PRETREATMENT OF COCOA WASTE USING IONIC LIQUID FOR BIOETHANOL PRODUCTION

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DEDICATION

This work is dedicated to my beloved sister Hasiya. May Allah (SWA) grant her Jannatul Firdaus, Ameen

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ABSTRACT

Bioethanol is a fuel derived from renewable sources of feedstock typically plants and agricultural waste such as cocoa waste. It has improved 'Lifecycle CO_2' performance because the plants used as feedstock take CO_2 from the atmosphere as they grown. This means that almost all the CO_2 produced by burning the fuel is balanced by CO_2 taken from the air. The reduced CO_2 emissions indicate that bioethanol is good for the environment. But unfortunately most of the chemicals used in the pretreatment processes for bioethanol production are not environmentally benign. In this study we employed the used of ionic liquid which is environmentally friendly in the pretreatment of coca waste, so that the whole process will be “green” (environmentally benign). To determine how effective Ionic liquid pretreatment is, it was compared to the untreated cocoa waste, sulphuric acid pretreatment and sodium hydroxide pretreatment. Ionic liquid pretreatment was found to showed minimal biomass destruction of 30.77% after pretreatment while H_2SO_4 showed 61.18% and NaOH 78.89% of biomass destruction after pretreatment. The untreated biomass has 10.23% amount of cellulose but pretreatment with ionic liquid exposed this amount up to 47.30%, H_2SO_4 to 49.13% and NaOH reduced this amount to 7.150%. Two types of yeast were also isolated from Tapai Ubi to do the fermentation. Using DNS method for determining reducing sugar, Ionic liquid pretreatment produced $6.3*10^{-2}$g/L of reducing sugar and untreated, H_2SO_4 pretreatment NaOH pretreatment produced $2.87*10^{-2}$ g/L, $7.4*10^{-2}$g/L and $3.37*10^{-2}$g/L respectively at the end of 24 hours of incubation. Bioethanol produced during the fermentation was analysed using gas chromatography. Ionic liquid produced a total of 7.885g/L, H_2SO_4 produced 7.911g/L NaOH produced 6.824g/L and untreated cocoa waste produced 5.116g/L of ethanol at the end of 24 hours.

ABSTRAK

Bioethanol adalah bahan api yang diperolehi daripada sumber yang boleh diperbaharui seperti bahan mentah biasanya tumbuh-tumbuhan dan bahan buangan pertanian seperti sisa koko. Ia telah meningkatkan prestasi 'Kitaran Hayat CO_2 kerana tumbuh-tumbuhan yang digunakan sebagai bahan mentah mengambil CO_2 dari atmosfera semasa mereka bertumbuh. Ini bermakna bahawa hampir semua CO_2 yang dihasilkan dengan membakar bahan api adalah seimbang oleh CO_2 yang diambil dari udara. Penghasilan CO_2 yang kurang menunjukkan bahawa bioethanol adalah baik untuk alam sekitar. Tetapi malangnya, kebanyakan bahan kimia yang digunakan dalam proses prarawatan untuk pengghasilan bioethanol tidak mesra alam. Dalam kajian ini, kami menggunakan cecair ionik yang mesra alam dalam prarawatan coca sisa, supaya keseluruhan proses akan menjadi "hijau" (mesra alam). Untuk menentukan keberkesanan prarawatan cecair ionik, ia dibandingkan dengan sisa koko yang tidak dirawat, prarawatan dengan asid sulfurik dan natrium hidroksida. sisa koko yang tidak dirawat,. prarawatan cecair ionik menunjukkan kemusnahan biomass yang minimum (30.77%) selepas prarawatan. Manakala H_2SO_4 menunjukkan 61.18% dan NaOH 78.89% daripada kemusnahan biomass selepas prarawatan. Biomass yang tidak dirawat mempunyai jumlah 10.23% selulosa tetapi sisa koko dengan prarawatan cecair ionik mempunyai jumlah 47.30% selulosa, H_2SO_4 parawatan mempunyai 49.13% selulosa dan NaOH parawatan mempunyai 7.150% selulosa. Dua jenis yis telah diisolasi daripada Tapai Ubi penapaian. Menggunakan kaedah DNS untuk menentukan gula sisa kok yand penurum, prarawatan cecair ionik yang menghasilkan $6.3*10^{-2}$ g/L gula penurum dan tidak dirawat, prarawatan dengan $H_2SO_{4,}$, dan NaOH prarawatan menghasilkan $2.87*10^{-2}$ g/L,$7.4*10^{-2}$g/L dan 3.3 *102g/L masing-masing pada akhir 24 jam pengeraman. Bioethanol yang dihasilkan semasa penapaian disulkat menggunakan kromatografi

