Abstract

The mitigation of CO_2 emission from energy sector is possible through the switching over from high carbon to low carbon fuels. The use of low-carbon renewable and sustainable biofuels, derived from waste biomass can serve the purpose of reaching the current energy targets along with reduction of CO_2 emissions. Transformation of biomass to bioenergy is traditionally conducted by employing different thermochemical (gasification, pyrolysis, torrefaction and hydrothermal liquefaction) and biochemical (fermentation and anaerobic digestion) processes or through their integration, e.g., syngas fermentation. Commercialization of bioethanol production from lignocellulosic biomass is one of the important areas under rigorous research and development to support the national ethanol blend-in targets of India. Under Ethanol Blending Program (EBP20) by 2025, pan India has to reduce crude import dependence and support "Atmanirbhar Bharat" and "Make in India" initiatives. Lignocellulosic biomass can be converted to ethanol either through sugar or syngas platform. Considering the necessity of energy transition to address the issue of CO_2 emission in India and the abundance of agricultural lignocelluloses biomass the thrust areas of the present research are: I) conversion of Indian agro-biomass to ethanol via sugar platform with possible analysis of each step along with kinetic analysis, mathematical modeling and optimization; II) conversion of Indian agro-biomass to ethanol via syngas platform with possible analysis of each step along with kinetic analysis, mathematical modeling and optimization; III) conversion of Indian agro-biomass through HTL and co-HTL and introspective analysis along with kinetic studies and optimization; IV) conversion of Indian agro-biomass through torrefaction with kinetic studies and product characterization

Pretreatment processes play the key role when lignocellulosic biomass has to be converted to biofuels through sugar. The release of fermentable sugars is the pre-condition for the conversion of lignocellulosic biomass (LCB) to biofuels via heterotrophic microorganisms. A cylindrical stainless steel reactor of 60 mm inner diameter and 150 mm height was used for the investigation of pretreatment of rice straw in batch mode. In the present study, 10 g rice straw was subjected to 100 mL of 0.1 M ferric chloride solution or 0.1 M sulfuric acid or water under isothermal condition at the temperature of 140, 150, 160, 170 and 180°C for 10 minutes respectively. Experiments were also conducted with $FeCl_3$ concentration of 0.15M and 0.2M. The enzymatic hydrolysis of pretreated solid is conducted in presence of enzyme. The glucose produced from enzymatic hydrolysis, is converted to bio-ethanol via fermentation using microorganism.

The salient findings of the present research (under sugar platform: pretreatment of rice straw followed by enzymatic hydrolysis and ethanol fermentation) are: (a) The analysis of hydrolysate and the pretreated solid clearly indicate the most efficient action of ferric chloride pretreatment (FCP) in comparison to acid pretreatment in the present range of temperature; (b) The maximum yield (g of product/ kg of rice straw) of glucose, xylose, furfural, 5-HMF, formic acid, acetic acid and levulinic acid have been determined as 93.1, 145.0, 52.5, 9.4, 7.4, 17.0 and 5.67 from 0.1 M ferric chloride treatment of rice straw at 180^{o}C for 10 minutes respectively; (c) The degradation rate constants of xylan and glucose for rice straw for liquid water pretreatment (LWP), sulfuric acid pretreatment (SAP) and FCP have been compared for the first time; (d) The glucose yields after 72 hours of enzymatic hydrolysis of untreated RS and pretreated solids (obtained from LWP, SAP and FCP) are determined as 27.9%, 32.3%, 45.4% and 78.9% respectively; (e) A deterministic mathematical model for conversion of xylan and cellulose into xylose and glucose (and valuable products) for ferric chloride pretreatment (0.2 M) of Indian rice straw has also been developed and validated for the first time; (f) A deterministic mathematical model for enzymatic hydrolysis has also been developed; (g) The effect of combined severity and enzyme loading on the yield of glucose have been investigated; (h) The yields of ethanol (kg ethanol / kg of rice straw) through LWP, SAP and FCP (0.1M $FeCl_3$) pretreatment of rice straw have been measured as 0.0444, 0.0609 and 0.0899 respectively. 0.0851 kg ethanol has been produced from 1 kg of rice straw when 0.2M $FeCl_3$ solution has been used for pretreatment; (i) The outcomes of this study would be quite worthwhile and can be used in scaling up of hydronium ion-driven pretreatment of LCB for the production of bio-fuels and bio-chemicals.

