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Abstract: The massive dependence on fossil fuels to produce ethanol has damaged the environment. This compels the quest for other alternatives using lignocellulosic materials (2nd generation bioethanol) so as not to compete and disturb food security purposes. The promising biomass to be valorized is corn cob because of its high productivity and short harvest period. Coupled with the fact that simulation studies of its fermentation with *Zymomonas mobilis* to produce bioethanol are still lacking, a corn cob sustainable valorization to fuel-grade bioethanol is hence disclosed. Superpro Designer 8.5® was employed for simulation. Corn cob undergoes pretreatment, 2-h hydrolysis of cellulose and hemicellulose, delignification, 48-h glucose and xylose anaerobic fermentation, cells removal, vaporation, and distillation. Bioethanol is produced at 10.85%-wt from direct fermentation. Subsequently, the 1st distillation (13 actual stages number) upgrades its concentration to 92.34%-wt. The second one (23 actual stages number) rectifies up to 99.96% and the product finally meets the criteria of fuel grade. Afterward, the calculated yield is 0.35 g/g corn cob or 44.30% based on glucose and xylose. Several by-products are also produced and to comply with the concept of sustainability, water is returned to the river, lignin and extractives are utilized for phenolic producers, wet CO_2 gas is proposed for microalgae inorganic carbon sources, and stillage is returned to nature as liquid fertilizer.

Keywords: Hydrolysis; Lignocellulose; Azeotropic; Pressure swing distillation; Cells; Water

1. Introduction

The environmental impact of fossil fuel exploitation is increasingly threatened[1–5]. In addition, the fact that fossil resources continue to be depleted also requires the search for alternative, renewable, and more sustainable resources[6–9]. Biomass from agricultural and forestry residues can be considered a potential source of production of biofuels or chemicals[10–12]. Most of the residues are overlooked and are just piled up in landfills. It adds to the negative environmental impact such as reducing soil absorption capacity, inhibiting mineral intrusion into the soil, and reducing land capacity[13,14].

One way to overcome those impacts is through biomass utilization through the bioconversion process. It converts biomass into products with the participation of microorganism activity[15]. Valuable compounds can be produced from the bioconversion process encompassing methane for biogas, ethanol for biofuel, hydrogen for clean energy, biodiesel, butanol for biofuel, biokerosene, aviation biofuel, as well as fatty acids and organic matter for chemicals[16,17]. The product with the highest demand in the world is bioethanol[6,18,19].

Until now, there are three possible routes to produce bioethanol from biomass which is mainly done by fermentation[20]. The 1st generation utilizes fermentation of molasses and/or starch-type carbohydrates containing amylose and amylopectin[21]. The starchy biomass is derived from corn, palm sugar, sorghum, cassava, cashew, and sweet potatoes. Besides, research related to strain improvement of yeast in the fermentation stage can produce bioethanol with a concentration above 99%-wt[19,22].

Actually, the 1st generation of bioethanol has a drawback since raw materials also play a role as main food needs. Long-term production following this route clearly competes with aspects of food security[23]. Therefore, the 2nd generation of bioethanol is born where the production applies lignocellulosic materials which cannot be digested by humans, so there is no potential to compete with food needs. The raw materials used can derived from rice husks, oil palm empty fruit bunches, banana stems, coconut shells, rice straws, corn cobs, and bagasse[24].

On the other hand, 3rd generation of bioethanol utilized microalgae and macroalgae as raw materials[25,26]. The development of bioreactors and related techniques is aimed at accumulating ethanol products which also relies on anaerobic fermentation[27,28]. Unfortunately, their cultivation takes weeks, the downstream processing is cost-intensive, and bioethanol yields are still low[26,29].

In order to support the achievement of bioethanol production in short, medium, and long terms, the potential of lignocellulosic materials needs to be studied further. Due to the large availability of lignocellulosic sources in Indonesia, the design of the 2nd generation bioethanol production is attractive to select and realize. The other benefits of the 2nd generation of bioethanol are reducing the amount of biomass residue piles, suppressing the exploitation of fossil resources, lowering global warming potential, and leading to sustainability[18,20,23,30].

Regarding local potential, the corn field area is large, the plant lifetime is relatively short, and the average after planting is 100 days[31]. The long-term impact that deserves attention is the accumulation of corn cob in landfill which create soil pollution. Coupled with the fact that the cellulose and hemicellulose content in corn cob is high, this biomass is attractive to be valorized as bioethanol[28].

In accordance with the extracted data from Scopus, the studies associated with the topic "corn cob fermentation to bioethanol" were pioneered in 2008. Nevertheless, it is still rarely communicated as nowadays only contains a total of 49 documents, as seen in Figure 1. The aforementioned list of studies is dominant in experimental mode focusing on hydrolysis, fermentation, or ethanol distillation separately[32–35].

