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Volume 12 No. 2, November 2021

FOCUS AND SCOPE

Jurnal Riset Teknologi Pencegahan Pencemaran Industri (Research Journal of Industrial Pollution Prevention Technology) seeks to promote and disseminate original research as well as review, related to following area:

Environmental Technology : within the area of air pollution technology, wastewater treatment technology, and management of solid waste and harzardous toxic substance.

Process Technology and Simulation : technology and/or simulation in industrial production process aims to minimize waste and environmental degradation.

Design Engineering : device engineering to improve process efficiency, measurement accuracy and to detect pollutant.

Material Fabrication : environmental friendly material fabrication as subtitution material for industry.

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PREFACE

Thanks to Allahu Robbie 'Alamin, Journal of Industrial Pollution Prevention Technology (JRTPPI) again will publish scientific articles, especially in the field of environmental technology for volume 12 no 2. Our high appreciation is directed to the authors and editorial board who have actively participated so as to maintain consistency of quality and punctuality of our periodic publications. We would like to acknowledge our high appreciation to the head at center of industrial pollution prevention technology, Ministry of Industry.

This edition of the issue is sixth series published that in full-text English. This continous policy is an attempt of the editorial board to improve the author's performance in delivering the results of their researches. Articles in full-text English are more likely to be read by broader audience so that it will increase the number of citations. This policy is also applied in order to actualize our hope of being a globally indexed international journal.

The articles contained in this edition consist of energy based on biogas, air monitoring, and material characterization. The biogas production use biological method as energy alternative, while characterization to identify and analysis the synthesized materials. Online monitoring as respon a current issue in Indonesia for real evaluation some emission industry and ambient quality. The five manuscripts accepted and published in this edition are from researcher and lecturer in Indonesia. The duration of submission, review, and editing of the manuscripts ranged from 1-8 months.

Hopefully, these scientific articles may be new source of knowledge and experience for readers from academic, researcher, industry, and society at large. We realize that nothing is perfect until the improvement of all parties involved is continuously done.

Semarang, Desember 2021

Chief Editor

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Environmental Critical Aspects of The Conversion of Biomass to Biogas for Sustainable Energy in Indonesia

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, November 2021, Vol. 12, No. 2, p. 1-14, 5 ill, 1 tab, 70 ref

Renewable energy will become the foundation for meeting the world's energy needs in the future. However, Indonesia has not done much research on the development and application of technology for sustainable energy. Indonesia has potential energy sources. However, biomass conversion into other forms of energy, such as biogas, will hurt the environment. The development of biomass-based bioenergy is one of the best solution for meeting Indonesia's current and future energy needs. Biogas is biomass-based bioenergy, which is the potential for future energy sources. Minimizing the environment's degradation is a significant aspect of preparing the biomass to biogas conversion model. Furthermore, the production of biogas with automatic monitoring and control will minimize new waste formation. Indonesian government regulatory support and total community participation will increase converting biomass into biogas as renewable energy into electrical energy. The paper analyzes the environmental impact of biomass conversion into biogas and proposed an environmentally friendly conversion model.

(Author)

Keywords: Renewable energy, Biomass, Biogas, Environmental impact, Conversion model

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Januar Arif Fatkhurrahman[1], Ikha Rasti Julia Sari[1], Yose Andriani[1] ([1]Balai BesarTeknologi Pencegahan Pencemaran Industri, Jalan Ki Mangunsarkoro No. 6 Semarang)

Environmental Critical Aspects of The Conversion of Biomass to Biogas for Sustainable Energy in Indonesia

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, November 2021, Vol. 12, No. 2, p. 15-24, 6 ill, 2 tab, 27 ref

Sulfur dioxide and Nitrogen dioxide were significant emissions emitted from coal-steam power plants that may cause health problems for humans and damage the environment. Studying the SO_2 and NO_2 gradients in Indonesian residential communities is critical for evaluating resident's SO_2 and NO_2 exposure. The method developed to assist analysis of spatial SO_2 and NO_2 gradients on a community scale combines a mesoscale Lagrangian dispersion model with field observations around coal-steam power plants using GRAL. The objectives of this study focused on GRAL dispersion of SO_2 and NO_2 in an Indonesian residential community near the coal-steam power plant, with a 6 km x 8 km resolution. Analysis of this model indicates a correlation between simulation and observation, with SO_2 coefficient correlation (R) within 0.5 – 0.82 and NO_2 coefficient correlation (R) within 0.30 – 0.59. Model performances analyze by NMSE and FB. The SO_2 model is comparable to observation data since it has a better average NMSE and FB than the NO_2 model. Due to data limitation of observation collected by grab sampling instead of continuous ambient measurement system affect different respond time compared with hourly data from the model.

(Author)

Keywords: GRAL, Dispersion, Sulfur dioxide, Nitrogen dioxide, Air quality model

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Muhammad Amin[1], Andini Yulian[2], Muhammad Al Muttaqii[3], Pulung Karo-Karo[2], David Candra Birawidha[1], Yusup Hendronursito[1], Kusno Isnugroho[1] ([1]Research Unit For Mineral Technology, [2]Lampung University, [3]Research Center of Chemistry)

Utilization of iron ore slag in the manufacture of calcium silicate boards

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, November 2021, Vol. 12, No. 2, p. 25-33, 7 ill, 5 tab, 26 ref

This study aims to determine the iron ore slag effect as an additive in particleboard based on the SNI 7705:2011 standard. Iron ore slag comes from the waste processing of iron ore into sponge iron. The iron

ore slag is reduced to a size of 200 mesh. Particleboard made with the composition of slag and silica is 0:40, 8:32, 16:24, 20:20, 24:16, 32:8, and 40:0 wt%. Meanwhile, other materials were made permanent, namely PCC cement and lime 16 wt%, coconut fiber 3wt%, and water 3 wt%. They are pressed with 3 tons of pressure for 1 hour using a hydraulic press. Drying at room temperature for one day, under the hot sun for two days, then in an oven at 110 °C for 8 hrs. Analysis of the chemical composition of X-ray fluorescence and X-ray diffraction crystalline phase, SEM-EDS micro-photographs, physical tests including density and porosity, and mechanical compressive strength tests. The dominant composition of SiO_2 and CaO affects the formation of silicon dioxide (SiO_2), calcium silicate ($CaSiO_3$), and dicalcium silicate (Ca_2SiO_4) phases. Silica has a positive effect on the compressive strength of particleboard but is different from Ca, which has an impact on reducing the compressive strength. The sem morphology shows that coconut fiber cannot withstand heating at 190 °C and results in agglomeration. The addition of 20% ore slag and silica has met the calcium silicate board SNI 7705-2011. These results can be used to develop slag waste from iron ore processing into much more useful objects.

(Author)

Keywords: Iron ore slag, Silica, Calcium silicate, Calcium silicate board, $CaSio_3$

Rustiana Yuliasni[1], Rieke Yuliastuti[2], Nanik Indah Setianingsih[1] ([1]Balai Besar Teknologi Pencegahan Pencemaran Industri, Jalan Ki Mangunsarkoro No. 6 Semarang, [2]Balai Riset dan Standardisasi Industri Surabaya)

Biogas Production from Sugarcane Vinasse: A Review

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, November 2021, Vol. 12, No. 2, p. 34-44, 3 ill, 3 tab, 44 ref

Biogas is a renewable energy sources that could replace the role of fossil fuel. Biogas could be produced from biomass or agro-industrial wastewater. Sugarcane vinasse has potential of biogas production due to its high BOD concentration (10–65 g BOD/L). However, the biogas production from sugarcane vinasse has several drawbacks that hinders the maximum biogas yield, such as: acidic pH (pH 3.5 – 5.0), high temperature (80–90°C) and high concentration of sulfuric acid (> 150 mg/L). Theoretically, the methane potential per gram COD is 0.35 L/gr COD, containing of 60% methane. However, up to date, the maximum biogas production from vinasse was less then its theoretical value. To get the full potential of biogas production from vinasse wastewater as well as to reduce the capital cost for full scale application, combination of suitable pre-treatment, selected microorganisms and bioreactor design-configuration are the most important parameters to be considered. This paper aims to explore the potential of sugarcane vinasse to produce biogas, by elaborating the aforementioned key parameters. In this review the basic characteristic and the potency of sugarcane vinasse wastewater will be elaborated. Furthermore, the effect of key parameters such as pH, temperature, and organic load to biogas production will also be discussed. The biogas technology will also be explored. Lastly, conclusion will be determined.

(Author)

Keywords: Agro-Industrial wastewater, Biogas, Methane, Sugarcane vinasse, Wastewter technology

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Iqbal Syaichurrozi[1,2], Suhirman Suhirman[1], Topik Hidayat[1] ([1]Department of Chemical Engineering, Faculty of Engineering, University of Sultan Ageng Tirtayasa, Jl. Jendral Soedirman Km 3, Cilegon 42435, Indonesia, [2]Master of Chemical Engineering, Postgraduate School, University of Sultan Ageng Tirtayasa, Jl. Raya Jakarta Km 4 Pakupatan, Serang 42118, Indonesia)

Effect of Substrate/Water Ratio on Biogas Production from the Mixture Substrate of Rice Straw and Salvinia molesta

Jurnal Riset Teknologi Pencegahan Pencemaran Industri, Nov 2021, Vol. 12, No. 2, p. 45-55, 5 ill, 3 tab, 20 ref

The substrate/water (S/W) ratio is one of the affecting parameters in anaerobic digestion (AD) since it affects the concentration of total solids (TS) in the biogas feedstocks. The appropriate S/W ratio has to be found to result in a high biogas yield. The goal of this study was to look into the influence of S/W ratio on biogas production from mixture substrate of rice straw and Salvinia molesta. Ratio of S/W was varied to be 1/7 w/v (TS 9.67%w/w), 1/10 w/v (TS 7.52%w/w), 1/13 w/v (TS 6.15%w/w), 1/16 w/v (TS 5.20%w/w). The results showed that S/W of 1/7, 1/10, 1/13, 1/16 resulted a total biogas yield of 22.86, 38.67, 42.71, 43.69 mL/g TS respectively. Decreasing TS from 9.67 %w/w (S/W of 1/7) until 6.15%w/w (S/W of 1/13) could increase the TS removal from 31.03% until 55.66%. However, at TS 5.20%w/w (S/W of 1/16), the TS removal was lower than that at TS 6.15%w/w (S/W of 1/13). The modified Gompertz (R^2 = 0.94 – 0.98) can predict evolution of biogas production with higher precision than the first order kinetic (R^2 = 0.91 – 0.98). The optimum TS was successfully predicted to become 5.40%w/w.

(Author)

Keywords: Biogas, Kinetic, Rice straw, Salvinia molesta, Substrate/Water, Total solid

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Environmental Critical Aspects of The Conversion of Biomass to Biogas for Sustainable Energy in Indonesia

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ABSTRACT

Renewable energy will become the foundation for meeting the world's energy needs in the future. However, Indonesia has not done much research on the development and application of technology for sustainable energy. Indonesia has potential energy sources. However, biomass conversion into other forms of energy, such as biogas, will hurt the environment. The development of biomass-based bioenergy is one of the best solution for meeting Indonesia's current and future energy needs. Biogas is biomass-based bioenergy, which is the potential for future energy sources. Minimizing the environment's degradation is a significant aspect of preparing the biomass to biogas conversion model. Furthermore, the production of biogas with automatic monitoring and control will minimize new waste formation. Indonesian government regulatory support and total community participation will increase converting biomass into biogas as renewable energy into electrical energy. The paper analyzes the environmental impact of biomass conversion into biogas and proposed an environmentally friendly conversion model.

1. INTRODUCTION

The development has a noble goal in the form of economic growth and welfare improvement. Energy is a significant component to drive development success. Energy comes from renewable energy sources and non-renewable energy sources that can produce energy either directly or through a conversion or transformation process(Mayer, Bhandari, & Gäth, 2019). Energy can be heat, light, mechanical, chemical, or electromagnetic(Zabek & Morini, 2019). Development also causes undesired side effects, namely environmental pollution, global warming, social inequality, and lack of natural resources.

Solar cells and bioenergy will become the foundation for meeting the world's energy needs in the future (Kumari & Singh, 2018; Prabakar et al., 2018; Roy & Dias, 2017; Zabaniotou, 2018). However, Indonesia has not researched developing and applying solar cells and bioenergy (Suryaningsih and Irhas, 2014; Papilo et al., 2018; Simangunsong et al., 2017). This condition is a challenge for researchers in Indonesia to prepare and implement renewable energy as an energy source immediately. It is crucial to start the development to not depend on foreign countries to provide solar cells and bioenergy facilities and infrastructure.

Indonesia is lagging compared to several countries in Asia, such as China, India, Singapore, South Korea, and Japan. These countries are very active in researching the

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development and application of solar cells and bioenergy (Huang et al., 2018; A. Kumar et al., 2018; S. Kumar et al., 2017; Yadav, Pandey, Bhatt, Kumar, & Kim, 2017). The high demand for solar cells related to fossil energy reduction has pushed some countries to be very active in research into solar cells' development. Singapore, South Korea, and Japan are very intensive in researching manufacturing new materials related explicitly to increasing solar cells' efficiency.

In the last decade, total energy consumption in Indonesia multiplied. Dependence on fossil energy, especially petroleum, in meeting domestic energy needs is still very high. On the other hand, efforts to develop and use renewable energy to reduce greenhouse gas emissions have challenging to proceed as planned. The use of energy tends to be very wasteful in various fields, especially industry, agriculture, households, and transportation. Besides the decline in fossil energy reserves such as petroleum, coal, and gas, discovering new energy reserves cannot be matched. The limited energy infrastructure available in Indonesia also limits people's access to energy. This condition makes Indonesia vulnerable to disruptions in the global energy market because most energy consumption, especially oil production such as Premium, Pertamax, and Avtur, is still met from imports. The development of biomass-based bioenergy is the best solution for meeting Indonesia's current and future energy needs. Bioethanol, biogas, and biodiesel are biomass-based bioenergy, which is the potential for future energy sources.

Indonesia can use renewable energy resources in hydro, geothermal, biomass, solar, wind, ocean, uranium, and biodiesel energy sources. (Azam, Khan, Bakhtyar, & Emirullah, 2015; Erahman, Purwanto, Sudibandriyo, & Hidayatno, 2016; Kurniawan, Sugiawan, & Managi, 2018; Liu, Zhang, & Bae, 2017; Purwanto, Sušnik, Suryadi, & de Fraiture, 2018; Sarrica, Richter, Thomas, Graham, & Mazzara, 2018) However, to date, only three types of renewable energy resources have been utilized by Indonesia, namely hydro, geothermal, and energy from biomass. Indonesia is still very dependent on non-renewable energy sources, namely oil, natural gas, and coal. Although Indonesia also has other non-renewable energy sources, namely coal, methane gas, and shale gas. Several countries have also developed new energy sources from nuclear, hydrogen, methane gas, liquefied coal, and confirmed coal. (Mirzoyan, Vassilian, Trchounian, & Trchounian, 2018; Ren, Zhao, Chen, Guo, & Cao, 2016; Sainati, Locatelli, & Smith, 2019; Sikder, Inekwe, & Bhattacharya, 2019) Nevertheless, Indonesia has not yet carried out development and research to keep abreast of global energy developments.

Another impact of development is the increase in energy needs derived from economic growth, population growth, industrial growth, office growth, hotels, and human welfare, and changes in daily human activities. (Bilgili, Koçak, Bulut, & Kuloğlu, 2017; Hidayatno, Destyanto, & Hulu, 2019; Vieira et al., 2019) Indonesia is in a condition of dependence on fossil energy sources, especially petroleum, in meeting domestic energy consumption, where most of the consumption is from imports. Other conditions include energy consumption that tends to be wasteful, a decline in fossil energy reserves, and the absence of new reserves. This condition has led to efforts to utilize renewable energy, which has not proceeded as planned until now. Besides, the limited available energy also limits people's access to renewable energy.

The utilization of renewable energy sources and non-renewable energy sources to produce energy, both directly and indirectly, such as conversion or transformation, must be managed appropriately not to cause adverse impacts on the environment. Energy management will prevent environmental pollution and environmental degradation and how many other negative impacts such as the meaning of acid rain, depletion of the ozone layer in the stratosphere, global warming due to the effects of greenhouse gases, and several other adverse effects.(Lee, 2017; Mishra, Roy, & Mohanty, 2019; Prabakar et al., 2018; Roy & Dias, 2017; Singh, Varanasi, Banerjee, & Das, 2019; Thi, Lin, & Kumar, 2016; Zabaniotou, 2018). In summary, a comparison of the various sources of renewable energy that can be applied in Indonesia is shown in Table 1.

The need for electrical energy in the industrial sector in Indonesia is increasing. The application of industrial technology 4.0 encourages industrial growth as well as the consumption of electrical energy. In addition, the high public interest in using electric vehicles is the driving force for increased consumption of electrical energy in the transportation industry sector. Data from the Ministry of Energy and Mineral Resources of the Republic of Indonesia in 2020 shows that 85.79% of electrical energy comes from non-renewable sources. Renewable energy production only reached 14.21%. Hydroelectric power (PLTA) contributed 5.84%, geothermal power plants (PLTPB) by 8.17%, and other renewable energies (Wind Power-PLTB, Solar Power-PLTS, Biomass Power Plants -PLTBm, Biogas power plant-PLTBg) by 0.20%. Indonesia's target in 2025 for the renewable energy mix of 23% (Direktur Jenderal EBTKE, 2020).

Indonesia has a potential biomass energy source and may become a source of energy in the future. However, biomass conversion into other forms of energy, such as biogas, bioethanol, and biodiesel, will hurt the environment. Indonesia has built many biogas production units (Bedi, Sparrow, & Tasciotti, 2017).

Biogas production can use pulp and paper waste, bagasse, grass and leaves, leftover food, wood, and fanfare. The hybrid, physical, chemical, and biological methods vary according to the type of media used. Most of the biogas production in Indonesia uses biological processes because of the low production costs is shown in Figure 1. Biogas from biomass can have several negative impacts, namely an increase in CO_2 emissions, odors, wastewater, and sludge that requires further processing (Hashemi, Sarker, Lamb, & Lien, 2021). Very few industries carry out advanced processing. If the waste is disposed of in the environment without treatment, it can cause increased greenhouse gas effects, water and air pollution, and soil contamination. It is necessary to analyze the environmental impact of converting biomass into biogas and developing an environmentally friendly conversion model.

Table 1. Comparison of different renewable energy sources in Indonesia

Source	Advantages	Ref.
Solar	Environmentally friendly	(Huang et al., 2018)
Hydropower	Environmentally friendly	(Tasri & Susilawati, 2014) (Tang et al., 2019)
Geothermal	Approximately 28.91 GW of 312 locations on different islands	(Pambudi, 2018)
Wind energy	The cheapest form of electricity generation with LCOE of 0.13 US$/kWh (±0.01 US$/kWh)	(Rogers, Ashtine, Koon Koon, & Atherley-Ikechi, 2019)
Biomass	Low investment	(Sgroi, Donia, & Alesi, 2018)
Biohydrogen	Source and prevent the organic wastewater contamination	(Chu, Hastuti, Dewi, Purwanto, & Priyanto, 2016)
Biogas	Potential source and conversion to electrical energy	(Harihastuti et al., 2021) (Steinhauser & Deublein, 2011)

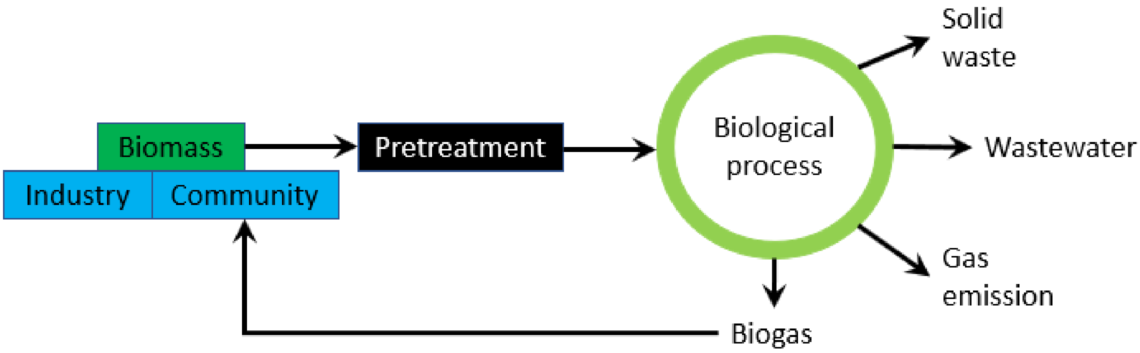

Figure 1. Conversion biomass into biogas production in Indonesia (Adapted from (Bharathiraja, Sudharsanaa, Bharghavi, Jayamuthunagai, & Praveenkumar, 2016; Guebitz, Bauer, Bochmann, Gronauer, & Weiss, 2015)

2. METHOD

This study was conducted systematically reviewed the available articles in ScienceDirect and Google Scholar up to 2021. The search terms we used are renewable energy and Biomass, and Biogas and treatment and sustainable energy. A manual search was also performed. The study selection based on biogas as a product resulted in biomass conversions. We selected literature based on the environmental impacts and their potential sustainable energy. Two proposed models developed scenarios based on the existing scenario and environmental scenario of converting biomass to biogas.

