Technology selection for rice straw-based second-generation bioethanol production in West Java

M Gozan

Biorefinery Lab., Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus Baru UI, Depok, 16424, Indonesia

E-mail: mrgozan@gmail.com

Abstract. Production of bioethanol from the abundant sources of agroindustrial cellulose has the potential to reduce world dependency on fossil fuel and, at the same time, represent a potentially negative environmental impact. Cellulose makes up nearly half of all plant biomass. Therefore, cellulosic ethanol may be the most potent source of biofuel in the near future. Rice straw is one of the most abundant lignocellulose materials in Indonesia. This study examines technology selection for rice straw-based second-generation bioethanol production. Selected possible process alternatives for bioethanol production are discussed in this work. Physical, chemical, and biological pretreatments, as well as a combination of those pretreatment processes, are elaborated in this study. The process chosen is process D, biomass–gasification – synthetic catalytic process – ethanol. In this alternative, the main processes are gasification and synthetic catalytic. Overall, fluidized bed reactors have more significant potential for use with biomass conversion than fixed bed reactors or other types of gasifiers. The gasification of carbonaceous biomass occurs via three main reactions, partial oxidation, complete oxidation, and the water-gas reaction.

1. Introduction

The second generation of bioethanol production needs sources of lignocellulosic biomass, such as forest woody feedstock (including different plant woody material like pine, fir, hemlock spruce, etc.), forestry and industrial residue, agricultural wastes, i.e., different crops residue such as corn stalks, rice straws, sugarcane bagasse, oil palm empty fruit bunch, durian skin, algae, waste paper [1-7], etc. Rice straw is produced in large amounts, as rice is the main course of Indonesian [8]. Hence, rice straw is one of the most potential lignocellulose (LC) sources for producing bioethanol in this region or perhaps in Asian countries. Several studies have suggested processing straw type biomass through bio-treatment and gasification pathways followed by fermentation and catalytic conversion [10-12]. This study examines the potential process routes of pretreatment and fermentation technologies for bioethanol production from rice straw. West Java province is one of the rice producer center in Indonesia [13] and the location of our University. Therefore, West Java is selected as the location of the study.

2. Materials and Methods

2.1. Process Observed

The potential process routes of pretreatment and fermentation technologies for bioethanol production from rice straw examined in this study are illustrated in Figure 1 and Table 1.
Table 1. Alternative process routes

| Alternative | Process Route |
|-------------|---------------|
| A           | Biomass – pretreatment – enzyme hydrolysis – fermentation – distillation |
| B           | Biomass – pretreatment – acid hydrolysis – fermentation – distillation – ethanol |
| C           | Biomass – gasification – fermentation – distillation – ethanol |
| D           | Biomass – gasification – synthetic catalytic process – ethanol |

Figure 1. Process routes of bioethanol production from rice straw.

2.2. Selection method

The process is evaluated and selected by using some criteria in engineering and economic aspects, i.e., Maturity; Product Conversion; Capacity; Treatment Process; Simplicity; Capital Expenditure (CAPEX; and Operational Expenditure (OPEX). The value of scoring is the value of scoring are 1: worse, 2: bad, 3: equal, 4: better, 5: very good.

Maturity means the process is proven and has been used in the real industry. The best process has a high conversion. Product conversion is one of the selecting factors. When the conversion reaches 80%, it means the process has high conversion and would be given score 5. Capacity means the sum of the feed or raw materials that could be processed. The higher capacity that would form into the ethanol would be chosen process. Some of the alternatives needed extra treatment before it goes to process, and some of the other produce the unneeded components like sulfur and tar, which needed to be removed. The extra treatment process and removal process may give the adding of equipment, and impacts the cost needed. Simplicity is how easy the process to convert the feed or raw materials to become the final product, ethanol. The more complex the process, the equipment needed to install and impact all of the cost spent. The capital expenditure (CAPEX) includes the costs needed to purchase, install the equipment, as well as providing the area and building. The details of the equipment are not shown in this study. The operational expenditure (OPEX) means the cost needed in the maintenance process and other operational processes. The technology is selected by using criteria (score 1-5), i.e., yield product, energy consumption, and costs.