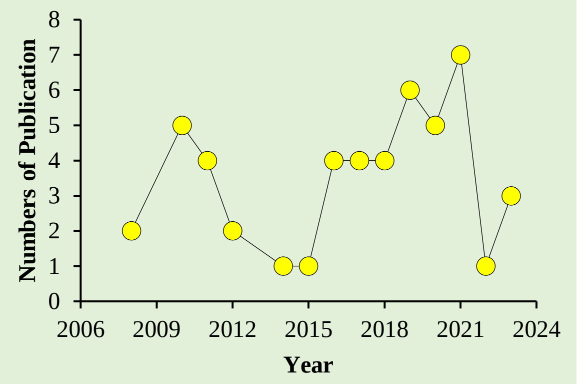


Fig. 1: Number of related publications along with time [processed from Scopus with TITLE-ABS-KEY: corn AND cob AND fermentation AND bioethanol].

Thus, a more specialized and integrated simulation study in corn cob sustainable valorization by fermentation using *Zymomonas mobilis* to produce bioethanol is believed to fill the gap and contribute to science and technology communities. Bioethanol is targeted to reach the fuel-grade category. For use as fuel, bioethanol should have a purity of above 99% to prevent phase mixing which causes engine problems and reduces machine efficiency[36].

This study is then aimed to analyze the production design of fuel-grade bioethanol from corn cob fermentation. Furthermore, the mass and energy balance, power requirement, utility amount needs, and unit specifications in downstream processing are examined. At last, several points of sustainability concepts in this production are also revealed.

2. Materials and methods

2.1 Raw materials, site locations, and simulation setups

This study employed corn cob which is cheap and contained high cellulose in it, 45%-wt. In addition, hemicellulose component was 35%-wt, lignin and extractives were total recorded at 15%-wt, and impurities were occupied at 5%-wt[16]. The production site was in Central Kalimantan Province, located close to the Kapuas River. The considerations lay on the water needs for process and utilities that can be completely complied from this river.

Subsequently, simulation was done in batch mode and assisted with Superpro Designer 8.5® software. The consideration for choosing batch mode is low capital cost and no need for robust control and instrumentation systems compared to continuous or fed-batch modes. Apart from that, the yield and productivity of the bioethanol produced are not much different from the other two modes[37].

The microorganism employed *Zymomonas mobilis* and the molecular formula can be written as $CH_{1.5}O_{0.5}N_{0.2}$. The desired specification of fuel-grade bioethanol was 1000 L with a concentration of surpassing 99.5%-wt (density of 790 kg/m^3). The capacity of bioethanol production was chosen following a study by Abeysuriya et al.[38]. There were four sections in corn cob fermentation to produce bioethanol, namely pretreatment, hydrolysis, fermentation, and downstream processing[39], as illustrated in the block flow diagram in Figure 2.

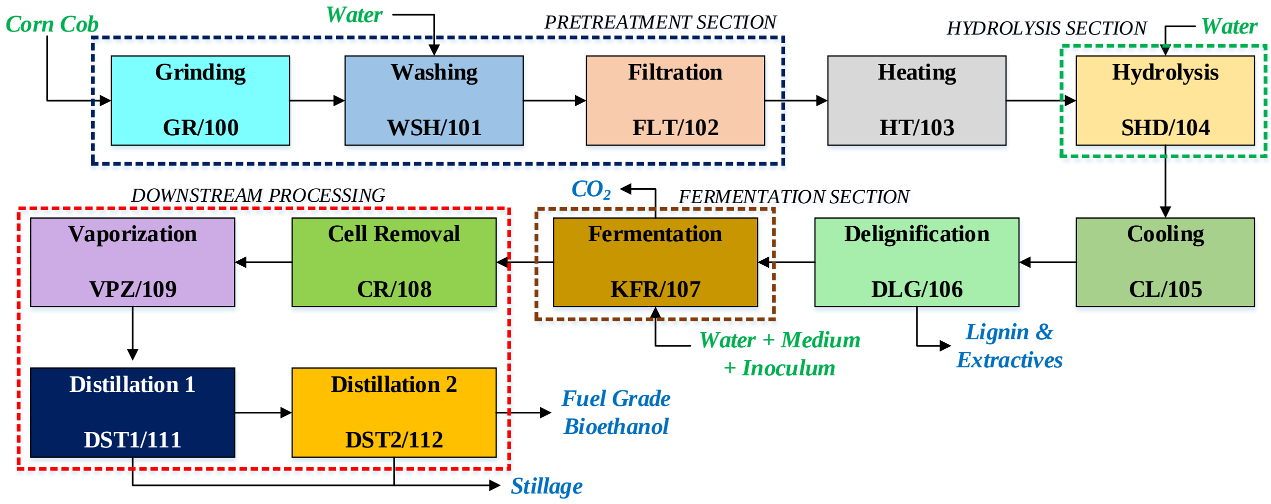


Fig. 2: Block flow diagram of bioethanol production from corn cob.

2.2 Detailed production process

Pretreatment was carried out by grinding and washing. First of all, corn cob was fed into the grinding unit (GR/100). The ground corn cob was then washed in unit WSH/101 to get rid of impurities. The impurities were dragged into the water. Afterward, washing water was clarified (FLT/102) and clean water was returned to the river.