3. RESULT AND DISCUSSION

3.1. *Renewable Energy Based Biomass*

Indonesia's strategic position on the equator raises several advantages, such as sunlight throughout the year so that various plants thrive. This condition increases the potential of Indonesia's biological resources, several types of energy plants that can potentially produce energy in Indonesia (Hasan, Mahlia, & Nur, 2012). Including sugar cane, sugar palm, sunflower, candlenut Sunan, sago, corn, sesame, sweet potato, cassava, avocado seeds, palm oil, and algae (Direktur Jenderal EBTKE, 2015).

Currently, Indonesia has still used biomass as a source of food and industrial raw materials. If the biomass is converted into an energy source, the techno-economic value could not match conventional energy conversion's economic value, although biomass has a relatively high biodegradable carbon component compared to biomass waste (Harihastuti et al., 2021). So that biomass waste is still the leading source for conversion to biogas in Indonesia.

3.2. *Biomass Waste*

Based on data from the National Waste Management Information System (Sistem Informasi Pengelolaan Sampah Nasional-SIPSN) in 2020, Indonesia's waste generation is 36.54 million tons. In 2020, there was an additional 5.47 million tons. Managed waste reaches 53.61%, and there is a potential for unmanaged waste of 16.95 million tons. This type of biomass waste is the most significant contributor to waste based on waste composition, namely 30.80% food scraps, 12% wood/twigs/leaves, 11.20% is paper/cardboard. The biomass waste sources are 32.40% households, 21.70% traditional markets, and 13.90% commercial centers (SIPSN, 2021).

The availability of biological resources in Indonesia encourages an increase in the agro-industry rate. However, on the other hand, the agro-industry operational processes also produce undesirable side effects, namely solid waste, liquid waste, and emissions. Some potential biomass waste to be converted into biogas are waste from the sugar cane industry and waste from the cassava flour industry (Rame, 2018).

Some other industries also produce biomass waste that is the potential to be converted into biogas. Namely the leather tanning industry, the palm oil industry, the rubber industry, tapioca, the milk processing industry. Including the soft drink industry, the vegetable oil product industry, the fruit and or vegetable processing industry. Also, fishery product processing industry, seaweed product processing industry, coconut processing industry, meat processing industry, soybean processing industry, cattle and pig farming industry, and wet process cooking oil industry (Direktur Jenderal EBTKE, 2015). There is also the potential for biomass waste originating from health service facilities, slaughterhouses, and domestic waste such as residential areas, office areas, commercial areas, apartments, restaurants, and dormitories (Zuli Pratiwi, Hadiyanto, Purwanto, & Nur Fadlilah, 2020).

3.3. *Bioenergy from Biomass*

Indonesia has enormous potential for developing bioenergy from biomass due to the potential of extensive land areas, the large number and types of plants available, and the abundant amount of biomass waste. However, current research in the world focuses on the field of solar cell development. However, bioenergy from biomass is still the majority of research focus, namely developing the biomass to hydrogen convention, especially in Taiwan and South Korea. (Eker & Erkul, 2018; Maaroff et al., 2019; Preethi, Usman, Rajesh Banu, Gunasekaran, & Kumar, 2019; Rambabu et al., 2019; Sinharoy & Pakshirajan, 2020). Development of biogas energy production not chosen to be developed by developed countries because the potential of methane gas emissions is more damaging to the ozone layer as a protector of the Earth than the destructive power of carbon dioxide gas (Dyominov & Zadorozhny, 2005; Sarkodie & Strezov, 2019; Sharifzadeh, Hien, & Shah, 2019).

World researchers are competing to research biohydrogen, which is believed to be the energy of the future. Nanotechnology supports the development of hydrogen energy by the rapid development that will produce enormous energy efficiency. Using nanotechnology, the energy produced from a hydrogen source in the form of a pen can move a motorized vehicle such as a car because even though the outer dimensions look small, the surface area inside is very high. One gram of nanomaterial will have a contact surface area similar to that of a soccer field. Nanomaterials support world energy development (Sinharoy and Pakshirajan, 2020; Srivastava et al., 2018, 2019).

Indonesia has the potential to develop nanomaterial basis biohydrogen energy if it is seriously developing. Hydrogen energy converted from biomass or bio solar in the future. Although hydrogen energy efficiency is lower when compared with nuclear energy efficiency. On the other hand, nuclear energy production has a considerable potential disaster risk.

Besides that, Indonesia's advantage is that it has an extensive sea area, an extensive land area that produces a very high potential for renewable energy sources. Indonesia's biomass waste is also very high as an alternative source of bio-energy, including in the form of residential or industrial waste. Biomass convert to biofuels. The utilization of biomass can be directly or indirectly. Biomass can be directly burned as a source of boiler energy to drive generators. Indirectly biomass can be converted into several energy sources such as biogas, bioethanol, biodiesel, biohydrogen, or fuel cells. In the short term, biohydrogen or fuel cell has not been used as a bioenergy source because investment costs are still relatively expensive.

Based on the Ministry of Energy and Mineral Resources data in 2109, biogas' supply is 166 thousand Barrel Oil Equivalent (BOE). Meanwhile, the supply of biofuel is 45.92 million BOE, and biomass is 61.39 million BOE (Adi et al., 2020), according to Figure 2. The National Waste Management Information System data provides information that there is a potential for unmanaged waste of 16.95 million tons (SIPSN, 2021). About 10 million tonnes is biomass can be converted into biogas.

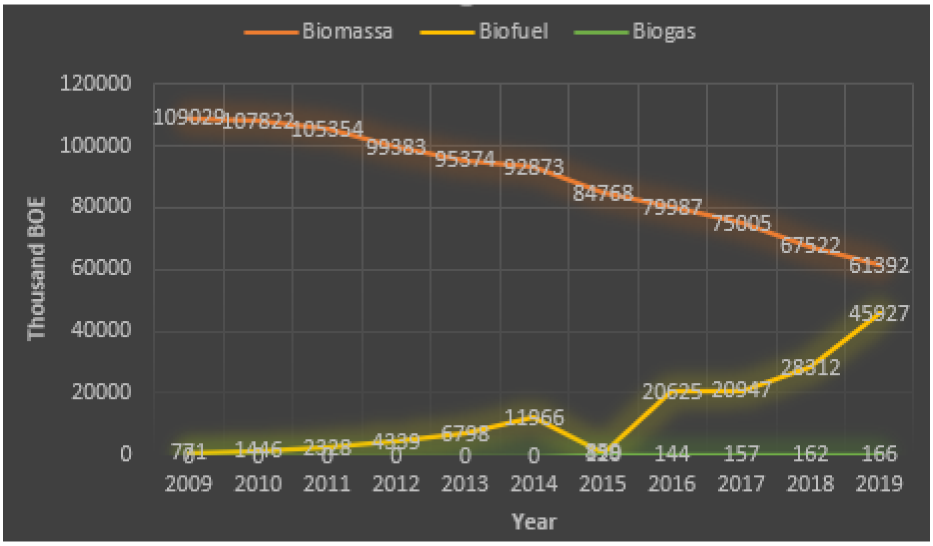

Figure 2. Bioenergy supply in Indonesia (Adi et al., 2020)

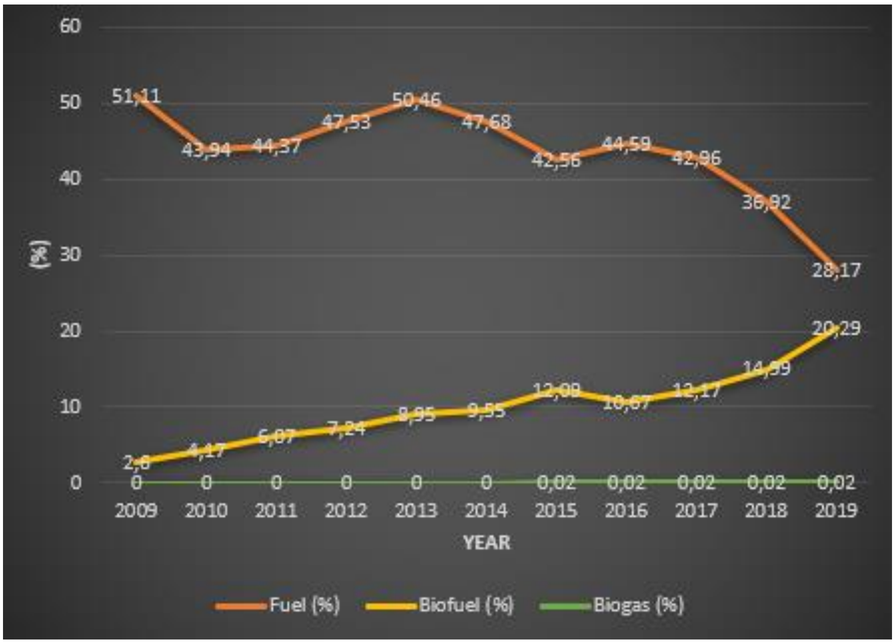

Figure 3. Share of bioenergy consumption in Indonesia (Adi et al., 2020)

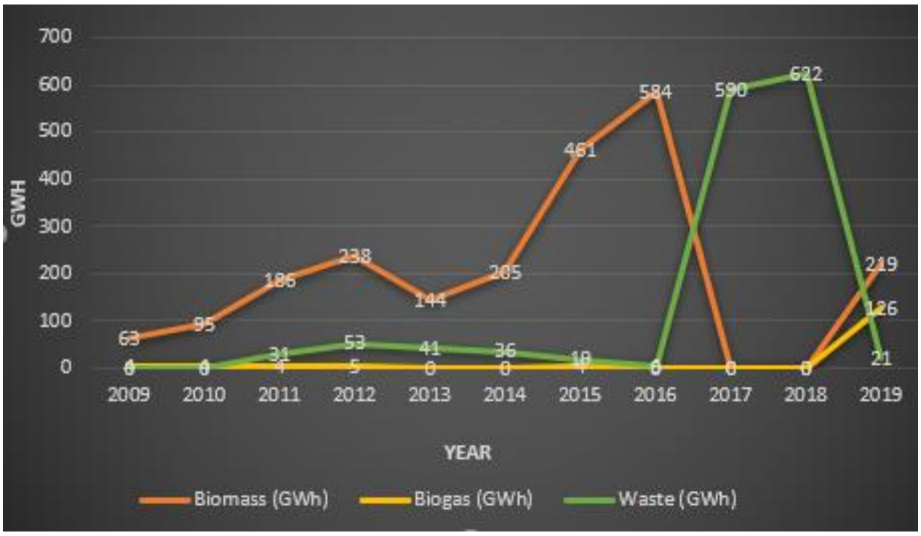

Figure 4. Bioenergy power plant production in Indonesia (Adi et al., 2020)

Although there is an increase in biofuel consumption by 20.29% in 2019, the actual percentage of energy consumption from biogas is only about 0.02% of Indonesia's total energy consumption, as shown in Figure 3. Bioenergy used in power plant production in Indonesia has decreased gradually, as shown in Figure 4. Although in 2019, the power plant production of biogas increased to 126 GigaWatt Hour (GWh) and biomass to 219 Gwh. On the other hand, power plant production from biomass has decreased drastically from 622 GWh to 21 GWh. In total, the contribution of bioenergy is still below 1%, with the 2019 PLN Power Plant Production of 278,942 GWh (Adi et al., 2020).

3.4. Biogas

Biogas is a product of the fermentation of biomass or organic material waste. A few years ago, there was a boom in converting coal into liquid fuels (Xiang, Yang, & Qian,

2016) and natural gas into liquid fuels, namely in various countries such as South Africa, Thailand, and Malaysia, and several other countries. Indonesia has developed biogas to liquid fuel, but only to the pilot plant stage and not yet to the industrial-scale production stage. Finally, Indonesia returned to the use of coal directly, which resulted in environmental pollution.

The Indonesian government must fully support the development of renewable energy. Although it cannot be denied, at this time, Indonesia is still very dependent on fossil energy sources, namely oil, coal, and natural gas. Indonesia is still very far behind in technology and the development of biogas fuels. On the other hand, methane gas is hazardous for the environment if not managed correctly. Indonesia still has not shown seriousness in developing biogas potential related to methane gas storage or methane gas production. Therefore, purification research and research on the storage and distribution of methane gas are the most urgent thing to support the development of energy directed towards reducing greenhouse gas emissions. The use of biomass for bioenergy is the right choice for Indonesia. Because when choosing solar cell development, Indonesia is still far behind related to solar cell material technology. Indonesia will be challenging to catch up with the rapid development of solar cell technology in the world today. South Korea, Taiwan, Europe, and America are currently very focused on developing semiconductor materials to support solar cells' efficiency.

Some countries have implemented biogas energy sources as transportation modes, such as Thailand, Malaysia, and several other countries. In the development of biogas, it is crucial to study the biogas composition before scale-up for industrial. Because each biogas raw material will produce different biogas characteristics, for example, tofu industry waste or livestock industry waste, or agro-industry waste will produce different biogas compositions. Different. For purification efficiency, comprehensive testing is needed to determine the composition of the gas and its fluctuations in a sufficient period. Then continue setting the purification conditions, the process of storage, and distribution. The latest development related to biogas is that converting methane to hydrogen has been successfully carried out. However, it has not been implemented on an industrial scale because the conversion process requires a relatively expensive investment and operational costs, making it challenging to implement in Indonesia. Also, the development of biogas conversion into biohydrogen is often constrained by hydrogen analysis, which requires unique accessories that are relatively expensive. Several research articles show the efficiency of various types of substrates to produce biogas.

3.5. Environmental impacts from conversion biomass to biogas

The characteristics of biomass wastes fluctuate with different organic and inorganic contamination levels at different input time ranges. This condition will indirectly change the input process parameters so that sometimes the biogas biodigester unit will experience interference. The occurrence of this disturbance can hamper biodigester operations, which is to inhibit the fermentation process. This condition has the potential to dispose of water in biodigesters that have not been appropriately treated to environmental bodies. The impact is in the form of water or soil pollution.

The current biogas production system from biomass still allows toxic gas release into the biodigester unit environment. At certain concentration levels, these gases will pose a risk of shortness of breath and poisoning. This condition will also occur if there is a gas leak. The danger of poisoning and shortness of breath is mainly due to the content of hydrogen sulfide in biogas, which is toxic even in low concentrations due to the potential for inhalation will produce these symptoms to cause fatal poisoning. (Barbusinski, Kalemba, Kasperczyk, Urbaniec, & Kozik, 2017; Indrawan, Thapa, Wijaya, Ridwan, & Park, 2018)

The combination of atmospheric air with specific concentrations of biogas under certain conditions can form explosive gases. (Bharathiraja, Sudharsanaa, Bharghavi, Jayamuthunagai, & Praveenkumar, 2016; Guebitz, Bauer, Bochmann, Gronauer, & Weiss, 2015; Monlau, Kaparaju, Trably, Steyer, & Carrere, 2015; Rosato, 2017) In addition to the potential for explosions due to the formation of explosive gas mixtures, there is a risk of fires surrounding biogas tanks and biodigesters. In areas that are far from the biodigester unit, although there is minimal risk of an explosion due to deficient biogas levels, there is the possibility of a fire due to sparks arising, sources of ignition, electrical short circuits, or natural lightning.

In addition to producing hydrogen sulfide gas, which can cause shortness of breath and poisoning, converting biomass into biogas also produces methane gas and carbon dioxide as a greenhouse gas emission that causes global warming. (Mayer et al., 2019; Vieira et al., 2019; Winter, Agarwal, Hrdlicka, & Varjani, 2019; Wu et al., 2017; Zhang, Bauer, Mutel, & Volkart, 2017) Methanogenic bacteria produced methane as a metabolic byproduct in anaerobic conditions, while the methane formation phase formed carbon dioxide during the hydrolysis phase.

The conversion of biomass into biogas also creates new problems in wastewater and sludge (Amirta, Herawati, Suwinarti, & Watanabe, 2016). The fermentation residue composition in the form of wastewater has different characteristics depending on the substrate used. The fermentation residue still contains some organic acids, ammonia, and several other intermediate compounds (Rahayu, Budiyono, & Purwanto, 2018). Fermented residual water is directly discharged to environmental bodies at the current conversion process without further processing (Harihastuti et al., 2021). Further processing is needed, but most of the biogas units in Indonesia have not yet carried out the processing. Biogas units that dispose of the fermented residual water can cause environmental pollution and environmental degradation.

3.6. *Renewable energy regulation in Indonesia*

The current position of the renewable energy mix in Indonesia requires a regulatory approach and community support to meet the energy mix target of 25% by 2025 (Suharyati, Pambudi, Wibowo, & Pratiwi, 2019). Increasing renewable energy consumption will reduce carbon emissions and reduce greenhouse gas emissions to reduce the greenhouse effect.

Several regulations have been made in developing new renewable energy and energy conservation, among others, regulations concerning the national energy policy, presidential regulation, national energy general plan, and utilization of renewable energy sources for electricity supply (Direktur Jenderal EBTKE, 2020). However, with these regulations, renewable energy development in Indonesia is still far from the renewable energy mix target.

Additional regulations are needed to support infrastructure development in the production and distribution of renewable energy in Indonesia based on the principle of equitable energy so that the energy independence of the Indonesian nation can be realized. Therefore, it is necessary to add government regulations to attract investors and the public to develop renewable energy. In addition, regulations related to community support in managing biomass waste into renewable energy, especially biogas, may accelerate the renewable energy mix.

The world's most formidable challenge in developing renewable energy is the significant investment required to produce and distribute this type of renewable energy. The Indonesian government needs to commit and realize developing renewable and sustainable energy as an alternative to sustainable and environmentally energy management. Currently, the level of the renewable energy mix is still around 14.21%. By increasing the conversion of biogas from biomass in the Biogas power plant, the achievement of the renewable energy mix is expected to reach 23%.

3.7. *Biogas Conversion Existing Scenario in Indonesia*

Converting biomass into biogas is an anaerobic fermentation process that converts biomass into biogas and several other byproducts. Biogas fermented from biomass is a mixture of methane gas (up to 70%), carbon dioxide gas (up to 50%), hydrogen sulfide gas, and other gases such as carbon monoxide and hydrogen gas (Harihastuti et al., 2021). The conversion process generally uses a doom reactor and a little use of a stirred tank reactor (Direktur Jenderal EBTKE, 2015).

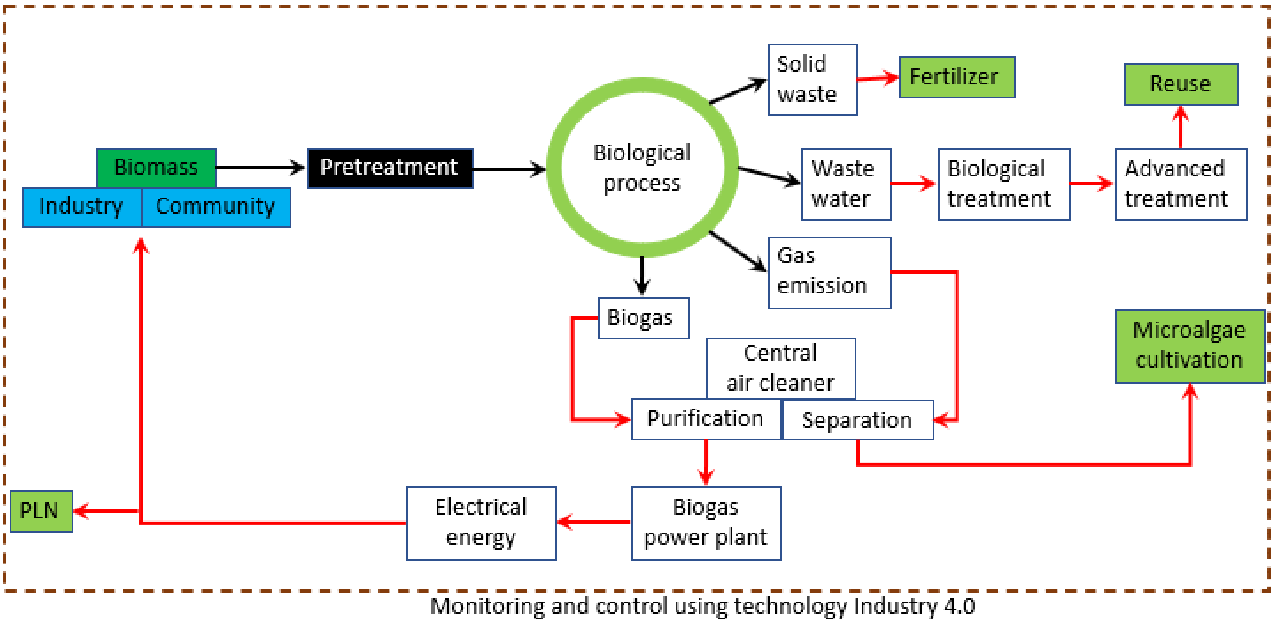

Figure 5. Proposed scenario new eco-friendly conversion biomass into biogas

The conversion of biomass into biogas generally consists of 5 stage components and the first is the equalization bath, the second is a mixing bath, the third is a hydrolysis tank, the fourth is a methane gas formation tank, and the last is a runoff bath. This conversion model makes it challenging to manage the optimization of conversion variables such as the rate of waste loading, fermentation time, the level of degradation, the quality of gas production, and the homogenization of the substrate (Direktur Jenderal EBTKE, 2015).

