design resulted in a second order model equation and the optimum temperature of 650^{o}C, nitrogen flow rate of 100ml/min and heating rate of 20^{o}C/min for obtaining maximum bio-oil and bio-char yields. There is an excellent agreement between experimental and predicted yields. The FTIR, GCMS and ^{H}NMR techniques have indicated that 2-furanmethanol, phenol, 2-methoxy-Creosol, phenol, 4-ethyl-2-methoxy- etc. is the major components of the bio-oil. The product bio-char is highly porous and has high carbon content and heating value indicating its use as soil conditioner, biocatalysts and adsorbent in waste water treatment.

The paper mill waste is a suitable industrial waste biomass for use as fuel. Its pyrolysis in presence of a solid catalytic material like Montmorillonite clay has a positive effect on its thermal degradation behaviour and related kinetic and thermodynamic parameters. Presence of catalyst resulted in reduced residual weight at each heating rate. The rate of thermal degradation increased significantly in presence of clay. The activation energy also decreased using all the models. The FWO model gave the lowest activation energy for both catalytic (PMW + clay) and non-catalytic (PMW) pyrolysis. Remarkable changes were observed in experimental curve of Z-master plot depicting the reaction mechanism.

10.2. Recommendations for Further Study

- Though several models (both iso-conversional and non-iso-conversional) are reported and used for analysing the kinetic data, it would however be appropriate to carry out a thorough comparative study of various models and to recommend the most efficient one out of these or if required an attempt should be made to come out with a new model incorporating the best features of available models.
- From the results presented and discussed in previous chapters it is clear that out of various Indian agro-waste biomasses, sugar cane leaves, banana trunk and peanut shell have no use as fodder hence could be good feedstock for pyrolysis and obtaining value added products. This will require pyrolysis studies using pilot scale units to generate information related to the optimal size of biomass particles and their feed rate, residence time, optimal heating rate, optimal

temperature range, and sweep gas flow rate and nature for the design and scale up of new and efficient pyrolyser.

- As the product bio-oil is a complex mixture of several compounds it would be useful to develop appropriate treatment processes to make it suitable for blending with diesel and fuel oil as well as separate the components having low fuel value but are suitable for other applications.
- Study of the effect of pre-treatment of biomass on its thermal degradation behaviour would be useful for obtaining basic information on the possible changes in the chemical composition of bio-char and bio-oil.
- All biomasses have inherent metallic salts that get converted to oxides/mixed oxides having catalytic properties and are likely to affect the pyrolysis process and product quality and quantity. Thus it would be interesting to study the effect of eco-friendly heterogeneous catalysts on the biomass pyrolysis for improving the product yield.