Process simulation of the pilot scale bioethanol production from rice straw by Aspen Hysys

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Abstract. This work is to implement a working model of an integrated process for bioethanol in the process simulation based on rigorous model using the Aspen HYSYS simulation software. As a case study, the simulation is applied to design a pilot plant that converts rice straw into ethanol. The model is based on the process for biochemical conversion of lignocellulosic biomass (rice straw) to ethanol, proposed by the pilot plant of producing bio-ethanol with capacity of 152 kg rice straw/batch. The plant for manufacturing bio-ethanol with rice straw as raw materials comprises basically three units: Pretreatment of rice straw by alkaline treatment; Simultaneous saccharification fermentation (SSF) of rice straw to produce bio-ethanol and the unit for separation and purification of bio-ethanol mixture from simultaneous and fermentation unit. Modeling of rice straw feedstock as a solid material in Aspen HYSYS, including the creation of necessary hypothetical components. Investigate and analyze the final ethanol yield of the simulation project in comparison with actual process. The model proposed was for easily evaluate and analyze various factors which affect to the final ethanol yield by changing operating conditions and being possible to find the optimal conditions for different input flow rate and many independent factors. The simulation model obtained in this study can be applied to any SSF processes with different biomass feedstock.

Keywords. Bioethanol, Process Simulation, Process Design, Rice Straw, Bio-refinery

1. Introduction
Nowadays, with the large amount of CO2 emission annually, fossil fuel has increasingly become a critical energy and environmental policy issue. Therefore, biofuel from ethanol seems to be a promising solution to meet the greenhouse gas reduction target and being as an alternative to conventional petroleum transportation fuels [1]. Among four generations of bioethanol production, lignocellulose-based bioethanol, which is a second one, is popular, abundant, not being against on food security and able to be utilized from agricultural waste [2]. From the figure of US Protection Environment Agency (EPA), cellulotic ethanol which can achieve at least 90% emission reduction show its huge potential. All these advantages have strengthened the interest from both academic and industrial field on recent years.

Lignocellulose conversion to bioethanol requires three major processes: physical and chemical pre-treatment to liberate cellulose and hemicellulose; enzymatic hydrolysis of cellulose and hemicellulose to produce fermentable sugars; and fermentation of sugars to bioethanol by microorganisms [3]. The actual bioethanol production plants have successfully implemented in many countries with various biomass material. In Vietnam, there are 7 bioethanol production plants being implemented in Vietnam [4]. However, the major raw material for bio-ethanol production is cassava which is a starch-based material. It leads to the problem that the food security is threatened and high cost of production.
Therefore, in term of a promising solution, bioethanol production plant in second generation need to be researched. With approximately 1200 million L bioethanol per year in total production (in 2013), Vietnam has a huge potential due to the high availability of agricultural residue [2].

The objective of this work is to implement a working model of an integrated process for bioethanol in the process simulation software Aspen HYSYS. As a case study, the simulation is based on the process for biochemical conversion of lignocellulosic biomass (rice straw) to ethanol at the pilot scale which established and operating at Hochiminh City University of Technology (HCMUT). Moreover, the investigation and analysis of the final ethanol yield also are applied in comparison with actual process. The simulation model achieved in the study is robust and can help for further investigation studies, such as optimization, process integration, dynamic control, etc.

2. Bioethanol production process

The flow sheet diagram is the process of bioethanol plant in Biomass Laboratory, the base study which is used to simulate and analyze in this research. The process is included 5 stages: pretreatment, hydrolysis, fermentation, product recovery and gasification. However, gasification is not be simulated in this study due to the research objective. Rice straw will be fed at 152 kg per batch with 20% moisture content. Firstly, among various ways of pretreatment, diluted sodium hydroxide solution (1 wt%) is used at 50°C for 12-24 hours. The alkaline pretreatment reacts with the ester bonds linking the lignin to the hemicellulose. As these bonds are broken, it allows lignin components to be solubilized. Due to the mild conditions, degradation of sugars to furfural, HMF and organic acids is limited.