3.8. Proposed new eco-friendly Scenario Biogas Conversion in Indonesia

Minimizing negative impacts on the environment is a significant aspect of preparing the biomass to biogas conversion model. This model aims to protect the environment by minimizing the negative impacts of converting biomass into biogas to the surrounding environment to prevent contamination into the air environment and the water and soil environment.

The model proposed in this review is shown in Figure 5, namely, the stage to deactivate germs and pathogens present in the water output of the conversion process. Air pollution's prevention stage protects the environment from the harmful effects of odor, pollutants, and dust emissions. The prevention phase of water pollution, to prevent the spread of contaminants in surface water or groundwater. The water treatment stage continues because the output water still contains high organic contamination. Phase Conversion on-site biogas to electricity /thermal/liquid fuel/biohydrogen prevents emissions from methane leakage.

This review finally recommends a proposed model for converting biomass to biogas shown in Figure 5. The biogas conversion process is monitored and controlled in real-time using sensors. After further processing in the central air cleaner, the output of CO_2 will be used as nutrients in microalgae cultivation. Biogas conversion wastewater can be treated using catalytic processes such as catalytic or electrocatalytic ozonation. Furthermore, treated water is used in microalgae cultivation or other processes. Convert biogas output into several products, namely biohydrogen, liquid fuel, thermal, or electricity.

4. CONCLUSION

Indonesia has an extensive sea area, an extensive land area that produces a very high potential for renewable energy sources. To develop and apply bioenergy, Indonesia still needs a transfer of technology developed rapidly from abroad. Indonesia needs to develop biomass-based bioenergy, such as biogas, to meet Indonesia's current and future energy needs. Environmental protection by minimizing biomass conversion to biogas in the environment is done by preventing contamination into the air environment, water, and soil environment. The pollution prevention model is carried out through wastewater treatment plants, Central air cleaner, utilization of CO_2 gas residues for microalgae cultivation, control and monitoring of sensor-based conversion and emission processes, and on-site conversion of biogas to electricity.

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Air Pollution Dispersion Modelling using GRAL in Area Near Coal-Steam Power Plant at Central Java

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ABSTRACT

Sulfur dioxide and Nitrogen dioxide were significant emissions emitted from coal-steam power plants that may cause health problems for humans and damage the environment. Studying the SO_2 and NO_2 gradients in Indonesian residential communities is critical for evaluating resident's SO_2 and NO_2 exposure. The method developed to assist analysis of spatial SO_2 and NO_2 gradients on a community scale combines a mesoscale Lagrangian dispersion model with field observations around coal-steam power plants using GRAL. The objectives of this study focused on GRAL dispersion of SO_2 and NO_2 in an Indonesian residential community near the coal-steam power plant, with a 6 km x 8 km resolution. Analysis of this model indicates a correlation between simulation and observation, with SO_2 coefficient correlation (R) within 0.5 – 0.82 and NO_2 coefficient correlation (R) within 0.30 – 0.59. Model performances analyze by NMSE and FB. The SO_2 model is comparable to observation data since it has a better average NMSE and FB than the NO_2 model. Due to data limitation of observation collected by grab sampling instead of continuous ambient measurement system affect different respond time compared with hourly data from the model.

1. INTRODUCTION

Sulfur Oxides, mainly Sulfur Dioxide (SO_2), emitted by coal-steam power plants may cause health impacts for humans with increased cardiovascular disease risk in long term exposures (Fatkhurrahman et al., 2020; Lin et al., 2018). Short-term exposures can make breathing difficult for people with asthma (Galán, Tobías, Banegas, & Aránguez, 2003). It also degrades the climate by producing acid rain in the environment (Jain, Cui, & Domen, 2016). The coal-steam power plant also releases massive Nitrogen Oxide as Nitrogen Dioxide (NO_2) into the atmosphere; the photochemical reaction may produce atmospheric ozone, which is harmful for lung function and other respiratory problems (Zhang, Wei, & Fang, 2019). In Indonesia, twenty coal-steam power plants utilize electricity generation, primarily built in Java, close together to dense housing.

In comparison, more than ten coal-steam power plants are planned for construction in future years (Quina, Fadhillah, Jiaqiao, & Zhao, 2017). Mainly, coal-steam power plants conduct emission tests using external testing laboratories; they could also install a continuous emission monitoring system (Simbolon et al., 2021). Therefore, studying the SO_2 and NO_2 gradients in Indonesian residential communities is critical for evaluating resident's SO_2 and NO_2 exposure. In Indonesia, there are several problems to conduct a comprehensive analysis of SO_2 and NO_2 exposure in the environment. The complexity of the emissions and building arrangements spreads in large areas.

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The lack of meteorological data available for the public makes the air pollution study take a difficult step.

Indonesian coal-steam power plants commonly built near the coast may cause air pollution dispersion through the coastal climate into the residents near the beach. It will be affected dominantly by sea windblown into the land, dispersing SO_2 and NO_2 from coal-steam power plants chimney for the entire year. As two significant seasons in Indonesia, the rainy and dry seasons, more pollution in the dry season will be possible than in the rainy season. The method was developed to assist in analyzing spatial SO_2 and NO_2 gradients on a community scale that combines a mesoscale Lagrangian dispersion model with field observations around coal-steam power plants. Popular air quality models like WRF-Chem and AERMOD can be utilized on regional to urban scales (Grell et al., 2005; Mijling, 2020). AERMOD is a paid software with more than USD 1000 cost to buy, while WRF-Chem is free software but needs advanced programming language knowledge. This study employs the Graz Lagrangian (GRAL) model for SO_2 and NO_2 simulation (Oettl, 2014; Romanov, 2020). GRAL can be applied for gaseous and particulates simulation and prediction for flat and complex terrain, mainly based on daily, monthly, and annual means (Anfossi et al., 2006). This GRAL system is entirely free, and study using GRAL seems to be applied both for urban scale, areas near industries, and even some tight tunnel openings (Ling, Candice Lung, & Uhrner, 2020). GRAL system is commonly prevalent in Europe, based on published validation studies by annual means (Kurz et al., 2014). There is also a GRAL limitation on chemical reaction modeling in the atmosphere that should be noticed when air dispersion simulation conduct in the area with chemical reaction happened. However, GRAL has not yet been validated in an Asian residential community, especially for Indonesian typical residential and population arrangement. In this study, SO_2 and NO_2 monitoring are compared with simulations at the residential level side by side with grab sampling of ambient measurement and evaluated as an hourly means. This study's novelty is Lagrangian mesoscale modeling to study SO_2 and NO_2 dispersion in typical Indonesian residential communities, which is free software, easy to operate with the large capacity of modeling computation with friendly GUI run in a familiar operating system like Windows. The main objectives were; to validate GRAL comprehensively on SO_2 and NO_2 dispersion in an Indonesian residential community near the coal-steam power plant, with a 6 km x 8 km resolution, and evaluate three-dimensional dispersion of coal-steam power plant SO_2 and NO_2 in areas near to it, with 48 square kilometres domain.

2. METHOD

2.1 Site description and observations

The community in this study was a typical Indonesian residential community near the coal-steam power plant in southern Java. Based on topographical characteristics, the residential community's mean building height was 3 meters. This coal-steam power plant has two-unit processes, with has a stack height of 240 meters and 220 meters, with 6.8-meters and 7.8-meters inside diameters. Based on this data, there is a possibility to simulate monthly SO_2 and NO_2 as dominant emissions from the coal-steam power plant. Simulation using GRAL was analyzed in quarterly periods as the ambient measurement was conducted every three months. Each parameter will be analyzed respectively. NO_2 concentration will convert from NO_x as empirical equation (1) (Middleton, Luhana, Sokhi, & Great Britain. Environment Agency., 2007), where NO_2 concentration would be equal as 1.58 times with NO_x order to 0.6887 as constant.

$$NO_2 = 1{,}58 \times NO_x{}^{0.6887} \quad (1)$$

SO_2 and NO_2 in ambient air measured in eleven points, within hundreds of meters to several kilometers from the coal-steam power plant, SO_2 measured by pararosaniline method on an hourly basis, while NO_2 measured by Griesz

Saltzman method also on one hourly. Intercomparison analysis for each receptor was evaluated using the statistical method.

2.2 *Modeling approach*

This study's GRAL model (v20.09) simulates the dispersion of multi-source gases and particulates using synoptic meteorological data. However, based on the typical topography of southern Java, where this coal-steam power plant is located, any obstacles were assumed to be ignored since there was typically flat terrain around the model domain region. Schematic for GRAL model as seen in figure 1 below.

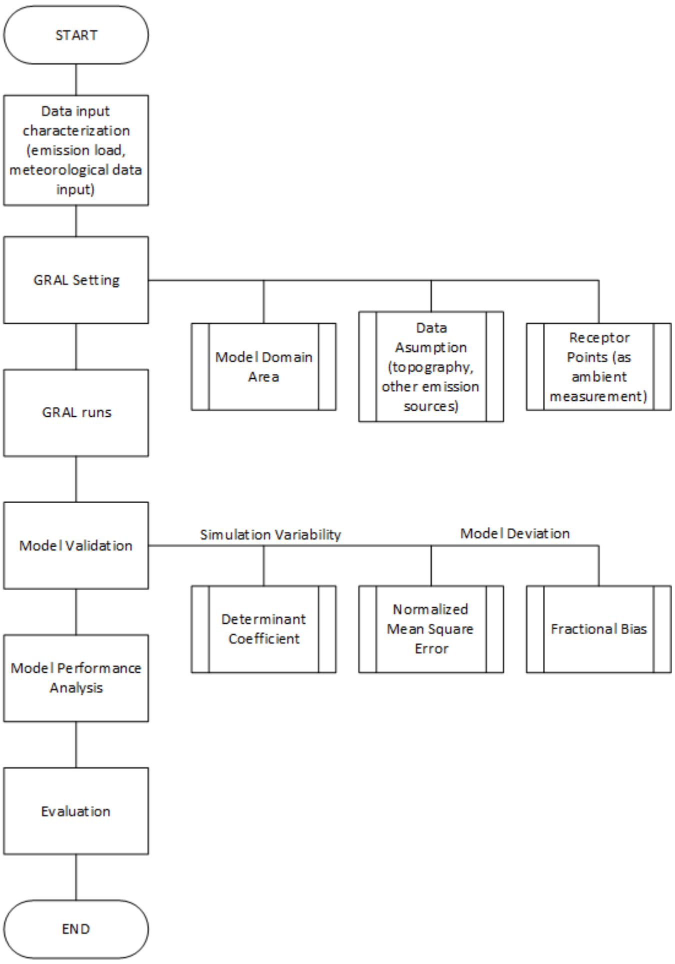


Figure 1. Schematic Run of GRAL Model

Most Gaussian dispersion models can be used for flat terrain simulation, such as CALINE 4 (Dhyani, Singh, Sharma, & Gulia, 2013), AERMOD, ADMS (Carruthers et al., 2011), and OSPM (Hu & Zhong, 2010). GRAL system can simulate dispersion for both flat terrain and complex terrain (Oettl, 2015). GRAL was efficient to its CPU time and minimum disk space computing requirements and can be used across microscales to mesoscales (Berchet et al., 2017). Meteorological wind data was collected using Copernicus ERA 5 Climate Reanalysis (Oses et al., 2020). Data was collected for the whole year in 2018 within hourly intervals, both for wind speed and wind direction meteorological data input. Data was collected through the model domain for 6 km x 8 km. As this research focused on the housing height from the ground, the vertical height was set to a minimum of 3 meters.

2.3 *Model limitation, validation, and evaluation*

The simulation result is initially outputted as the SO_2 and NO_2 concentration field from each emission source. At the receptor point, the total SO_2 and NO_2 concentration (C_{total}) was calculated using this equation (2);

$$C_{total} = C_{blank} + C_1 + C_2 \qquad (2)$$

C_{blank} as background concentration for SO_2 is 13.5 µg/Nm^3 based on (Rogers et al., 1999) and NO_2 are 14.8 µg/Nm^3 based on (Jarvis, Adamkiewicz, Heroux, Rapp, & Kelly, 2010) both are atmospheric concentration trend similar in large Indonesia cities (Susanto, 2005). C_1 and C_2 are the specific SO_2 and NO_2 increments related to each SO_2 and NO_x emission source. Here C_1 and C_2 were SO_2 and NO_x emissions from each coal-steam power plant stack chimney. Normalized mean square error (NMSE) and fractional bias (FB) were used to determine the optimum parameters and assess the model performance (Ling et al., 2020). This assessment can be calculated using equations (2) and (3).

$$NMSE = \frac{(C_{obs}-C_s)}{C_{obs}\times C_s}; \text{(ideal value 0, accepted value} \leq 4) \qquad (2)$$

$$FB = \frac{C_{obs}-C_s}{0{,}5\times(C_{obs}+C_s)}; \text{(ideal value 0, accepted value -0,3} \leq \text{FB} \leq \text{0,3)} \qquad (3)$$

C_{obs} are observed SO_2, and NO_2 concentration and C_s are simulated SO_2 and NO_2 concentration as hourly means, respectively.

3. RESULT AND DISCUSSION

3.1 Characteristics of the Area and Emission

Studying the dispersion of SO2 and NO2 near the coal-steam power plant in southern Java can evaluate over the near region around the coal-steam power plant. This coal-steam power plant is located in coastal south Java, verge with Hindian ocean in the south. Around the coal-steam power plant, there is another coal-steam power plant 8 km to the east. Emission source data for this coal-steam power plant does not include in this study. There are two major emission sources at the western side of the coal-steam power plant: cement industries and oil and gas refinery plants within the 8 km range.

This coal-steam power plant has two chimneys; chimneys 1&2 are one chimney from two separate processes, and chimney 3 emits dominant SO_2 and NOx to the atmosphere. Each quarter, an external laboratory conducts emission monitoring and emission load, as seen in table 1. Ministry of Environment Regulation No. 21 the year 2008 stated there is no emission load limit while emission rate should follow that regulation strictly.

Figure 2. Geographical Characteristics Around Coal-steam Power Plant

Table 1. Emission load from coal-steam power plant

No	*Parameter*	*Chimney 1&2*				*Chimney 3*				
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Value
1	SO2	2941	605.4	201.8	634.8	2536.8	545.5	28.2	209.6	kg/h
2	NOx	943.3	2224	1964.4	864.3	428	1865.7	455.1	688.4	kg/h
3	Q	1175	1509.8	1175.7	1183.3	1199.8	1867.1	1216.1	940.8	m^3/s

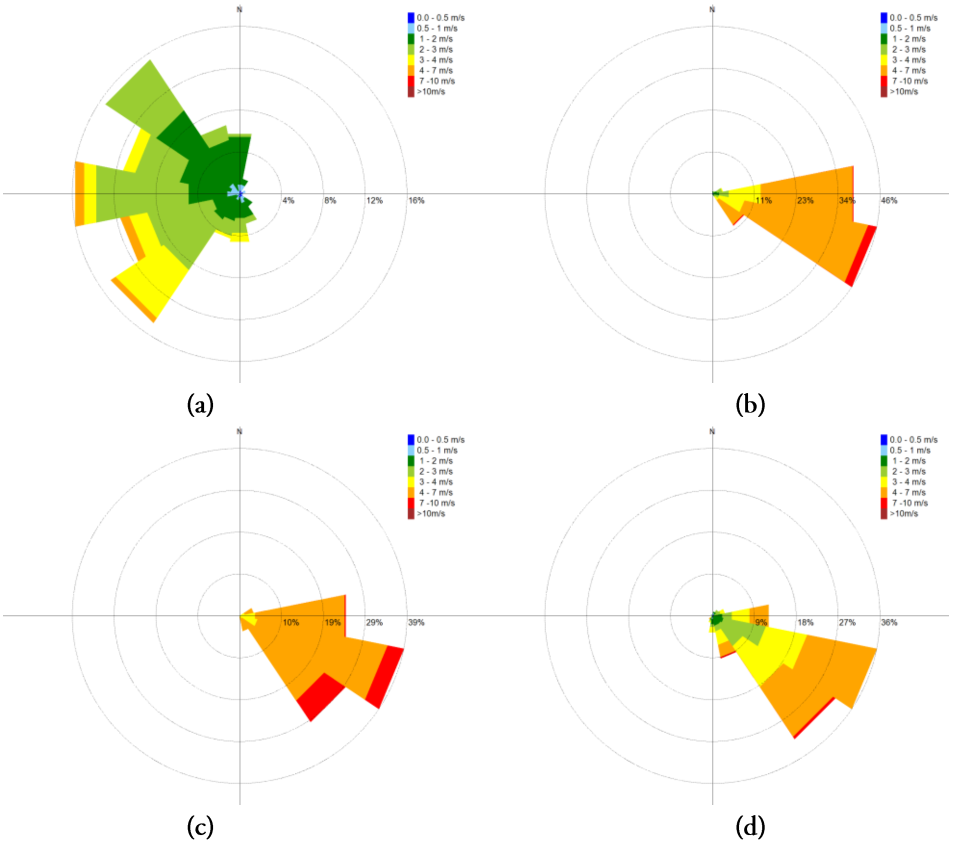


Figure 3. Spatial wind direction dominant around coal-steam power plant ; (a) 1st quarter, (b) 2nd quarter, (c) 3rd quarter, (d) 4th quarter

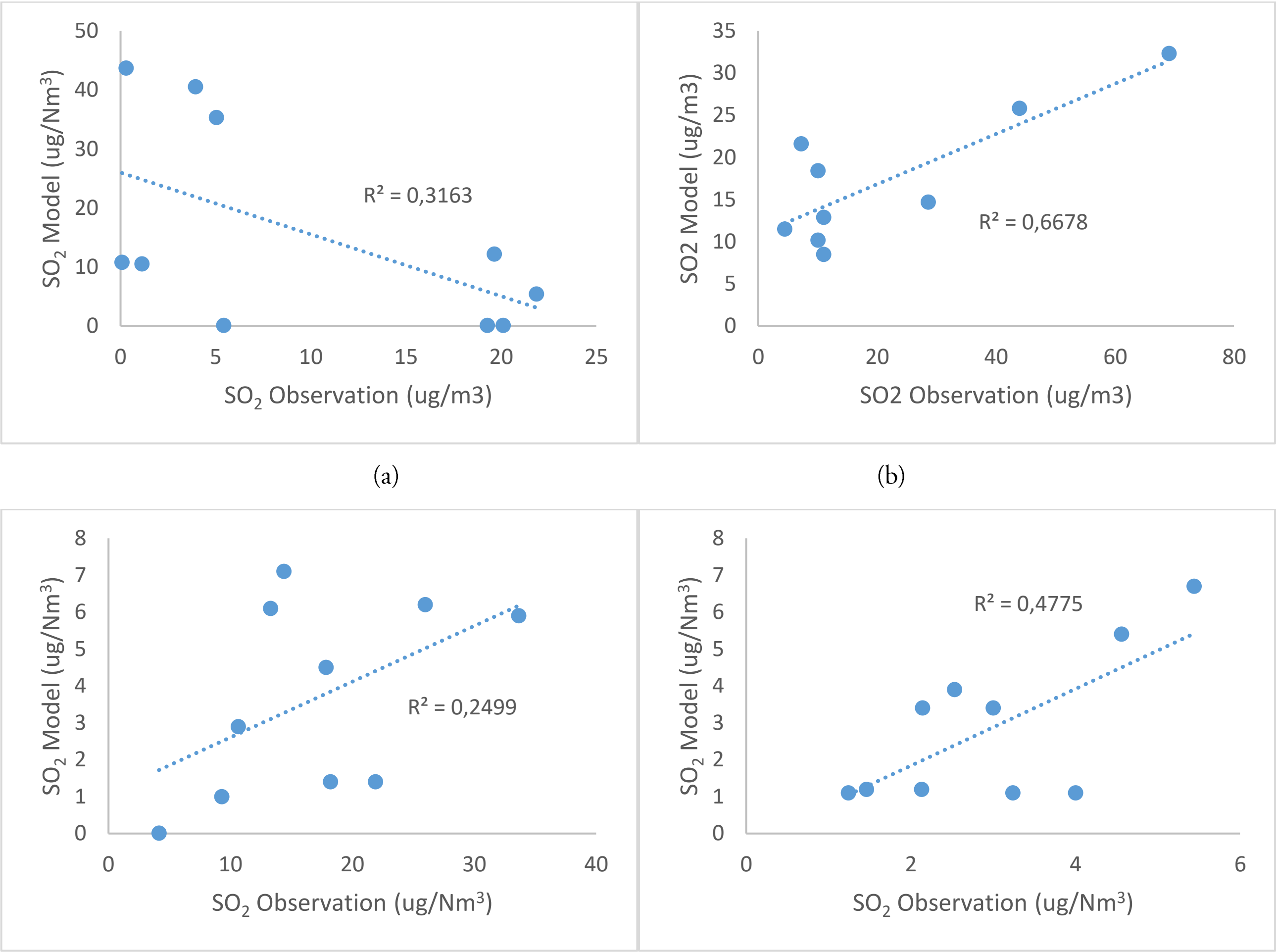
Around the coal-steam power plant, ten receptor points are measured manually for SO_2 and NO_2 quarterly based on the AMDAL document, similar to emission data from the coal-steam power plant.

