

Quality of gaseous biofuels: Statistical assessment and guidance on production technologies

Guohui Song^a, Jun Xiao^b, Chao Yan^c, Haiming Gu^a, Hao Zhao^{d,e,*}

^a School of Energy and Power Engineering, Nanjing Institute of Technology, Nanjing, Jiangsu, 211167, China

^b Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing, Jiangsu, 210096, China

^c Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ, 08544, USA

^d College of Engineering, Peking University, Beijing, 100871, China

^e Institute of Energy, Peking University, Beijing, 100871, China

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ABSTRACT

The wide variation in the properties of gaseous biofuels pose a major challenge to the practical application. This study focused on composition-related qualities of various purified gaseous biofuels excluding the effects of residual impurities. It built an informative compositional database of 20 types of existing and predicted gaseous biofuels. The ranges of the major constituent gases are as follows, CH₄: 0.01–98.00 vol%, H₂: 0.01–72.74 vol%, CO: 0–56.84 vol%, C₂H₄: 0–8.89 vol%, C₂H₆: 0–2.78 vol%, CO₂: 0.01–87.40 vol%, N₂: 0.01–94.98 vol%, O₂: 0–6.53 vol%. The quality indicators, such as heating values, explosive limits, toxicity, and interchangeability, were statistically investigated. Subsequently, two methods for classifying gaseous biofuels regarding heating value and toxicity were proposed. The results show that synthetic natural gas, biogas, and methanation products of producer gases from gasification with steam, high-purity O₂ (nearly 100%), and O₂-enriched air (50–70% purity) are the preferred gaseous biofuels for different application scenarios. The CO and H₂ contents are recommended to be limited to 2 vol% and 5 vol%, respectively. Then, suitable source and upgrading technologies are selected based on the quality results. Furthermore, the concept of electrification of biomass conversion including electricity-driven gasification and synthesis technologies was proposed. Diverse electricity-driven gasification technologies were analyzed with their applications and limitations. The results point out that the biomass and power-to-X pathway provides promising solutions for biomass and organic waste management, grid stability, sustainable fuel production, and decarbonization.

1. Introduction

Natural gas is a desirable energy resource for both economic and social development, especially in developing Asia countries, as they are in the energy transition from coal towards lower-carbon fuels [1]. However, imbalance is one of the most notable characteristics of natural gas in resource, production, and consumption [2]. The lack of access to affordable natural gas has become a stumbling stone for many developing countries [3]. Additionally, non-renewable natural gas is not a sustainable option in the decarbonization race. Instead, alternative gaseous fuels have been highly expected to reduce disparities in natural gas, mitigate its resource depletion and accelerate global decarbonization.

Biomass is renewable organic material including dedicated energy

crops, agricultural and forestry residues, and algae, etc., which is receiving increasing interest due to a spatially broad distribution of feedstock, friendly environmental impact, renewable characteristics, and comparable cost. Two major source technologies are generally available to produce gaseous biofuels (Fig. 1): (i) Anaerobic digestion, the product is generally called biogas; and (ii) Thermochemical gasification, the product is named as producer gas or syngas [4,5]. Subsequently, several upgrading technologies (Fig. 1), such as the methanation synthesis, CO₂ separation, and trace compounds removal, can be applied to substantially adjust the composition and properties of these gaseous biofuels [5–7]. Raw gaseous biofuels generally need to be purified to remove most contaminants, e.g., particulate matter, tar, sulfur compounds, and hydrogen chloride. The purified gaseous biofuels are focused on in this work.

Gaseous biofuels are potential alternatives in all areas of the energy

* Corresponding author.

E-mail address: h.zhao@pku.edu.cn (H. Zhao).

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Nomenclature**Abbreviations**

AD	anaerobic digestion
AR	air gasification
AS	air-steam gasification
B&PtG	biomass and power-to-gas
B&PtX	biomass and power-to-X
E	excellent
ER	equivalence ratio
G	good
GHS	globally harmonized system
GWP	global warming potential
HHV	higher heating value
L	upper or lower explosive limit
LEL	lower explosive limit
LHV	lower heating value
LC ₅₀	50% Lethal Concentration
M	marginal
OE	O ₂ -enriched air gasification
P	prohibitive
PO	high-purity oxygen gasification

PtG	power-to-gas
S/B	steam-to-biomass ratio
SN	stoichiometric number
SNG	synthetic natural gas
STM	steam gasification
UEL	upper explosive limit
WI	Wobbe Index
db	dry basis
cSNG	crude synthetic natural gas
3R, 4R or 5R	classification labels of city gas based on WI and HHV
10T or 12T	classification labels of natural gas based on WI and HHV

Subscripts

m	conventional methanation
ms	conventional methanation plus CO ₂ separation
hm	hydrogenation methanation

Variables

d_r	relative density
f	molar fraction
v	volume fraction

sector, including power generation, transport fuel, cooking, and heating [8,9]. However, gaseous biofuels have very different H₂, CO, CO₂ and CH₄ contents [10,11], and thus exhibit distinct thermodynamic properties and combustion characteristics [12,13]. For example, when biogas is used in a gas turbine, a series of modifications must be made to the device, such as the installation of compressors and fuel-delivery nozzles [13]. In addition, problems that arise during premix combustion, such as flame flashback, auto ignition, lean blowout, and instability, should be handled properly for different gaseous biofuels [14]. The syngas composition also affects the volumetric efficiency, output power, and pollutant emissions of spark-ignition engines [15]. Therefore, variations of syngas composition and quality must be considered in the case of

engine and burner applications to ensure efficient utilization, facility compatibility, safety, and low emissions. However, there have been few comprehensive analyses of the effects of syngas quality on its utilization.

Quality evaluation and classification are necessary for gaseous biofuels whose compositions show significant variations. Previous studies have generally characterized the quality of gaseous biofuels based on their composition [16], lower/higher heating values (LHV/HHV) [17, 18], Wobbe Index (WI) [17,18], H₂/CO ratio, and CH₄/H₂ ratio [15, 19–21]. However, systematic and statistical investigations of their components and important properties, such as their interchangeability, are crucial for choosing the appropriate source technology as well as constructing gas grids and developing suitable combustors. To be able to

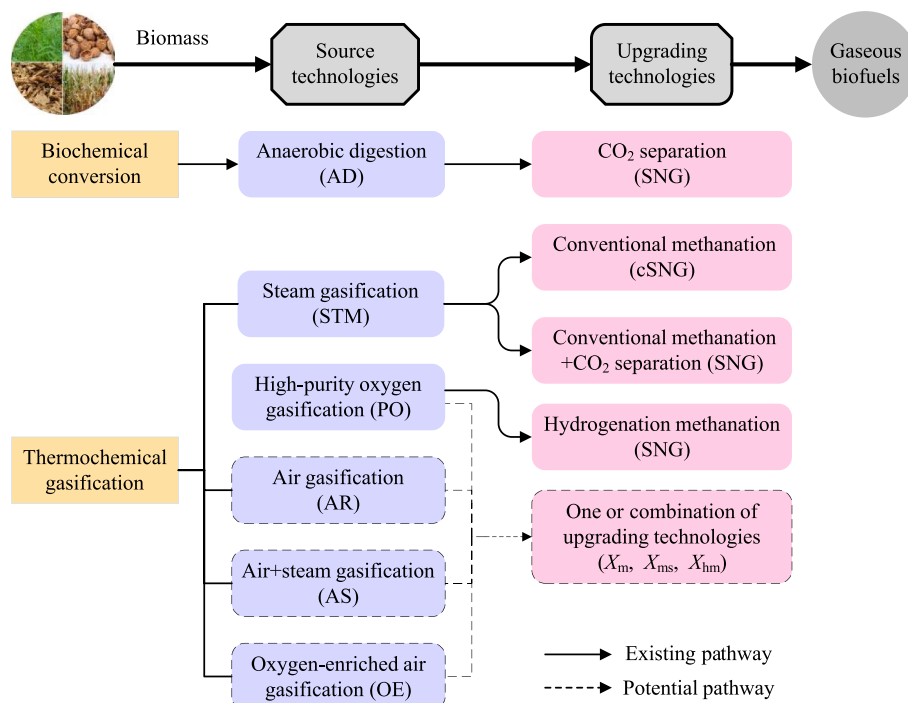


Fig. 1. Scope and classification of gaseous biofuels assessed in this study.

perform such an assessment, sufficient data on compositions of various gaseous biofuels need to be collected and processed.

Most classifications of biogas are based on production technique, feedstock, and digester [22,23]. Jenkins [24] suggested classifying syngas into three categories based on the HHV: 3.35–7.1 MJ/m³, 9.3–20.5 MJ/m³, 33.4–43.0 MJ/m³. The Ministry of Agriculture of China requires that the LHV of qualified syngas should be greater than 4.6 MJ/m³ for use in the specialized syngas grid [25]. Most studies on the topic have been limited to performing preliminary classifications of syngas based on the HHV and LHV. Furthermore, the safety and cleanability are always concerns in the case of liquid and gaseous fuels within the scope of sustainable development [26]. Gaseous biofuels commonly consist of flammable and toxic components. For example, CO is a major component of some types of syngas [27]. Gaseous biofuels can accidentally cause fires and explosions and result in toxic emissions to humans and the environment. Thus, the explosivity and toxicity of gaseous biofuels must be evaluated during the production, transport, and end-use stages. Molino et al. [28] assessed the explosive limits and risks of hydrogen-rich syngas from a biomass gasification plant. Xie et al. [29] studied the pressure history of the syngas/air/H₂O explosion in a constant-volume vessel over a wide range of equivalence ratios at elevated temperatures. In addition, the explosive limits of H₂/CO/O₂-CO₂/H₂O mixtures were analyzed both computationally and theoretically by Liu et al. [30]. Although the H₂ and CO concentrations were between 5–100 vol% and 0–95 vol%, respectively, only 6 cases were considered, and CH₄ was not included. Zhou et al. [31] focused on the variations in the fuel composition (H₂ and CO: 10–40 vol%, CH₄: 6.7–80 vol%) and diluent ratio on the explosion characteristics of syngas/air mixtures in a constant-volume vessel. Thus, the explosive limit, adiabatic explosion pressure, and explosion time are the commonly used indices. However, to date, there have been few comprehensive statistical studies on the explosion characteristics of gaseous biofuels.

In addition, there have been few specialized quantitative studies on the toxicity of gaseous biofuels. Recently, this topic has attracted considerable attention with respect to syngas production, transport, storage and usage [32,33]. Stolecka and Rusin assessed the lethal toxicity of syngas using a method based on the 50% Lethal Concentration method (LC₅₀) [34]. Although these studies provided valuable information regarding the lethal toxicity of syngas, a broad range of syngas compositions was not covered. The appropriate production technologies should be selected or developed to produce safe gaseous biofuels. Thus, in this study, the characteristics of explosion and toxicity of gaseous biofuels will be focused on with quantitative analysis.