![Figure 1. Actual process of bioethanol production at HCMUT [5]](image)

At relatively low temperatures (<100°C) and low alkali concentrations (<4%), structural changes for cellulose and hemicellulose are insignificant. After alkaline pretreatment, the pretreated rice straw will experience the squeeze stage to reduce the excessive amount of alkaline solution (2 times) and be neutralized by diluted HCl. Pre-treated rice straw is loaded into an 800-L SSF reactor and then was sterilized on 30 minutes at a temperature of more than 90°C with steam, then cool down and maintain at 35°C during hydrolysis and fermentation process. Then, pre-cultivated yeast and enzyme are added into fermenter. The process happens in 3 hours before moving the recovery stage. Simultaneous Saccharification and Fermentation (SSF) has been used in this small-scale bio-refinery. In this process, the enzymatic hydrolysis takes place together with the fermentation in one tank. Cellulose is hydrolyzed by enzyme Cellulase to be glucose and then by fermented by S.cerevisiae yeast.
to get ethanol. SSF is claimed to result higher ethanol yield due to the fact that hydrolysis inhibitions are solved by fermentation process. However, it is a challenging task to control the solution environment since enzymes and microorganisms are employable only within the preference temperature and pH. Some reactions happening in the hydrolysis and fermentation step will be listed below.

\[
\text{Cellulase} \quad (\text{C}_6\text{H}_{12}\text{O}_6)_n + \text{H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 \\
\text{Saccharification} \quad \text{C}_6\text{H}_{12}\text{O}_6 \rightarrow \text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2
\]

The final ethanol from fermentation is distilled in two ordinary distillation columns, producing a pure ethanol production. The fermentation broth is distilled in a batch crude distillation column to obtain approximately 35-37 wt% ethanol. Subsequently, this aqueous ethanol is separated in a batch purification distillation column to obtain approximately 91 wt% ethanol as the final product.

### 3. Simulation procedure

In this design, the Aspen HYSYS Ver 8.8 process simulator is used to model the given process. Areas concerning feedstock storing and handling, mechanical pretreatment of the raw material such as rice straw, physical-chemical method steam-explosion pretreatment by puffing machine, storing and management of finished products are not included in this HYSYS case. Additionally, a thorough implementation of waste water treatment and the process of gasification to produce syngas have not been included. The work will not be done without completing 3 compulsory parts:

- Adding all of the components that will be existed in the simulation project. It can be added by the available sources of Aspen Database or create the hypothetical components if this component cannot be found out in the sources.
- Choosing the appropriate fluid packages which suit for all of the components. The wrong decision might give the inaccurate simulation results.
- Input all of the existed reactions during the process with the reactants and products, stoichiometry coefficients, conversion, etc. If the reaction follows the kinetic model, many parameters for the kinetic equation must be provided.

#### 3.1. Component list

The component list consists of 9 individual components, which most is “pure components” retrieved from the native HYSYS source databank. Some components which have different names but same chemical and physical properties of the compounds using in practice also are choose. However, the HYSYS database is limited, in that it mostly contains components specific to oil and gas processing. Therefore, components associated with biomass are created as hypotheticals. Most of the critical properties of the hypothetical component are taken from Aspen database using Aspen Properties Manager or from the NREL design report [1].

#### 3.2. Thermodynamic model

In process simulation, choosing an appropriate property package is one of the most important consideration to achieve a successful simulation. If the property package is unsuitable, that can lead to an inaccurate simulation. Two of the most important factors should be concerned with are the component list (what components will be involved) and the other is based on the operating conditions. The Fluid-package Association function can be helpful to recommend and guide you in deciding the fluid package. Other way the users can used is reading some valuable publications and professional literature that deal with the process in question or with the components that participate in the process.

The property package includes a set off specialized methods for calculating the properties of components and values for properties in the simulation itself. HYSYS consists of a wide range of different property packages for selection. A system consisting of mainly water, ethanol is considered as non-ideal system. Mixture water-ethanol forms azeotrope mixture and NaOH is a polar solution. Therefore, the Extended Non-Random-Two-Liquid (NRTL) equation has been used to successfully represent such system. This model uses a combination of temperature and non-temperature dependent parameters to calculate each component activity coefficient. It is a good choice for representing both vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE).
3.3. Building PFD
The feedstock input is 152 kg rice straw for a batch process. The composition in this work is indicated in Table 1.

