Contents lists available at ScienceDirect

Materials Letters: X

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Integrated technique to produce sustainable bioethanol from lignocellulosic biomass

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ARTICLE INFO	A B S T R A C T
Keywords: Lignocellulosic biomass Gasification Fermentation Syngas Bioethanol	This study focuses on the utilization of mostly available renewable energy resources, such as lignocellulosic biomass, to generate syngas and bioethanol through a hybrid gasification and syngas fermentation process. The lignocellulosic biomass was characterized using TGA, XRD, FESEM with EDX analysis, and gasifying parameters were optimized using Aspen Plus®. In the first stage of this integrated process, hydrogen-containing syngas was generated, and the final product was bioethanol. The forest waste-based syngas produces higher bioethanol than EFB and coconut shell in the presence of biocatalyst. Therefore, bioethanol will be a sustainable biofuel that will satisfy the world's future energy demands.

1. Introduction

Lignocellulosic biomass, which is composed of forestry and agricultural waste, is used as a sustainable feedstock for bioenergy production [1]. These are the most abundant natural biomass, with an estimated natural output of 200 billion tons per year [2]. Renewable energy resources are more feasible than non-renewable energy resources because of their renewability and carbon-neutrality [1]. Bioethanol, as a sustainable energy produced from lignocellulosic biomass, does not release as many greenhouse gases (GHGs) as fossil-based fuels (coal, peat, oil, gas) [3,4]. Syngas is produced through thermochemical conversion of lignocellulosic biomass via pyrolysis (torrefaction), hydrothermal treatment, gasification, and combustion [5]. It is converted to bioethanol using yeast and bacteria in a tar-free bioreactor [6].

The development of metabolically microbial systems for fourthgeneration biofuels and high-value biochemicals has made significant progress [7]. Hydrogen fuel is a viable alternative of fossil fuels due to its high energy content and minimal emissions [8]. Highly efficient photocatalysts are employed for water treatment and hydrogen generation [9,10] and barium titanate nanostructures are used for photocatalytic hydrogen production [11]. Metal nitrides and graphitic carbon nitrides as novel photocatalysts used for hydrogen production and environmental remediation [12].

In the literature, bottleneck work has been attempted to achieved

sustainable bioethanol through integrated technique. Therefore, the purpose of this article is to produce clean and sustainable syngas and bioethanol by means of a hybrid gasification and syngas fermentation process.

2. Methodology

Syngas was produced (Stage 1) from lignocellulosic biomass including empty fruit bunches (EFB) of palm oil, coconut shell, and forest waste through thermochemical process in a downdraft gasifier (Fig. 1a). In the second stage, bioethanol was generated through biochemical process in a tar-free bioreactor utilizing two different types of biocatalysts (yeast and bacteria).

The lignocellulosic biomass was characterized in order to validate their feasibility for gasification reactions. Three distinct characterizations of TGA (Thermogravimetric analysis), XRD (X-ray powder diffraction), and FESEM (Field emission scanning electron microscopy) with EDX (Energy-dispersive X-ray) were performed. The simulation process was run before running the gasification using Aspen Plus® to optimize the gasification parameters. Three separate gasification experiments using EFB, coconut shell, and forest waste were carried out applying the optimized parameters of temperature (1000 °C) and pressure (30 bar). GC-TCD (Gas Chromatography-Thermal Conductivity Detector) analysis was used to identify the composition of syngas (H₂,

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https://doi.org/10.1016/j.mlblux.2022.100127

Received 8 August 2021; Received in revised form 30 December 2021; Accepted 19 January 2022 Available online 24 January 2022 2590-1508/© 2022 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0).







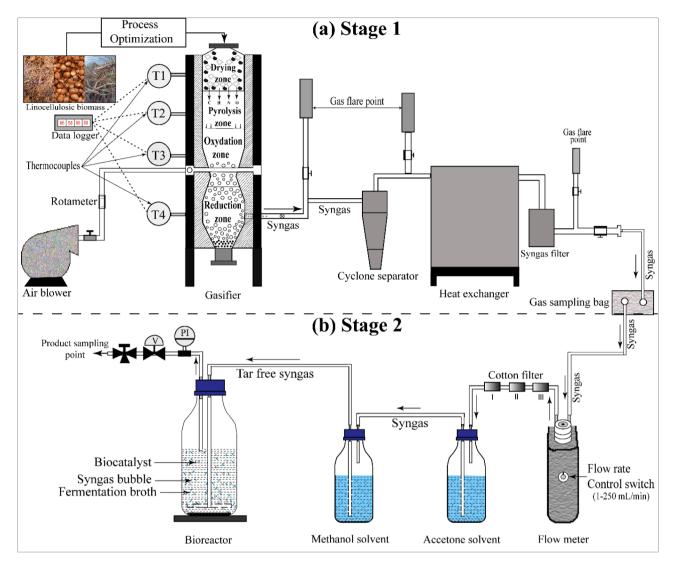


Fig. 1. Schematic diagram of an integrated process: (a) Stage 1. Syngas production in a downdraft gasifier (b) Stage 2. Bioethanol production in a bioreactor.

