CHAPTER 1

Introduction

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1.1 Principle and Background

In the present situation, Thailand is confronting important problem of energy shortage because it has to import energy from foreign countries in very large quantity. In 2010, Thailand imported the commercial energy from several countries in quantity of 63,958,000 tons, compared with crude oil (41,766,000 tons). It is certain that crude oil price of world market always increases and fluctuates. This causes Thailand to face several disadvantages in economical aspect. To solve the problem, the consideration for finding new energy sources to replace crude oil is very significant. Therefore, Thai government decided to implement renewable energy development plan which takes approximately 15 years from 2008 to 2022 with the main purpose to increase the proportion of renewable energy consumption to 20% higher than total energy consumption in 2003. This can help reduce imported energy over 460,000 million/year and the plan is divided into 3 phases. The first one is short-term phase (2008-2011) which aims at proving accepted technological support and efficacy of the greatest renewable energy products such as biofuel, electricity generation, biomass heat, biogas and NGV. The second one is half-term phase (2012-2016) which involves industrial promotion, proven technology, renewable energy technology as well as supports new technological model development such as ethanol production, biodiesel from seaweeds, biomass oil production and hydrogen fuel. This is to earn economic worthiness including promotion of new technologies in biofuel production, develop Green City model and conduct strength for community's renewable energy production. The last one is long-term phase (2017-2022) to promote the new type of renewable energy technologies which areeconomically valuable including extended Green City results and energy for

community as well as support Thailand to be the export center of Asian for biofuel and renewable energy technologies.

Ethanol biofuel is one of the objectives in adjusted plans for renewable energy in 15 years which supports production and consumption of ethanol not to be lower than 9 million liters/day within the year 2022. There are many advantages for this plan. Firstly, to decrease petroleum use, increase value, earn stabilities for agricultural productivities by sustainable ethanol production. Secondly, to prepare knowledge campaign and contribute commitment to consumers conscientiously, and finally to promote completely and environmentally friendly ethanol industries as well as logistics development purpose for reducing cost of both research and development. However, ethanol production ranking of the year 2010 was only 1.2 million liters/day.Ethanol or ethyl alcohol is the alcohol of which chemical formula is C₂H₅OH and its characteristics are clear liquid, colorless, inflammable as well as it has high research octane value. It can be used for many purposes such as food, alcoholic beverage or act as solvent in many industries and fuel. Ethanol can be produced either from chemosynthesis method using ethylene as essential material or chemical method using plants or agricultural crops which contain some materials such as flour and sugar. The latter method is popular and has various alternative materials which can be easily found in each countryside area such as corn, millet, cassava, sugar cane, molasses and weed. Besides, there has been a technological development of ethanol production which contains high cellulose such as rice straw, sawdust, dried grass. Because Thailand is one of the countries that heavily relies on agriculture. There could be many kinds of materials to produce ethanol such as sugar cane, cassava, corn, millet. For the main materials at the present, ethanol industry uses molasses, which is the product from sugar and cassava production method, surplus of tapioca chip, cassava pellet, and cassava flour products. However, this main material to produce ethanol will be insufficient if the demand is higher than 9 million liters/day in 2022 and cultivated areas for energy product are severely limited.

Therefore, the efficient way for ethanol production is necessary for research and development to increase the cultivation of cassava, sugar cane and other alternative plants. To produce consumable plants as energy source could increase the food price in the country. At the present, there are some researches for ethanol production from

cellulose which is regarded as the second generation bio-energy with materials such as wood and agricultural crops which consist of lignocellulose material with organic compounds. Carbohydrate is the main component of plant cells arise from Glucose suborders bridging together as line or polymer of glucose. Ethanol made of cellulose has the similar chemical properties and qualities as ethanol made of sugar and flour. To produce ethanol, a group of lignocelluloses is combined with other groups of lignocellulose which have sugar in their structural element, when these groups of lignocellulose change and decay, they would increase the amount of monosaccharide which can be converted to ethanol. Ethanol production method from lignocellulose material groups is composed of the following main stages. (1) Pretreatment (2) Hydrolysis (3) Fermentation and (4) Distillation. To produce ethanol from materials with simple structure such as sugar and flour is not so complicated. Thus, it is preferred to use elementary materials such as sugar cane, molasses, cassava and corn because sugar can be converted to ethanol by using yeast. Lignocellulose has rather complex molecular structure to make sugar with more complex structure decay to become another kind sugar with simpler structure. Nevertheless, restriction of ethanol production from cellulose is that the decaying process of lignocellulose to be sugar takes longer time than the conversion of sugar to be ethanol.

Lignocellulose pretreatment has been studied for a long time. The purpose of this method is to separate lignin and hemicellulose, decrease cellulose crystallization and increase porous material. The requirements in lignocellulose pretreatment are (1) increase sugar number (2) reduce the carbohydrate loss (3) avoid restraining production in hydrolysis and fermentation processes and (4) decrease production cost.

For ethanol production from lignocellulose, lignocellulose substance is very hard for decay so it must be prepared for softening process so that enzyme can access and react well (Sun and Cheng, 2002). From the studies of Krishna and group (1998) in hydrolyzed trashes with enzyme, the results were that the prepared trashes were changed to be sugar higher than 40% but the unprepared trashes were changed to be sugar lower than 20% and ethanol production from unprepared alfalfa fiber would give only 6.4 g/L of ethanol whereas prepared alfalfa fiber could provide ethanol at 18.0 g/lL (Sreenath et al., 2001).

