Waste gas utilization potential for solid oxide fuel cells: A brief review

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ABSTRACT

This work is centered on the comparative appraisal of various waste gas mixtures which can be utilized for electric power and heat generation using solid oxide fuel cells (SOFCs), on the main sources of these gases, and on technological aspects related to their use. Particular emphasis is given to the waste gases produced by municipal solid waste landfills and industry, including coke oven, blast furnace and converter gases from metallurgy, gas from underground coal mines, agricultural and food industry produced biogas, and hydrogen-containing wastes from chemical industrial processes. The advantages and limitations of SOFCs are analyzed with respect to the mature technologies based on reciprocating internal combustion engines and gas turbines, where successful pilot projects of the waste gas utilization were well documented in the literature, and other types of fuel cells. The high-calorific waste generation dynamics, gas purification methods and state-of-the-art SOFC developments are briefly addressed.

1. Introduction

Every year the problems of environmental pollution are becoming more acute, particularly due to rapidly increasing amount of generated municipal solid wastes (MSWs) and industrial emissions. At present, one of the widely used approaches of waste disposal is to transmit it to landfills, often without sorting. From the energetic point of view, such landfills (about 8 years after start of their operation [1]) present a very specific source of renewable hydrocarbon-containing fuel located in the vicinity of cities. The relevance of this subject is stipulated due to toughening of the environmental safety requirements, problems associated primarily with the operation of MSW landfills, and efforts to introduce energy-efficient waste utilization technologies. The calorific gases produced by industrial enterprises as by-products (if not used in further technological processes) may also serve as a fuel to produce electrical and thermal energy. Therefore, adaptation of various energy-related technologies for use of these resources is being actively analyzed. Another issue refers to the development of alternative power sources providing a high efficiency and minimum environmental pollution. Whilst the reciprocating internal combustion engines (ICEs) are already employed in this niche, the use of fuel cells is mainly limited

to pilot projects with the main emphasis on an increased efficiency of these systems compared to heat engines [2]. As an example, the molten carbonate fuel cells (MCFCs) were installed for the utilization of landfill gas at the urban landfill of Giugliano in Campania (Italy) in addition to four ICEs and one gas turbine (GT) unit, operating in the cogeneration mode [3]. The technologies based on solid oxide fuel cells (SOFCs) are also considered as a feasible and efficient solution for the waste gas utilization problems [4–13]. SOFCs attract a great interest due to their high energy-conversion efficiency, fuel flexibility including the prospects to directly operate on methane-containing gases, environmental safety, and a possibility to recover exhaust heat [14].

This work is focused on the survey of promising technologies for the utilization of various waste gases generated by MSW landfills and industry, including coke oven, blast furnace and converter gases from metallurgical industries, gas from underground coal mines, agricultural and food industry produced biogas, and hydrogen-containing wastes from chemical industries. Particular attention was centered on the potential application of SOFCs operating with the use of waste gases, their advantages and limitations. Selection of the references for this brief review is focused on the last 10–15 years, with the main emphasis on the newly reported information and recent trends. Priority was also given to providing an overview of waste gas resources and state-of-the-art SOFC

developments, which may be useful for specialists working in these and closely-related scientific fields.

2. Processes and technologies exhausting calorific gases

Selected sources emitting high calorific gases which can be used by power plants, include:

- MSW landfills and wastewater treatment plants (WWTPs), which may be considered as sources of biogas forming due to the waste decay. The main components of biogas are methane and CO_2.
- Iron and steel making: the gases generated as by-products (blast-furnace, FINEX-off, converter and coke-oven gases) contain methane, carbon monoxide and hydrogen [15].
- Coal mining industry: mines (including abandoned ones) are the sources of mine methane, which is mainly a product of natural processes occurring in the bulk of coal seams [16].
- Oil and gas sector where the main by-product is the associated petroleum gas and natural gas. These gases are widely used for various applications and are, therefore, excluded from consideration in this review.
- Power engineering sector where a part of unburned fuel may often leave the technological cycle together with exhaust gases.
- Enterprises of food industry [17], agro-industrial sector [6], and forestry and woodworking industries where a variety of liquid and solid wastes can be used for biogas production.
- Chemical industry: the production of chlorine, sodium hypochlorite and caustic soda which emit large amounts of relatively pure hydrogen. Such hydrogen is already used for proton-exchange membrane fuel cells (PEMFCs) in a number of countries [18].

Table 1 presents a summary on typical compositions of selected high-calorific gases generated by various industries [1,15,19–28]. Notice that carbon monoxide formed due to incomplete oxidation of fuels in the internal combustion engines (ICEs) is difficult to extract. Similar situations take place for the fuel cell technologies. For example, the power plants based on MCFCs can be equipped with the systems for after-burning of the fuel residues and for capturing of carbon dioxide [29]. Further analysis takes into account the possibility to collect target gaseous products for their further use for energy production, including the fuel cell-based technologies.

Converter gas (or basic-oxygen-furnace gas), blast furnace gas and FINEX-off gas are formed in the course of steel making and contain high amounts of CO [15,24,30]. These gases have relatively high calorific values (3.4–9.2 MJ/m^3) and high toxicity. Coke-oven gas (17–21 MJ/m^3) contains hydrogen, methane and carbon monoxide (Table 1)

Table 1

Main components in high-calorific waste gases[a] [1,15,19–28,30–32,33].

Gas type	Composition, vol%					
	CH_4 (37.7 MJ/m^3)	N_2	CO (12.0 MJ/m^3)	CO_2	H_2 (12.1 MJ/m^3)	O_2
Landfill gas	35–65	<1 - 25	–	24–60	0.1–3	0–6
Coal mine gas	25–95	≤35	–	2–6	–	1–15
Coke oven gas	20–42	4–6	4–10	1–5	39–65	–
Blast furnace gas	0.4	49–59	21–43	4–25	1–4	–
Converter gas	0–0.5	13–25	56–90	10–21	1–4	0–1

[a] Gross calorific values or higher heating values (the amount of heat produced by the complete combustion at standard conditions, MJ/m^3) are given in parentheses.

and is also contaminated by H_2S [30,31]. All these by-product gases are derived in the smelters and used for various purposes, including the production of electricity and heat. In particular, the amount of coke-oven gas globally produced in 2020 is estimated as 93×10^9 Nm^3 [31]. Only about a half of this gas is however re-utilized within the steelmaking processes, while the balance is often flared and discharged into the atmosphere [32].

Another necessary comment is that a number of waste gases listed in Table 1 have fossil origins. Taking into account the global intentions for decarbonization of industrial processes, their generation is expected to decrease with time in the long run. In the short and medium perspectives, however, these emissions represent an important challenge requiring to develop utilization solutions appropriate from the environmental, technical and economic points of view.

2.1. Waste methane

Emissions of methane-containing gases to the atmosphere present a wasted potential source of energy and an environmental threat, increasing the greenhouse effect. Fig. 1 displays the sources of methane-containing waste gases and main advantages of their potential use. Typical distributions of the methane emissions between different sources [22,34] are illustrated by Fig. 2.

2.1.1. Coal mining

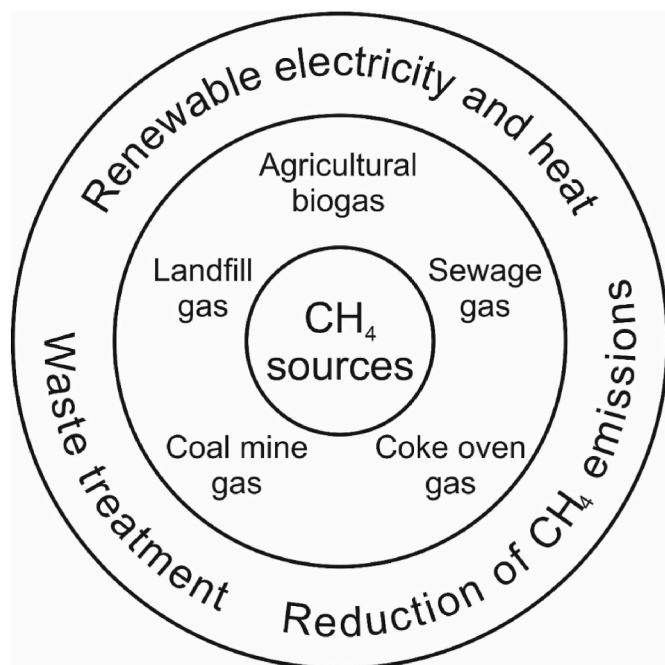Coal continues being an important source of energy in the world, and

