FINAL REPORT OF
INTERNATIONAL RESEARCH COLLABORATION

Alkaline-Dilute Acid Pretreatment and Simultaneous Saccharification Fermentation for Production of Bioethanol From Rice Husk (Experimental and CFD Modeling)

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Research Title : Alkaline-Dilute Acid Pretreatment and Simultaneous Saccharification-Fermentation for Production of Bioethanol From Rice Husk (Experimental and CFD Modeling)

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Research Duration : 3 years
Research Budget

Year	**Proposed to Unsri**
Year 1	196.832.705
Year 2	193.388.025
Year 3	199.993.768

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1. Introducion

1.1. Problem Statement

The crisis of energy and climate change has caused the interest of renewable energies in many countries such as Indonesia significantly increases. The combustion of fossil fuels provides the largest source of carbon in the earth's atmosphere. Carbon dioxide greenhouse gases trap heat inside the earth's atmosphere which contributes to climate change. The technology involves utilizing and converting biorenewable resources to meet the petroleum fuel and product demands (Wyman, 1999) which will substantially reduce net greenhouse gas emissions. The conversion of lignocellulosic biomass to biofuels especially bioethanol as transportation fuels provides the best optional to reduse the greenhouse emission. Bioethanol can be used in various blends with gasoline, such as 5% bioethanol (Demirbas 2008), 10% & 20% (E10 & E20) or even 85% (E85) (Balat et al. 2008).

Rice husk is one of the abundant lignocellulosic waste materials that can be utilized to become renewable energy. The rice husk has the huge potential to be converted to the second generation of bioethanol. It has high cellulose and hemicelluloses content that can be readily hydrolysed into fermentable sugars. The rice husk predominantly contains cellulose (42.2 %), hemicellulose (18.47 %) and lignin (19.4 %) (Banerjee et al. 2009).

The production of bioethanol involves different process steps including biomass pre-treatment, enzymatic hydrolysis, fermentation and product recovery. Biomass pre-treatment is one of the most crucial and expensive process steps that has been widely discovered (Rabelo et al. 2009). The pretreatment process is important for increasing the enzymatic digestibility of lignocellulosic materials (Chang et al. 2011). The purpose of the pretreatment is to remove lignin and hemicellulose, avoid the degradation or loss of carbohydrate, avoid the formation of byproducts inhibitory to the subsequent hydrolysis and fermentation processes; and be cost-effective (Sun & Cheng 2002).

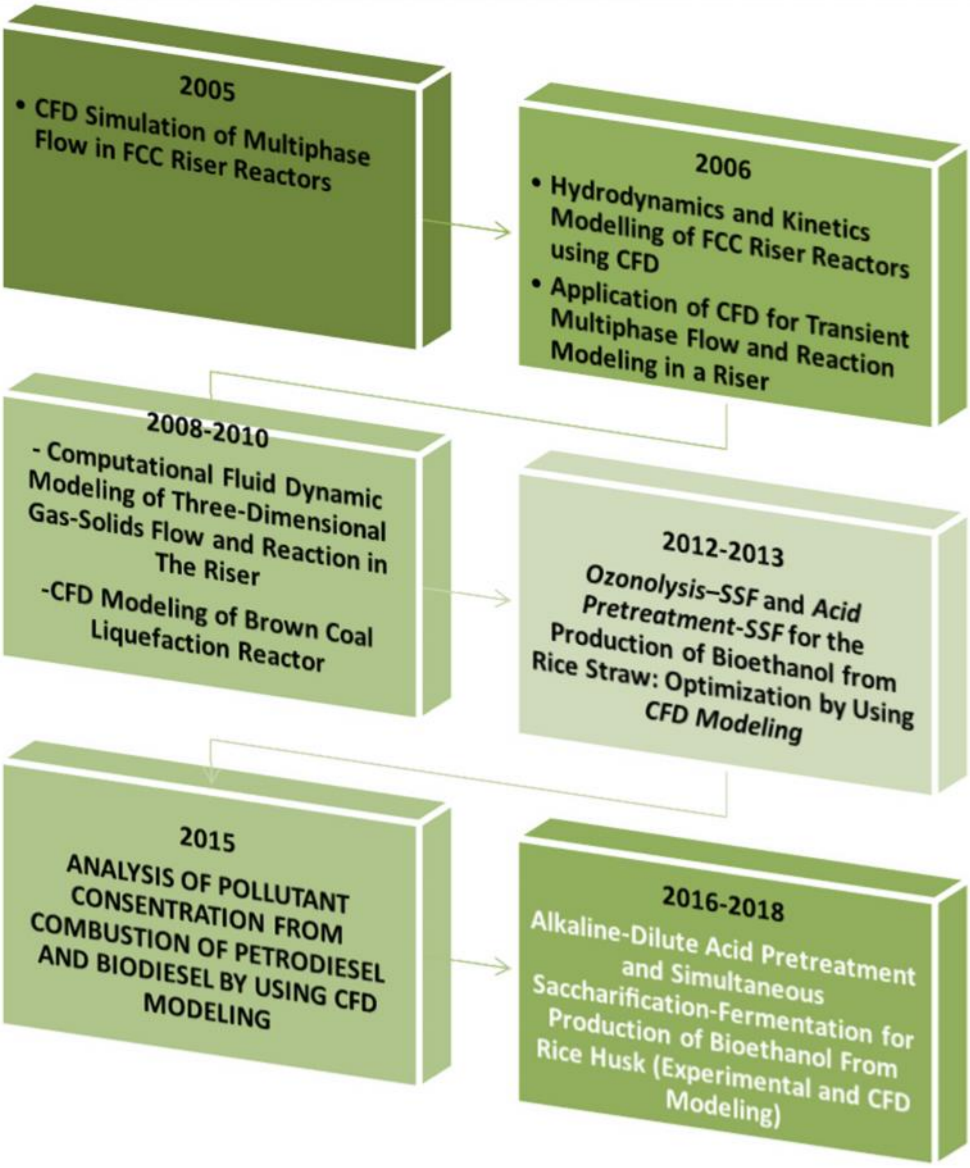
This study aimed to evaluate delignification process by using alkaline-dilute acid pretreatment experimentally and CFD modeling . The rice husk pretreated at various alkaline concentrations and continued to the acid pretreatment with various concentrations and time heating. The Simultaneous Saccharification and Fermentation process was used to produce ethanol by using the cellulose enzyme and *Saccharomyces cerevisiae.*

1.2. Research Objectives

The Purpose of this research is for producion of bioethanol from risk husk by using Alkaline-Dilute Acid Pretreatment and *Simultaneous Saccharification and Fermentation (SSF)* Method Experimentally and CFD Simulation. For realized this objective, several steps to be done as follow:

1. Investigate the Alkaline-Dilute Acid Pretreatment to degradate the lignin content in the lignosellulosic biomass by Experimental Research
2. Modeling of the Alkaline-Dilute Acid Pretreatment by using CFD
3. Verification of the Alkaline-Dilute Acid Pretreatment by Experimentally and CFD Modeling
4. Investigate *Simultaneous Saccharification and Fermentation (SSF)* by Experimental Research
5. Formulate the correlation between the Alkaline-Dilute Acid Pretreatment and *Simultaneous Saccharification and Fermentation (SSF)*.
6. Design of Alkaline-Dilute Acid Pretreatment Reactor
7. Design of *SSF* Bioreactor

1.3. Road Map of Research



2005
- CFD Simulation of Multiphase Flow in FCC Riser Reactors

2006
- Hydrodynamics and Kinetics Modelling of FCC Riser Reactors using CFD
- Application of CFD for Transient Multiphase Flow and Reaction Modeling in a Riser

2008-2010
- Computational Fluid Dynamic Modeling of Three-Dimensional Gas-Solids Flow and Reaction in The Riser
-CFD Modeling of Brown Coal Liquefaction Reactor

2012-2013
Ozonolysis–SSF and Acid *Pretreatment-SSF* for the Production of Bioethanol from Rice Straw: Optimization by Using *CFD Modeling*

2015
ANALYSIS OF POLLUTANT CONSENTRATION FROM COMBUSTION OF PETRODIESEL AND BIODIESEL BY USING CFD MODELING

2016-2018
Alkaline-Dilute Acid Pretreatment and Simultaneous Saccharification-Fermentation for Production of Bioethanol From Rice Husk (Experimental and CFD Modeling)

2. Literarute Review

The government programs on energy conversion should be supported by seeking the alternative sources of renewable energy. A large number of studies regarding the utilization of lignocellulosic biomass as a feedstock for producing bioethanol has been carried out (Chen et al. 2011; Xavier et al. 2010; Karimi et al. 2006).

The production of bioethanol second generation is more complex compared than the first generation of bioethanol. The lignin content in lignocellulosic biomass must be removed in order to access the digistability of enzymatic hydolysis. Therefore, a pretreatment process is very essential in order to remove lignin and hemicellulose, reduce cellulose crystallinity, and increase the porosity of the materials (Karimi et al. 2006). Pretreatment is required to change the structure of cellulosic biomass to make cellulose more accessible to the enzymes that convert the carbohydrate polymers into fermentable sugars (Mosier et al. 2005). The cellulose and hemicellulose fractions can be enzymatic hydrolysed to monomeric sugars after a pretreatment process. The pretreatment process is highly cost, so the good pretreatment can decrease the amount of enzyme for enzymatic hydrolysed. Pretreatment also enhanced the yield of glucose. Without pretreatment results less than 20 % of glucose, meanwhile with the pretreatment process produces the yield of glucose is about 90% (Hamelinck et al. 2005). Several methods for the pretreatment of ligncellulosic materials to enhance saccharification have been developed in laboratories by using steam explosion and alkaline peroxide (Cara et al. 2006), alkaline pretreatment (McIntosh & Vancov 2010; Harun et al. 2011); and hydrothermal pretreatment (Thomsen et al. 2008). These technologies are usually implemented under severe reaction conditions with a large capital investment, high processing costs and great investment risks (Li et al. 2009). Some of these methods produce strong acidic, toxic residues in the treated lignocellulosic and inhibit compounds for saccharification and subsequent ethanol fermentation. Meanwhile, alkaline pretreatment was shown to be more effective on agricultural residues than on wood materials (Taherzadeh & Karimi 2008). Also, alkali pretreatments selectively remove lignin portion mainly. Alkali pretreatment processes use lower temperatures and pressures compared to other pretreatment technologies (Mosier et al. 2005). The process of lime pretreatment involves slurrying the lime with water, spraying it onto the biomass material, and storing the material for a specific duration, usually from days to weeks (Mosier et al. 2005). Ammonia has been widely used in alkali pretreatments, its use leads to many environmental problems because of which recovery and recycling processes must also be used along with this pretreatment. Removal of hemicellulose and lignin could affectedly improve enzyme digestibility by increasing the enzyme accessibility to cellulose. The pretreatment with dilute sulfuric acid followed by aqueous ammonia would then be needed for efficient saccharification and lignin isolation. Based on the advantages of dilute acid and alkaline pretreatment, this research studied the combination of dilute acid-alkaline pretreatment to remove the lignin content in the rice husk. Pretreatment is the most expensive process in lignocellulosic biomass to be converted to fuels, but it has the huge potential for improving the efficiency and reducing of the costs through further research and development.