Synthetic natural gas (SNG) or biomethane is one of the most attractive gaseous biofuels because of its similarity to natural gas and low CO and H₂ contents. Generally, SNG is produced by upgrading biogas or syngas [35]. Recently, power-to-gas (PtG) technology is receiving increasing attention because of the demand for electricity storage. Clausen et al. developed a high-efficiency SNG production method by integrating biomass gasification with the co-electrolysis of CO₂ and H₂O in pressurized solid oxide electrolysis cells [36]. Gutiérrez-Martín and Rodríguez-Antón compared the PtG technologies with hydrogenation methanation of CO₂, biogas, and syngas [37]. Analogously, upgrading treatments, including CO methanation, CO₂ separation, and hydrogenation methanation, can also be employed with syngas produced using different gasifying agents. A single or a combination of the upgrading treatments may produce new types of gaseous biofuels with different compositions and properties. Thus, the effects of these upgrading treatments as well as those of related issues on gaseous biofuel evaluation must also be considered.

Based on the above analyses and motivations, the objectives of this study are as follows: (i) to collect and statistically analyze data related to the compositions of various existing gaseous biofuels; (ii) to assess the quality of gaseous biofuels in terms of their thermodynamics and safety properties; (iii) to predict possible gaseous biofuels based on applying individual or combined upgrading treatments to the existing gaseous

biofuels, and then to evaluate the quality of these new gaseous biofuels; and (iv) to analyze and guide the selection and development of matched source and upgrading technologies based on the quality evaluation results. The results of this study should provide guidance for the selection of gaseous biofuels, and the development of source and upgrading technologies as well as end-use models and technologies. In addition, assessing the explosion and toxicity characteristics of gaseous biofuels can aid the development of environmental and social policies for reducing related accidents and potential illnesses.

2. Collection scopes and composition data

Anaerobic digestion and thermochemical gasification are the two primary methods for the production of raw gas from biomass (Fig. 1). Anaerobic digestion is a biological process that occurs in the absence of oxygen. During this process, microorganisms break down complex biodegradable organic matter into biogas, which mainly consists of CH₄ and CO₂. Biomass gasification is a relatively mature technique for converting biomass into H₂, CO, CO₂, and other products without combustion using gasifying agents in a controlled process. Gasifying agents such as air, oxygen, steam, and their mixtures are commonly used to initiate gasification, and their choice significantly affects the characteristics of the gasification process as well as the quality of the gaseous biofuel [5].

The following collection and assessment mainly involve well-developed technologies and commonly used gasifying agents. Fig. 1 shows the scope of data collection. The technologies and products marked with the solid lines are used widely and have been studied extensively. The existing gaseous biofuels are first listed and then divided into the following 8 categories (Fig. 1): biogas produced by anaerobic digestion (AD), syngas produced by air gasification (AR) or air-steam gasification (AS), syngas produced by O₂-enriched air gasification (OE) or high-purity oxygen gasification (PO), and syngas produced by steam gasification (STM). Crude SNG (cSNG), produced by the methanation of STM, has compositions similar to those of biogas; while SNG upgraded using the CO₂ separation technique with AD or cSNG has compositions similar to those of natural gas. Thus, cSNG and SNG were classified as two different types.

There are several types of contaminants in syngas and biogas, including particulate matter, tar, sulfur compounds, nitrogen compounds, alkali metals, and hydrogen chloride. The contaminants, particularly tar, must be removed for conversion technologies to be commercially successful. Hot, cold, and warm gas cleaning technologies that can remove most of the contaminants are currently available [38]. Specifically, physical, thermal, and catalytic tar reduction technologies can achieve removal efficiencies of up to 98% and higher. A combination of these technologies is typically used for deep purification in industrial plants [39]. The limits for the contaminants in purified gaseous biofuels vary substantially depending on the end-use technologies and/or national emission standards (Table S1). For example, the upper limits for particulate matter and tar for internal combustion engines are 50 and 100 mg/Nm³, respectively, while those for gas turbines are 30 and 5 mg/Nm³, respectively [38,39]. As per a Chinese standard (NY/T 443–2016), the contents of dust, tar, and H₂S in producer gas for civil use must not exceed 15, 15, and 20 mg/Nm³, respectively [25]. The contents of the contaminants in purified gaseous biofuels are too low to pose obvious influences on the concerned properties in the study. For example, the calculation with the greatest limits of individual contaminants in Table S1 indicates that the total LHV of the main combustible contaminants (tar, H₂S, and NH₃) is less than 0.005 MJ/Nm³, which is very small compared with those of the various producer gases. Thus, the following assessment was performed on a purified dry basis.

482 sets of composition data were collected and listed in Table S2 in the Supplementary Material. 8 species of constituent gases were collected and processed, i.e., CH₄, H₂, CO, CO₂, C₂H₄, C₂H₆, N₂, and O₂. A part of the data was obtained by digitizing data from graphs. In

addition, there were few technological attempts to apply the methanation and CO₂ separation to the syngas except STM (as shown by dashed lines in Fig. 1), which may produce new types of gaseous biofuels. The details of such attempts will be discussed in Section 5.

2.1. AD samples

The samples of biogas are marked as “AD”. 43 sets of the AD samples were collected from the literature [40–49]. CH₄ and CO₂ are the major components of this type of gaseous biofuels. The CH₄ concentration varies from 38.4 to 70.08 vol%; and the CO₂ concentration varies from 29.92 to 61.60 vol%. Low-level concentrations of O₂ (0.1–3.65 vol%) may exist in the AD samples (Table S2).

2.2. AR samples

This type of gaseous biofuel refers to the syngas produced by biomass gasification only with air. 74 sets of the AR samples were collected from the literature [27,50–60]. The samples of plasma-assisted air gasification were also included in this group. In the case of gasification with air or oxygen, the equivalence ratio (ER) is usually applied to evaluate the gasification characteristics. ER is the ratio between the oxygen content in the oxidant supply and that required for complete stoichiometric combustion. Alternatively, a few studies reported the amounts of air used for gasification in the form of air ratio, i.e. in kg of air per kg of biomass. The ER for these samples is 0.12–0.48, and the air ratio is 0.46–2.29. The gasification temperature involved in these studies is approximately 617–1450 °C.

N₂ in the AR samples makes up the largest portion (33.53–76.13 vol %) due to air's characteristics. Except N₂, the other major components are H₂, CO, and CO₂, of which the concentrations vary from 2.10 to 36.41 vol%, 4.37–29.59 vol% and 1.75–20.10 vol%, respectively. The AR samples usually have low-level concentrations of O₂ (0.27–2.04 vol %). Additionally, H₂/CO ratio in the AR samples is 0.17–1.88, and has an average of 0.9 (Table S2).

2.3. AS samples

This type of gaseous biofuel refers to the syngas produced by biomass gasification with both air and steam. 71 sets of the AS samples were collected from the literature [50,51,53,54,56,58,60–64]. The samples of air-steam gasification assisted with plasma were also enrolled into this group. Similarly, ER and steam-to-biomass ratio (S/B) are commonly used to evaluate the characteristics of air-steam gasification. The ER for the AS samples is 0.04–0.37, and the S/B is 0.02–1. The gasification temperature is approximately 586–1300 °C.

N₂, H₂ and CO₂ are the major components of the AS samples, which change more widely than those of the AR samples. The concentrations of N₂, H₂, CO and CO₂ vary from 7.90 to 65.59 vol%, 7.42–50.76 vol%, 3.70–41.64 vol% and 0.05–27.40 vol%, respectively. AS also has more lower concentrations of O₂ (<0.95 vol%), compared with AR. The C₂H₄ concentration of the AS samples is 0.28–8.89 vol%, which is higher than that of the AR samples (0.81–3.34 vol%). Additionally, the H₂/CO ratio is 0.43–6.01 with an average of 0.43 (Table S2). Most of the ratios are less than 2, and only several ratios are greater than 2.5 caused by their very low CO content (<10 vol%).

2.4. OE samples

This type of gaseous biofuel refers to the syngas produced by biomass gasification with both O₂-enriched air and steam. O₂-enriched air gasification conceptually includes high-purity O₂ gasification. A large proportion of previous investigations used the O₂-enriched air with 30–70% O₂ purity; the other employed the O₂-enriched air with O₂ purity of 99.5% and higher. Because the latter barely brings in inert gas N₂, the N₂ in syngas is mainly formed by the intrinsic nitrogen element in biomass.

The compositions of syngas from gasification using O₂-enriched air with O₂ purity of 30–70% are essentially different from those with high-purity O₂. Thus, here O₂-enriched air specifically refers to the air with O₂ purity of 30–70%.

46 sets of the OE samples were collected from the literature [51,57, 65–68]. The ER and S/B are 0.1–0.4 and 0–1, respectively, and the gasification temperature is approximately 617–1025 °C. Table S2 shows that in the case of OE, the addition of O₂-enriched air causes an increase in CO₂ concentration and a decrease in N₂ concentration compared with those of AR and AS. O₂ concentration is 0.27–0.56 vol%. H₂/CO ratio is 0.08–2.25 with an average of 0.79.

2.5. PO samples

The purity of the oxygen for this type of gasification is not lower than 99.5%. 52 sets of the PE samples were collected from the literature [54, 58,67,69–73]. The samples included the syngas produced through chemical looping gasification by using oxygen carriers. The ER in the reviewed papers is 0.15–0.625, and most of them do not exceed 0.4. Additionally, the S/B is 0–1.25. The gasification temperature is approximately 660–1108 °C.

Table S2 shows that when high-purity O₂ is used as the gasifying agent, the CO₂ concentration is much higher (up to 67.93 vol%). The H₂ and CO concentrations are also higher than those of the OE samples, mainly depending on the S/B parameter. Additionally, the PE samples have the highest O₂ concentration (0.35–6.53 vol%). The H₂/CO ratio is 0.48–2.25 with an average of 0.99.

2.6. STM samples

This type of gaseous biofuel is produced by steam gasification. 105 sets of the STM samples were collected from the literature [18,74–87]. Dual fluidized beds were commonly used as the reactor to indirectly supply heat for the endothermic process of steam gasification. Additionally, the data of solar thermochemical gasification were enrolled into this group. Affected by the requirements of different gasifiers, the S/B is 0–6, and most of them are within 0.2–2. The gasification temperature is between 690 and 1400 °C.

Table S2 shows that when steam is used as the gasifying agent, the maximum H₂ concentration is up to 65.98 vol%, and the minimum concentration (22.42 vol%) is much greater than those of other types of gaseous biofuels. The CO concentration is also higher, ranging from 11.31 vol% to 51.25 vol%. Correspondingly, the H₂/CO ratio is 0.45–3.61 with an average of 1.78. The H/CO₂ ratios of approximately 90% of these samples are less than 3, indicating that H₂ in syngas is not sufficient to convert CO to very low level by CO methanation reaction.