There were twenty-one receptors for ambient measurement around it, but only ten-point measures of SO_2 and NO_2, in figure 2, are signed by A4, A6, A8, A10, A11, A12, A15 A16, A17, and A18. Evaluating this potential dispersion pollutant possibility from the coal-steam power plant to the receptor point needs meteorological data in a quarterly period. Meteorological data from Copernicus ERA 5, wind speed, and wind direction data were collected hourly for 2018 data. Both wind speed and wind direction data around coal-steam power plant as seen in figure 3.

Annual average of wind direction based on figure 3 wind rose originally come from South-East. The pollutant dispersion tends to disperse to the land at the Westside to the Northside of the coal-steam power plant. By quarterly analysis, only 1st quarter tends dispersion will happen from the West side of the coal-steam power plant to the Eastside. While wind speed distribution in figure 3 indicates an average annual wind speed as high as 3 – 6 meters per second. Wind speed indicates how pollutants will be diluted over the dispersion period (Kim, Lee, Woo, & Bae, 2015). The concentration contour of SO_2 and NO_2 for each quarter can be seen in Figure S1-S8.

3.2 *Intercomparison Model to Observation*

SO_2 and NO_2 concentration from GRAL simulation for each receptor point was analyzed by intercomparison using ambient measurement in ten receptor points. This ambient data was collected by grab sampling method using the pararosaniline method for SO_2, and Griesz Saltzmann method for NO_2 the data compared as seen in Figure 4 and figure 5.



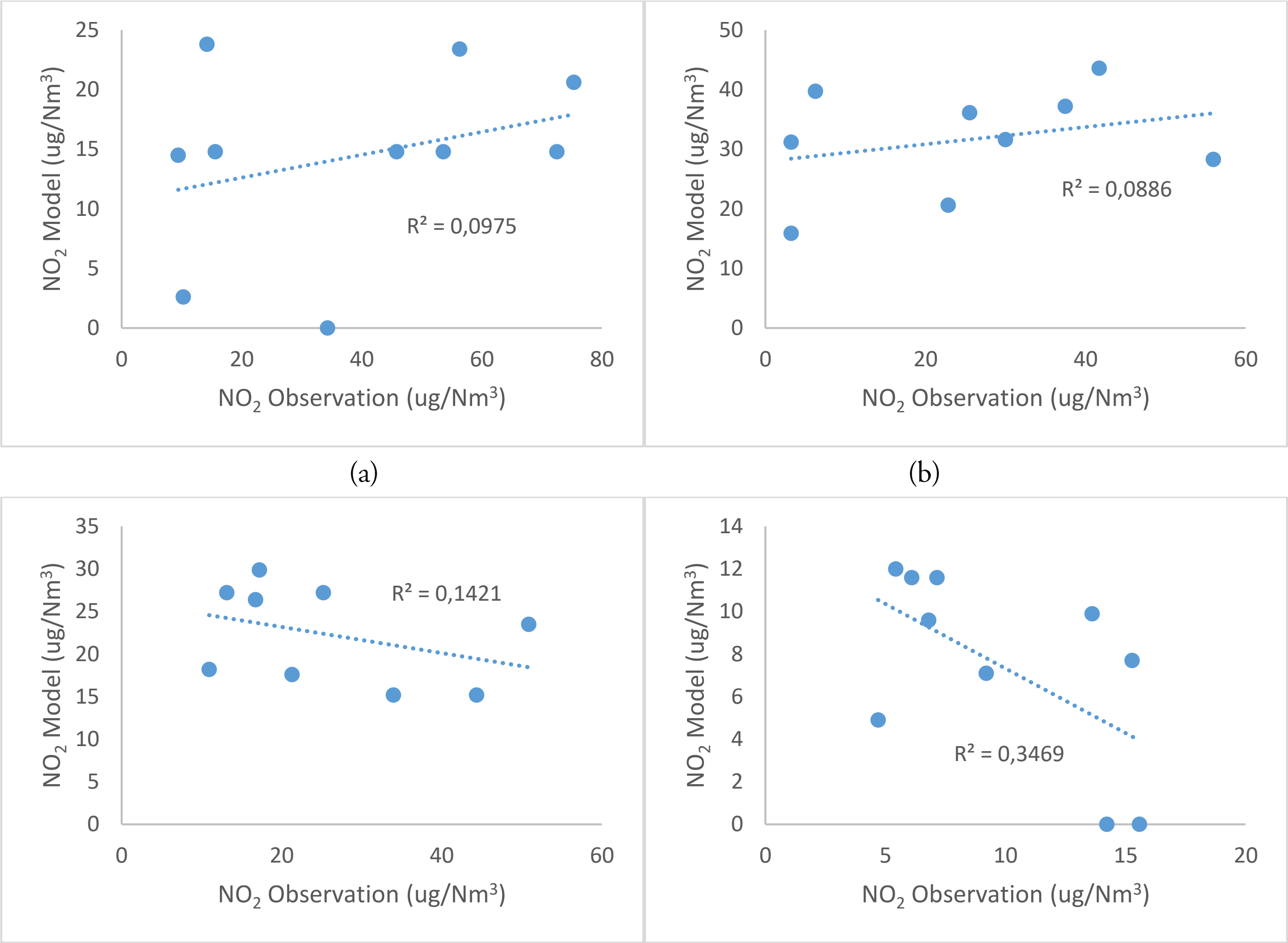
(a) (b)

(c) (d)

Figure 4. Scatter plot showing the relationship between SO_2 observation and model; (a) 1st quarter, (b) 2nd quarter, (c) 3rd quarter, (d) 4th quarter

Observation data and modeled data relationships are shown by coefficient correlation (R). Based on simulation and observation data, there is a coefficient correlation within the range of 0.5 – 0.82, which is good enough for modeled-based air pollution dispersion since it compared grab sampling and hourly modeled data. At Q1, based on the wind rose in figure 3, dominant dispersion happened from the west to the east that caused no dispersion of the pollutant from the coal-steam power plant to the receptor in the west side (A12, A10, A18, A16, A15, A6, A11, and A4). A receptor (A8) is located far to the north side to get minimum pollutant dispersion from the coal-steam power plant. This concentration is relatively equal to ambient measurement, shown below the detection limit of the pararosaniline method. In Q3 and Q4, wind direction dominantly came from the south-east and east sides; this result underestimates simulation results compared to observation data.

NO_2 variability in figure 6 is shown as coefficient correlation. It has a range between 0.30 – 0.59. Q3 and Q4 shown the best linear correlation between simulation and observation data. These phenomena could happen because the domestic combustion process and transportation can produce NO_2. At receptor points A6, A6, A8, and 18, where measurement site near the public street, NO_2 observation data shown higher than simulation data. Deviation of the simulation as model performance analysis by NMSE and FB (Chang and Hanna, 2004), NMSE, and FB value for SO_2 and NO_2 are seen in table 2 and table 3.



(a) (b)

(c) (d)

Figure 6. Scatter plot showing the relationship between NO_2 observation and model; (a) 1st quarter, (b) 2nd quarter, (c) 3rd quarter, (d) 4th quarter

Table 2. NMSE and FB for SO_2 for each location and quarter

NO	*Location*	*Q1*		*Q2*		*Q3*		*Q4*	
		NMSE	FB	NMSE	FB	NMSE	FB	NMSE	FB
1	A4	0.139	1.208	-0.002	-0.020	0.669	1.760	0.364	0.559
2	A6	9.950	1.980	0.027	0.256	0.659	1.714	0.600	0.986
3	A8	0.031	0.468	-0.013	-0.159	0.166	1.194	-0.173	-0.455
4	A10	9.815	1.928	0.016	0.520	0.140	1.403	-0.139	-0.426
5	A11	9.948	1.979	0.033	0.641	0.892	1.612	0.148	0.195
6	A12	-0.229	-1.645	0.016	0.725	0.071	0.678	-0.035	-0.208
7	A15	-12.728	-1.971	-0.139	-0.887	0.251	1.143	0.103	0.120
8	A16	-0.795	-1.614	-0.045	-0.587	0.089	0.742	-0.039	-0.125
9	A17	-3.299	-1.973	below detection limit		99.758	1.990	0.659	1.137
10	A18	-0.170	-1.500	-0.093	-1.001	0.123	1.229	-0.034	-0.169
	Average	1.266	-0.114	-0.022	-0.057	10.282*	1.347*	0.145	0.161

Table 3. NMSE and FB for NO_2 for each location and quarter

NO	*Location*	*Q1*		*Q2*		*Q3*		*Q4*	
		NMSE	FB	NMSE	FB	NMSE	FB	NMSE	FB
1	A4	0.035	1.141	0.005	0.102	0.010	0.190	0.032	0.257
2	A6	0.054	1.322	0.017	0.656	0.043	0.979	99.930	1.997
3	A8	0.025	0.825	0.0002	0.007	0.023	0.736	-0.043	-0.342
4	A10	0.003	0.051	-0.001	-0.045	-0.025	-0.538	-0.101	-0.754
5	A11	0.046	1.023	-0.250	-1.330	0.036	0.763	-0.009	-0.043
6	A12	0.049	1.135	-0.012	-0.345	-0.003	-0.076	-0.078	-0.622
7	A15	-0.028	-0.504	-0.280	-1.628	-0.037	-0.499	0.064	0.659
8	A16	99.971	1.999	-0.002	-0.053	-0.039	-0.697	0.027	0.315
9	A17	-0.037	-0.425	below detection limit		below detection limit		99.936	1.997
10	A18	0.287	1.193	-0.135	-1.457	-0.022	-0.450	-0.054	-0.477
	Average	10.040*	0.776	-0.073	-0.455	-0.001	0.045	19.970*	0.299

*) : Unaccepted NMSE and FB range

Model performance by NMSE and FB indicate that the SO2 model is better than the NO2 model as the average range of NMSE and FB for SO2 qualified in accepted NMSE and FB interval. It can be concluded that the SO2 model is more comparable to observation data than the NO2 model (Bhat, Kumar, & Czajkowski, 2011; El-Fadel, Abi-Esber, & El-Fadel, 2012). The NO2 model is slightly incomparable to the observation data. It can happen due to the origin of the NO2 produced by internal combustion processes like domestic and transportation which did not include an emission source in this model. Eastern side coal-steam power industries, cement industry, and oil and gas refinery within eight kilometers range were dominant NO2 emitters which the data does not include in this study. As model input, both SO2 and NO2 were simulated using GRAL based on emission load, wind speed, and wind direction.

4. CONCLUSION

GRAL study as air pollution model near the coal-steam power plant showed a medium correlation between simulation and observation, with SO_2 coefficient correlation (R) within 0.5 – 0.82 and NO_2 coefficient correlation (R) within 0.30 – 0.59. Model performances analyze by NMSE and FB, SO_2 model seems to be more comparable to observation data since has better average NMSE and FB than NO_2 model. NO_2 emissions may be produced from the domestic and transportation process, and several industries within the region did not include an emission source in this study. Due to data limitation of observation collected by grab sampling instead of continuous ambient measurement system affects different response times compared with hourly data from the model. A comprehensive study needs to be conducted to alter this limitation. Serial observation ambient data is a must to analyze comparison between simulation and observation data on an hourly basis.

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Utilization of iron ore slag in the manufacture of calcium silicate boards

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ABSTRACT

This study aims to determine the iron ore slag effect as an additive in particleboard based on the SNI 7705:2011 standard. Iron ore slag comes from the waste processing of iron ore into sponge iron. The iron ore slag is reduced to a size of 200 mesh. Particleboard made with the composition of slag and silica is 0:40, 8:32, 16:24, 20:20, 24:16, 32:8, and 40:0 wt%. Meanwhile, other materials were made permanent, namely PCC cement and lime 16 wt%, coconut fiber 3wt%, and water 3 wt%. They are pressed with 3 tons of pressure for 1 hour using a hydraulic press. Drying at room temperature for one day, under the hot sun for two days, then in an oven at 110 °C for 8 hrs. Analysis of the chemical composition of X-ray fluorescence and X-ray diffraction crystalline phase, SEM-EDS micro-photographs, physical tests including density and porosity, and mechanical compressive strength tests. The dominant composition of SiO_2 and CaO affects the formation of silicon dioxide (SiO_2), calcium silicate ($CaSiO_3$), and dicalcium silicate (Ca_2SiO_4) phases. Silica has a positive effect on the compressive strength of particleboard but is different from Ca, which has an impact on reducing the compressive strength. The sem morphology shows that coconut fiber cannot withstand heating at 190 °C and results in agglomeration. The addition of 20% ore slag and silica has met the calcium silicate board SNI 7705-2011. These results can be used to develop slag waste from iron ore processing into much more useful objects.

1. INTRODUCTION

The metal industry in Indonesia continues to increase in line with the development and industry developments. According to data from the Indonesian Ministry of Industry, the population of the Metal industry continues to grow with the addition of 142 sectors in 2019 (kemenperin.go.id). Metal production produces various products, especially iron/steel, nickel, and aluminum. The production process of metal smelting from iron ore produces solid waste known as slag (Siradjuddin, 2011). The management of steel slag waste in practice has challenges and the increase in the steel industry (Yang, 2017). The slag content of iron ore contains calcite oxide compounds (CaO), silica (SiO_2), alumina (Al_2O_3), and magnesia (MgO) (Feng et al., 2013). Iron ore slag contains gehlenite ($2CaO.Al_2O_3.SiO_2$) and akermanite (2CaO.MgO.2SiO) (Puertas and Jimenez, 2003). Technically, steel slag can be used as an aggregate material in civil works, such as cement mixture in concrete (Pane et al., 2021), road aggregate (Theresia & Susanti, 2017), to use as fertilizer (Rosidah et al., 2018). The dominant oxide compounds in iron ore slag in CaO and SiO_2 are very close to calcium silicate compounds. Calcium silicate is the result

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of the reaction of calcium carbonate (CaO) and silicon dioxide (SiO_2) using a reliable method to form $CaSiO_3$ (Jacob, 1976) and Ca_2SiO_4 (Budiman and Asmi, 2013). The response can be seen as follows:

$$CaCO_3(s) + SiO_2(s) \longrightarrow CO_2(g) +$$

$$CaO(s) + SiO_2(s) \longrightarrow CaSiO_3(s) \quad (1)$$

$$CaSiO_3(s) + CaO(s) \longrightarrow Ca_2SiO_4(s) \quad (2)$$

Calcium silicate contains calcium (Ca), silica (Si), and oxygen (O_2) (Newport, 2006). Calcium silicate can be made from natural and artificial minerals. Calcium silicate contains calcium (Ca), silica (Si), and oxygen (O_2) (Newport, 2006). Calcium silicate can be made from natural and artificial minerals. Minerals derived from nature are classified as impure because they still contain iron, magnesium, manganese, sodium, and potassium, so it is necessary to carry out a purification process to obtain pure calcium silicate. Iron ore slag from industrial waste also still contains many other chemical compounds, which are impure calcium silicates, especially the content of hematite (Fe_2O_3). The average silica content in iron ore slag is 41.54% (Syarif, 2010). The advantage of using iron ore slag with a high silica content is that its ability to provide a strong bond between cement and aggregate (Anggraeni, 2017). The content of iron ore slag is close to that of cement and natural sand. Iron ore slag can be used as a substitute for cement with alternative materials such as silica, portland cement, coconut fiber, and water. Based on (SNI 7705: 2011), cement functions as a binder, cellulose for flexibility, silica sand as a space provider or matrix, aluminum hydroxide or clay media for fire resistance (Hariadi, 2010). Types of sheet boards include magnesium, calcium silicate, and gypsum boards (Hariadi, 2010). This type of calcium silicate board has better advantages over other sheet materials. The weakness of the calcium silicate board is that it is not strong enough to be applied as a structural wall and has not been able to absorb sound waves (Asmi et al., 2011).

Standards for determining the percentage of the chemical composition of calcium silicate boards are not yet available. This study examines calcium silicate boards based on their chemical composition according to SNI 7705:2011. The standard is about a building material made of silica sand, portland cement, cellulose, and water with or without additives if needed, which is formed into a flat shape. The chemical reaction occurs at temperature and pressure between the elements of silica and calcium. So that the dominant chemical compounds on the calcium silicate board are SiO_2 and CaO, based on SNI 7705:2011, particleboard is grouped into five classes based on flexural strength. Classification of flat sheets for the flexural strength of calcium silicate boards is shown in Table 1.

Tabel 1. Classification of calcium silicate board

No	Class	Type A (Mpa)	Type B (Mpa)
1	Class 1	4	4
2	Class 2	7	7
3	Class 3	13	10
4	Class 4	18	16
5	Class 5	24	22

Category A is the saturated condition for products that are used outdoors. Category B is the ambient condition intended for indoor (interior) (SNI 7705-2011).

This research aims to make calcium silicate boards from iron ore slag. Flexural strength test based on SNI 7705-2011 standard. Chemical composition, crystal phase, SEM morphology, and physical examinations were used to support the properties analysis of the calcium boards made.

2. METHOD

Slag obtained from processing iron ore is cleaned of other impurities. Subsequently, the slag and silica materials were milling used a ball bill machine to get a powder. The powder of iron ore slag and silica are then sieved through an ASTM 200 mesh sieve. The coconut fiber used has a size of 40 mesh. The parameters for the manufacture of calcium silicate boards are shown in Table 2.

The process of mixing all the ingredients using a mixing machine is then formed in a mold measuring 200 x 50 x 20 mm using the hand layup method. Three-ton compaction to molds used the pressure press machine for 6hrs. The samples were then left at room temperature for 24hrs. Drying in the sun for two days and continued using the oven at 110 °C for 8hrs. Flexural strength test using UTM HT 2404 100kN. Physical examinations include density, porosity, absorption, and water content based on the ASTM C 642-90 test standard, using equations (3) to (5).

$$\text{Porosity (\%)} = \frac{W2-W1}{W2-W3} \text{ x } 100\% \quad (3)$$

$$\text{Absorption (\%)} = \frac{W2-W1}{W1} \text{ x } 100\% \quad (4)$$

$$\text{Porositas (\%)} = \frac{W1}{W2-W3} \text{ x } \rho\text{air} \quad (5)$$

Table 2. The composition of calcium silicate board

Compotitions (wt%)	TS1	TS2	TS3	TS4	TS5	TS6	TS7
Iron ore Slag	0	10	15	20	25	30	40
Silica	40	30	25	20	15	10	0
PCC cement			Fixed 15				
Lime			Fixed 15				
Aquades			Fixed 25				
Coconut fiber			Fixed 5				

The chemical compositions of the raw material were characterized by Epsilon 4 XRF Spectrometer from Malvern Panalytical with operating at 50 kV and three mA. The board's crystallinity and phase were measured by Panalytical Xpert 3 Powder X-RD with a Cu-Kα as a source of X-ray operating at 40 kV and 30 mA. The sample was scanned in the range 2θ of 0-80. Meanwhile, to determine the morphology used Nixon Eclipse MA100.

3. RESULT AND DISCUSSION

Results on the chemical composition test using X-ray fluorescence obtained from chemical compounds, as shown in Table 3.

Slag from iron ore processing has a dominant chemical composition of 38.73% SiO_2, 24.36% CaO, 16.31% Fe_2O_3, 8.64% Al_2O_3, and 6.19% SO_3. At the same time, other chemical compounds are less than 2%. The high CaO content in the slag is influenced by lime ($CaCO_3$) during the iron ore reduction process. In the iron ore smelting process, limestone serves to bind iron ore impurities and coke ash (C), including silicon, phosphorus, and manganese (Syarif, 2010).