Cellulose $[C_6H_{10}O_5]_n$ is a straight-chain polysaccharide containing covalently linked β-1,4 glycosidic bonds. It is the most abundant organic polymer found in nature and is located, nearly entirely, within the plant cell wall where it is embedded in a complex lignin structure. Enzymatic hydrolysis occurs in two steps which are degradation of cellulose to cellobiose by endo-p-1,4-glukanase and ekso- B-1,4 glukanase, subsequent by degradation of cellobiose by B-1,4 glukosidase (Martins et al. 2008; Ahamed & Vermette 2008). Aspergillus Niger produce high content ofp-glukosidase and low content of endo-p-1,4-glukanase and ekso-B- 1,4-glukanase. Saccharification is carried out by adding cellulase enzym and p-glukosidase.

Enzymatic hydrolysis has several advantages (1) reduce the negative impact to environmental (2) the enzymatic hydrolysis can be performed together with the fermentation, instead of subsequent to the enzymatic hydrolysis (Olofsson et al. 2008). This is called as Simultaneous Saccharification and Fermentation (SSF). In the simultaneous saccharification and fermentation (SSF) process, the saccharification and the fermentation take place within the same reaction vessel. Furthermore, the hydrolytic enzyme and the fermenting organism are fed to the same reactor addressing the glucose formed during the saccharification to be immediately consumed by the fermenting organism. Several advantages of SSF include (Sun & Cheng 2002):

1. Lower enzyme requirement
2. The immediate removal of glucose and the production of ethanol reduce the requirements for sterile
3. Shorter process time
4. Higher product yields

The research of bioethanol from lignocellulosic biomass has been studied by several researchers (Adsul et al. 2005; Cerveró et al. 2010; McIntosh & Vancov 2010; González-García et al. 2009; Harun et al. 2011; Erdei et al. 2010; Lee et al. 2010). This research studied the simultaneous saccharification and fermentation (SSF) of pretreated rice husk for the production of bioethanol. Figure 1 desribes the complexity of the various metabolic pathways involved in ethanol production from sugars.

Simulation of the Alkaline-Dilute Acid Pretreatment using computational fluid dynamics (CFD) modelling is still a challenging domain. The fundamentals research to understand the processes occurring in reactive flow systems have been studied. Several works are being carried out to develop computational methods suitable for coupling the many important aspects of chemistry and physics in a way that is efficient enough for solving the pretreatment problems. The CFD modeling can provide a wide range of information for the design of pretreatment reactorr. The using of CFD modeling can reduce the cost of time-consuming experimental investigations.

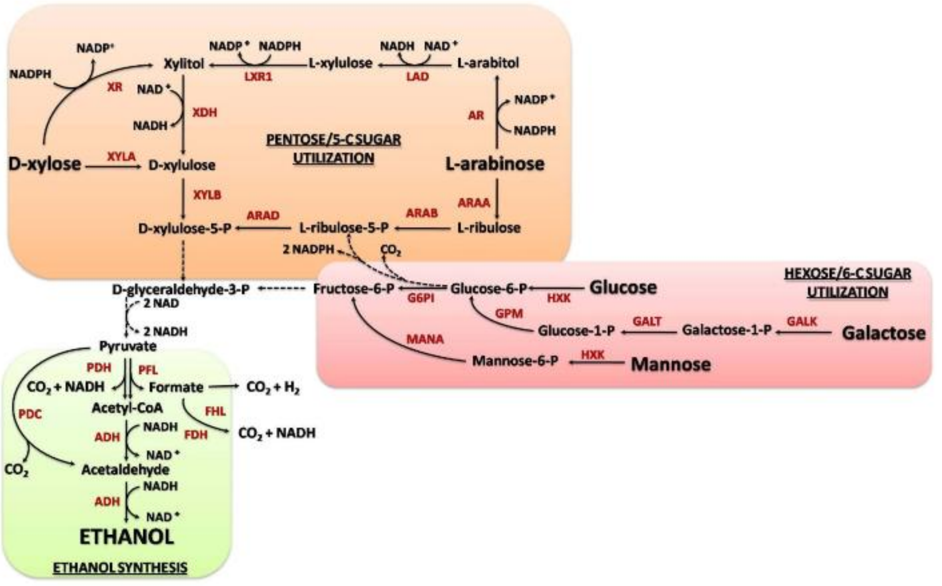


Figure 2 Engineered pathways for microbial production of ethanol from carbohydrates. Orange, red and green boxes indicate pathways for pentose and hexose sugars utilization, and ethanol synthesis respectively. The dashed lines indicate multiple steps. Abbreviations: ADH, alcohol dehydrogenase; AR, aldose reductase; ARAA, L-arabinose isomerase; ARAB, L-ribulokinase; ARAD, L-ribulosephosphate 4-epimerase; FDH, formate dehydrogenase; FHL, formate hydrogen lyase; LAD, L-arabitol 4-dehydrogenase; LXR1, L-xylulose reductase; PDC, pyruvate decarboxylase; PDH, pyruvate dehydrogenase; PFL, pyruvate formate lyase; XDH, xylitol dehydrogenase; XR, xylose reductase; XYLA, xylose isomerase; XYLB, xylulokinase.

Figure 1. The metabolic pathways involved in ethanol production (Dellomonaco et al. 2010).

3. Research Methodology

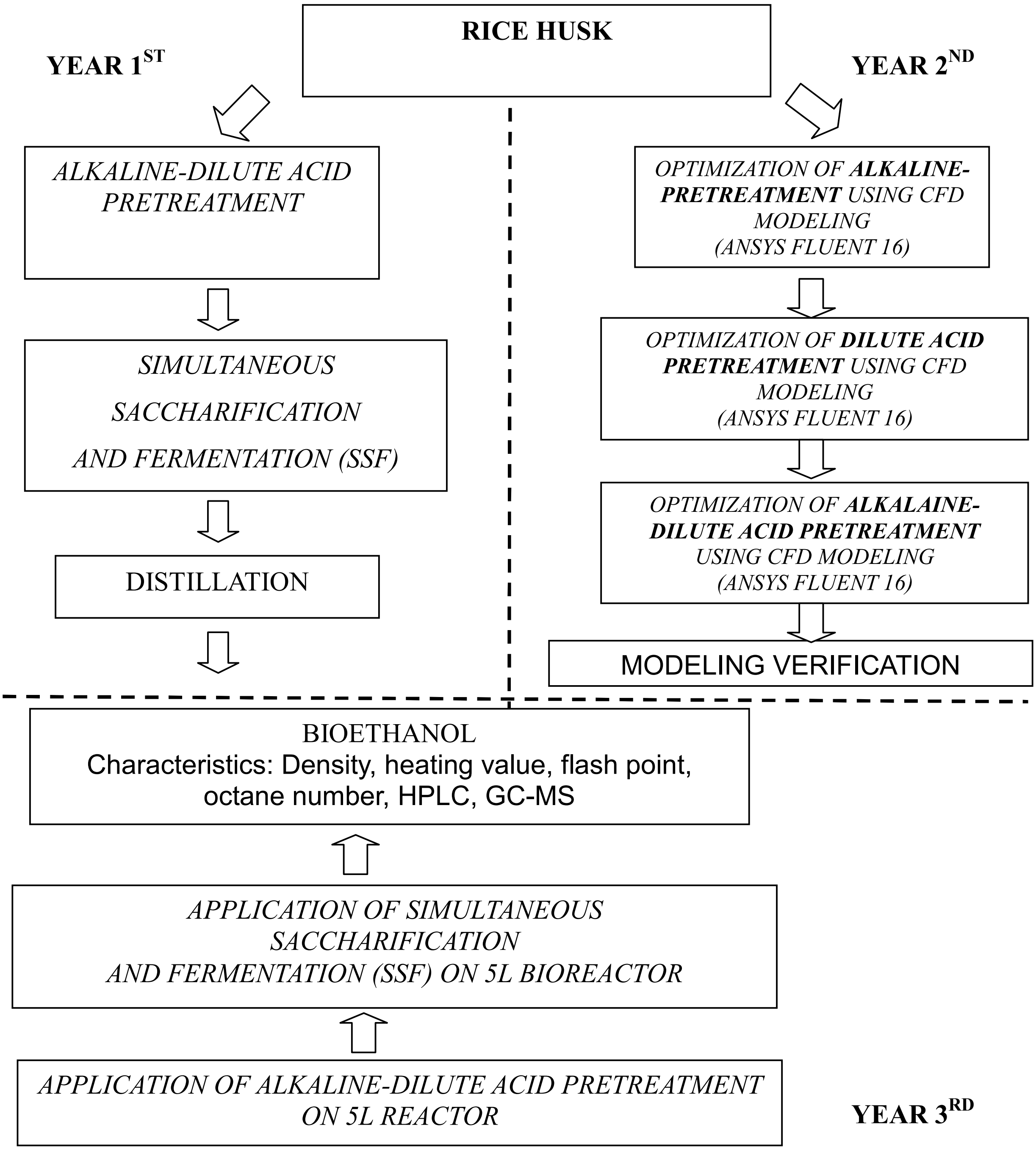


Figure 2. Scheme of Research Work During Three Years

3.1. Research collaboration

The research at Sriwijaya University (Indonesia) is part of a project done together with the School of Cemical and petroleum Engineering (Curtin University, Western Australia). The principal researchers at Sriwijaya University will investigate he Alkaline-Dilute Acid Pretreatment and Simultaneous Saccharification-Fermentation for Production of Bioethanol From Rice Husk Experimentally, while the researchers at Curtin University will focus on CFD modeling.

3.2. Research Activites on First Year

3.2.1. Biomass

Rice husk samples were collected locally (South Sumatera). The moisture content was determined and the samples were stored in plastic bags at 5^oC. The rice husk was collected from the location of Inderalaya in the city Ogan Ilir, South Sumatera, Indonesia. The rice husk was then air-dried and stored at room temperature. The rice husks were milled and sieved.