2.7. cSNG samples

The cSNG refers in particular to the methanation product of the syngas from steam gasification, i.e., STM. cSNG is the key intermediate stream in conventional biomass-to-SNG processes. Although the composition of cSNG is similar to that of biogas, this study took it as an independent group. 34 sets of the cSNG samples were collected from the literature [4,35,88–98], which included some samples of hydrothermal gasification.

Table S2 also shows that CH₄ and CO₂ are the major components of cSNG, of which the concentration ranges (29.23–54.09 vol% and 40.56–62.76 vol%, respectively) are comparable with but narrower than those of AD. Additionally, cSNG also has visible-level concentrations of H₂, CO and C₂H₄, which differs from AD.

2.8. SNG samples

The biomass-based SNG is produced by applying CO₂ separation to either biogas and or cSNG (Fig. 1). 57 sets of the SNG samples were

collected from the literature [8,18,36,42,93,95–103], which included some samples from hydrothermal gasification and biomass and power-to-gas processes. Depending on different methanation techniques and CO₂ separation efficiencies, the CH₄ concentration varies from 79.80 to 98.00 vol%, the H₂ concentration varies from 0.06 to 14.00 vol%; while the CO₂ concentration varies from 0.06 to 11.10 vol% (Table S2).

The compositions in this collection cover the following ranges, CH₄: 0.01–98.00 vol%, H₂: 0–72.74 vol%, CO: 0–56.84 vol%, C₂H₄: 0–8.89 vol%, C₂H₆: 0–2.78 vol%, CO₂: 0.05–67.93 vol%, N₂: 0.01–76.13 vol%, O₂: 0–6.53 vol%. Apparently, the compositional data in this study are much wider than those in previous studies [10,11,34] and even cover gaseous biofuels produced by biomass CO₂ gasification [104–106] and supercritical water gasification [107–109]. Therefore, the presented database is valuable to related studies of those technologies.

3. Indicators of assessments and classifications

The specification for gas quality can be national or area specific. To judge the quality of gaseous fuels, many properties need to be taken into account, such as flame speed, adiabatic flame temperature, Wobbe Index, flame stability and extinction limits [110]. As the basic and most commonly used properties, heating values and Wobbe Index are widely used as the quality indicators. Additionally, the safety performances of gaseous biofuel are particularly focused on to guide its application in relevant transport, combustion, and leakage precaution. Note that the reference conditions in the following assessment are 15 °C and 101.325 kPa.

3.1. Heating values

Heating value is the amount of heat obtained from burning chemicals per unit quantity. The LHV and HHV of gaseous biofuel are calculated as follows:

$$\text{LHV} = \sum f_i \cdot \text{LHV}_i \quad (1)$$

$$\text{HHV} = \sum f_i \cdot \text{HHV}_i \quad (2)$$

where LHV_{*i*} and HHV_{*i*} are the lower and higher heating values of component *i*, respectively (Table 1) [111], and *f_i* is the molar fraction of component *i*.

Table 2 lists the requirements of the LHV for different gaseous fuels as specified in Chinese technical standards. Thereinto, the LHV of natural gas is converted from its HHV. According to these standards, gaseous biofuels with a LHV <4.4 MJ/m³ should not be used as fuels because of the problems related to ignition, steady combustion, and poor economic competitiveness.

Based on the characteristic values in Table 2, the gaseous biofuels are divided into 5 classes according to LHV values as indicated in Table 3. The upper limit of Class High (34 MJ/m³) is converted by the LHV of pure methane.

3.2. Safety indicators

Gaseous biofuels may result in fire or explosion hazards owing to their flammability. They may also contain toxic gases, such as CO and

Table 1
Properties of flammable components in gaseous biofuel.

Component	HHV (kJ/mol)	LHV (kJ/mol)	UEL (%)	LEL (%)
CH ₄	891.51	802.65	15	5
H ₂	286.15	241.72	75.9	4
CO	282.91	282.91	74.2	12.5
C ₂ H ₄	1412.12	1323.26	36	2.7
C ₂ H ₆	1562.14	1428.85	12.5	3

Table 2

Requirements of LHV for different gaseous fuels in Chinese technical standards.

No.	gas type	technical standard	LHV (MJ/m ³)
1	bio-syngas	NY/T 443–2016 [25]	≥4.4
2	manufactured gas (Class II)	GB/T 13612–2006 [112]	10–14
3	manufactured gas (Class I)	GB/T 13612–2006 [112]	>14
4	natural gas	GB 17820–2018 [113]	≥28
5	city gas	GB/T 13611–2018 [114]	≥9.99

Table 3

Classification of gaseous biofuels according to LHV and HHV.

Class	LHV (MJ/m ³)	HHV (MJ/m ³)
High	28 ≤ LHV ≤ 34	31.1 ≤ HHV ≤ 37.8
Medium	14 ≤ LHV < 28	15.5 ≤ HHV < 31.1
Low	10 ≤ LHV < 14	11.1 ≤ HHV < 15.5
Ultralow	4.4 ≤ LHV < 10	4.8 ≤ HHV < 11.1
Subpar	LHV < 4.4	HHV < 4.8

SO_x. In this study, both the explosivity and toxicity are investigated as safety indicators.

3.2.1. Explosivity

The potential hazards related to the uncontrolled release of flammable gases depend on the composition and explosive limits of the gas in question [34], which are calculated as follows [115]:

$$L = \frac{(1 - 4.76 \cdot f_o)}{\sum_{i=1}^n \frac{f_i}{L_i} + 0.01(f_N - 3.76 \cdot f_o)} \quad (3)$$

where L is the upper or lower explosive limits of the fuel/oxidizer mixture, respectively, %. L_{*i*} is the upper or lower explosive limits of flammable component *i*, %, respectively (Table 1) [116]. *f_o* is the molar fraction of oxygen; and *f_N* is the total molar fraction of inert components (N₂ and CO₂).

3.2.2. Toxicity

LC₅₀ value is frequently used as a general indicator of the acute toxicity of a substance. The LC₅₀ of a gas mixture is defined as follows:

$$\text{LC}_{50} = \frac{1\,000\,000}{\sum_i^n \frac{v_i}{\text{LC}_{50,i}}} \quad (4)$$

where *v_i* is the ppm value (volume fraction) of toxic component *i*, and LC_{50,*i*} is the Lethal Concentration 50 value of toxic component *i* in ppm. CO, which has a LC₅₀ of 1880 ppm (4 h, rat), is the major toxic component in gaseous biofuels [117]. The other components in gaseous biofuels have very large LC₅₀ values (up to 820000 ppm) [117,118], which means they have very low or no acute toxicity. Therefore, it can be speculated from Eq. (4) that the LC₅₀ of a gaseous biofuel exhibits a power function relationship with its CO concentration when the gaseous biofuel contains CO.

In the Globally Harmonized System (GHS), the inhalation toxicity levels are: Category 1: Fatal if inhaled, 0 ppm < LC₅₀ ≤ 100 ppm; Category 2: Fatal if inhaled, 100 ppm < LC₅₀ ≤ 500 ppm; Category 3: Toxic if inhaled, 500 ppm < LC₅₀ ≤ 2500 ppm; Category 4: Harmful if inhaled, 2500 ppm < LC₅₀ ≤ 20000 ppm. Here the LC₅₀ values correspond to 4 h exposure.

3.3. Interchangeability

Gas interchangeability ensures that any gas-fired equipment using a substitute gas will continue to meet the performance standards corresponding to the original gas. The Wobbe Index is commonly used to evaluate the interchangeability of gaseous biofuel, which is represented

as below:

$$WI = \frac{HHV}{\sqrt{d_r}} \quad (5)$$

where d_r is the relative density respect to air (Table S2). The WI is used to compare the rate of heat release of different fuel gases in combustion equipment. For two fuels with identical WI, the heat release will be the same or closer for given pressure and valve settings.

The regulation of interchangeability is also either national or area specific. Honus et al. [119,120] investigated the replacement of conventional fuels in the USA, Europe, and the UK with plastic pyrolysis gases using the WI, the Knoy index, the Dutton factors, Weaver's method, the AGA method, and the Delbourg interchangeability indices. Zhang et al. [121] corrected the interchangeable limit of the AGA lifting index for domestic gas cookers burning multi-source natural gases. Currently, the gas interchangeability commonly used in South Korea is simply defined based on the range of the WI and maximum combustion potential [122]. The latest Chinese technical standard GB/T 13611–2018 uses a combination of the WI and HHV to measure and classify the interchangeability of city gases [114]. Manufactured gas is classified into 5 types: 3R, 4R, 5R, 6R, and 7R (WI range: 12.65–33.12 MJ/m³, and HHV range: 9.99–20.21 MJ/m³). Similarly, natural gas is classified into 4 types: 3T, 4T, 10T, and 12T (WI range: 12.42–54.77 MJ/m³, and HHV range: 11.62–43.57 MJ/m³). In this study, the technical standard GB/T 13611–2018 was employed to assess the interchangeability of gaseous biofuels.

Furthermore, Table S2 shows that the WI and HHV of many gaseous biofuels are lower than the minimum values in the technical standard GB/T 13611–2018 (WI: 12.42 MJ/m³, HHV: 9.99 MJ/m³), respectively. The regression analysis on the standard value and range of every class in the technical standard indicates that the WI and HHV differences are within –7%–8% and ±10%, respectively. Here the WI and HHV differences can be used as the preliminary requirements to judge the interchangeability of the gaseous biofuels with WI less than 12.42 MJ/m³ or HHV less than 9.99 MJ/m³.

4. Assessment of existing samples

4.1. LHV

Fig. 2 and Table S2 show that the LHVs of the AR, AS and OE samples

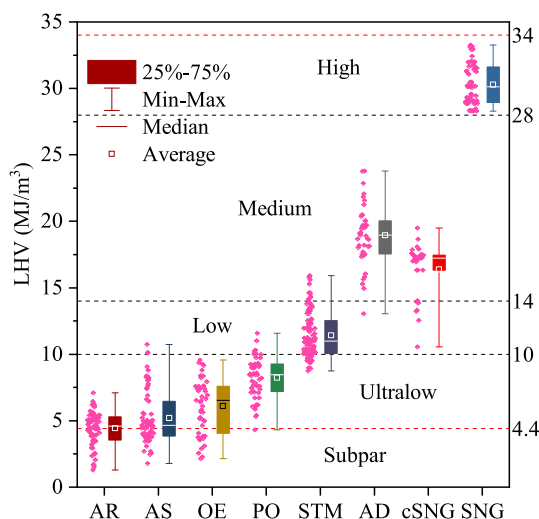


Fig. 2. LHV ranges of 8 types of gaseous biofuels (LHV: lower heating value; AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; STM: steam gasification; AD: anaerobic digestion; cSNG: crude synthetic natural gas; SNG: synthetic natural gas).

vary between 1.29 and 7.10, 1.08–10.7 and 2.1–9.6 MJ/m³, respectively. According to the required minimum LHV, nearly half of the AR and AS samples, and a quarter of the OE samples should not be used as gaseous fuels. The LHVs of the PO and STM samples are 4.3–12.6 and 8.3–15.92 MJ/m³, respectively. According to Table 2, most PO samples can be classified into the manufactured gas Class II, while more than half of the STM samples can be classified as manufactured gas Class I. Additionally, most of the AD and cSNG samples have LHVs of 14–28 MJ/m³, while all the SNG samples have eligible LHVs that could classify them as Class High (≥28 MJ/m³).

