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Full Length Article

Comparative study of three optimized acid-based pretreatments for sugar recovery from sugarcane leaf waste: A sustainable feedstock for biohydrogen production

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ABSTRACT

This paper reports the development and comparison of three optimized pretreatment models for xylose and glucose recovery from sugarcane leaf waste (SLW) using HCl, H_2SO_4 and HNO_3. The input variables for each model consisted of acid concentration, temperature, solid to liquid ratio and heating time in the range of 0.5–5.0% (v/v), 60–100 °C, 30–50% (w/v) and 60–240 min respectively. All models showed high coefficients of determination (R^2) above 0.78. Process optimization gave xylose and glucose yields of 78 and 11.48 g/L, 50.75 and 7.15 g/L, 30.82 and 3.99 g/L for HCl, H_2SO_4 and HNO_3 pretreatments respectively. The HCl-based model gave up to 160% more sugar while simultaneously requiring a 2.5-fold lower heating time compared to H_2SO_4 and HNO_3. The highest hemicellulose removal (93.15%) was also observed with the HCl model. Preliminary assessment of sugars from the optimized HCl pretreatment on dark fermentation gave a peak hydrogen fraction of 40.11% and a yield of 18.6 ml H_2 g^{-1} fermentable sugar. The optimized pretreatments showed high efficiency at releasing xylose and glucose from SLW. In addition, the recovered sugars are excellent substrates for various fermentation bioprocesses and biofuel generation.

1. Introduction

The global dependency on nonrenewable fossil fuels and the current emission of greenhouse gases are propelling research towards a cleaner more sustainable source of energy [15,55]. A major factor which influences the production cost of biofuels is the feedstock [45]. Plant biomass is increasingly being considered a suitable feedstock due to its low costs, high availability and the added environmental benefits [28,26,48]. Annually, 200 billion tons of biomass is produced [61] and the current disposal practice involves mainly burning or landfill dumping [41].

Sugarcane is an important agricultural crop cultivated worldwide [20] with annual yields of 65 million tons in Thailand [37], 590 million tons in Brazil [42] and 20 million tons in South Africa [50]. The leaf component of the sugarcane, commonly referred to as trash, constitutes 40% of the sugarcane plant [37,50]. Harvesters are the primary method for sugarcane recovery. In this process, much of the extraneous material is discarded, where the sugarcane sorters have the ability to collect all the trash [50]. Cellulose and hemicellulose found in the cell wall of the leaves and culm comprise two thirds of the total energy content in sugarcane [65]. Furthermore, the dry leaves possess the energy equivalent to ten tons of coal per hectare, which is a major advantage of this feedstock [50]. The leaves are considered waste and are often burnt in the field [20]. Several studies have reported an increase in the emission of harmful mutagenic particulate matter such as benzo (b) fluoranthene and benzo(a)pyrene during harvesting periods [46,5,9]. These polycyclic aromatic hydrocarbons have been found to affect the functioning of the lungs as well as other health ailments during exposure [39].

Sugarcane leaves are composed of 36% cellulose, 21% hemicellulose and 16% lignin [14]. Lignocellulosic biomass is recalcitrant towards microbial decomposition owing to its rigid and crystalline structure of cellulose which is enclosed by a cross-linked matrix of hemicellulose and lignin [23]. Thus appropriate low cost and efficient pretreatments are essential for the release of the fermentable sugars for industrial bioprocesses [40]. The pretreatment regime is dependent on the type of lignocellulose present since biomass has a high level of variability in complexity [63]. Current pretreatment strategies include physical milling, extrusion, microwave),

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Table 1
Coded and actual levels of the input variables for the experimental design.

Independent variables	Symbols	Coded		
		−1	0	1
Acid Concentration (%, v/v)	A	0.5	2.75	5.0
Solid: Liquid Ratio (%, w/v)	B	30	40	50
Temperature (°C)	C	60	80	100
Heating time (min)	D	60	150	240

chemical alkali, acid, ionic liquid) and physico-chemical steam, ammonia fiber explosion) [32,49].

Dilute acid hydrolysis is a widely used pretreatment technique for lignocellulosic biomass [18,19]. The advantages of dilute acid pretreatment include its high solubilization of hemicellulose, reducing cellulose crystallinity and simplistic operation whereas the disadvantages include the requirement for corrosive-free reactors under certain circumstances as well as the production of fermentation inhibitors [12,21]. During acid hydrolysis, glycosidic bonds are cleaved leading to the conversion of polysaccharides into monosaccharides [21]. Significant strides have been made towards optimizing sugar release following acidic pretreatment on a variety of lignocellulosic material [28,16,8,22]. The pretreatment of sugarcane leaves is scarcely reported [20,35]. Furthermore, there is a lack of substantial studies detailing modeling the interaction of pretreatment input parameters on the release pattern of both xylose and glucose from lignocellulosic biomass. In addition, several lignocellulosic-based substrates have been reported for biohydrogen production [27] whereas sugarcane leaves are scantily reported.

