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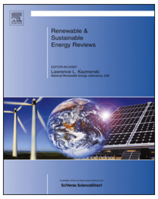

A review of methane production from agricultural residues in China

Kun Li [a,b], Ronghou Liu [a,b,*], Chen Sun [a,b]

[a] *Biomass Energy Engineering Research Centre, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China*

[b] *Key Laboratory of Urban Agriculture (South), Ministry of Agriculture, 800 Dongchuan Road, Shanghai 200240, PR China*

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ABSTRACT

Anaerobic digestion is an effective technology for resources recycling. The application of anaerobic digestion has been a hotspot due to its capability of converting solid organic waste into methane. The metabolism of acetoclastic methanogens, anaerobic digestion features and strategies of three main agricultural residues and current situation of large, medium biogas plant built in China are summarized, hoping to promote the application of this technology to deal with agricultural residues. Also, the current problems are presented and future research and development of biogas technology are proposed.

Contents

1. Introduction

China has abundant biomass resource which refers to residues and by-products of agriculture, forestry and other related industries, as well as the biodegradable fraction of industrial and municipal waste [1,2]. 21% of total biomass resource was occupied by agricultural residues which are associated with manure of

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* Corresponding author at: Biomass Energy Engineering Research Centre, School of Agriculture and Biology, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, PR China. Tel.: +86 21 34205744.
E-mail address: liurhou@sjtu.edu.cn (R. Liu).

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livestock, fruits and vegetable wastes produced during store, transportation and handling of vegetables, and lignocellulosic biomass such as rice straw, wheat straw, corn Stover, etc. [3–6]. They are biodegradable, rich in organic matter and can be used for methane production by anaerobic digestion [7]. In 2012, 846 million tons crops residues and 3.21 billion tons livestock manure were produced in China. If these wastes are utilized for anaerobic fermentation, 4.23×10^{11} m^3 biogas could be produced [8]. However, these resources have not been used efficiently. 72.5% of crop straw is combusted, lost or discarded, left only 0.5% for biogas production [9]. Besides, the uncontrolled decomposition of animal manures have caused serious environmental problems. Obviously, technologies for biomass utilization are urgently needed in China, either for energy or for environmental purpose.

Biomass can be converted to gaseous, liquid and solid biofuels by technologies like anaerobic digestion and gasification, pyrolysis and carbonization [10,11]. Compared with other bioenergy technologies, biogas technology is quite mature and has already been at its industrialization stage. Furthermore, biogas project combines together the ideas of ecological agriculture and recycle agriculture, and develops several practical agricultural production patterns like the "Pig-Biogas-Fruit" model in south China and the "Four in One" model in north China [12,13]. Extensive fundamental researches about biogas have also been conducted. For example, microbial community shifts during thermophilic methane fermentation, fermentation characteristics of crop straw pretreated by microbial community or steam explosion [14], and trace elements' stabilizing effects on long-term anaerobic digestion have been studied [15]. It has also been found that digested liquid swine manure can control soybean cyst nematode [16], and biogas fertilizer can improve the yield of cherry tomato [17].

However, understanding the process of methane fermentation is difficult because of various influence factors. The broad application of biogas technology is greatly limited by the disconnection of practical operation from its mature research status. So, in order to improve the practical efficiency of anaerobic digestion, to grasp the current study of anaerobic digestion for biogas production in China is necessary.

This article reviews the metabolism of methanogens and the present situation of biogas technology dealing with three main agricultural residues including livestock manure, fruit and vegetable waste (FVW) and lignocellulosic biomass in China. The current status of large, medium biogas plant built in China are also summarized. In addition, problems and recommendations for future development are put forward based on current situation of biogas technology, with the hope of improving anaerobic digestion efficiency and promoting the application of biogas technology in China.

2. Methanogens in anaerobic digestion

Methanogens are strictly anaerobic archaea and have limited substrate range. Thus the bioconversion of organic waste to methane generally needs the consortia of interacting microorganisms including fermentative bacteria, H_2-producing acetogenic bacteria and methanogens, and the final generation of methane by methanogens is the rate-limiting step.

