
Abstract

In the present study, two different types of biomass materials (agricultural residue like pigeon pea stalk and commercial farm wood such as eucalyptus) have been used for the possible generalization of torrefaction and pyrolysis of torrefied biomass on other different biomass materials for the enhancement of bio-fuel properties through pre-treatment process. The research work mainly focuses on torrefaction of these biomass materials and thereafter pyrolysis leading to the drastic improvement bio-fuel properties in sharp contrast to the pyrolysis of raw biomass and co-combustion with coal. The present scope of research work also covers the optimization and the statistical analysis for both torrefaction and pyrolysis process using response surface methodology (RSM). The present study includes the energy and the exergy aspects of torrefaction and pyrolysis process in order to improve the existing process by introducing energy recuperation from byproducts, and thus decreasing the energy consumption and helping in achieving an energy efficient process for obtaining high grade bio-fuels from biomass.

Torrefaction of pigeon pea stalk and eucalyptus have been carried out in a quartz tube reactor. For the torrefaction process, temperature (X_1) varied from 200-300 °C; residence time (X_2) varied from 0-60 min, and heating rate (X_3) varied from 5-20 °C/min. Based on the statistical analysis, for both biomass materials, the impact of operating parameters on responses (HHV and energy yield) have been found as $X_1 > X_2 > X_3$. Based on ANOVA and validation of optimum condition, it can be attributed that reduced quadratic models for HHV and energy yield of torrefied pigeon pea stalk and eucalyptus have been efficient to

operate in the design space. The optimum torrefaction condition for pigeon pea stalk and eucalyptus have been obtained at 248 °C, and 253 °C, respectively, with residence time at 60 min, and heating rate at 20 °C/min. Maximum increase in HHV for torrefied pigeon pea stalk and eucalyptus have been 43.53 and 39.49 %, respectively, as compared to their raw biomass. The solid fuel properties like HHV, FR, CI, and VI have been improved for the torrefied biomass, making it compatible with the existing coal based power plants available in South Asian and African countries. FTIR results confirmed the removal of oxygen containing functional groups in pigeon pea stalk and its extent increased with severity of torrefaction. XRD analysis showed a decrease in crystallinity index for torrefied biomass as compared to raw biomass. SEM micrographs indicated increase in porosity and generation of cracks for torrefied biomass. HHV and water content of liquid product have been in the range of 6.91-11.94 MJ/kg and 50.2-84.3 wt%, respectively. GC-MS results suggested the high presence of phenol and furan derivatives with acetic acid and ketones derivatives being on the lower side. Kinetic parameters revealed that the total activation energy decreased by 54.4 % and 45 % for eucalyptus and pigeon pea stalk, respectively, at the most severe torrefaction condition as compared to their respective raw biomass.

Pyrolysis have been performed for the torrefied biomass obtained at the optimum condition. Statistical analysis revealed that impact of operating parameters on bio-oil yield (BY) for both types of biomass has been $X_1 > X_3 > X_2 > X_4$ (where X_4 denotes nitrogen sweeping rate). Based on maximum bio-oil yield (BY), the optimum conditions have been obtained at 461 °C, 1 min, 42.3 °C/min, and 73 ml/min for pigeon pea stalk and at 442 °C, 0 min, 55.4 °C/min, and 42 ml/min for eucalyptus. On comparing the BY obtained from

torrefied to that of raw biomass at the same condition revealed that BY has been decreased substantially. However, the fuel properties of bio-oil obtained from the pyrolysis of torrefied biomass have been significantly improved as compared to bio-oil obtained from raw biomass. Both elemental and FTIR analysis confirmed that oxygen content in the bio-oil from pyrolysis of torrefied biomass decreased significantly.

In torrefaction process energy and exergy values of solid products have been decreased, whereas for non-condensable gases (NCG) and liquid, these values have increased with increase in temperature. Energy and exergy values of solid have been the highest followed by liquid and then NCG. CO has been the main contributor in the total energy and exergy of NCG. Exergy efficiency of solid product has been in the range of 52 to 54% under moderate torrefaction. Irreversibility has been found to be increased with increase in temperature. Recuperation of energy from byproducts (liquid and NCG) could increase the energy recovery in solid by 8 to 9 %. The present study shows that the moderate torrefaction condition for biomass seems to be the most promising condition in achieving a balance between overall efficiency and desired physicochemical properties. During the energy and exergy analysis for the pyrolysis of torrefied biomass there was a significant increase in the chemical energy of CH₄ which confirmed the quality enhancement of pyrolytic gas on using torrefied biomass as a feed. Similarly the energy or exergy value of bio-char from torrefied biomass also witnessed a sharp increase in its value. However, on analyzing the energy-exergy value of bio-oil there was a decrease in its value for the torrefied biomass as compared to raw biomass feed but considering the yield of bio-oil the quality of bio-oil increased significantly in terms of HHV.