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Anaerobic conversion of microalgal biomass to sustainable energy carriers – A review

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HIGHLIGHTS

- Microalgal biomass is amenable to anaerobic energy carrier production.
- The highest energy yields have been reported for ethanol and CH_4.
- The highest butanol and H_2 fermentation yields are still relatively low.
- Simultaneous and sequential production of several energy carriers is also considered.
- Energy yields from microalgae are similar to those from other feedstocks.

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ABSTRACT

This review discusses anaerobic production of methane, hydrogen, ethanol, butanol and electricity from microalgal biomass. The amenability of microalgal biomass to these bioenergy conversion processes is compared with other aquatic and terrestrial biomass sources. The highest energy yields (kJ g^{-1} dry wt. microalgal biomass) reported in the literature have been 14.8 as ethanol, 14.4 as methane, 6.6 as butanol and 1.2 as hydrogen. The highest power density reported from microalgal biomass in microbial fuel cells has been 980 mW m^{-2}. Sequential production of different energy carriers increases attainable energy yields, but also increases investment and maintenance costs. Microalgal biomass is a promising feedstock for anaerobic energy conversion processes, especially for methanogenic digestion and ethanol fermentation. The reviewed studies have mainly been based on laboratory scale experiments and thus scale-up of anaerobic utilization of microalgal biomass for production of energy carriers is now timely and required for cost-effectiveness comparisons.

1. Introduction

Biomass-based energy produced in microbial processes is one prospect of the sustainable supplements and alternatives to fossil fuels but has yet to reach its full potential. Advantages of photosynthetic biomass-based feedstocks (i.e., terrestrial plants, microalgae) include their carbon neutral CO_2 emissions and increased energy security and independence in regions without fossil fuel reserves. Microalgae have several advantages over terrestrial plants such as higher photosynthetic efficiencies, lower need for cultivation area, higher growth rates, more continuous biomass production, no direct competition with food production, and possibility to use saline waters and wastewater streams for biomass production (Schenk et al., 2008). Microalgae, like terrestrial crops, can be used in energy and fuel production in several ways. Microalgal biomass can be anaerobically processed to gaseous (methane, hydrogen) or liquid (alcohols) biofuels. Chemical and physical processes at high temperatures and in the absence of oxygen can produce bio-oil and bio-syngas. Further, dewatered biomass can be incinerated, and lipids can be extracted from the cells to produce biodiesel or renewable diesel. Biodiesel is considered by many to be an ideal fuel that can be derived from microalgal biomass because areal productivities of microalgal lipids are substantially higher compared to the most efficient terrestrial crops and because biodiesel can be used with little or no modification in diesel engines of motor vehicles (Schenk et al., 2008; Lam and Lee, 2012). However, recent life-cycle assessments indicate that microalgal biomass cultivation and use for biodiesel production consume more energy than can be harvested from the process (Lardon et al., 2009; Beal et al., 2012). For example, Lardon et al. (2009) demonstrated that the requirement to dry microalgal biomass prior to lipid extraction significantly reduces overall energy efficiency. Anaerobic conversion of algal biomass to energy carriers

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does not require cost-intensive drying of the biomass. In addition, high content of lipids, starch and proteins and the lack of recalcitrant lignin make microalgal biomass a promising substrate for anaerobic microorganisms (Schenk et al., 2008).

Different microalgal biofuel production processes and especially microalgal use in diesel production have been thoroughly reviewed (for reviews, see Chisti (2007), Schenk et al. (2008), Brennan and Owende (2010) and Lam and Lee (2012)). Previous reviews have not focused on many anaerobic processes such as dark fermentative hydrogen production and microbial fuel cells. The purpose of this review is to focus on recent research on anaerobic processes for conversion of microalgal biomass to sustainable energy carriers all of which are within the sustainable biorefinery concept. The current status of each anaerobic process is considered and possible integration of these processes is discussed. For comparison, selected examples of energy yields from other aquatic and terrestrial biomasses are presented.

2. Anaerobic digestion for methane generation

Anaerobic digestion of organic matter in the absence of terminal electron acceptors such as sulfate, nitrate or ferric iron produces methane (55–75 vol%), CO_2 (25–45 vol%) and fermentative metabolites. Anaerobic degradation is carried out by heterogeneous microbial populations involving multiple biological and substrate interactions. Anaerobic biodegradation can be divided into four main phases: hydrolysis, acidogenesis, acetogenesis and methanogenesis. Anaerobic digestion (sometimes also called methanogenic fermentation) is widely applied in digestion of manure, sewage sludge and organic fraction of municipal solid wastes in industrial and agrarian societies.

Anaerobic digestion of microalgal biomass has been studied from many freshwater and marine microalgae in various combinations. Ranges of process temperatures, reactor configurations, pretreatment methods as well as use of co-substrates are summarized in Table 1. The digestibility of microalgal biomass varies significantly even between closely related species (Mussgnug et al., 2010). CH_4 yields from microalgae vary due to variation in cellular protein, carbohydrate and lipid content, cell wall structure, and process parameters such as the bioreactor type and the digestion temperature. Theoretically, proteins, carbohydrates and lipids yield 0.851, 0.415 and 1.014 L CH_4 per g of volatile solids, respectively (Sialve et al., 2009). Chemical composition of microalgal biomass varies among microalgal species and even within the same species under different growth conditions (Sheehan et al., 1998). Thus, CH_4 production from microalgae should be examined under different experimental conditions to seek high growth yields and to determine optimal biomass composition for anaerobic digestion.