Fig. 1. Sources of methane-containing waste gases and main advantages of their potential use for electrical energy and heat production.
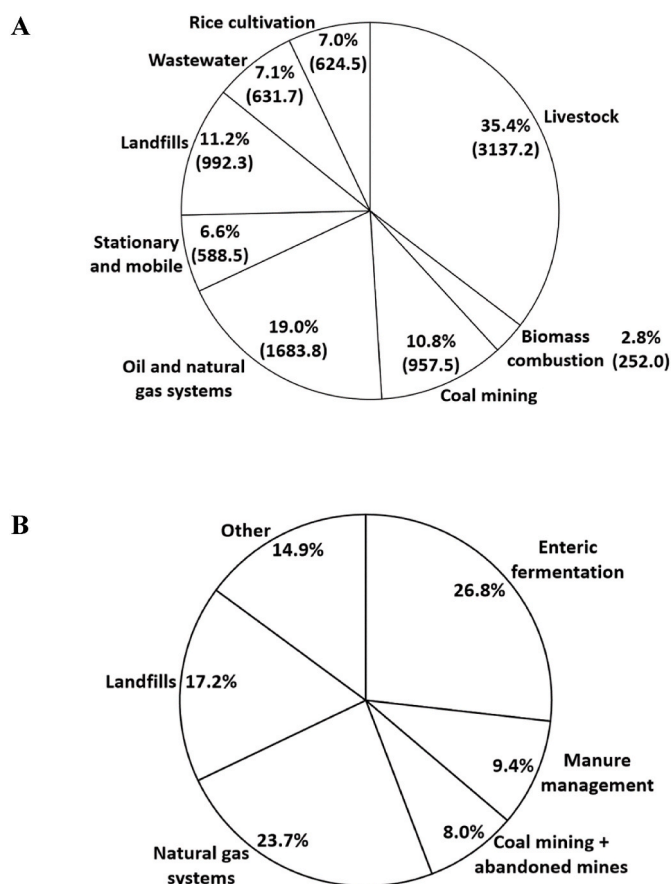

Fig. 2. Contribution of methane emissions by source for the whole world in 2020 (A) and for the United States of America in 2019 (B) [22,34]. The numbers in brackets are in million tons of carbon dioxide equivalents, MtCO$_2$e.

the coal production is expected to further grow [19,21,22,28,35,36]. China is a leading coal producer; USA and Russia have the largest coal reserves in the world. Russian coal mines are among most gas-rich, with an average level of 11.6 m^3 of methane per ton of coal [21,28,37], Table 2. Note that the coal mine gas must be extracted not only for economic benefit, but primarily for the safety reasons. The composition of coal mine gases is usually unstable and may often be explosive. The ignition range for CH$_4$ concentration in air is 5–16 vol% at room temperature and becomes larger on heating, especially for the higher concentration limit (~28 vol% at 700 °C) [36,38,39]. The estimates of yearly methane emissions to atmosphere due to the underground coal-mining activities around the world vary from 28 × 10^9 to 125 × 10^9 m^3 [34,35]. Even abandoned mines continue releasing of methane for a long period of time, i.e., during decades [22,36]. The gases derived from coal mines may be classified into 4 groups: coal seam methane or coal bed methane (CSM/CBM, CH$_4$ content of 80–98 %), coal mine methane or working mine methane (CMM/WMM, CH$_4$ content of 5–75 %), abandoned mine methane (AMM, CH$_4$ content of 20–80 %) and ventilation air methane (VAM, CH$_4$ content of 0.1–1.2 %) [22,25,34]. CMM is also defined as the methane released from coal and the surrounding rock strata due to mining activities [34]. VAM contributes over 60 % to the total emissions [25,34]. Table 3 lists the potential applications of CMM, based on the CH$_4$ concentration and corresponding calorific value [22,28,39–43]. As an example, in Russia the most prevalent application of CMM is to generate heat and electricity at the mining facility or to provide operation of thermal coal dryers [28]. Currently the use of extracted methane, especially the low-concentration drainage gas, for energy production is insufficient, although its amounts are quite large (Table 3). In China, the high- and medium-concentration gas ($\geq$30 % CH$_4$), low concentration gas (1–30 % CH$_4$) and VAM ($\leq$1 % CH$_4$) contribute 6, 11 and 83 % of total coal-mine methane emissions, respectively [43]. The utilization of such diluted gas mixtures is problematic due to the explosion risks mentioned above, and to their low calorific value. The use of VAM is essentially limited to the catalytic combustion in order to mitigate methane emissions to the atmosphere [42,44]. When the average methane concentration is lower than 0.3 %, VAM emission mitigation is not economically and technologically feasible for state-of-the-art technologies [45].

2.1.2. Agriculture and food industry

A high emission of calorific waste gases is well known for the animal husbandry enterprises (Fig. 2). For instance, estimates of methane emissions from cows show that one cow emits about 20 g of methane per

Table 2
Coal production by country, average methane content in coal and emissions of CMM[a] [28,36].

Country	Coal production[a], Mt/year [36]	Average methane content, m^3/t [28]	Annual methane emissions [36]	
			Mt CO$_2$e20[b]	Mt CO$_2$e100[b]
China	3326	9.3	3176	1147
USA	538	7.0	240	87
Russia	412	11.6	194	70
Australia	500		171	62
South Africa	234		101	36
India	770		84	30
Poland	95		69	25
Indonesia	557		58	21
North Korea	21		36	13
Kazakhstan	99		35	13
Germany	140	5.0		
UK	1	10.3		

[a] Updated July 2022.
[b] CO$_2$e20 and CO$_2$e100 denote CO$_2$-equivalent on a 20- and 100-year horizon.

Table 3
Recovery and use of coal mine methane [22,28,39–43].

Mine gas	Methane concentration, %	Recovery technologies	Calorific value, MJ/m^3	Utilization options and facilities
VAM	0.5–1	Mine ventilation systems	<0.3	Regenerative thermal or catalytic oxidation, substitute of combustion air in boilers, GTs or engines
Drained CMM	1–6	Drainage systems	0.3–2	Catalytic combustion, porous media combustion, fuel cells, methane enrichment
	6–30		2–11	Internal combustion, fuel cells, methane enrichment, metal fiber burner
	30–50		11–17	Heat and power generation (internal combustion engines, GTs, fuel cells), heating greenhouses
	50–95	Drainage systems (including CMM enrichment)	17–32	Heat and power generation, utility gas, transport engines
	95–100	Degasification of seams and gas accumulations Drainage systems	32–36	Chemical raw materials, motor fuel, utility gas, heat and power generation, feeding into gas pipelines, making LNG

kg of dry matter in feed. However, collection of these gases is very difficult. The mandatory ventilation of the animal husbandry premises leads to low concentrations of methane in the exhaust gas mixture. Therefore, the animal husbandry enterprises equipped with anaerobic waste fermentation plants (onsite sewage facilities) can be considered as sources of high calorific waste gases for energy generation. In the projects for methane utilization from agricultural wastes, the gas produced by anaerobic utilization (fermentation) of manure is widely considered [22,46–52]. In this case, the concentration of methane in biogas may reach 70–80 %; the biogas yield is up to 0.6 m^3/kg of dry matter loaded in the onsite bioreactor [46], Table 4. The approximate output of physiological waste per head of livestock and poultry is summarized in Table 5, [50–52]. The agricultural biogas plants may also use vegetable

Table 4
Methane output during fermentation of agricultural and other types of wastes [46].

Organic waste	CH$_4$ output, m^3/kg of dry organic substrate	CH$_4$ content in biogas, %
Pig manure	0.58	78
Cattle manure	0.2–0.3	60
Chicken litter	0.37	54
Cow dung	0.40	65
Sewer drains	0.60	70
Dairy waste	0.64	82
Municipal solid waste	0.60	50

Table 5
Average output of physiological waste per head of livestock and poultry [50,51].

Animal	Annual output of fresh manure, kg [50]	Annual output of fresh manure, kg [51]	Annual output of dry solids, kg [51]
Cattle	10950 (85% humidity)	7300–11700	750–1150
Horses, mules, asses, camels		4600–7300	900–1500
Goats, sheep (small cattle)	1460 (70% humidity)	400–600	75–150
Pigs	1460 (85% humidity)	1300–1600	200–250
Egg-laying hen	73 (75% humidity)	20–40[a]	5 - 10[a]
Broiler	42 (75% humidity)		

[a] Average for poultry.

wastes, glycerol from the biodiesel manufacture, palm oil mill effluent or vegetable processing wastewater or co-digestion of livestock and vegetable-origin wastes [6,25,48,49,52,53]. Mixtures of organic industrial, municipal and agricultural wastes were considered for processing in an anaerobic digester [49,53]. The digestion of two or more co-substrates yields often higher quantities and concentrations of methane and smaller contents of hydrogen sulfide in biogas [49,53]. The latter factor is important for the further utilization of biogas, as discussed below. Using the data from olive kernel steam gasification, an approach integrating the biomass gasification and SOFCs was suggested as highly efficient for the renewable power generation [6]. The typical composition of gas produced by an agricultural biogas plant is presented in Table 6.

