Bifurcation of lignocellulosic biomass (*Areca catechu*) using alkaline pretreatment: An efficient method.

Adhirashree Vannarath[1], Arun Kumar Thalla[2]

[1]Department of Civil Engineering, National Institute of Technology Karnataka, Surathkal, 575025, India
[2] Department of Civil Engineering, National Institute of Technology Karnataka, Surathkal, 575025, India
Keywords: Lignocellulosic biomass, alkaline pretreatment, biomass composition, value-added product
Presenting author email: adhirashree28@gmail.com

Introduction: Second generation biofuels (SGB) is considered to be a promising resource for the hike in energy usage which can balance the bridge gap between energy demand and supply. One among the major contributors to these biofuels are the lignocellulosic biomass and helps in mitigating greenhouse gases (GHG) effects. The renewable nature and immense availability of these clean resources have fascinated the researchers and studies are pointing towards the conversion of agro wastes to value-added products. In view with the global production of the various agro wastes, India has a large leading production of arecanut husk (*Areca catechu*) (40%- 50%) and China comes the next (Singh et al., 2017). A major portion of these wastes is disposed on open lands causing nuisances by spreading diseases and pest growth due to their slow deterioration. The recalcitrant nature of this arecanut husk is primarily because of the persistence of lignin in it. Various pretreatment methods can be employed to facilitate the removal and recovery of lignin and hence, increasing its digestibility. Alkaline pretreatment at an optimised level has proved to be a best-suited method for the fractionalisation of the arecanut husk (Singh and Trivedi, 2013). Only a few studies were reported on the arecanut husk previously. The fractionalisation, lignin study and its recovery from the arecanut husk in the present research brings the novelty in it.

Materials and methods: The dehusked arecanut husk collected from the Central Plantation Crops Research Institute (CPCRI) Kasargod, Kerala, India, was washed, dried and size reduced to 0.2-0.5 cm. The moisture content, TS, VS, TOC, TKN were analyzed. The basic elements of any biomass such as carbon, hydrogen, nitrogen, sulphur and oxygen were quantified by CHNSO analyser. The determination of extractives and lignin content were done using NREL protocol (Sluiter et al., 2012) and biomass composition such as cellulose and hemicellulose using Tappi method (Ayeni et al., 2015). The confirmation of the biomass composition is done by TGA analysis and FT-IR analysis. To 1 g of arecanut husk, targeted concentration such as 5, 10, 15 and 20% (w/v) of alkaline solution (sodium hydroxide) was added at 1:10 ratio. The mixture is incubated at 35^{0}C for soaking periods (12hr, 24hr, and 48 hr) at 150 rpm. The fractionation of the biomass composition was checked for the soaked residues after washing with distilled water. The morphological and physiochemical analysis was performed for the residues after pretreatment.

Result and discussion: The fractionalization of cellulose, hemicellulose and lignin in the Arecanut husk makes them the perfect substrate for the production of value-added products. The TS, VS, moisture content and ash content in AH was found to be 88.09%, 97.22%, 11.91% and 2.78% respectively. The characteristics of the AH is shown in table 1 given below.

Table 1 Biomass compositional analysis of Arecanut husk

Parameter	Value
TOC	54.64%
Total extractives	2.156%
Cellulose	45.02%
Hemicellulose	28.25%
Lignin	22.47%
Ash content	2.1%

Weight loss and fragility of the pretreated sample was found to be increased. The colour of the husk was lightened. The TS was found to be decreased with the increase in the soaking periods. The maximum weight loss was recorded for 10% NaOH at 24 hrs soaking, i.e., 5.24% of weight reduction. This can be due to lignin removal during the pretreatment process (Dulermo et al., 2016).