3. Results and Discussion

3.1. Biochemical Conversion

The cellulose would be converted to ethanol by the biochemical process, which is known as fermentation. During the fermentation, specialized microorganism (primarily fungi and bacteria) is used to convert the glucose in biomass to ethanol. Before the fermentation, cellulose is pretreated and is converted into glucose by hydrolysis. Fermentation is helped by yeast, the microorganism containing an enzyme that acts as a catalyst. Fermentation works in warm conditions, between 18 and 35 °C and at a neutral or acidic pH between 4 and 7.

As seen in table 1, the alternative used the biochemical conversion as a process is in the alternative A, B, and C. The alternative A and B have mostly common pathways to produce the ethanol, they differ in the hydrolysis process. By using alternative: A and B, the biomass would go to pretreatment in the beginning. This pretreatment would separate the lignin and hemicellulose from the cellulose because only the cellulose could be converted to ethanol. In another way, alternative B gives the process in which the lignin and hemicellulose do not need to be separated, but it converts into gases. Alternative A uses enzymes while alternative B uses acid in the hydrolysis process.
3.1.1. Hydrolysis
There are two basic types of hydrolysis, using enzyme or acid. Most of the acid processes are limited to a sugar recovery efficiency of around 50%. The advantage of acid processes is their fast rate of reaction, which facilitates continuous processing yet low sugar yield. Another process is by using enzymes. Enzymes are naturally occurring plant proteins that cause certain chemical reactions to occur. However, for enzymes to work, they must obtain access to the molecules to be hydrolyzed. For enzymatic processes to be effective, some kind of pretreatment process is thus needed to break the crystalline structure of the lignocellulose and remove the lignin to expose the cellulose and hemicellulose molecule.

3.1.2. Fermentation
Ethanol fermentation is the biological process in room temperature and atmospheric conditions. The main objective process converts the glucose into ethanol by using the microorganism like Saccharomyces cerevisiae, classified to the yeast types. It is commonly used in ethanol production, and it has good prosperity in ethanol fermentation. The fermentation process is started by mixing the source of sugar, water, and yeast and the yeast to act in an oxygen-free environment. Bacterial fermentation of CO, CO₂, and H₂ to ethanol gives the following equations:

\[
\begin{align*}
6 \text{CO} + 3 \text{H}_2\text{O} & \rightarrow \text{C}_2\text{H}_5\text{OH} + 4 \text{CO}_2 \\
\Delta G &= -216 \text{kJ/mol} \\
6 \text{H}_2 + 2 \text{CO}_2 & \rightarrow \text{C}_2\text{H}_5\text{OH} + 3 \text{H}_2\text{O} \\
\Delta G &= -97 \text{kJ/mol}
\end{align*}
\]

3.2. Thermochemical Conversion
The conversion with the thermochemical process uses heat and chemicals to break cellulose into syngas (CO and H₂) and reassemble it into products such as ethanol. The cellulose with lignin-rich parts cannot be easily converted biochemically. Cellulose in biomass is burned into syngas. The gases formed then go to the tar reformer to be cleaned to get closer to pure CO and H₂. The cleaned gas to compress and run across a catalyst that make the gases back up into molecules like ethanol or hydrocarbons. The process conversion biomass into ethanol is in the catalytic synthesis process.

3.2.1. Gasification
The cellulose in the form of biomass would be dried and goes to the gasification process. Biomass gasification means the combustion of biomass, resulting in the production of combusting gases consist of carbon monoxide (CO), hydrogen (H₂), and traces of methane (CH₄). Actually, this produces gas contains other contaminants to likes tar and sulfur that must be treated [14].

There are four distinct processes that take place in a gasifier as the fuel makes its way to gasification. They are drying of fuel, pyrolysis, combustion, and reduction. Gasification of biomass could be considered as two-stage processes, begin with pyrolysis, which then is followed by gasification. The gasifier is the most important part of the process of turning biomass into syngas: the gasifier turns the feed into syngas. There are several types of gasification processes.