Generally, gaseous biofuels exhibit a wide LHV range. When the biomass gasification with air, air-steam or O₂-enriched air is applied, all efforts must be made to improve the LHV to meet the related lowest requirement. From this perspective, these gasification technologies, especially air gasification and air-steam gasification, are not recommended for producing gaseous biofuel.

4.2. Explosivity

Fig. 3 shows that most of the AR, AS and OE samples have both relatively higher UELs (60–85%) and LELs (10–25%); whereas most of the AD, cSNG and SNG samples have both relatively lower UELs (15–25%) and LELs (5–10%). The PO and STM samples exhibit higher UELs and lower LELs. Correspondingly, the AD, cSNG, and SNG samples show relatively narrower explosive ranges (UEL–LEL), while the other samples show relatively broader explosive ranges (Fig. 4). The difference in explosive limits of the STM and cSNG samples suggests that CO methanation can have a significant positive effect on the explosive hazard risk. As the LELs of the STM, AD, cSNG, and SNG samples are relatively low, more attention should be paid to preventing leakage during their use.

4.3. Toxicity

The ranges of CO concentrations of various types of gaseous biofuels are listed in Table S2, and the results of the GHS indicator are listed in Table 4. Generally, the LC₅₀ values of various gaseous biofuels vary from 3303 ppm to 2135417 ppm. All the OE, PO and STM samples are rated as “harmful”, while approximately 75% of the AR and AS samples are rated as “harmful”. On the other hand, all the AD, cSNG, and SNG samples are

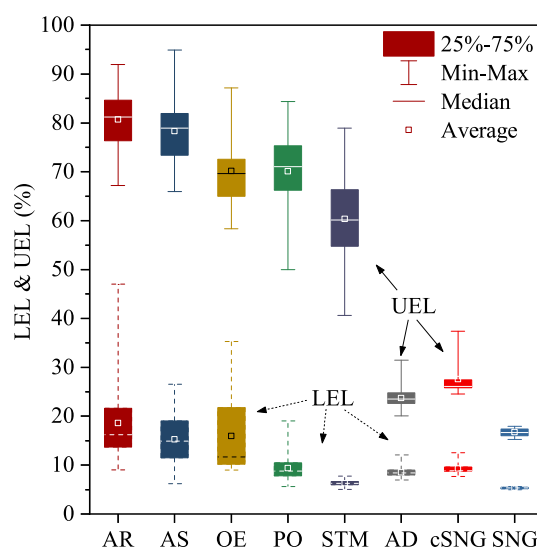


Fig. 3. LEL and UEL ranges of 8 types of gaseous biofuels (LEL: lower explosive limit; UEL: upper explosive limit; AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; STM: steam gasification; AD: anaerobic digestion; cSNG: crude synthetic natural gas; SNG: synthetic natural gas).

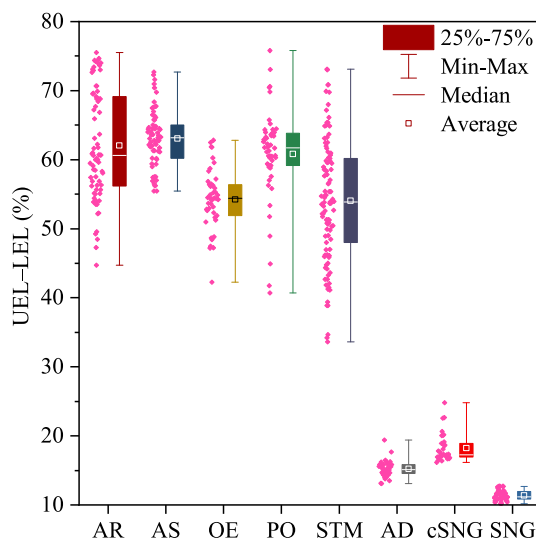


Fig. 4. (UEL–LEL) ranges of 8 types of gaseous biofuels (LEL: lower explosive limit; UEL: upper explosive limit; AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; STM: steam gasification; AD: anaerobic digestion; cSNG: crude synthetic natural gas; SNG: synthetic natural gas).

Table 4
LC₅₀ of 8 types of gaseous biofuels.

LC ₅₀ (ppm)	Max	Average	Min
AD	2,135,417	1,491,528	1,170,014
AR	42,899	14,417	6345
AS	50,343	16,520	4507
OE	18,778	10,251	5989
PO	11,219	6538	3303
STM	18,275	7486	3661
cSNG	1,943,128	875,470	54,862
SNG	925,572	636,075	205,968

nontoxic. Therefore, syngas produced by gasification should not be directly used as a civil gaseous fuel because of its toxicity. The difference in the LC₅₀ values of the STM and cSNG samples suggests that CO methanation can also play a significant role in reducing the toxicity hazard potential. Thus, CO methanation should be performed to all the syngas obtained by gasification.

Fig. 5 shows that there is a typical power function relationship between the LC₅₀ value and the CO concentration of the CO-containing gaseous biofuel samples without methanation treatment (coefficient of determination, $R^2 = 0.9999$). This confirms the feasibility and reliability of the above-mentioned method of evaluating the toxicity based on CO

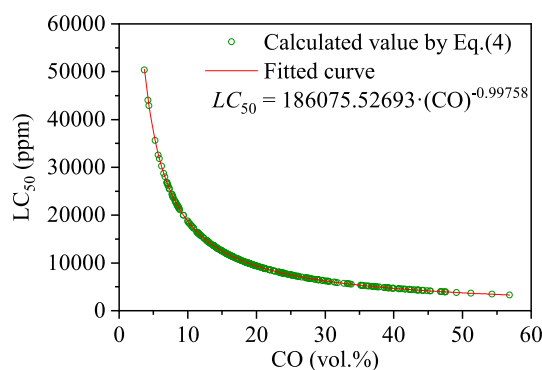


Fig. 5. Variation in LC₅₀ with CO concentration (LC₅₀: 50% Lethal Concentration).

concentration.

Fig. 6 shows the range of CO concentrations of the existing gaseous biofuel samples. Based on the power function relationship between LC₅₀ and CO concentration (Fig. 5), the CO concentration is approximately 9.4 vol% corresponding to the 20,000 ppm LC₅₀ in GHS (the threshold value). If the CO concentration is less than 9.4 vol%, the gaseous biofuel is rated as “not harmful” as per the GHS classification scheme. The related Chinese technical standard requires that the CO concentration in manufactured gas of Class I should be less than 10 vol% [112], which is almost equivalent to the value obtained using the GHS indicator. In addition, other Chinese technical standards (GB/T 13612–2006 [112], NY/T 443–2016 [123]) require that the manufactured gas of Class II and syngas should have a CO concentration of less than 20 vol%. Moreover, as Mao et al. reported [124], European manufacturers had supplied manufactured gases with stricter CO concentration limits (as low as 2 vol%) in the past. Inspired by these facts, the concentration of CO is attempted to be directly used as the toxicity index of gaseous biofuels for two reasons: (a) it is easy to determine and use; (b) by tightly controlling the CO concentration, it should be possible to increase the safety of gaseous biofuels. Based on the above-mentioned requirements and references, all the gaseous biofuels are classified into 4 groups (Table 5): Prohibitive (P), Marginal (M), Good (G) and Excellent (E).

According to the classification based on the CO concentration, most of the PO and STM samples, approximately half of the OE samples and a quarter of the AR samples are rated as “P” (Fig. 6). This implies that the PO and STM samples should not be used as civil gaseous fuels. A large proportion of the AR, AS, and OE samples with CO concentrations of 10–20 vol% are rated as “M”, meaning that these samples can be used as gaseous fuels but are not recommended. These samples are rated as “harmful” based on the LC₅₀ indicator in GHS. Approximately a quarter of the AR and AS samples are rated as “G”, and only one cSNG sample has a CO content greater than 2 vol% (Table S2); this sample was produced by hydrothermal gasification. Except for the outlier, all the AD, cSNG and SNG samples are rated as “E”. A comparison of the SNG and STM samples indicates that the CO methanation significantly reduces the toxicity of gaseous biofuels.

4.4. Interchangeability

The WI and HHV values of the existing gaseous biofuel samples are

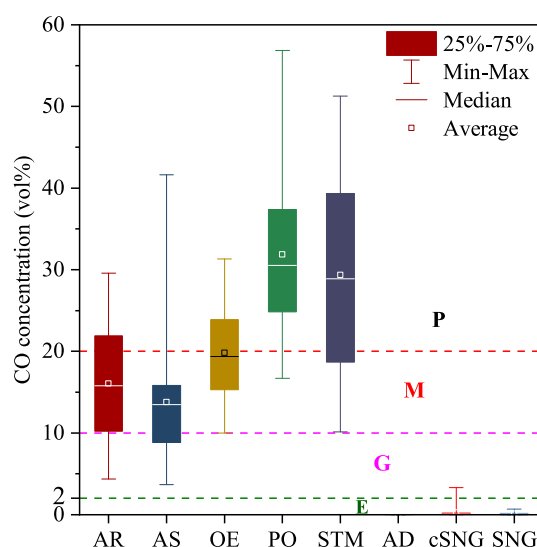


Fig. 6. CO concentration ranges of 8 types of gaseous biofuels (AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; STM: steam gasification; AD: anaerobic digestion; cSNG: crude synthetic natural gas; SNG: synthetic natural gas; E: excellent; G: good; M: marginal; P: prohibitive).

Table 5

Classification of gaseous biofuel's toxicity according to CO concentration.

Concentration	Classification
CO > 20 vol%	Prohibitive (P)
10 vol% < CO ≤ 20 vol%	Marginal (M)
2 vol% < CO ≤ 10 vol%	Good (G)
CO ≤ 2 vol%	Excellent (E)

shown in Fig. 7 (a) and (b), respectively. Firstly, SNG does not exhibit interchangeability with the other types of gaseous biofuels. According to the minimum values of WI (12.42 MJ/m³) and HHV (9.99 MJ/m³) in the standard [114], the STM, AD, cSNG, and SNG samples can be evaluated using the interchangeability indicators in the standard, while most of the AR, AS, OE, and PO samples can not be assessed by these indicators. Thus, the AR, AS, OE, and PO samples generally do not show interchangeability with the STM, AD, and cSNG samples, and vice versa. This also means that most of the AR, AS, OE, and PO samples are not compatible with the existing proven combustors. Data backdating shows that the AR and PO samples that are exceptions are mainly related to plasma gasification [54,56], which can reduce the amount of air or oxygen required for gasification and increase the concentrations of the flammable components.