Treated corn cob was initially heated until 90°C in unit HT/103. After heating, it was hydrolyzed to produce glucose (from cellulose) and xylose (from hemicellulose)[40,41]. The hydrolysis was aided with water at 99°C in unit SHD/104. The working volume was 80% of the total volume. The output stream from the hydrolyzer was later called crude mash. The crude mash was cooled in unit CL/105 until reached the fermentation temperature, 37°C. Crude mash still contained lignin and extractives so it should be processed in a delignification unit (DLG/106)[42]. The output stream was treated mash.

The treated mash was fermented in unit KFR/107 until glucose and xylose were converted to ethanol. The fermenter's working volume occupied 80% of its total volume. Into this unit was added 1 ppm *Zymomonas mobilis* inoculant and nutrient. The microorganism was chosen due to its excellent performance in ethanol fermentation[43].

The metabolic pathway for glucose to ethanol followed Entner-Doudoroff pathway and for xylose to ethanol accompanied phosphoketolase pathway[44,45]. In a macroscopic view, reactions that occur are written in Eq. (1) for glucose fermentation and Eq. (2) for xylose fermentation. Since glucose and xylose fermentations to produce bioethanol are categorized as mixed growth association, they comply Luedeking-Piret kinetic model which is combined with the 1st-order microorganisms' maintenance reaction as expressed in Eq. (3)[15]. Other than that, product yield is calculated using Eq. (4). All of the involved kinetic data are summarized in Table 1.

$$1.14\ C_6H_{12}O_6 \rightarrow CH_{1.5}O_{0.5}N_{0.2} + 2\ CO_2 + 2\ C_2H_5OH \quad (1)$$

$$3.18\ C_5H_{10}O_5 \rightarrow 1.1\ CH_{1.5}O_{0.5}N_{0.2} + 5\ CO_2 + 5\ C_2H_5OH \quad (2)$$

$$r = q_p.X \quad (3a)$$

$$q_p = \alpha\mu_g + \beta = \alpha\left(\mu_{max}\frac{S}{K_S+S}\right) + \beta \quad (3b)$$

$$Y_{p/s} = \frac{m_p}{m_s}\times 100\% \quad (4)$$

where r is rate of ethanol formation [g/L/h], q_p is specific ethanol production rate [h^{-1}], X is cells concentration [g/L], α is growth associated factor for ethanol production, μ_g is specific growth rate of cells [h^{-1}], β is maintenance parameter or growth independent factor for ethanol production [h^{-1}], μ_{max} is maximum growth rate of cells [h^{-1}], S is substrate concentration [g/L], K_S is saturation constant [g/L], $Y_{p/s}$ is product yield [% or g/g], m_p is product amount [g], and m_s is substrate amount [g], either in corn cob base or in glucose and xylose base.

Table 1. Kinetic parameter data in glucose and xylose fermentation, processed from[41,46–49].

Parameters	Units	Glucose Fermentation	Xylose Fermentation
α	-	1	1
β	h^{-1}	0.23	0.20
μ_{max}	h^{-1}	0.27	0.09
K_S	g/L	1.45	4.32

After fermentation, there were two output products, i.e. bottom product (liquid) and top product (gas). The CO_2 gas from the top product was collected in storage. In order to meet the fuel grade criteria, this solution should enter a consecutive phase of downstream processes. The cells still remained in liquid product so they should be separated in unit CR/108 to be reused or destructed if cells have already lost their ability to convert glucose and xylose.

The cells-free liquid contained low-concentration ethanol. To rectify the concentration, vaporation in unit VPZ/109 and two stages of distillation in units DST1/111 and DST2/112 were conducted. Distillation operated at different pressures due to azeotropic phenomena[50]. Before entering the first distiller unit, the feed was vaporized until two phases of liquid and vapor were formed. The first distiller worked at atmospheric pressure and the second distiller operated at 0.507 bar. The relative volatility of ethanol compared to water is chosen at distillation operating temperature. The bottom product streams from the two distillers were mixed in unit MX/113. This stream was named stillage. A list of process units, their equipment name, and their detailed operating conditions were all served in Table 2.

Table 2. Process units equipped with their operating conditions.

