Hydrogen Production from Sewage Sludge by Biological and Thermochemical Process: An Overview

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Abstract

Hydrogen is a kind of clean effective resource. Sewage sludge is regarded as a promising material for hydrogen production because it owns a wide range of sources and the methods are consistent with the goal of sustainable development. This work summarizes existing hydrogen production technologies from sewage sludge, including photo-fermentation, dark-fermentation, sequential dark- and photo-fermentation, pyrolysis, gasification, and supercritical water gasification (SCWG). Overall comparison for the involving approaches is conducted based on their inherent features and current development status along with the technical, environmental, and economic aspect. Results show that sequential dark- and photo-fermentation and SCGW have improved hydrogen yields while the emissions of carbon dioxide are higher than those of other methods. Biological processes have an advantage in cost, but the reaction rates are inferior to those of thermochemical method. Enhancing methods and improvements are proposed to guide future research on hydrogen production from sewage sludge and promote the effectiveness both technically and economically.

Keywords: hydrogen production; sewage sludge; renewable resource; waste to energy

1. Introduction

Hydrogen as a promising kind of clean energy can be produced from both fossil fuels [1], and renewable resources, like biomass, wind energy and solar energy [2,3]. Currently, natural gas took the majority of hydrogen production (48%) by steam reforming method, followed by heavy oils and naphtha (30%), and coal (18%) [1,4–6], which indicates that present hydrogen production exhibits a high dependence on fossil fuels. To relieve the pollution and dependence on fossil fuels, renewable resources based hydrogen production technologies are attracting attention all over the world [2].

Due to the large amount of production [7,8], the disposal for sewage sludge, which is a kind of byproduct generated during wastewater treatment, has become another popular topic in recent years. Present options for sludge disposal include the agricultural usage [9], the waste treatment plants, landfilling, incineration [10] and construction reuse [11–13]. Although there exist various types of treatment options for sewage sludge, practical operation is still dissatisfactory and limited by the immature development of technologies, high investment, and incomplete on the relevant legislation [7,8]. If sewage sludge is discharged to the environment directly without fully treatment, it would result in serious secondary pollution because of the compositions of heavy metal [14], toxic pollutants, and pathogens [15,16]. Therefore, exploration of harmless disposal and recycling utilization for sewage sludge is necessary and significant, especially the latter which is consistent with the requirement of sustainable development.

Sewage sludge, a kind of biomass with a wide range of sources, can be applied to produce hydrogen [1]. The feasibility of this production approach has been recognized by many researchers from different perspectives, including anaerobic digestion [17], pyrolysis [18] and supercritical water gasification [19]. Various experiments were also carried out to figure out the optimal conditions of photo- and dark-fermentation [20,21]. Guo et al.[15] conducted a brief introduction of three main approaches of hydrogen production from sewage sludge, including biological fermentation, gasification, and supercritical water gasification approaches. The products from the thermochemical transformation of sewage sludge were studied by Manara and Zabaniotou [22], where hydrogen was a major product of the pyrolysis process. Nipattummakul et al. [23] conducted a series of steam gasification for sewage sludge aiming to investigate the compositions and major properties of the produced syngas. Since the only by-product of the production is CO_2, which is regarded to be neutral to the environment, hydrogen-rich biogas production from sewage sludge can be regarded as a highly clean method that effectively provides energy and disposes waste simultaneously [11].

As an emerging branch of hydrogen production, however, the maturity of many technologies is relatively low and relevant research is insufficient and incomplete. Although there has been a certain amount of research regarding several hydrogen production technologies from sewage sludge, most of them were only focus on one or some aspects of the specific technology.

To demonstrate the state-of-the-art developments and supply the scientific basis for the future research of sludge-to-hydrogen process, this work is carried out with a systemic overview regarding the complete process of sludge-based hydrogen production. A comprehensive introduction and relevant data of pretreatment and manufacturing techniques for hydrogen production from sewage sludge are carried out. The basic principles of operations and characteristics of different techniques are presented, and the strengths and weaknesses are analyzed respectively. Finally, a comparison is made based on the former analysis and propose possible directions for future improvement of sustainable hydrogen production.

2. Methodology and scope

According to the current articles on sewage sludge and hydrogen production, the Scopus [24] was applied to identify the articles characterized by these terms in their title, abstract, and keywords. The search results are shown in Figure 1 classified by their publication year.

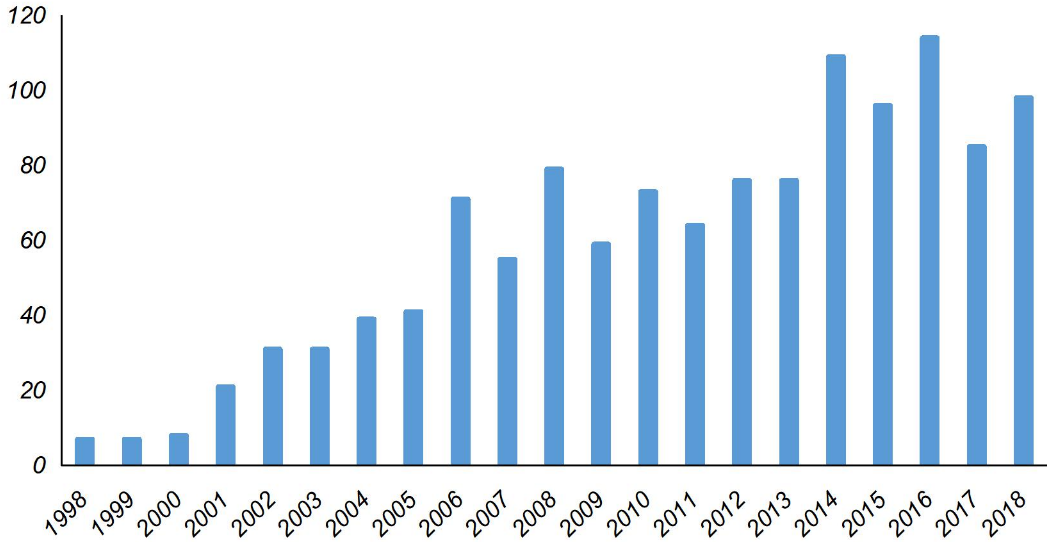


Figure 1 Publications on sewage sludge and hydrogen production by Scopus [24] since 1998

The increasing trend of research on this topic reveals the fact that the huge study potential existing in this domain has been gradually recognized by the academics. However, the review work for this topic is limited, with only 1.9% of the total literature based on the results from Scopus [24]. Hence, it is necessary to provide a comprehensive overview of the current work of hydrogen production from sewage sludge.

This study focuses on describing the basic process and major features of existing hydrogen production method from sewage sludge and exhibiting their merits and shortcomings under current state of art, aiming to guide the development of future manufacturing and research. Since it is an emerging technology, this review is conducted not only based on the literature of sludge as material to produce hydrogen, but also some overviews regarding hydrogen or biogas production to cover the possible approaches as comprehensively as possible.

3. Development of the sludge-to-hydrogen production technologies

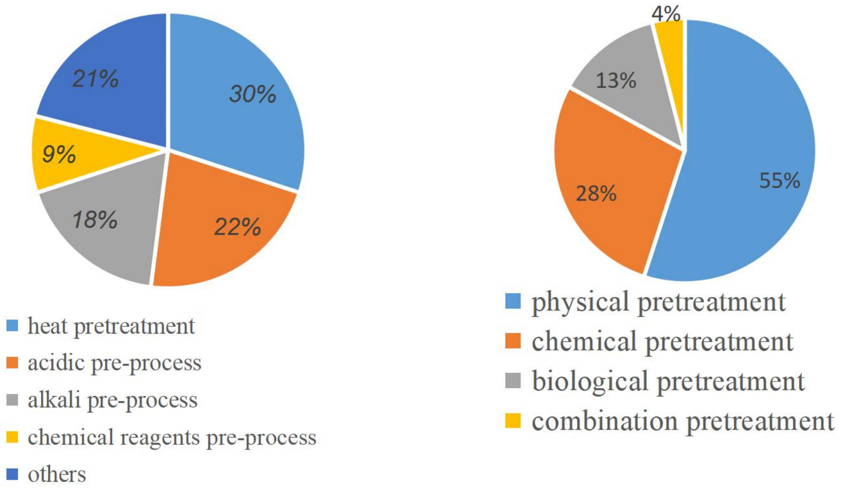
The various treatment process which is feasible for hydrogen production from biomass can apply to sewage sludge as well. The major process techniques for sewage sludge include biological methods and thermochemical approaches. Supercritical water gasification (SCWG) as a technology with unique advantages has also caused researchers' attention. These three categories will be introduced in detail in the following parts.

3.1. Biological process

Hydrogen production from sewage sludge by biological technology mainly refers to two methods – photo-fermentation and dark-fermentation. Both methods convert organic materials, such as glucose and acetic acid, into bio-hydrogen, carbon dioxide and some other volatile fatty acids (VFA) by the bacterial colony or algae under different conditions. Besides individual fermentation process, sequential dark- and photo-fermentation have also been proved to have an outstanding improvement on the hydrogen production [25,26].