The silica has a composition of 95.26% SiO_2, while other compounds such as Al_2O_3, CaO, P_2O_5, and Fe_2O_3 are less than 2%. SiO_2 concentrations above 90% are good silica. Lime contains 95.91% CaO, while MgO, Al_2O_3, SiO_2, K_2O, TiO_2, Cr_2O_3, MnO, and Fe_2O_3 are below 2%. Based on SNI 15 7064 2004 standard, PCC cement contains 60-67% CaO, 17-25% SiO_2, 3-8% Al_2O_3, and a maximum of 4.0% SO_3.

The chemical composition of the calcium silicate board can be seen in Table 4.

Tabel 3. Chemical composition for raw materials

No	Compound	Iron ore slag (%)	Silicate (%)	Lime (%)
1	MgO	1.30	-	0.30
2	Al_2O_3	8.64	0.70	0.78
3	SO_3	6.19	-	-
4	SiO_2	38.73	95.26	1.93
5	K_2O	1.89	-	-
6	CaO	24.36	0.98	95.91
7	TiO_2	0.59	-	-
8	MnO	1.44	-	-
9	Fe_2O_3	16.31	2.12	0.73
10	P_2O_5	-	0.74	-
11	PbO	0.14	-	

Tabel 4 . The chemical composition of the calcium silicate board

Compound	TS1	TS2	TS3	TS4	TS5	TS6	TS7
MgO	0.206	0.206	0.996	1.156	1.241	1.831	2.065
Al_2O_3	1.399	1.411	3.157	4.453	3.470	4.644	5.028
SO_3	0.288	0.311	0.473	0.374	0.229	0.759	0.366
SiO_2	40.468	29.364	47.069	33.395	29.307	28.667	21.04
K_2O	0.479	0.950	0.861	1.325	1.322	1.422	2.038
CaO	53.193	62.499	42.613	55.243	59.666	57.477	63.094
TiO_2	0.137	0.224	0.245	0.303	0.270	0.335	0.372
MnO	0.134	0.389	0.512	0.741	0.729	0.934	1.288
Fe_2O_3	1.524	4.399	3.825	3.758	3.513	3.639	3.620
SrO	0.111	0.149	0.131	0.134	0.140	0.193	0.162

Tabel 5. The physical and mechanical tests of the calcium silicate board

Sample	Physical				Mechanical
	Porosity (%)	. Absorbtion (%)	Density (g/cm^3)	Water content (%)	Flexural content (Mpa)
Standard	-	≤60 (oversea, 1987)	≥1,3 (overseas, 1987) dan ≥ 0,8 (SNI 7705-2011)	5-15 % (JIS A 5905-2003)	4 (1A/B) 7 (2 A/B) 16 (4B) 18 (4A) 22 (4B) 24 (4A)
TS1	47.895	41.264	1.160		2.50
TS2	41.309	30.809	1.340	Average: 0.53-5.32	2.50
TS3	39.572	28.522	1.388		2.00
TS4	37.586	27.199	1.382		4.00
TS5	38.204	26.466	1.367		3.00
TS6	42.499	32.173	1.320		3.50
TS7	43.011	32997	1.308		3.25

Based on SNI 7705:2011 calcium silicate board in terms of SiO_2 and CaO elements. From the study results, the highest SiO_2 was found in samples of 15% slag and 25% silica, which was 47.069%. SiO_2 content is influenced by the use of slag but does not dominantly change the composition of the calcium silicate board. The CaO content affects high CaO compounds in limestone, and cement is more dominant. 40 wt% slag without the addition of silica has made the CaO content of calcium silicate board high.

Other chemicals did not significantly change based on XRF analysis, even with added iron ore slag variations. The total content of Fe_2O_3 itself is an average of 2% so that Fe_2O_3 is not too influential. Calcium silicate boards with a small iron oxide content are particularly advantageous. More Fe can cause a decrease if it reacts with water (Cahyono & Kusdarini, 2019). The physical and mechanical tests of the calcium silicate sample board can be seen in Table 5.

The density of the average calcium silicate board is 1.323 g/cm^3. The most negligible density is obtained when the panels are made without slag. At the same time, the addition of 10-40 wt% slag has a density that is not much different, which is around 1.3 g/cm^3. The addition of slag and silica with concentrations of 15/25, 20/20, and 25/15 wt% gave higher board density than the other percentages.

The relationship between the porosity and density of the calcium silicate board in this study is shown in Figure 1.

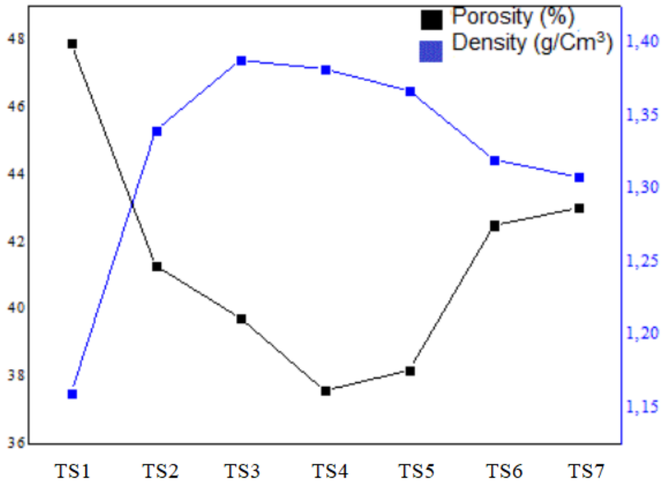


Figure 1. The relationship between porosity and specimen density

The board with the percentage of slag and silica 0/40 wt% showed the highest porosity value and the lowest density. Based on the XRF results, the CaO, SiO_2, Al_2O_3, Fe_2O_3, and MgO compounds were less. The density of iron ore slag is 3.5 g/cm^3. The sample board with 0/40 wt% slag and silica has the lowest density value because it uses the least iron ore slag. The more iron ore slag used, the higher the density value and the porosity decreases until the optimum point is added to 40/40 wt% slag and silica. The high porosity is due to the dominant composition of iron ore slag and higher CaO content. The heating process affects the particle size and surface area of CaO. Heating limestone for too long will result in the agglomeration of CaO particles so that the CaO surface increases significantly and causes porosity (Khaira, 2011). Overall, calcium silicate boards with the addition of iron ore slag showed an average density of 1.3 g/cm^3, following those on the market (Asmi et al., 2011). The specific gravity of iron ore slag is heavier than other materials and affects density (Amin et al., 2018). The board density value based on SNI 7705:11 has met the density standard, a minimum of 0.8 g/cm3.

The relationship between porosity and absorption is shown in Figure 2.

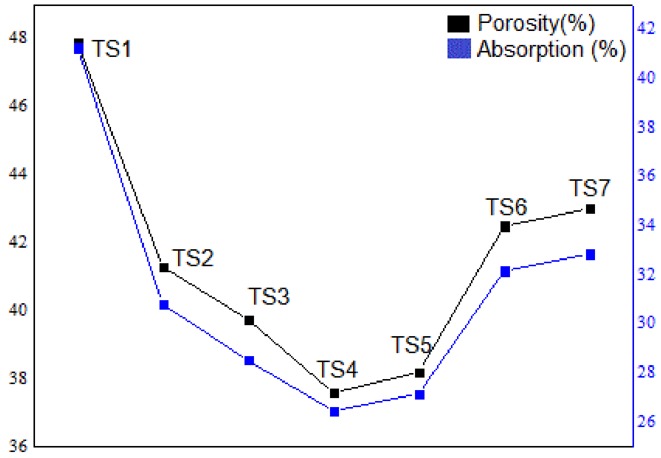


Figure 2. The relationship between porosity and absorption

The composition of iron ore slag and silica affects the porosity and absorption of the calcium silicate sample board so that the porosity and absorption values are directly proportional. The absorption function determines the absorption of the sample to water (Sagel et al., 1997). The absorption value is directly proportional to the porosity value. The higher the percentage of iron ore slag and the lower the percentage of silica, the lower the porosity value. In addition, the specimen contains coconut fiber. In natural fibers, cellulose and lignin are the most significant composition. These components are insoluble in water, but cellulose can absorb water (Pohan and Setiawan, 2000). Drying at high temperatures will result in the loss of some of the swelling properties. Heating at a temperature of about 100°C will reduce the ability to expand by about 50% (Putera, 2012). In addition, due to the heating process at 110°C, the coconut fiber changes its structure and mass. As a result, the board shrinks, and pores are formed. The water absorption capacity of the board is also affected by the high silica content (Sagel et al., 1997). The lowest water absorption was a sample of slag and silica 40/40 wt% with SiO_2 of 33.395%. SiO_2 can still fill the empty spaces on the board surface to reduce the water absorbed. The moisture content of the calcium silicate board is between 0.53%-5.32%.

Figure 3 shows the moisture content of the calcium silicate board. The higher the heating temperature of a material, the higher the percentage loss of water content. When heated in a temperature range of 110 to 190°C, the fiber and CaO will be lost. It makes a significant change in water content.

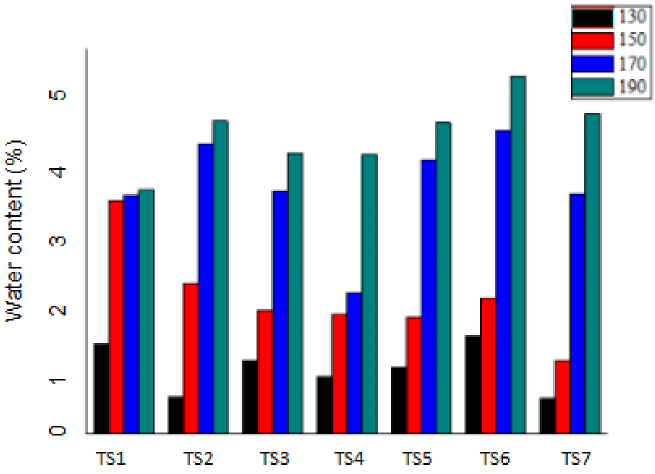


Figure 3. Water content of calcium silicate boards.

The results of the flexural strength test of calcium silicate board are shown in Figure 4.

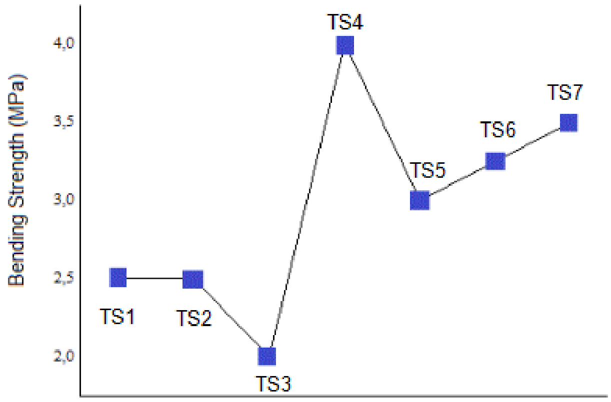


Figure 4. The flexural strength test of calcium silicate board

The highest flexural strength was found in the 40/40 wt% silica slag sample board at 4.0 MPa with the silica and ore slag percentage each of 20.16%. The addition of the slag percentage will increase the compressive strength, tensile strength, and flexural strength (Stiati & Halim, 2018). In addition, the acquisition of the elastic properties of coco fiber affects the flexural strength of the sample. Judging from the percentage of slag used, the piece with the best flexural strength was slag - silica 0/40wt%. However, this board has a high CaO compound. The nature of CaO, along with the increase in calcium dioxide, will decrease its compressive strength and flexural strength. Silica properties, the higher SiO_2 can increase the compressive strength and flexural strength of calcium silicate (Astuti et al., 2012). The mixing of materials in the manufacturing process also affects the flexural strength of the sample, for inhomogeneous mixing will cause the flexural strength graph to be formed imperfectly (Kanti, 2014).

The results of the XRD analysis are shown in Figure 5.

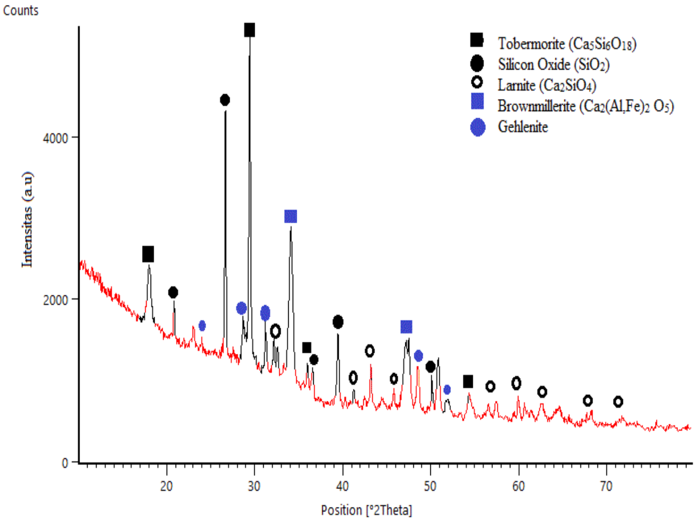
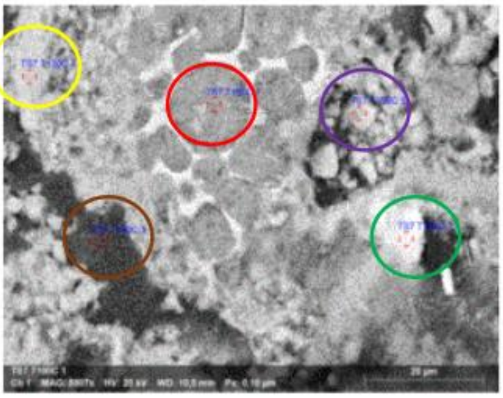


Figure 5. The results of the XRD analysis

Calcium silicate board phases include silicon dioxide, wollastonite, brownmillerite, gehlenite, and tobermorite. The silicon oxide (SiO_2) phase has a hexagonal crystal structure and is the highest peak on the graph. Wollastonite ($CaSiO_3$) phase with the monoclinic crystal structure. Brownmillerite ($Ca_2(AlFe)_2O_5$) phase with orthorhombic crystal structure and gehlenite phase. The diffraction peak in calcium silicate is a typical peak for dicalcium silicate. High CaO tends to produce calcium silicate. This silicate is a type of dicalcium silicate (Ca_2SiO_4). Dicalcium silicate (Ca_2SiO_4) is optimum at a ratio of SiO_2/CaO 4:6 (Haryono et al., 2018).

Figure 6 depicts the morphology of the particle size with a magnification of 5000X.



Gambar 6. The morphology of the particle size at 190 °C

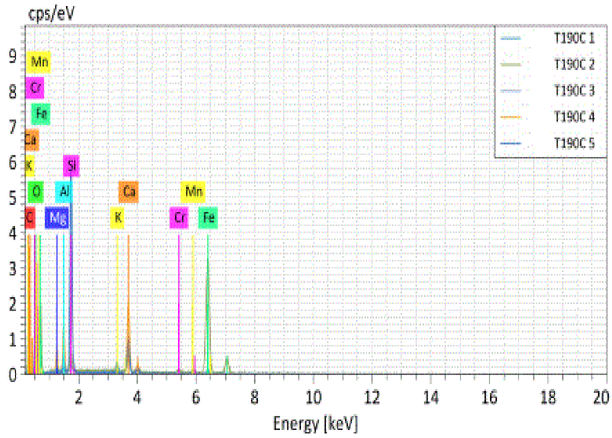


Figure 7. The results of SEM-EDS at 190°C

The distribution of the constituent elements is shown using colored circles. Colored circles of red, green, orange, yellow, purple are indicated in order. In SEM-EDS results, the area with purple color displays the distribution of calcium silicate minerals ($CaSiO_3$) as evidenced by the absence of other elements except Ca and Si with mass percentages of 11.20% 11.12%, respectively.

The constituent materials are still visible, pores are formed in the board, not yet fully integrated, and some grains have accumulated (agglomerated). The phenomenon caused by the minerals that make up the sample, such as fiber, has melted at 190°C, so there are still some inhomogeneous constituent minerals.

The results of SEM-EDS are shown in Figure 7. Wherein In the energy spectrum of 0-2 KeV, there are the elements of carbon (C), oxygen (O), potassium (K), iron (Fe), chromium (Cr), manganese (Mn), magnesium (Mg), aluminum (Al) and silicon (Si) are present. In the energy spectrum 2-4 KeV, there are elements of potassium (k) and calcium (Ca) detected, and in the energy spectrum 4-7 KeV, there are elements of chromium (Cr), manganese (Mn), and iron (Fe) observed.

4. CONCLUSION

The manufacture of calcium board from iron ore slag and silica with a percentage of 20.16% of each material on a 40/40 wt% slag-silica sample board has met the class 1 standard of SNI 7705:2011. The phases formed in the sample are silicon dioxide (SiO_2), calcium silicate ($CaSiO_3$), and dicalcium silicate (Ca_2SiO_4). The highest water content in the test object is 4.76, with a heating temperature of 190°C. SEM morphology shows that the constituent minerals and pores can still be seen clearly, but not yet wholly mixed, and some grains accumulate (agglomerate). The agglomerates caused by the fibers have undergone melting at 190°C. The EDS results show the formation of a distribution of calcium silicate ($CaSiO_3$) minerals as evidenced by the absence of other elements except Ca and Si with mass percentages of 11.20% and 11.12%, respectively. This research shows that iron ore waste slag can be developed as calcium silica board manufacture.

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Biogas Production from Sugarcane Vinasse: A Review

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ABSTRACT

Biogas is a renewable energy sources that could replace the role of fossil fuel. Biogas could be produced from biomass or agro-industrial wastewater. Sugarcane vinasse has potential of biogas production due to its high BOD concentration (10–65 g BOD/L). However, the biogas production from sugarcane vinasse has several drawbacks that hinders the maximum biogas yield, such as: acidic pH (pH 3.5 – 5.0), high temperature (80–90°C) and high concentration of sulfuric acid (> 150 mg/L). Theoretically, the methane potential per gram COD is 0.35 L/gr COD, containing of 60% methane. However, up to date, the maximum biogas production from vinasse was less then its theoretical value. To get the full potential of biogas production from vinasse wastewater as well as to reduce the capital cost for full scale application, combination of suitable pre-treatment, selected microorganisms and bioreactor design-configuration are the most important parameters to be considered. This paper aims to explore the potential of sugarcane vinasse to produce biogas, by elaborating the aforementioned key parameters. In this review the basic characteristic and the potency of sugarcane vinasse wastewater will be elaborated. Furthermore, the effect of key parameters such as pH, temperature, and organic load to biogas production will also be discussed. The biogas technology will also be explored. Lastly, conclusion will be determined.

1. INTRODUCTION

Indonesia is amongst the biggest ethanol producer in the world, alongside Brazil, India, and China (OECD/FAO, 2019). At recent days, the ethanol production demand increases due to the extreme need for disinfectant. In Indonesia, sugar cane and molasses are the major feedstocks in the ethanol agro-industry. There are big, as well as small-medium scale of agro-industries that produce ethanol from molasses. For instance, one big ethanol industry in Central Java-Indonesia, PT Indo Acidatama has maximum production capacity of 80 million liter ethanol per year (Harihastuti & Marlena, 2018). As for small scale industries, there are about 130 industries in Polokarto, Sukoharjo, Central Java that produce alcohol total amount of 13,000 L/per day (around 80-100 L alcohol/industry/day) (Harihastuti et al., 2020; Harihastuti & Marlena, 2018)

The environmental problem related to the developing ethanol agro-industry is vinasse wastewater, as a by-product of ethanol production. For every liter of ethanol production, approximately 10 – 15 liters vinasse is generated (Bernal et al., 2017; Naspolini et al., 2017). Figure 1 depicts a flowchart of ethanol production from sugarcanes and pollution prevention strategies. Figure 1 shows that vinasse is a wastewater that generated from stripping and distillation process. Vinasse wastewater has low pH, high COD, dark-colored, high concentration of

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sulfur and bad odor (Cristiano E Rodrigues Reis, Hu, & Hu, 2017). The easiest way to utilize vinasse wastewater is using it as fertilizer/fertirrigation. Technologies, such as anaerobic digestion (AD), advanced oxidation process (AOP), biological based treatment using algae and fungi are also commonly used as treatment strategy. The aforementioned technologies could treat vinasse wastewater so that the effluent can fulfil the water reuse standard. The effluent could be reused in the fermentative process. Bagasse, the solid waste that comes from juice extraction process, is used as feed to the boiler to produce steam and heat.

