Madras Agric.J., 2018; doi:xxxxxxxxx

RESEARCH ARTICLE

Delignification of corncob using catalytic hydrodynamic cavitation reactor

Kiruthika Thangavelu [a], Ramesh Desikan [a*] and Sivakumar Uthandi
[a]Department of Bioenergy, Agricultural Engineering College and Research Institute,
[b]Department of Agricultural Microbiology, Tamil Nadu Agricultural University, Coimbatore, Tamil Nadu, India – 641 003

ABSTRACT

The optimization of pretreatment conditions for effective delignification of the corncob biomass using catalytic hydrodynamic cavitation reactor was presented in this paper. Response surface methodology (RSM) was adopted to optimize pretreatment parameters: lime loading (0.05-0.15 g/g), biomass loading (2.5–5 %) and time (5–60 min), in terms of three responses *viz.,* lignin reduction, hemicellulose reduction and cellulose increase. The percentage of lignin reduction was found to be highest as 38.13 under optimized conditions of 5 % of biomass loading, 0.1 g g^{-1} of lime loading and the process time of 60 min. The cavitational yield obtained under optimized conditions was calculated as 2.86×10^{-5} g J^{-1}. The developed reactor consumes less energy input for the pretreatment process and it can be easy to scale up.
Keywords: Corncob, delignification, lime, pretreatment, hydrodynamic cavitation reactor

1. *Introduction*

Principally, lignocellulosic biomass feedstocks comprises of 75% of carbohydrates (40-50 % of cel- lulose, 25-30 % of hemicellulose) and 25 % of lignin. Corncobs are one of unexploited potential lignocel- lulosic feedstocks for biofuel production. Pretreat- ment for lignocellulosic biomass is essential process for production of biofuels via biochemical conver- sion route. The design of reactors used in the down- stream process *viz.,* saccharification and fermentation strongly based on final products produced at the end of the biomass pretreatment process. Based on the literature review, the main drawbacks of most of the current biomass pretreatment methods used for lig- nocellulosic biomass feedstocks were involved more complex processes, energy intensive, higher process- ing cost and difficult to upscale. Recently, application of cavitation technology is gaining momentum in many fields due to its added advantages (low ener- gy input and operated at ambient conditions). This technology has been successfully employed in di- versified fields such as wastewater treatment, food processing and bio-processing operations. Cavitation is the process of generation, growth and violent col- lapse of vapour bubbles at millions of locations in the corncob biomass and experimental results are presented in this paper.

2. *MATERIALS AND METHODS*

Materials

The size of dried corncob biomass was reduced in a sequence shredder, pin mill, and grinder. The powdered corncob sample was sieved using ASTM 70 sieve and the size of the biomass particles used for the pretreatment experiment was <212 μm.

Computational Fluid Dynamics analysis

The computational fluid dynamics (CFD) analysis was carried out with software ANSYS Fluent 15.0 to stimulate fluid flow in the hydrodynamic cavitation reactor for selected orifice plate with 9 holes of 2 mm diameter. Analysis was done with the finite volume method for a fluid geometry and grid generation.

Hydrodynamic cavitation –lime pretreatment

The hydrodynamic cavitation reactor consist- ed of circulation tank (5 litre capacity), orifice plate, flanges, orifice plates, centrifugal pump, electrical motor, gate valves for priming and bypass lines, pres- sure gauges and pipe accessories. Two pressure gaug- es (P and P) fixed at both downstream and upstream working liquid, which leads to rise in temperature and pressure within the cavity and subsequent reduction to ambient conditions in a few microseconds (Pandit and Pinjari, 2010). An attempt was made to apply this technology combined with lime catalyst for pretreat- sides of the orifice plate were used to measure the pressure drop. An orifice plate with 9 holes of 2 mm diameter was used in this reactor. The inlet pipe of the pump was connected at the base of the circula- tion tank. The main pipe line was connected to out-let side of the centrifugal pump. The main pipe line was divided into three pipe lines to serve for three purposes viz., priming, bypass line, sub mainline to accommodate flanges and orifice plate. In order to make a closed loop circulation, the biomass slurry (ie., reactant mixture of corncob biomass and lime catalyst) was supplied from circulation tank to orifice plate with the help of centrifugal pump and then sent back to circulation tank. The purpose of bypass valve was used to regulate the pressure of working liquid at upstream side of an orifice plate.