3.1.1. Pretreatment methods for anaerobic digestion

The pretreatment methods of sewage sludge, usually seed sludge or waste activated sludge [27–29], are carried out for producing hydrogen by anaerobic digestion to inhibit the activity of Hydrogen-consuming bacteria (HCB) and improve the yield of H_2 from Hydrogen-producing bacteria (HPB) [29]. Physical/mechanical pretreatments, chemical methods, thermal options, biological process, and thermochemical techniques are the five sorts belong to the major pretreatment technologies [29,30]. Application proportion of different pretreatment methods has been shown in Figure 2.



(a) pretreatment for HPB enrichment (b) pretreatment for substrate sludge

Figure 2 Application proportion of major pretreatment methods. (modified from [31])

Physical/mechanical Pretreatment

Physical or mechanical pretreatment technologies mainly limit the activity or eliminate HCB by physical ways. This category includes ultrasonication, microwave (especially ultraviolet) irradiation, aeration, freeze and thaw, electro-kinetic disintegration, and high-pressure homogenization [29,30]. The former four technologies are frequently used in sludge pretreatment for hydrogen generation. Ultrasonication is a developed technology in this category and the core thought is to promote the process for the break-up of sludge flocs and the liberation of intercellular material [30] and destruction of cell walls of HCB. To prevent the same damage on HPB, the duration and strength of pretreatment should be well controlled [32,33]. Effects of sterilization, microwave, and ultrasonication on sludge pretreatment for hydrogen generation were investigated by Guo et al. [34]. Researchers have proved that ultrasonication method could improve the anaerobic digestion of sewage sludge significantly [35]. The maximum hydrogen production obtained by this approach was

1.03 mol H_2/mol glucose, i.e. 8% of the theoretical value that can be gained from 1mol of glucose, which can be seen from Eq.(1) [29].

$$C_6H_{12}O_6 + 6H_2O \rightarrow 12H_2 + 6CO_2 \quad (1)$$

This indicates that further optimization for this approach is required. Future research could take the strength of ultrasonic wave, operation duration, the usage of chemicals and heat control into consideration to improve the yield of hydrogen and decrease the energy consumption.

Microwave irradiation is a common option in conditional heating (CH) technology. The damages to sludge sell caused by microwave irradiation have been investigated in the study of Zhen et al. [30]. Ultraviolet irradiation is a method used to pretreat the sewage sludge for hydrogen production among the diverse microwaves. After 15 min of ultraviolet irradiation, which is the recommended condition, the method has a considerable influence on eliminating HCB and methanogens and increasing the production of hydrogen to 0.39 fold when compared with the yield from untreated sludge [29]. However, this approach is not efficient enough because the microwave is only accessible to the sludge in smaller granules with light color, which leads to the HCB being protected by the larger and darker sludge particles [29,36]. Therefore, this method could be combined with other pretreatment techniques to improve the effectiveness.

Deactivating anaerobic HCB and reducing oxygen sensitive methanogens by oxidative stress, aeration is regarded as an ineffective pretreatment method due to the relatively low yield. The main weakness of this technique is that it destructs HCB and brings damages to obligate anaerobic HPB and facultative HCB simultaneously [29].

Freeze and thaw process handles seed sludge through freezing and thawing under extreme temperature. Experiments have shown that the yield of H_2 from this way is the lowest one, with only 0.15 mol H_2/mol glucose. The negative influence on the bacterial activity of HPB makes the freeze and thaw method not a valid one to increase the production of hydrogen [29].

Chemical Pretreatment

Chemical pretreatment methods mainly include pH treatment (acidic and alkali pre-process), chemical activation and inhibition, and oxidation. The first two methods have been applied to improve the yield of hydrogen production from sewage sludge, while the last one is mainly implemented in methane recovery [29,30].

By applying acid or alkali, the pH of sludge is adjusted to an extreme value (e.g. pH 3 or 12) to reserve HPB and lyse HCB. Due to the difference of the reactions of HPB and HCB toward extreme pH, HPB can be well protected by spores and survive while most HCB does not have such a defense mechanism, which leads them to be eliminated [29,37–40]. Experiments have shown that compared to alkali pretreatment, process with acid is more effective on improving the production of hydrogen from seed sludge (1.67 times of the hydrogen's yield from seed sludge treated by alkali) [29]. An obvious disadvantage of this method pointed out by Zhen et al. [30] is that special equipment is needed for the extreme pH during the operation.

Chemical activation and inhibition uses a proper substrate or medium to spike or impact sludge, aiming at enhancing the performance of HPB. It has a relatively high application value when enriching selective HPB and thermophilic HPB [29,41]. The major shortcoming of this method is that it is not feasible for the common situation where the particular medium or substrate for the targeted HPB cannot be recognized [29]. On the other hand, some toxic chemicals, which can inactivate HCB, also destruct HPB [29]. Meanwhile, the negative influence is obvious toward human being and the total environment as well. It is challenging to find access to balance the production propose and environment protection as for chemical method. Thus, it is still an issue under discussion that whether it is worthwhile to apply this method to produce hydrogen.

Heating Pretreatment

Heating pretreatment, or thermal hydrolysis is regarded as one of the most frequently used physical methods. It can effectively eliminate HCB with relatively low investment and bring a considerable improvement on the yield of hydrogen. Plenty of studies have shown the huge potential of this method on processing seed sludge, that is not only successfully eliminate HCB, but also enhance the reduction of chemical oxygen demand (COD) to a great extent [29]. Mu et al. [42] tested the hydrogen yield from sewage sludge processed through heating, acid and alkaline approach respectively and proved that heat-treatment had a better performance than the other two methods. The major challenge is to find out the optimal alternative of heating temperature and operation time-length to maximize the yield of hydrogen. Wong et al. [29] proposed the changes of hydrogen production from sludge pretreated by heating and found out that seed sludge is more likely to be suitably pretreated by moderate temperature for relatively long time (65 ℃ for 30min) or a little high temperature with a short period (100 ℃ for 15min) to guarantee the complete elimination of HCB. However, the yield of hydrogen still depends on various factors, especially the sludge source which leads to the difference of bacteria species. Hence, figuring out the categories of HCB and HPB to determine the optimal conditions of temperature and heating period could be one of the research topics for future work.

Combined Pretreatment

Mechanical and chemical pre-process technologies can be combined to enhance the enrichment of HPB and eliminate HCB. Wong et al. [29] made a comparison of different pretreatment combinations, such as repeated heating and combinations of several technologies. Some combination pretreatments have a significant improvement on the hydrogen production compared to individual pretreatment, especially heating coupled with pH pretreatment or ultrasonic, which is at least twice production as that sludge treated by a single method. When pretreated by individual approach is insufficient, combination pretreatment can be regarded as an alternative to continue the process of HPB enrichment.

Other pretreatment methods, including electro-kinetic disintegration, high-pressure homogenization (HPH), oxidation technologies and biological pretreatment, are emerging technologies with various uncertainty and limited awareness. Some of these methods are used for methane production from sewage sludge while the application for hydrogen production is rare. Future research may attempt to explore the effectiveness of these new methods for hydrogen production from fermentation using sewage sludge.

3.1.2. Photo-fermentation

Photo-fermentation is a kind of biological process happened in photosynthetic bacteria. Using organic acids or VFA as substrate, photosynthetic non-sulfur (PNS) bacteria can produce hydrogen with carbon dioxide as a byproduct. Carbon sources, such as glucose, also can be used for hydrogen production by PNS bacteria [20]. Major photosynthetic organisms include oscillaria, Rhodospirillum rubrum [15], Rhodopseudomonas spheroids O.U001, and Rhodopseudomonas palustris [20]. Eq. (2) shows an example of hydrogen generation using acetic acid by photo-fermentation [20].

$$CH_3COOH+2H_2O \rightarrow 4H_2+2CO_2 \quad (2)$$

The core mechanism of hydrogen producing by photosynthetic microorganisms can be briefly described in Figure 3 [15]. Nitrogenase and hydrogenase enzyme play a nonnegligible role during the bio-hydrogen production. A detailed description of the mechanism of photo fermentation can be found in the study of Hay et al. [43].

Photo fermentation is strongly stimulated by the sunlight under anaerobic conditions [20,43]. Therefore, sufficient surface area for enough sunlight absorption and strict anaerobic environment are required to guarantee the normal photo fermentation process.

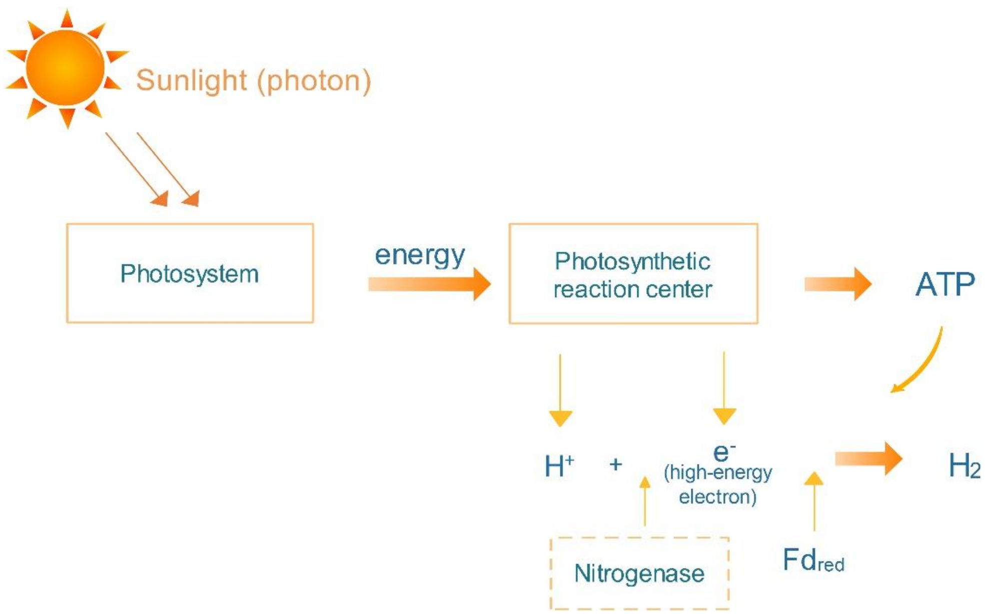


Figure 3 Flow diagram of the photo-fermentation process

Operation conditions control is nonnegligible for effective hydrogen production by photo fermentation. Besides abundant sunlight and anaerobic environment, pH value, temperature and the contains of some metal elements which are necessary for the nitrogenase enzymes to form H_2, are also important factors to consider [20]. The control of nitrogen source is essential due to the possible inhibition (recorded that even 20 μm of ammonia has influence) on nitrogenase enzyme to producing hydrogen effectively. The optimal ranges of some key parameters to reach a higher yield of hydrogen are listed in Table 1.