3.2.2. Methods

3.2.2.1. Alkaline-Dilute Acid Pretreatment

Lignocellulosic materials were pretreated with the following procedures. 50 gram supply of each dry material was placed in a 500 mL glass beaker and mixed well with 500 ml of NaOH solution with the concentration of 1%, 2%, 3%, 4% and 5% (w/v). Ratio rice husk and NaOH solution was (1:10 w/v). The slurry was incubated in a rotary air bath at 120 rpm and 85 ^oC for 1 hour. After the reaction, the slurry was poured into 1.2 L of pre-cold acetone and mixed thoroughly. The mixture was centrifuged at 8000 rpm for 10 min, and the supernatant was collected. Moreover, the solid residue was washed in 1.2 L of distilled water and centrifuged. The lignin content before and after alkaline pretreatment was analysed by standard methods of $ZnCl_2$-CH_3COOH.

The alkaline pretreated samples were continued by dilute acid pretreatment to enhance the removal of lignin content in the rice husk. Various concentration of sulfuric acid (H_2SO_4) of 1%; 2%; 3%; 4% and 5% (v/v) and performed in the autoclave reactor at 121^oC with the varied residence time of 30 minutes, 45 minutes, 60 minutes, 75 minutes, and 90 minutes. The slurry was filtrated and separated into solid and liquid fraction. 100 ml sodium hydroxide at the concentrate of 4% (w/v) fed to the pretreated samples and inserted to the autoclave at 121^oC for 30 min. The pretreated solids were washed with water until the filtrate registered a neutral pH. Then they were dried in the oven at 105^oC. The lignin content after dilute acid pretreatment was analysed by standard methods of $ZnCl_2$-CH_3COOH.

3.2.2.2. Simultaneous Saccharification and Fermentation

A 30 grams of rice husk pretreated were put into 1000 ml Erlenmeyer, then it was added the solution of media (yeast extract of 5 g / L, $(NH_4)\ {}_2SO_4$ 7.5 g / L; K_2HPO_4 3, 5 g / L; $MgSO_47H_2O$ 0.75 g / L and $CaCl_22H_2O$ 1 g / L) with a ratio of 1: 10 (w / v) and be adjusted the pH of ± 5. Then it was sterilized in the autoclave at 121 ° C for 60 minutes (Li, Kim, Jiang, Kang, & Chang, 2009). Once in the autoclave, rice husk pulp is allowed to cool and then added with a cellulase enzyme concentration of 3 ml (1-5 ml). The fermentation time was varied between 72 hours to 168 hours, while the treatment of the yeast Saccharomyces cereviseae concentration of 5 ml to 20 ml. Furthermore erlenmeyer shut with a cork. Then placed on a rotary shaker at 120 rpm for each fermentation time. Ethanol was analyzed by 2010 Plus Series Gas Chromatography.

3.2.2. Research Activites on Second Year

3.2.2.1. Modeling of Alkaline-Dilute Acid Pretreatment by Using CFD

The governing conservation equations of fluid flow represent the statement of the conservation laws of mass, momentum and energy. For reacting flows, the chemical species transport and mixing can be estimated by using species-transport equations.

The mass conservation of phase *i* (*i* = fluid, solid):

$$\frac{\partial}{\partial t}\left(\rho_i \varepsilon_i\right) + \nabla.\left(\rho_i \varepsilon_i \mathbf{U}_i\right) = r_i \tag{1}$$

With definition: $\varepsilon_f + \varepsilon_s = 1$

The conservation of momentum of phase *i* (*i* = fluid, *k* = solid, *k* ≠ *i*) can be written as:

$$\frac{\partial}{\partial t}\left(\rho_i \varepsilon_i \mathbf{U}_i\right) + \nabla.\left(\rho_i \varepsilon_i \mathbf{U}_i \mathbf{U}_i\right) = -\varepsilon_i \nabla P + \nabla.\boldsymbol{\tau}_i + \rho_i \varepsilon_i \mathbf{g} - \beta(\mathbf{U}_i - \mathbf{U}_k) \tag{2}$$

The conservation of energy for phase *i* yield:

$$\frac{\partial}{\partial t}\left(\varepsilon_i \rho_i H_i\right) + \nabla.\left(\varepsilon_i \rho_i \mathbf{U}_i H_i\right) = -\varepsilon_i \frac{\partial P_i}{\partial t} + \boldsymbol{\tau}_i : \nabla \mathbf{U}_i - \nabla.\mathbf{q}_i + S_i \tag{3}$$

Where: $H_i = \sum_i \varepsilon_i \int_{Tref}^{T} Cp_i dT$ (4)

Additional Equations

Interphase Exchange Coefficients:
From the Syamlal-O'Brian model for the drag force formulation (Fluent, 2006):

$$\beta = \frac{3}{4} C_D \frac{\varepsilon_s \varepsilon_g}{v_{r,s}^2} \frac{\rho_g}{d_s} \left(\frac{\mathrm{Re}_s}{v_{r,s}}\right) \left|\mathbf{U}_s - \mathbf{U}_g\right| \tag{5}$$

The drag coefficient, C_D is given by:

$$C_D = \left(0.63 + \frac{4.8}{\sqrt{\mathrm{Re}_s / v_{r,s}}} \right)^2 \tag{6}$$

$$\mathrm{Re}_s = \frac{\rho_g d_s \left| \mathbf{U}_s - \mathbf{U}_g \right|}{\mu_g} \tag{7}$$

where $v_{r,s}$ is the terminal velocity correlation for the solid phase:

$$v_{r,s} = 0.5A - 0.03\,\mathrm{Re}_s + 0.5\sqrt{(0.06\,\mathrm{Re}_s)^2 + 0.12\,\mathrm{Re}_s (2B - A) + A^2} \tag{8}$$

where:

$$A = \varepsilon_g^{4.14} \tag{9}$$

$$B = 0.8\,\varepsilon_g^{1.28} \quad \text{for } \varepsilon_g \le 0.85 \tag{10}$$

$$B = 0.8\,\varepsilon_g^{2.65} \quad \text{for } \varepsilon_g > 0.85 \tag{11}$$

Solids Pressure

The solids phase pressure (P_s) consists of a kinetic term and the particle collisions term. It is calculated from the equation of state which is the same as the van der Waals equation of state for gases (Chapman and Cowling, 1970):

$$\begin{aligned} P_s &= (1 + 2(1 + e_s)\varepsilon_s g_o)\varepsilon_s \rho_s \Theta_s \\ &= \rho_s \varepsilon_s \Theta_s + 2 g_o \rho_s \varepsilon_s{}^2 \Theta_s (1 + e_s) \end{aligned} \tag{12}$$

Where Θ_s is the granular temperature. e_s is the coefficient of restitution for particle collisions. g_o, the radial distribution function (Sinclair and Jackson, 1989) is given by:

$$g_o = \left[1 - \left(\frac{\varepsilon_s}{\varepsilon_{s,\max}} \right)^{\frac{1}{3}} \right]^{-1} \tag{13}$$

The value of maximum solid packing, $\varepsilon_{s,\max}$ for this simulation is 0.6.

Solids Shear Stress

The solids stress tensor contains bulk and shear viscosities. The solid phase bulk viscosity can be expressed as:

$$\mu_b = \frac{4}{3} \varepsilon_s \rho_s d_s g_o (1 + e_s) \left(\frac{\Theta_s}{\pi} \right)^{1/2} \tag{14}$$

The solids phase shear viscosity is given by:

$$\mu_s = \frac{2\mu_{s,dil}}{(1+e)g_o}\left[1+\frac{4}{5}(1+e_s)g_o\varepsilon_s\right]^2 + \frac{4}{5}\varepsilon_s\rho_s d_s g_o(1+e_s)\left(\frac{\Theta_s}{\pi}\right)^{1/2} \tag{15}$$

The solid phase dilute viscosity is:

$$\mu_{s,dil} = \frac{5}{16}\rho_s\varepsilon_s l_s\sqrt{2\pi\Theta_s} \tag{16}$$

Where is $l_s = \frac{\sqrt{2}}{12}\frac{d_s}{\varepsilon_s}$ (17)

Granular Temperature

The granular temperature, Θ_s, is calculated by solving the turbulent kinetic energy equation for solid phase:

$$\frac{3}{2}\frac{\partial}{\partial t}(\rho_s\varepsilon_s\Theta_s)+\nabla.(\rho_s\varepsilon_s\mathbf{U}_s\Theta_s)=T_s:\nabla\mathbf{U}_s+\nabla.(k_{\Theta s}\nabla\Theta_s)-\gamma_s \tag{18}$$

The diffusion coefficient for granular energy $k_{\Theta s}$ is represented by:

$$k_{\Theta s} = \frac{2k_{\Theta s,dil}}{(1+e_s)g_o}\left(1+\frac{6}{5}(1+e_s)g_o\varepsilon_s\right)^2 + 2\varepsilon_s^2\rho_s d_s g_o(1+e_s)\left(\frac{\Theta_s}{\pi}\right)^{1/2} \tag{19}$$

where:

$$k_{\Theta s,dil} = \frac{75}{64}\rho_s\varepsilon_s l_s\sqrt{2\pi\Theta_s} \tag{20}$$

The collisional energy dissipation, γ_s, is given by:

$$\gamma_s = 3(1-e_s^2)\varepsilon_s^2\rho_s g_o\Theta_s\left[\frac{4}{d_s}\left(\frac{\Theta_s}{\pi}\right)^{1/2}-\nabla\mathbf{U}_s\right] \tag{21}$$

k-∈ Turbulence Models

Generally, the FCC riser reactor is under turbulent flow conditions. Therefore, it is important to use an appropriate turbulence model to describe the effect of turbulent fluctuations of velocities and scalar variables for the basic conservation equations. A *k-∈* model was used to describe the turbulent motions in both phases. In the *k-∈* model, the turbulent viscosity is defined as:

$$\mu_{t,i}^{(t)} = \rho_i \varepsilon_i C_\mu \frac{k_i^{2}}{\in_i} \tag{22}$$

The turbulence kinetic energy, *k*, and its rate of dissipation, $\in$, can be calculated from the following transport equations:

$$\frac{\partial}{\partial t}(\rho_i \varepsilon_i k_i) + \nabla.(\rho_i \varepsilon_i k_i U_i) = \nabla.\left(\varepsilon_i \frac{\mu_t}{\sigma_k} \nabla k_i\right) + (\varepsilon_i G_k - \varepsilon_i \rho_i \in_i) \tag{23}$$

$$\frac{\partial}{\partial t}(\varepsilon_i \rho_i \in_i) + \nabla.(\rho_i \varepsilon_i \in_i U_i) = \nabla.\left(\varepsilon_i \frac{\mu_t}{\sigma_k} \nabla \in_i\right) + \frac{\in_i}{k}(C_{1\in} \varepsilon_i G_k - C_{2\in} \varepsilon_i \rho_i \in_i) \tag{24}$$