Experimental design

RSM was employed to optimize the operating parameters for the hydrodynamic cavitation based biomass pretreatment to attain higher percentage of lignin reduction. Response was assumed to be affect- ed by three independent variables, catalyst concen- tration (A), biomass to liquid ratio (B) and reaction time (C). The range of selected three independent variables used for pretreatment process is: lime load- ing of 0.05- 0.15 g/g of biomass, biomass loading of

– 5.0 % and reaction time of 5 – 60 min. A total of 17 trials of the three variables were designed by Box– Behnken design using the Design-Expert software 10.0 (Stat-Ease, Inc., USA) (Box and Behnken, 1960).

2.5 Biomass characterization analysis

FTIR analysis, thermogravimetric analysis, X- ray diffraction analysis and scanning electron microscopy were performed to study the characterization chang- es before and after pretreatment.

3. *Results and discussion*

3.1 CFD analysis of HCR

By using ANSYS software, the velocity streamline profile was obtained to study the velocity flow distri- bution before and after the orifice plate in HCR (Fig 1). The velocity of the working fluid (indicated by blue colour) before reaching and after leaving the orifice plate remains the same (37.07 m/s). At the orifice plate, the velocity of the orifice plate increases to sev- eral times (indicated by red colour) due to sudden re- duction in the cross sectional area of the orifice plate (28.26 mm^2) when compared to the cross sectional area of the pipe (283 mm^2), this sudden increase of velocity, causes the formation of cavities that leads to breakdown of biomass in the working fluid.

3.2. Hydrodynamic cavitation – lime pretreatment

All the experiments were performed by using orifice plate at an inlet pressure of 50 kPa. RSM was adopted to assess the parametric effect of three inde- pendent variables on maximum lignin reduction (%), hemicellulose reduction (%) and cellulose increase (%). Among the 17 runs, run 4 resulted in optimum responses in percentage of lignin reduction (38.13 %), hemicellulose reduction (5.11 %) and cellulose in- crease (22.58 %) with biomass loading of 5 per cent at catalyst concentration of 0.1 g/g in 60 min time. A similar study of the HC based feed pretreatment showed that a maximum lignin removal was observed (53 %) was achieved at conditions of 5 per cent of NaOH, 5 per cent biomass loading and 40 min. of HC operation (Kim *et al*., 2015). The response surface plot was shown in Figure 2.

Thermal behaviour of raw and pretreated bio- mass

Thermal degradation of raw corncob biomass sample represents two different peaks in the DTG curves due to the degradation of hemicelluloses, fol- lowed by cellulose. Decomposition of lignin occurs in a wide range that overlaps partially with that of hemicelluloses and cellulose. The temperature of two distinct DTG peaks of pretreated corncob samples was shifted to higher temperatures than that of raw corncob samples. By comparing the DTG peaks of the tested corncob samples appeared between 200 and 400°C, it clearly showed that they differ in position and height. The reason may be due to bio-molecular compositional changes occurring due to effect of pre- treatment *viz.*, lignin reduction, hemicellulose reduc- tion and cellulose increase. Details of temperature at peak 1 and 2 obtained from DTG curves for tested samples are furnished in Table 1. This results supports lignin removal, cellulose increase and hemicellulose reduction concept from the corncob samples after biomass pretreatment.

FTIR analysis of raw and pretreated biomass samples

Pretreated corncob was analyzed by FT-IR, dif- ferent wave numbers, functional groups and their corresponding polymer are furnished in Table 2.

Reduction in hemicelluloses peak intensity is at- tributed to solubilization of hemicelluloses owing to biomass pretreatment treatment, wave number 1157 cm^{-1} with a functional group of C-O-C was greatly re- duced. Similarly reduction in peak intensity for lignin functional groups was noticed. For instance, greater

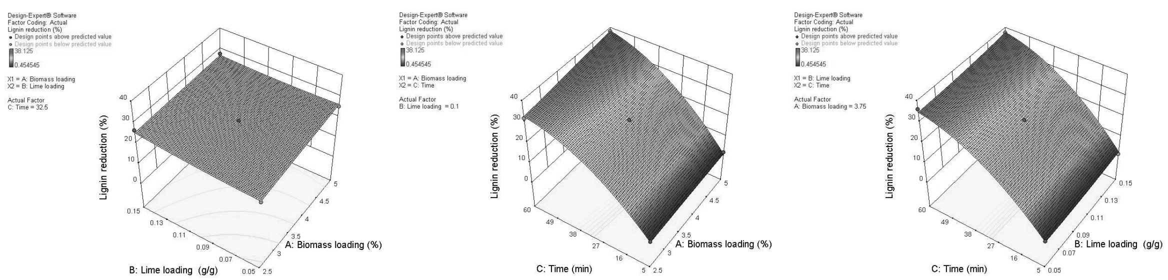

Fig. 2. 3D plots for response lignin reduction of corncob pretreated with HC (A) Lime loading vs. biomass loading;
(B) biomass loading vs. time; (C) lime loading vs. time.