Table 1 Optimal ranges of some important factors through photo-fermentation [20]

Factor	Optimal Range
pH	6.8-7.5
Temperature	31-36℃
Wavelength	400-1000 nm
Light intensity	6-10 klux

Malate/glutamate ratio	≥ 1
VFA concentrations	1800-2500 mg/L

The assessment for the performance of photo fermentation of PNS bacteria includes two aspects – hydrogen production and light efficiency. The optimal H_2 yield ratio was recorded as 80% while the light efficiency was only between 0.2% and 9.3% [20]. Light energy has a great contribution to the process taken place in photo-bioreactors. Enhancing the efficiency of light converting into hydrogen is the major propose for future study [20,44].

Photo-fermentation can be further classified into batch, continuous and fed-batch photo-fermentation due to the differences in operation process. Batch photo-fermentation has caused extensive concerned in recent years, in which hydrogen is generated from various substrates. Research on hydrogen production under continuous photo fermentative condition is quite limited, because the considerable quantity of studies realizes continuous fermentation by two-step fermentation. Fed-batch operation denotes that the photo-fermentation is conducted through fed-batch under high cell density. Relevant research on fed-batch is insufficient. These three operation methods have been reviewed by Argun and Kargi [20]. Some examples of the yield of hydrogen production from photo-fermentation have been listed in Table 2.

Table 2 Examples of hydrogen yield from photo-fermentation [20,43]

Substrate	Micro-organisms	Process (Batch - Y or others)	Hydrogen production

			H_2 content (%)	Yield (mol H_2/mol substrate)	Yield coefficient (%)[a]
Brewery wastewater	Rhodobacter sphaeroides O.U.001	Y	90%	0.009	-
Dairy wastewater	Rhodobacter sphaeroides O.U.001	Y	≥90%	0.308	-
Olive mill wastewater	Rhodobacter sphaeroides O.U.001	Y	-	0.559	-
Olive mill wastewater	Rhodobacter sphaeroides O.U.001	Y	-	1.267	-
Olive mill waste water	Rhodobacter sphaeroides O.U.001	Y	98%	0.670	-
Soy sauce wastewater	Rhodobium marinum (Sanur)	Y	60%	0.107	-
Glucose	Rhodobacter sphaeroides	Y	-	110 mL H_2/h glucose	6.6%
Glucose	Rubrivivax gelatinosus	Y	-	1.1	9.2%
butyrate	ZX-5	Y	-	118 mL H_2/(L h)	-
DL -Malate	Rhodobacter sphaeroides OU 001	Y		4.45-4.55	75%
carbon monoxide and water	R. rubrum. A 2 L	Continuous		397.5 mL H_2/h	80%
Acetate	Rhodopseudomonas faecalis strain RLD-53	Fed-batch		3.17mol/h (highest)	80%

a: the ratio of produced to the theoretical maximum

Photo-fermentation has obvious drawbacks, such as sufficient surface area required for light absorption [1], sensitive to oxygen and quite long duration. Nevertheless, researchers still made efforts to improve the hydrogen production from various bacteria cultures and substrates by photo-fermentation. Ike et al. [45,46] found that Lactobacillus amylovorus could convert starch glucose into lactic acid, and then lactic acid could be transformed into H_2 by rhodobacter sphaeroides, obtaining 5mol H_2 obtained from 1mol starch glucose. It could generate a considerable amount of hydrogen and omit the pretreatment for sewage sludge which contributes to reducing the investment simultaneously [15]. Hay et al. [43] also reviewed some hydrogen yields from different waste, including POME, olive mill wastewater, and tofu wastewater. Dasgupta et al. [44] developed a method to reduce the pigment content in bacteria, improve the efficiency of nitrogenase enzyme and decrease the absorption of hydrogenase enzymes. Therefore, there is still a wide space for the development of photo fermentation.

3.1.3. Dark-fermentation

Dark-fermentation denotes that bacteria degrade carbonhydrates (mainly glucose) and generate hydrogen accompanied with VFAs and CO_2 [20] under the functions of nitrogenase or hydrogenase enzymes under dark, anoxic conditions [15]. Organic matters, like formic acid, pyruvic acid, and other short-chain fatty acids, are also common substrates for dark-fermentation [15]. Some widely used cultures for this process include spore forming Clostridium species (e.g. Clostridium butyricum) [15], Bacillus sp, and various thermophile microorganism [20]. Selecting glucose as the substrate, the related reactions can be expressed as Eq. (3) and Eq. (4). The major procedures of dark fermentation are described in Figure 4.

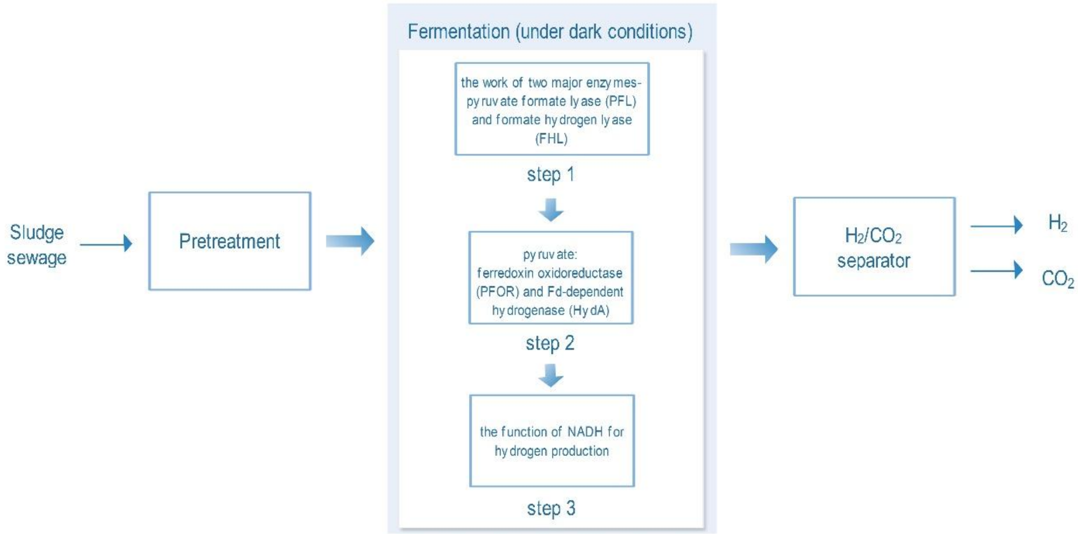


Figure 4 Flowchart of the dark fermentation for hydrogen production from sewage sludge (modified from [1,43])

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \quad (3)$$

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CH_2COOH + 2H_2 + 2CO_2 \quad (4)$$

Eq. (3) is the reaction for acetate fermentation while Eq. (4) represents the principle of butyrate fermentation [1]. The butyric acid formation is usually accompanied by the acetate fermentation. The theoretical yield of hydrogen when both of the two reactions exist simultaneously is 2.5 mol [20,47].

Dark-fermentation faces the challenge caused by HCB which have a significant influence on the production of hydrogen from the mixed cultures. Therefore, the pretreatment method, as it has been mentioned before, is necessary to conduct this process. When discussing the yields of different dark-fermentation approaches, taking the pretreatment techniques into consideration is important.

Except for the pretreatment method, the process of dark-fermentation is also affected by inoculum, substrate, reactor type, nitrogen, phosphate, sulfur, iron, temperature, and pH [20,48]. In fact, the influence of different factors toward the fermentation process depends on operation conditions. Many researchers have made the attempted to figure out the optimal range for hydrogen production, but sometimes they may draw a completely opposite conclusion due to the interactions between the various parameters. For instance, pH ranging 5.5-6.5 was considered as the best extent [49–51] because hydrogen is generated at acidogenic stage; while Zhao et al. [52] believed that controlling the pH value at 10 could contribute to avoiding the generation of propionic acid and inhibiting the activity of HCB when activated sludge was applied as substrate [20]. Anyway, acid base environment plays an essential role during the process of dark-fermentation. The optimal ranges of some other important factors have been presented in Table 3. More detailed analysis of the influence of these parameters was referred to the study of Wang and Wan [48].