Process Unit	**Process – Category**	**Equipment name**	**Operating Conditions**
Grinder	Grinding – Pretreatment	GR/100	• Specific power = 0.1 kWh/kg • Power dissipation to heat = 0.5%
Washer	Washing – Pretreatment	WSH/101	• Impurities removal = 100% • Water temperature = 25ºC
Clarifier	Filtration – Pretreatment	FLT/102	• Impurities removal = 100% • Filter mesh size = 2 mm
Heater	Heating – Pretreatment	HT/103	• Type = Plate and frame • Exit temperature = 90ºC • Heating agent = Saturated steam 152ºC • Heat transfer coefficient = 1500 W/m^2.K • Heat transfer efficiency = 80%
Hydrolyzer	Hydrolysis – Hydrolysis	SHD/104	• Final temperature = 99ºC • Heat transfer agent = Saturated steam 152ºC • Specific power for agitation = 3 kW/m^3 • Power dissipation to heat = 0.5% • Reaction progress = 99% • Duration = 2 h • Working volume = 80% • Reaction progress = 100% based on reaction-limiting component
Cooler	Cooling – Hydrolysis	CL/105	• Type = Plate and frame • Exit temperature = 90ºC • Cooling agent = Chilled water 5ºC (in) 10ºC (out) • Heat transfer coefficient = 1000 W/m^2.K • Heat transfer efficiency = 80%
Centrifuge	Delignification – Hydrolysis	DLG/106	• Lignin and extractives removal = 100% • Feed-to-concentrate ratio = 20
Fermenter	Fermentation – Fermentation	KFR/107	• Final temperature = 37ºC • Heat transfer agent = cooling water 25ºC (in) 30ºC (out) • Specific power for agitation = 3 kW/m^3 • Power dissipation to heat = 0.5% • Reaction progress = kinetic in Table 2 • Duration = 48 h • Working volume = 80% • Venting operating mode = open vessel atmospheric at 25ºC • Gas product emission component = 100%
Centrifuge	Cells Removal – Downstream processing	CR/108	• Cells removal = 100% • Feed-to-concentrate ratio = 20
Vaporizer	Vaporation – Downstream processing	VPZ/109	• Type = Thin film vaporizer • Feed quality = 50% • K-value = Gamma-Phi model • Liquid fugacity = NRTL • Vapor fugacity = Soave-Redlich-Kwong • Heating agent = Saturated steam 152ºC • Heat transfer coefficient = 2905 W/m^2.K • Heat transfer efficiency = 80%
Mixer	Vapor-Liquid Mixing – Downstream processing	MX1/110	• None
Distiller	Product enriching – Downstream processing	DST1/111	• Light key = ethanol • Heavy key = water • Ratio of reflux and minimum reflux = 1.25 • Feed quality = 50% • Colum pressure = 1.013 bar • Vapor flow = 3 m/s • Stage efficiency = 75% • Condenser temperature = 50ºC (agent = cooling water 25ºC (in) 30ºC (out)) • Reboiler temperature = 105ºC (agent = Saturated steam 152ºC)
Distiller	Product enriching – Downstream processing	DST2/112	• Light key = ethanol • Heavy key = water • Ratio of reflux and minimum reflux = 1.25 • Feed quality = 100% • Colum pressure = 0.507 bar • Vapor flow = 3 m/s • Stage efficiency = 75% • Condenser temperature = 35ºC (agent = cooling water 25ºC (in) 30ºC (out))

Process Unit	Process – Category	Equipment name	Operating Conditions
			• Reboiler temperature = 105°C (agent = Saturated steam 152°C)
Mixer	Stillage Mixing – Downstream processing	MX2/113	• None