An example of the food industry enterprises generating potentially useful wastes for biogas production, refers to distilleries. The wastes of alcohol production are stillage, carbon dioxide and fusel oils. The methods for their processing include: drying of distillery stillage or production of fodder yeast on its basis, used as feed additives in animal husbandry; cleaning and liquefying carbon dioxide or making dry ice; distillation of fusel oils in order to obtain higher alcohols (amyl, butyl, propyl) used in the medical, paint and varnish, and perfume industry. Processing of stillage by methane fermentation is not widespread. The project introduced by Asahi Quality and Innovations [37] presents a successful example of using biomethane, a byproduct of the wastewater treatment process at breweries, in SOFCs for power generation instead of conventional combustion. The long-term continuous power generation using a 200 kW SOFC stack has been demonstrated [37].

Table 6
Composition of landfill gas and biogas obtained from wastewater treatment and farm plants [1,23,26,27,47,49,54].

Component	Content, % in dry volume		
	Landfill gas	Sewage digester gas	Farm biogas
Methane	37–70	58–65	49–69
Carbon dioxide	24–60	34–39	29–44
Nitrogen	<1 - 17	0.1–8	<1 - 13
Oxygen	0–3	<1	0.2–3
Paraffin hydrocarbons	0.1		
Aromatic and cyclic hydrocarbons	0.2	3 - 12[a]	1 - 2[a]
Hydrogen	<0.01–3		
Hydrogen sulfide	0–2.4	0–0.06	7 × 10^{-4} - 0.7
Carbon monoxide	0.1		

[a] Total content of benzene and toluene, in mg/m.^{3}.

2.1.3. MSW landfills and WWTPs

Another important source of calorific gases originates from the fact that the world generates over 2×10^9 tons of MSW every year (Fig. 3) and this amount tends to further increase [55,56]. A major part of this waste is related to food, green (yard trimming) and paper (Fig. 4A), which may be used to produce biogas. Most wastes are currently dumped or disposed of in landfills, but only 8 % fraction is disposed of in sanitary landfills equipped with gas collection systems [56], Fig. 4B. Uncontrolled emission of biogas generated in the landfill bulk due to anaerobic fermentation of biomass (landfill gas) may lead to release of a number of gaseous components including toxic ones, into the environment (Table 6 [12,23,26,27]), and to spontaneous combustion of landfills. The MSW landfills, due to their location, large waste disposal and relatively long duration of the operation, can be considered as one of the main sources of high calorific gases.

For the spatial analysis of resources (gross potential) of high-calorific gases, a series of maps were constructed for Russian territory using the MapInfo 12 software. The annual amounts of produced waste gases were first estimated for each source assuming that the landfill site is operated in stable mode (after 3–5 years after the operation start). The landfill gas (and methane) production rate can be roughly estimated from the amounts of solid wastes delivered to landfills every year [51,57,58]. The volume of generated methane was assumed to be 0.086 m^3 per 1 kg of MSW [12]. Fig. 5A shows the estimated annual methane volumes generated at large-scale MSW landfills in 2019. The total amount of methane was estimated around 2.7 Mt/year (4.1×10^9 m^3/year) [12,13]. The technical potential for this amount was shown to achieve 3278 $\times 10^6$ kWh per year for electrical energy and 1512×10^6 kWh per year for thermal energy in the case of SOFC application for landfill gas utilization in Russia [13].

Sewage collected in municipal systems should be transported to the WWTP. Many WWTPs employ anaerobic digestion of sludge, in the course of which a series of biological processes result in the biogas formation [25,59,60]. The daily amount of municipal sewage sludge is about 0.10–0.26 kg per capita [47,48]. An overview of the combined heat and power (CHP) utilization technologies for biogas produced at the WWTPs is presented in Ref. [61]. In particular, a techno-economic feasibility of ICEs, micro GTs and fuel cells, and their combinations was assessed. As for the agricultural wastes, co-digestion of the sludge with other organic wastes seems preferable [59]. Typical composition of the biogas obtained from anaerobic digestion of the wastewater sludge is given in Table 6.
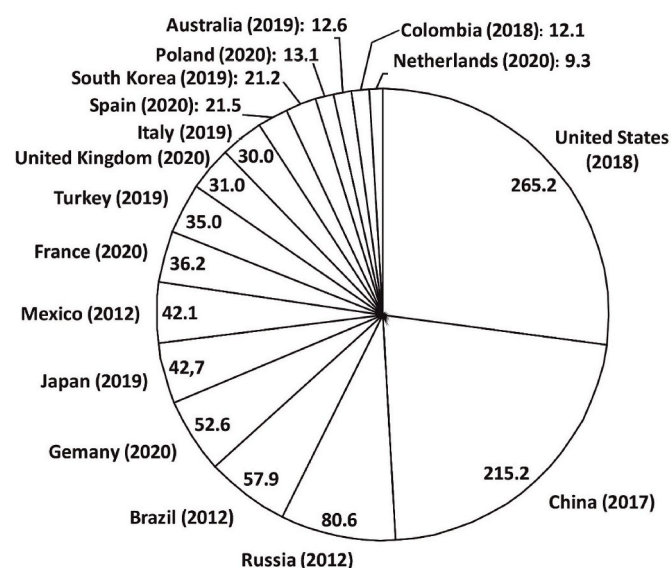
2.2. By-product hydrogen

Several industries produce hydrogen with different levels of purity as a by-product. For example, hydrogen forms in the course of chlorine, sodium hypochlorite, sodium chlorate and caustic soda production [12,62,63]. If compared to the chlorine and caustic soda production by the chlor-alkali plants, hydrogen from the chlorate factories has a lower quality and may contain up to 0.5 % chlorine, 2 % oxygen, 1–2% CO and other impurities [12,62,63]. The amount of by-product hydrogen was estimated [62] as 0.028 kg per kg of chlorine; the global annual market of chlorine increased up to approximately 92.3 Mt in 2021 [55]. The global sodium chlorate market reached 4.74 Mt in 2022 [64], which corresponds to ~0.3 Mt of by-product hydrogen [63]. Caustic soda produced mainly by the electrolysis of NaCl aqueous solution, yields about 0.025 kg of hydrogen per kg of NaOH. The global caustic soda market attained a value of about 78 Mt in 2019 [64]. In 2019, the total production of caustic soda in Russia was estimated as 1291×10^6 kg [55], whilst the average annual sodium chlorate production was approximately 87×10^6 kg. In this case, the total amount of high-purity hydrogen released from chlorine and caustic soda production can be assessed as 426×10^6 m^3/year; the amount of hydrogen from chlorate production, which needs an additional purification, is close to 148×10^6 m^3/year [12]. Considering the limited chemical stability of sodium chlorate, municipal water-treatment facilities may prefer its production on-site, using available sodium chloride, water and electricity (Fig. 5B). Such production was not included in the statistical data discussed above; this may lead to slightly underestimated amounts of hydrogen. The annual production of hydrogen generated by the water-treatment facilities in the cities of the Russian Federation is summarized in Fig. 5B. These amounts clearly indicate, in particular, a substantially high potential for the application of fuel cell plants with modular structure which can be adopted to hydrogen-exhausting industrial processes. Notice that the PEMFCs provide a high efficiency in cases when pure hydrogen is available [12,62,63], whilst the use of contaminated hydrogen is more feasible for SOFCs.

3. Release dynamics of high calorific gaseous wastes

The analysis of technological processes in various industries provides a basis for studying the dynamics of high calorific gas production. Of course, the generation rates of high calorific gases at industrial enterprises and landfills/WWTPs should be considered separately from one another. In the former case, the gas production rate over time is almost constant as uniform loading of equipment is important for extending its service life and for economic consumption of the necessary resources. Therefore, even for the processes with characteristic consumption peaks, their smoothing is usually used. This may be achieved either via continuous supply of new portions of raw materials (metallurgy), or via parallel use of technological units of the same type but implementing different technological stages within the cycle (food and petrochemical industries). One exception should refer to the agricultural industry where the amount of wastes, especially those of the vegetal origin, is season-dependent.

The amount of generated coal mine gas depends also on numerous factors including the mine productivity, gassiness of the coal seam and any underlying and overlying formations, operational variables and geological conditions [40]. Consequently, the release rate of the coal mine gas exhibits large variations with time, in addition to the compositional instabilities mentioned above.