CO, CO₂, CH₄). After the completion of syngas fermentation (16 days), yield was taken from fermentation broth, extracted using chloroform solvent, and analyzed by GC–MS (Gas chromatography-Mass spectrometry).

3. Results and discussion

3.1. Characterization

The TGA analytical results for EFB, coconut shell, and forest waste show three key weight loss regions (A-zone, B-zone, C-zone), which correspond to dehydration (moisture removal), devolatilization (volatile material removal) and solid disintegration, respectively (Fig. 2a). Cellulose and hemicellulose have effectively decayed at temperatures between 120 °C and 400 °C in all biomass samples, with weight losses of 0.06 (wt%) at 235 °C, 0.08 (wt%) at 223 °C, and 0.07 (wt%) for forest waste at 255 °C. The cellulose and hemicellulose were pyrolysed by raising temperature of 400 °C leaving trace amount of ash (~12 wt %/°C). The degradation rate for EFB, coconut shell and forest waste was 0.41 (wt%/°C) at 355 °C, 0.38 (wt%/°C) at 365 °C, and 0.38 (wt%/°C) at

400 °C. The highest lignin-breakdown temperature was 900 °C with weight loss of 0.92 (wt%/°C), 0.94 (wt%/°C) and 0.77 (wt%/°C), respectively. It is also found that lignin part is the most complex part of biomass to degrade, and its breakdown occurred very slowly throughout the whole temperature profile (upto 900 °C). As a result, in order to achieve optimal energy efficiency, minimum temperature required for biomass gasification using a downdraft gasifier was 900 °C.

The XRD pattern (Fig. 2b) confirmed three strong diffraction peaks at 2θ values of 44.03° , 64.36° , and 77.48° which correspond to the (110), (200), and (211) crystal faces for EFB. Similar patterns were confirmed for coconut shell and forest waste. The crystalline structure of all samples were revealed by the sharp high-intensity peaks. The broad range peaks in all biomass samples, indicated amorphous in nature [13].

The FESEM images of EFB, coconut shell, and forest waste correspond to morphology and surface characteristics (Fig. 2c–e). The EDX analysis of these samples revealed two main elements of carbon and oxygen. In this study, very low concentration of sulfur was detected and confirmed that studied lignocellulosic biomass was environmentally acceptable. Metal traces such as iron, zinc, copper, etc. were shown to be favorable for microbial cell growth during syngas fermentation [14,15].

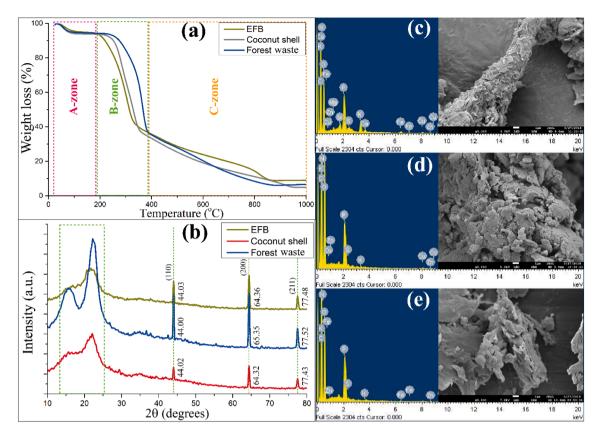


Fig. 2. Characterization of lignocellulosic biomass: (a) TGA analysis (b) XRD analysis, and FESEM images with EDX: (c) EFB (d) Coconut shell (e) Forest waste.

3.2. Simulation for gasification optimization

Fig. 3a shows the simulation results. Syngas composition (H₂, CO) together with CO₂ and CH₄ were simulated to identify best-operating parameters. According to the simulation curve, optimum temperature (T) and pressure (P) for performing gasification were 900–1000 °C and 30–35 bar, respectively. Therefore, the required temperature for cellulose, hemicellulose and lignin breakdown was 900 °C which consistent with TGA results.