Alkaline pretreatment removes lignin and facilitates the accessibility to the cellulose. A significant increase in VS to 98.76% can be seen w.r.t increase in concentrations and soaking hours (3.14% increase from raw AH) at 15% NaOH concentrations for a soaking period of 24 hours. For varying soaking hours (12hrs, 24hrs, 48hrs), the %TS showed a non-significant decrease for particular NaOH concentrations. Ash content was reduced to 1.24% for 15% NaOH- 12hrs soaking (70.8% reduction). Biomass composition of pretreated AH showed a rise in cellulose content to 46.56% from 43.76% at 15% NaOH – 24hrs soaking as given in table 2. This rise in cellulose was due to the breakdown of the lignin-hemicellulose complex (Amin et al., 2017; Fu et al., 2015). The above statement can be justified by the profound decrease in the lignin content to 17.54% at 20% NaOH addition for 24 hours. The recovered lignin can be used for various applications which increase the value of these agro wastes. The removal of lignin enhances the digestibility of the substrate making them easily degradable and can be used for biofuel generation applications. Strong alkaline concentrations cause hydrolysis, peeling of end groups, degradation and decomposition of polysaccharides.

Table 2 Effect of soaking hours and pretreatment concentration on the biomass compositional of the arecanut husk

Biomass composition analysis	Soaking hours	Control	NaOH pretreatment			
	(hrs)	%	5%	10%	15%	20%
Extractives (%)	12	2.156	1.824	1.748	1.636	1.62
	24	2.098	1.764	1.644	1.632	1.622
	48	2.148	1.756	1.648	1.63	1.624
Hemicellulose (%)	12	31.62	32.89	33.36	34.06	34.53
	24	31.58	33.01	33.65	34.11	34.68
	48	31.57	33.12	33.91	34.37	34.97
Cellulose (%)	12	43.76	45.04	46.23	46.53	46.11
	24	43.79	45.03	46.18	46.56	46
	48	43.75	45.8	46.33	46.23	45.85
Lignin (%)	12	22.46	20.24	18.66	17.78	17.73
	24	22.47	20.19	18.52	17.69	17.69
	48	22.41	19.32	18.11	17.78	17.54

Conclusion: Alkaline pretreatment is one of the best methods can be employed for the fractionalisation of the arecanut husk. It helps in the removal of lignin and increases the accessibility to the cellulose. The recovered lignin can be utilised for the various applications and can also be used for the synthesis of various chemicals and value-added products.

Reference

Amin, F.R., Khalid, H., Zhang, H., Rahman, S., Zhang, R., Liu, G., Chen, C., 2017. Pretreatment methods of lignocellulosic biomass for anaerobic digestion. AMB Express 7, 1–13. https://doi.org/10.1186/s13568-017-0375-4

Ayeni, A.O., Adeeyo, O.A., Oresegun, O.M., Oladimeji, E., 2015. Compositional analysis of lignocellulosic materials : Evaluation of an economically viable method suitable for woody and non-woody biomass American Journal of Engineering Research (AJER) 14–19.

Dulermo, T., Coze, F., Virolle, M., Méchin, V., Baumberger, S., Froissard, M., 2016. Bioconversion of agricultural lignocellulosic residues into branched-chain fatty acids using Streptomyces lividans. oilseeds fats Crop. Lipids 23, 1–10.

Fu, L., Mccallum, S.A., Miao, J., Hart, C., Tudryn, G.J., Zhang, F., Linhardt, R.J., 2015. Rapid and accurate determination of the lignin content of lignocellulosic biomass by solid-state NMR 141, 39–45.

Singh, D.P., Trivedi, R.K., 2013. Acid And Alkaline Pretreatment Of Lignocellulosic Biomass To Produce Ethanol As Biofuel 5, 727–734.

Singh, R.D., Bhuyan, K., Banerjee, J., Muir, J., Arora, A., 2017. Hydrothermal and microwave assisted alkali pretreatment for fractionation of arecanut husk. Ind. Crop. Prod. 102, 65–74. https://doi.org/10.1016/j.indcrop.2017.03.017

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Nrel, D.C., 2012. Determination of Structural Carbohydrates and Lignin in Biomass, Laboratory Analytical Procedure, NREL.