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The Effects of Mineral Acids and Bases on Physico-Chemical Pretreatment and Bioethanol Yield from Some Selected Agro-Peel Wastes

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***Abstract*— *This research work investigated suitable mineral acids and bases that could be utilized for physico-chemical pretreatment of agro-peel wastes for optimal bioethanol yield. Each substrate was physico-chemically pretreated with water, 1% NaOH, 1% KOH, 1% $Ca(OH)_2$, 1% H_2SO_4 1% HCl and 1% HNO_3 in order to identify the reagent that has the best hydrolytic effect. Thereafter, the concentration of the identified reagents with the best hydrolytic effects in each case was scaled up to 2% and 3% reagent concentrations in order to identify the optimum concentration for optimal bioethanol yield. Simultaneous Saccharification and Co-fermentation strategy using Trichoderma ressi, P. stipitis and S. cerevisiae inoculums were adopted under aseptic condition. It was found that the amount of sugars liberated depended on the type of chemical reagent utilized during physico-chemical pretreatment. The substrates seemed to be chemically selective; however, 1% NaOH, 1% H_2SO_4 and 1% HCl gave the best hydrolytic results. It was also found that mild pretreatment conditions were necessary for optimum bioethanol yield. Bioethanol production and yield took place optimally in samples physico-chemically pretreated with 1% reagent concentration when compared with 2% and 3% reagent concentrations.*

Keywords*— *Bioethanol, Agro-peel Wastes, Pretreatment, Saccharification, Fermentation, Mineral Acids and Bases

I. INTRODUCTION

Bioethanol is a renewable, clean liquid biofuel made by fermenting sugars or converting starch or cellulose from plant-based materials. Unlike alcohol produced synthetically from petroleum, bioethanol is made through fermentation. It is colorless, volatile, and flammable, which makes it an ideal biofuel that can be blended with gasoline in any proportion [1, 2]. This fuel has been of interest in recent years as an alternative fuel to the present fossil fuels; as it looks very promising for changing environmentally non-friendly fossil hydrocarbon raw materials [3].

Most agro-peel wastes are made up of lignocellulosic materials that are composed of cellulose, hemicellulose and lignin, as well as other minor components. Lignocellulosic biomass is plentiful in tree branches, stalks, stumps, stems; sawmill residues, shrubs, seaweeds, straw, sawdust, tree bark and agricultural peel wastes. The composition of hemicellulose, cellulose, and lignin varies, typically consisting of 40–60% cellulose, 20–40% hemicellulose, and 10–25% lignin. Through pretreatment, hemicellulose and cellulose are isolated from lignin and can be easily converted into fermentable sugars, which are then fermented to produce biofuel. Both cellulose and hemicellulose are sugar polymers and serve as potential sources of fermentable sugars [4]. Hemicellulose can be broken down under mild acidic or alkaline conditions, whereas the cellulose fraction is more resistant and needs more intensive treatment to become accessible for further conversion or hydrolysis [5]. Basically, the adopted pretreatment can be physical, chemical or biological depending on the action mechanism applied to the substrate. Sometimes, a combination of two or more of these methods is considered to achieve synergistic effects and better hydrolysis [6]. A successful pretreatment should fulfill the following conditions: (1) eliminate the lignin layer and de-crystallize cellulose; (2) boost sugar production or enhance the capacity for sugar formation through enzymatic hydrolysis; (3) reduce carbohydrate degradation or loss; (4) avoid generating byproducts that hinder subsequent hydrolysis and fermentation processes; and (5) be economically viable [7].

Various studies have been done on the effect of pretreatment on bioethanol yield; however, the authors did not find evidence of comparative study to evaluate mineral acids and bases optimization trials during pretreatment for optimal bioethanol yield. The aim of this research paper therefore is to investigate suitable mineral acids and bases that could be utilized for physico-chemical pretreatment of agro-peel wastes for optimal bioethanol yield.

II. MATERIALS AND METHODS

2.1 Collection and Preparation of Samples

Ripped peels were collected from food items bought from the market. These food items were washed with distilled water, air-dried and their peels collected. The peels were cut with knife into pieces of about 3-5 cm length prior to further treatments.

2.2 Physico-chemical Pretreatment of Substrates

Chemical hydrolysis was performed concurrently with mechanical comminution. In each instance, 15 grams of substrate were mechanically pulverized in a high-speed blender with 100 milliliters of each of the specified reagents for a duration of 5 minutes. The reagents were: (1) H_2O (2) 1% NaOH (3) 1% KOH (4) 1% $Ca(OH)_2$ (5) 1% H_2SO_4 (6) 1% HCl and (7) 1% HNO_3.

The broth was further incubated for 10 min at 120°C to achieve further hydrolysis. This was done to identify the reagent that has the best hydrolytic effect on the substrate. The concentration of the identified reagents that had the best hydrolytic effects was scaled up to 2% and 3% reagent concentrations in order to identify the optimum concentration for optimal bioethanol yield.

2.3 Hydrolysate Sugar Level Measurement

A refractometer was used to test and measure hydrolysate sugar levels. Samples were dropped on its glass surface and their sugar levels measured. The degree Brix results were then converted into sugar weight using Equation 1 below [1, 2, 8, 9].

$$\text{Hydrolysate sugar weight (g/L)} = {}^\circ\text{Brix} \times 10 \times \text{Specific gravity} \quad (1)$$

2.4 pH Adjustment and Sterilization

Prior to the addition of micro-organisms to the above pretreated samples, their pH values were adjusted to prevent the micro-organism from dying in either hyper acidic or basic conditions. The pH of the pretreated biomass was adjusted to 5.0 in a bowl using 4 M NaOH and 2.5 M H_2SO_4. Subsequently, samples were sterilized using an autoclave at a temperature of 120°C for 20 min and cooled to appropriate temperature before the introduction of microorganisms [1, 2].