3.2.2. Steam Gasification
The steam gasification reaction is endothermic, which is requires heat input for the reaction to proceed in its forward direction. This reaction is typically combined with other gasification reactions in practical applications, while The H₂-to-CO ratio of the product syngas depends on the synthesis chemistry as well as process engineering.

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \\
\Delta H^\circ_{298K} = 131.3 \text{kJ/mol}
\]

3.2.3. Carbon Dioxide Gasification
The carbon dioxide gasification is endothermic, similar to the steam gasification reaction. The reaction of carbon dioxide gasification is shown below.
\[ C + 2 \text{CO}_2 \rightarrow \text{CO} \quad \Delta H_{298K} = 172.5 \text{kJ/mol} \quad (4) \]

However, this reaction in practical gasification applications is almost never attempted as a single chemical reaction, because of a variety of factors including low conversion, slow kinetic rate, low thermal efficiency, unimpressive process economics, etc.

### 3.2.4. Hydrogasification

The hydrogasification process is the direct addition of hydrogen to biomass under high-pressure forms methane.

\[ C + 2 \text{H}_2 \rightarrow \text{CH}_4 \quad \Delta H_{298K} = 172.5 \text{kJ/mol} \quad (5) \]

This reaction is exothermic and is thermodynamically favored at low temperatures; therefore, the high temperature is needed for the kinetic.

### 3.2.5. Partial Oxidation

The partial oxidation reaction is known as the combustion process. The reactions for partial oxidation are shown as follows.

\[ C + \frac{1}{2}\text{O}_2 \rightarrow \text{CO} \quad \Delta H_{298K} = -111.4 \text{kJ/mol} \quad (6) \]
\[ C + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2 \quad \Delta H_{298K} = -393.5 \text{kJ/mol} \quad (7) \]

The presence of both gas phase homogenous reactions and heterogeneous reaction between gaseous and solid reactants make the reaction pathway is further complicated.

### 3.2.6. Catalytic Synthesis

Catalytic synthesis is the main process to convert the syngas into ethanol in thermochemical. This catalytic synthesis uses a metallic catalyst like modified methanol catalysts (Cu/Zn and Cu/Mn-based), modified molybdenum sulfide catalysts, and modified molybdenum oxide catalysts. Gasification of biomass to synthesis gas, followed by catalytic conversion of syngas, produces ethanol, plus C3-C4 alcohols.

All the alternatives above is then scored as illustrated in Table 2.

| Criteria                  | Weight [%] | A Score | A Weight | B Score | B Weight | C Score | C Weight | D Score | D Weight |
|---------------------------|------------|---------|----------|---------|----------|---------|----------|---------|----------|
| Engineering Aspect        |            |         |          |         |          |         |          |         |          |
| Maturity                  | 20         | 5       | 1        | 5       | 1        | 4       | 0.8      | 4       | 0.8      |
| Product                   | 20         | 4       | 0.8      | 4       | 0.8      | 5       | 1        | 5       | 1        |
| Capacity                  | 15         | 4       | 0.6      | 4       | 0.6      | 5       | 0.75     | 5       | 0.75     |
| Treatment                 | 15         | 3       | 0.45     | 3       | 0.45     | 4       | 0.6      | 4       | 0.6      |
| Simplicit                 | 10         | 4       | 0.4      | 4       | 0.4      | 4       | 0.4      | 4       | 0.4      |
| Economic Aspect           |            |         |          |         |          |         |          |         |          |
| Capital                   | 10         | 5       | 0.5      | 5       | 0.5      | 3       | 0.3      | 4       | 0.4      |
| Operation                 | 10         | 3       | 0.3      | 3       | 0.3      | 4       | 0.4      | 5       | 0.5      |
| Total Scores              |            |         |          |         |          |         |          |         |          |
|                           | 4.05       |         | 4.05     |         | 4.25     |         | 4.45     |         |          |

Based on the scoring process, the process with a high score is the chosen process. The process chosen is process D: biomass–gasification-synthetic catalytic process-ethanol. In this alternative, the main processes are gasification and synthetic catalytic.