Fig. 8 shows the interchangeabilities of the STM, AD, cSNG and SNG samples. Most of the SNG samples can be classified as 10T (62.50%) or 12T (33.93%), implying that SNG is highly compatible with the existing natural gas facilities. About three quarters of the STM and AD samples can be labeled as 3R, 4R, 5R, or 6R, meaning they can be used with the existing devices for manufactured gas. Although the composition of cSNG is similar to that of AD as per a preliminary estimation, only 39.39% of the cSNG samples are interchangeable with the manufactured gas of 3R, 4R, and 5R. The primary reason for the samples that cannot be classified using the technical standard is that their WI values lay outside the classification ranges. For example, the WI values of a dozen of cSNG samples are 19.23–19.61 MJ/m³ (Table S2), these are greater than the upper limit of 4R (19.03 MJ/m³, Fig. 8) and less than the lower limit of 5R (19.81 MJ/m³, Fig. 8). Considering the narrowness of these invalid intervals, it is easy to improve the interchangeability of cSNG by adjusting its composition.

Meanwhile, the interchangeabilities of the AR, AS, OE, and PO

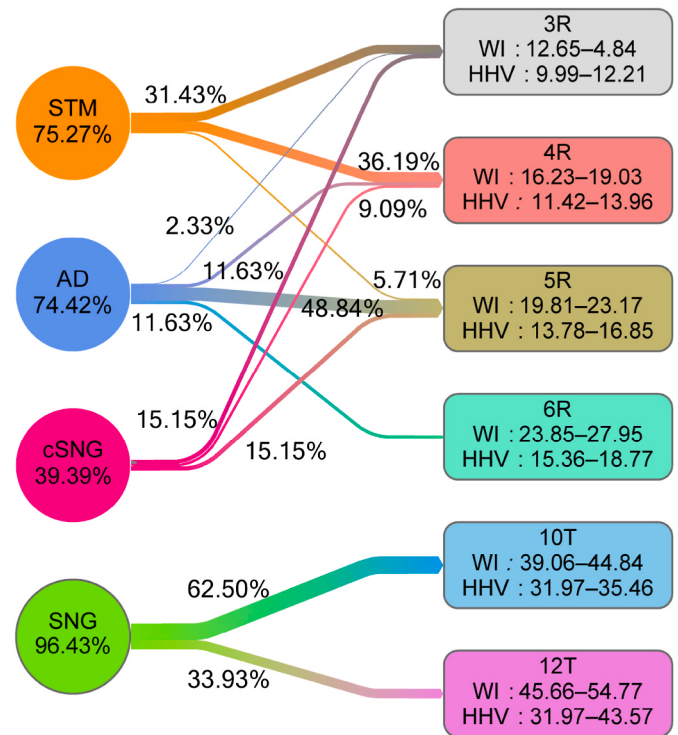


Fig. 8. Interchangeability of STM, AD, cSNG and SNG samples (WI: Wobbe Index; HHV: higher heating value; STM: steam gasification; AD: anaerobic digestion; cSNG: crude synthetic natural gas; SNG: synthetic natural gas; 3R, 4R, 5R, 10T, and 12T: classification labels of city gas).

samples are preliminarily investigated using the above-mentioned rules: the WI difference is within -7% – 8% and the HHV difference is within $\pm 10\%$. Fig. 9 shows that, except for the AR and PO samples ($\leq 54\%$), most of the AR, AS, OE, and PO samples (59% – 88%) are interchangeable with each other. Specifically, 54% of the AR samples can be interchanged with the PO samples, while only 40% of PO samples can interchange with the AR samples. This indicates that high-purity O₂ gasification is a distinctive technology. The results also highlight the

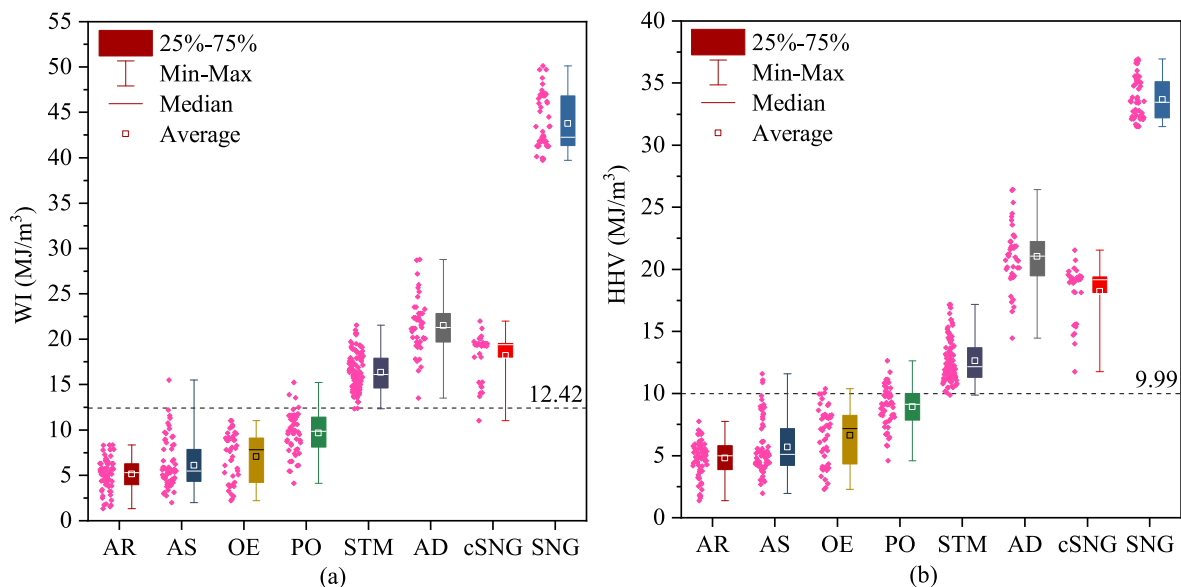


Fig. 7. WI (a) and HHV (b) value ranges of 8 types of gaseous biofuels (WI: Wobbe Index; HHV: higher heating value; AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; STM: steam gasification; AD: anaerobic digestion; cSNG: crude synthetic natural gas; SNG: synthetic natural gas).

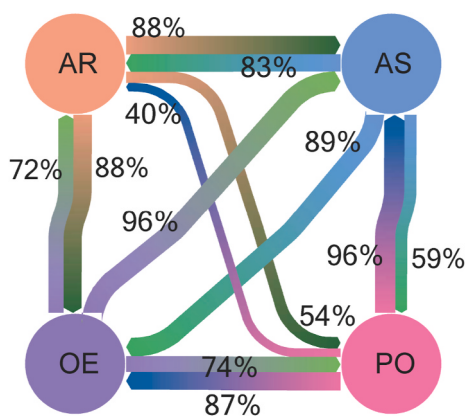


Fig. 9. Interchangeability of AR, AS, OE and PO samples (AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification).

feasibility and compatibility of the different gasification technologies and feedstocks that can be used with one gaseous biofuel grid. In terms of interchangeability, the differences between air gasification, air-steam gasification and O₂-enriched air gasification are not significant. Therefore, only one of the three gasification technologies should be researched further for gaseous biofuel production.

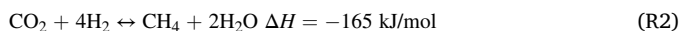
5. Assessment on predicted samples

Previous studies mainly used the methanation technology as the post treatment for STM and performed CO₂ removal to AD and cSNG. In contrast, only a few studies involved the hydrogenation methanation in studies on PtG processes. In this study, by applying the conventional methanation, CO₂ separation, and hydrogenation methanation processes, 12 new types of gaseous biofuels could be obtained from syngas produced by gasification using air, air-steam, O₂-enriched air, and high-purity O₂ as the gasifying agents (Fig. 1). The upgrading treatments and their applications were discussed below.

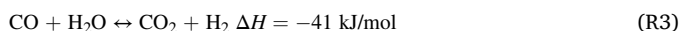
5.1. Upgrading treatments

5.1.1. Conventional methanation

The aim of methanation synthesis is to produce CH₄ from CO (CO methanation) and/or CO₂ (CO₂ methanation) with H₂ through the following reactions:



The H₂/CO ratio of the AR, AS, OE, and PO varies from 0.08 to 2.25 (Table S2), indicating that the original amount of H₂ is too small to significantly reduce the CO concentration to a very low level. Without the addition of H₂, the water promotes water-gas shift reaction (R3) to shift towards the right side to generate H₂ and CO₂:



The conversion rate of H₂ can reach 89.5% [125] or higher [92], while that of CO approaches 100% [92,126]. Therefore, the conversion rates of H₂ and CO were assumed to be 90% and 99%, respectively, to predict the compositions of the new gaseous biofuels upgraded using the conventional methanation. In this study, “conventional methanation” refers to the syngas methanation without using external H₂.

5.1.2. CO₂ removal

CO₂ is generally separated from AD or cSNG to improve their heating values. Fig. 10 shows the existing technologies of CO₂ removal with

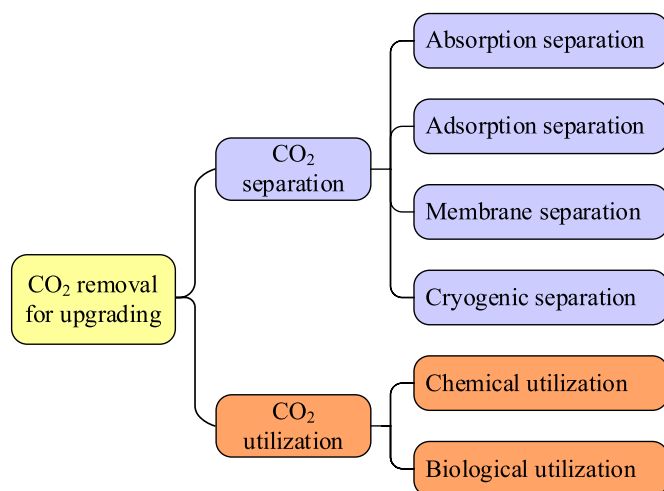


Fig. 10. Current technologies of CO₂ removal for gaseous biofuel upgrading.

good readiness for upgrading gaseous biofuels, including CO₂ separation and CO₂ utilization. Absorption (physical and chemical), adsorption, membrane separation (polymer and inorganic), and cryogenic separation are the commonly used CO₂ separation technologies [8,10]. Note that trace contaminants, such as H₂O, H₂S, and siloxanes, usually need to be removed from biogas, however, that was not the focus of this study.