The amount and composition of biogas formed at various landfills are unstable, depending on the ambient temperature, humidity, air access, waste composition and time period from the landfill operation start (Fig. 6). The following main stages of organic waste decomposition are usually distinguished [65–68]: (i) aerobic oxidation, (ii) decay of hydrolysis products under anaerobic conditions, (iii) unstable methane yield, (iv) sustainable formation of methane, and (v) post-closure stage.
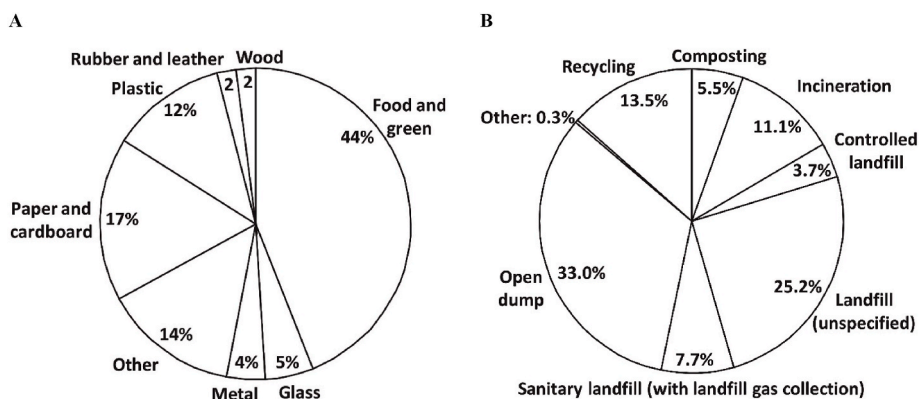

Fig. 3. Amounts of MSW generated annually by different countries, in Mt [55].

Fig. 4. Global waste composition (A) and major methods of treatment and disposal of waste (B), in % [56].

Duration of these stages is strongly influenced by the climatic conditions. At the short initial stage of landfill operation, the organic part of MSW decomposes under aerobic conditions when atmospheric oxygen is consumed and high concentrations of carbon dioxide are formed. After adding new amounts of MSW, the underlying layers are compacted. As a result, the decomposition continues under anaerobic conditions when methane and carbon dioxide are mainly produced. The resulting biogas rises to upper layers of the landfill, where methane is partly oxidized into carbon dioxide under aerobic conditions [65]. The processes of methanogenesis commence during the first 2–7 years after the start of landfill operation. After 12–17 years, the maximum yield of biogas can be achieved (first half of Stage 4 in Fig. 6) with subsequent gradual decrease. This anaerobic stage lasts for the time period necessary for degradation of over 90 % putrescible matter [66] followed by landfill closure when air starts to slowly infiltrate into the waste mass, again creating aerobic conditions. Then, after 25–30 years from the moment of closing the landfill, the biogas flow decreases to safe concentrations of methane [67]. As the process of biogas formation in the landfill bulk occurs during many years, the closed landfills remain sources of methane. Notice that, due to the complex dynamics of biogas formation and its dependence on many factors [23,66,68], the corresponding estimates can only be very approximate and should be related to a specific landfill.

As one particular example, Ref. [69] illustrates the environmental benefits and feasibility of utilizing landfill gas as alternative energy source in Trinidad and Tobago, where most solid waste is currently disposed of in open areas without any preliminary treatments. The methane generation model (LandGEM) was proposed taking into account the statistical data on MSW landfills and assuming average gas composition of 50 % CH_4 and 50 % CO_2. Both the total landfill gas and methane generation flowrates were found to rapidly increase during the first ~40 years of landfill operation and continue to increase slower until the closure, reflecting the larger amounts of waste added to the landfill [69]. A different situation was reported for an Italian MSW landfill where the gas generation passed through a maximum during the landfill operation [70].

The production rate of biogas from mixed sludge varies typically in the range of 0.75–1.12 m^3 per kg of volatile suspended solids destroyed [60].

4. Waste gas pretreatment and utilization technologies: an overview

### 4.1. Fuel contaminants and their role for various power generation technologies

In addition to the components listed in Table 1, the digester gas from WWTPs and landfill gas may often contain sulfur-, silicon- and chlorine-containing compounds, higher hydrocarbons and other gaseous species,

the presence of which in the fuel for power plants may lead to a failure of the plant equipment and/or environmental pollution. For example, over 140 trace volatile organic compounds including alkanes, aromatic compounds, cycloalkanes, terpenes, alcohols and ketones, and halogenated compounds were identified in the landfill gas at seven waste disposal facilities in the United Kingdom [23]. Therefore, complex purification of the waste gases is always required. The purification level and methods are always determined by further applications of the resultant gas mixtures. Whilst thermal energy alone is usually obtained using the boiler-furnace equipment, four technologies are commonly considered to generate electric power using methane-containing gases (Fig. 7): ICEs, GTs (including micro GTs), MCFCs and SOFCs. The latter two, operating at high temperatures, make it possible to electrochemically oxidize mixtures of hydrogen and carbon monoxide, generated internally within the fuel cell stack or in the external fuel converter [14, 71–74]. Their efficiency is substantially higher with respect to ICEs and GTs, Fig. 7. If comparing SOFC and MCFC technologies, the former provides a higher tolerance with respect to some fuel components and impurities. In particular, the tolerance limit of MCFCs with respect to CO is 0.1 g/l [72]. Approximate tolerance limits with respect to the fuel contaminants are compared in Table 7.

Low-temperature fuel cells such as phosphoric acid fuel cells (PAFCs), alkaline fuel cells (AFCs) and PEMFCs require quite a complex external fuel processor to produce H_2 and to remove CO, leading to a lower system efficiency and to a higher complexity and cost [71,72,78], Fig. 7. Note that PAFCs may only tolerate <5 % CO, whereas CO concentration in the case of PEMFCs should not exceed 10 ppm [63,71,78].

Nonetheless, purification of fuel gases is still important for the high-temperature SOFC- and MCFC-based technologies ([70,71] and references therein). For internal combustion engines, the requirements are less strict (Table 7), but the fuel purity also has a significant impact on the engine life duration [23]. The issues of SOFC operation using biomass gasification products were reviewed in Ref. [7] with the main emphasis on the analysis of acceptable content of impurities; a relatively small number of experimental works employing real or model gas mixtures was noted. Approaches for the direct use of biogas in SOFCs without preliminary reforming were reviewed in Ref. [9]. It was mentioned that the most dramatic negative impact on the service life of SOFCs is associated with the formation of carbon deposits and poisoning with impurities such as H2S, siloxanes and halides. The possibility to use landfill and digester gases as a fuel for power generation is also affected by the concentrations of certain trace volatile organic compounds [23]. Organosulfur or organochlorine compounds react with oxygen and water during the combustion process forming H_2SO_4 and HCl, which contribute to the combustion chamber corrosion [23]. For instance, three internal combustion engines of the waste gas utilization plant at Braunschweig's sanitary landfill were seriously damaged by corrosion after 900–1000 h working [79]. Although removal of aggressive impurities reduces maintenance costs and increases the efficiency and uptime
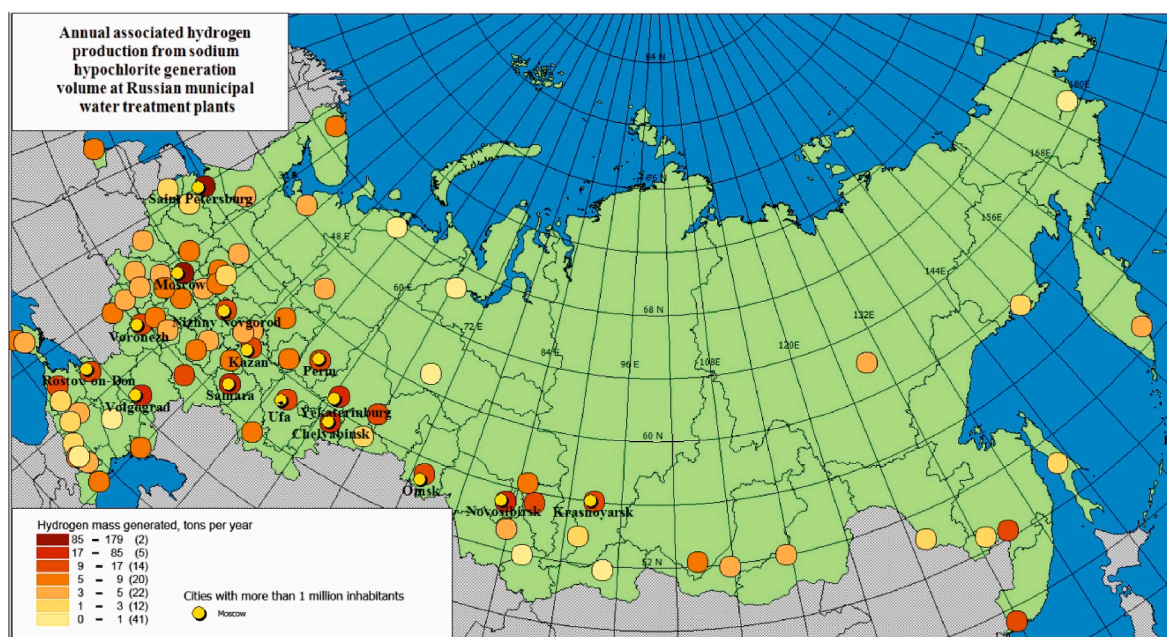
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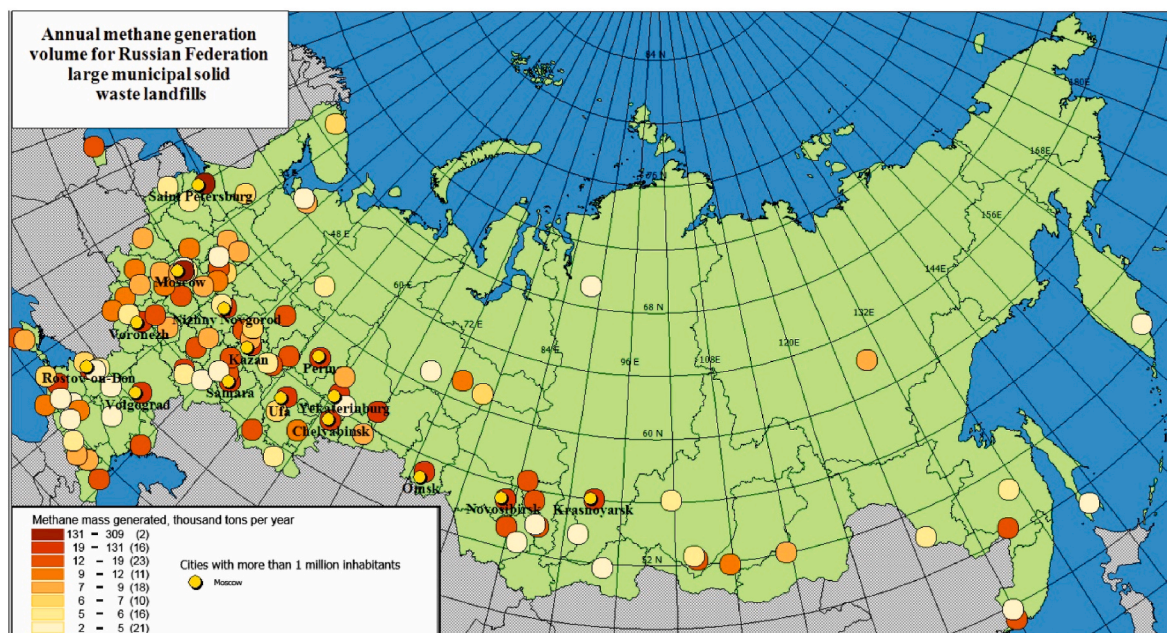
B