Response surface methodology RSM) has been widely employed for the modeling and optimization of bioprocesses [57]. Various studies have modeled the release of fermentable sugars using RSM with high efficiency [8,23,33,13].

This study aims to compare the efficiency of three acid-based models to optimize the release of fermentable sugars from sugarcane leaf waste (SLW) with a focus on the influence of main operational parameters viz. acid concentration, temperature, heating time and solid: liquid ratio. Additionally the use of these fermentable sugars in dark fermentation for hydrogen production is assessed.

2. Materials and methods

2.1. Raw material

The sugarcane leaves used in this study were collected at 8 months old from The South African Sugarcane Research Institute-SASRI located on the North Coast of South Africa (29° 42′ 18″S, 31° 02′ 44″E) at an altitude of 96 m. This area is characterized by a warm climate with an annual mean rainfall of 951 mm. The leaves, cut roughly at the 3rd–6th leave, were transported in sealed plastic bags, then dried at 60 °C for 72 h followed by milling using a centrifugal miller (Retsch ZM-1, Durban South Africa) with a 1 mm sized mesh to yield particles sized $\leq$ 1 mm. Milled leaves were stored in sealed paper bags prior to use.

2.2. Experimental design

The optimization window for the input pretreatment parameters was selected with the view to minimize the energy input, while enhancing xylose and glucose recovery and guided by previous reports [35,62,16,33]. The input parameters consisted of acid concentration, temperature, solid to liquid ratio and heating time in the range of 0.5–5.0% (v/v), 60–100 °C, 30–50% (w/v) and 60–240 min respectively. Three acid types used were HCl, H_2SO_4, and HNO_3. The Box-Behnken design was used to generate 29 experiments with varied pretreatment input conditions for each of the acid-based pretreatment models (Table 1), thus a total of 87 experiments were carried out in duplicate consequently a total of 174 experiments were evaluated.

Table 2
Xylose and glucose released from HCl based pretreatment.

Run	A: HCl (%)	B: Heat time (Min)	C: Temperature (°C)	Solid : Liquid %	Response 1 Xylose (g/L)	Response 2 Glucose (g/L)
1	2.75	240	80	50	57.82	8.94
2	0.50	60	80	40	0.79	3.99
3	2.75	240	60	40	5.83	4.66
4	0.50	240	80	40	0.43	3.29
5	0.50	150	80	50	0.39	2.46
6	5.00	150	60	40	5.83	3.46
7	2.75	150	100	30	50.96	10.10
8	2.75	150	80	40	0.29	3.42
9	2.75	60	80	50	34.58	7.89
10	5.00	150	100	40	62.13	14.57
11	2.75	60	80	30	8.38	5.24
12	0.50	150	100	40	0.50	3.42
13	2.75	150	80	40	44.04	7.98
14	5.00	240	80	40	46.09	9.30
15	2.75	60	100	40	57.61	9.25
16	2.75	240	80	30	31.94	4.96
17	5.00	150	80	30	39.57	6.73
18	5.00	60	80	40	54.83	8.11
19	5.00	150	80	50	63.38	10.99
20	0.50	150	80	30	0.43	4.13
21	2.75	150	80	40	37.32	5.15
22	2.75	240	100	40	37.37	7.67
23	2.75	150	80	40	23.81	6.14
24	2.75	150	60	50	0.51	3.98
25	2.75	150	60	30	3.30	4.27
26	2.75	150	80	40	47.71	7.43
27	2.75	150	100	50	30.80	6.79
28	2.75	60	60	40	1.74	5.55
29	0.50	150	60	40	0.45	3.67

2.3. Pretreatment process

Milled SLW was transferred to 250 ml Schott bottles and 20 ml of varied concentrations of acid (0.5, 2.75, 5.0% (v/v)) was then added. The contents were mixed and heated using a PolyScience Analogue water bath. The solid to liquid ratio (S: L), acid concentration, heating time and temperature setpoints were maintained as specified in the design (Tables 2–4). Timing was initiated once the temperature of the substrate reached the specified set point. The pretreated SLW were filtered and the solid fraction was washed three times with distilled water for chemical and morphological examination. The liquid fraction was analyzed for the concentration of glucose and xylose.

2.4. Scanning electron microscope analysis

Physical changes in native and pretreated SLW were analyzed by scanning electron microscopy (ZEISS EVO LS 15). All samples were mounted on conductive adhesive tape, sputter coated with gold (Eiko IB-3 Ion Coater) and observed at 5 kV voltages. Images were taken at 277× and 350× magnification.

2.5. Preliminary assessment for hydrogen production

2.5.1. Seed inoculum

The anaerobic sludge used in this study was obtained from The Darville Wastewater treatment plant Pietermaritzburg, South

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