CO₂ separation can significantly improve the quality of gaseous biofuels. The available CO₂ separation technologies were reviewed based on the development principles, process configurations, equipment, separation performance, and environmental impact [127–130]. The methane loss during CO₂ separation is 0.05–4%, and the electricity consumption rate is 0.05–0.43 kWh/Nm³_{biogas}, or 0.5–10 MJ/kg CO₂ [128,129,131]. The operating cost of CO₂ separation in China is 0.26–0.37 CNY/m³ [132], accounting for approximately 10% of the typical selling price of natural gas. To predict the compositions of the new gaseous biofuels obtained after CO₂ separation, 98% of CO₂ in syngas was assumed to be separated, and methane loss was assumed to be 1% [133].

5.1.3. Hydrogenation methanation

Fig. 10 shows that CO₂ utilization mainly involves chemical and biological processes [6]. As a significant amount of energy is needed to break the C=O bonds in CO₂, renewable energy or excess electricity must be used to keep the process sustainable. With the development of PtG technology, CO₂ removal via hydrogenation methanation is a promising method for upgrading syngas obtained from biomass gasification, resulting in an improved SNG yield with no CH₄ loss. PtG technology has been evaluated extensively in recent years to convert biogas/syngas/CO₂ streams into storable methane using excess renewable electricity [134,135]. Because of this trend, hydrogenation methanation has become an attractive upgrading technology as CO and CO₂ can be converted readily into CH₄ with the addition of H₂. The amount of H₂ required for the complete reforming of CO and CO₂ into CH₄ can be determined from the stoichiometric coefficients of R1 and R2. The stoichiometric number (SN) of the incoming gas stream was used to characterize the achievable methane yield [89]. When biomass gasification is combined with PtG through water electrolysis, a massive amount of H₂ is required to unify the SN, and that the by-product, O₂, is produced in excess, even for high-purity O₂ gasification. Thus, for a biomass and power-to-gas (B&PtG) process integrating with water electrolysis and hydrogenation methanation, high-purity O₂ gasification should be used.

The primary technical challenge related to the use of PtG and B&PtG technologies is the energy inefficiency of water electrolysis (65–90%, based on HHV), especially at the industrial scale [136,137]. These

processes would be profitable if the cost of renewable electricity were to become very low or zero [98,138–140]. Considering the future decreases in both electricity price and electrolyzer cost, the technical benefits of hydrogenation methanation were explored in this study. Based on a related experimental report [141], a CO₂ conversion rate of 90% was modeled during the assessment. Based on the modeling and verification using Aspen Plus, the H₂ conversion rate was approximately 97.5% for AR and AS and 98.5% for OE and PO.

In the study, the subscripts “m” refers to the conventional methanation without addition of H₂, “ms” refers to the conventional methanation and CO₂ separation, and “hm” refers to the hydrogenation methanation of CO and CO₂ with external H₂.

5.2. Assessment and comparison

5.2.1. Compositions

Table S2 lists the ranges of the compositions and properties of the predicted 729 sets of gaseous biofuel samples on dry basis. Generally, the concentration ranges of combustible components of the predicted gaseous biofuel samples are similar to those of the existing samples. However, the inert components CO₂ and N₂ of the predicted samples have wider ranges of 0.01–87.40 vol% and 0.09–94.98 vol%, respectively. Table S2 also shows that conventional methanation sharply reduces H₂ and CO concentrations of all syngas samples. Although CO₂ separation has few benefits in improving the CH₄ concentration for the AR_m and AS_m samples, it can considerably or substantially increase the CH₄ concentration for the OE_m and PO_m samples. Hydrogenation methanation leads to a significant enhancement in the CH₄ concentration for the PO and PO_m samples as CO₂ is a major component. The results demonstrate that conventional methanation, CO₂ separation, hydrogenation methanation can create new types of gaseous biofuels.

5.2.2. LHV

In the cases of AR and AS and the predicted samples, Fig. 11 shows that conventional methanation has slight effects on LHV. The reason is that inert gases (N₂ and CO₂) are still the major components in the AR_m and AS_m samples (Table S2). Since the CO₂ concentration of most of these samples is below 28 vol%, CO₂ separation has limited effects on increasing LHV. Therefore, most AR_{ms} and AS_{ms} samples still belong to Class “Ultralow”. Considering the cost of CO₂ separation, it is not practical to apply CO₂ separation to AR_m and AS_m. Indicated by the AR_{hm} and AS_{hm} samples, LHV can be substantially improved by hydrogenation methanation, because it converts CO₂ into CH₄ and then substantially increases CH₄ concentration compared with AR_{ms} and AS_{ms}

(Table S2). Fig. 11 shows that the Class of AR_{hm} and AS_{hm} based on LHV is generally one level higher than that of AR_{ms} and AS_{ms}. However, because of the above-mentioned high cost associated with water electrolysis and excess by-product of O₂ in the B&PtG process integrated with water electrolysis, the justification is poor to apply hydrogenation methanation to AR and AS.

In the cases of OE and the predicted samples, the difference in LHVs of OE_m and OE samples indicates that the conventional methanation has limited effects on LHV (Fig. 11), because CO₂ and N₂ are the main components (totally 58 vol%). Most of the OE_m samples belong to Class “Ultralow”, a part of them belongs to Class “Subpar”. Indicated by the OE_{ms} samples, CO₂ separation can significantly improve LHV (Fig. 11), and a quarter of OE_{ms} belong to Class “Medium”. The comparison between OE_{hm} and OE_{ms} shows that hydrogenation methanation can further significantly increase LHV as well the class. Generally, LHVs of the OE_{hm} samples are similar to those of the AD and cSNG samples. However, LHVs of all OE_{hm} samples are less than 28 MJ/m³, and most of them are less than 22 MJ/m³. Taken together, the results imply that O₂-enriched air (O₂ purity: 30–70%) gasification is useable but recommended to produce high-LHV gaseous biofuels.

Furthermore, Table S2 indicates that the LHVs of the OE_m samples over 50–70% O₂ purity range exceed 7 MJ/m³. This indicates that O₂ purity is an effective measure for improving the heat values and ensuring the qualities. O₂-enriched air gasification over 50–70% O₂ purity range may be a compromise technology for gaseous biofuel production, which theoretically balances LHV and oxygen production cost. It has potentials for low-income areas without a gas grid, which is discussed in Section 6.

In the cases of PO and the predicted samples, Fig. 11 shows that the conventional methanation has more obvious effects on LHV, although most of the PO_m samples still belong to Classes “Ultralow” or “Low”. Very few of the PO_m samples belong to Class “Subpar”, suggesting that high-purity O₂ gasification plus conventional methanation is a potential technical route to generate high-safety gaseous biofuels. This technical route may gain the development opportunity in the PtG framework by taking advantage of the by-product O₂ [98]. As the PO_m samples have few inert N₂, their LHVs can be significantly improved by CO₂ separation. Note that the LHVs of both PO_{ms} and PO_{hm} samples are equivalent to those of SNG (Fig. 11), indicating that high-purity O₂ gasification plus either conventional methanation and CO₂ separation or hydrogenation methanation is a feasible way for SNG production [98]. Taken together, high-purity O₂ gasification is a powerful and flexible technology for generating gaseous biofuels.

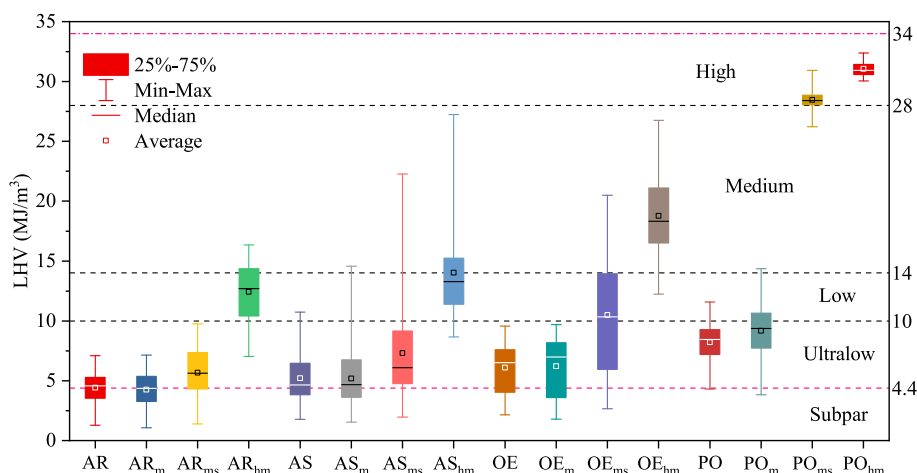


Fig. 11. Influences of methanation and CO₂ removal on LHV of 12 types of predicted gaseous biofuels (LHV: lower heating value; AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; m: conventional methanation; ms: conventional methanation plus CO₂ separation; hm: hydrogenation methanation).

5.2.3. Explosion limit

Fig. 12 shows that the conventional methanation substantially lowers the ULE and considerably enlarges the LEL. CO₂ separation further reduces both ULE and LEL. However, the explosion range (UEL–LEL) changes little with CO₂ separation. The hydrogenation methanation can further reduce both ULE and LEL, as well as the explosion range. Note that after CO₂ separation, the average and median values of H₂ concentration of the PO_m sample are approximately 14.5 vol%, which is much higher than those in other predicted samples (generally <5 vol%). However, ULEs and LELs of the PO_m samples are similar to those of PO_{hm} samples, indicating that H₂ concentration is not a crucial factor any more for these types of gaseous biofuels. As the LELs are quite low, close attention is needed to prevent leakages. To sum up, conventional methanation, CO₂ separation, and hydrogenation methanation are beneficial to reduce the explosive hazard risk.

5.2.4. Toxicity

Fig. 13 shows that all types of gaseous biofuels produced by methanation synthesis, either conventional or hydrogenation, have very low toxic hazard potential and can be rated as “Excellent” according to Table 5. Furthermore, although the CO concentration rises slightly by CO₂ separation, all the samples with “ms” are still excellent enough. These results confirm that the CO methanation must be carried out to all the syngas produced by gasification for civil utilization.

Note that about half of the AR_m and AS_m samples, a large proportion of the OE_m and PO_m samples meet the lowest requirement of LHV for civil use (≥ 4.4 MJ/m³, Table 2) and have lower explosive and toxic hazard potentials. With proper controls, the process of biomass gasification only with conventional methanation can be a compromise method to produce affordable gaseous biofuels for low-income areas.