Table 3 Optimal ranges of some important factors through dark-fermentation [20]

Factor		Optimal range	Remark
Temperature	mesotherm	25-40℃	More widely used due to less energy requirement
	thermophile	40-65℃	Higher H_2 yield due to the effective inhibition on the activity of HCB
	Hyper-thermophile	>80℃	-
Oxidation-reduction potentials (ORP) (for Clostridium sp.)		-200- -250mV	Range out of this may lead to an unsuitable environment for HPB
COD/N		11.4/1-200/1	-
COD/P		73/1-970/1	-

Hydrogen generation rate and the total yield are the two basic indices for choosing the most suitable culture of bacteria in dark fermentation [20]. Hydrogen formation rate refers to the quantity of hydrogen generated per unit time. The hydrogen yield in per unit volume or per unit biomass is two other production rates which are called volumetric rate and specific rate respectively [20,53].

Similar to photo-fermentation, dark-fermentation also has three specific handing methods - batch, continuous and fed-batch fermentation. Among these three approaches, batch dark-fermentation is the most frequently used one, although it is usually limited by the types of substrates and low production rate [20]. Studies on dark-fermentation are more than those of photo-fermentation. Besides applying simple sugars for bio-hydrogen production, which are regarded as relatively expensive substrates, the yields of hydrogen gas from waste and sewage sludge were also investigated by previous research. Several data about hydrogen yields by dark-fermentation from sewage sludge are shown in Table 4.

Table 4 Examples of hydrogen production through dark-fermentation from waste [20]

Substrate, inoculum culture	Process	Hydrogen production		Reference
		Total yield (mol H_2/mol glucose)	Generation rate	
Vegetable waste with sewage	Batch	25.2-26.4 mol H_2/kg COD	About 20 mmol /day (highest)	[54]
Heat pretreated anaerobic sludge, corn stover	Batch	3.0	275 mL H_2/(L h)	[55]
Heated pretreated anaerobic sludge, sucrose	Batch	1.06±0.05	73-75.4 mL H2/(g VSS)/h	[56]
Carbohydrate rich organic wastewater, pretreated anaerobic	Batch	2.53 mol H_2/mol sucrose	-	[57]

sludge				
Cheese processing wastewater, heat pretreated anaerobic sludge	Continuous	22mmol H2/g COD corresponding to 590 mL H_2/g glucose	62.3 mL H_2/(L h)	[58]
Waste sugar media, 20 L CSTR inoculated with anaerobic sludge	Continuous	1.78	-	[47]
AGSB fed with starch, anaerobic sludge	Continuous	0.83 (highest)	(corresponding to highest yield) 700 mL H_2/(L h) (lowest rate)	[59]
Boiled waste WP	Fed-batch	3.1	36 mL H_2/h	[60]

Note: CSTR: continuous stirred tank reactor; AGSB: agitated granular sludge bed reactor; WP: wheat powder

Compared with hydrogen production through photo-fermentation, dark-fermentation has more advantages over many aspects [15]:

- HPB for hydrogen producing by dark-fermentation show better performances than that of microorganisms for photo-fermentation.
- The process is simple without requirement for light. Hence, the production can continuously proceed stably day and night. Meanwhile, the design for related equipment, operation and management can also be simplified.
- Hydrogen production equipment can be large enough to improve the yield of each equipment. On the other hand, transportation and conservation of facultative bacteria for hydrogen production by fermentation are more convenient.
- Materials, such as sewage sludge and other waste with a wide range of sources, can greatly reduce the investment of industry.

Thus, the industrialized and formalized production of hydrogen through dark fermentation is more promising and easier than that of photo fermentation.

However, the major limitation for further development of this method is low hydrogen yield. Many efforts were made by plenty of researchers to improve the performance of dark fermentation. Datar et al. [55] and Lee et al. [61] observed that the production rate of hydrogen could be significantly increased when substrate (glucose and starch) concentration had a considerable improvement, but it should not exceed a proper range because of the accumulation of suppressive VFAs in the process. Wu et al. [62] investigated the hydrogen yield from immobilized sewage sludge and obtained the highest production rate as 0.93 L/h/L with 2.67 mol H_2/mol sucrose as the best yield. Many reports recorded that sludge co-digesting with other materials can obviously improve the activity of HPB and increase the yield of hydrogen. The materials applied to co-digestion with sewage sludge are classified into two categories – municipal solid waste (MSW) where food waste is the main part [63,64], and agriculture solid waste [31]. Kim et al. [17] explored the viability of producing H_2 through sludge co-process with food waste. Wang et al. [31] listed a table to analyze hydrogen production of different ratios of mixtures. Membrane cell recycles reactor (MCR) also could be used together with a CSTR to obtain a higher hydrogen generation rate through continuous dark-fermentation [61]. Zheng et al. [65] performed an "activated sludge – biological film" hybrid anaerobic baffle reactor (ABR) hydrogen production system and found that the yield of hydrogen reached a peak with 44.75 L/d when inflow COD was about 3500 mg/L.

Hydrogen production by biological approach remains in the experiment stage. This mainly reflects from the following basic facts: i) major source of natural anaerobic bacteria species is limited to activated sludge; ii) carbohydrate is still most frequently used hydrogen donor; iii) many studies concentrated on the immobilization technology for cell and enzyme [15]. More investigations need to be conducted to realize the industrialization for hydrogen production by biological method.

3.1.4. Sequential dark- and photo- fermentation

Using the products from dark-fermentation (VFAs) as the substrates for photo-fermentation, a hybrid system can be developed which combines the advantages of both biological methods and improves the total yield of hydrogen. The reactions of two-step fermentation can be described by Eq. (5) and Eq. (6) [1]. These principles take the dark-fermentation which generates acetic acid as an example. The theoretical yield of hydrogen of the hybrid process improves to 12 mol/mol glucose (see Eq. (1)).

Stage I – dark-fermentation:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2 \qquad (5)$$

Stage II – photo-fermentation:

$$2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2 \qquad (6)$$

The basic procedures of sequential fermentation are shown in Figure 5 [1,20]. Usually, the pretreatment methods used before dark-fermentation include acid hydrolysis (type I in Figure 5). Dark-fermentation can also be conducted together with bio-hydrolysis step, followed by photo-fermentation for hydrogen production (type II in Figure 5). It is also possible to proceed direct photo-fermentation after the acid hydrolysis process (type III in Figure 5).

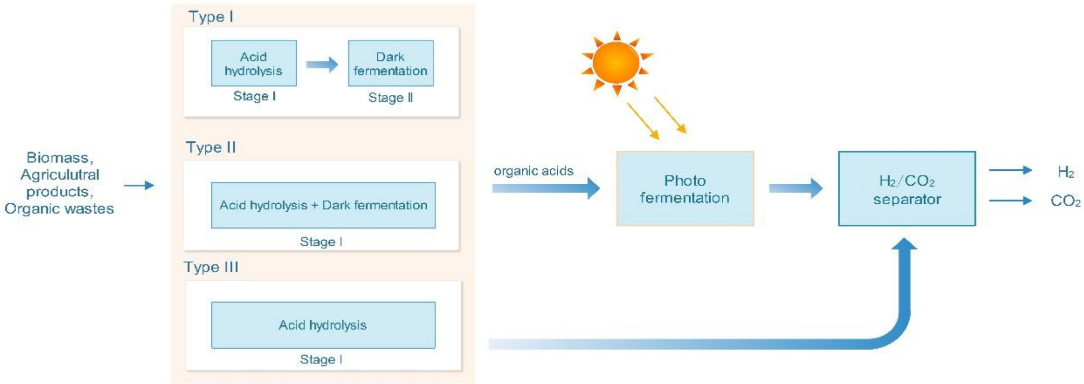


Figure 5 Flowchart of three different types of sequential dark- and photo-fermentation

Temperature, pH value and major properties of dark-fermentation effluent (DFE) have considerable impact on hydrogen yield. The increase of temperature can improve the yield of hydrogen, and the pH should be controlled within 4.5-6.5 and above 7 for dark-fermentation and photosynthetic process respectively [1,66]. The total volatile fatty acid (TVFA) of DFE should be reduced below 2500 mg/L and the concentration of NH_4^+ should below 40 mg/L. In addition, residual glucose also put adverse force on the H_2 yield rate during dark-fermentation. Therefore, DFE has to go through the treatment in order to meet the certain conditions for ammonia, glucose, and VFA to realize effective hydrogen gas production by subsequent photo-fermentation [20].

Although the theoretical total amount of H_2 from two-step fermentation is considerable, the output in practice is still far from the ideal value because of the generation of VFAs compounds and the employment of portion of the feedstock for

PHB's cultivation [20]. The maximum yield obtained by Yokoi et al. [67] was 7.2 mol H_2/mol glucose, while the total yield at least reaches 8 mol H_2/mol glucose could be regarded as an economically feasible pathway [20,68]. Chen et al. [68] proposed that a combination system, which has optimal conditions for dark-fermentation and a novel photobioreactor for photo-fermentation, could ultimately reach a total yield of hydrogen by 7.88 mol H_2/mol sucrose. Information regarding hydrogen generation through two-step fermentation from waste and pure carbon sources have been briefly presented in Table S1 in the Supplementary Information, where the overall yields of hydrogen are much higher than those from single dark-fermentation, but the generation speeds in two-step fermentation are inferior to the latter. This means that PNS bacteria needs a longer period to realize effective conversion of VFAs to hydrogen [20]. Nevertheless, the considerable improvement in conversion efficiency and reduction of the negative influence of untreated fermentation effluents toward the environment are still attractive. Present studies mainly focus on the single carbohydrate as substrate to produce hydrogen by two-step fermentation. Further research can attempt to test hydrogen production by sequential fermentation from food waste and pretreated sewage sludge for dark-fermentation.