Table 1. Details TGA profile of raw and pretreated corncob biomass samples

Plate number / biomass	Catalyst & process used	Catalyst Concentration	Temperature at peak 1	Temperature at peak 2
Raw corncob	-	-	290.72 (0.5753 %/°C)	333.7 (0.7088 %/°C)
Pretreated corncob	Combined lime and hydrodynamic cavitation	0.1 g/g of dry biomass	315.7 (0.6956 %/°C)	353.5 (0.9529 %/°C)

Table 2 Assignment of functional groups and their corresponding polymers in pretreated corncob

Wavenum	Functional groups	Corresponding polymer

ber		
3340	O-H stretch	Lignin
2833	C-H stretch	Lignin
1634	Aromatic ring vibration	Lignin
1509	C=C	Lignin
1422	CH_2	Lignin
1321	C-O-CH vibration	Lignin
1247	C-O stretching	Syringyl units
1157	C-O-C asymmetrical stretching	Hemicellulose (Xylose)
1031	C-O,C=C,C-C-O stretching	Cellulose, Hemicellulose and lignin

reduction in intensity at wave number 1247 cm^{-1} of syringal groups of lignin was observed for combined lime and hydrodynamic cavitation biomass pretreat- ment. Furthermore, functional groups representing lignin reduced significantly at wave numbers 1329 and 1509 cm^{-1} for orifice plate. It was interesting to note that the functional group representing lignin at wave number 1422 cm^{-1} was completely absent. In addition to hemicelluloses and lignin removal, vibra- tional changes were apparent in the biomass at wave numbers 1037 cm^{-1} and 2892 cm^{-1} indicating the na-ture of lime to alter the cellulose and lignin structure.

Scanning Electron Microscopy (SEM) image of raw and pretreated biomass

Raw corncob retained it smooth surface without any disruption whereas alterations in the surface of the pretreated corncob biomass in the form of remov- al of fibers and disintegration of fibre structures due to combined pretreatment. These structural changes are due to bursting of cavitation at the surface of bio- mass leading to a shear of bio-molecular structures. In addition to the surface changes, separation of fibre was more evident for lime treatment and the typical formation of globules as the hemicelluloses and lignin condensation due to alkaline lime catalyst. Apart from

surface changes, disintegration of bundles was more; it is due to the collapse of cavities at the vicinity of biomass created such breakdown.

X-ray diffraction study of HCR treated biomass

Untreated and pretreated corncob samples were estimated for cellulose crystallinity changes. There was no significant change in crystallinity of cel- lulose, which indicates that the treatments performed under combined hydrodynamic cavitation with lime pretreatment improved the accessibility of cellulose without modifying the cellulose structure.

4. Conclusion

Lignin and hemicelluloses removal consequent- ly makes cellulose more accessible to saccharifying enzymes without modifying its structure is the im- portant aspect of any pretreatment process. The performance evaluation of combined hydrodynamic cavitation and lime biomass pretreatment using RSM showed promising results, the maximum percentage of lignin reduction and cavitational yield under opti- mized conditions were found as 38.13 and 2.86×10^{-5} g J^{-1} at 5 % biomass loading, 0.1 g g^{-1} lime loading and 60 min. The result of other studies (FTIR, TGA, SEM and XRD) indicates that the reduction in lignin and hemicellulose in the pretreated biomass due to this combined biomass pretreatment. Hence, the de- signed hydrodynamic cavitation reactor for biomass pretreatment may be used for effective delignification of any lignocellulosic biomass by combination of ei- ther chemical, biological catalysts.

References

Box, G.E.P. and D.W. Behnken. 1960. Some new three level designs for the study of quantitative variables. Tech- nometrics 2:455–475.

Kim, I., I. Lee, S. H. Jeon, T. Hwang and J. I. Han. 2015. Hy- drodynamic cavitation as a novel pretreatment ap- proach for bioethanol production from reed. Biore- sour. Technol, 192:335–339.

Pandit, A. B. and D. V. Pinjari. 2010. Cavitation milling of nat- ural cellulose to nanofibrils. Ultrasonics Sonochemis- try, 17:845–852.