Fig. 5. Estimated spatial distribution of calorific waste gas sources in Russia (this work): annual amount of methane generated by large MSW landfills (A), and annual amount of hydrogen associated with sodium hypochlorite production by municipal water treatment plants (B). The numbers of sources are given in brackets.

of engines, GTs, micro GTs, boilers and fuel cells, the total cost of such plants should also unavoidably increase due to the fuel purification [80].

4.2. Siloxane poisoning

The concentration of siloxanes in biogas, wether landfill or sewage gas, tends to increase due to a growing use of silicon-containing compounds (such as polydimethylsiloxanes) in lubricants, cosmetics, personal care products, detergents, pharmaceuticals, glues, paints and other industrial and domestic applications [60,81,75]. At least some of the siloxanes may present environmental and health risks [75]. Si-containing compounds are found in all types of biogas. The content of

siloxanes in the landfill gas can reach 112 mg/Nm^3 [76] but is usually at ppm level [49,52,60]. In the case of biogas from wastewater, the siloxane amount varies in a wide range up to 417 mg/Nm^3 [47,60, 75–77,81]. The agricultural wastes are characterized by very low amounts of siloxanes [49]. It was concluded [77] that the removal of siloxanes is more important for ICEs, whereas hydrogen sulfide is most critical for gas-distributing networks and fuel cells.

The impact of siloxanes on the performance of ICE units operating on landfill gas was analyzed in Ref. [33]. The main degradation mechanism is the deposition of solid but not aggressive sediments on the walls of the combustion chamber and in the area of engine sealing ring channels [33]. These deteriorate heat transfer, resulting in engine overheating, in
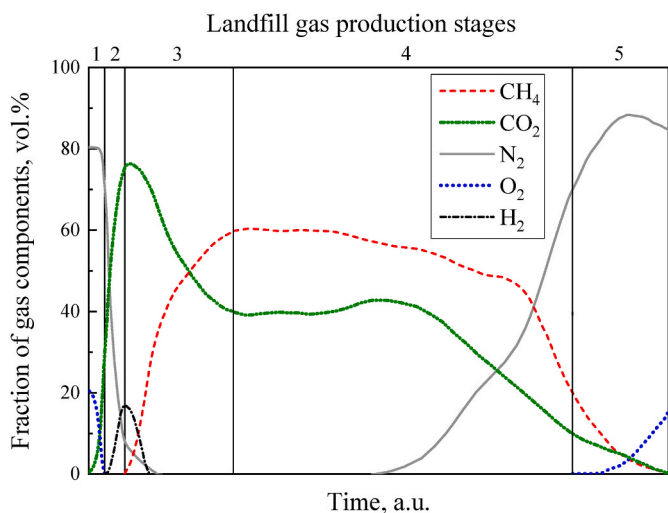
Fig. 6. Schematic presentation of the formation rates of main decomposition products of organic waste at MSW landfills [66,68]. Note that the stage duration depends on the waste type and landfill conditions.

an increase in friction losses during piston movement and, as a consequence, in decreasing efficiency and increasing wear of the pistons and gaskets. The solid sediment analysis made it possible to identify its origin, namely high-temperature decomposition of silicon-organic compounds with the formation of silicic acid and formaldehyde [33]. A similar problem was discussed in Ref. [82], where quantitative content of siloxanes in the landfill gas (approximately 10 mg/Nm^3) and their composition (with a predominance of octamethyltetraoxysiloxane) were determined. Cleaning of the fuel with an activated carbon filter enabled to reduce silicon fraction in the sediment by an order of magnitude, but the amount of sulfur was increased [82]. The same authors analyzed general technical and economic aspects of the ICEs operating on landfill gas at the Odaeri landfill near Istanbul [54]. According to three-year observations, the gas from this landfill contained an average of 49 % methane, 37 % carbon dioxide, 300 mg/m^3 hydrogen sulfide, 10.2 mg/m^3 siloxanes, and other impurities. High concentrations of hydrogen sulfide, as well as the presence of aggressive chlorine-containing impurities, led to accelerated corrosion of the engine parts.

In GTs, silica deposits usually form on the nozzles, blades and

bearings, causing their erosion and subsequent irreversible decrease in the operating efficiency and GT failure ([81,75] and references therein). The use of micro GTs for the utilization of biogas from sewage was considered in Ref. [83]; gas pretreatment was needed in order to remove impurities, including siloxane and water, and to increase biogas pressure. The electrical power consumption rate for the biogas pretreatment was approximately 7 % of the power generated by the micro GT [83].

The presence of siloxanes in the fuel causes the formation of silica at the conventional Ni-stabilized zirconia cermet anodes of SOFCs. The irreversible degradation of SOFC performance was observed at the octamethylcyclotetrasiloxane (D4) concentration level of 111 ppb(v) (1.35 mg/Nm^3) at 750 °C [2] and 69 ppb(v) at 800 °C [84]. Possible mechanisms are based on the condensation-type processes involving the decomposition of siloxanes followed by chemical reduction of SiO_2 to gaseous SiO (predicted by thermodynamic calculations) and its electrochemical reoxidation at the triple-phase boundary [85], siloxane interaction with water leading to the formation of gaseous $Si(OH)_4$ and then solid SiO_2 [84,86], or adsorbtion of siloxanes with subsequent methane release and carbon deposition [87–90]. The cyclic siloxanes were found to have a higher degradation effect on the SOFC performance compared to the linear siloxanes [89]. Steam additions to the fuel may inhibit not only carbon but also silica deposition at the SOFC anodes [87,90]. In general, the presence of siloxanes in the fuel gas seems unacceptable for the SOFC technology [8]. Notice that, as for siloxanes, sulfur compounds (primarily hydrogen sulfide) are subject to mandatory removal [77].

Table 7
Requirements for the impurity content in fuel gases for various energy technologies [2,8,60,61,72,75–77].