### 3.3. Technology Selection

The alternative chosen is alternative D with thermochemical conversion through gasification technology. There are two main types of gasifiers, indirect and direct gasifier. In a direct gasifier, the
fees are heated directly, or partial oxidation gasifier will be generated the heat required for gasification inside the reactor. On the other hand, an indirect gasifier transfers heat from an external source into a gasifier. The differences between the two gasifiers are depicted in Table 3.

Table 3. Indirect versus direct gasifier (modified from [14])

| Factor             | Unit     | Direct | Indirect |
|--------------------|----------|--------|----------|
| Feed               | MTPD     | 2200   | 2200     |
| Products           | mmgal/y  | 45     | 43       |
| Power Consumption  | MW       | 14.5   | 34.7     |
| Power Generation   | MW       | 26.8   | 30.2     |
| Fuel Products      | %        | 30.1   | 28.7     |
| Thermal Efficiency | %        | 44.8   | 42.5     |
| Capital Cost       | mm$      | 480    | 356      |
| Operating Cost     | $/gal    | 3.07   | 2.71     |

The heat from external sources came from the heat generated through the combustion of by-product created during gasification. The feed into the reactor then sealed and filled with pressurized CO2 recovered from the gas purification and conditioning section of the plant. The raw untreated gas from the gasifier is sent to a primary cyclone separator where char is captured and sent to the char combustor [14]. The indirect gasifier contains both a gasifier and a separate combustor. The feed into the low-pressure indirectly heated gasifier while a portion of the heat required for the gasifier comes from the steam in the steam cycle. The wet solids are transported to a landfill, and the hot gas is then cooled by a boiler in order to use for biomass drying as depicted in Table 4.

Table 4. Gasification technology scoring.

| Criteria            | Weight | Direct Gasifier | Indirect Gasifier |
|---------------------|--------|-----------------|-------------------|
|                     | [%]    | Score           | Weight | Score | Weight |
| Product Yields      | 25     | 4               | 1.00   | 4     | 1.00   |
| Energy Efficiency   | 25     | 4               | 1.00   | 5     | 1.25   |
| Equipment Needed    | 25     | 4               | 1.00   | 4     | 1.00   |
| Cost                | 25     | 4               | 1.00   | 5     | 1.25   |
| **Total Score**     |        | **4.00**        | **4.5** |       |        |

Based on the scoring process, the technology chosen is an indirect gasifier. In addition, technology by heat supplied, there are several types of gasifiers that can be used to produce syngas from biomass, counter-current fixed bed (updraft), counter-current fixed bed (downdraft), fluidized bed and entrained bed. In a fixed bed reactor, the oxygen or air as the gasifying agent flows up or down through a fixed pile of biomass. Co-current fixed bed reactor (updraft) gasifier consists of fixed bed biomass with counter-current flow of steam, oxygen, and air flowing upward through the fuel bed while the Co-current fixed bed reactor (downdraft) gasifier the steam, oxygen, and air flows downward with the fuel. Gas exit temperatures for updraft gasifiers are low, which improves thermal efficiency but increases tar and methane impurities in the gas. The exit temperature of the gas is higher, resulting in lower overall efficiency.

In a fluidized bed gasifier, biomass is added to a fluid bed. Some particles remain entrained with the gas so that inert material exits with the syngas, where it is separated from each other by cyclone separator, and the particle re-circulated to the reactor. The fuel in a fluidized bed gasifier is gasified in an oxygen/air and steam mixture. Fuel throughput is higher than for fixed bed gasifiers and has the advantage of uniform temperature distribution achieved in the gasification zone resulting in cleaner reactions. However, conversion rates are lower, requiring the recycling of part of the exit gas back to the gasifier.

