ABSTRACT
The quest for alternative sources of energy generation that are inexpensive, eco-friendly, renewable and can replace fossil fuels is owing to the increasing demands of energy. Production of biofuels from lignocellulosic biomass, holds remarkable potential to meet the current energy demand as well as to mitigate greenhouse gas emissions for a sustainable clean environment. Lignocellulose biomass feedstocks compulsorily undergo pretreatment process to release the fermentable sugars. The most of the existing pretreatment processes is energy intensive and consumes more cost. Low cost and effective pretreatment is essential to overcome the hurdles in commercialization of biofuel production from lignocellulose biomass. Catalytic Downflow liquid contact reactor (CDLCR) is an innovative method used to pretreat the lignocellulosic biomass, which consists of pump, electrical motor, circulation tank and pipe accessories. The present study deals with the pretreatment of pearl millet biomass using alkali catalyst (Ca (OH) \(_2\)) in a CDLCR under ambient conditions. Results of experimental trial show that there was significant reduction in lignin and hemicellulose observed for pearl millet biomass. The minimum and maximum total reducing sugars observed at 10 and 60 min. of reaction time were 77.80 and 160.15 mg/g of biomass.

Keywords : Lignocellulosic biomass, Pretreatment, Catalytic Downflow Liquid Contact Reactor
Lignocellulosic biomass feedstocks mainly made of a mixture of carbohydrate polymers viz., cellulose, hemicelluloses and lignin. Production of biofuels, especially bio-ethanol from lignocellulosic biomass, holds remarkable potential to meet the current energy demand. Pearl millet (Pennisetum glaucum) is a warm season annual grass and grows in semiarid conditions with very low (≤300mm) or inconsistent rainfall. Pearl millet serves as a good offset for biofuel production. The basic process steps in producing bioethanol from lignocellulosic materials are: pretreatment, hydrolysis, fermentation and product separation/distillation. So, pretreatment is one of the main preprocessing operations for lignocellulosic biomass based biofuel production. A number of pretreatment technologies based on numerous physical, chemical and biological methods have been developed, which alter/damage the structure of lignocelluloses and remove lignin (Chaturvedi and Verma, 2013). In the alkaline treatment, biomass is treated with alkali such as sodium, potassium, calcium and ammonium hydroxides at normal temperature and pressures. The main advantage of the process is efficient removal of lignin from the biomass and cost of lime required to pretreat a given quantity of biomass is lowest among alkaline
The study aims in optimization of conditions for lignin reduction of pearl millet biomass in catalytic downflow liquid contact reactor and test results are presented in this paper.

**Materials and methods**

The pearl millet biomass variety C07 was collected dried in the ambient temperature and it was powdered with help of shredder and grinder. The biomass size 212 µ was used in this experiment. Catalytic Downflow liquid contact reactor was developed and used in this study. In this reactor, there is no mechanical device used mixing. It consists of pump, electrical motor, circulation tank and pipe accessories. The biomass slurry was prepared by mixing of catalyst, powdered biomass sample and water. In order to make a closed loop circulation, the biomass slurry was supplied from circulation tank to reactor column with the help of centrifugal pump and returned to circulation tank. The electrical power required for one hour operation of this reactor was found as 373 W. The conditions selected and used in the experiment were 10% of alkaline catalyst, 10% biomass loading and reaction time (10, 20, 30, 60 min.). The alkaline catalysts selected for this study was calcium hydroxide and test results are presented. In order to compare the change in the biomass before and after pretreatment, the FTIR spectra of the raw and pretreated biomass samples were obtained using a FT-IR (FT-IR 6800 JASCO, Japan). Absorbance spectra were recorded between 4000 to 400 cm\(^{-1}\) wave numbers with a spectral resolution of 4 cm\(^{-1}\) and 64 scans per sample.

**Results and discussion**

The Catalytic Downflow liquid contact reactor treatment have a potential effect on biomass pretreatment under milder conditions, providing localized high energy to break down crystalline cellulose and facilitate the formation of radical species to degrade lignin as shown from the results. Alkali treatment of lignocellulose disrupts the cell wall by dissolving hemicellulose, lignin, and silica, by hydrolyzing uronic and acetic esters, and by swelling cellulose. Total reducing sugar (TRS) content in biomass was found in the range of 77.80 mg/g to 160.15 mg/g biomass (Table 1). The alkaline pretreatment with 10 percent alkali loading resulted in the lignin reduction and part of hemicellulose and increased the reactivity of cellulose for further hydrolysis steps (Hamelinck et al., 2005). The reaction conditions are generally

| Reactor time, min. | Glucose | Xylose | Arabinose | Mannose | Galactose | Cellobiose | TRS  |
|-------------------|---------|--------|-----------|---------|-----------|-----------|------|
| 10                | 13.70   | 9.39   | 11.25     | 14.09   | 13.02     | 16.36     | 77.80|
| 20                | 13.00   | 8.85   | 10.61     | 13.30   | 12.34     | 15.50     | 73.59|
| 30                | 19.34   | 13.82  | 16.55     | 20.65   | 18.68     | 23.49     | 112.54|
| 60                | 27.09   | 19.90  | 23.80     | 29.65   | 26.44     | 33.27     | 160.15|

All values are in mg g\(^{-1}\).
Figure 1. FTIR analysis of pretreated pearl millet biomass
mild, which prevent condensation of lignin leading to its high solubility and greater removal (Sharma et al., 2012).

Studies showed that in case of raw biomass sample, clear peaks appeared in the spectra for cellulose, hemicelluloses and lignin with their respective wave numbers as presented in Figure 1. For alkaline pretreatment in the developed reactor, there was evident for lignin removal. Because, the peaks at wave numbers related to lignin compound (1321, 1422, 1509, 1634 and 3340 cm$^{-1}$) for pretreated sample was disappeared or lower peak intensity as compared to that of raw sample. Similarly, there was low intensity peak appeared for pretreated samples for hemicellulose compound (1157 cm$^{-1}$).

Conclusions

Development of low cost pretreatment is essential for reducing the price of biofuel. Results of FTIR study showed that there was reduction in lignin and hemicellulose. The total reducing sugars was increased with increase in reaction time. Maximum total reducing sugars observed in this reactor under tested conditions for a reaction of 60 min. was 160.15 mg/g of biomass. An increase in catalyst loading to 15 percent was effective in lignin reduction to 63 percent in 20 mins. time. However additional confirmation studies are required. Further studies on the geometry and construction of CDLCR system will bring out an efficient high throughput system for industrial treatment of lignocellulosic biomass for biofuel production.

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