Technology	Tolerable impurity concentration, (vol.) ppm in the fuel gas			
	Hydrogen sulfide	Siloxanes (D4, D5)	Halides	Ammonia
Reciprocating engines	20 - 2200[a]	5 - 109[b]/0.4–9	100 - 713[a]	55 - 105[a]
Gas turbines	$(1–7) \times 10^4$	0.03–0.1[b]/ $(2–10) \times 10^{-3}$		
Molten carbonate fuel cells	0.1–5	1–100	0.1–10	$(1–3) \times 10^4$
Solid oxide fuel cells	1–2	0–0.1[b]/0–0.01	few - 40	

[a] mg/Nm^3 in CH_4 partial volume.
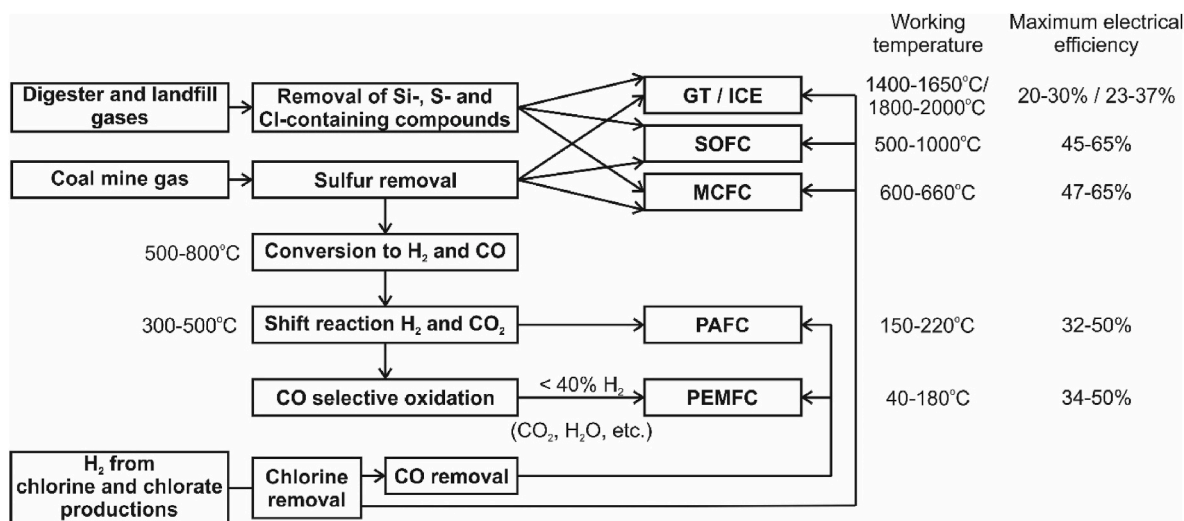[b] mg/Nm^3 in total fuel gas volume.

Fig. 7. Fuel purification and processing reactions, and the efficiency of fuel utilization using different technologies [7,71,73,74]. The maximum efficiency is given for hydrogen fuel.

4.3. H₂S, halides and other impurities

The landfill and digester gases may contain up to 5400 ppm and 1200 ppm H_2S, respectively ([52,60] and references therein). Although the composition of biogas varies depending on the feed stock of the digesters, generally the H_2S content in landfill gas is low compared to the biogas from WWTPs [47,52]. The poisoning mechanisms of Ni-containing cermet SOFC anodes by fuel impurities, including sulfur-containing compounds (such as H_2S, CH_3SH and COS) and chlorine were studied for humidified H_2 and CH_4 fuels [86]. The initial cell voltage drop was found essentially independent of the type of sulfur compounds, whereas an additional gradual decrease in the cell voltage with time was detected in case of CH_3SH poisoning. 20 ppm(v) of the latter compound (methanethiol) in biogas caused a drastic performance decrease, up to the cell break [91].

In Ref. [8], the composition of biogas was carefully analyzed; impurities were removed using carbon sorbents and alkali metal oxides; then a model gas mixture with similar composition was prepared and tested. It was shown that, for SOFC, the approximate limit of hydrogen sulfide concentration should be below 1 ppm(v) [8]. Notice that the tolerable level of hydrogen sulfide for SOFCs is determined by the cell operating temperature and current density as well as catalytic activity of the anode; differences in the operation conditions and anode compositions may result in some discrepancies in the literature data. In the case of 1 ppm H_2S at 1000 °C, a reversible 9 % drop in the operating voltage occurs; at 800 °C, the decrease is much larger and irreversible [92].

Halogenated compounds were found in the landfill and sewage digester gases at the concentrations of 0.3–1.3 and <0.1 mg/m^3, respectively [47]; their levels up to 11–20 and 0.8–1.4 ppm were also reported [52], but in some cases these values may even be considerably higher [52,93]. The poisoning effects of hydrogen chloride on anode-supported SOFCs, namely single cell and short stack, were compared in Ref. [94] using hydrogen or syngas fuels at 750 °C. The poisoning was more severe in the former case, whilst HCl did not affect stack performance in syngas even at the concentrations up to 500 ppm (v). Performance loss was attributed to the effects of HCl adsorption onto nickel surfaces, which lowered the catalyst activity. Chlorine was found to present on the nickel particles in the form of adsorbed species rather than forming a secondary phase of nickel chloride [94,95]. The presence of HCl, already at 20 ppm level, caused the degradation of glass-sealant [91]. At the SOFC operation temperature of 850 °C, both methane utilization and performance were unaffected by the presence of 12 ppm(v) HCl in biogas fuel; the poisoning effects appeared however at lower temperatures [93].

In order to reduce the poisoning effects of H2S, siloxanes and halides, the use of structured fibrous anode materials based on $Mg_6Al_2(OH)_{16}CO_3 \bullet 4H_2O$ with a well-developed surface, control of the methane/carbon dioxide/water vapor ratio in the fuel gas, and introduction of molybdenum, copper or cerium dioxide into the anode material were considered [9]. The optimum fuel composition is strongly dependent of temperature and operating voltage [9]. The W- or Mo-containing $Ni–CeO_2$ anodes of direct-biogas electrolyte-supported SOFCs showed better tolerance to siloxanes, HCl and H_2S compared to conventional $Ni–Y_2O_3$-stabilized ZrO_2 (YSZ)) and Ni-GDC anodes, whereas NH_3 had no impact on the cell performance [95–97]. Nevertheless the presence of 1 ppm of D4 siloxane in biogas caused a progressive performance degradation. In the case of biogas utilization using SOFC-based technologies, the fuel purification is absolutely necessary.

4.4. Purification and upgrade of waste gases

The technologies for landfill gas and biogas purification for further energy production were reviewed in Refs. [52,60,61,76,77,98,99]. The main purification methods include absorption, adsorption, membrane separation and precipitation of components by cooling of the gas stream and biodegradation. Cooling provides an opportunity to remove moisture from the landfill gas and reduce the content of siloxanes by 10–50 %. A relatively new method is the adsorption of siloxanes at elevated temperatures (400 °C) on alumina, silica, calcia and magnesia, although the latter two are also characterized by an increased absorption of carbon dioxide. Activated carbon has a high sorption capacity for siloxanes, but its regeneration is also most difficult [77]. The highest performance was achieved using superhydrophobic polymer sorbents; an additional feature of these expensive materials is the loss of sorption capacity of less than 10 % per cycle with 10 regeneration cycles (heating in air up to 100 °C). One should also account for competing sorption (especially carbon dioxide) as these processes reduce sorption capacity for the target component. The main sorbents for hydrogen sulfide are porous media based on iron oxide. The sorption capacity of such sorbents was estimated as 12 wt%. (gram of S per gram of sorbent) [60].

Taking into account the relatively high costs and sensitivity of various sorbents to the impurity concentration, the multistage purification suggested in Ref. [100] seems one of the most appropriate approaches. In this case, the first purification stage was based on cooling of the biogas with water down to 10 °C; the second stage was based on sorption using activated carbons selected to remove silicon-organic compounds as well as traces of hydrogen sulfide [100]. Apart from the widely used adsorption, absorption and deep chilling techniques, the concepts based on biotrickling filters, catalysts and membranes, and, in the case of sewage gas, sludge stripping, peroxidation and filtration at the point inlet source, were also considered in Ref. [101]. For the small-scale SOFC applications, biological cleaning technologies are suggested as economically suitable, although these have limitations due to slow response with respect to the gas composition variations and should often be combined with additional cleaning technologies [98]. Biodegradation is advantageous due to high treatment capacities, reduced operating costs and environmental impact: it is characterized by moderate (10–74 %) removal efficiency for siloxanes and high efficiency for H_2S [75,76]. An approach combining adsorption and biological degradation seems more feasible. The use of in-situ cleaning technologies such micro aeration by air and/or O_2 or additions of iron salts (usually $FeCl_2$) may also be useful [49,60,98].