Reaction Kinetics Model

The scheme of the reaction in this model is assumed as below:

$$\boxed{\text{RH}} \xrightarrow{K_1} \boxed{\text{Cellulose}}$$

Where: RH is representative of rice husk. It is assumed the irreversible and pseudo first-order reactions. The reaction kinetics is enclosed to the hydrodynamic model by solving the species equation of the components in the form of the reaction rates as following:

$$\frac{dA}{dt} = -K_1 A \phi \tag{25}$$

3.2.3. Research Activites on Third Year

3.2.3.1. Design of Alkaline-Dilute Acid Pretreatment Reactor

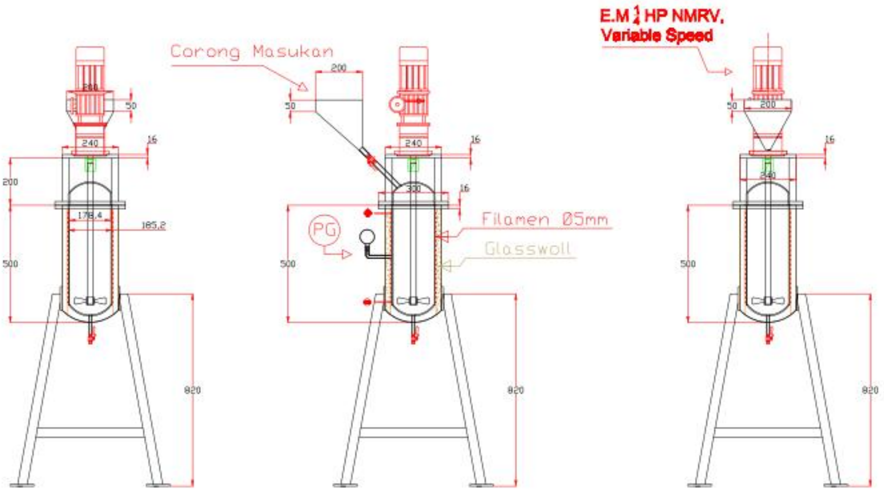


Figure 3. Design of Alkaline-Acid Pretreatment Reactor

3.3.3.2. Design of SSF Bioreactor

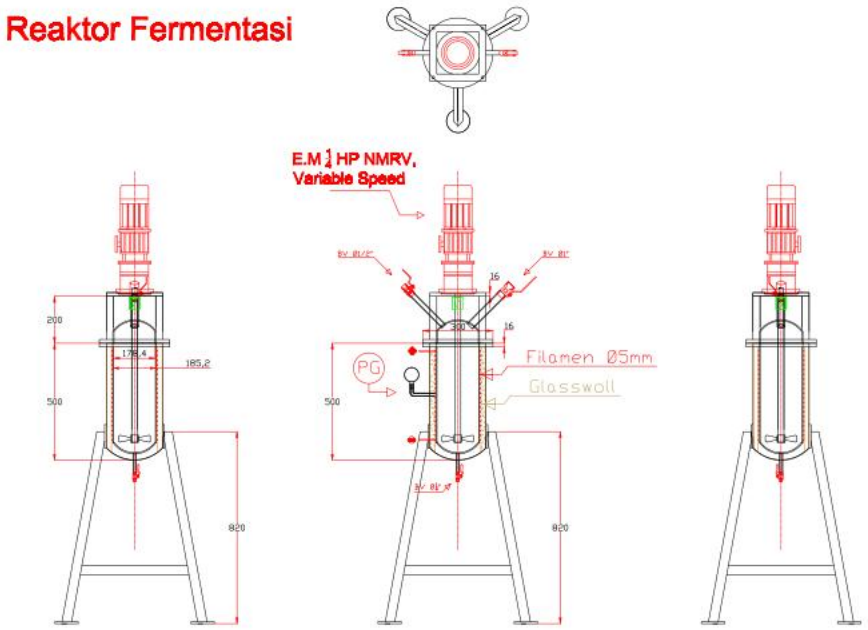


Figure 4. Design of Simultaneous Saccharification and Fermentation (SSF) BioReactor

4. Time Schedule and work plan for the research project

The project is to be completed in a three years period. The work plan of the research can be seen in Table 1. The first part of the project, with duration of one year, has been focused on investigating the Alkaline-Dilute Acid Pretreatment and Simultaneous Saccharification-Fermentation for Production of Bioethanol From Rice Husk Experimentally. The second part of the research will focus on the Alkaline-Dilute Acid Pretreatment using CFD Modeling. After successful application of Alkaline-Dilute Acid Pretreatment and Simultaneous Saccharification-Fermentation from previous part, the development of Pretreatment reactor and SSF bioreactor will be studied and figured out. This part is scheduled in the third year of the project.

Table 1. Work plan of the project

No	Activity	Coordinator	2016		2017		2018	
			I	II	I	II	I	II
1	Literature Review	Team Member	▨	▨	▨	▨	▨	▨
2	Investigate the Alkaline-Dilute Acid Pretreatment Experimentally	Novia, Tuty, Vishnu	▨	▨				
3	Investigate *Simultaneous Saccharification and Fermentation (SSF)* by Experimental Research	Novia, Tuty, Vishnu	▨	▨				
4	Formulate the correlation between the Alkaline-Dilute Acid Pretreatment and *Simultaneous Saccharification and Fermentation (SSF)* .	Novia, Tuty, Vishnu	▨	▨				
5	Modeling of the Alkaline-Dilute Acid Pretreatment by using CFD	Novia, Vishnu			▨	▨		
6	Verification of the Alkaline-Dilute Acid Pretreatment by Experimentally and CFD Modeling	Novia, Vishnu			▨	▨		
7	Application of Alkaline-Dilute Acid Pretreatment on Bench Scale Reactor	Novia, Tuty, Vishnu					▨	▨
8	Application of SSF on Bench Scale Bioreactor	Novia, Tuty, Vishnu					▨	▨
9	Pubication	Team Member		▨		▨		▨

5. Results and Duscussion

5.1. Singe Stage Pretreatment

5.1.1. Effect of NaOH concentration on Cellulose, Hemicellulose and Lignin Content

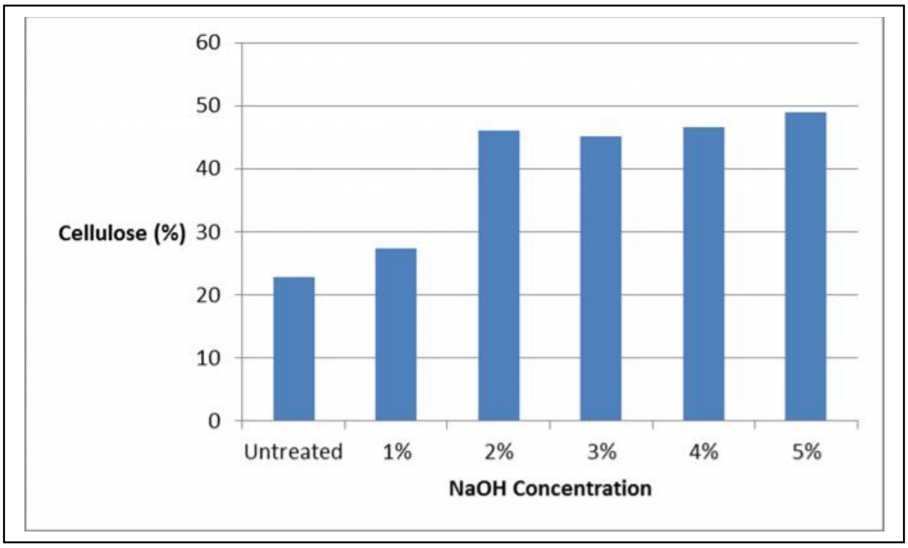


Fig.1. Cellulose Content of Rice Husk After Alkaline Pretreatment

It was illustrated from fig 1 that the cellulose content raised with the increasing of NaOH concentration. The figure shows the highest content of cellulose is about 48,99 % at the NaOH concentration of 5%. The value of 5% of NaOH concentration was used to treat the biomass further.

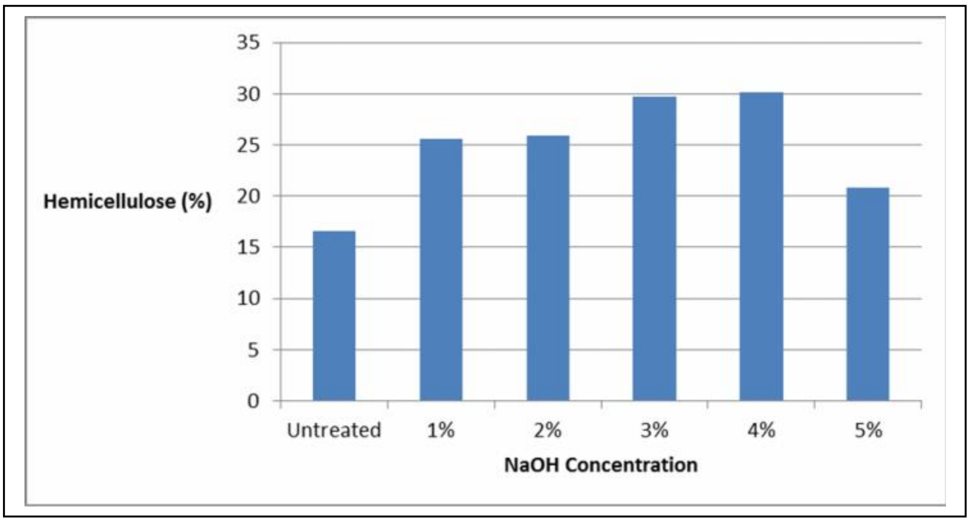


Fig.2. Hemicellulose Content of Rice Husk After Alkaline Pretreatment

Interestingly after alkaline pretreatment, the lowest content of hemisellulose was found at the NaOH concentration of 5%.