gas. Cecair ionik telah menghasilkan sejumlah 7.885g/L, H_2SO_4 menghasilkan 7.911g/L NaOH menghasilkan 6.824g/L dan biomass yang tidak dirawat menghasilkan 5.116g / L ethanol akhir 24 jam.

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LIST OF ABBREVIATIONS

IL	-	Ionic Liquid
LB	-	Lignocellulose biomass
DCM	-	Dichloromethane
DNS	-	Dinitrosalicyclic acid
GC	-	Gas chromatography
M	-	Molar
g	-	Gram
g/L	-	Gram per Litre
ml	-	Mililter
m	-	Slope
w/v	-	weight / volume
v/v	-	volume / volume
^{o}C	-	Degree Celsius
OD	-	Optical density
PDA	-	Potato Dextrose Agar
PYS	-	Peptone Yeast Extract Starch Medium

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CHAPTER I

INTRODUCTION

1.1 Background of the study

Green chemistry simply refers the use of chemistry in preventing pollution. It is a philosophy of science, particularly chemical research and engineering that encourages the design of products and synthetic processes that minimize the use and generation of hazardous substances. It involves the use of chemicals substances and chemical processes that are designed to eliminate or reduce negative environmental impacts. The use and production of these chemicals may involve reduced waste products, non-toxic components, and improved efficiency. The twelve principles of green chemistry, according to Anastas, and Warner (1998), are:

1. “ **Waste prevention**: this principle advocates the concept of preventing waste from the source as the best method of preventing pollution than cleaning waste after it has been created.
2. **Economy of atom**: the production process should involve all the components of the materials used in production. If possible the by-products can also be converted to other valuable goods to minimize the production of waste.
3. **Chemical process with less hazardous substances**: this involves the substitution of hazardous chemical process (substances) with less hazardous ones use in synthetic processes.

4. **Chemical are designed for safer use**: chemical should be designed in such a way that their impact to the environment is reduced to a minimal level.
5. **Use of auxiliaries and safer solvent**: solvent and auxiliary substances used in chemical process should be minimized and if possible less toxic ones should be used.
6. **Synthetic processes are designed for energy efficiency**: energy require for chemical process should be determined and minimized. Chemical process should be carried out at room temperature (if possible) to reduce their economic and environmental impact.
7. **Minimum use of derivatives**: Synthesis processes should minimize the use of derivatives (related chemical product) to reduce the additional reagent which generate waste.
8. **Maximum use of renewable resources**: this step encourages the use of renewable raw materials in the synthetic process rather than non-renewable resources.
9. **Rate of reaction**: speeding up of chemical reaction using catalyst should be encouraged over using stoichiometry.
10. **Degradation design**: synthetic process should be designed in such a way that can be degraded to substances that are harmless to the environment.
11. **Pollution control through real-time analysis**: analytical methods should be used to monitor, evaluates and provides possible solutions to potential environmental damages.
12. **Accident prevention through the use of safer chemistry**: this involves the selection of chemical that either prevent or reduced chemical accident, example explosion". (Anastas and Warner, 1998).