Table 1. Compositional data of rice straw

| Type          | AIL | ASL | AII | Hemicellulose | Cellulose | Others |
|---------------|-----|-----|-----|---------------|-----------|--------|
| Raw           | 16.11 | 6.5 | 3.66 | 20.79         | 35.88     | 17.05  |
| Puffed        | 14.73 | 5.93 | 7.88 | 18.98         | 34.85     | 17.63  |
| Pretreated    | 11.11 | 4.06 | 7.55 | 18.62         | 46.09     | 12.58  |

3.3.1 Pretreatment area

![Figure 2. Process flow diagram of rice straw pretreatment area](image)

The split factor is adjusted in some major component such as cellulose to make the simulation case become more practical with the actual case. Because of lacking data for the after-squeezer stream, all of the split factor must be assumed in a reasonable way. The squeezed stream is sent to a neutralization tank (V-101) to neutralize any remaining alkaline solution. Dilute hydrochloric solution (HCl) 2 wt% is pumped to the tank to react with excessive NaOH solution and keep the slurry to get pH= 6. The amount of HCL loading in the tank is calculated by the following formula.

Let take x = mass flowrate of HCl stream loading. To get pH=6, we have the concentration of H+ after neutralization should be 10^-6.

![Figure 3. HYSYS simulation flowsheet of pretreatment area](image)

The raw material is mixed with water stream in a mixer to get a 17% water content in rice straw. It is then fed to an alkaline pretreatment reactor (CRV-100). The pretreatment reactor is modeled as a conversion reactor. Duty of the conversion reactor is used to control the reactor temperature at 50oC by adjust tool. NaOH 1 wt% is loading with the rate 20g NaOH / 100g biomass based on the research of [7]. The delignification takes place in order to solubilize the lignin solid into liquid phase so that easily
hydrolysis for further step. The conversion of delignification base on [8, 9] is 39.66%. On the other hand, hemicellulose remains mostly intact with the cellulose fraction and degradation of sugars to furfural, HMF and organic acids is limited [6].

The alkaline pretreatment slurry from CRV-100 is sent to a solid/liquid separation unit. The squeezer will use a pressing filtration at pressure up to 11-13 kgf/cm² to remove waste alkaline solution and a huge amount of liquid. However, in this HYSYS case, the separation is modeled as a simple component splitter (Squeezer 1). The separation yield is assumed to be 0.8, which become the split factor for most of soluble components.

$$[H^+] = \frac{0.02x}{36.5} - \frac{\text{mole NaOH}}{\text{Volume of squeezed stream}} + \frac{x}{\text{density of HCL loading stream}}$$

Subsequently, neutralized stream is sent to a solid/liquid separation unit again to remove the excessive liquid amount and keep the insoluble solid loading for hydrolysis is 12 wt%. The 12 wt% insoluble fraction is considered as an optimal condition for hydrolysis and fermentation step [5].

### 3.3.2 Enzymatic hydrolysis and fermentation area

![Process flow diagram of rice straw hydrolysis and fermentation area](image)

**Figure 4.** Process flow diagram of rice straw hydrolysis and fermentation area

![HYSYS simulation flowsheet of hydrolysis and fermentation area](image)

**Figure 5.** HYSYS simulation flowsheet of hydrolysis and fermentation area

A process flow diagram and a HYSYS simulation flowsheet for enzymatic hydrolysis and fermentation unit are shown in figure 4 and figure 5 respectively. Although it is a simultaneous process, it seems quite impossible to simulate in one reactor tank in HYSYS. Therefore, the simulation case is assumed at 2 separated reactor tanks with the same operating conditions, which is mentioned in the biomass report. The pretreated stream from pretreatment area is cooled 35°C (E-101), which is an operating temperature for simultaneous saccharification fermentation process at Biomass Laboratory. Cellulase is mixed in at a rate of 15 mg cellulase / g dry biomass.
The insoluble solids content in the resulting slurry is just above 12% making the moving of pretreated material challenging. The cellulase hydrolysis stream is feed to an enzymatic hydrolysis process. It is modeled as a single tank in the simulation and the conversion for hydrolysis reaction is 90%.