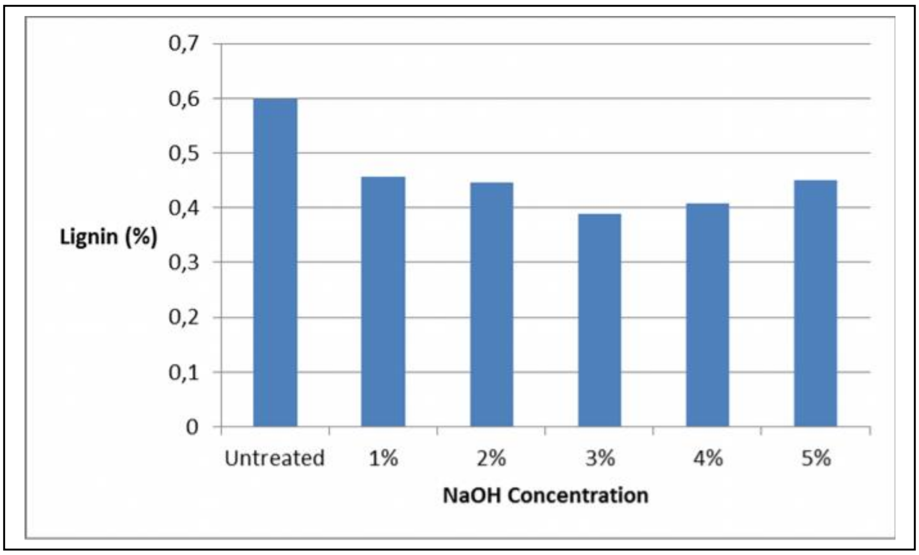


Fig.3. Lignin Content of Rice Husk After Alkaline Pretreatment

5.1.2. Effect of sulfuric acid concentration on Cellulose, Hemicellulose and Lignin Content

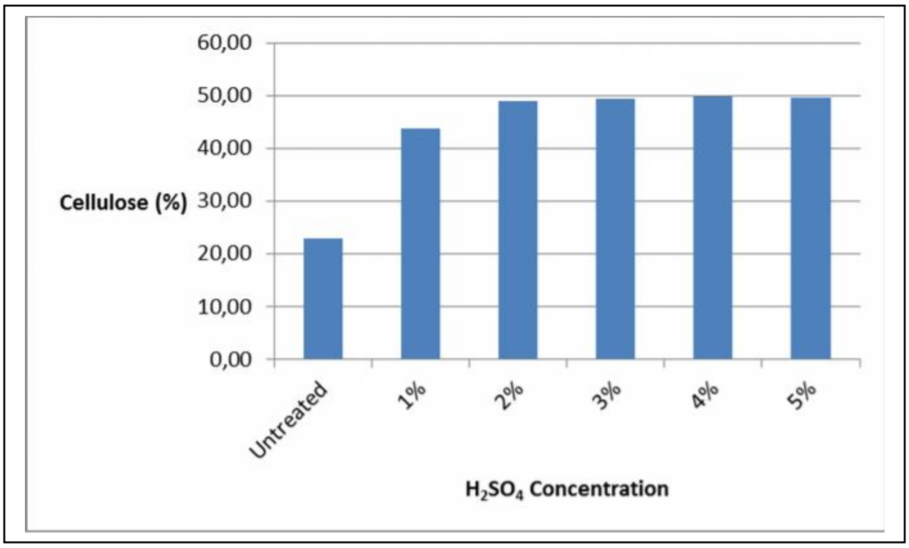


Fig.4. Cellulose Content of Rice Husk After Acid Pretreatment

Fig 4 shows that the cellulose started to increase at the acid concentration of 2 %, then have stagnant value above 3% of the acid concentration. This NaOH concentration was used as fived parameter on the next two stage step of pretreatment.

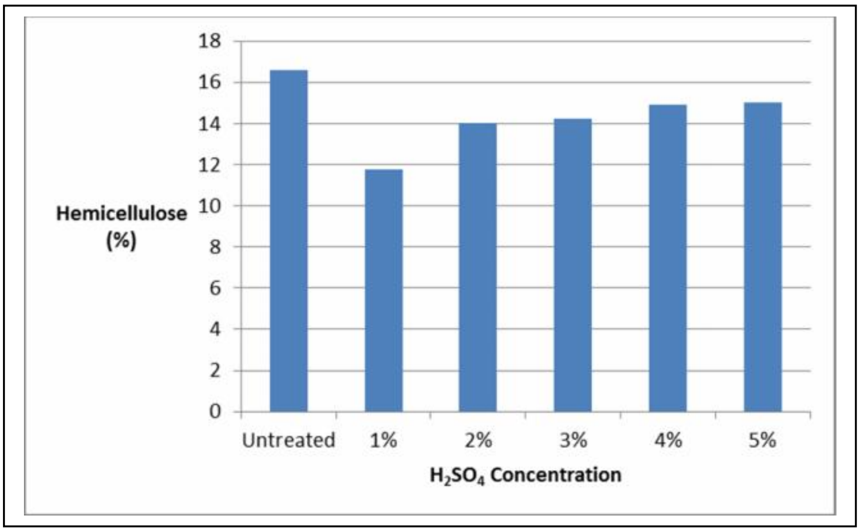


Fig.5. Hemicellulose Content of Rice Husk After Acid Pretreatment

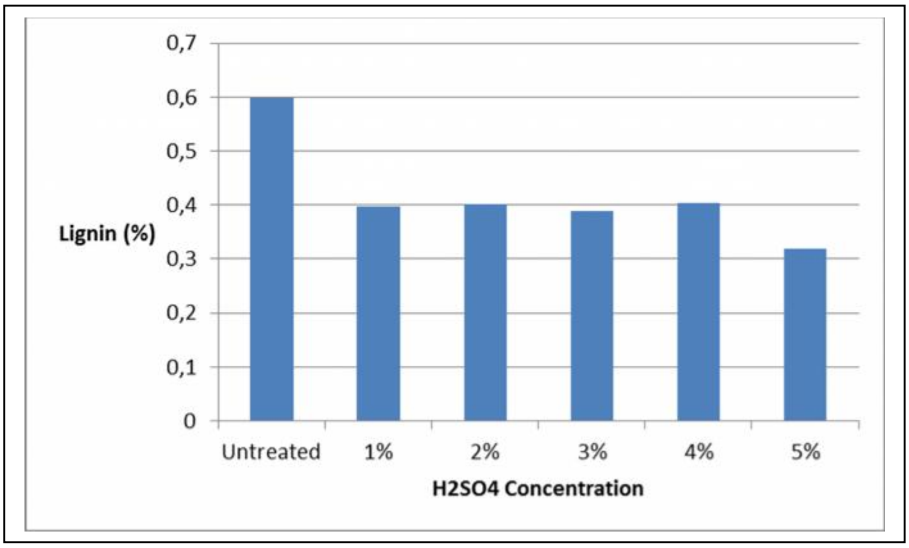


Fig.6. Lignin Content of Rice Husk After Acid Pretreatment

It was cocluded from fig 6 that the lowest content of lignin is 0,32 % at the acid concentration of 5 %.

5.2. Two Stage Pretreatment

5.2.1. Effect of sulfuric acid concentration on Cellulose, Hemicellulose and Lignin Content by Using Alkaline-Acid Pretreatment

The effect of sulfuric acid concentration of rice husk pretreatment on the content of cellulose, hemicellulose and lignin content, respectively, are shown in Figs. 1–3. The cellulose content after sulfuric acid-pretreated increased as the acid pretretament times were increased. The cellulose content of the pretreated rice husks ranged from 75.02% (3%, 30 min) to 88,84% (2%, 90 min) (Fig. 1). Previous researchers (Silverstein et al. 2007) reported 28.72 % (1%, 30 min, 90°C) to 40.68% (2%, 60 min, 121°C of glucan preservation. During pretreatment, it is desirable for the cellulose portion of the biomass to be virtually unaffected.

As a result of the solubility of lignin, the cellulose content in the solid phase increased with the higher of the acid pretreatment time as shown in fig. 1. However, for similar pretreatment time, the highest cellulose content was found at the acid concentration of 2%. This is due to the solubility of some cellulose occurring over 2% of acid concentration. The highest value of cellulose content was achieved about 88.84 % for material acid pretreated at the H_2SO_4 concentration of 2% and 90 minutes acid pretreatment time. After enzymatic hydrolysis this cellulose-rich solid leads a highest concentrated of glucose solution.

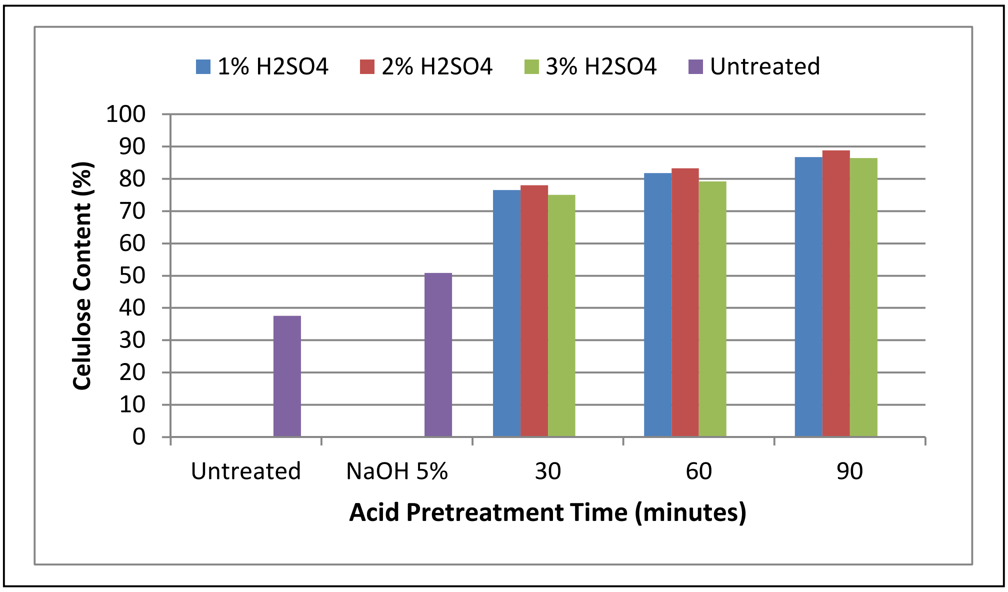


Fig.7. Cellulose Content of Rice Husk Before and After Alkaline-Acid Pretreatment

Figure 2 ilustrates the pretreatment caused the reducing of hemicellulose content. For similar pretreatment times, the higher pretreatment time leads the lower value of hemicellulose content. This is due to depolymerisizing of xylan to xylose then hydrated to furfural.