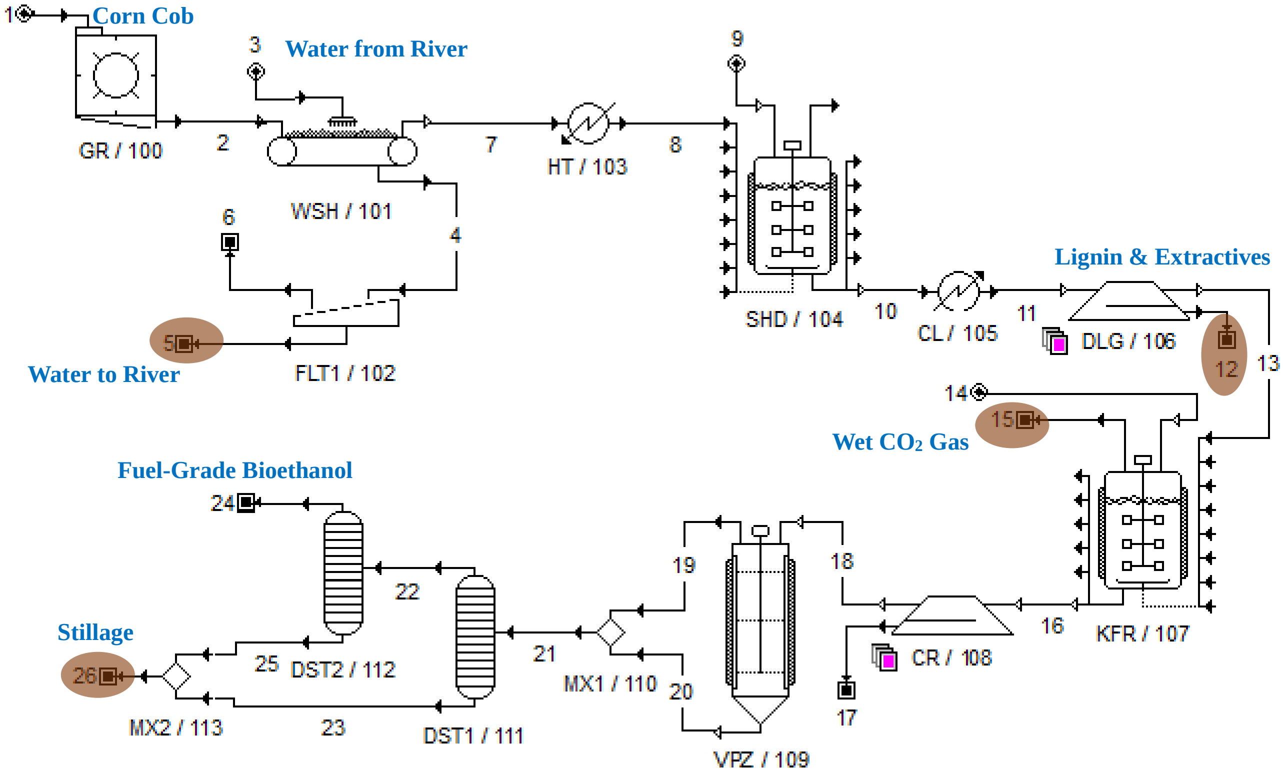
3. Results and discussion

3.1 Requirement amount of raw materials and utilities

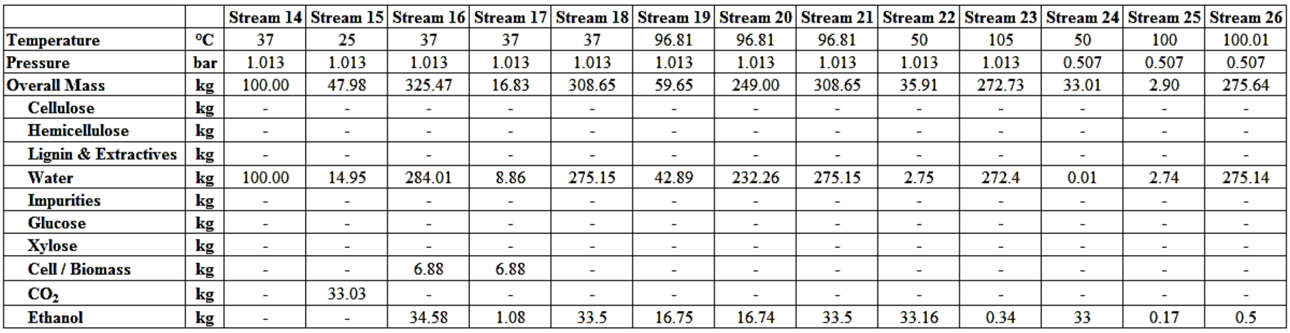
There are 26 streams in the process flow diagram of fuel-grade bioethanol production using Superpro Designer 8.5® as illustrated in Figure 3. The target for fuel-grade bioethanol production in the international system unit is 33 kg. The amount of corn cob is initially estimated at 500 kg, but the produced bioethanol exceeds the target. Consequently, iterative calculation is carried out and the calculated corn cob (stream 1) is 94.25 kg. In other words, the product yield is acquired at 0.35 g/g corn cob.

The utility that stands out is water. In this design, water is used for process purposes such as raw material washing (stream 3), hydrolyzing media (stream 9), and fermentation medium (stream 14). On the other hand, water also acts as utilities for cooling (chilled water or cooling water) and heating (steam). Air is of less use considering the process is facultatively anaerobic.

The total process water requirement is 500 kg with details of 200 kg for washing, 200 kg for hydrolysis, and 100 kg for fermentation. For process purposes, water from the river should be initially treated to gain demineralized water prior to usage. To avoid water scarcity and to meet the goal of water sustainability, this study strongly proposes water recycling for the river (stream 5).



		Stream 1	Stream 2	Stream 3	Stream 4	Stream 5	Stream 6	Stream 7	Stream 8	Stream 9	Stream 10	Stream 11	Stream 12	Stream 13
Temperature	**°C**	25	33.22	25	25.18	25.18	25.18	28.3	90	25	99	37	37	37
Pressure	**bar**	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013
Overall Mass	**kg**	94.25	94.25	200	204.71	200	4.71	89.54	89.54	200	289.54	289.54	16.09	273.45
Cellulose	**kg**	42.41	42.41	-	-	-	-	42.41	42.41	-	0.42	0.42	0.42	-
Hemicellulose	**kg**	32.99	32.99	-	-	-	-	32.99	32.99	-	0.33	0.33	0.33	-
Lignin & Extractives	**kg**	14.14	14.14	-	-	-	-	14.14	14.14	-	14.14	14.14	14.14	-
Water	**kg**	-	-	200	200	200	-	-	-	200	199.83	199.83	0.87	198.96
Impurities	**kg**	4.71	4.71	-	4.71	-	4.71	-	-	-	-	-	-	-
Glucose	**kg**	-	-	-	-	-	-	-	-	-	41.99	41.99	0.18	41.81
Xylose	**kg**	-	-	-	-	-	-	-	-	-	32.82	32.82	0.14	32.68
Cell / Biomass	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-
CO_2	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-
Ethanol	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-



