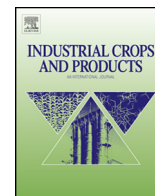




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Exploiting the potential of gas fermentation

Stephanie Redl^{a,1}, Martijn Diender^{b,1}, Torbjørn Ølshøj Jensen^a, Diana Z. Sousa^b,
Alex Toftgaard Nielsen^{a,*}

^a Novo Nordisk Foundation Center for Biosustainability, Technical University of Denmark, Hørsholm, Denmark

^b Laboratory of Microbiology, Wageningen University, Wageningen, The Netherlands

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ABSTRACT

The use of gas fermentation for production of chemicals and fuels with lower environmental impact is a technology that is gaining increasing attention. Over 38 Gt of CO₂ is annually being emitted from industrial processes, thereby contributing significantly to the concentration of greenhouse gases in the atmosphere. Together with the gasification of biomass and different waste streams, these gases have the potential for being utilized for production of chemicals through fermentation processes. Acetogens are among the most studied organisms capable of utilizing waste gases. Although engineering of heterologous production of higher value compounds has been successful for a number of acetogens, the processes are challenging due to the redox balance and the lack of efficient engineering tools. In this review, we address the availability of different gaseous feedstock and gasification processes, and we focus on the advantages of alternative fermentation scenarios, including thermophilic production strains, multi-stage fermentations, mixed cultures, as well as mixotrophy. Such processes have the potential to significantly broaden the product portfolio, increase the product concentrations and yields, while enabling the exploitation of alternative and mixed feedstocks. The reviewed processes also have the potential to address challenges associated with product inhibition and may contribute to reducing the costs of downstream processing. Given the widespread availability of gases, such processes will likely significantly impact the transition towards a more sustainable society.

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1. Introduction

There is an increasing demand for processes that reduce carbon-emissions and ensure carbon neutral and sustainable production of energy and commodities for the steadily growing population (Pachauri et al., 2014). Previous advances in the production of first generation biofuels have raised the feed vs. fuel debate. A promising technology that has gained increasing attention within recent years is gas fermentation, a process in which microorganisms anaerobically convert a gaseous substrate into biofuels and biochemicals. Several microorganisms have the ability to utilize CO₂ and CO as

energy and carbon source. Acetogenic bacteria are the most studied and have the greatest industrial potential, making use of the Wood-Ljungdahl pathway (WLP) to convert CO₂ (and CO). Compared to the Calvin-Benson-Bassham cycle, which is used by plants, algae, cyanobacteria, purple bacteria, and some proteobacteria, the WLP is a highly energy efficient CO₂ fixation pathway (Hawkins et al., 2013). Microorganisms employing the WLP are therefore relevant as biotechnological platforms for the production of biofuels and biochemicals from one-carbon compounds, and potentially decrease our dependence on fossil resources.

Metabolic traits of gas-fermenting bacteria have been reviewed recently (Daniell et al., 2016; Dürre and Eikmanns, 2015; Latif et al., 2014). The scope of this article is to assess the potential of gas fermentation and ways to exploit this potential. We would like to draw attention to alternative production scenarios, including multi-stage processes, co-cultures, mixotrophy, and thermophilic production strains. To date, pure cultures of mesophilic strains are deployed, with a focus mainly on ethanol, and on 2,3-BDO production. The aforementioned alternative production scenarios on the contrary would broaden the spectrum of products that can be produced from CO and CO₂. Additionally, it would be possible to explore combina-

Abbreviations: 3HP, 3-hydroxypropionic acid; 4HB, 4-hydroxybutyrate; ATP, adenosine triphosphate; BDO, butanediol; GHG, greenhouse gas; MEK, methyl ethyl ketone; MSW, municipal solid waste; NADH/NAD⁺, nicotinamide adenine dinucleotide; NADPH/NADP⁺, nicotinamide adenine dinucleotide phosphate; NETL, National Energy Technology Laboratory; PFOR, pyruvate:ferredoxin oxidoreductase; PHA, polyhydroxyalkanoates; VFA, volatile fatty acids; VSS, volatile suspended solids; WLP, Wood-Ljungdahl pathway.

* Corresponding author.

E-mail address: atn@biosustain.dtu.dk (A.T. Nielsen).

¹ These authors contributed equally.

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tions of different industrial feedstock streams (gas and sugar) and to take advantage of variable process conditions.

2. Feedstock availability

The present review focuses on the conversion of CO and CO₂ as carbon source by gas fermenting microorganisms. Hereby, CO serves as carbon source and electron donor. When CO₂ serves as sole carbon source, an additional electron donor is required. Below, we describe some of the sources of CO, CO₂, and electron donors, as well as their industrial availability.

2.1. Off-gases from industry, heat and energy generation

CO- and CO₂-rich waste gases are an attractive substrate for gas fermentation. Many industrial processes produce large amounts of carbon-rich gases that are often left unused, thereby contributing to elevated concentrations of CO₂ and CO in the atmosphere. In 2011, about 23% of the total CO₂ emissions were derived from industrial processes (van der Hoeven, 2013), the second largest sector contributing to CO₂ emissions, after electricity- and heat-generation installations. More than 40% of the CO₂ emissions in 2011 were derived from generation of electricity and heat (van der Hoeven, 2013), which worldwide relies heavily upon coal combustion (Gutmann, 2014). Overall, the anthropogenic CO₂ emissions account to 38 Gt/year (Edenhofer et al., 2014).