3.1.5. Combined dark- and photo-fermentation

This approach means to conduct dark- and photo-fermentation simultaneously in the same equipment, where VFAs generated from the former process are directly utilized by photo-fermentation. Still, the theoretical yield of hydrogen from single glucose as substrate is 12 mol (see Eq.(1)). Existing studies on hydrogen formation by this method are limited, so does the discussion and analysis for the application of sewage sludge. Thus, detailed information about this pathway is not provided here. Further description of this approach can be obtained by the research of Argun and Kargi [20] and Rai and Singh [69].

3.2. Thermochemical process

Thermochemical process for sewage sludge to produce hydrogen or hydrogen-rich gas mainly consists of pyrolysis and gasification. During the process, hydrogen is generated together with some other gases, like CH_4 and CO [23,70], which can be further processed by steam reforming method and water gas shift (WGS) aiming to obtain more hydrogen yield [1]. Hydrogen-rich gas production through this method could have an outstanding contribution toward the sustainable development due to the elimination of greenhouse gases emission [1,71]. In addition, thermochemical pathways have obvious advantages over that of biological methods, such as high conversion efficiency and ease of management. Apart from pyrolysis and gasification, combustion and liquefaction also belong to this category. However, the latter two methods are regarded as less effective ways to produce hydrogen due to the low yield and strict operation conditions [1,72]. Hence, this section focuses on sludge as material for hydrogen production through pyrolysis and gasification, related analysis for combustion can refer to the studies of Syed-Hassan et al. [73] and Magziara and Werle [74].

3.2.1. Pyrolysis

Operation temperature varying from 300 ℃ to 900 ℃, pyrolysis is a thermochemical process of degradation for chemical molecules of fuel in an inert environment, accompanied by the formation of liquid oils, gaseous products, and solid char [22]. The generation of methane and water vapors during the process can be further treated by steam reformation and WGS reaction for more hydrogen production. The typical reactions occurring in this treatment are described by Eq. (7) – Eq. (9) [1]. Figure 6 shows the basic pyrolysis mechanism of sewage sludge.

$$\text{pyrolysis of sludge sewage} \rightarrow H_2 + CO_2 + CO + \text{hydrocarbon gases+tar+char} \quad (7)$$

$$C_nH_m + nH_2O \rightarrow nCO+(n+\frac{1}{2}m)H_2 \quad (8)$$

$$CO+H_2O \rightarrow CO_2+H_2 \quad (9)$$

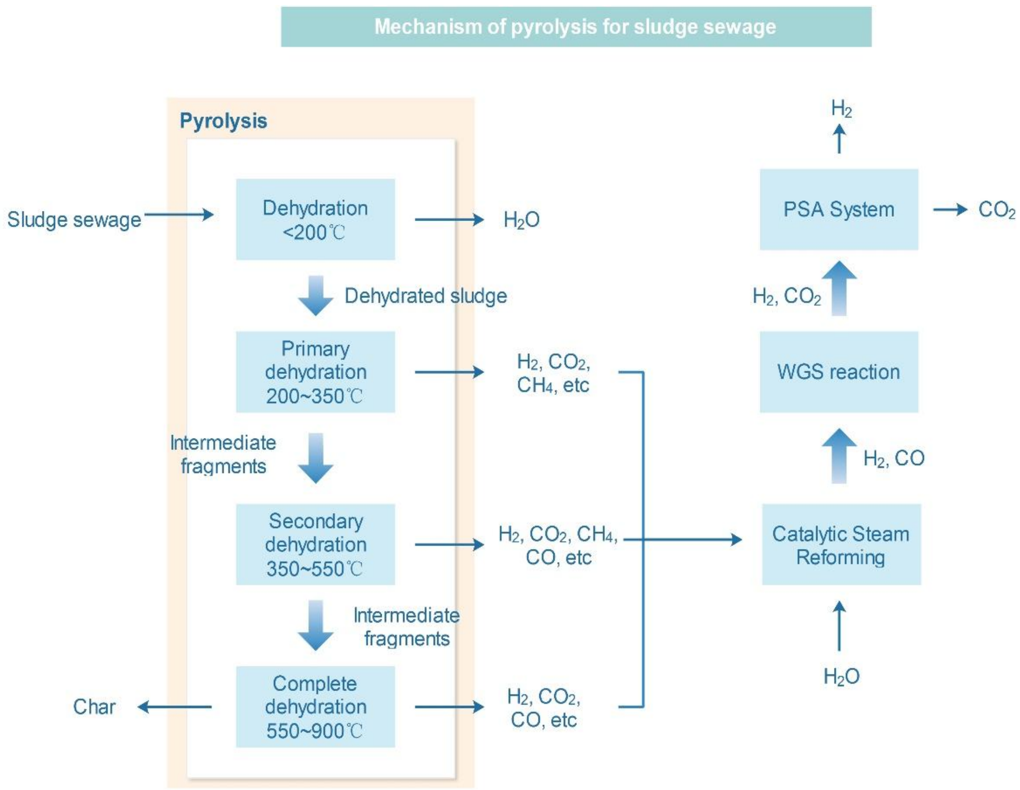
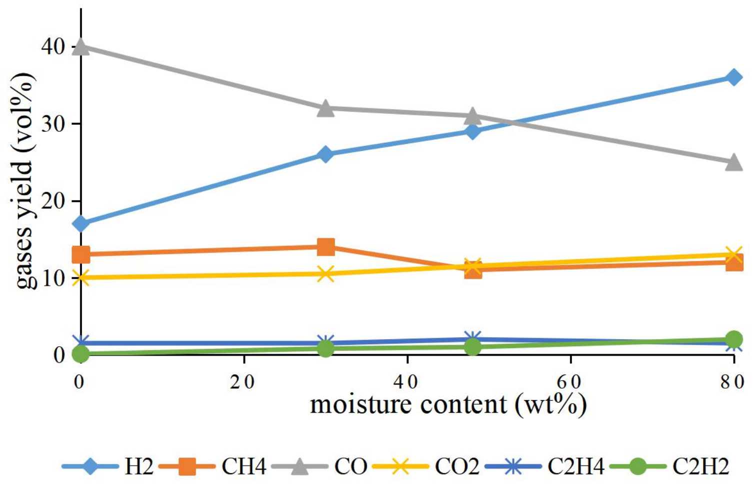
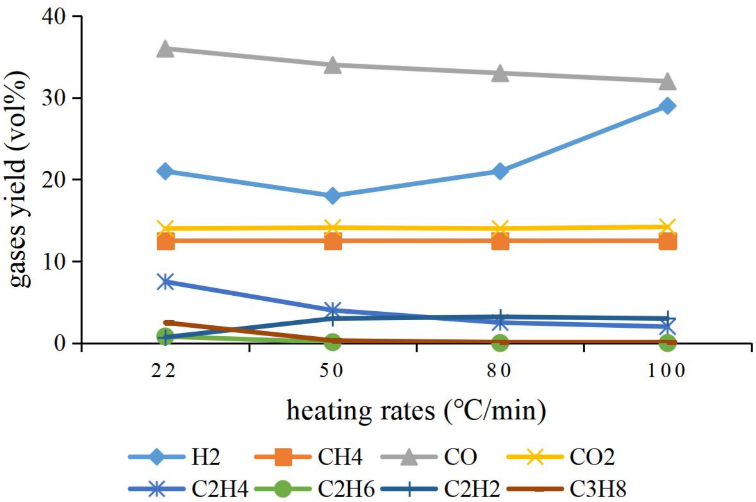


Figure 6 Mechanism flowchart of pyrolysis for sewage sludge (modified from [1,22])

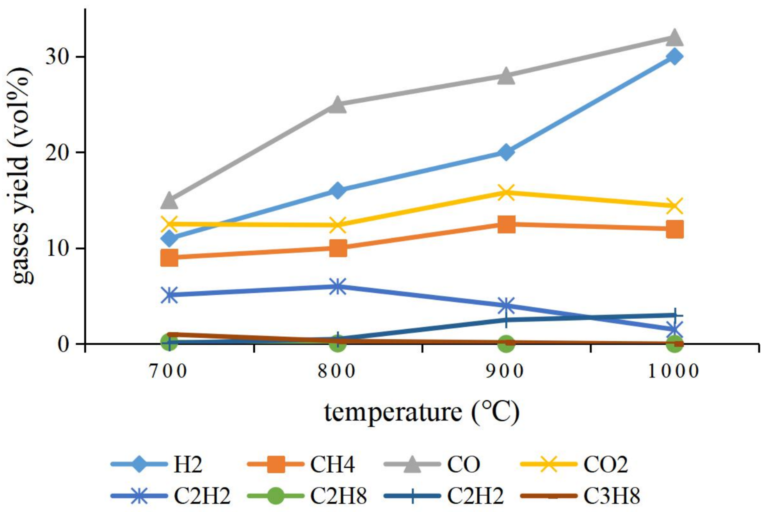
Temperature, residence time and intermediate products, pressure, turbulence and the type of feedstock are the major factors to influence the yield of pyrolysis products [22] and the applied catalyst, temperature and duration have a close relationship with the hydrogen yield from sewage sludge [1]. The influence of moisture content, heating rates, and temperature is illustrated in Figure 7. Increasing moisture content and temperature and keeping heating rates larger than 5 ℃ /min tend to provide favorable conditions for hydrogen generation.



