Inorganic Gasses into Organic Acids for Polyhydroxyalkanoates Production: An Integrated Lab-Scale System for the Syngas Fermentation Coupled PHA Production

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Keywords: Biorefinery, Gas-to-Material, C1 Gasses, VFA, Anaerobic Digestion
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Introduction

Thermochemical technologies are promising processes to generate energy and useful-materials in the form of gas (syngas), liquid (bio-oil), and solid (biochar) from biomass resources (e.g. lignocellulosic garden waste, kitchen waste, sewage sludge). The gas portion is mainly composed from inorganic gases such as carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2) and methane (CH_4) which corresponds a significant potential to be used as a direct gas-fuel or converted into other useful end-products. H_2 and CH_4 content with a high energy value, can be used as a direct fuel and subsequently emitted as a CO_2 which is known to be the primary greenhouse gas. However, CO as the main component in syngas has a relatively poor potential to be used as a direct gas-fuel. Alternatives to the gas-fuel approach are; conversion of syngas into liquid-hydrocarbons (e.g., diesel fuel) via chemical-catalysis based well-known method Fischer–Tropsch (FTS), or microbial bioconversion of syngas into the variety of valuable end-products such as biogas, ethanol, butanol, acetic acid, propionic acid, etc. via anaerobic digestion (AD) technology (Gunes, 2021). Although FTS is considered as an art-of-state technology with many industrial applications, it requires a certain range of ratio between CO/H_2 which is a challenging operational problem especially in case of biomass based thermochemical conversion systems. On the other hand, anaerobic bioconversion is an improving interesting approach to produce variety of products with an advantage of more flexibility in influent and the cost-efficiency. Even though methane is the thermodynamically most stable product of the anaerobic systems, natural gas-grade production of biomethane is a challenging task in anaerobic digestion systems. Besides, upgrading of biogas mixture mainly composed of 50-70% of CH_4 and 50-30% of CO_2, which does not allow to use as a direct biofuel in transportation systems, is another challenge for the biomethanization of gas materials. On the other hand, acidogenic fermentation of gas materials can be a promising method for the alternative production of value-added products such polyhydroxyalkanoates (PHA) via a coupled PHA-accumulation system. PHA molecules are frequently called as bioplastics due to their physicochemical structures' similarities to the fossil-based traditional plastics. A variety of microbes can intracellularly store them under stressing conditions. The most known PHA accumulation pathway is requiring organic acid rich influent for the PHA-accumulator microorganisms. In case of biochar as a conductive material with a highly porous physical structure can be used as a microbial booster in such hybrid thermochemical-biological systems (Wu et al., 2021).

Inorganic gas materials such as mono-carbon (C1) gasses (CO and CO_2), and H_2 gas can be converted into volatile fatty acids (VFA) via anaerobic fermentation, followed by bioplastic production by PHA-accumulating bacteria. In this study a lab-scale integrated system was developed for conducting Gas-to-VFA and VFA-to-PHA subsequential bioconversions in continuous operation mode. The primary tests of the integrated system will be shared together with preliminary results.

Material and Methods

The gas substrates used as feedstock in the fermentation reactor was produced by intermediate pyrolysis of lignocellulosic biomass (CO-rich syngas). Fir-tree sawdust was used as a representative lignocellulosic biomass material at batch-feeding conditions with a gas-recirculation approach (N_2 used as carrier gas) for minimizing syngas dilution. Residence time was 30 minutes, constant temperature at 550 °C was applied, and 5.0 grams of raw biomass was pyrolyzed in each run to obtain syngas materials to be used in anaerobic bioreactor.

Since the main limitation for the gas-fermentation process has been argued to be as gas-to-liquid mass transfer issue due to the poorly soluble character of the target inorganic gasses (CO and H_2), a special attention was given to the increase the productivity of the gas-fermentation system (Geinitz et al., 2020; Sun et al., 2019). For this purpose, a special type of gas-bubbler was manufactured by biochar and polystyrene (PE) mixture to maximize both the biologically active surface area to increase gas-to-biofilm direct encountering possibility and also the gas-to-liquid mass transfer rate via forcing the gas substrates to pass through the bio-active surface area.

A lab-scale continuous and integrated Gas-to-VFA (anaerobic fermentation, AF) and VFA-to-PHA (anoxic/aerobic SBR) consequential biorefinery system was proposed, designed, and constructed by us. For this niche and complex experimental set-up, Arduino microcontroller was used to control and monitor (via online sensors) the whole lab-scale biorefinery system. A general overview of the designed integrated system is visualized in the following Figure 1.

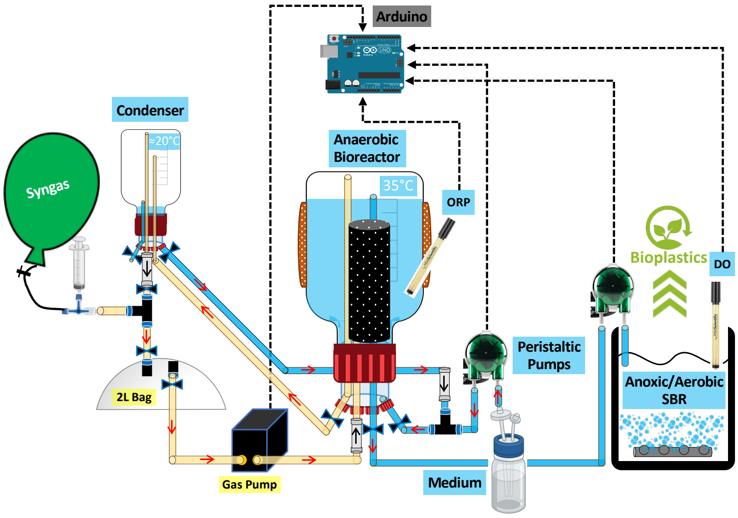

Figure 1. A simplified overview of the proposed complete set-up for the Gas-to-VFA-to-PHA biorefinery system

Results and Discussion

During the first tests of the gas fermentation part of the integrated system, which is considered to be the more challenging section in terms of structure due to the easily-permeable gasses existence, the bioreactor set-up has satisfied all critical expectations such as; maintaining stable temperature conditions, provision of no significant gas and liquid leaking, and supplying enough liquid mix via gas-bubbling. Those mentioned issues are quite critical for obtaining a COD (namely chemical oxygen demand) closed system which is required to obtain trustworthy results. COD was proposed and used to track chemical energy flow throughout the integrated biorefinery systems, since it is directly correlated to the chemical energy compound due to the stoichiometry of redox reactions (Torri et al., 2022).

During the first fermentation experiments with pyrolysis derived real syngas feeding at an average rate of 0.5 g-COD/L-day at 25 days of hydraulic retention time (HRT), it was succeeded to maintain a stable liquid COD around 7 g/L that is consisted of more than 70% of VFA. The VFA composition was mainly consisted of acetic acid (90%) together with some minor propionic, butyric acids at the end of 22 days of continuous fermentation experiment, which corresponds a perfect stream for the subsequential PHA-accumulation reactor. The critical point of this test was showing us that raw pyrolysis gas obtained from lignocellulosic biomass can be bio-utilized by acidogenic microbial mixed cultures (MMC) without any toxification or inhibition effect at continuous operation.

Conclusion

This study was shown that real pyrolysis gas (syngas) can be continuously bioconverted into acetic acid rich bioliquids, without any gas treatment prior to the fermentation, to be used as the carbon source of the PHA-accumulating bacteria.

Acknowledgments

The authors are gratefully acknowledging the financial support of TÜBİTAK for funding the presenting author's abroad research stay under the scope of 2214A fellowship program.

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