After hydrolysis simulation step, the slurry is cooled by the cooler to maintain the fermentation conditions at 35°C. Following the cooled hydrolysed slurry, a 1/10 fraction is diverted by Tee-100 into a seed train tank for production of yeast Saccharomyces cerevisiae, an industry standard yeast for fermentation glucose into ethanol. Corn Steep Liquor (water, protein and lactic acid) and Diammonium Phosphate (DAP) are used as nutrients for dry yeast cultivation. DAP loading is assumed to be 0.67 g/L broth while CSL is assumed to be 0.5wt%. Glucose will be fermented to be ethanol, with 90% conversion, whereas glucose with lactic acid and DAP are used to grow the S.cerevisiae yeast with 4% conversion.

After mixing seed train slurry stream and remaining hydrolysate stream, additional nutritional agents are charged to keep CSL loading rate and DAP loading rate is unchangeable. The formation of lactic acid from sugars are not included in this reaction set. There is no clear research modeling of huge inhibitory effects from furans and acetic acid. Loss reactions of acetic acid does be mentioned in the NREL report, however, the conversion is not sufficiently large to be considered. The fermentation tank is continued modeled as a single tank with the temperature maintained at 35°C. Glucose is fermented to ethanol with 95% conversion.

Figure 6 and 7 illustrate the actual process and the simulation case of product recovery area. The fermentation broth from hydrolysis and fermentation area, containing 2.5 wt% ethanol is fed by the pump (P-100) to increase the pressure stream and heated by a heater (E-100) to increase the feeding stream to nearly boiling liquid mixture, which will reduce the duty in the reboiler of distillation column. The heated broth which has 100°C and approximately 400 kPa is fed to the crude distillation column. The crude distillation column is designed to remove most of the amount of dissolved CO2 as a top vapor stream. While at the same time, most of the water (91.5 wt%) is removed in the bottom stream. The specifications in this crude distillation column are the mass flow rate of ethanol in the distillate stream, which is 90 wt% of ethanol mass flow rate containing in feed stream and the distillate stream flow rate in which ethanol flow account for 37 wt% in total flow rate of this stream. Another specification is vent flow rate, which is assumed that CO2 contain 85 wt%.

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![Figure 7. HYSYS simulation flowsheet of product recovery area](image)

4. Simulation result and comparison to the actually process

Figure 8 shows the completed HYSYS simulation flowsheet of bioethanol production process. The figure shows the whole process by connecting each stage. The process is rigorously simulated starting from the raw rice straw with 17 % moisture and reaching to the final product pure ethanol. This simulation model provides a robust basis for further studies of process integration, environmental assessment, and optimization studies leading to innovative solutions to the energy scarcity problems. Moreover, it can be applied on any type of biomass sources reaching to liquid ethanol production as a sustainable model of a bio-refinery.

4.1. Pretreated composition comparison

The purification distillation column is designed to purify the ethanol from 37 wt% to 91% at the top stream. The two specifications in this column are the mass flow rate of ethanol in the distillate stream, which is 95 wt% of ethanol total mass flow rate containing in feed stream and the distillate stream flow rate in which ethanol flow account for 91 wt% in total flow rate of this stream.

On the other hand, in actual process, duty of the reboiler in two distillation columns are supplied by the steam which is generated by syngas from gasification process of rice husk. However, with the objective and limited time of this study, the gasification unit from rice husk is ignored and the steam supplying to the distillation columns is assumed being available without syngas heat exchanger. Process saturates steam with 152°C and 1 atm is used to supply the heat flow for reboilers of two distillation columns. Process steam will be split into 2 streams which the amount is sufficient to generate the specific amount of duty for distillation columns reboilers. The steam is gone through the cooler to change to the saturated liquid state, which the duty of that process is used to supply to the separation unit.