Currently, two acetate-utilizing methanogens, *Methanosarcina* and *Methanosaeta*, are most explored among methanogens, partly because 70% methane in nature derives from methyl group of acetate [18]. *Methanosarcina* have one times larger genomes than obligate hydrogenotrophic methanogens, which reflects powerful metabolic capabilities. For example, it has the broadest substrate spectrum, acetate, methylated C_1 compounds and H_2/CO_2. The key enzymes for methane formation from acetate in *Methanosarcina* are the same with the ones of *Methanosaeta* except enzymes in the process of acetyl-CoA synthese. As a result, *Methanosaeta* has lower minimum threshold acetate concentration than *Methanosarcina*. While *Methanosarcina* species grow faster than *Methanosaeta* species when acetate concentrations are beyond 1 mM [19].

The methanogens population are not only affected by acetate concentration, but also by temperature [20] or substrate [21]. When temperature is increased within a certain range, methanogens can grow and multiply. Generally, mesophilic anaerobic digestion is more stable than thermophilic fermentation for lower ratio of free ammonia to total ammonium ion, as well as greater diversity and evenness of bacterial communities [22]. *Methanosarcinales* is a common major methanogenic order in mesophilic conditions [23], but in thermophilic reactor hydrgenotrophic methanogens dominated [24]. The order of *Methanosarcinales* only occupied a percentage of 10% in methanogenic population at temperatures of 55 °C, in which *Methanosaeta* was almost absent. Additionally, reducing digester feeding frequency can increase *Methanosarcina* predominance, and *Methanosarcina*-enriched reactor has better performance than *Methanosaeta*-enriched reactor [25]. In the industry application, *Methanosaeta* is important for the upflow anaerobic sludge blanket (UASB) reactor, due to its enhancing granulation [26] and attachment ability [27]. Hydrogenotrophic methanogens can tolerate the ammonium concentration of 6000 mg/L which is sixfold higher than the threshold ammonium concentration of *Methanosaeta* and twofold higher than that of *Methanosarcina* [24,28]. Therefore, the stable methane production when ammonia level increases may be explained by the increasing activity of hydrogen-utilizing methanogens.

Overall, several species of methanogens participate in the terminal steps of methane generation. They are high susceptible to the environmental conditions. As a result, anaerobic digestion process is fragile and highly sensitive to external influences. The prevalence of certain members of archaeal methanogens depends on physical and chemical conditions like temperature, pH, NH_3-N and VFA etc. The shifting of this anaerobic microbe community might influence the biogas yield as well as the stability of biomethanation.

3. The adaptability of substrate materials for methanogenic fermentation

The feedstock of anaerobic digestion is widely tolerant, but if the maximum biogas yield is expected to obtain, several factors should be concerned, including C/N ratio, substrate concentration, physical and chemical property of feedstock.

In terms of C/N ratio, low C/N ratio may lead to ammonia releasing [29], while methanogenesis inhibition also occurs when the ratio is high either due to nitrogen shortage or to organic acid accumulation caused by excess carbon [30,31]. As a result, various feedstock with various C/N should be matched properly to produce a proper ratio range, generally proposed 20/1 to 30/1 [32,33].

Substrate concentration refers to the proportion of total solids accounting for the reactor medium [34]. Proper solid content is important for biogas production. Too much water in the fluid can cause low organic loading rate and too little can lead to organic matter accumulation resulting in fermentation inhibition, both of which will decrease biogas yield. The substrate concentration capable of producing biogas is quite wide. TS content ranging from 1% to 40% [35], even to 55% is feasible [36]. In rural area of China, substrate concentration of 6–12% is generally adopted during anaerobic digestion [37].

Physically, anaerobic digestion can be divided into liquid anaerobic digestion (L-AD) and solid-state anaerobic digestion (SS-AD), with solid concentrations between 0.5% and 15%, and higher than