3.3. Product analysis

Produced syngas contains combustible (H₂, CO, and CH₄) with noncombustible gases (CO₂, N₂, etc) (Fig. 5a). Previous studies are agreed this syngas concentration [1,16,17]. The highest H₂ concentration was produced in forest waste-based gasification whereas EFB-based gasification produced least amount of H₂. However, coconut shell-based H₂ concentration was higher than EFB-based gasification and lower than forest waste-based gasification. The CO concentration follows same pattern as H₂ in all gasification. Moreover, CO₂ concentration in coconut shell-based gasification was quite significant, while other two gasification produced more CO₂. During the whole process, CH₄ concentration was almost same for three different gasification.

Fig. 3b shows GC–MS analytical results of end product (Stage 2). The MS fraction of extracted samples were comparable to standard MS fraction of 15:29:31:45. The concentration of bioethanol produced using biocatalysts (yeast and bacteria) were 15.02–15.31 mmol/L and 14.23–14.97 mmol/L, respectively. This results agreed with the

literature [3,18]. According to the results, highest bioethanol was generated through forest waste based syngas fermentation using yeast, and lowest bioethanol was produced from EFB based syngas fermentation using bacteria. In this integrated process, lignocellulosic biomass based syngas is suitable for bioethanol production.

4. Conclusion

This research performed an integrated gasification and syngas fermentation technique to produce sustainable bioethanol, reduce dependency on non-renewable energy sources. Temperature and pressure were optimized using Aspen Plus® and gasification was run producing syngas. This syngas was further performed fermentation process with presence of biocatalysts. The highest amount of bioethanol (15.31 mmol/L) was produced during forest waste-based syngas fermentation in the presence of yeast, and lowest amount of bioethanol (14.23 mmol/ L) was generated during EFB-based syngas fermentation in the presence of bacteria. This study is limited to small-scale bioethanol production using a tar-free bioreactor. In this study, concentration of bioethanol was found to very low when its yield was compared to other fermentation processes. Therefore, further advanced research is needed to improve bioethanol production and potential of its commercialization.

CRediT authorship contribution statement

Minhaj Uddin Monir: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing.

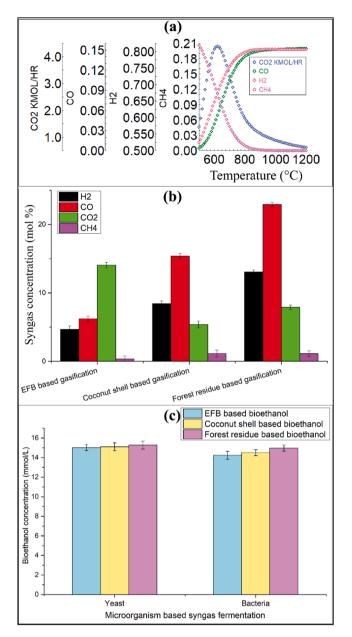


Fig. 3. (a) Simulation model using Aspen Plus® for gasification process, and bioethanol concentration through the integrated process: (b) syngas concentration (c) bioethanol concentration.

Azrina Abd Aziz: Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing. Abu Yousuf: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors want to acknowledge the funding of Malaysia Ministry of Higher Education via Fundamental Research Grant Scheme (FRGS) No. FRGS/1/2017/TK02/UMP/02/20 and Universiti Malaysia Pahang for the provision of laboratory facilities.