| Type            | Simulated flow rate (kg/h) | Actual process flow rate (kg/h) | Error (%) |
|-----------------|----------------------------|---------------------------------|-----------|
| Cellulose       | 42.46                      | 45.90                           | 7.49      |
| Hemicellulose   | 17.42                      | 18.54                           | 6.04      |
| Lignin          | 13.63                      | 15.10                           | 9.73      |
| Ash             | 7.23                       | 7.51                            | 3.72      |
| Others (Extractives) | 12.14                    | 12.53                           | 3.11      |
Table 2 shows the detail comparison of rice straw after pretreatment unit between simulated streams and actual streams. Cellulose accounts for approximately 50%, which is appropriate for further hydrolysis and fermentation process. The result of pretreated composition in Biomass report is slightly different with the figures in simulation project. Lignin shows a huge gap between actual process and simulated project, with precisely 9% difference in flow rate. The other components show minor differences with around 3-7% error. The existed difference can be understood with some reasons. Firstly, Alkali-treatment efficiency in [7],[9] is assumed to neglect the hemicellulose and cellulose degradation throughout the alkaline pretreatment process because the amount of these changes insignificantly. It leads to the result that some errors in cellulose, hemicellulose, lignin, etc. should be accepted in a minor range (< 15% error). Moreover, the experiments used to evaluate the alkali-efficiency are conducted in a laboratory scale whereas the actual process is implemented in pilot scale, which is larger and more complicated. With the difference in scale and some unexpected errors in measurement, it is quite impossible to get a perfectly accurate conversion.

Secondly, a solid/liquid separation unit which is modeled as two component splitter equipment may have some limitation. In actual, a pressing filtration is used to squeeze rice straw slurry to remove waste alkaline solution and lignin soluble liquid. However, when applying this process in simulation term, many assumptions of split factors must be done. The wash yield is assumed to be 0.8 as a split factor for most of the soluble component whereas there are some changes in 0.9-0.95 as split factors for insoluble component. The effort is taken to get the most similar results with the actual process with some accepted errors.

| Stream                  | Type                     | Simulation process | Actual process | Error (%) |
|-------------------------|--------------------------|--------------------|----------------|-----------|
| Ethanol Fermented       | Mass flow rate (kg/h)    | 20.53              | 24.8           | 17.21     |
| Pure Ethanol            | Mass flow rate (kg/h)    | 17.55              | 19.6           | 10.45     |

A performed result from HYSYS simulation indicates that 20.53 kg/h bio-ethanol and 17.55 kg/h bio-ethanol are obtained after saccharification fermentation process and purification stage. On the other hand, the figures for actual process are slightly higher with 24.8 kg/h bio-ethanol after SSF process and 19.6 kg/h bio-ethanol as a final product. Errors are calculated and shown that just above 17% difference between actual process and simulation one in ethanol fermented stream and 10% in pure ethanol stream. This difference can be known by some explanation. Firstly, simultaneous saccharification fermentation process, which enzymatic hydrolysis and fermentation happens simultaneously in one reactor are
restricted with the tool of HYSYS simulation software. As a result, the hydrolysis and fermentation process are assumed to be separated into two tanks with same reaction conditions with the actual stage. It may leave some gaps in the ethanol in the final product. In addition, kinetic reaction sets for the enzymatic hydrolysis and fermentation are not added, which is replaced by the conversion reactions.

5. Conclusions

Being based on analyzing a lot of inventions, technical documents, books relating to the bio-ethanol production from rice straw; and comparing the advantages and disadvantages of different simulation models, the basic simulation for producing bio-ethanol is achieved with just above 17 kg/h of a batch rate. Following what was discussed, the plant for manufacturing bio-ethanol with rice straw as raw materials which successful operating at HCMUT, comprises basically 3 units: Pretreatment of rice straw by dilute NaOH, which is make the material suitable for hydrolysis and fermentation; Simultaneous saccharification fermentation of rice straw to produce bio-ethanol; The unit for separation and purification of bio-ethanol mixture from simultaneous and fermentation products unit. Moreover, the project may need to take some improvement to be more accurate for further investigation studies. Kinetic model should be developed in pretreatment stage to make the pretreatment efficiency more precise, whereas the hydrolysis enzyme should be adjusted to take advantage of the hemicellulose fraction.

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