The syngas fermentation is a hybrid process through which syngas, mainly constituted of CO and H_2, is generated from lignocellulosic biomass in the first step, and subsequently the gas is fermented to bioethanol in the second step. The pyrolysis of rice straw was carried out in a semi-batch reactor (35 mm diameter and 210 mm long) under isothermal condition at the temperature of 400, 450, 500, 550, 600, 650 and 700 ^{o}C in an inert atmosphere maintained by nitrogen. The reactor equipped with furnace, temperature controller (PID controller) and digital weight box. Rice straw was pyrolysed at a rate of 10g/hand nitrogen flow rate was maintained at 2.5g/h, i.e., .The nitrogen flow rate was maintained at value so that sufficient time is available for the reaction of higher molecular weight volatile compounds to form gaseous compounds. Experiments were conducted in a 3L glass bioreactor of 135mm diameter and 235mm height equipped with two

50mmRushton gas dispersion impellers, each with six flat blades mounted vertically around a central horizontal disc and gas sparger. The impellers were spaced at a distance of 60mm. The lower impeller is situated 30mm above the bottom. The bioreactor was provided with inlet and outlet lines for both gas and liquid streams. The main gas sparger, connected with the gas outlet was located in between the lower impeller and the bottom of the bioreactor.

The salient findings of ethanol production from rice straw through syngas platform are: (a) Deterministic mathematical models along with experimental data on the bioconversion of pyro-syngas to ethanol and acetic acid in a gas-sparged stirred tank reactor, operated in semi-batch and continuous modes, have been reported for the first time; (b) The locally isolated clostridial consortium *UACJUChE1* was proved to be capable of utilizing CO, CO_2, and H_2 present in the pyro-syngas; (c) The mathematical models have been validated through the comparison of the predictions with the experimental results; (d) The optimization of the performance of the semi-batch and continuous modes of operation was achieved using response surface methodology; (e) The optimum level of the independent variables, pyrolysis temperature, V_G/V_L, and q_G giving the maximum ethanol concentration (=13.122 g/L) after 30 h of semi-batch operation are 648 °C, 0.46, and 6.7 L/h, respectively; (f) The optimum level of the independent variables, V_G/V_L and $q_{G/}q_L$, giving the maximum ethanol concentration (=29.450 g/L) after 300 h of continuous operation are 0.28 and 336.148**,** respectively; (g) Since pyrolysis is used as the precursor process for syngas fermentation, other valuables products like pyro-oil and pyro-char are also generated, and the criterion of zero-waste generation for the circular economy concept is fulfilled; (h) The outcome of this research study can also be useful for the utilization of other lignocellulosic agro-wastes of Indian and other origins.

Lignocellulosic biomass (LCB) can be converted into four fractions namely, hydrochar, bio-oil, aqueous and gaseous phase products during hydrothermal liquefaction (HTL) in the temperature range of 200-400 ^oC. In HTL pretreatment method, the lignocellulosic feedstocks are easily hydrolyzed to sugar molecules (poly-, oligo and mono-saccharides) which are subsequently converted to cyclic ketones, phenols etc. via isomerization step. Some alcohols, aldehydes for instance, are also formed particularly during the decomposition of lignin. A part of xylan and glucan in biomass are also converted into small organic compounds, obtained in aqueous phase. The gases namely, carbon mono-oxide (CO), carbon di-oxide (CO_2), hydrogen (H_2), methane (CH_4), nitrogen (N_2) and ethane (C_2H_6) are present in the gaseous fraction. Solid products are usually formed due to the re-polymerisation of oligosaccharides. The oxygen and water contents of bio-oil, obtained from biomass HTL, are less and the higher heating values (HHV) are, in turn more than those of oil products of conventional pyrolysis.