These principles guide firms in designing new products and processes in such a way that their impact on the environment is reduced. This may unknowingly eliminates some serious environmental problems before we even know they exist. This is a very good method of controlling pollution because it applies innovative scientific solutions to real-world environmental situations. The concept of "green chemistry" is well-known among scientists today, especially the exploration of novel solvents that can replace the volatile organic compounds that is used in synthesis, catalysis, and separation processes**,** (Kazunori Nakashima, *et al.,* 2005). One of the developments in green chemistry is to substitute the volatile organic solvent with ionic liquids.

Ionic liquids (ILs) are ionic, salt-like materials that are liquid below 100°C. ILs have ambient temperature and possess many attractive properties such as negligible volatility, non-flammability, high thermal stability, and controllable hydrophobicity, (Kojiro Shimojo *et al.*, 2006). ILs has solvent properties and is miscible with organic solvents and water. Their non-flammability and negligible vapour pressure make them not readily lost to the environment. In recent years, ILs has been extensively studied as an alternative to organic solvent. They have been widely examined as extracting phases in liquid-liquid extraction systems and show good extraction performance and separation ability for metal ions when compare with organic solvents, (Kojiro Shimojo *et al.*, 2006). Dai *et al.*, (1999) studied the extraction of alkaline and alkaline metal in ILs and achieved high extraction efficiency compared to that of ordinary organic solvent. The extraction behaviour of strontium into imidazolium cation based ILs was also examined by Dai *et al.* (1999), and obtained a high distribution coefficient compared to that of ordinary organic solvent. From these studies, it can be deduced that apart from being environmentally benign, ILs also show high extraction performance compared to conventional organic solvents.

Although several works have been done on ILs, this particular work focuses on demonstrating the use of IL in pretreatment of cocoa waste for production of bioethanol. This study also compared the efficiency of using ILs and other chemical pretreatments methods, such as H_2SO_4 and NaOH.

1.2 Aim and objectives of the study

The aim of this study is to introduce the concept of ionic liquids as a solvent in pretreatment of cocoa waste. Specifically, the study was designed to address the following objectives:

a. To determine the effect of IL, H_2SO_4, NaOH pretreatments on cocoa waste

b. To determine the amount of cellulose, hemicelluloses and lignin content of IL, H_2SO_4, NaOH pretreatments and compare to the untreated cocoa waste

c. To compare the sugar produced by IL, H_2SO_4, NaOH pretreatment with the one produced by untreated cocoa waste

d. To detect the present of ethanol produced by IL, H_2SO_4, NaOH pretreatments as evidence that fermentation has taken place.

1.3 Scope of the study

This study is limited to a single type of lignocelluloses biomass; cocoa waste which was obtained from JB Koko. The study focused on the usage of ILs to pretreat cocoa waste and compare with several known physical and chemical pretreatment. The sugar and bioethanol produced was measured and the best pretreatment method was determined.

1.4 Significant of the study

To achieve enzymatic degradation in production of ethanol, a pretreatment process is necessary. The purpose of all pretreatments is to remove lignin and hemicellulose, reduce cellulose crystalinity and increase the porosity of the materials. According to Mohammad J and Keikhosro K, (2008), all kinds of pretreatment must meet the following requirements:

- Production of reactive cellulosic fiber for enzymatic attack
- Avoiding destruction of hemicelluloses and cellulose,
- Avoiding formation of possible inhibitors for hydrolytic enzymes and fermenting microorganisms,
- Minimizing the energy demand
- Reducing the cost of size reduction for feedstocks,
- Reducing the cost of material for construction of pretreatment reactors,
- Producing less residues,
- Consumption of little or no chemical and using a cheap chemical.

Most of the pretretment methods fail to meet all these requirements, thus there is need to exploit some other alternative methods which are environmentally friendly and are in line with the green chemistry. Hence the significant of this study is to exploit other alternative method for pretreatment of lignocelluloses biomass which is environmentally friendly and may possibly meet the above requirements.

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