(a) Impact of moisture content



(b) Impact of heating rates



(c) Impact of temperature

Figure 7 Influence of different factors on gas contents from pyrolysis (modified from [75])

Due to the effective concentration of heavy metal [76] and energy recovery during pyrolysis process for sewage sludge, it has attracted much attention and been regarded as an environmental benign method in recent years [22]. Domínguez et al. [77] explored the pyrolysis of wet sewage sludge at high temperature and obtained that a higher hydrogen concentration (>35 vol%) occurred in the pyrolysis of anaerobically digested sludge. Same authors conducted experiments to maximize the bio-fuels production by high temperature pyrolysis of sludge applying traditional and microwave heating and got a maximum value of 38% for hydrogen and 66% for hydrogen and carbon monoxide [78]. An analysis of dried sludge pyrolysis by thermogravimetric analysis and mass spectrometry was provided by Magdziarz and Werle [74] and they pointed out that the maximum peaks of H_2 occurred at 600-700 ℃. The cost for hydrogen production by pyrolysis is estimated between 8.86 \$/GJ and 15.52 \$/GJ (i.e. 1.25 \$/kg – 2.20 \$/kg), which depends on the equipment scale and the characteristics of materials [1,72].

3.2.2. Gasification

Gasification is a thermochemical process where high concentration of combustible gases and small quantities of char and ash are generated in a net reducing atmosphere [2,22]. Under a high temperature between 500 and 1400 ℃ and pressure varying from atmospheric to 33 bar [1], a combination of hydrogen, methane, carbon monoxide, nitrogen, and carbon dioxide is produced [2]. Eq. (10) and Eq. (11) reveal the gasification process of sewage sludge [1]. Due to a higher requirement for temperature, temperature-rise period can also combine with pyrolysis [22] in the oxygen-free environment as it is shown in Figure 8.

$$\text{Sludge sewage+Air} \rightarrow H_2 + CO_2 + CO + N_2 + CH_4 + \text{other CHs+tar+}H_2O\text{+char} \tag{10}$$

$$\text{Sludge sewage+Steam} \rightarrow H_2 + CO_2 + CO + CH_4 + \text{other CHs+tar+char} \tag{11}$$

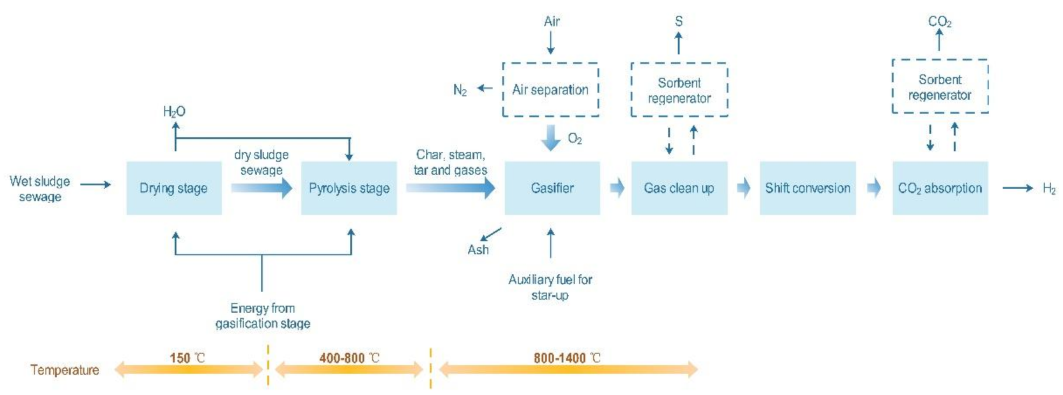
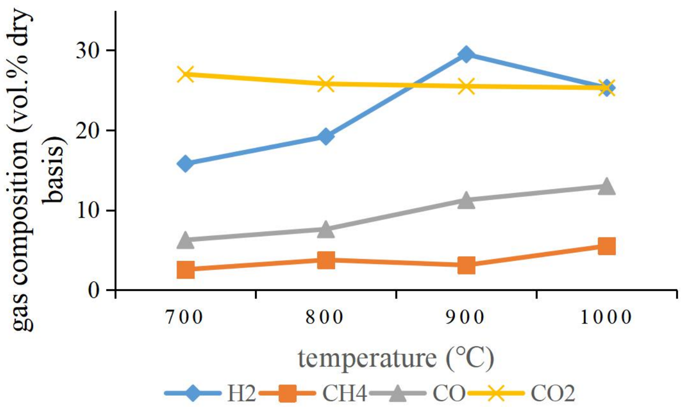
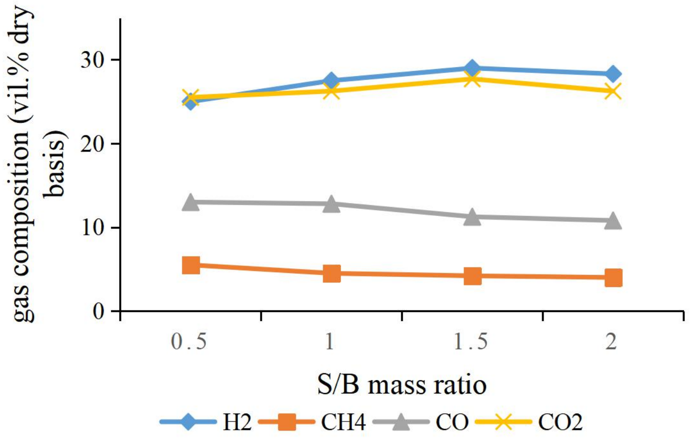


Figure 8 Flow chart of the sewage sludge gasification (modified from [1,22])

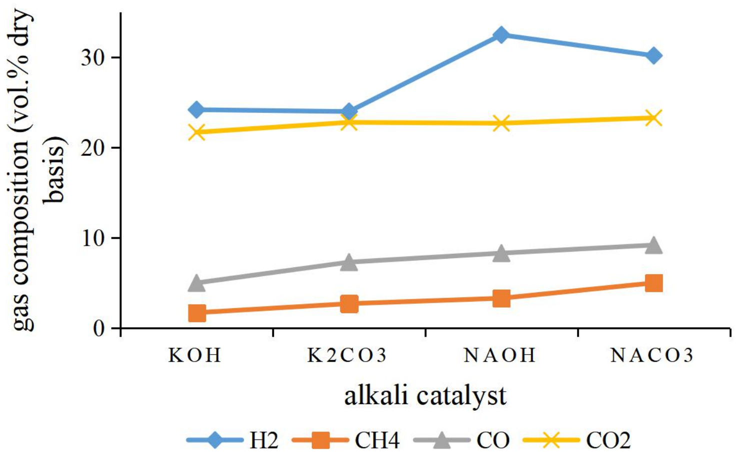
The generated syngas can be further treated by steam reformation and WGS to increase the yield of hydrogen just as the gaseous production from pyrolysis process. The temperature range of gasification for sewage sludge is usually between 800 and 1500 ℃ [22]. Factors including heating rate, temperature, residence time, properties of sewage sludge, types of reactors and types of catalyst have influence on hydrogen yield. The effect of temperature, S/B mass ratio and alkali catalyst applied on produced gas composition are exhibited in Figure 9. Nipattummakul et al. [23] made a comparison of the hydrogen production from sewage sludge by steam gasification and pyrolysis when temperature was in the range of 700-1100 ℃. They found that the yield of H_2 has an uptrend as the temperature increasing and the hydrogen composition from gasification is higher than that from pyrolysis. On the other hand, fluidized bed for sludge gasification has a better performance on efficiency compared to fixed bed reactors [79]. Experiments also revealed that steam as gasification medium can enhance hydrogen production [22].



(a) Influence of temperature



(b) Influence of S/B mass ratio



(c) Influence of alkali catalyst

Figure 9 Influence of three factors on gas composition by gasification (modified from [80])

Typical combustible gas composition by gasification from sewage sludge summarized by Manara and Zabaniotou [22] is between 8.89 and 11.17 vol %. Midilli et al. [70] applied a downdraft gasification technique by fixed bed and obtained 10-11% (V/V) hydrogen of the produced gaseous products. Dogru et al. [81] employed a throated downdraft gasifier for gasification of sewage sludge combined uncertainty analysis and eventually got the composition of hydrogen between 8-12%.

Gai et al. [80] proved that higher hydrogen content could be obtained with the increased presence of Fe, Ni, alkali and alkaline earth metals, and the application of alkali catalysts. Hydrogen gas composition (Vol. % dry basis) of steam gasification from sewage sludge was found within the range of 15-30%. If an industry has an expectation of 139,700 kg/day hydrogen output and the expenses on feedstock between 46-80 $/dry-ton, then the production investment is estimated to be 1.77-2.05 $/kg [1,82].

Hydrogen production through gasification from sewage sludge presents a good performance on production efficiency and yield. However, it requires higher temperature than pyrolysis due to the poor reaction rates [23], which may lead to higher consumption of energy and strict requirements for production equipment. In addition, the low content of hydrogen in sewage sludge may become a major limitation of the hydrogen yield [2,83]. Future study can consider the hydrogen concentration methods for the sewage sludge treatment.