		Stream 14	Stream 15	Stream 16	Stream 17	Stream 18	Stream 19	Stream 20	Stream 21	Stream 22	Stream 23	Stream 24	Stream 25	Stream 26
Temperature	**ºC**	37	25	37	37	37	96.81	96.81	96.81	50	105	50	100	100.01
Pressure	**bar**	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	1.013	0.507	0.507	0.507
Overall Mass	**kg**	100.00	47.98	325.47	16.83	308.65	59.65	249.00	308.65	35.91	272.73	33.01	2.90	275.64
Cellulose	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-
Hemicellulose	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-
Lignin & Extractives	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-
Water	**kg**	100.00	14.95	284.01	8.86	275.15	42.89	232.26	275.15	2.75	272.4	0.01	2.74	275.14
Impurities	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-
Glucose	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-
Xylose	**kg**	-	-	-	-	-	-	-	-	-	-	-	-	-
Cell / Biomass	**kg**	-	-	6.88	6.88	-	-	-	-	-	-	-	-	-
CO_2	**kg**	-	33.03	-	-	-	-	-	-	-	-	-	-	-
Ethanol	**kg**	-	-	34.58	1.08	33.5	16.75	16.74	33.5	33.16	0.34	33	0.17	0.5

Fig. 3: Process flow diagram in bioethanol production from corn cob equipped with overall and component mass balance.

However, used water certainly contains high impurities in the form of total solids[51]. Hence, water treatment should be applied again before being returned to the river. It can be done by physical treatment (filtration, adsorption), chemical treatment (coagulation, flocculation, chemical precipitation), or combinations[51]. From this study, it is also calculated that total utility requirement is as much as 29211.5 kg of water and the details are presented in Table 3.

Table 3. Summary of energy and utility requirements in this process.

Equipment Name	Power (kW)	Utility (kg)	Utility Category
GR/100	9.43	-	-
HT/103	0.08	0.14	Saturated steam
SHD/104	17.17	29.33	Saturated steam
CL/105	21.51	3685.98	Chilled water
DLG/106	18	-	-
KFR/107	0.26	45.35	Cooling water
CR/108	24	-	-
VPR/109	69.6	118.9	Saturated steam
DST1/111	137.2	234.4	Saturated steam
DST1/111	136.3	23467.1	Cooling water
DST2/112	9.7	1613.8	Saturated steam
DST2/112	9.4	16.5	Cooling water
Total	452.65	29211.5	

3.2 Simulation performance and results analysis

3.2.1 Pretreatment section

Figure 3 also serves the overall and component mass balance as seen therein. A total of 94.25 kg of corn cob is ground in unit GR/100. As a consequence of power dissipation to heat, the outlet temperature escalates from 25ºC to 33.22ºC. Ground corn cob (stream 2) is then washed with 200 kg of water (stream 3) until all impurities are removed.

After washing (stream 4), impurities in water are separated and obtained at 4.71 kg (stream 6). The pretreated corn cob (stream 7) now has a temperature of 28.3ºC and is heated until 90ºC prior to hydrolysis (stream 8) to elongate the thermal exposure on materials which eases the further process. The power requirement for heating in unit HT/103 is fulfilled by 0.14 kg saturated steam.

3.2.2 Hydrolysis section

Hydrolysis is carried out with 200 kg of water at 99ºC (stream 9) to break the lignin structures in corn cob which leads to perfect heat and mass transfer between materials and hydrolyzing agent[52,53]. Cellulose is hydrolyzed to glucose, C_6 sugar, and follows Entner-Doudoroff pathway in its fermentation[44,54]. Hemicellulose is hydrolyzed to xylose, C_5 sugar, and complies phosphoketolase pathway in its fermentation[45]. Lignin and extractives stand still in the solutions. In accordance with the simulation, the working volume of hydrolyzer is gained at 554.78 L. Also, the saturated steam required for enhancing the inlet temperature (90ºC) until setup hydrolysis temperature (99ºC) is 29.33 kg.

The output of the hydrolysis reactor, crude mash (stream 10), has a composition of 14.5%-wt glucose, 11.3%-wt xylose, 4.9%-wt lignin and extractives, 0.15%-wt cellulose, 0.11%-wt hemicellulose, and the rest is water. It is then cooled until reaches fermentation temperature, 37ºC (stream 11). Cooling in unit CL/105 needs 3685.98 kg of chilled water.

Lignin and extractives in cold crude mash have a high possibility of inhibiting microorganisms' performance due to their toxic nature[24]. After delignification process, stream 12 is 16.09 kg which contains lignin and extractives of as much as 87.9%-wt. It is then accommodated to be further processed into phenolic derivative chemicals[55].

3.2.3 Fermentation section

Treated mash (stream 13) which contains as much as 41.81 kg glucose and 32.68 kg xylose in 198.96 kg of water is then fermented using *Zymomonas mobilis*. It is a microorganism that can operate at facultative anaerobic[56].

Besides, inside the fermenter is added 100 kg of medium and water (stream 14). During fermentation, there is an increase in temperature in the reactor due to exothermic microbial metabolism. To prevent overheating, the fermenter is equipped with a heat exchanger system with cooling water as the medium. The consumed cooling water is calculated at 45.35 kg.

According to the calculation, the fermenter has 17559.8 L of working volume and has product yield of 0.35 g/g corn cob or 44.30% based on glucose and xylose. This value is comparable to the common yield from corn cob feedstock, 46%20). Also, the value is in line with the theoretical or maximum yield according to reactions 1 and 2 is calculated at 46.51% based on glucose and xylose.

