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Pretreatment of cassava stems and peelings by thermohydrolysis to enhance hydrolysis yield of cellulose in bioethanol production process

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ABSTRACT

The potential of wastes obtained from the cultivation of *Manihot esculenta* Crantz as raw material for bioethanol production was studied. The objective was to determine the optimal conditions of hemicellulose thermohydrolysis of cassava stems and peelings and evaluate their impact on the enzymatic hydrolysis yield of cellulose. An experimental design was conducted to model the influence of factors on the pentose, reducing sugar and phenolic compound contents. Residues obtained from the optimal pretreatment conditions were hydrolysed with cellulase (filter paper activity 40 FPU/g). The hydrolysates from pretreatment and enzymatic hydrolysis were fermented respectively using *Rhyzopus* spp. and *Sacharomyces cerevisiae*. The yield of enzymatic hydrolysis obtained under the optimal conditions were respectively 73.1% and 86.6% for stems and peelings resulting in an increase of 39.84% and 55.40% respectively as compared to the non-treated substrates. The ethanol concentrations obtained after fermentation of enzymatic hydrolysates were 1.3 and 1.2 g/L respectively for the stem and peeling hydrolysates. The pentose and phenolic compound concentrations obtained from the multi-response optimization were 10.2 g/L; 0.8 g/L and 10.1 g/L; 1.3 g/L respectively for stems and peelings. The hydrolysates of stems and peelings under these optimal conditions respectively gave ethanol concentrations of 5.27 g/100 g for cassava stems and 2.6 g/100 g for cassava peelings.

1. Introduction

In the recent years, the production of value-added compounds from lignocellulosic wastes has been of great interest for economic as well as environmental reasons [1]. These wastes constitute an attractive and renewable raw material for bioethanol production due to their abundance, availability and low cost [2,3]. In Cameroon, cassava (*Manihot esculenta* Crantz), with an annual production of 2.3 million tons, is amongst the most consumed agricultural products. This production generates a great amount of residues which include cassava peelings and stems (444 tons per hectare) [4], often considered as waste. In some parts of Cameroon, the stems are used as fuel or animal feeds while the peelings are used as fertilizers. However, the use of these wastes for bioethanol production would be of greater interest.

Lignocellulosic biomass is principally composed of cellulose, hemicellulose and lignin whose contents vary depending on the species [5]. The bioethanol production process from lignocellulosic feedstocks is very complex and involves pretreatment, hydrolysis and fermentation [5,6]. The biomass pretreatment is necessary to alter the physical and chemical properties, thereby enhancing enzymatic hydrolysis [7,8]. Many factors related to lignocellulosic substrate (lignin, hemicellulose, porosity …) or specifically to cellulose characteristics (crystallinity index, degree of polymerization, accessible specific surface …) are responsible for low rate of enzyme hydrolysis of cellulose [5,7]. Amongst these factors, the lignin-hemicellulose matrix surrounding the cellulosic fraction of the biomass has been reported to be one of the main factors influencing the yield of hydrolysis. It acts as a physical barrier preventing the access of cellulase on the cellulose surface [7,8]. Zhu et al. [9] reported that the hemicellulose hydrolysis increases the pore size and substrate specific surface, thus facilitating the access of cellulase on the cellulose structure. Some authors [10,11] have shown that the removal of acetyl groups on hemicellulose chains,

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greatly improves enzymatic hydrolysis yields of the substrate. Recent studies have shown that xylooligomers obtained from hemicellulose hydrolysis are cellulase inhibitors. Their release during enzymatic hydrolysis could lead to a low yield of hydrolysis. This provides evidence of the need of hydrolyzing hemicellulose during pretreatment [2,12].

Amongst the pretreatments presented in literature, thermohydrolysis which uses pressure to maintain water in the liquid state at high temperatures (160–240 °C) results in a good solubilisation of hemicellulose [7,13,14]. This pretreatment, also called autohydrolysis, hydrothermal treatment, hot compressed water or liquid hot water [14], is very economical since there is no use of chemical reagents such as sulfuric acid and ammonia [13] and avoids the presence of inhibitors during fermentation of the hydrolysates obtained during the pretreatment stage. Hinman et al. [15] reported that the use of sugars from the hydrolysis of hemicellulose offers an opportunity to reduce the cost of lignocellulosic ethanol production in the order of 25%. However, during hydrolysis of hemicellulose into monosaccharides, there is the simultaneous cleavage of 1–4 alkyl-aryl bonds of lignin and lignin-hemicellulose bonds resulting in the release of soluble phenolic compounds [16,17]. These are inhibitors for the fermentation strains, and therefore constitute a barrier to the use of hemicellulosic hydrolysates obtained during pretreatment.