3.3. Super critical water gasification (SCWG)

SCWG, an emerging technique for sewage sludge process and hydrogen production, is characterized by the unique properties of super critical water (SCW). It refers to apply super critical water which is above its critical point (i.e. temperature is above 374.15 ℃ and pressure is more than 220.64 bar) as the gasifying agent [84]. Water below the critical conditions does not dissolve sewage sludge components of various organic matters, while water possesses the miscibility with organic materials under super critical conditions [2]. This characteristic leads to a rapid rate and tar-free gasification to produce gas-rich products including H_2, CH_4, CO, and CO_2 [84]. During the reaction period, the molecules of SCW evolve in different reaction stages as different roles (reactant or catalyst). Generally, the reaction of SCWG can be classified into three major categories, which are shown by Eq. (12) –Eq. (14) [2]. A schematic diagram for the hydrogen production process by SCWG from biomass was drawn by Hosseini and Wahid [2] (see Figure 10). An experiment designed for hydrogen production from sewage sludge through SCWG technique was proceeded by Amrullah and Matsumura [85].

Steam reforming:

$$\text{Sludge sewage} + H_2O \rightarrow CO + H_2 \quad (12)$$

WGS reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (13)$$

Methanation reaction

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad (14)$$

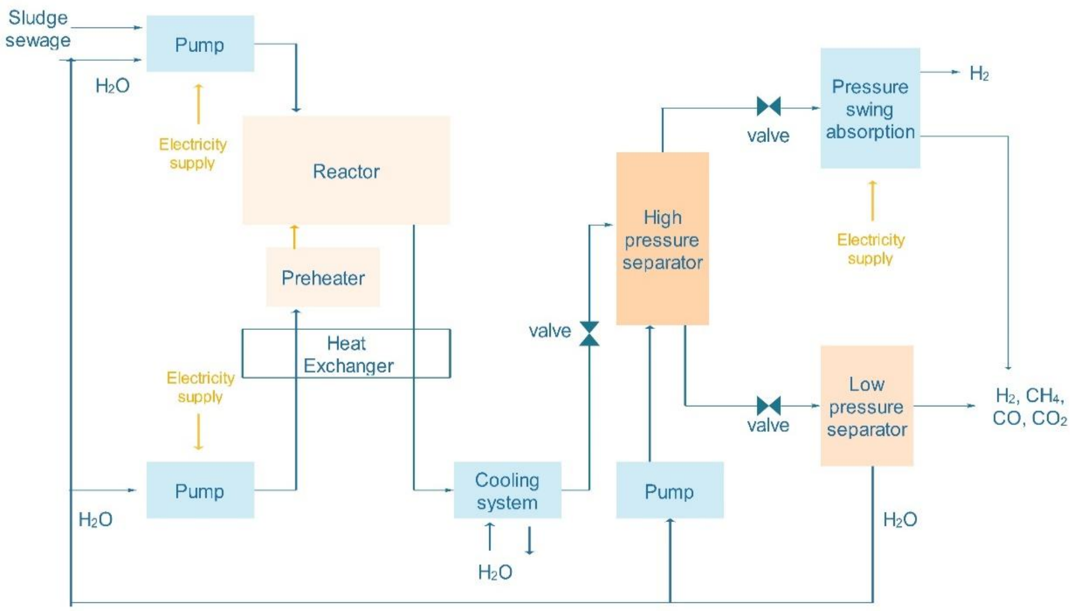
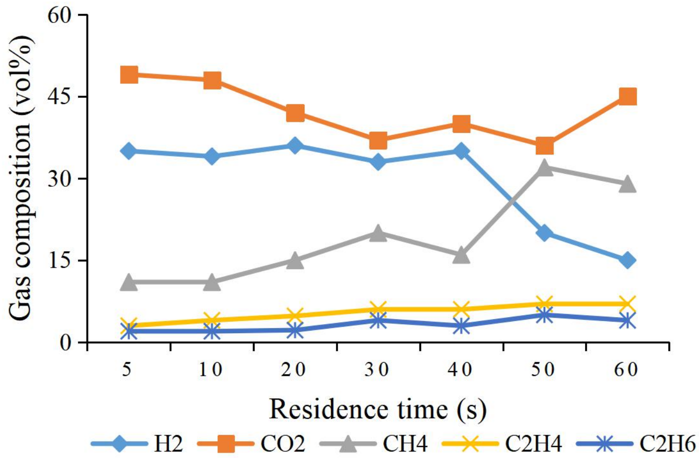


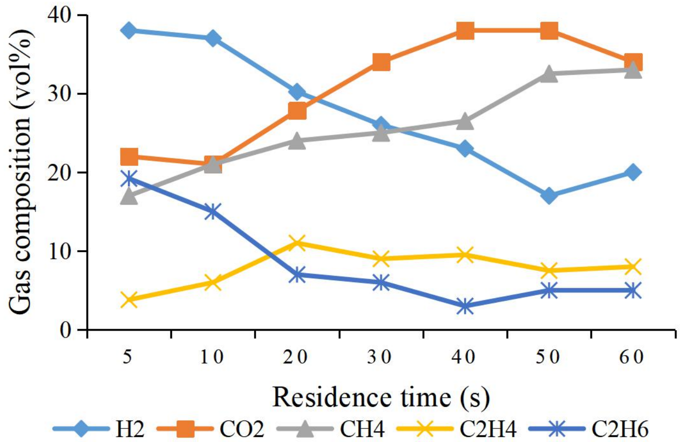
Figure 10 Hydrogen production process from sewage sludge by SCWG [2]

The factors influencing reaction pathways and performance of SCWG can be divided into two categories: the components of feedstock and the operation conditions [86]. The latter category main refers to feed concentration, temperature, pressure, residence time and catalysts [87]. Figure 11 reveals the impact of temperature and residence time on generated gas components， which shows that higher temperature favors the yield of H_2 and CO_2. The effect of pressure on hydrogen production through SCWG is complex because of interrelation with other factors. On the other hand, higher concentrations of feedstock are against SCWG process for hydrogen production. The presence of catalyst makes this method more attractive and economical due to the reduction on the investments for extreme requirement of operation conditions and the improvement on the yield of hydrogen [87,88]. Alkali metal catalysts (e.g. $NaCO_3$, KOH, and NaOH) and transition metals (e.g. Bi, Ru, Cu, and Co) are supposed to have pronounced positive influence to SCWG process [87].

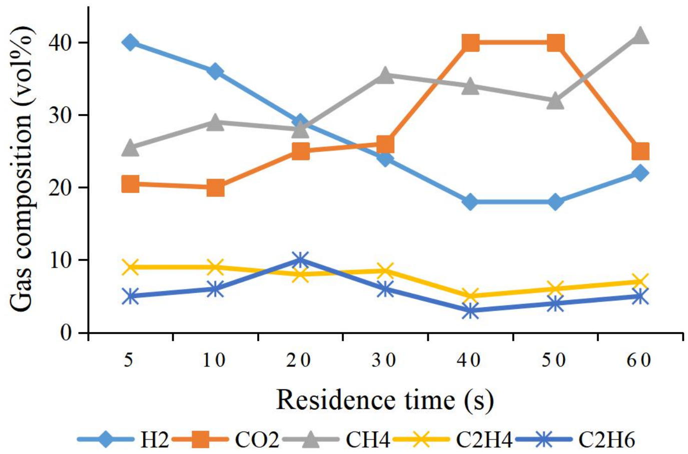
Gong et al. [89] examined the impact of NaOH and Ni catalyst on treating sewage sludge in SCWG process. The highest yield of H_2 was 4.8 mol/kg organic matter under the condition of participation of 3.33 wt% Ni and 1.67 wt% NaOH, which was nearly five times as much as that of non-catalytic.



(a) 500 ℃



(b) 550℃



(c) 600℃

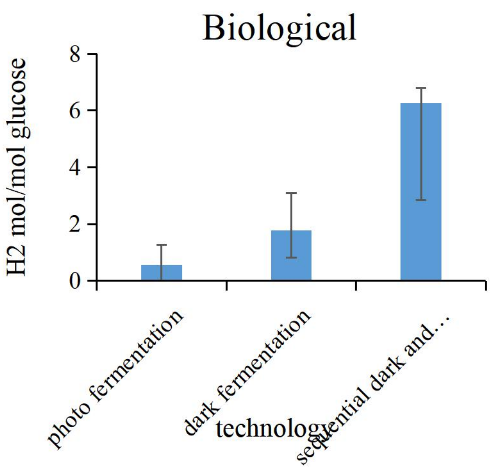
Figure 11 Gas components by SCWG of sewage sludge at different temperature (modified from [85])

The feasibility of applying SCWG for sewage sludge treatment and H_2 production has been explored by groups of researchers. Acelas et al. [90] investigated the viability of gas production combined with phosphorus recovery under different temperature (400 ℃, 500 ℃, 600 ℃) and residence time (15 min, 30min, 60min) by SCWG from dewatered sewage sludge and ultimately got approximate 15 vol% of dry hydrogen at 500 and 600 ℃. He et al. [19] proposed that a higher industrial application value for the hydrogen production from SCWG can be shown when the sludge with a solid concentration higher than 15%. Wilkinson et al. [91] made a comparison of the performance of SCWG for primary sewage sludge and anaerobic digestion system and results showed that SCWG could formulate more energy per gram of raw material with the destruction of more volatile solids at the same time. Reported by Fan et al. [92], dewater sewage sludge with the addition of formic acid could have a significant increase in the yield of hydrogen from 0.16 to 10.07 mol/kg organic matter with the acid increasing from 0 to 6 wt%.