In comparison with other studies, Table 4 outlines the yield obtained from this study and other researchers. It is found that there is a result discrepancy which is caused by dynamics that happen in each experimental condition while this study is a simulation that does not experience that dynamism. However, it is quite lower than yield reported by Jerry et al.33) which might be caused by the excellent cell strain in their research.

Table 4. Comparison of bioethanol yield from corn cob fermentation using *Zymomonas mobilis.*

Process Conditions	Bioethanol Yield	Ref.
- Hydrolysis: water at 99°C for 5 h - Fermentation: at 37°C for 48 h	44.30% (glucose-xylose base) 0.35 g/g corn cob	This study
- Hydrolysis: 2% (w/v) NaOH at 80°C for 6 h - Fermentation: : at 30-40°C for 96 h	28.56-40.16% (glucose-xylose base)	32)
- Hydrolysis: 10% (w/v) citrate at 50°C for 7 h - Fermentation: at 28°C for 48 h	49% (hydrolysate base)	33)
- Hydrolysis: 1% (v/v) H_2SO_4 a at 170°C for 5 mins - Fermentation: at 30°C for 48 h	35.93% (glucose base) 0.21 g/g corn cob)	34)

The top flow of the fermentation reactor (stream 15) is wet CO_2 gas containing 33.03 kg CO_2 and 14.95 kg of water vapor from 5%-wt of water vapor that is set to be carried over out of the fermenter. To meet the criteria of low carbon footprint, CO_2 capture and utilization should be realized57–60). This wet CO_2 gas can be proposed for microalgae inorganic carbon sources29,61–63).

3.2.4 Downstream processing section

The outlet of fermentation solutions (stream 16) still contains 2.11%-wt cells, so it should be separated by centrifugation. Centrifugation results in 16.83 kg of concentrated cells (stream 17) with composition of 40.91% cells, 52.68% water, and 6.41% ethanol. Further, cells can be reused or destroyed by ultrasonication or heating if it has low viability. This is done to prevent mutations64).

Cells-free solution (stream 18) contains 10.85%-wt ethanol. The result is in line with the rule of thumb that the maximum ethanol concentration from direct fermentation process is about 6-12%-wt. This occurs to prevent microorganism death due to product accumulation in the fermentation broth which leads to inhibition phenomenon54,65).

To upgrade the bioethanol concentration, this study used pressure-swing distillation (PSD), a distillation technique that includes operating two columns at two distinct pressures, high pressure and low pressure. It is chosen considering the azeotropic phenomenon in ethanol-water mixture66). Iqbal et al. showed that PSD can produce bioethanol with a purity of up to 99.7%67).

In the distillation column, if the feed has 100% liquid phase, the reboiler burden becomes dominant. If the feed enters the distillation column in 100% vapor phase, the condenser burden becomes large. Therefore, the ethanol-water mixture should be vaporized to form two phases before entering the distillation unit. Raw bioethanol solution is vaporized until forming 2-phase in the form of liquid vapor with feed quality of 50% (streams 19-20).

By applying Gamma-Phi model for K-value, NRTL for liquid fugacity, and Soave-Redlich-Kwong for vapor fugacity, the vaporation temperature to reach the desired condition is 96.81°C as depicted in Figure 4. Under this condition, ethanol relative volatility compared to water has a value of 10.5868). Additionally, vaporation requires 118.9 kg of saturated steam and produces a solution with ethanol concentration of 28.09% in the vapor phase. It then undergoes distillation to meet the goal of fuel grade criteria.

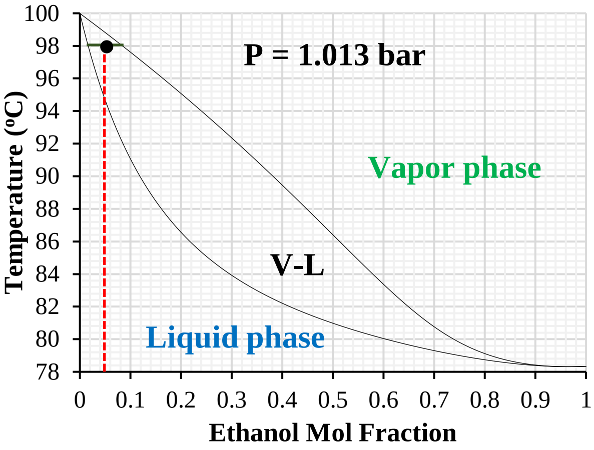
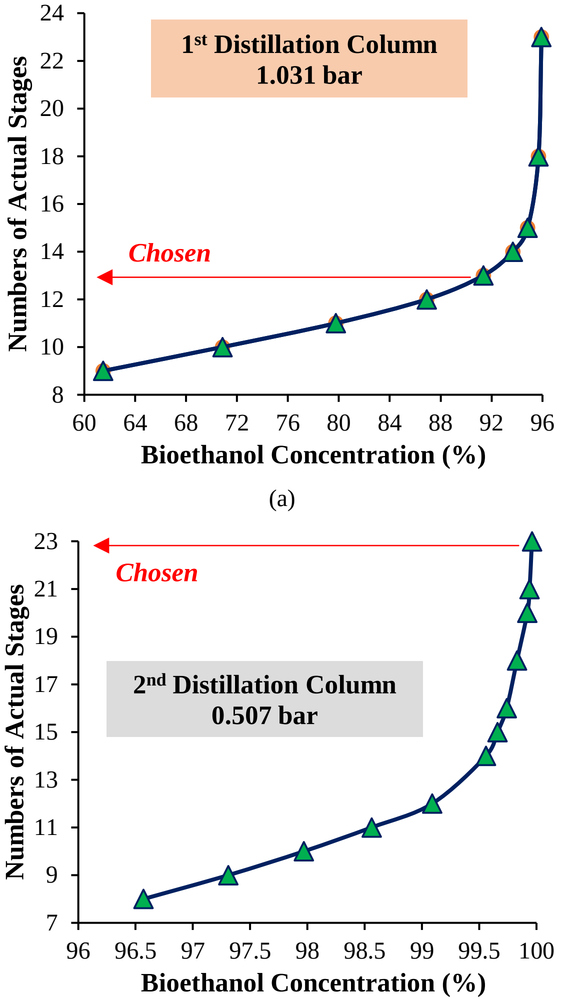