References

- M.U. Monir, A.A. Aziz, R.A. Kristanti, A. Yousuf, Syngas Production from Cogasification of Forest Residue and Charcoal in a Pilot Scale Downdraft Reactor, Waste Biomass Valorization 11 (2) (2020) 635–651.
- [2] F. Wang, D. Ouyang, Z. Zhou, S.J. Page, D. Liu, X. Zhao, Lignocellulosic biomass as sustainable feedstock and materials for power generation and energy storage, J. Energy Chem. 57 (2021) 247–280.
- [3] M.U. Monir, A.A. Aziz, A. Yousuf, M.Z. Alam, Hydrogen-rich syngas fermentation for bioethanol production using Sacharomyces cerevisiea, Int. J. Hydrogen Energy 45 (36) (2020) 18241–18249.
- [4] M.U. Monir, M.Y. Hasan, M.T. Ahmed, A.A. Aziz, M.A. Hossain, A.S. M. Woobaidullah, P.K. Biswas, M.N. Haque, Optimization of Fuel Properties in Two Different Peat Reserve Areas Using Surface Response Methodology and Square Regression Analysis, Biomass Convers, Biorefin, 2021.
- [5] M.W. Seo, S.H. Lee, H. Nam, D. Lee, D. Tokmurzin, S. Wang, Y.-K. Park, Recent advances of thermochemical conversion processes for biorefinery, Bioresour. Technol. 343 (2022), 126109.
- [6] M.U. Monir, A. Yousuf, A.A. Aziz, Syngas fermentation to bioethanol, in: A. Yousuf, D. Pirozzi, F. Sannino (Eds.), Lignocellulosic Biomass to Liquid Biofuels, Academic Press, 2020, pp. 195–216.
- [7] M. Aamer Mehmood, A. Shahid, S. Malik, N. Wang, M. Rizwan Javed, M. Nabeel Haider, P. Verma, M. Umer Farooq Ashraf, N. Habib, A. Syafiuddin, R. Boopathy, Advances in developing metabolically engineered microbial platforms to produce fourth-generation biofuels and high-value biochemicals, Bioresour. Technol. 337 (2021), 125510.
- [8] P. Sampath, Brijesh, Kakarla Raghava Reddy, C. Venkata Reddy, Nagaraj P. Shetti, Raghavendra V. Kulkarni, Anjanapura V. Raghu, Biohydrogen production from organic waste–a review, Chem. Eng. Technol. 43 (7) (2020) 1240–1248.
- [9] M. Jyothi, V. Nayak, K.R. Reddy, S. Naveen, A. Raghu, in: Non-Metal (Oxygen, Sulphur, Nitrogen, Boron and Phosphorus)-Doped Metal Oxide Hybrid Nanostructures as Highly Efficient Photocatalysts for Water Treatment and Hydrogen Generation, Nanophotocatalysis and Environmental Applications, Springer, 2019, pp. 83–105.
- [10] K.R. Reddy, M. Jyothi, A. Raghu, V. Sadhu, S. Naveen, T.M. Aminabhavi, in: Nanocarbons-Supported and Polymers-Supported Titanium Dioxide Nanostructures as Efficient Photocatalysts for Remediation of Contaminated Wastewater and Hydrogen Production, Nanophotocatalysis and Environmental Applications, Springer, 2020, pp. 139–169.
- [11] K. Karthik, C.V. Reddy, K.R. Reddy, R. Ravishankar, G. Sanjeev, R.V. Kulkarni, N. P. Shetti, A. Raghu, Barium titanate nanostructures for photocatalytic hydrogen generation and photodegradation of chemical pollutants, Journal of Materials Science: Materials in Electronics 30 (23) (2019) 20646–20653.
- [12] Sudesh Kumar, Kakarla Raghava Reddy, Ch. Venkata Reddy, Nagaraj P. Shetti, Veera Sadhu, M.V. Shankar, Vasu Govardhana Reddy, A.V. Raghu, Tejraj M. Aminabhavi, in: Nanostructured Materials for Environmental Applications, Springer International Publishing, Cham, 2021, pp. 485–519, https://doi.org/ 10.1007/978-3-030-72076-6_19.
- [13] Nurain Johar, Ishak Ahmad, Alain Dufresne, Extraction, preparation and characterization of cellulose fibres and nanocrystals from rice husk, Industrial Crops and Products 37 (1) (2012) 93–99.
- [14] Konstantinos Asimakopoulos, Hariklia N. Gavala, Ioannis V. Skiadas, Reactor systems for syngas fermentation processes: A review, Chemical Engineering Journal 348 (2018) 732–744.
- [15] Vineet Singh Sikarwar, Ming Zhao, Paul S. Fennell, Nilay Shah, Edward J. Anthony, Progress in biofuel production from gasification, Progress in Energy and Combustion Science 61 (2017) 189–248.
- [16] M.U. Monir, A.A. Aziz, R.A. Kristanti, A. Yousuf, Co-gasification of empty fruit bunch in a downdraft reactor: A pilot scale approach, Bioresour. Technol. Rep. 1 (2018) 39–49.
- [17] M.U. Monir, A.A. Aziz, R.A. Kristanti, A. Yousuf, Gasification of lignocellulosic biomass to produce syngas in a 50 kW downdraft reactor, Biomass Bioenergy 119 (2018) 335–345.
- [18] M.U. Monir, A.A. Aziz, F. Khatun, A. Yousuf, Bioethanol production through syngas fermentation in a tar free bioreactor using Clostridium butyricum, Renewable Energy 157 (2020) 1116–1123.