5.2.5. Interchangeability

Fig. 14 shows that conventional methanation has few effects on the WI and HHV values of the AR, AS, OE, and PO samples, as well as the interchangeabilities. Concretely, more than half of the samples can interchange with each other. 14% of the AS_{ms} samples and 37% of the OE_{ms} samples are interchangeable with the manufactured gases (mainly 3R and 4R, Fig. 8). However, no AR_{ms} samples can be interchanged with those manufactured gases in the technical standard. Note that 81% of the PO_{ms} samples are interchangeable with the natural gases (10T and 12T, Fig. 8). When hydrogenation methanation is employed, 55% of the AR_{hm} samples, 77% of the AS_{hm} samples, and 72% of the OE_{hm} samples are interchangeable with the manufactured gases (mainly 3R, 4R, 5R and 6R, Fig. 8). 83% of the PO_{hm} samples can be interchanged with the

natural gases (10T and 12T, Fig. 8).

With respect to interchangeability, the most notable result is that a majority of PO_{ms} and PO_{hm} samples are interchangeable with natural gas. This confirms that SNG can be produced based on high-purity O₂ gasification regardless of oxygen production methods.

5.2.6. Statistical relation between HHV and LHV

Different countries and organizations have different selections with regard to HHV or LHV. Thus, the classification of gaseous biofuels according to HHV is also useful, which should be studied for the convenience of application. Based on the 1211 sets of samples (Table S2), the statistical study indicates that there is a strong positive linear relationship between LHV and HHV as below:

$$\text{LHV} = 0.8978 \cdot \text{HHV} + 0.0493 \quad (6)$$

where LHV and HHV are in MJ/m³, and the R^2 is 0.9999. Based on the correlation, the HHV values of the demarcation points were calculated and listed in Table 3, which forms the method for classifying gaseous biofuels according to HHV.

6. Selection of gaseous biofuels and guidance on production technologies

6.1. Recommended gaseous biofuels

Based on the above-described results, the matching relationships for the source and upgrading technologies are listed in Table 6. The available gaseous biofuels are as follows: (i) high-LHV (SNG), as shown in Figs. 11 and 14, PO_{ms} and PO_{hm} are actually SNG; (ii) medium-LHV (AD and cSNG); and (iii) low and ultralow-LHV (OE_m, OE_{ms} and PO_m). The CO concentration should be limited to 2 vol% (Figs. 6 and 13). The average and median values in Table S2 indicate that it is feasible to limit the H₂ concentration to 5 vol%, although it is not a crucial safety factor for these types of gaseous biofuels. AR_m and AS_m are not recommended because approximately half of the samples belong to the Class “subpar”. As more than a quarter of the OE_m samples belong to the Class “subpar”, various factors, such as ER, gasification temperature, and residence time, must be considered during OE production to improve the heating value. O₂-enriched air gasification with O₂ purity of 25–40% can generate qualified gaseous biofuels when the S/B is small (generally ≤ 0.6). Conservatively, O₂-enriched air with an O₂ purity of less than 50% can satisfy this purpose. The results also indicate that upgrading technologies have a determining effect on the quality of gaseous biofuels,

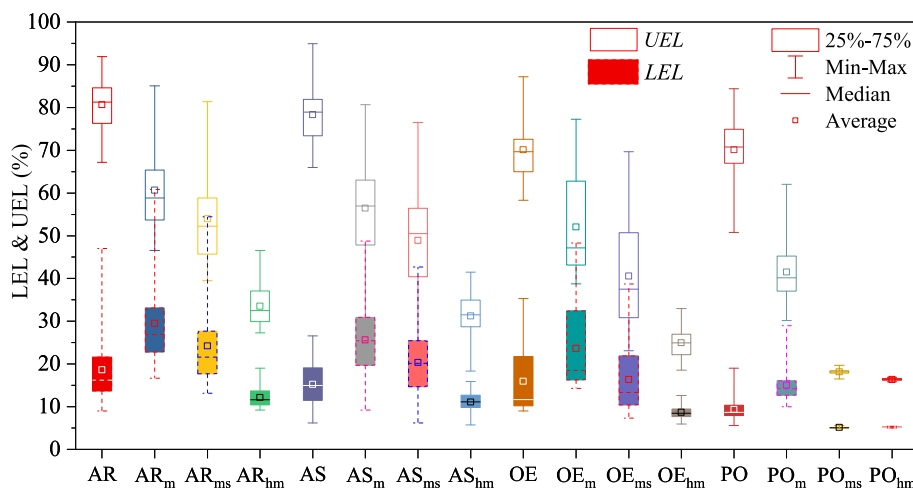


Fig. 12. Influences of methanation and CO₂ removal on LEL and UEL of 12 types of predicted gaseous biofuels (LEL: lower explosive limit; UEL: upper explosive limit; AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; m: conventional methanation; ms: conventional methanation plus CO₂ separation; hm: hydrogenation methanation).

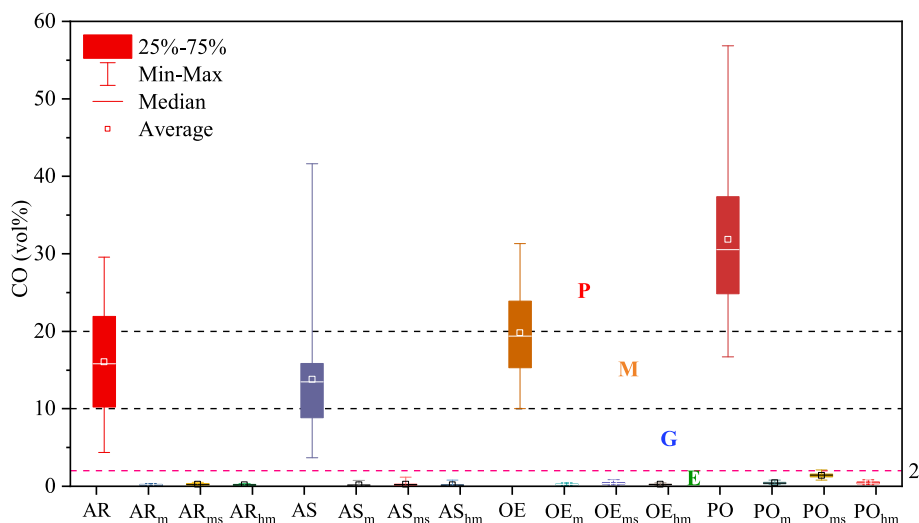


Fig. 13. Influences of methanation and CO₂ removal on toxicity of 12 types of predicted gaseous biofuels (E: excellent; G: good; M: marginal; P: prohibitive; AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; m: conventional methanation; ms: conventional methanation plus CO₂ separation; hm: hydrogenation methanation).

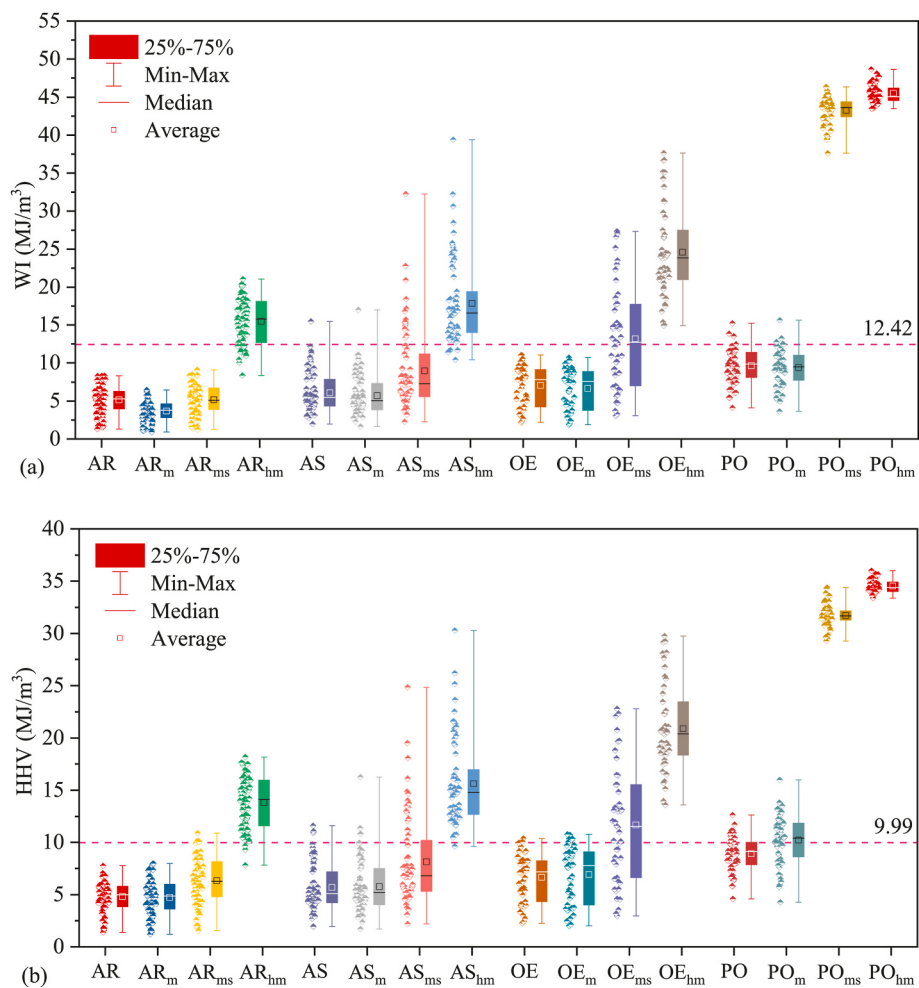


Fig. 14. Influences of methanation and CO₂ removal on WI (a) and HHV (b) of 12 types of predicted gaseous biofuels (WI: Wobbe Index; HHV: higher heating value; AR: air gasification; AS: air-steam gasification; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification; m: conventional methanation; ms: conventional methanation plus CO₂ separation; hm: hydrogenation methanation).

Table 6

Relationship between source and upgrading technologies and recommended gaseous biofuels.

Source technology	Upgrading technology		
	Conventional methanation	CO ₂ separation	Hydrogenation methanation
AD		√ (SNG)	√ (SNG)
AR	Not recommended	×	×
AS	Not recommended	×	×
OE	√ (OE _m , O ₂ purity ≥50%)	√ (OE _{ms})	×
PO	√ (PO _m)	√ (PO _{ms})	√ (PO _{hm})
STM	√ (cSNG)	√ (SNG)	√ (SNG)

especially when hydrogenation methanation is employed.