An enrichment of biogas with methane using hollow fiber membranes removing carbon dioxide was suggested in Ref. [101]. The authors proposed the use of asymmetric hollow fiber membranes based on polyester-carbonates resistant to hydrogen sulfide. The single-stage cleaning process provides a significant reduction in the operating costs compared to high-pressure gas drying (by 50 %) and a 20 % reduction in the capital costs; the content of biomethane after passing through such a membrane was up to 96 %. The energy consumption for gas compression in front of the membrane reactor is approximately 2 MJ/Nm^3 [101]. The diffusion tests of siloxanes (D4 and decamethylcyclopentasiloxane/D5) together with other biogas impurities (limonene, toluene and hexane) through polydimethylsiloxane membranes demonstrated effective cleaning of the biogas obtained by sewage fermentation [102]. The process of biomethane separation from the biogas, obtained by waste fermentation in two food and one dairy industries, using a mobile membrane module was described in Ref. [17]; the pilot module had a capacity of 100 Nm^3/h for the feed biogas. Purification from the impurities including alkanes, hydrogen sulfide and siloxanes, was mainly carried out using coalescing filters prior to gas supply into the module. A part of the impurities was condensed together with water when the flow was cooled down to +5 °C in the heat exchanger downstream of the filters. Next, the gas passed through adsorbent (porous alumina) and then entered the membrane reactor based on polyimide hollow fiber membranes. The energy consumption was approximately 0.35 kWh/Nm^3 of biogas [17].

The composition of gases from coal deposits includes methane and other products of the coal metamorphism, namely heavy homologues of methane, hydrogen, hydrogen sulfide as well as gases of air origin (CO_2, N_2 and inert gases), which penetrate the coal seam in the process of gas weathering [103]. In general, the CMM requires less extensive

purification compared to any sort of biogas. For the high-temperature utilization technologies, the particulate removal, deoxygenation (for safety reasons) and sulfur removal may be necessary (Fig. 7). There are four basic processes that are commonly used for mine gas purification: solvent adsorption, pressure swing adsorption, cryogenic separation and membrane separation [41].

The hydrogen purity for PEMFC technology should fulfil the ISO 14687–3 or ISO 14687-2 standards. The methods of hydrogen purification are reviewed in Ref. [104] comparing the output hydrogen recovery and purity for different processes. The cryogenic separation is considered as a pre-purification step necessary to remove CO_2, H_2S and H_2O. The pressure swing adsorption and catalytic purification are necessary to produce hydrogen with moderately high purity (99.999 %), while the purity of >99.9999 % may only be achieved using palladium membrane diffusion [104]. Only palladium membrane diffusion and catalytic purification can yield high recovery levels (up to 99 %) from hydrogen-rich gas mixtures; the combination of cryogenic separation and solid polymer electrolyte techniques can provide 95 % recovery [104]. The metal hydride separation, pressure swing adsorption and polymer membrane diffusion yield lower recovery levels, 70–85 %.

4.5. Concluding remarks

In summary, three main groups of the purification methods for waste gases can be distinguished: (i) those based on simple cooling or cryogenic separation, (ii) technologies based on membrane gas separation, and (iii) sorption which is most expensive and effective. Among the sorbents, activated carbon is most widespread due to the availability of raw materials and possibilities to control its morphology by varying activation parameters. The inexpensive methods based on the condensation of impurities provide an insufficient purification depth for their use in combination with fuel cell technologies, but are mainly suitable for the gas treatment prior to supply in ICEs. Nevertheless, these methods make it possible to significantly reduce the impurity concentration in order to decrease costs of further application of the sorbents. The membrane techniques are mainly used to enrich mixtures with methane and have a limited use for separating impurities other than CO_2. Therefore, a combination of condensation with several sorbents (activated carbon plus iron or aluminum compounds) seems to be promising for the practical applications, as each of the sorbents primarily captures its own target impurity.

The requirements to impurity content in the fuels for various energy technologies are compared in Table 7. Exceeding of these concentrations leads either to corrosion of the plant components (hydrogen sulfide, ammonia, halides), or to precipitation of solid deposits on rubbing parts and catalysts (hydrogen sulfide, siloxanes). Note that the tolerance to contaminants present in the fuel is strongly dependent on temperature, pressure, gas composition, construction components, and system operation conditions. If comparing different technologies, relatively low requirements to the fuel purity are characteristic for ICEs, except for ammonia. In the case of SOFCs, ammonia can be directly used as a fuel. Also, the efficiency of SOFC-based systems is higher with respect to ICEs (Fig. 7). The application-specific solutions for each type of fuel are determined by relationships between these factors and costs.

Another limitation related to the SOFCs fueled with contaminated waste gases is the necessity to use elevated operating temperatures, such as 750–850 °C. This makes it impossible to use a part of materials, catalysts and microstructures developed for the so-called intermediate temperature range (450–700 °C), and leads to higher costs. On the other hand, elevated operating temperatures provide an opportunity to achieve higher efficiency combining SOFC- and GT-based systems.

In the field of fuel processor development, a number of scientific laboratories, institutes and companies achieved significant progress during the last decade (e.g., see Refs. [105–111]). Most developments are centered on compactization and universalization of the fuel processors, the catalysts resistant to carbonization and poisons (primarily

sulfur), novel materials and new technological solutions enabling to reduce size and weight of the processors.

5. State-of-the-art SOFC systems and utilization of waste gases in SOFCs

Table 8 presents an overview of selected SOFC projects which were started or substantially updated in 2019–2022 [112–126]. These projects reflect state-of-the-art SOFC technology becoming quite mature; the target power of the developed plants and systems varies from 0.7 kW up to 2 MW. The range of planned applications covers (but is not limited to) marine, domestic, military and transportation areas and a variety of other technological fields where modular power plants are necessary. Most of the developed SOFC systems are oriented on the use hydrocarbon-based fuels, including natural gas, propane, liquefied natural gas (LNG), liquefied petroleum gas (LPG), biogas, and also ammonia. One should separately mention that such systems often use an approach of fuel partial internal conversion or pre-reforming [127–129], when a part of the fuel is converted into a mixture of hydrogen and carbon oxides in separate fuel processor (reformer or converter) and the rest is supplied onto the SOFC anode. Their ratio varies from system to system, but the fraction of externally converted fuel is usually up to a half of the total fuel supply [130–132]. Another necessary comment is that only a few projects are specifically centered on the use of waste gases (Table 8). However, the adaptation of SOFC systems to the use of biogas opens a wide perspective towards utilization of other waste gases, including those from the MSW landfills. This is reflected by increasing number of publications focused on the SOFC performance evaluation in these conditions and on the comparative assessment of SOFCs with respect to other technologies used in this area, primarily ICEs or GTs.

The results of techno-economic modelling and experimental analysis of various biogas-utilizing technologies, including GTs [[61,133]] and SOFCs [[8,48,61,134]], demonstrated a high potential of these technologies and their combination. The optimization of biogas-fueled anode-supported SOFC system design was performed in Ref. [134] in order to maximize electrical efficiency and optimize thermal integration. Four schemes with different reforming options and different types of anode off-gas recirculation were considered. The tests with the use of model biogas [8] were performed employing anode-supported SOFCs with 8 mol.% Y_2O_3-stabilized ZrO_2 (8YSZ) solid electrolyte, Ni - 8YSZ anode, and GDC - $(La,Sr)(Fe,Co)O_{3-\delta}$ (LSCF) cathode. The possibilities of direct use of biogas in SOFCs (without pre-reforming) were analyzed in Ref. [9]. Addition of a small amount of hydrogen to the fuel mixture [10] was shown to suppress the degradation of nickel-containing anodes, caused by chlorine impurities in biogas. Reforming of the biogas obtained by anaerobic digestion of municipal wastewater sludges, was tested [11]. The stack of tubular anode-supported SOFCs with YSZ electrolyte, Ni - YSZ anodes and Sr-doped $LaMnO_3$ - YSZ cathodes was fueled with a simulated biogas reformate mixture (66.7 % H_2 - 16.1 % CO - 16.5 % CO_2 - 0.7 % N_2, humidified to 2.3 or 20 mol% H_2O). Higher humidification yields a better SOFC performance. On the basis of experimental results, a model predicting system efficiency and emissions was developed [11]. The technical and economic feasibility of operating a 174 kW SOFC unit in a WWTPs was demonstrated [100]; the fuel for three SOFC modules was biogas available on-site from the anaerobic digestion of sludge collected from treated wastewater. The net electric efficiency of 50–55 % was achieved [100].

The feasibility of SOFC operation over a wide compositional range of biogas and landfill gas was studied using a small tubular SOFC system working at 850 °C [4,5]. In the case of Cannock landfill gas, an efficiency of 18.5 % was obtained at a current density of 524 mA/cm². The introduction of cobalt additives in the anode catalyst increases its tolerance with respect to sulfur impurities and carbonization. The SOFC operation using biogas was found possible even at low concentrations of methane, when the conventional heat engines would not function, thus

Table 8
Summary of selected new and updated SOFC projects in 2019–2022.