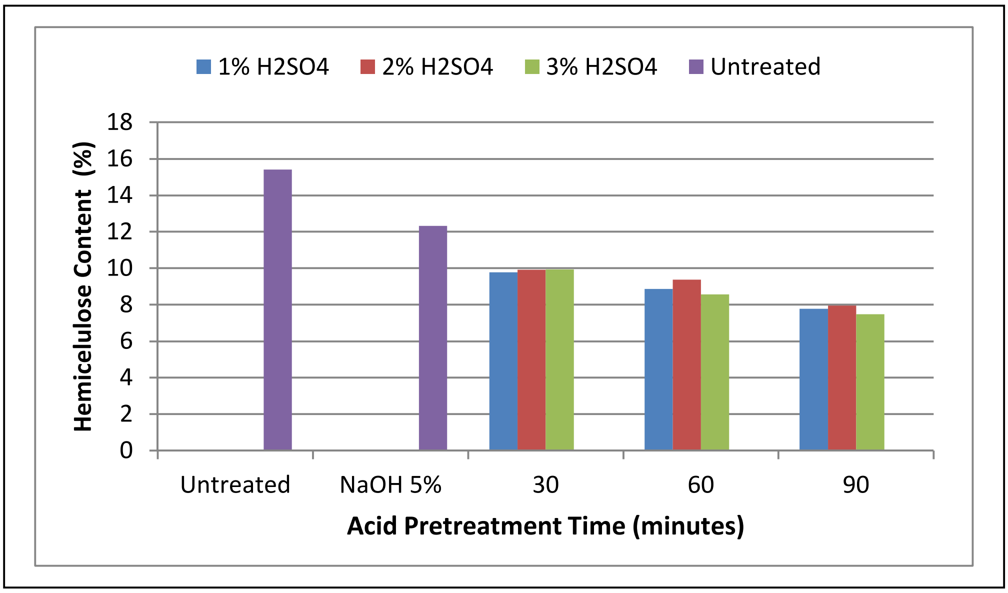


Fig.8. Hemicellulose Content of Rice Husk Before and After Alkaline-Acid Pretreatment

The increasing of acid concentration and pretreatment time significantly improved the delignification. The lowest of lignin content is about 3.46 % for solids pretreated at the acid concentration of 2% and 90 minutes of pretreatment time. It can be seen from the figure that higher concentration of acid results in a deeper breakdown of lignocellulosic structure, thus facilitating the solubilization of lignin in the delignification step.

Compared with untreated samples, dilute acid treatments resulted in an increase in the total lignin content of the material due to the removal of carbohydrates from the structure. The lignin content of the samples varied from 3.46% (3% H_2SO_4, 90 min) to 8.78% (1% H_2SO_4, 30 min) depending on the treatment conditions. On the other hand, the lignin reduction ranged from 47.46% to 79.29%. The findings of this study are comparable to Silverstein et al. (2007), who observed 24.2% lignin reduction for cotton stalks treated with 2% H_2SO_4 at 121^{o}C for 90 min.

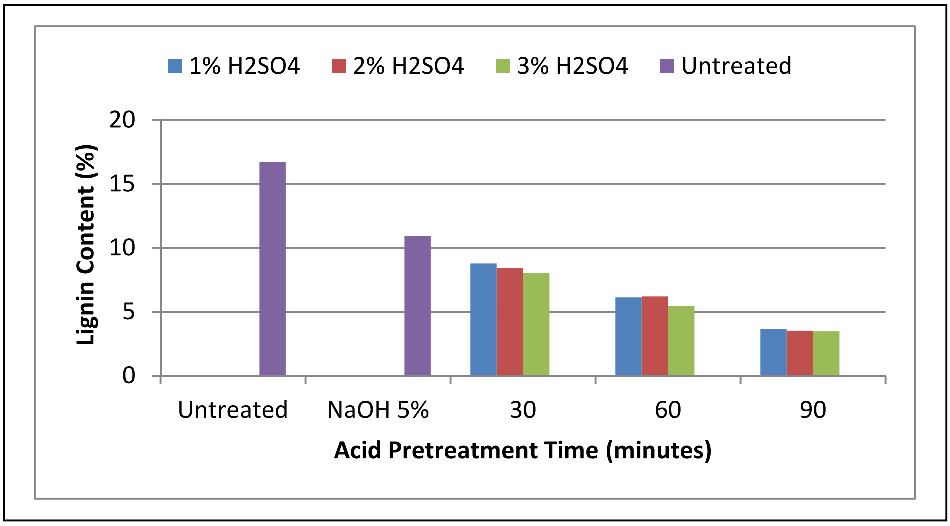


Fig.9. Lignin Content of Rice Husk Before and After Alkaline-Acid Pretreatment

5.3. Effect of sulfuric acid concentration on bioethanol concentration

Rice husk was pretreated at 121°C for 60 minutes with different sulfuric acid concentrations. The simultaneous saccharification and fermentation (SSF) of preteated samples were conducted by the commercial cellulase enzyme (Novozyme) and the *Saccharomyces Cerevisiae* for various SSF time of 72-160 hr. When 3% sulfuric acid was used, the concentration of ethanol was slightly increased comparing with the other sample.

One of the factors affecting the enzymatic hydrolysis yield is the inhibition caused by the accumulation of glucose and cellobiose on the enzymes. The simultaneous saccharification and fermentation (SSF) has been recommended as a possible solution (Olofsson et al. 2008). Figure 4 shows the ethanol concentration during the SSF using the commercial cellulase enzyme (Novozyme) and the *Saccharomyces Cerevisiae*. The highest ethanol concentration obtained was 13.68 g/L for the SSF time of 120 hours and the sulfuric acid concentration of 3 %. Similar results (15.8 g/L ethanol) were obtained by previous study (Camesasca et al. 2015).

The two-stage the sodium hydroxide-dilute sulfuric acid pretreatment could successfully fractionate the main components of rice husk into a low-lignin hydrolysate and cellulose-rich residual solid. This is reasonable result with the previous study (Kim et al. 2011).

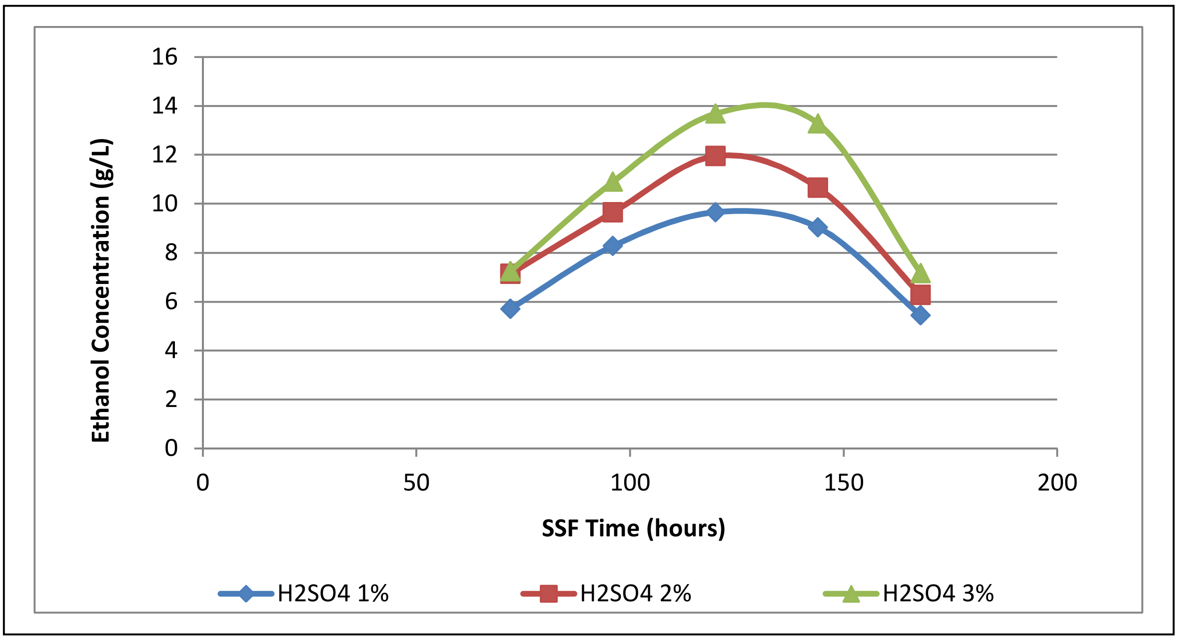


Fig.10. Ethanol Concentration of SSF process for different sulfuric acid concentration

5.4. Effect of sulfuric acid pretreatment time and SSF Time on Bioethanol concentration

Fig. 10 describes for acid pretreatment time of 30 and 40 minutes, the concentration of ethanol increased with the raising of SSF time, then reduced regulery after 4 days of SSF. This is due to the death phase of microbe at SSF process. The highest concentration of bioethanol os about 3,67 %.

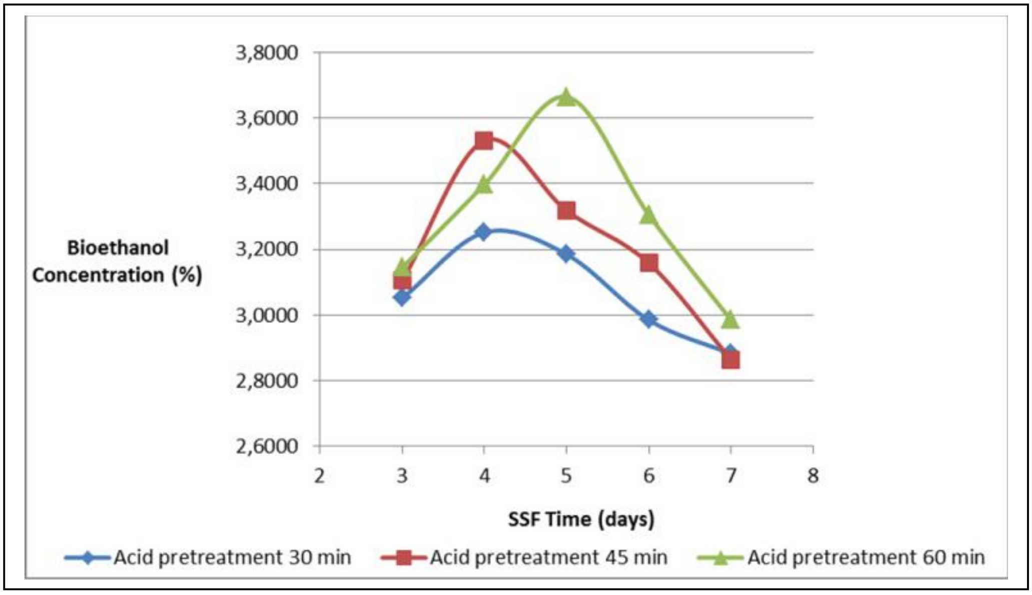


Fig.10. Ethanol Concentration of SSF process for different acid pretreatment time

6. Conclusions

A two-stage pretreatment of rice husk with sodium hydroxide followed by dilute sulfuric acid pretreatment at lower temperature was highly effective in removing lignin and hemicellulose, enhancing enzymatic digestibility.This process could be used to sequentially fractionate major components of rice husk to glucose, xylose, and lignin. The lignin content of the samples varied from 3.46% (3% H_2SO_4, 90 min) to 8.78% (1% H_2SO_4, 30 min) depending on the treatment conditions. The highest value of cellulose content was achieved about 88.84 % for material acid pretreated at the H_2SO_4 concentration of 2% and 90 minutes acid pretreatment time. The lignin reduction ranged from 47.46% to 79.29%. The highest ethanol concentration obtained was 13.68 g/L for the SSF time of 120 hours and the sulfuric acid concentration of 3 %.