6.2. Selection of upgrading treatments

6.2.1. CO₂ separation

The CO₂ in gaseous biofuels and their flue gas can be regarded as biogenic, of which the global warming potential (GWP) is usually excluded from the environmental impact assessments [142,143]. However, the GWP of biogenic CH₄ cannot be excluded. The current CO₂ separation technologies lead to a methane loss of approximately 0.05–4% [128,129,131]. As the GWP of CH₄ is 25 times that of CO₂, a small amount of methane loss during CO₂ separation will have an obvious impact on the GWP. Ardolino et al. [144] performed a life cycle assessment of biomethane production from anaerobic digestion and membrane separation and reported a CH₄ loss of 0.69%, which results in a considerable emission of biogenic CH₄. Thus, biomethane production and utilization would increase global warming compared with the direct burning of raw biogas. Although there have been a number of environmental assessments related to biogas/cSNG upgrading, the effects of CH₄ loss during CO₂ separation have not been sufficiently elucidated, owing to the following factors: either the CH₄ loss was not taken into account [142,143,145], or the CH₄ loss was considered but a quantitative analysis of its impact was not performed [89,130,146]. As both SNG and AD are currently used as fuels worldwide [48,147], the direct use of cSNG and AD may be an alternative to avoiding CH₄ loss during CO₂ separation and reducing the plant-to-grave GWP.

6.2.2. Hydrogenation methanation

The great challenge with respect to PtG and B&PtG technologies is that the energy efficiency of H₂ production by water electrolysis is relatively low, and the production cost is too high. CO₂ removal based on hydrogenation methanation is not competitive currently. In addition to the future decreases in both the electricity price and electrolyzer cost, approaches that can either improve the conversion efficiency of water electrolysis or reduce the electricity consumption per unit SNG are essential for this technical pathway. In addition, hydrogenation methanation can be used to modestly adjust and upgrade various types of gaseous biofuels. As shown by the interchangeability analysis results (Figs. 7 and 8), the AD and cSNG samples have similar compositions, but only a few samples exhibit interchangeability. To supply gaseous biofuels with satisfactory interchangeability and equivalent qualities for a distributed and isolated gas grid, the partial conversion of CO₂ by hydrogenation methanation could be an alternative for the fine adjustment of the composition of the gaseous biofuel.

The investment cost of CO₂ separation technologies is 2300–3400 €/Nm³ biogas/h, and the specific energy consumption is 0.15–0.42 kWh/Nm³ biogas [130]. In contrast, the investment cost of water electrolysis technologies is 800–2320 €/kW_{el} and higher for solid oxide electrolysis cells. The specific energy consumption of water electrolysis is 3.7–6.6 kWh/Nm³ H₂ [148]. Based on the stoichiometric coefficients for CO₂ methanation and the CO₂ concentration in biogas or cSNG, it can be speculated that, to upgrade the same amount of biogas or cSNG, the

investment cost and energy consumption for hydrogenation methanation are undoubtedly much higher than those for CO₂ separation. However, the product of hydrogenation methanation also has distinct advantages over that of CO₂ separation, both in terms of the volume flow rate and energy flow rate. Thus, the levelized cost of energy for these CO₂ removal technologies should be analyzed in the future, especially while considering the fluctuating price of electricity.

6.3. Selection of source technologies

From the perspective of the quality of gaseous biofuels, anaerobic digestion is an excellent source technology for producing medium to high-LHV and high-safety biofuels without methanation. The theory and technical route of anaerobic digestion are well understood and developed; however, the optimization of the feeding composition and co-digestion process [49], pre-treatment enhance technologies [147], and upgrading technologies [8] need to be investigated further [149]. Regarding thermochemical gasification, the following guidelines should be used for selecting the source technology.

- (1) Air gasification or air-steam gasification is not recommended as source technology because the LHVs of most samples are very low, even after upgrading treatments.
- (2) O₂-enriched air gasification with a proper control can be used. Table S2 shows that the LHVs of all the OE_m samples with an O₂ purity of 50–70% exceed 7 MJ/m³. Therefore, a process integrating O₂-enriched air gasification with 50–70% O₂ purity and subsequent conventional methanation is recommended for low-cost gaseous biofuel production, as a compromise technology for low-income areas.
- (3) High-purity O₂ gasification is an adequate source technology. This technology was once compared with steam gasification [150], and integrated into PtG processes [36,37,98]. The available technologies for O₂ production must be compared to determine the most appropriate scenarios.
- (4) Steam gasification is a suitable technology for medium- and high-LHV gaseous biofuel production. The most crucial equipment for this technology is the indirect heating gasifier (dual fluidized beds in most cases), which is complex and difficult to design, operate, and maintain [151]. Thus, this technology may not be attractive in undeveloped areas lacking advanced manufacturing abilities and skilled workers. Similar problems also exist with the chemical looping gasifiers used for biomass oxygen gasification [152].

6.4. Outlook on production technologies

Facing the global transmission to renewable energy-dominated energy structures, B&PtG processes integrated with water electrolysis can play an important role in electricity storage [98]. However, the primary limitations of this pathway are the low energy conversion efficiency of water electrolysis and high production costs. Other electricity-driven gasification technologies are theoretically applicable. High-efficiency plasma torch (70–94%) and electric resistance heating (nearly 100%) can both drive and promote gasification reactions [54,153]. As the products are easy-to-use fuels for regenerating electricity, these electricity-driven gasification technologies can be utilized to indirectly and equivalently store electricity.

The relevant electricity-driven gasification technologies are classified as “Direct” and “Indirect” technologies (Fig. 15). Direct technologies integrate conversion components that transform electricity into heat energy without a medium. However, microwave-assisted heating is not recommended because of its relatively low energy efficiency [154–156]. In contrast, plasma gasification and electrical heating gasification are more efficient and suitable for industrial applications [157]. In this case, biomass gasification can be performed in a single reactor,

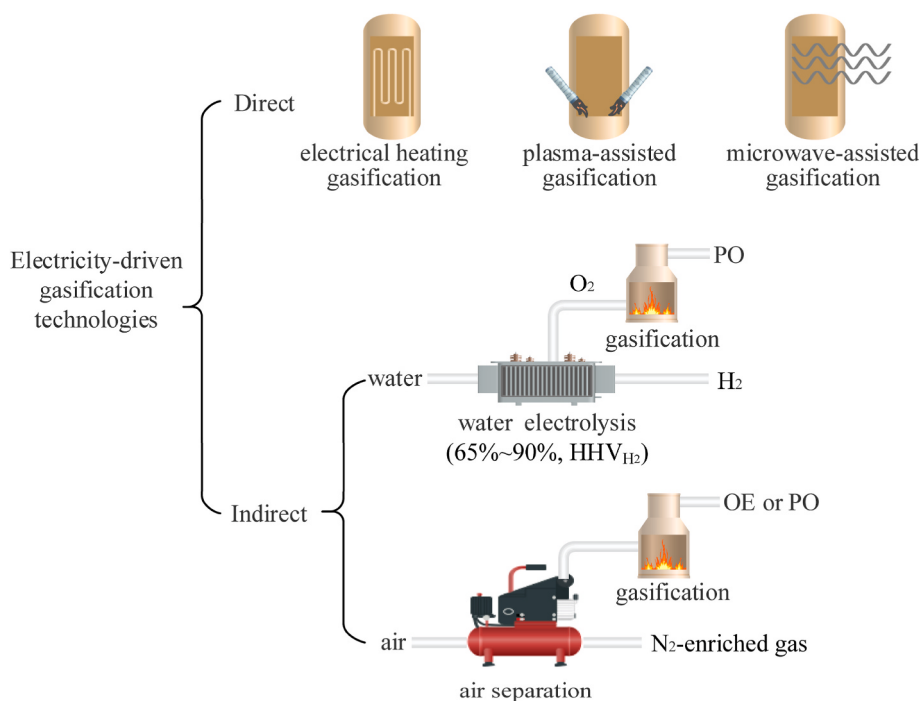


Fig. 15. Classification and examples of some electricity-driven gasification technologies (HHV: higher heating value; OE: O₂-enriched air gasification; PO: high-purity oxygen gasification).

and dual fluidized beds are not necessary. Furthermore, the restrictions related to the moisture content of the feedstock become more lenient when direct electricity-driven gasification technologies are employed. Distributed pyrolysis plants with central gasification plants are a promising approach [158], and direct electricity-driven gasification technologies can be employed in the pyrolysis processes.

In contrast, indirect technologies involve at least one medium. In addition to water electrolysis, biomass gasification with oxygen produced by various air separation technologies can also be regarded as an indirect electricity-driven gasification technology, which may be better than indirectly heated gasification using steam in terms of thermo-economic performances [159]. Note that the above-described electricity-driven technologies can be applied in a hybrid manner and thus create more opportunities for tackling the challenges related to biomass conversion.

In addition, the electricity-driven synthesis of biogas and syngas are attractive options. Grim et al. [160] reviewed the direct and indirect (via an energy carrier such as H₂) reductive pathways for CO₂ utilization for chemical production. Most of the pathways can also be utilized for the synthesis of biogas and syngas. Furthermore, renewable power-to-X (PtX) is a promising platform for storing excess renewables and providing a low-cost decarbonization pathway [161–163]. The integrated process of biomass and power-to-X (B&PtX) via the above-mentioned electricity-driven technologies can produce various fuels even from organic wastes (biogenic and non-biogenic) in a clean and sustainable way. The B&PtX process can potentially provide solutions for the following demands: biomass and organic waste management, renewable power utilization and storage, sustainable fuel production, and decarbonization. Renewable power utilization and storage are crucial for grid stability. The B&PtX pathway should be subjected to additional technical, economic, and environmental studies to evaluate its competitiveness and potential for renewable power storage. In summary, the proposed concept of the electrification of biomass conversion provides new opportunities for boosting biomass conversion and the production of alternative fuels.

7. Conclusions

An informative database of the compositions of various gaseous biofuels containing 20 types (1211 sets) of samples was built, and the suitable gaseous biofuels were screened. This study should contribute significantly to analyses of the properties of gaseous fuel as well as the development of their production technologies and chemical synthesis. Statistical findings were obtained, such as the relationship between toxicity and the CO concentration, and the correlation between the HHV and LHV. In addition, two practical methods for classifying gaseous biofuels were proposed based on their heating values and CO concentrations, respectively.

Anaerobic digestion, steam gasification, and high-purity O₂ gasification are the primary suitable source technologies to produce eligible gaseous biofuels. O₂-enriched air gasification with O₂ purity of 50–70% is a suitable technology for Ultralow-LHV gaseous biofuels production. O₂-enriched gasification with O₂ purity between 80 and 93% is a potential competitive source technology and deserves investigations in the future. For the areas with excess renewable power, the electricity-driven gasification technologies are promising and preferable.

Conventional methanation is a necessary upgrading technology to sharply reduce toxicities for all syngas from biomass gasification. Conventional methanation, CO₂ separation, and hydrogenation methanation are beneficial to reduce the explosive hazard risk. For the application of CO₂ separation, the influence of CH₄ loss should be paid attention to.

Moreover, the electrification of biomass conversion is an encouraging direction in this field. Particularly, the electricity-driven gasification technologies deserve future investigation and demonstration. As a specific pathway of this concept, the biomass and power-to-X processes provide promising solutions for biomass and organic waste management, grid stability, sustainable fuel production and decarbonization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.rser.2022.112959>.

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