Anaerobic digestion (AD) is proven to be the most beneficial treatment for vinasse wastewater mitigation management. AD produces bioenergy (methane) that can be utilized as fuel replacing fossil fuel in the distillation process, as well as generate bio-fertilizer. Theoretically, the methane potential per gram COD is 0.35 L/gr COD, with 60% methane content. From 1 m^3 vinasse, about 115–312 m^3 of biogas can be produced, from which 169 kW of energy can be generated (Meyer, Rein, Turner, Administrative, & Mcgregor, 2011). The energy efficiency of the biogas produced from the vinasse in reciprocating combustion engines is 29%, while it is 32% in the gas turbines and microturbines (Parsaee, Kiani, Kiani, & Karimi, 2019). The total energy in vinasse is about 18% of the energy produced by bioethanol produced in the plant (Meyer et al., 2011). Unfortunately, methane production from vinasse cannot reach to its maximum potential due to many factors, such as: high level of inhibitors (Jesus, Bastos, & Altenhofen, 2019), low C/N ratio than the optimum C/N yield in biogas system (Janke, Leite, Nikolausz, Schmidt, & Liebetrau, 2015; Kayhanian & Rich, 1995), the needed HRT to achieve full organic degradation (Janke et al., 2015), low pH (Harihastuti et al., 2021; Cristiano E Rodrigues Reis et al., 2017), type of microorganisms (Oliveira et al., 2020), etc. Hence, for full scale application, addressing those factors is important thing to do.

Literatures about biogas potential from vinasse wastewater are still limited. This paper will generally review the potential of biogas production from vinasse wastewater. Specifically, the characteristic of vinasse along with its environmental effect and treatment technology will be elaborated. In addition, this paper also addresses the various aspects that have to be considered to enhance biogas generation of vinasse. Furthermore, its full-scale applications are also discussed. Lastly, the conclusion is determined.

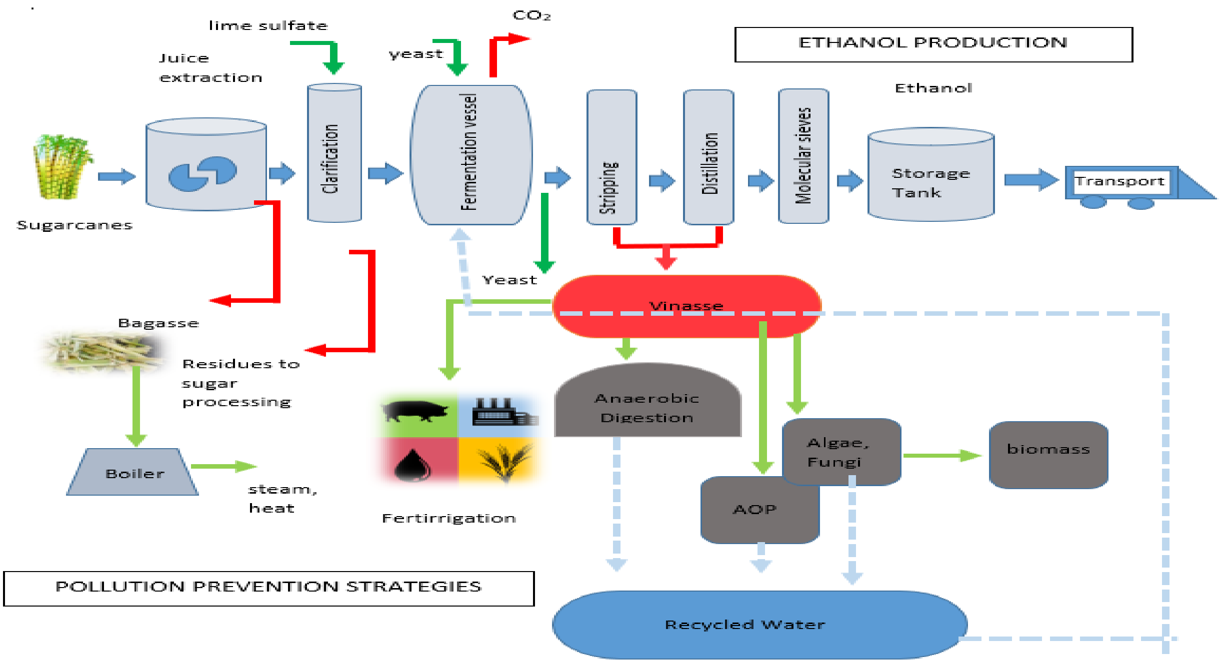

Figure 1. Flowchart of ethanol production and pollution prevention strategies

Table 1. Properties of sugarcanes vinasse wastewater

Parameter	Unit	Concentration range	Ref.
pH	-	3.0 – 5.0	(Harihastuti et al., 2021; Iqbal Syaichurrozi, 2016)
Temperature	°C	40 - 50	(Harihastuti & Marlena, 2018)
Biochemical Oxygen Demand (BOD)	mg/L	23,182 -109,038	(Harihastuti & Marlena, 2018; Soares et al., 2019; Iqbal Syaichurrozi, 2016)
Chemical Oxygen Demand (COD)	mg/L	32,400 – 353,797	(Harihastuti & Marlena, 2018; Janke et al., 2015)
Total Organic Carbon (TOC)	mg/L	30,750	(Iqbal Syaichurrozi, 2016)
C/N ratio	-	11-15/1	(Janke et al., 2016)
Total Suspended Solid (TSS)	mg/L	7,200	(Harihastuti & Marlena, 2018)
Total Solid (TS)	mg/L	27,000 -81,500	(Parsaee, Kiani, et al., 2019)
Volatile Suspended solid (VSS)	mg/L	1,620 –15,860	(Parsaee, Kiani, et al., 2019)
Total Nitrogen (TN)	mg/L	17,920	(Janke et al., 2016)
Total Phosphate (TP)	mg/L	1 – 102	(Iqbal Syaichurrozi, 2016)
Sulfide (H_2S)	mg/L	6.55 - 39.7	(Harihastuti et al., 2020, 2021)
Volatile Fatty Acid (VFA)	mg/L	1,310	(Lebrero & Zaiat, 2017)
Bicarbonate Alkalinity	mg $CaCO_3$/L	295	(Parsaee, Kiani, et al., 2019)
Phenols	mg/L	0.45–0.469	(Parsaee, Kiani, et al., 2019)
Iron (Fe)	mg/L	200 – 488	(Janke et al., 2015)
Manganese (Mn)	mg/L	55.4 - 194	(Janke et al., 2016, 2015)
Nickel (Ni)	mg/L	0.47 – 2.30	(Janke et al., 2016, 2015)
Copper (Cu)	mg/L	3.62 – 7.96	(Janke et al., 2016, 2015)
Zinc (Zn)	mg/L	29.4 – 36.8	(Janke et al., 2016, 2015)
Cobalt (Co)	mg/L	0.53 -0.62	(Janke et al., 2016, 2015)
Molybdenum (Mo)	mg/L	0.48 -0.84	(Janke et al., 2016, 2015)
Selenium (Se)	mg/L	0.08	(Janke et al., 2015)

2. CHARACTERISTICS OF SUGARCANES VINASSE WASTEWATER

The characteristics of vinasse wastewater depends on the raw materials (i.e. the variety of sugarcanes and the quality of molasses) and the process technology (i.e. the operating condition of the ethanol production, type of fermentation and distillation process , the quantity of the chemicals used, etc (Soares, Zaiat, Augusto, & Tadeu, 2019;

Wilkie, Riedesel, & Owens, 2000). Sugarcanes wastewater, that comes from ethanol distillation process, is considered as recalcitrant. It has temperature of 65–107 °C and a pH of 3–5 (Albuquerque, Ratusznei, & Rodrigues, 2019; Harihastuti & Marlena, 2018). Sugarcane vinasse contains of 93-97% water (Pazuch et al., 2017), 5% organic matter and 2% inorganic insoluble solid (Parsaee, Kiani, et al., 2019). It easily dissolves in water and has dark brown color. The dark brown pigment is derived from phenolic compounds (tannin and humic acids), melanoidins and caramels that makes vinasse is toxic to microorganisms. The characteristic of sugarcanes vinasse can be seen in Table 1.

3. ENVIRONMENTAL IMPACT

Sugarcane vinasse is considered very polluting because of high organic load that causes proliferation of microorganisms that reduces the dissolved oxygen (DO) in the water body that makes water unconsumable. Sugarcane vinasse also has low pH and corrosive. Its degree of pollution can be 100 times more dangerous than domestic waste (Marafon, Salomon, & Lucena, 2020). The lowest maintenance utilization of vinasse wastewater is using it as fertirrigation, as it requires low initial investment, low maintenance cost and simple technology (Marafon, Salomon, & Lucena, 2020). However, the bad effect of the excessive use of vinasse as fertirrigation are ground water contamination, soil salinization, metal leach and greenhouse gas emission (GHG) such as nitrous oxide, which is about 300 times more polluting than carbon dioxide (CO_2) (Marafon, Salomon, Amorim, & Peiter, 2020). Furthermore, over a long period of time, frequent discharges to the soil, rivers or lake could be harmful to the biota. However, vinasse wastewater fertirrigation could be very beneficial to improve soil fertility, with optimum dosage supplement that should not be exceed the soil's ion retention capacity (Tadeu, Loureiro, & Zaiat, 2018). Thus, the optimum dosage should be determined based on soil properties.

4. SUGARCANES VINASSE TREATMENT METHODS

Due to its high organic content, the treatment of vinasse wastewater should not be only rely on single method. The combination of several technology should be applied for the effluent in order to fulfill stream standard regulation. Biological treatment is till most common preference. The combination of biological anaerobic and aerobic treatment is the best solution to treat vinasse wastewater (Harihastuti et al., 2021). To improve the effluent's quality for re-use, another add-on advance technology such as ozonation catalytic might be used. Beside proven technologies, there are also several advance methods that also able to treat sugarcane vinasse wastewater effectively. Table 2 shows sugarcanes vinasse wastewater treatment technology.

5. ANAEROBIC DIGESTION OF SUGARCANE VINASSE

Sugarcane vinasse anaerobic digestion follows the already known mechanism of anaerobic process that involves anaerobic bacteria. Anaerobic process is consisting of four phases that works simultaneously, namely : hydrolysis, acidogenesis, acetogenesis and methanogenesis phase. Figure 2 shows anaerobic digestion phase of sugarcane vinasse wastewater. The process begins with the decomposition of complex organic compound into smaller molecules such as polysaccharide, lipid and protein. The second stage is called hydrolysis, where polysaccharide would be hydrolyzed into glucose, lipid was hydrolyzed into fatty acid, and protein into amino acid. Third phase, acidogenesis, is where glucose degrades into different types of VFA's (acetic, butyric, propionic, etc), ethanol and CO_2. The forth phase is called acetogenesis, where all VFA's change into acetic acid and CO_2. The last phase is methanogenic, where methane, CO_2 and water are the only products left. The type microorganism involved in the anaerobic process was also a mixture of different types of bacteria that follows syntrophic reaction. The dominant microbial community is shifting at each phase, as shown in figure 3 (Zimmerman, 2016).

Table 2 Reviews several methods that are able to treat sugarcanes vinasse wastewater. Better formatting of the table below

Treatment methods	COD in (g/L)	% COD removal (%)	Design Parameter	Type of Application	Ref.
Two stages anaerobic digestion (AD) with sodium hydroxide addition (ph adjustment) and effluent recirculation	• Acidogenesis stage : 84.2 kg-COD m^{-3} d^{-1} • methanogenesis stage= 25 kg-COD m^{-3} day^{-1}	• Acidogenesis stage: 21.2% • methanogenesis stage = 73.9%	HRT 232 days (harvested time)	• Acidogenesis stage : packed bed reactor lab scale • Methanogenesis stage: structured-bed reactors	(Tadeu, Messias, Júnior, Loureiro, & Zaiat, 2017)
Two-stage Anaerobic Membrane Bioreactor	16.706	97	HRT 3.1 – 5.3 days. With two separated acidogenic and methanogenic tank	Membrane bioreactor (MBR) Lab scale	(Santos, Ricci, Neta, & Amaral, 2017)
Single stage Thermophilic UASB	35.2 ± 2.6	71.7	HRT = 34 - 56 hrs	UASB reactor, Lab scale	(Ferraz, Koyama, Araújo, & Zaiat, 2016)
Two-stage Thermophilic UASB	24.0 ± 1.8	90.3	HRT = 32-39 hrs	UASB, Lab scale	(Ferraz et al., 2016)
Combination coagulation flocculation and fenton oxidation	6.836	69.2	1)pH adjustment with NaOH and H_2SO4 2)Coagulant $FeCl_3$, stirring 150 rpm for 3 mins 3)Flocculation = 15 mins, 4)Settling = 20 hrs 5)Fenton $FeCl_3$ + H_2O_2, HRT 3 hrs	Lab scale	(Guerreiro et al., 2016)
Two stage Up flow Anaerobic Filter, with pH adjustment and effluent recirculation	61 – 104	71	Addition of $CaCO_3$ to pH 6, 25% effluent recirculate, HRT 30 days	Two stages UAF, Full scale	(Harihastuti et al., 2021)
Anaerobic digestion using UASB, with Ozonation (AOP) post treatment	120	AD removes 95% to the level COD of 4.5 g/L (as bio recalcitrant color). AOP post treatment removes 80% of the color.	Sludge granules from settled UASB reactor, VFA/Alk = 0.4, pH 7.5 Optimum Ozone dosage of 90 mg/L/ min	UASB, Lab scale	(Otieno & Apollo, 2020)
Ozone, anaerobic, aerobic	39.4	95%	120 mins ozonation followed with aeration and peroxide removal with using a Na_2CO_3 dosage at 20 g L−1 following heating at 90 °C and magnetic stirring for 14 h. Aerobic treatment was using *M. circinelloides*	Lab scale	(Cristiano E R Reis, Bento, Alves, Carvalho, & Castro, 2019)

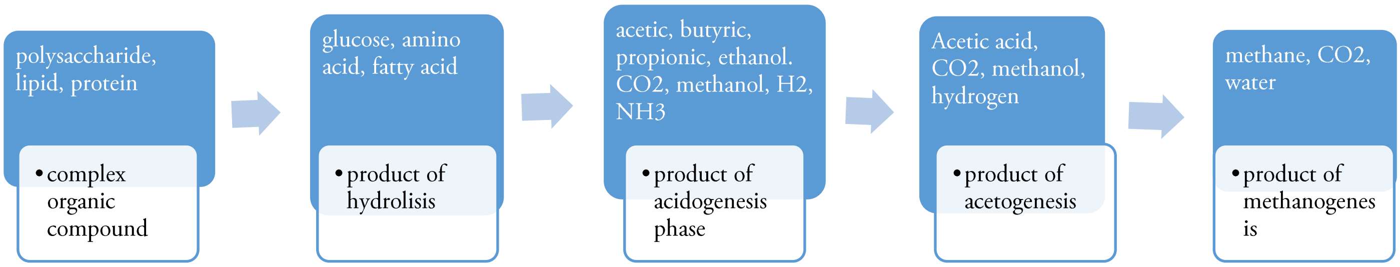

Figure 2. Anaerobic degradation phase of vinasse wastewater

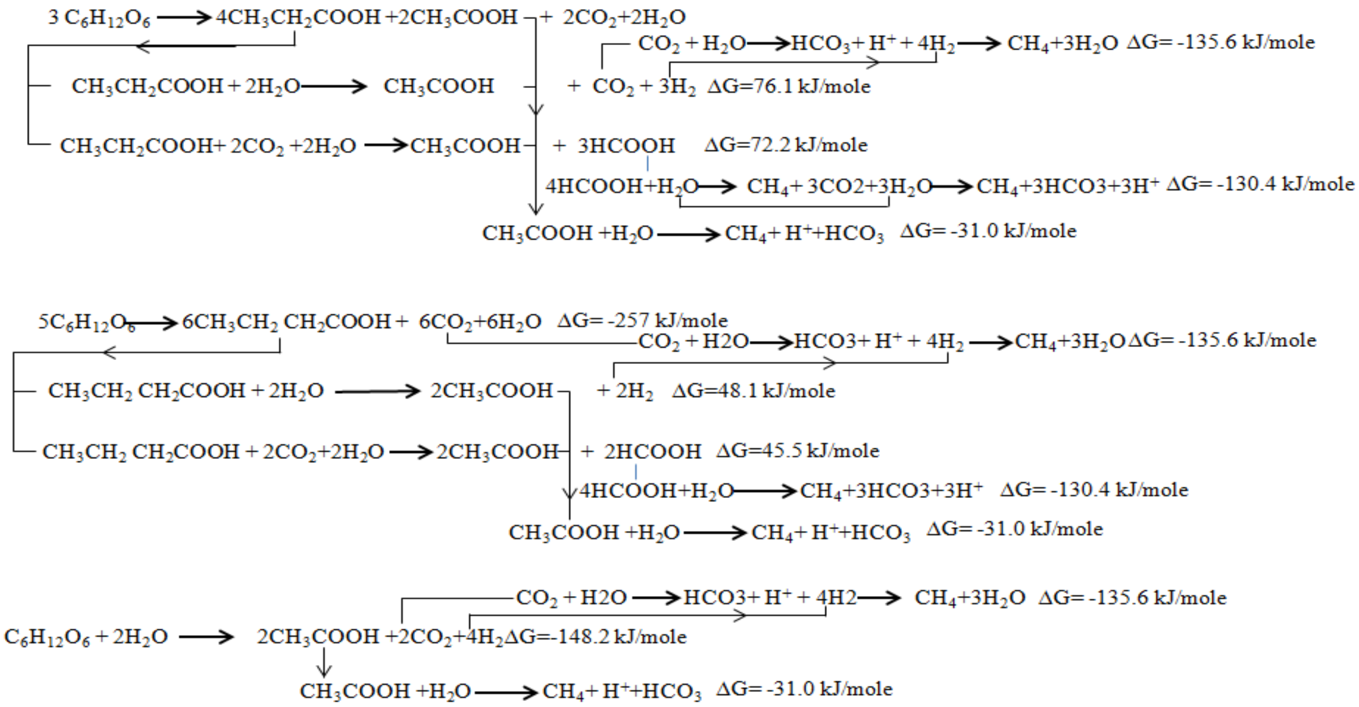

Figure 3. Biological reaction in anaerobic digestion, as referred from Al-mashhadani et.al (Zimmerman, 2016)

6. VINASSE BIOGAS GENERATION

A full-scale application for sugarcane vinasse treatment could be costly due to its high investment of infrastructure. To reduce the cost, utilization of biogas generated from sugarcane vinasse, as alternative energy, could be the better option. Sugarcane vinasse has high methane potential. Approximately, for every 1 m^3 vinasse, 10–26.4 m^3 of biogas could be produced, and equal to1.5–10 kW energy that could power engine-generator with a thermal power of 6.5 kWh/m^3 (Barrera, Spanjers, Dewulf, Romero, & Rosa, 2013; Pazuch et al., 2017). If sugarcane vinasse is converted into bioethanol, from 1m^3 bioethanol, about 115–312m^3 of biogas can be produced, from which 169 kW of energy can be generated (Meyer et al., 2011). The total energy in vinasse is about 18% of the energy produced by bioethanol produced in the plant (Parsaee, Kiani Deh Kiani, & Karimi, 2019). Sugarcane vinasse wastewater has high organic loading, so anaerobic system would be suited to lower down the concentration of organic, as well as utilized by-product biogas for alternative energy, prior treatment using aerobic system to fulfill stream standard. Thus, for full-scale application and to completely treated sugarcane vinasse wastewater with low cost technology, the combination of anaerobic-aerobic treatment technology could be the best option.

Anaerobic technology is still the main tools for vinasse wastewater treatment. However, there are expected conditions that should be met in order to generate maximum biogas production. Nutrients are important due to the low ratio of carbon-to-nitrogen (Moraes, Triolo, Lecona, Zaiat, & Sommer, 2015). The optimum range is reported as being between 25 and 35 for biogas production (Moraes et al., 2015). To modify carbon-to-nitrogen ratio, addition of materials with high carbon-to nitrogen ratio such as bagasse, straw or filter cake could be done(Moraes et al., 2015). Another preferable co-substrate could be domestic wastewater (Tena, Perez, & Solera, 2021a, 2021b), wastewater from biodegradable food beverage industries (Boncz, Formagini, Santos, Marques, & Paulo, 2012) or agriculture waste (Meng et al., 2020; Moraes et al., 2015; Oliveira et al., 2020).

Dilution as a pretreatment is proven to be necessary to lower down the levels of inhibitors, thus it should be maintained. It was shown that vinasse to water ratio of 1:3 produced biogas of 37.409 mL/g COD (Budiyono & Sumardiyono, 2013; I Syaichurrozi & Sumardiono, 2014). Harihastuti, et al (Harihastuti et al., 2021) also proved that theoretical methane yield of diluted vinasse sample (with ratio vinasse to water: 1:4) was higher than undiluted sample. Acidic pH in vinasse wastewater is not an optimum growth condition for methanogenic bacteria, hence the amount of certain level of alkalinity should be maintained to ensure the buffering capacity in wastewater. To enhance the alkalinity, addition of urea is one of the option. In the anaerobic digestion (AD), urea will be converted into OH^- + NH_4^+. However, the urea addition could not higher than C:N : 20-40:1 to prevent process failure caused by ammonia inhibition (Boncz et al., 2012). Beside Nitrogen, the addition of phosphate is also important for the stability of anaerobic digestion system, but the phosphate cannot be directly injected to the system. Therefore, urea, ($CO(NH_2)_2$) and sodium phosphate, (NaH_2PO_4), are added as soluble to optimize nitrogen phosphorus, respectively (Taylor, Siqueira, Damiano, & Silva, 2013). A study conducted by Boncz, et.al,(Boncz et al., 2012) showed that the optimum urea concentration was 0.215 g/g COD for maximum biogas production of 10 L/g COD. Review of key parameters for vinasse degradation process is shown in table 3.