7. Research Outcomes

1. Presented paper on International Conference “Sriwijaya International conference on Engineering, Science and Technology” 9-10 November, Bangka Island, Indonesia
2. Submitted paper to Matec Web of Conference (Indexed Scopus)

SICEST

Certificate
of Participation

We certify that Ms/Mr

Novia

has participated as

Oral Presenter

in the Sriwijaya International Conference on Engineering,
Science & Technology held in Bangka Island,
Indonesia 8-10 November 2016

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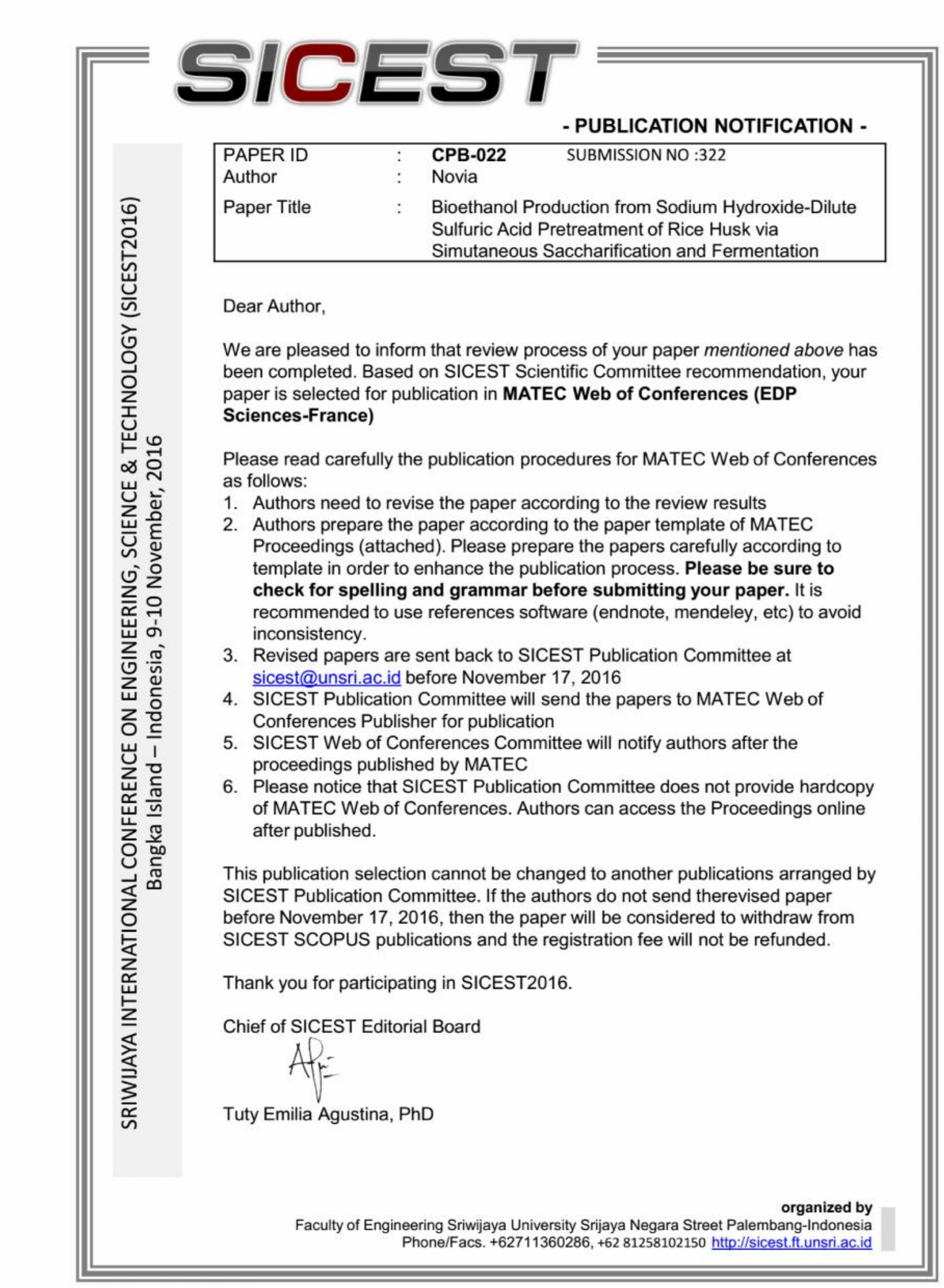

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SRIWIJAYA INTERNATIONAL CONFERENCE ON ENGINEERING, SCIENCE & TECHNOLOGY (SICEST2016)
Bangka Island – Indonesia, 9-10 November, 2016

- PUBLICATION NOTIFICATION -

PAPER ID	:	**CPB-022**	SUBMISSION NO :322
Author	:	Novia	
Paper Title	:	Bioethanol Production from Sodium Hydroxide-Dilute Sulfuric Acid Pretreatment of Rice Husk via Simutaneous Saccharification and Fermentation	

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ATTACHMENT:

RESEARCH DOCUMENTATION

➢ Size Reduction of Rice Husk

After Size Reduction

Screening Process of rice husk to **(60) mesh**

➢ Alkaline Pretreatment

Rice Husk + NaOH 10% before alkaline Pretreatment

Put mixture in waterbath at alkaline pretreatment

After Alkaline Pretreatment

Alkaline Pretreated of Rice Husk

Alkaline Pretreated of Rice Husk after drying in oven

- **Acid Pretreatment**

Alkaline Pretreated of Rice Husk + 200 ml H_2SO_4 2% before acid pretreatment

Autoclavation of rice husk by using two stage of pretreatment

Chesson Datta Method

Refluks of sample by using 150 ml aquadest

Filtration

Drying

Refluks of solid using 150 ml H_2SO_4 1 N

Filtration using H_2SO_4 1 N

Drying after refluks

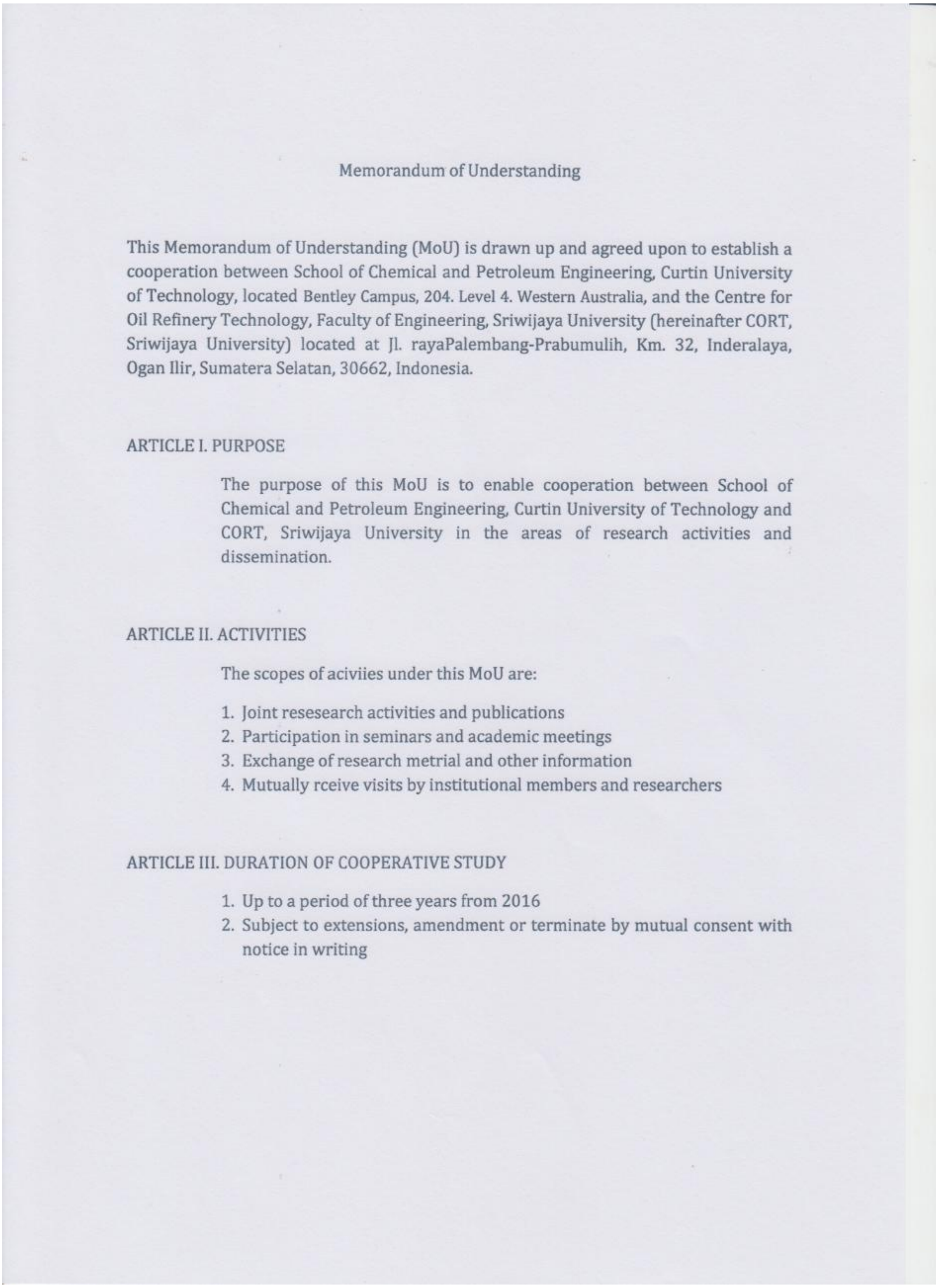
Refluks of residue using 10 ml H_2SO_4 72%

Filtration using H_2SO_4 72%

Drying with H_2SO_4 72%

PREPARATION OF ENZYM SELULASE DAN *YEAST SACHAROMICESS CEREVISIAE*

SIMULTANEOUS SACCHARAIFICATION-FERMENTATION (SSF)



Memorandum of Understanding

This Memorandum of Understanding (MoU) is drawn up and agreed upon to establish a cooperation between School of Chemical and Petroleum Engineering, Curtin University of Technology, located Bentley Campus, 204. Level 4. Western Australia, and the Centre for Oil Refinery Technology, Faculty of Engineering, Sriwijaya University (hereinafter CORT, Sriwijaya University) located at Jl. rayaPalembang-Prabumulih, Km. 32, Inderalaya, Ogan Ilir, Sumatera Selatan, 30662, Indonesia.