2.5 Hydrolysate Simultaneous Saccharification and Co-fermentation

Under sterile conditions, the pretreated substrates were inoculated simultaneously with 25 milliliters each of Trichoderma ressi, S. cerevisiae, and P. stipitis inoculums. The mixture was incubated at 38°C with an agitation rate of 150 rpm for a duration of 72 hours on a shaker [1, 2]. This procedure was then repeated with broths that had 2% and 3% pretreatment reagent concentrations. The percentage ethanol yields were calculated according to the methods used by Tsunatu *et al*. [10].

III. RESULTS AND DISCUSSIONS

The results of different trials from different mineral acids and bases utilized in physico-chemical pretreatment for maximum sugar and ethanol yields are presented in Table 1 below.

Table 1: The Weight of Hydrolysate Sugars (g/L) Achieved After Physico-chemical Pretreatment

Pretreatment Conditions	Weight of Hydrolysate Sugars (g/L) from Pretreatment						
	PIP	**BP**	**PLP**	**POP**	**CP**	**YP**	**RH**
15g/100ml of H_2O	26.3	23.2	36.5	47.9	26.3	20.2	56.2
15g/100ml of 1% NaOH	**48.9**	**42.7**	**61.4**	59.3	59.3	48.9	**104.5**
15g/100ml of 1% KOH	34.5	37.5	48.9	49.9	48.9	33.4	61.4
15g/100ml of 1% $Ca(OH)_2$	28.3	22.2	34.5	28.3	26.3	23.2	48.9

15g/100ml of 1% H_2SO_4	43.7	40.6	52.0	**69.8**	63.5	**51.0**	93.2
15g/100ml of 1% HCl	39.6	41.7	54.1	68.8	**65.6**	48.9	92.2
15g/100ml of 1% HNO_3	38.6	39.6	51.0	68.8	56.2	47.9	87.9

PIP = Pineapple peels, BP = Banana peels, PLP = Plantain peels, POP = Potato peels, CP = Cassava peels, YP = Yam peels and RH = Rice husk

The results in Table 1 showed that considerable amounts of hydrolysate soluble sugars were liberated during physico-chemical pretreatment and this depended on the type of chemical reagent involved. 1% NaOH, 1% H_2SO_4 and 1% HCl were best in hydrolyzing the substrates which seemed to be chemically selective.

1% NaOH gave the best hydrolysate sugar weight result for sugar based substrate peels (ripped pineapple, ripped banana and ripped plantain peels) and rice husk while 1% H_2SO_4 gave the best result for starch based substrate peels of yam and potato. 1% HCl was the best for cassava peels. This showed that the substrates have target chemicals for optimum pretreatment or hydrolysis. 1% $Ca(OH)_2$ gave the most discouraging result in the test. 1% HNO_3 was equally good but did not come first in any of the tested substrate.

The utilized mineral acids and bases optimum concentration for optimal bioethanol yield is shown in Table 2 below.

Table 2: The Effect of Concentration Changes in Chemical Reagent used in Physico-chemical Pretreatment on Bioethanol Yield

Substrates	**Chemical reagent involved**	**Bioethanol yield (% w/v) with 3% reagent concentration**	**Bioethanol yield (% w/v) with 2% reagent concentration**	**Bioethanol yield (% w/v) with 1% reagent concentration**	**Bioethanol yield (% w/v) from other workers**
Pineapple peels	NaOH	3.10	3.78	4.94	1.67 (Aophat, *et al*., [11])
Banana peels	NaOH	2.24	2.79	3.85	2.30 (Ajay *et al*., [12])
Plantain peels	NaOH	2.90	3.43	4.57	3.18 (Itelima *et al*., [13])
Cassava peels	HCl	3.00	3.57	4.87	1.78 (Ezebuiro *et al*., [14])
Yam peels	H_2SO_4	2.51	2.72	3.78	2.70 (Akponah, [15])
Potato peels	H_2SO_4	3.92	4.21	5.31	3.90 (Sanat *et al*., [16])
Rice husk	NaOH	5.94	6.40	6.45	6.00 (Prasad *et al*., [17])

The results in Table 2 showed that mild pretreatment conditions were necessary for optimum bioethanol yield. One percent reagent concentration achieved the best bioethanol yield in all considered substrates. The decrease in yield with the increase in reagent concentration can be attributed to the degradation of hydrolysate sugar after physico-chemical pretreatment and possible formation of inhibitors detrimental to the fermentative microorganisms.

IV. CONCLUSION

It was found that considerable amounts of hydrolysate soluble sugars were liberated during physico-chemical pretreatment; and the amount of liberated sugars depended on the type of chemical reagent utilized during physico-chemical pretreatment. The substrates seemed to be chemically selective; however, 1% NaOH, 1% H_2SO_4 and 1% HCl gave the best hydrolytic results. 1% NaOH gave the best hydrolysate sugar weight result for sugar based substrate peels (ripped pineapple, ripped banana and ripped plantain peels) and rice husk while 1% H_2SO_4 gave the best result for starch based substrate peels of yam and potato. 1% HCl was the best for cassava peels. 1% $Ca(OH)_2$ gave the most discouraging result in the test.

It was also found that mild pretreatment conditions were necessary for optimum bioethanol yield. Bioethanol production and yield took place optimally in samples physico-chemically pretreated with 1% reagent concentration when compared with 2% and 3% reagent concentrations. The decrease in yield with the increase in reagent concentration can be attributed to the degradation of hydrolysate sugar after physico-chemical pretreatment and possible formation of inhibitors detrimental to the fermentative microorganisms.

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