Fig. 4: T-x,y diagram for ethanol-water mixture [processed from Superpro Designer 8.5®].

The sensitivity of columns in PSD is presented in Figure 5. Results imply that more stages in the 1st distillation column lead to the asymptotic condition of bioethanol concentration at approximately 96% due to the azeotropic phenomenon[35]. Likewise, the greater actual stages in the 2nd column reflect the intensive cost that should be required to rectify bioethanol from 96% to 99.96%. It can be concluded that more stages are involved in the distillation column to obtain a purer component.



(a)

(b)

Fig. 5: Numbers of actual stages vs. bioethanol concentration in 1st (a) and 2nd (b) distillation column.

The first column has a chosen ideal number of stages of 10.1. By applying efficiency per stage of 75%, the actual number of stages is calculated at 13. The reflux ratio involved is 12.48. The cooling water requirement is 23467.1 kg whereas the steam requirement is 234.4 kg. Within this condition, the output product of the first column (stream 22) is bioethanol 92.34%-wt.

After that, the second column has an ideal number of stages of 16.9, actual number of stages of 23, and reflux ratio of 0.15. The need for cooling water is 1613.8 kg and the steam requirement is 16.5 kg. The output product of the second column (stream 24) has met fuel grade criteria with an ethanol concentration of 99.96%-wt. This study shows that the number of stages in the 2nd distillation column is approximately 2-fold higher than in the 1st distillation column. This is also in line with the pattern that was reported by Pachón et al[66].

The bottom product from PSD (streams 23 and 25) is mixed to form stillage (stream 26) of as much as 275.64 kg. It consists of 99.82% water and 0.18% ethanol. Again, to achieve water sustainability, it is recommended to return the stillage to nature as liquid fertilizer.

3.3 Sizing results of several important types of equipment

This simulation also provides sizing results of several important equipment that are involved in fuel-grade bioethanol production. Those types of equipment are heat exchangers (heaters and coolers), hydrolyzers (in the hydrolysis section), fermenters (in the fermentation section), vaporizers (in the downstream processing section), and distillers (in the downstream processing section). The summary of these sizing results is given in Table 5.

Table 5. Sizing results of several important types of equipment.

Equipment	Sizing Results
Heater	- Type = Plate and frame - Heat transfer area = 0.001 m^2
Hydrolyzer	- Total volume = 693.47 L - Working volume = 554.78 L - Height = 1.996 m - Diameter = 0.665 m - L/D (height/diameter) = 3
Cooler	- Type = Plate and frame - Heat transfer area = 0.386 m^2
Fermenter	- Total volume = 21949.70 L - Working volume = 17559.76 L - Height = 6.312 m - Diameter = 2.104 m - L/D (height/diameter) = 3
Vaporizer	- Type = Thin film vaporizer - Heat transfer area = 0.434 m^2
Distiller 1 (ASME Vessel)	- Actual stages = 13 - Stage height = 0.4 m - Column height = 4.4 m - Column diameter = 0.2 m - Volume = 137.922 L
Distiller 2 (ASME Vessel)	- Actual stages = 23 - Stage height = 0.4 m - Column height = 8 m - Column diameter = 0.075 m - Volume = 34.887 L

4. Conclusions

The sustainable production of fuel-grade bioethanol with a capacity of 1000 L per batch has been successfully carried out by 94.25 kg corncob valorization. Corncob undergoes a sequential process of pretreatment, hydrolysis, fermentation, and downstream processing. Referring to the results, direct fermentation has succeeded in producing 10.85%-wt bioethanol. Downstream processing rectifies its concentration up to 99.96%-wt allowing bioethanol to meet the fuel grade criteria. Furthermore, this study also emphasizes the sustainability concept in utilizing produced by-products such as water recycling to the river, 16.09 kg lignin and extractives which can be further processed into phenolic-based chemicals, 47.98 kg wet CO_2 gas for inorganic carbon sources in microalgae cultivation, and 275.64 kg stillage (consisting 99.82% water) which is targeted as a liquid fertilizer.

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