ARTICLE I. PURPOSE

The purpose of this MoU is to enable cooperation between School of Chemical and Petroleum Engineering, Curtin University of Technology and CORT, Sriwijaya University in the areas of research activities and dissemination.

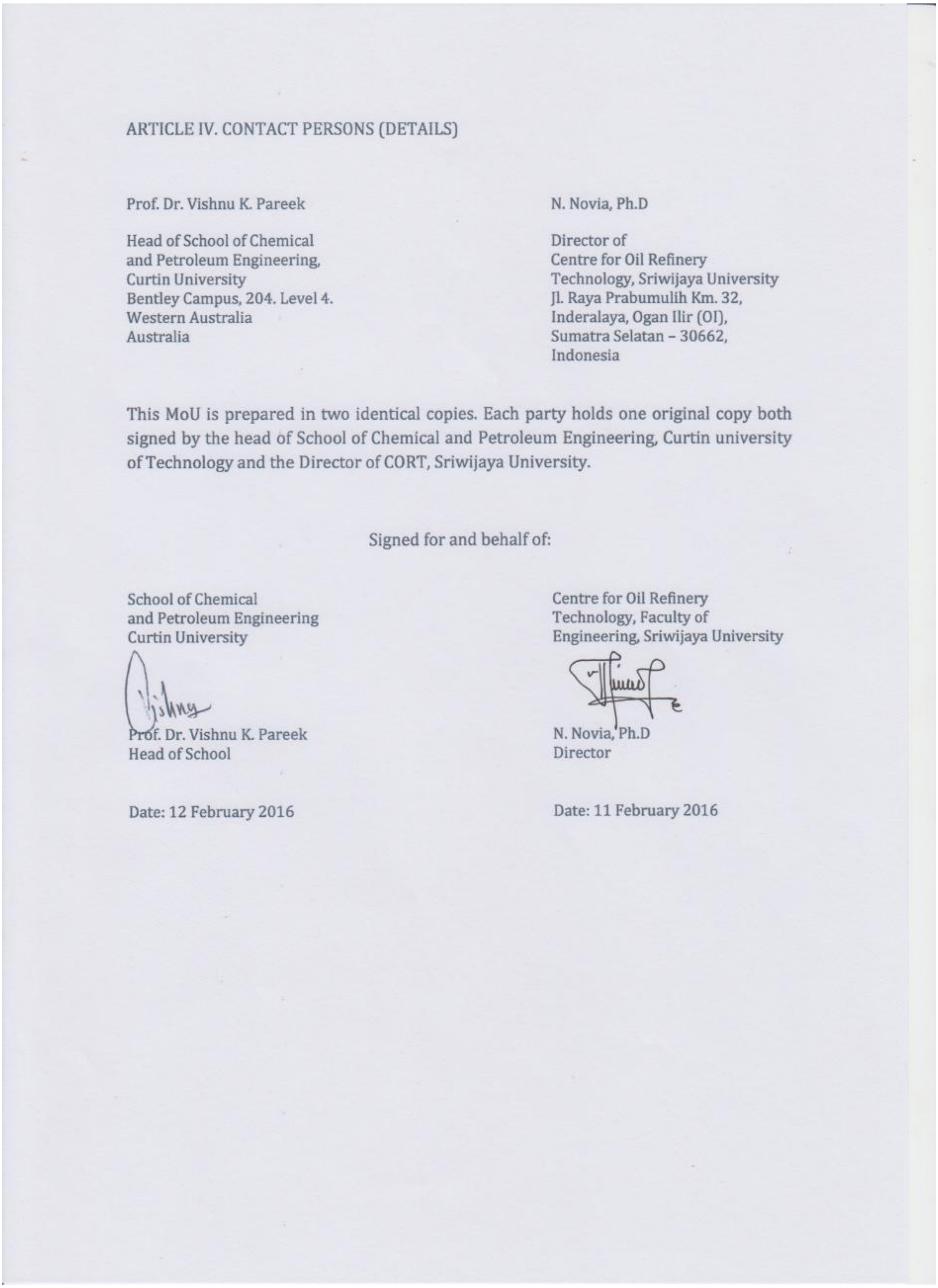
ARTICLE II. ACTIVITIES

The scopes of aciviies under this MoU are:

1. Joint resesearch activities and publications
2. Participation in seminars and academic meetings
3. Exchange of research metrial and other information
4. Mutually rceive visits by institutional members and researchers

ARTICLE III. DURATION OF COOPERATIVE STUDY

1. Up to a period of three years from 2016
2. Subject to extensions, amendment or terminate by mutual consent with notice in writing



ARTICLE IV. CONTACT PERSONS (DETAILS)

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Sumatra Selatan – 30662,
Indonesia

This MoU is prepared in two identical copies. Each party holds one original copy both signed by the head of School of Chemical and Petroleum Engineering, Curtin university of Technology and the Director of CORT, Sriwijaya University.

Signed for and behalf of:

School of Chemical
and Petroleum Engineering
Curtin University

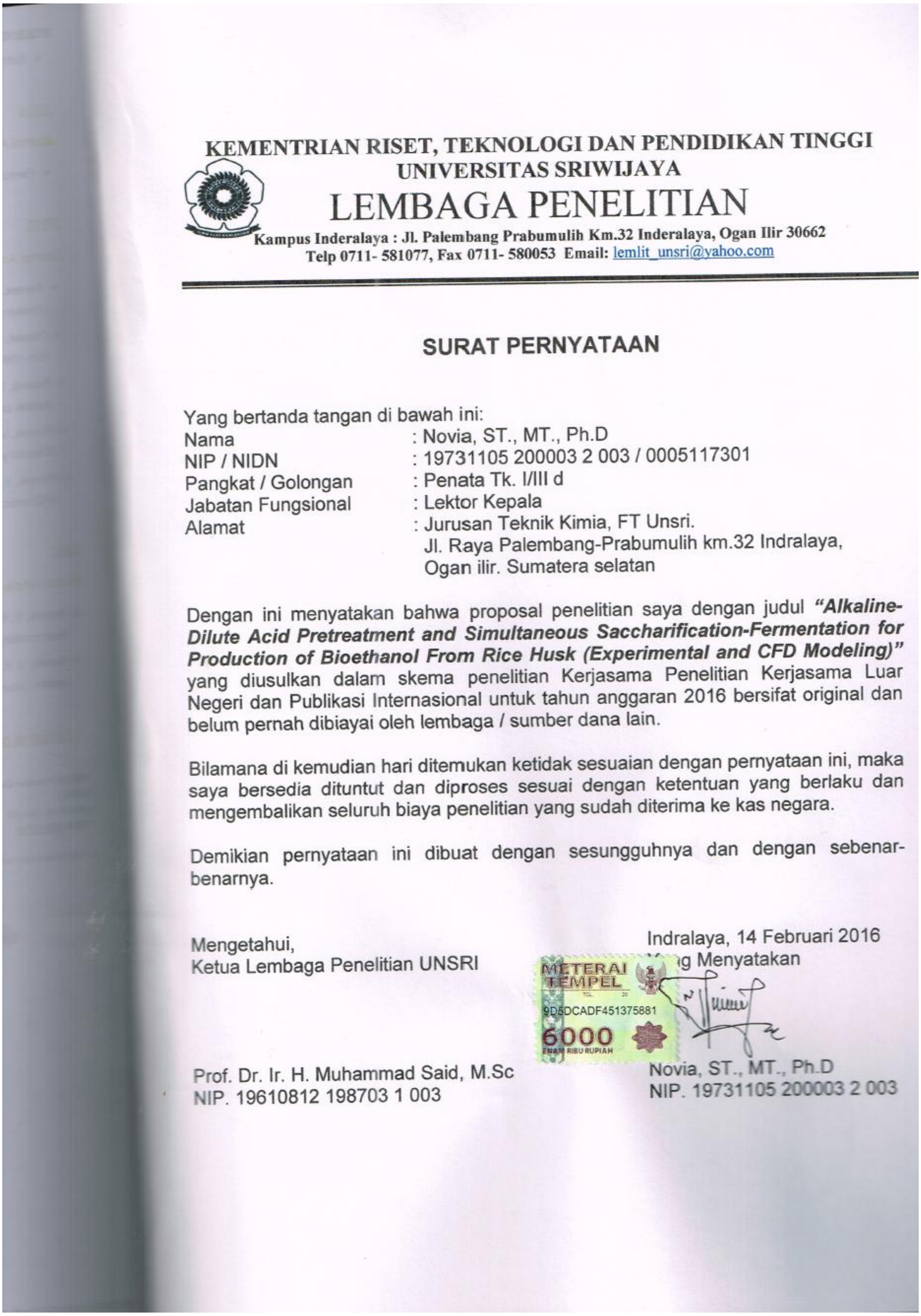
Prof. Dr. Vishnu K. Pareek
Head of School

Date: 12 February 2016

Centre for Oil Refinery
Technology, Faculty of
Engineering, Sriwijaya University

N. Novia, Ph.D
Director

Date: 11 February 2016



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SURAT PERNYATAAN

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Jl. Raya Palembang-Prabumulih km.32 Indralaya,
Ogan ilir. Sumatera selatan

Dengan ini menyatakan bahwa proposal penelitian saya dengan judul ***"Alkaline-Dilute Acid Pretreatment and Simultaneous Saccharification-Fermentation for Production of Bioethanol From Rice Husk (Experimental and CFD Modeling)"*** yang diusulkan dalam skema penelitian Kerjasama Penelitian Kerjasama Luar Negeri dan Publikasi Internasional untuk tahun anggaran 2016 bersifat original dan belum pernah dibiayai oleh lembaga / sumber dana lain.

Bilamana di kemudian hari ditemukan ketidak sesuaian dengan pernyataan ini, maka saya bersedia dituntut dan diproses sesuai dengan ketentuan yang berlaku dan mengembalikan seluruh biaya penelitian yang sudah diterima ke kas negara.

Demikian pernyataan ini dibuat dengan sesungguhnya dan dengan sebenar-benarnya.

Indralaya, 14 Februari 2016

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