Lignocellulose materials preparation could be proceeded by various methods. There might be physical, chemical and biological processes such as by minimizing materials size with cutting, grinding in order to reduce crystallization of cellulose. The cut sizes are approximately 10-30 mm., grinded sizes are approximately 0.2 to 2 mm. Grinding is used to dissolve crystallization of cellulose and increase decay. (Sun and Cheng, 2002), Zhu and group (2005a, 2005b) used rice straw in ethanol production. Before the preparation with sodium hydroxide (NaOH) solution, cut as 1-2 cm. and after NaOH solution preparation, cut as small size 10 to 20 millimeters again would increase amount of cellulose.

Steam explosion is the most regular method for preparing lignocellulose materials. This process materials shall be prepared with high steam pressure and then reduce pressure rapidly for effects of explosion and decomposition. Steam Explosion starts from 160 - 260 °C as pressure 0.69-4.83 MPa two or three seconds long after that put into normal temperature (Sun and Cheng, 2002) The advantage of steam exploding preparation is low energy consumption compare with cutting, grinding, physical process that use more energy than steam explosion process at 70%. Steam explosion shall be highly activated with hardwoods and agriculture crops but lowly activated with softwoods, restriction of steam explosion is splitting lignin and carbohydrate incompletely, rise microorganisms restrained substances (Sun and Cheng, 2002)

Chemical process preparation by decomposing ozone with lignin and hemicellulose in various materials such as rice straw, bagasse, dried grass, peanut, sawdust. Disintegration activates only with lignin and hemicellulose but cellulose is hard. Ozone preparation method has advantages to be able to remove lignin, does not produce prison or occurs as an inhibitor in temperature reaction and normal pressure, large amount ozone use would be high because high price (Sun and Cheng, 2002) or has used some kinds of acid such as sulfuric acid (H₂SO₄) and hydrochloric acid (HCl) in lignocellulose preparation. Although acids are chemicals for good cellulose hydrolysis but the acid concentration is harmful, abrasive and dangerous so reactor which can endure corrosion need to be used. At present development by acid dilution in lignocellulose preparation till can be used for cellulose hydrolysis increase but acid using it would stimulate the cost and pH would be affected in fermentation process as well (Sun and Cheng, 2002)

Some base solution could also be used for preparing lignocellulose material and factors of preparation depend upon the amount of lignin. To prepare lignocellulose with diluted ammonium hydroxide (NH₄OH), the results need to be dilated to make surface area much larger as well as decompose polymer state, reduce crystallization and destroy lignin structure. Furthermore, NaOH solution could reduce amount of lignin in hardwood from 24%-55%, only 20% is left, but diluted acid would be left out of Lignin over about 20% (Millet and group, 1976 refer to Sun and Cheng, 2002). Some base solution types could damage bonds between groups of lignin, damage bonds between lignin and polysaccharide (Sun et al., 1995).

Besides lignocellulose material preparation with physical and chemical processes, there are some microbes such as brown, white, and soft-rot fungi in damaging lignin and hemicellulose in the materials, brown-rot fungi are used only for cellulose, while white-rot fungi and soft-rot fungi could be for both cellulose and lignin. White-rot fungi are in fungi group which is highly efficient for lignocellulose preparation, white-rot fungi are able to decay lignin and release cellulose. Brown-rot fungi could damage cellulose.

Advantages of preparation with biological process is low energy using and simple condition needed but hydrolysis with microorganisms or biological processes occur in very low number of products.

Bana grass is hybrid Napier grass (P.purpureum x P. americanum hybrid) when grew up completely tall as 3-4 m., it is well grown up on sandy soil as well as clay soil but need drainage soil in high abundant amount.

Bana grass can be harvested in high yield per hectare, an output product per time estimate as 25-37.5 tons, in a year can be able to harvest around 5-6 times. So output product is estimated weight at 156.2-187.5 tons/hectare/year, humidity approximates 70%, as dried weight has cellulose 33-35%, hemicellulose 25-26% and lignin estimates 4-7%. cellulose and hemicellulose product that produced from Bana grass is equal to 28.1-33.7 tons/hectare/year. Regarding this product, Bana grass must be high efficient product for material of ethanol production from cellulose, which is the second generation biofuel.

This research would study about Lignocellulose material pretreatment which is from Bana grass in order to expel lignin by using alkaline and ozone and study about condition of proper factors using in expelling lignin out of Bana grass compares with biomass amount in high number of lignin. Obtained data would be analyzed and evaluated fund for Bana grass pretreatment process to answer the proposition in technology development of renewal energy in the country in the near future.

1.2 Objectives

1.2.1 This is to study the influence of delignification processes, i.e. alkaline with ozone and ozone only. Both kinds of processes are used to break down lignin from Bana grass for the production of ethanol fuel.

1.2.2 To optimize the delignification conditions that are used to break down lignin from biomass with low lignin content, i.e. Bana grass and compare it with another high lignin content biomass.

1.3 Scopes of this study

1.3.1 The selected delignification process is low concentrated alkaline with ozone. Result of the study will be compared with that from alkaline only.

1.3.2 Bana grass having 80 - 90 days of age and 8.20 % lignin is used in this study.

1.3.3 The selected high lignin biomass is the leaves and stems of corn obtaining from livestock breeding. It is collected not more than 5 days of harvest and has 16.86% of lignin.

1.3.4 Three selected alkaline are NaOH, Ca(OH)₂ and NH₃.

1.3.5 Pretreatment parameters used in the process of alkaline with ozone and alkaline only are as follows;

1.3.5.1 Concentrations of alkaline are NaOH 0.5–10.5%, NH₃ 5–20% Ca(OH)₂ 20-100 %

1.3.5.2 Impregnation time of alkaline are 0.5 to 8 hours.

1.3.5.3 Impregnation temperature are 30 to 90 0 C.

1.3.5.4 Flow of ozone are 10-30 mins.