Table 3. Review of key parameters to maximize vinasse degradation process

Key parameters	**Range value**	**remarks**	**reference**
Ratio C/N	20-40 : 1	Above the value can cause ammonia inhibition that lead to reactor failure	(Boncz et al., 2012)
Dilution factor	vinasse : water = 3 : 1	Could lower down the concentration of inhibitors, thus enhance methanogenic activity. Dilution could also lower down the concentration of Total Solid to improve the vinasse biodegradability	(Budiyono & Sumardiyono, 2013; I Syaichurrozi & Sumardiono, 2014)
Effluent recirculation	15% ratio	Effluent recirculation could stabilize pH. Recirculation could be applied after initial addition of alkaline at start up period.	(Fuess, de Araújo Júnior, Garcia, & Zaiat, 2017)
pH	Feed stock has to be pH 6 at minimum by adding alkaline with concentration not more than 4 g/g COD.	Alkaline such as urea ($CO(NH_2)_2$,) and sodium phosphate (NaH_2PO_4) could be used	(Janke et al., 2016)
HRT	10- 40 days	Sufficient HRT range to achieve at least 80% degradation	(Janke et al., 2015)
Co-digested substrate	Addition of bagasse, straw, filter cake, cow manure, sludge	Sludge has typical methanogenic activity of 0.25 – 0.30 mg CH4/g VS	(España-gamboa, Mijangos-cortés, Hernández-zárate, & Maldonado, 2012; Gomes, Barros, Maria, Alves, & Oliveira, 2016)

7. CONCLUSION

This paper reviews the characteristic, the environmental effect, treatment methods, and the key parameters for maximum biogas production from vinasse. Vinasse has high organic load, thus it is one of the main source of industrial pollution that potentially harmful to the environment. Anerobic digestion is still the most effective treatment method for mitigation, because it can produce biogas as renewable energy. To enhance biogas production, key parameters such as : C/N ratio, dilution factor, recirculation, pH, HRT and co-digested substrate should be maintained. To reduce cost and to fulfil the stream standard regulation, the combination of several technologies should be applied for wastewater management strategy.

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Effect of Substrate/Water Ratio on Biogas Production from the Mixture Substrate of Rice Straw and Salvinia molesta

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ABSTRACT

The substrate/water (S/W) ratio is one of the affecting parameters in anaerobic digestion (AD) since it affects the concentration of total solids (TS) in the biogas feedstocks. The appropriate S/W ratio has to be found to result in a high biogas yield. The goal of this study was to look into the influence of S/W ratio on biogas production from mixture substrate of rice straw and Salvinia molesta. Ratio of S/W was varied to be 1/7 w/v (TS 9.67%w/w), 1/10 w/v (TS 7.52%w/w), 1/13 w/v (TS 6.15%w/w), 1/16 w/v (TS 5.20%w/w). The results showed that S/W of 1/7, 1/10, 1/13, 1/16 resulted a total biogas yield of 22.86, 38.67, 42.71, 43.69 mL/g TS respectively. Decreasing TS from 9.67 %w/w (S/W of 1/7) until 6.15%w/w (S/W of 1/13) could increase the TS removal from 31.03% until 55.66%. However, at TS 5.20%w/w (S/W of 1/16), the TS removal was lower than that at TS 6.15%w/w (S/W of 1/13). The modified Gompertz (R^2 = 0.94 – 0.98) can predict evolution of biogas production with higher precision than the first order kinetic (R^2 = 0.91 – 0.98). The optimum TS was successfully predicted to become 5.40%w/w.

1. INTRODUCTION

Anaerobic digestion (AD) is one of the best methods to treat organic wastes. By AD, organic substances in the wastes will be degraded to biogas with the help of bacterial activity (Kougias & Angelidaki, 2018). Logically, the higher organic waste concentration in the digester, the higher concentration of biogas will be produced. However, study conducted by Budiyono et al., 2014) (Budiyono, Syaichurrozi, & Sumardiono, 2014) proved that when total solid (TS) of organic material was higher than 9%, total biogas yield decreased. Study by Shankar et al., 2013 (Shankar, Patil, Muralidhara, Ramya, & Ramya, 2013) found that a mixture of water hyacinth and water produced high concentration of biogas if the TS value was in range of 7-9%. Another study by Budiyono et al., 2010 (Budiyono, Widiasa, Johari, & Sunarso, 2010) had the same conclusion that TS of 7.4-9.2% was good concentration to generate biogas from cattle manure. Furthermore, the study from Yavini et al., 2014 (Yavini, Chia, & John, 2014) also informed that the good TS level in AD of agricultural wastes was 9%. Hence, in conclusion, some authors have agreed that the optimum range of TS was 7-9.2%.

On the other side, a study from Igoni et al., 2008 (Igoni, Abowei, Ayotamuno, & Eze, 2008) stated that TS of 10% (more than 9%) was better than that of 6-8% in AD

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of municipal solid waste. Furthermore, based on research conducted by Kalia et al., 2000 (Kalia, Sonakya, & Raizada, 2000) found that TS of 2-4% (lower than 7%) was the best level to produce methane from AD of banana stem waste. Moreover, the authors (Sinbuathong, Munakata-Marr, Sillapacharoenkul, & Chulalaksananukul, 2011) also proved that TS of 4.8% produced higher CH_4 yield than that of 9-13%. Based on information above, the optimum range of TS was not always in 7-9%, but the range can be lower than 7% or higher than 9%, but depends on the type of substrates as well.

The optimum TS concentration is not solely based on certain values but also depends on the kind of substrates used in AD. Thus, in this research, we used mixture substrate of rice straw (RS) and *Salvinia molesta* (SM). In the previous study, we found that the best chemical composition in the mixture substrate, producing the highest biogas yield, was obtained by the ratio of RS:SM was 60:40 (mass basis) (I. Syaichurrozi, 2018). The RS is a waste that resulted when Indonesian farmers harvest their rice plants. Approximately 58% of mass of single rice plant is to be the RS (I. Syaichurrozi, 2018; Iqbal Syaichurrozi, Suhirman, & Hidayat, 2018). Furthermore, the SM is alike water hyacinth, which is a free-floating aquatic plant having high doubling time and growth rate. It is one of the problems in Indonesian agriculture because it can decrease the irrigation system efficiency and disturb the rice plant growth (I. Syaichurrozi, 2018; Iqbal Syaichurrozi et al., 2018).

The existing studies have not reported about the effect of S/W in mixture substrate of RS and SM yet. Therefore, this study aims to investigate the influence of TS concentration on biogas yield from mixture substrate of RS and SM (with ratio of 60:40) (I. Syaichurrozi, 2018), to investigate the effect of ammonium, ammonia and VFA on the digestion process and to compare the biogas evolution through modified Gompertz and first order kinetic models. Finally, the prediction of optimum TS was estimated by making correlation between TS and biogas yield.

2. METHODS

2.1. *Materials*

The RS and SM used in this study were same as those used by the author (I. Syaichurrozi, 2018). They were collected from some paddy fields located in Bayah Regency (Indonesia). They were cleaned using water. Furthermore, they were dried under the sun. After dry, they were blended to reduce their size to be 18 mesh. Detailed chemical compositions of RS and SM were presented in Table 1. The rumen fluid (as inoculums) was collected from the cow slaughterhouse in Cilegon City (Indonesia). It had TS level of 4%w/v.

Table 1. Characteristics of RS and SM

Component	RS	SM
Total solid (TS) (%)	94.48	86.98
Crude fiber (%TS)	38.00	25.40
Crude carbohydrate (%TS)	67.93	53.95
Crude protein (%TS)	9.19	3.53
Crude lipid (%TS)	0.92	0.93
Lignin (%TS)	8.17	13.49
Hemicellulosa (%TS)	6.49	3.19
Cellulosa (%TS)	9.52	2.10
Volatile solid (VS) (%TS)	78.04	58.42

2.2. *Experimental Set Up*

Laboratory batch digesters used in this study were adapted from other authors (I. Syaichurrozi, 2018; Iqbal Syaichurrozi, Basyir, Farraz, & Rusdi, 2020; Iqbal Syaichurrozi et al., 2018). They were made by modifying the 600-mL-polyethylene bottles. To make anaerobic condition, the rubber was used to plug the bottles. The experimental schematic diagram in this study is shown in Figure 1.

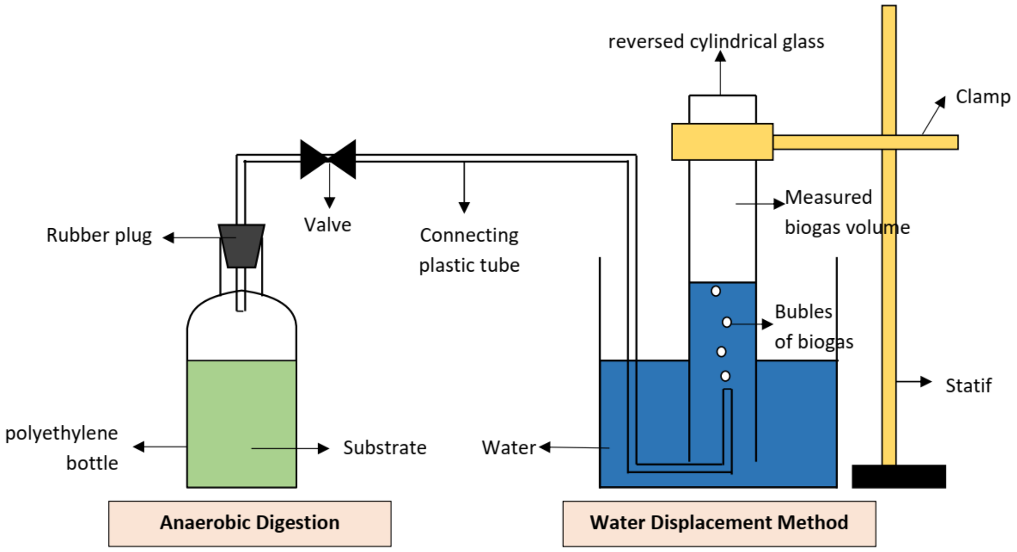

Figure 1. The experimental schematic diagram

Table 2. Total runs in this study

Substrate			S/W (w/v)	Water (mL)	Rumen fluid (mL)	Total Solid (TS)	
RS (g)	SM (g)	Total (g)				g	%w/w
6	4	10	1/7	70	25	10.15	9.67
6	4	10	1/10	100	25	10.15	7.52
6	4	10	1/13	130	25	10.15	6.15
6	4	10	1/16	160	25	10.15	5.20

Remarks: RS, Rice straw; SM, *Salvinia molesta*;; TS, Total solid; S/W, Substrate/Water ratio

2.3. Experimental Design and Procedures

Total mixture mass of RS and SM of 10 gram with the RS:SM ratio of 60:40 (mass basis) was used as substrates (I. Syaichurrozi, 2018). Water was mixed to adjust ratio of S/W to be 1/7, 1/10, 1/13, 1/16 w/v. Furthermore, 25 mL of rumen's fluid was added as inoculum (I. Syaichurrozi, 2018; Iqbal Syaichurrozi et al., 2018). For all variables, initial pH was conditioned at 7.0±0.1 by using NaOH 1 N. Total runs in this study were presented in Table 2.

The anaerobic digestion process was running for 40 days under room condition. Daily volume of biogas was determined using water displacement method, referred to Syaichurrozi et al., 2018 (Iqbal Syaichurrozi et al., 2018). Meanwhile, the change in pH was monitored using a digital pH meter (Hanna-Digital-PHEP-98107-1, Hanna instruments, Rumania) every two days. The concentration of ammonium ion (NH_4^+-N) was analyzed via Standard Methods (APHA, 2012). The concentrations of ammonia (NH_3-N) and volatile fatty acids (VFAs) were estimated using equation (1) (El-Mashad, Zeeman, Van Loon, Bot, & Lettinga, 2004) and (2) (Paul & Beauchamp, 1989). The TS removal was calculated using equation (3).

$$(\mathrm{NH_3-N}) = (\mathrm{NH_4^+-N}) \times \left[1+\frac{10^{-\mathrm{pH}}}{10^{-\left(0.1075+\frac{2725}{T}\right)}}\right]^{-1}$$, T in Kelvin (1)

$$\mathrm{pH} = 9.43 - 2.02\,\frac{\mathrm{VFAs}}{[(\mathrm{NH_3-N})+(\mathrm{NH_4^+-N})]} \quad (2)$$

$$\text{TS Removal (\%)} = \frac{\text{initial TS (g)} - \text{final TS (g)}}{\text{initial TS (g)}} \times 100\% \quad (3)$$

2.4. Kinetic Model

The biogas evolution during AD was simulated via models of modified Gompertz (equation (4); (Iqbal Syaichurrozi et al., 2020) and first order kinetic (equation (5); (Tri Mardiani, Budiyono, & Sumardiono, 2015). The value of ym, λ, μ, k was searched by using non-linear regression with help of polymath 5.0 educational version.

$$\mathbf{y(t) = ym.\exp\left\{-\exp\left[\frac{\mu.e}{ym}\,(\lambda - t) + 1\right]\right\}} \tag{4}$$

$$\mathbf{y(t) = \ ym\left(1 - \exp(-k.t)\right)} \tag{5}$$

where: ym, maximum biogas yield (mL/g TS); y(t), biogas yield at t days (mL/g TS); λ, adaptation time (days); μ, biogas production rate (mL/g TS.day); t, digesting time (days); k, biogas rate constant (/day); e, mathematical constant (2.718282)

3. RESULT AND DISCUSSION

3.1. Biogas Production

The different values of the S/W ratio affected the difference of initial TS concentration in the substrates (Table 2). The more water was added, the lower the TS concentration of the substrates. The standard of S/W was 1/7, because this ratio was used in the previous study (I. Syaichurrozi, 2018).

The daily biogas yields (mL/g TS) during fermentation at different S/W ratios were shown in Figure 2(A). There were some zones in daily biogas yield patterns from all variables. In Zone 1, daily biogas yield increased from day 0 to 8. The non-fiber carbohydrates in substrates were converted to biogas in this zone because it was easy to be degraded in the first fermentation time (Iqbal Syaichurrozi et al., 2018). In Zone 2, the availability of non-fiber carbohydrates was low because a lot of that had been degraded in Zone I. Hence, daily biogas yield decreased from day 8 to 18. In Zone 3, daily biogas yield increased drastically from day 18 to 26. The biogas was resulted from degradation of complex organic matters (fiber carbohydrates) in this zone. It was difficult to be degraded so it could be converted into biogas after day 18. In Zone 4, daily biogas yield decreased from day 26 to 40 because the biodegradable substrate was limited.

Cumulative biogas yield was shown in Figure 2(B). It was 22.86±6.11, 38.67±3.00, 42.71±3.79, 43.69±2.51 mL/g TS for S/W ratio of 1/7, 1/10, 1/13, 1/16 respectively. The total biogas yield increased with decreasing TS from 9.67%w/w (S/W = 1/7) until 5.20%w/w (S/W = 1/16). The S/W of 1/10 resulted 69,18% more total biogas yield than S/W standard (1/7). Furthermore, the S/W of 1/13 and 1/16 produced 86.85% and 91.16% more total biogas yield than S/W standard. Based on Figure 2, the best S/W ratio for biogas production was 1/16 with TS 5.20%w/w because it resulted the most total biogas yield.

Figure 2(B) showed that biogas production at a period of day 0-18 (Zone 1 and 2) was almost same for all variables. That means, the difference in the S/W ratio did not affect the degradation rate of non-fiber carbohydrates to biogas. Furthermore, on day 18-40 (Zone 3 and 4), biogas production rate was different. That means the difference in the S/W ratio is very influential in degradation of fiber carbohydrate to biogas. By water addition, biogas production rate in period of day 18-40 was higher compared to standard S/W (1/7). Dilution could increase substrate solubility thus increase substrate consumption, and then increase the anaerobic digestion. This phenomenon indicated that substrate containing high fiber carbohydrate was suitable to be processed with TS concentration lower than 7%w/w. Meanwhile, substrate containing high non-fiber carbohydrates was enough using TS concentration of more than 7%w/w. The authors (Panico et al., 2014) also reported that chemical composition of substrates affects the hydrolysis rate. The substrate containing high readily biodegradable compounds (such as carbohydrates) is easy to be disintegrated in water. Meanwhile, the substrate containing high slowly biodegradable compounds (such as cellulose, hemicellulose, lignin) is difficult to be hydrolyzed. Therefore, the level of water was dominantly affected in Zone 3 and 4 where the degradation of non-fiber carbohydrates occurred.

The S/W ratio did not affect the pH changes significantly (Figure 2(C)). The pH level during AD for 40 days was in the range of 6.7 - 6.9 (Figure 2(C)). Furthermore, the final pH level was in range of 6.8 - 6.9.

The fluctuation of pH during AD period was due to production of VFAs and ammonium/ammonia. The pH value from beginning until end of fermentation was still in optimum range of biogas production which was 6-8, where pH in range of 6-8 did not give a significant impact on biogas yield (Iqbal Syaichurrozi et al., 2018).

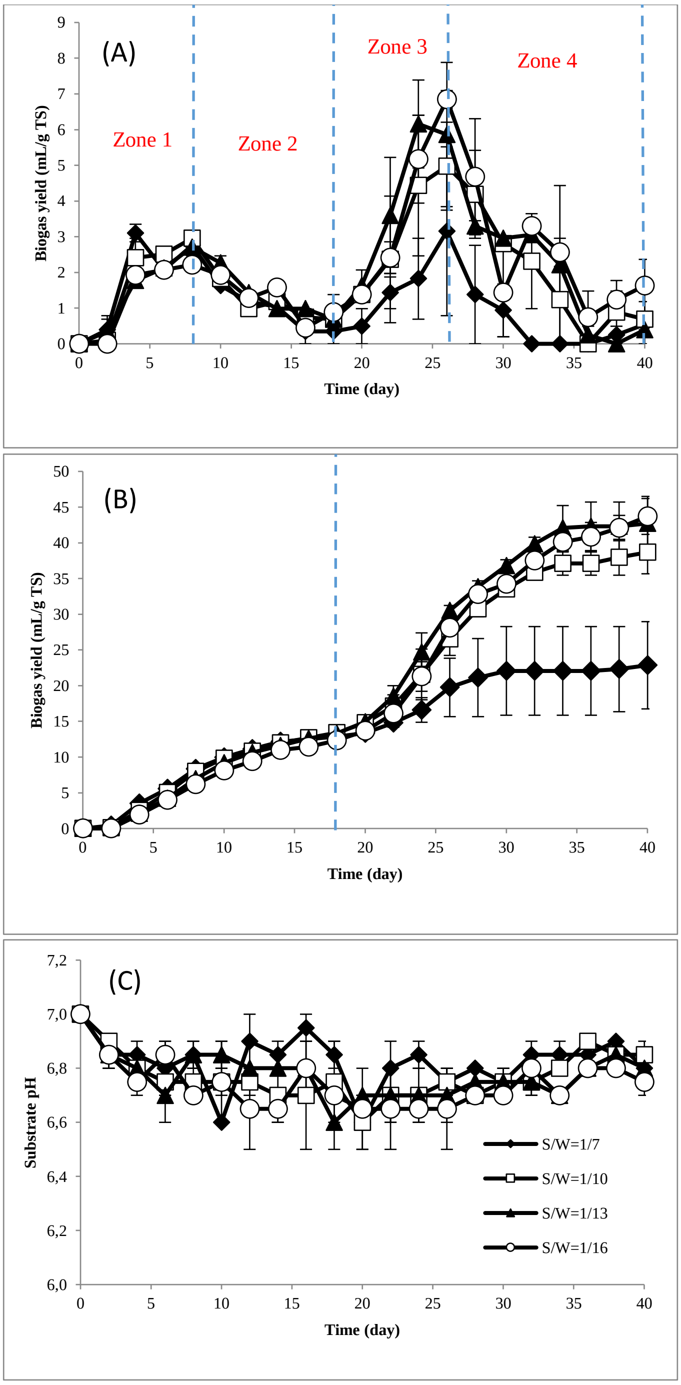

Figure 2. Effect of S/W ratio on (A) daily biogas yield, (B) cumulative biogas yield and (C) substrate pH

3.2. Ammonium, Ammonia, VFA

Ammonium ion (NH_4^+) and ammonia (NH_3) were generated by decomposition of nitrogen (protein) source in the substrates. They were uptaken by bacteria to make their cell structure. However, ratio of NH_4^+ and NH_3 in substrates relied on the pH level. Permanent equilibrium between NH_4^+ and NH_3 was shown in equation 6 and 7 (Sung & Liu, 2003).

$$NH_4^+ \boxed{\leftrightarrow} NH_3 + H^+ \quad (6)$$

$$NH_4^+ + OH^- \boxed{\leftrightarrow} NH_3 + H_2O \quad (7)$$

The more acidic pH level, the higher the ratio of NH_4^+:NH_3 in substrate. According to Deublein and Steinhauser (Deublein & Steinhauser, 2008), at pH level of 7.0, the ratio of NH_4^+:NH_3 was equal to 99:1. Furthermore, at pH below 7.0, ammonium ion is fully dominant (Iqbal Syaichurrozi et al., 2020). In this study, pH level during AD for all variables was 6.7 - 6.9 (close to 7.0) (Figure 2(C)) and the range of NH_4^+ and NH_3 during AD was 144.90±0.00 - 810.45±0.00 and 0.97±0.03 - 3.40±0.10 mg/L respectively (Figure 3(A and B)). Hence the ratio of NH_4^+:NH_3 was 99.22:0.78 - 99.69:0.31. It means the NH_4^+ was much more dominant than NH_3 in the AD process.