Year of project launch or update	Project name	Country	Power, kW	Fuel	Application description	Ref.
2022	HELENUS	EU	500	Carbon-neutral maritime fuels	Integration of a 500 kW SOFC module operating in CHP mode, in an MSC World class series ocean cruise vessel is planned.	[112]
2021	SO-FREE	EU	5	Any fuel mixture from natural gas and biogas to H_2	Realization of a flexible SOFC platform that allows to integrate multiple SOFC stack technologies within any CHP system, fed with any fuel mixture ranging from natural gas to biogas and to pure hydrogen, is planned	[113]
2021	ShipFC	EU	2000	Ammonia	The project plans to equip an offshore vessel, Viking Energy, with a large 2 MW ammonia fuel cell retrofitted, allowing it to sail solely on the clean fuel for up to 3000 h annually.	[114]
2021	Waste 2 Watts	Switzerland, EU	2–30 10–100 >100	Biogas from wastes	An integrated biogas-Solid Oxide Fuel Cell combined heat and power system with minimal gas pre-processing, focusing on low-cost biogas pollutant removal and optimal thermal system integration.	[115]
2020	PACBOAT	EU	50	LNG	MSC Cruises project PACBOAT integrates a CEA Liten 50 kW SOFC onboard the LNG-powered Europa cruise ship.	[116, 117]
2020	Wärtsilä LPG cargo	Finland	2000	Ammonia	Wärtsilä designs LPG cargo handling systems, which is also used for ammonia transportation. The ship is planned to have a 2 MW ammonia fueled SOFC power plant.	[117]
2020	Aisin Seiki Type S (SOFC) system	Japan	0.7	Natural gas	Aisin Seiki in cooperation with Toyota Motor and Kyocera presented a new Type S system working on SOFCs, which has electrical efficiency of 55 % (increased from 53 %), and total efficiency of 87 %. Service life is up from 10 to 12 years.	[117]
2020	MEGAMIE pressurised SOFC hybrid system	Japan	250	Natural gas	The 250 kW MEGAMIE system, an SOFC stack with a GT driven by the high temperature exhaust from the SOFC, is in early commercial deployment status.	[117, 118]
2020	Sunfire-Home	Germany, EU	0.75	LPG/Propane or natural gas	Sunfire has a variant of its Sunfire Home SOFC system using LPG/Propane or natural gas, with outputs of 750 W power and 1.25 kW heat, at an advertised electrical efficiency close to 40 % and overall efficiency at 89 %.	[119]
2020	Sunfire Remote	Germany, EU	0.4–1.2 (optionally 3.6)	Propane/Natural gas	SOFC stack (named PowerCore) is used in the Sunfire-Remote system with the power output from 400 W up to 1.2 kW, and optionally up to 3.6 kW.	[120]
2020	Bosch's Buderus SOFC micro-CHP system	Germany, EU	5–11	Natural gas	The BlueGEN technology is used in Bosch's Buderus SOFC micro-CHP system. Units with the power output of 5–11 kW are announced to have electrical efficiencies of up to 60 %.	[117]
2020	SOLIDpower BlueGEN BG-60	EU	6	Natural gas, Biogas	Commercial scale system for stationary CHP application with the efficiency of 60 %.	[121]
2020	SOLIDpower large system	EU	180	Natural gas	The system incorporates thirty 6 kW stacks. The market focus for this system is data centers and other applications in grid congested locations.	[117]
2020	Convion C60	Finland, EU	60	Natural gas, Biogas	Convion C60 is a modular power generator capable of CHP generation.	[122]
2020	WATT Fuel Cell's Imperium	USA	1	LPG	Power source for recreational boating.	[123]
2019	Weichai bus range extender	China, UK	30	Natural gas	Weichai electric bus range extender based on CeresPower SteelCell technology.	[124]
2019	Viessmann CHP system	Germany, UK	0.75	Natural gas	Stationary CHP power plant for households.	[117]
2019	Precision Combustion	USA	1–10	JP-8[a]	JP-8 fueled SOFC generators for US Department of Defense.	[125]
2019	Atrex	USA	1.5	JP-8	JP-8 fueled SOFC generators for US Department of Defense.	[126]

[a] JP-8 (Jet Propellant 8) is the kerosene-based jet fuel.

offering a valuable and environment-friendly utilization of poor-quality biogas that is currently wasted to the atmosphere [5]. The maximum power was obtained at 45 % methane concentration which corresponds to the maximum production of H_2 and CO via the internal dry reforming. SOFCs are also tolerant to ammonia present in biogas [5], thus having potential as an environmental clean-up system decomposing the pollutant into N_2 and water vapor without any formation of nitrogen oxides.

The operation of a SOFC stack comprising two membrane-electrode assemblies (MEAs) working on model landfill gas without external steam reforming of methane, was experimentally confirmed [13]. For the model landfill gas (47.4 % CH_4 - 52.6 % CO_2) humidified at 65 °C, the maximum power density of 0.18 W/cm^2 was achieved at 850 °C. The methane content in the exhaust gas flux was 0.01 vol%, indicating a sufficiently high utilization degree. A fuel consumption of 6.3 dm^3/min in terms of dry gas was estimated for 1 kW system [13].

The large variations of methane and oxygen concentrations in the coal mine gas may cause serious problems for its utilization in conventional engines [39]. On the other hand, the mine gas with low methane content is currently underutilized. The minimum CH_4 concentration requirements for fuel cell applications need further investigations but, in any case, SOFCs can operate using mine pre-drainage and medium quality post-drainage gas [41]. The SOFC-based technologies adapted for the use of coal mine gas are considered efficient to produce electrical power and heat [39,42,135–137]. Approximately 2 kW SOFC stacks equipped with a pre-reformer were developed [36]. One of the fuel cell stacks was installed into the experimental facility in Luisenthal (Germany) and operated on the coal mine gas under real conditions for 130 h; the concept was concluded suitable when the methane concentration varies between 30 and 45 % [39]. SOFCs fueled by coal mine gas with a low (1–30 %) methane content were recently proposed and modified to improve safety, efficiency and stability [42,135]. In order to overcome the explosion risk problem, a combination of SOFCs with the kinetic vacuum pressure swing adsorption was suggested for fuel deoxygenation

and CH₄ concentrating [42,135]. The direct utilization of air-diluted methane in SOFCs seems doubtful not only for safety reasons but also due to nickel oxidation in the cermet anodes. Although several recent reports claim a possibility of feeding the Ni-YSZ anode-supported SOFCs with a 30 % CH₄ - 70 % air mixture at 750–850 °C using NiO–BaO–CeO₂ (13-2-85 wt%) catalyst [136] or with the gas mixtures of 8.7–25 % CH₄ and 0–4.4 % O₂ at 800 °C using Mo-doped NiTiO₃ catalyst [137], the long-term stability and performance of such cells may be questionable.

At the same time, information on the oxidation mechanisms of multicomponent gas mixtures containing hydrocarbons, CO and other redox-active species in SOFCs is still often insufficient. This appears due to serious experimental limitations, namely, the presence of several parallel processes that are current- and overpotential-dependent, involve solid surfaces and electrode-electrolyte interface, and occur with gas volume and temperature changes affecting multicomponent diffusion in the porous media (see Ref. [14] and references cited therein). In fact, experimental testing of SOFC-based systems in the target multicomponent gas mixtures is necessary in many particular cases. A variety of approaches are being tested to overcome problems arising from carbon deposition in the SOFCs fueled by hydrocarbon-containing gas mixtures, including the incorporation of components with high catalytic activity towards carbon oxidation in the Ni-containing anode layers and addition of large amounts of steam or CO₂ in the fuel [14, 138]. For instance, the surface enhanced Raman spectroscopy (SERS) enabled identification of various stages of carbon formation process and electrode materials which are more or less susceptible to this effect [139].

6. Conclusions

MSW landfills and sewage treatment plants, coal mining, steel making, agricultural industry, production of chlorine and caustic soda, and other industries are considered as sources of high-calorific waste gases. In this short review, typical compositions and generation rates of the waste gases were analyzed. All these gases may and should be utilized for electrical energy and heat co-generation using not only ICEs and GTs, but also SOFCs. The SOFC-based generators operating at elevated temperatures provide a high efficiency, fuel flexibility and tolerance with respect to many impurities characteristic of the waste gases. The state-of-the-art SOFC technology is already able to widely contribute to the waste gas utilization, thus solving important environmental problems and reducing use of fossil fuels. The limitations associated with carbon deposition at the SOFC electrodes and significant variations in the waste gas composition with time can be overcome via optimization of the SOFC operation control systems and operational regimes, including those for fuel processing. The landfill gas, coal mine gas and various types of biogas are considered among the fuels having a highest potential for utilization in SOFCs. At the same time, gas purification from a number of impurities, primarily siloxanes, H₂S and halide-containing species, is necessary in many cases, especially for the landfill gas. The combined purification methods, including the condensation of water vapor with dissolved impurities, sorption and membrane technologies, were identified as most promising for the practical applications. The limiting impurity concentrations for SOFCs with respect to other power generation technologies were briefly discussed.

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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