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Soaking assisted thermal pretreatment of cassava peels wastes for fermentable sugar production: Process modelling and optimization

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ABSTRACT

This study reports a hybrid pretreatment strategy for optimum fermentable sugar (FS) release from cassava peels waste. The Response Surface design method was used to investigate the effect of soaking temperature, soaking duration, autoclave duration, acid concentration and solid loading on reducing sugar yield. The model gave a coefficient of determination (R^2) of 0.87. The optimum pretreatment conditions of 69.62 °C soaking temperature, 2.57 h soaking duration, 5 min autoclave duration, 3.68 v/v acid concentration and 9.65% w/v solid loading were obtained. Maximum reducing sugar of 89.80 ± 2.87 g/L corresponding to a fermentable sugar yield of 0.93 ± 0.03 g/g cassava peels was achieved upon model validation. A percentage sugar recovery of 90.79% was achieved with a 31% improvement in the FS yield from the enzyme pretreatment. The combined severity factor (CSF) of 0.77 and the low concentration of inhibitory compounds achieved further demonstrates the efficiency of this technique.

1. Introduction

The production of value-added products such as biofuel, organic acids, and enzymes continues to attract great interest for economic and environmental sustainability. Meanwhile, the agro-industrial sector generates large volumes of lignocellulosic biomass, most of which are underutilized and their disposal continues to raise environmental concerns due to pollution [1]. This raw material has been considered as one the most attractive and sustainable feedstock for biofuel production [1]. Cassava, (*Manihot esculenta* Crantz) is a staple crop for over 800 million people and approximately 263 million tons are produced annually across the world [2,3]. This often leads to the generation of a huge volume of residues in the form of peels which usually makes up to approximately 20–35% of the whole tuber [4]. Cassava peels are lignocellulosic waste containing polymeric structures such as cellulose, hemicellulose, lignin and very rich in starch [5].

Pretreatment is essential to disrupt the physical and chemical structure of lignocellulosic biomass in order to enhance its accessibility to the enzyme and microbial degradation [5]. Therefore, the liberation of the cellulose and hemicellulose components from the lignocellulosic complex remains impetuous for an efficiently developed pretreatment process [6]. This reduces the crystallinity of these components and enhances their susceptibility to hydrolytic processes characteristic of biofuel production. Several pretreatment methods have been reported for lignocellulosic biomass pretreatment which includes biological, physical, chemical and physicochemical methods [7]. For instance, chemical methods can be performed using dilute or concentrated acid, alkali, ionic liquids and organic solvents [8]. Among the chemical methods, acid pretreatment has been commonly employed due to its merits of a low cost of operation and high sugar recovery [9].

Recently, combined pretreatment methods such as microwave-alkali-acid [6], thermal assisted acid hydrolysis [10] and steam assisted acid treatment [11] have been considered as a promising approach to overcome some of the challenges limiting the application of the aforementioned methods. This can also improve the efficiency of sugar recovery, decreased the formation of inhibitory compounds and a more economic process.

Although dilute acids are low cost and are considered effective for pretreatment processes, an additional enzymatic treatment step is usually required for optimal sugar recovery [12], especially for starchy based substrates like cassava peels. However, it is obviously predictable that the complications associated with such additional processes coupled with the high cost of enzymes will significantly impact on the techno-economic value. This therefore, justifies the need for a cheaper and simpler pretreatment technique for optimum fermentable sugar yield.

Lignocellulosic biomass pretreatment under high temperature and acidic conditions often lead to the formation of inhibitory compounds such as 5-Hydroxymethyl furfural (HMF), furfurals, and formic acid. The effects of these inhibitory compounds include longer microbial lag

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phase, lower cell density and overall low productivity [13]. The variation in the chemical composition of different feedstock has a major impact on the formation of inhibitors during pretreatment [14]. There are limited reports on the profile of inhibitors generated during chemical or thermal pretreatment of cassava peels waste, which therefore necessitates the need for their evaluation.

An efficient biomass pretreatment process often involves the combination of various factors, for this reason, modeling and optimization techniques can be employed to improve the efficiency of the process. Moreover, the archetypal method of varying a variable at a time while keeping the other constant does not always depict the comprehensive effects of all the variables and their interactions [15,16]. The Response Surface Methodology (RSM) is a statistical modeling technique that analyses the responses from a number of planned experiments by studying the influence of identified parameters coupled with the individual and interactive effects [17]. The RSM has been employed previously in combined pretreatment studies that focused on preservation of food texture using Pressure Assisted Thermal Processing (PATP) [18]. Also, soaking in aqueous solvents such as ammonia and water was reported as a pretreatment method for the improvement of xylan digestibility and fermentable sugar yield [19,20]. However, to the best of our knowledge there are no reports on the optimization of Soaking Assisted Thermal Pretreatment (SATP) to improve fermentable sugar yield from starch based substrates.

Therefore, this study is aimed at the production of optimum fermentable sugar from cassava peels biomass using a hybrid Soaking Assisted Thermal Pretreatment technique (SATP). The individual and interactive effects of soaking duration, soaking time, autoclave duration, dilute acid concentration and solid loading on the fermentable sugar release from cassava peels biomass was investigated using the RSM. The pretreatment severity, profile of inhibitors and morphological changes on the substrate were also investigated.