Industrial processes produce CO₂ emissions through chemical reactions that do not involve combustion, of which the following three sub-sectors are the main-contributors: iron and steel (27%), non-metallic minerals (27%), and chemicals and petrochemicals (16%) (International Energy Agency, 2007). For example, 60% of the CO₂ emissions from cement production come from inevitable chemical reactions in the process (Cement Sustainability Initiative, 2014). Those emissions cannot be prevented by heat and energy generation with renewables, thus alternative strategies for reducing GHG emission are required. According to the world steel association, 1.7 × 10⁹ t of crude steel were produced worldwide in 2014 (World Steel Association, 2015a) and 1.9 tons CO₂ are emitted per ton crude steel produced (World Steel Association, 2015b), which accounts to an annual CO₂ emission of 3.2 × 10⁹ t. In conclusion, large amounts of carbon rich off-gases are available and their conversion into chemicals and fuels has the potential to significantly decrease GHG emissions (Handler et al., 2015; Ou et al., 2013).

Off-gases from electricity and heat generation, as well as industrial waste gases are supposedly a substrate that comes free of charge. Currently, gas fermentation processes closest to commercialization are based on industrial waste gases (LanzaTech, 2016). However, not all waste gases are equally suitable for microbial gas fermentation, since there are demands with regards to the continuity of the gas stream, the carbon content, as well as the purity of the gas.

The CO and CO₂ content of the off-gas is dependent on the sector, but is also heavily dependent on process parameters and can therefore vary between production sites. For example, the off-gas from power plants contains only 3–4% (gas-fired) to 13–14% (coal-fired) CO₂, but process improvements such as chemical looping combustion and oxyfuel-technology (O₂-fired instead of air-fired) can increase the power-efficiency and the CO₂-content of the off-gas (International Energy Agency, 2014). The off-gases of other industrial processes contain high percentage of CO₂, for example the production of ethylene oxide emitting nearly 100% CO₂ (International Energy Agency, 2014). As it is the case for electricity and heat generation, the off-gas composition can be greatly influenced by the process parameters: for example, the CO₂ content of

cement kiln waste gas increases from <50% CO₂ (air-fired) to up to 100% when being O₂-fired (International Energy Agency, 2014).

2.2. Gasification of low-value carbonaceous materials to syngas

The availability of substrate for gas fermentation is broadened immensely when considering the amount of feedstock that can be converted into carbon- and energy-rich gas streams via gasification. Gasification is defined as the “thermo-chemical conversion of carbonaceous feedstock to gaseous products through a partial oxidation process at elevated temperatures” (Mohammadi et al., 2011). Besides fossil fuels, there is a broad range of more sustainable options: lignocellulosic energy crops such as willow, switchgrass, etc. can serve as feedstock for syngas production. The use of lignocellulosic energy crops has the advantage that their prices are “more stable as they only participate in the energy market” (Daniell et al., 2016). Also algae is an abundant biomass that is suitable as feedstock for gasification (Azadi et al., 2015).

Another option is lignocellulosic biomass waste, which is not suitable for food production or starch- and sugar-based production of chemicals and biofuels. The impact of this option is even more significant when taking into account that the lignin-fraction is not utilized in sugar-based production (both 1st and 2nd generation production). In wheat straw the lignin content is around 20% (Sheldon, 2014), and can be as high as 44.5% in some woody biomass (Vassilev et al., 2012). This kind of lignin-rich feedstock, suitable for gasification, accumulates as agricultural residues or as forestry by-products. Crop production (for food, feed, or production of 1st generation biofuels), generates large amounts of residue, with a residue/crop ratio of 1:1.4 for conventional crops (Kim and Dale, 2004). Another interesting source for lignocellulosic biofuels include residues from 2nd generation biofuels production. In the process of ethanol production from corn stover, for example, 5.9-times (by mass) more lignocellulosic residues are generated than ethanol (McAloon et al., 2000).

Municipal solid waste (MSW) or industrial waste could also serve as feedstock for gasification. A total of 251 × 10⁶ t of MSW was generated in the US in 2012 after annual increases during the last decades (U. S. Environmental Protection Agency, 2014). Especially those parts of the complex waste that are of organic origin possess great potential as starting material for gasification. Although their carbon content is high, with 13% by mass (Staley and Barlaz, 2009), they are currently left unrecycled. In particular, the biodegradation of the aforementioned waste fraction has been identified as one of the main challenges for direct exploitation (Drzyzga et al., 2015). Additionally, sludge from waste water treatment could act as potential feedstock for gasification, but is of lesser relevance, since its carbon-content is relatively low (Drzyzga et al., 2015).

The feedstock requirements for gasification technologies are generally considered flexible (Daniell et al., 2016). However, there are certain requirements, for example with regards to the moisture content of the feedstock (Piccolo and Bezzo, 2009). Additionally, the technology of large-scale gasifiers restricts the feed rate to around 2000 t per day (Griffin and Schultz, 2012). There are different gasification technologies available, and fluidized bed gasification is most suitable for large scale gas production, when taking throughput, costs, complexity, and efficiency into account (Alauddin et al., 2010; Mohammadi et al., 2011). The efficiency of conventional biomass gasification, when comparing the lower heating value of the produced syngas with that of the gasification feedstock, is around 85% for biomass and coal (Ptasinski, 2008). Currently, advances in biomass gasification technologies are made (Heidenreich and Foscolo, 2015), thus more efficient gasification technologies are likely to emerge.

The syngas composition depends on the feedstock (Tiquia-Arashiro, 2014), but can be greatly influenced by the gasification

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