In entrained flow gasifiers, the fuel is fed either as a dry pulverized solid or the fuel slurry in tandem with oxygen or air. This gasifier has the highest operating temperature and pressure, which
decreases the number of tars and methane formed during gasification. Because of the entrainment requirement, the high space velocity of the gas stream and fine powdery coal particles are essential to the operation of this type of process. Because of the very short residence time (i.e., high space velocity) in the reactor, a very high temperature is required to achieve good conversion in such a short period of reaction time. Each gasifier design has different advantages and disadvantages, such as cost, tar yield, sensitivity to moisture, and volume potential. Gasifier manufacturers indicate that of the commercial gasifiers in use, 75% are co-current, 20% are fluidized beds, 2.5% are counter-current, and 2.5% are other designs [15]. The gasification reactor scoring is depicted in Table 5.

| Criteria          | Weight (%) | Fixed Bed Score | Weight (%) | Fixed Bed Score | Fluidized Bed Score | Weight (%) | Entrained Bed Score | Weight |
|-------------------|------------|-----------------|------------|-----------------|---------------------|------------|---------------------|--------|
| Product Yields    | 25         | 0.75            | 3          | 0.75            | 3                   | 0.75       | 4                   | 1.00   |
| Energy            | 25         | 0.75            | 4          | 1.00            | 4                   | 1.00       | 4                   | 1.00   |
| Equipment         | 25         | 1.00            | 4          | 1.00            | 5                   | 1.25       | 3                   | 0.75   |
| Cost              | 25         | 1.00            | 4          | 1.00            | 5                   | 1.25       | 3                   | 0.75   |
| **Total Score**   | **3.50**   | **3.75**        | **4.25**   | **3.50**        |                     |            |                     |        |

Overall, fluidized bed reactors have greater potential for use with biomass conversion than fixed bed reactors or other types of gasifiers. The gasification of carbonaceous biomass occurs via three main reactions, partial oxidation, complete oxidation, and the water-gas reaction.

4. Conclusion

The process chosen is process D, biomass – gasification – synthetic catalytic process – ethanol. In this alternative, the main processes are gasification and synthetic catalytic. Overall, fluidized bed reactors have more significant potential for use with biomass conversion than fixed bed reactors or other types of gasifiers. The gasification of carbonaceous biomass occurs via three main reactions, partial oxidation, complete oxidation, and the water-gas reaction.

References

[1] US Dept of Biomass Program. September 11, 2009.
[2] Limayem M and Ricke SC 2012 Prog. Energy. Combust. Sci, 38 449
[3] Sahlan M, Muryanto, Hermansyah H, Wijarnako A, Gozan M, Lischer K, Ahmudi A and Pujianto P 2020 Evergreen 7 1
[4] Hans M, Kumar S, Chandel AK and Polikarpov I 2019 Process Biochem. 85 125
[5] Dave N, Selvaraj R, Varadavenkatesan T and Vinayagam R 2019 Algal Res. 42 101606
[6] Darmawan, M.A., Hermawan, Y.A., Samsuri, M., Gozan, M., 2019. Conversion of paper waste to bioethanol using selected enzyme combination (cellulase and cellobiase) through simultaneous saccharification and fermentation, AIP Conference Proceedings 2085 020018
[7] Abdurachman and Gozan M 2016 Warta IHP 33 1
[8] Badan Pusat Statistik 2019 Luas Panen dan Produksi Padi di Indonesia 2019, No. 16/02/Th.XXIII, 4 Feb., 2020.
[9] Ayodele BV, Alsaffar MA and Mustapa SI 2019 J. Clean. Prod. 245 118857
[10] Ferreira JA, Brancoli P, Agnihotri S, Bolton K and Taherzadeh MJ 2018 Process Biochem. 75 173
[11] Carrillo-Nieves D, Magdalena J, Alanís R, Quiroz RC, Ruiz HA, Iqbal HMN and Parra-Saldívar R 2019 Renew. Sust. Energ. Rev. 102 63
[12] Rastogi M and Shrivastava S 2017 Renew. Sust. Energ. Rev. 80 330
[13] Badan Pusat Statistik 2017 ‘Kecamatan Indramayu dalam Angka’ (PDF). Badan Pusat Statistik Kabupaten Indramayu. Indonesian Bureau of Statistics. Retrieved 20 July 2017
[14] U.S Department of Energy, PNNL-19009
[15] Van Loo, S, Koppejan, J 2008 *The handbook of biomass combustion and co-firing* (London: Earthscan)

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