2. Materials and methods

2.1. Substrate preparation

Cassava tubers (*Manihot esculenta*) were obtained from a commercial market, in Durban, South Africa. The tubers were cleaned, peeled and oven dried at 50–55 °C until complete drying was observed. These were subsequently milled to a particle size of 1–2 mm using a centrifugal miller (Retsch ZM-1, South Africa) and stored for further use.

2.2. Experimental design

Optimization of the fermentable sugar yield was carried out using the Response Surface Methodology (RSM). The input variables selected in this study were soaking temperature, soaking duration, hydrochloric acid concentration (v/v), autoclave duration (min) and solid loading (w/v) while the output parameter was reducing sugar (g/L). The independent variables selected were varied within the range of 30–70 °C [20], 0–24 h [20], 5–20 min [21], 0–5% [22], and 2–10% [22] in order to investigate the effects of soaking temperature, soaking duration, autoclave duration, acid concentration and solid loading respectively on the release of reducing sugars from the cassava peels biomass (Table 1). A five-factor Box-Behnken design of the RSM was used to generate a total of forty-six experimental runs (Table 2).

2.2.1. Pretreatment technique

2.2.1.1. Soaking Assisted Thermal Pretreatment (SATP). SATP was carried out using a water bath and an autoclave. The milled cassava peels were soaked in dilute hydrochloric acid at varying concentration and temperature followed by autoclave thermal treatment (121 °C) according to the Box-Behnken design (Table 2).

Table 1
Experimental design.

Factors	Factors levels		
	−1	0	1
Soaking temperature (°C)	30	50	70
Soaking duration (h)	0	12	24
Autoclave duration (min)	5	12.5	20
Acid concentration (% v/v)	0	2.5	5
Solid loading (% w/v)	2	6	10

2.2.2. Modelling and pretreatment optimization

The experimental data obtained from the experimental runs were used to fit a polynomial equation relating the total reducing sugar with the input variables. The general form of the model is shown in Eq. (1).

$$\begin{aligned} Y= {} & \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_4 x_4 + \alpha_5 x_5 + \alpha_{12} x_1 x_2 + \alpha_{13} x_1 x_3 + \alpha_{14} x_1 x_4 \\ & + \alpha_{15} x_1 x_5 + \alpha_{23} x_2 x_3 + \alpha_{24} x_2 x_4 + \alpha_{25} x_2 x_5 + \alpha_{34} x_3 x_4 + \alpha_{35} x_3 x_5 \\ & + \alpha_{45} x_4 x_5 + \alpha_{11} x_1^2 + \alpha_{22} x_2^2 + \alpha_{33} x_3^2 + \alpha_{44} x_4^2 + \alpha_{55} x_5^2 \end{aligned} \quad (1)$$

where 'Y' represents the process output (i.e. the fermentable sugar determined as total reducing sugar), α_0 is the free or offset term. The linear coefficients are α_1, α_2, α_3, α_4 and α_5 while α_{11}^2, α_{22}^2, α_{33}^2, α_{44}^2 and α_{55}^2 and α_{12}, α_{13}, α_{14}, α_{15}, α_{23}, α_{24}, α_{25}, α_{34}, α_{35}, and α_{45} are the quadratic and the interactive coefficients respectively.

The fitness of the model was assessed by the Analysis of Variance (ANOVA) using Design-Expert Version 8 (Stat-Ease, Inc., USA). Process optimization was carried out by solving the polynomial equation using the method of Montgomery and Myers [23].

2.3. Combined Severity Factor (CSF)

The Severity of the SATP pretreatment technique was evaluated using the combined severity factor (CSF). The CSF defines the severity of a pretreatment technique as a function of temperature (°C), treatment duration (min) and the pH [24].

The CSF is generally defined as shown in Eq. (2)

$$CSF = log\{t.\ exp[(T_H - T_R)/14.75]\} - pH \quad (2)$$

where t is the pretreatment reaction time in minutes, T_H is the reaction temperature in °C, T_R the reference temperature usually 100 °C and pH is the acidity of the aqueous solution in terms of acid concentration. In this study, the general CSF Eq. (2) was modified to include the autoclave and soaking temperature as shown in Eq. (3)

$$CSF = log\left\{ts.\ exp\left[\frac{T_{Hs} - T_R}{14.75}\right] + ta.\ exp\left[\frac{T_{Ha} - T_R}{14.75}\right]\right\} - pH \quad (3)$$

where t_s is the soaking time in minutes, T_{Hs} is the soaking temperature in °C, T_{Ha} is the autoclave temperature in °C, t_a is the autoclave time in minutes and T_R is the reference temperature usually 100 °C.

2.4. Comparison of SATP with enzymatic hydrolysis

The enzymatic hydrolysis was carried out in two major stages. The liquefaction stage was carried out using Termamyl 120 L (3000 U/ml; ≥500 units/mg protein), while the Saccharification stage was carried out using amyloglucosidase AMG 260 U/ml and Celluclast 1.5 L (≥700 units/g) (Novozymes, Denmark). These steps were carried out using the optimum enzymatic pre-treatment conditions reported by Khawla et al. [22] and Marx and Nquma [25]. Milled cassava peels (9.65 g) was mixed with 100 mL distilled water and the mixture was treated with 1 µl/g of Termamyl 120 L at 90 °C and pH 7 for 1 h followed by a denaturing step by incubating the mixture at 96 °C for 10 min after which the mixture was cooled to room temperature. The saccharification process was then carried out by the addition of 2.3 µl/g