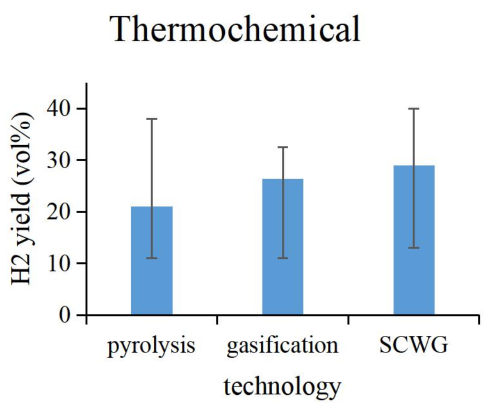
Except for the conspicuous property of SCW which provides the chance of dissolving organic matters, SCWG also possesses some other remarkable advantages. It allows highly moisturized feedstock (even more than 50%) to be directly applied for hydrogen production, which leads to the elimination of drying process as pretreatment and a reduction on the relevant cost [2,93]. Meanwhile, less energy is needed to pressurize hydrogen for its storage because of the high pressure required during the production process. On the other hand, the formation of tar and char dramatically decreases [2,94] and phosphorus recovery can proceed with hydrogen production simultaneously [95]. Moreover, SCWG shows a higher gasification efficiency at low temperature than that of other thermochemical gasification methods, such as steam or air gasification [2,96]. From the perspectives of technique and economy, SCWG is supposed to be a competitive method to obtain H_2 from sewage sludge under specific conditions. An evaluation for the cost and benefits from sludge process by SCWG suggested that it can be comparable with natural gas reforming (6.82 €/GJ) and electrolysis (26.82 €/GJ) method when sludge profits reach 211 €/t dry matter and 62 €/t dry matter, respectively [97]. However, the existence of three challenges, including corrosion, plugging, and high running investment, impedes the development and active application of SCWG in practice [19,98]. Therefore, future research needs to address these problems to promote the development and wide acceptance of industrial applications.

4. Overall comparison and discussion

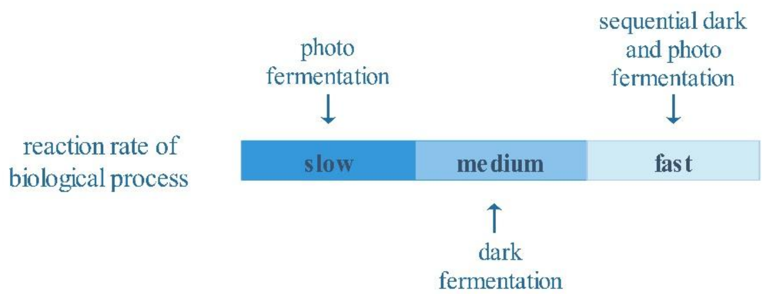
In the section, an overall comparison for the major hydrogen production methods from sewage sludge is conducted. The evaluation is involved with technical, environmental and economic aspects to obtain a basic recognition of the performance for existing production technologies. Related data and some other important remarks are collected in Figure 12.



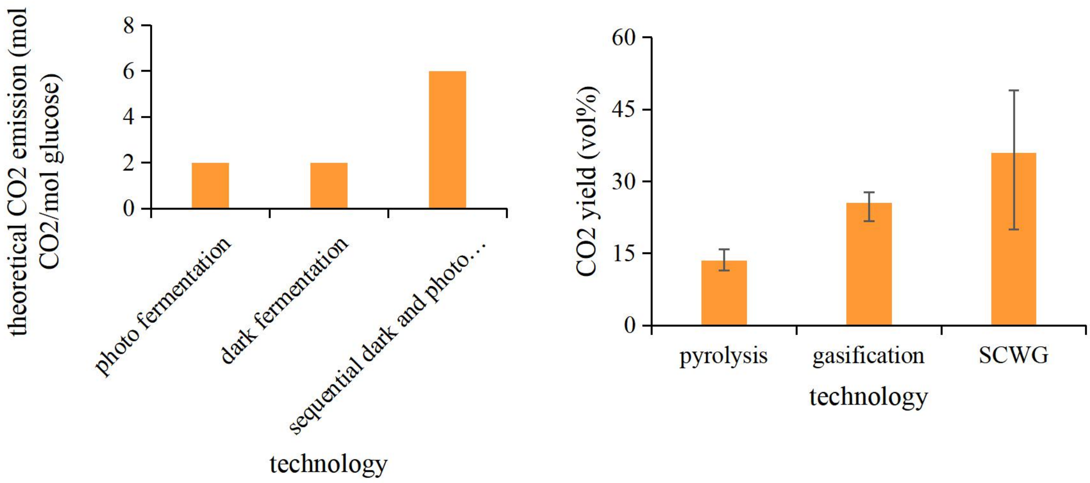
(a)



(b)



(c)



(d) (e)

Figure 12 Overall comparison of hydrogen production from sewage sludge ((e) is drawn based on [75,80,85])

4.1 Technological aspect

The general hydrogen yields from selected approaches are summarized in Figure 12 (a) and (b). Currently, a unified standard for the measurement of hydrogen production efficiency is still missing. The yields from biological processes are addressed by material efficiency while the generation from thermochemical methods are measured by H_2 content in the syngas. According to the figures, two-step fermentation possesses the highest H_2 generation in the total process among the three biological methods and SCWG is the highest one compared with other thermochemical ways.

As for the reaction rate, thermochemical methods usually own the advantages over the biological pathways in this aspect. Based on the literature review and Figure 12 (c), the reaction rate of photo fermentation is the lowest one. Although sequential dark- and photo-fermentation shares the highest yield, its reaction rate is inferior to that of dark-fermentation.

Hydrogen production from sewage sludge as an emerging branch of hydrogen producing, none of these existing techniques can be regarded as mature technologies. Biological pathways remain laboratory stage which is far from industrialization. SCWG is also a developing method which needs to be further explored. Gasification and pyrolysis are relatively mature compared to others, but they are lack of commercial applications and production normalization [99].

4.2 Environmental aspect

Though CO_2 may be regarded as environmental neutral gas, it is still an important concern for the environment due to the global warming potential. CO_2 emissions from biological and thermochemical ways are estimated by reaction functions and experiments from previous studies respectively. Figure 12 (d) shows that theoretically there are 6 mol CO_2 generated if 1 mol glucose is the substrate during the whole process of two-step fermentation. Figure 12 (e) indicates that the CO_2 content from SCWG is the highest one (20-49 vol%), followed by gasification (21.7-27.7 vol%) and pyrolysis (10.5-15.8 vol%).

4.3 Economic aspect

There are few studies reporting economic assessment for sludge-to-H_2. Many investigations evaluate the cost of biomass-to-hydrogen. Due to the similar production process, these results could be a reference for the cost of sewage sludge as material to produce hydrogen. SCWG is estimated to be the most expensive one and pyrolysis is the cheapest way. Limited researches investigate the investment for biological methods, but they are generally lower than those for thermochemical processes under certain conditions [43].

4.4 Discussion

Based on the comparison above, there exist conflict features of these technologies. For instance, sequential dark- and photo-fermentation and SCWG both have improved hydrogen production, but the CO_2 emissions are also remarkably higher than other methods in the same category. Meanwhile, corrosion, plugging and expensive running cost for SCWG are three mainly obstacles for the promotion of this technology. The corresponding solutions were provided by Kritzer [100] which are omitted here. Hence, plenty of efforts are still required to offer a competitive price for the hydrogen generating from sewage sludge, including the improvement for the yield of hydrogen and production rate, and optimization for the equipment and process design. Taking the trade-off into account, comprehensive evaluation for these technologies are also necessary to judge the method is whether to promote and develop furtherly.

5. Conclusions

Hydrogen production from sewage sludge is an emerging method to obtain the efficient and clean energy and deal with the waste simultaneously. This paper reviews the principle and characteristics of the present major technologies along with the basic assessment in respect to technology, environment, and economy. Among these techniques, thermochemical processes are relatively developed with established facility while biological methods are far from industrialization due to the limitation researches. Pretreatment procedure is generally needed before biological fermentation to realize the enrichment for hydrogen production. For the current sludge-to-hydrogen production technologies, the production cost and low yield are major limitations for their future development. Fermentation methods could be low-cost but rather time-consuming and related studies are at the fundamental stage. Thermochemical approaches can be high-effective but relatively high-cost as well, and some of them are limited by technical problems, like SCWG. Alternatives processes still need to be improved both from the yield of hydrogen and overall economic benefit in order to be more competitive.

Researchers could investigate an effective production process according to the essential properties of different methods in the future study. The proper combination of various pathways and co-processed with other feedstock, like food waste, may also provide an available way for high-effective hydrogen production. Membrane reactor tends to be a popular option for integration in other hydrogen production methods recently, which may be employed for the improvement of thermochemical processes. Noted that hydrogen production form sewage sludge is a promising approach which could provide clean energy to the public and recycle the waste at the same time, government should give strong support to relevant industries on economic and technological aspects, which would greatly relieve the price pressure from competition. Above discussion clearly indicates that it is necessary to conduct further research on hydrogen production from sewage sludge together with detailed evaluation standards and alternatives optimization.

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