The salient findings of hydrothermal liquefaction of jute stick and rice straw are: (a) The first attempt has been made to study the hydrothermal liquefaction of jute stick; (b) The yield of hydrochar decreases from 43.97% to 22.15 % for hydrothermal liquefaction of jute stick and 48.36% to 25.17% for hydrothermal liquefaction of rice straw when the temperature is increased from 240 to 360^{o}C; (c) The yield of bio-oil increases from 22.15% - 33.81% for jute sticks and 20.39% to 30.34% for rice straw when the temperature is increased from 240 to 300^{o}C. When, the temperature is increased from 300 to 360 ^{o}C, the yield of bio-oil decreases from 33.81% - 32.09% for jute sticks and 30.34% to 28.31% for rice straw. The maximum bio-oil yield obtained at 300^{o}C; (d) The kinetic parameters of hydrothermal liquefaction (HTL) of jute stick (JS) and rice straw (RS) have been determined; (e) The convention of Van Krevelen diagram, used for the assessment of quality of fuel, H/C values of hydrochar and bio-oil have been plotted against the corresponding O/C values for JS and RS respectively; (f) The higher heating value of bio-oil samples obtained from hydrothermal liquefaction of jute stick and rice straw have been determined as 28.74 kJ/kg and 25.94 kJ/kg respectively; (g) The optimum bio-oil yield obtained from co-hydrothermal liquefaction of jute stick and rice straw has been measured as 32.8% at 317.2 ^{o}C for 28.1 minutes with 83.1% blend ratio; (h) The higher heating value of bio-oil obtained from co-hydrothermal liquefaction of jute stick and rice straw has been measured as 28.56 kJ/kg; (i) The area of GC-MS spectrum of bio-oil produced from co-HTL of JS and RS is dominated by phenolic compounds (45.59%) followed by aromatic (24.28%), cyclic (11.79%) and aliphatic (0.04%) compounds; (j) It is observed that hydrochar, obtained from hydrothermal liquefaction of jute stick, could be efficiently used for Congo red dye removal; (k) It is expected that the results of individual and co-HTL of JS and RS will open up a new arena in their application in bioenergy sector of India.

Torrefaction has been considered as a promising technology for the production of valuable products like biochar, volatile liquid, and non-condensable gaseous component from biomass at lower temperature range (200 - 400 ^{o}C) in absence of air or oxygen. Other than production of char, bio-oil and gas through structural decomposition, torrefaction also improves flow properties and grindability of biomass. Torrefaction also enhances the hydrophobicity of biomass and hence reduces the susceptibility to microbial degradation. Under the scenario of the necessity to transport biomass from the sources and subsequent mixing with coal etc. for power generation, torrefaction is considered as one of the promising pretreatment technology. Compared to pyrolysis, torrefaction is low energy intensive process. All torrefaction products, namely bio-char, bio-oil and gas have prospective usage. The salient findings of torrefaction of mustard stalk are: (a) The yield of biochar decreases from 67.91% - 34.33 % when the temperature is increased from 200 to 400^{o}C. The maximum bio-oil yield is 21.32% at 300^{o}C. The yield of gas increases from 20.31% - 44.75 % when the temperature is increased from 200 to 400^{o}C; (b) Parameters for lumped kinetic and distributed activation energy model of torrefaction of mustard stalk have been determined; (c) The fuel ratio (FR) of raw-mustard stalk and biochar are 0.21 and 0.29 respectively; (d) The HHV of raw MS, biochar and bio-oil have been measured as 14.25 MJ/kg, 16.37 MJ/kg and 19.85 MJ/kg respectively. The values of energy yield (EY) of biochar and bio-oil are 50.05% and 29.63% respectively; (e) The % area occupied by aliphatic, cyclic, aromatic and phenolic compounds, have been determined as 25.70, 12.82, 12.91 and 20.41; (f) The area of GC-MS spectrum of bio-oil produced from torrefaction of mustard stalk is dominated by aliphatic compounds (25.70%) followed by phenolic (20.41), aromatic (12.91%) and cyclic (12.82%) compounds; (g) The environmental impact of the torrefaction of mustard stalk has also been assessed using life cycle analysis in SimaPro software; (h) It is expected that the results of torrefaction of mustard stalk will be of use for the development of in bioenergy sector of India.