The sum of ammonium ion and ammonia is called total ammonia nitrogen (TAN). According to Figure 3(C), the TAN concentration increased from beginning fermentation until day 30 for all variables. S/W of 1/7 (TS 9.67%) resulted TAN easily than the other ratios. S/W of 1/7 had TAN of 573.30±0.00 and 561.16±0.20 mg/L at day 10 and day 20 respectively. Meanwhile, the other ratios had TAN of 329.88±0.04 - 354.46±0.27 mg/L and 341.75±0.12 - 378.44±0.08 mg/L at day 10 and day 20 respectively. On day 30, the peak value of TAN concentration was obtained to be 708.11±0.08, 813.85±0.10, 573.90±0.07, 695.74±0.00 mg/L for S/W ratio of 1/7, 1/10, 1/13, 1/16 respectively. From day 20 to 30, the TAN concentration increased drastically for S/W of 1/10-1/16. This path of TAN production was similar to the path of biogas production (Figure 2(B)). From Figure 2(A), biogas was generated drastically from day 20 to 30 for S/W of 1/10-1/16. Meanwhile, biogas production rate from S/W of 1/7 from day 20 to 30 was still low. This path was also similar to its low TAN production rate from day 20 to 30. Furthermore, after day 30 (which was at day 40), the TAN concentration decreased for all variables. As explained before, the anaerobic bacteria utilized TAN (ammonium ion and ammonia) as a direct nitrogen source to build their cell structure. From day 0 to 30, the TAN production rate was higher than its consumption rate. Meanwhile, on day 30 to 40, its production rate was lower than its consumption rate.

In the AD process, TAN concentration between 50-200 mg/L is considered to be good for bacterial growth. Meanwhile, when the value increased to 200-1000 mg/L, they still do not have negative effect on the growth (Rajagopal, Massé, & Singh, 2013). In this study, the TAN value ranges from 271.22±0.00 - 813.85±0.10 mg/L (Figure 3(C)). It means the TAN concentration during AD would not disturb the bacterial activity in this study due to a low TAN concentration (below 1000 mg/L).

Volatile fatty acids (VFAs) were resulted from degradation of carbon compounds in the substrates. High concentration of VFAs affected in dropping pH. The very low pH level could interrupt the AD process stability (Rajagopal et al., 2013). Methanogenic bacteria growth was more intolerant with acid condition than acidogenic bacteria growth. Based on Figure 2(C), pH level during digestion was 6.7 - 6.9. That value was still in good pH range for AD. The VFAs accumulation did not decrease the pH, because its concentration was not excessive. According to Figure 3(C and D), it shows that there is a positive correlation between TAN and VFAs. It illustrates that the higher the TAN concentration, the higher the VFAs concentration. This phenomenon was in line with the study of Syaichurrozi, 2018 (I. Syaichurrozi, 2018).

3.3. *TS Removal*

The mount of TS that was removed during AD was called TS removal. The results show that for S/W of 1/7, 1/10, 1/13, 1/16 were 31.03, 40.88, 55.66, 31.03% respectively. Generally, the higher TS removal was obtained, the higher the biogas yield was generated. However, this study showed interesting phenomena. The S/W of 1/16 produced the higher biogas but it had the lower TS removal than S/W of 1/7-1/13. In AD, the good collaboration between acidogenic and methanogenic bacteria was very important. Before biogas was produced, the organic substrate had to be degraded to VFAs by acidogenic bacteria. At S/W of 1/7-1/13 (TS 9.67-6.15%w/w), acidogenic bacteria degraded organic matters to VFAs easily so that the TS removal was high. However, the condition substrate of 1/7-1/13 was not good enough for methanogenic bacteria. S/W of 1/7, 1/10, 1/13, 1/16 contained lignin concentrations of 8.86, 6.89, 5.64, 4.77 g/L respectively. Substrates containing higher lignin concentrations were easier to produce phenolic compounds during AD. It might be more toxic against methanogenic bacteria than against acidogenic bacteria. The acidogenic bacteria were more dominant than methanogenic bacteria in the S/W of 1/7-1/13. Meanwhile, S/W of 1/16 gave a comfort condition for the methanogenic bacteria and acidogenic bacteria so that the both bacteria were in good syntrophic condition.

3.4. *Kinetic Analysis*

Simulation of biogas production during AD was successfully conducted. The kinetic parameters in the two models (such as ym, λ, μ, k) were presented in Table 3. Furthermore, a plot between experimental data and simulation data was depicted in Figure 4.

3.4.1. *Modified Gompertz Model*

S/W ratio of 1/16 (TS = 5.20%w/w) had more value of ym than ratio of 1/7-1/13 (TS = 9.67-6.15%w/w) (Table 3). That means the ratio of 1/16 resulted the maximum biogas yield in a larger amount (70.97 mL/g TS) compared with ratio of 1/7-1/13 (26.83-62.81 mL/g TS). It showed that bacteria were in the suitable metabolism conditions provided by the S/W of 1/16. The authors (Iqbal Syaichurrozi et al., 2020) stated that the value of μ is positively correlated with the value of ym. That means that the biogas production rate is in line with the total biogas yield. The substrate of 1/13-1/16 had a higher value of μ (1.53 mL/g TS.d) than the substrate of 1/7-1/10 (0.68-1.28

mL/g TS.d). The good range of S/W ratio was 1/13-1/16 and the best TS was 5.20%w/w obtained from S/W of 1/16.

The kinetic parameter of λ showed the adaptation time was needed by bacteria in the new environment. Bacteria in S/W ratio of 1/7 needed lower time to adapt which was 0.00 days. However, bacteria in substrate of 1/10-1/16 needed a longer time (5.72-8.71 days) than that in substrate of 1/7. This result was in line with a study conducted by Budiyono et al., 2014 (Budiyono et al., 2014) which reported that lag time to degrade substrate (vinasse) with TS 27.910% (0.423 days) was shorter than the need to degrade substrate with TS 7.015% (0.959 days).

3.4.2. First order kinetic model

The result from the first order kinetic model shows that the variable of S/W of 1/16 had ym value of 131.53 mL/g TS. Meanwhile, S/W of 1/7-1/13 had ym value of 33.82-126.34 mL/g TS. The S/W of 1/16 (TS=5.20%w/w) was a good ratio for bacterial activity. The k constant showed the biogas production rate per day, and it shows that the higher the k value, the faster the biogas production (Kafle, Kim, & Sung, 2013). Substrate of 1/7 had the highest k value (0.03/day) of all variables. Although S/W of 1/7 had the highest k value, it produced the lowest biogas yield. The S/W of 1/7 contained a higher TS concentration (which was 9.67%w/w) than the others, so the distance between organic matter and bacteria was closer and then the biogas was produced easily in the first digestion process. However, the high fiber carbohydrate in the substrate caused that the bacteria were difficult to degrade, so the biogas production process only lasted a short time and the biogas yield was low. The value of λ in modified Gompertz had a good correlation with the k value in first order kinetic model, which was the lower value of λ, the higher value of k would be.

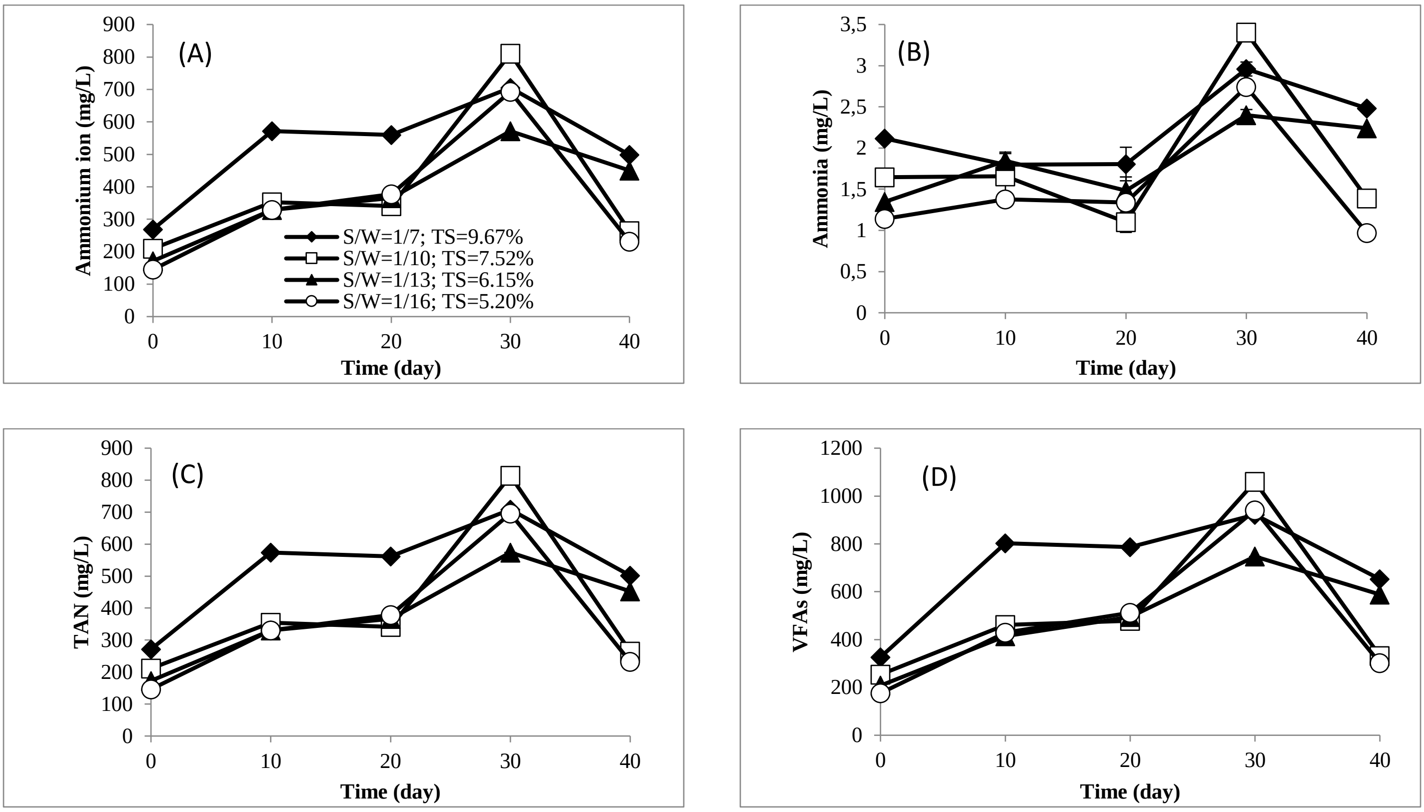

Figure 3. Concentration of (A) ammonium ion, (B) ammonia, (C) TAN, (D) VFAs during fermentation for 40 days at variation of S/W

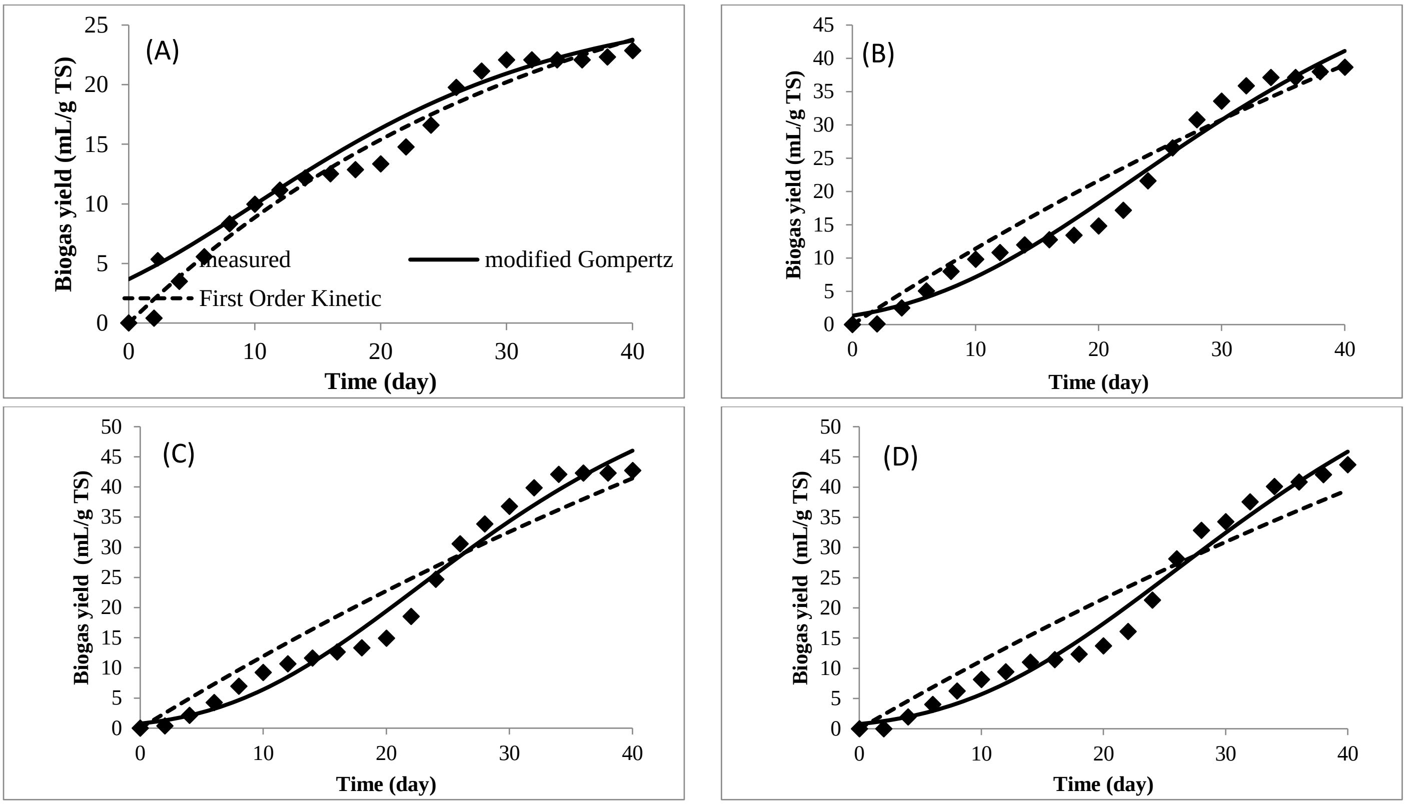

Figure 4. Comparison of measured and predicted biogas yield using modified Gompertz and first order kinetic at variation of (A) S/W=1/7 (TS 9.67%w/w), (B) S/W=1/10 (TS 7.52%w/w), (C) S/W=1/13 (TS 6.15%w/w), (D) S/W=1/16 (TS 5.20%w/w)

Table 3. Kinetic analysis results

	S/W Ratio			
	1/7	1/10	1/13	1/16
Modified Gompertz Model				
λ (days)	0.00	5.72	7.36	8.71
μ (mL/g TS.d)	0.68	1.28	1.53	1.53
R^2	0.94	0.98	0.98	0.98
ym (mL/g TS)	26.83	59.18	62.81	70.97
Predicted biogas yield (mL/g TS)-40 d	23.70	41.10	46.03	46.87
Measured biogas yield (mL/g TS)-40 d	22.86	38.67	42.71	43.69
Fitting error (%)-40 d	3.69	6.29	7.76	4.98
First-Order Kinetic Model				
k (/day)	0.03	0.01	0.01	0.01
R^2	0.98	0.94	0.92	0.91
ym (mL/g TS)	33.82	110.13	126.34	131.53
Predicted biogas yield (mL/g TS)-40 d	23.77	38.99	41.43	39.52
Measured biogas yield (mL/g TS)-40 d	22.86	38.67	42.71	43.69
Fitting error (%)-40 d	3.40	0.83	2.99	9.55

$$\text{Fitting error (\%)} = \frac{|\text{measured biogas yield} - \text{predicted biogas yield}|}{\text{measured biogas yield}} \times 100\%$$

3.4.3. Comparison between the two models

The error between the experimental data and simulation data of biogas yield for 40 days obtained from the modified Gompertz model was 3.69-7.76 % and in the first order kinetic model was 0.83-9.55 % (Table 3). Clearly, both kinetic models could fit in with the measured biogas evolution successfully because they have a low fitting error (below 10%). However, the former was better than the latter because the former had a higher R^2 value, which was 0.94 – 0.98 for the Gompertz model compared to 0.91 – 0.98 for first order kinetic.

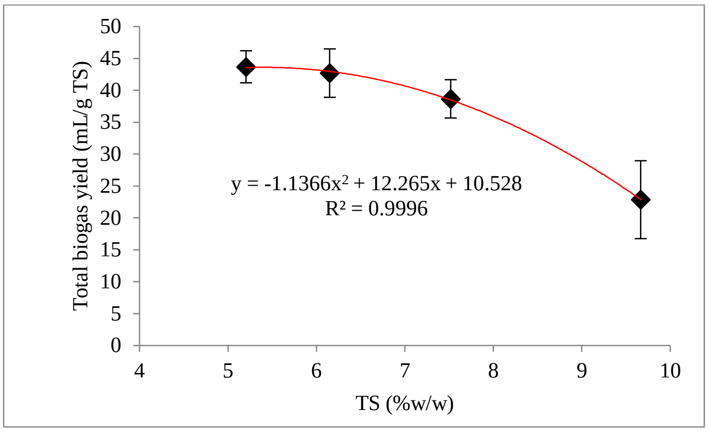

Figure 5. Correlation between TS and total biogas yield

3.5. Prediction of optimum TS

Correlation between TS and total biogas yield could be seen in Figure 5. The curve made by correlation between them had equation of $\boldsymbol{y = -1.136x^2 + 12.26x + 10.5}$ $\boldsymbol{(R^2 = 0.999)}$ (equation (8)), where $\boldsymbol{y}$ was total biogas yield (mL/g TS) and $\boldsymbol{x}$ was TS (%w/w). This equation could be used to predict the optimum TS producing biogas maximally.

$$\boldsymbol{y = -1.136x^2 + 12.26x + 10.52} \tag{8}$$

Differential of equation (8)

$$\boldsymbol{\frac{dy}{dx} = -2.272x + 12.26} \tag{9}$$

Maximum $\boldsymbol{y}$ could be obtained at optimum $\boldsymbol{x}$. Hence, we had to obtain the value of $\boldsymbol{x}$. The optimum $\boldsymbol{x}$ could be obtained using equation (9) with $\boldsymbol{\frac{dy}{dx} = 0}$.

$$\boldsymbol{0 = -2.272x + 12.26}$$
$$\boldsymbol{-12.26 = -2.272x}$$
$$\boldsymbol{x = 5.4} \tag{10}$$

By the calculation, the value of optimum $\boldsymbol{x}$ was 5.4. That means, the optimum TS was 5.40%w/w.

4. CONCLUSION

Variation of S/W ratio influenced TS concentration of substrates, where S/W of 1/7, 1/10, 1/13, 1/16 resulted the TS concentration of 9.67, 7.52, 6.15, 5.20%w/w respectively. The S/W ratio of 1/7, 1/10, 1/13, 1/16 resulted total biogas of 22.86, 38.67, 42.71, 43.69 mg/L respectively. The more the water was added into digesters, the more the biogas was produced. Compared to S/W of 1/7, The S/W of 1/10, 1/13, 1/16 could increase total biogas 69.18, 86.85, 91.16%. The TS 5.20%w/w (S/W of 1/16) resulted the highest biogas for all variables. Furthermore, the modified Gompertz and first order kinetic successfully simulated the biogas production from all variables, with the fitting error of 3.69-7.76% and 0.83-9.55% respectively. By prediction, the optimum TS concentration was 5.40%w/w.

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