Rigid eukaryotic cell walls of microalgae can limit the anaerobic digestion of the biomass (Golueke et al., 1956; Chen and Oswald, 1998). Rates and yields of CH_4 formation from microalgal biomass often increase with digestion temperature. They can also be enhanced with pretreatment of microalgal biomass prior to digestion (Table 1). For example, Golueke et al. (1956) reported 5–10% increase in digestibility of microalgal biomass, when the digestion temperature was increased from 35 to 50 °C. Chen and Oswald (1998) increased the CH_4 yield by 33% by heat pretreating microalgal biomass at 100 °C for 8 h. In both examples, however, the amount of energy consumed in the heating and pretreatment was higher than the corresponding energy gain from increased CH_4 production (Yen and Brune, 2007; Sialve et al., 2009). Drying of microalgal biomass prior to digestion would also increase energy consumption and has been reported to reduce CH_4 yields (Mussgnug et al., 2010). These findings together with data on terrestrial plant materials (Lakaniemi et al., 2012b) indicate that pretreatment of microalgal biomass does not increase the energy gain of CH_4 production.

Biomass slurries of salt water algae contain sodium, calcium and magnesium ions that are inhibitory to anaerobic digestion at high concentrations. Methanogens are sensitive to excessively high salt levels but the susceptibility varies. Lakaniemi et al. (2011a) reported significantly lower CH_4 yields from NaOH-flocculated marine microalga *Dunaliella tertiolecta* than from chitosan-flocculated freshwater microalga *Chlorella vulgaris*. Mussgnug et al. (2010) reported similar or higher CH_4 production from marine microalga *Dunaliella salina* than from freshwater species. Factors affecting the level of inhibition of methanogenesis include biomass feedstock type and concentration, and source and previous growth history of microbial consortia in anaerobic digestion. Potential salt inhibition can be reduced by using cultures from saline environments and by successive enrichment at incremental concentrations of salt ions (Feijoo et al., 1995).

Microalgae cultivated under optimal growth conditions often contain high proportion of proteins. Consequently, the biomass has a relatively low C/N ratio, which may reduce digestibility and cause ammonium accumulation (Yen and Brune, 2007). C/N ratio can be adjusted to more optimal values with C-rich co-substrates such as cellulose (e.g., waste paper) (Yen and Brune, 2007) or glycerol (Ehimen et al., 2009). The C/N ratios of algal biomass can also be modified by selecting growth conditions that reduce cellular protein synthesis and favor lipid or carbohydrate production; an example is nitrogen limitation (Sheehan et al., 1998). High lipid content would increase the theoretical CH_4 yield, whilst it can also cause problems in the digestion due to adhesion of fat on cell surfaces. This leads to mass transfer limitations and unwanted flotation of digester biomass. Nitrogen limited cultivation would be useful for energetic balance and sustainability of microalgal biomass production because nitrogen fertilizer production consumes significant amount of energy (Hulatt et al., 2012). When normalized to surface area, microalgal biomass production requires substantially more nitrogen as compared to most terrestrial plants (Sialve et al., 2009).

Retention times required to obtain high CH_4 yields from untreated microalgal biomass are relatively long, 20–30 days (Ras et al., 2011; Zamalloa et al., 2011). Anaerobic digestion of microalgal biomass has been investigated in batch and fed-batch systems as well as in continuously stirred tank reactors (De Schamphelaire and Verstraete, 2009; Sialve et al., 2009). Zamalloa et al. (2011) suggested that anaerobic sludge blanket reactors, anaerobic filter reactors and anaerobic membrane bioreactors should be tested due to their high volumetric conversion rates. These processes have, however, been designed for wastewater treatment and high solids content of microalgal slurry may interfere with generation of anaerobic biomass and clog the membranes.

3. Dark fermentative hydrogen production

Many microalgae produce H_2 via photobiological pathways (for a review, see Levin et al. (2004)). Photosynthetic H_2 production, $2H_2O + \text{light} \rightarrow 2H_2 + O_2$, does not generate CO_2 and provides direct conversion of microalgal biomass to H_2. The hydrogenases involved in this reaction are relatively sensitive to high partial pressure of H_2 and O_2 and their activity is contingent on intact photosynthetic apparatus. The rates and conversion efficiencies of H_2 synthesis are considerably higher with dark fermentation than with the photobiological pathway. Dark fermentative H_2 production of biomass in anaerobic digestion is also more amenable for practical application (Levin et al., 2004; Levin and Chahine, 2010). The rates and yields of the photobiological H_2 production by microalgae are not comparable to anaerobic digestion systems because the process parameters are quite different. Therefore, only H_2 production studies where microalgal biomass has been used as a substrate for fermentative organism are included in this review.