In this work, thermohydrolysis is used to pretreat cassava stems and peelings while determining the optimal pretreatment conditions for the different fractions. From literature, very little work has been done on thermohydrolytic pretreatment of cassava stems and peelings. Most of the optimizations done use classical methods consisting of varying each independent variable with time while maintaining the other variables fixed. This is costly in terms of time and does not permit a good appreciation of the possible interactions between the factors. For this reason, the central composite design response surface methodology was used to visualize and determine the effects of time, temperature, solid concentration and possible interactions between them during thermohydrolysis of cassava peelings and stems. Thereafter, optimal operating conditions for solid residues without hemicellulose and secondly, hemicellulose hydrolysates with maximum pentose content and minimum phenolic compound content were determined. Enzymatic hydrolysis of the residues permitted the evaluation of its impact on the yield of cellulose hydrolysis. Fermentation of hydrolysates and products from enzymatic hydrolysis by *Rhizopus* spp. and *Saccharomyces cerevisiae* respectively were conducted.

2. Materials and methods

Experiments were carried out as presented on Fig. 1.

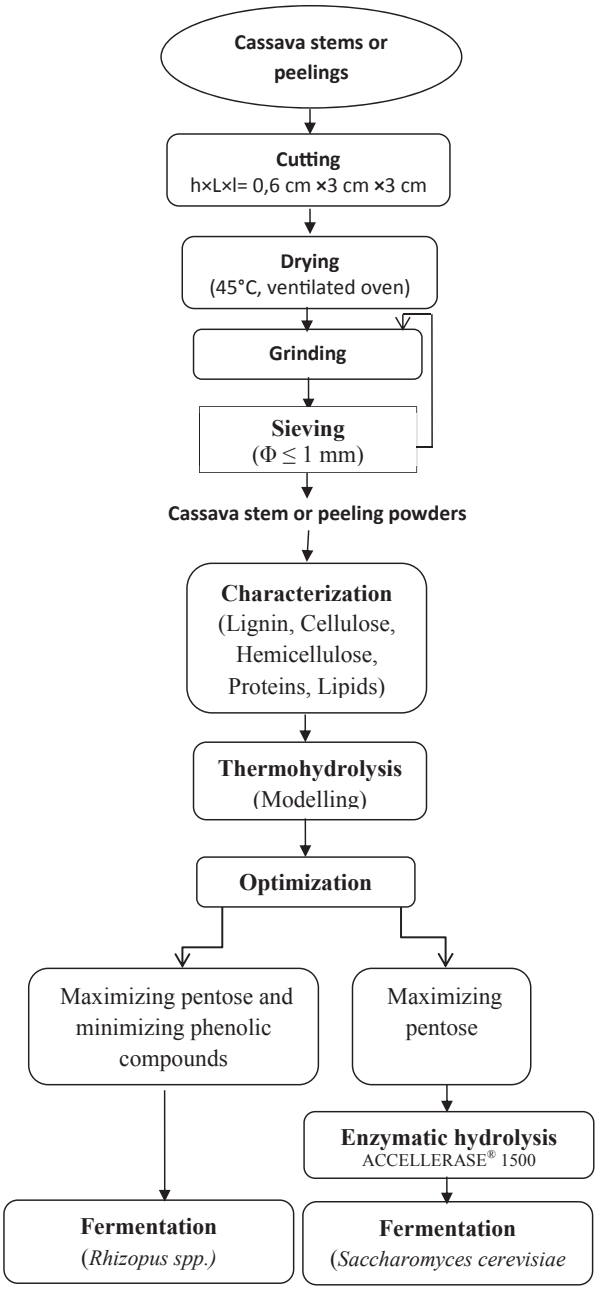

Fig. 1. Experimental approach.

2.1. Raw materials

Sweet cassava stems and peelings were harvested from a plantation, in the month of November, in the Nom-Kandi locality, located 60 km from Ngaoundere in the Adamawa region (Cameroon). The stems were sun dried till about 10% moisture content and milled to a 1 mm particle size. The powders obtained were conditioned in sealed plastic bags and stored at ambient temperature (25 ± 2 °C) till use. The moisture content was determined using a *Heraeus* oven at 105 °C according to NREL procedure [18]. Van Soest and Robertson [19] method was used to evaluate the cellulose, lignin and hemicellulose content. Ash content was determined in a muffle furnace using LAP-NREL procedure [20].

2.2. Preculture and activation of microorganisms

Fermentations were conducted using *Rhizopus* spp. for the pretreatment hydrolysates or *Saccharomyces cerevisiae* for the enzymatic hydrolysis products. The *Rhizopus* genus was obtained from the Microbiology Laboratory of the National Advanced School of Agro-Industrial Sciences (ENSAI) of the University of Ngaoundere in Cameroon. The *Saccharomyces cerevisiae* strain was an instant yeast ("safe-instant", packaged in white 11 g-composite packaging, 59703-Marcq-France) bought from a local supermarket in Ngaoundere-Cameroon.

The *Rhizopus* genus was identified following the identification key used by Chabasse et al. (2002) [32]. After 8 days of culture in Sabouraud medium at 25 °C, the *Rhizopus* had a cotton-like texture. At the beginning of the rapid and extensive growth, the colonies are