Journal of Physics: Conference Series

PAPER • **OPEN ACCESS**

Hydrogen energy in Russia - industrial waste gases utilization potential

To cite this article: S Kiseleva *et al* 2021 *J. Phys.: Conf. Ser.* **1960** 012010

Hydrogen energy in Russia - industrial waste gases utilization potential

S Kiseleva[1,2,*], A Tarasenko[2], V Shakun[1] and D Agarkov[3]

[1]Lomonosov Moscow State University, Faculty of Geography, Moscow, Russian Federation
[2] Joint Institute for High Temperatures of the Russian Academy of Sciences, Moscow, Russian Federation
[3]Institute of Solid State Physics of the Russian Academy of Sciences, Chernogolovka, Moscow District, 2 Academician Ossipyan str., 142432

[*]E-mail: k_sophia_v@mail.ru

Abstract. Hydrogen is supposed to be prospective energy carrier and even commercial product for the nearest future. One of the hydrogen energy main problems is hydrogen production problem with high energy consumption in electrolysis case and CO/CO_2 co-production in case of steam hydrocarbon reforming. At the same time several branches of industry are able to produce hydrogen as a by-product with different purity degree. Sodium and chlorine production plants can be a source of high-purity hydrogen. Low-purity hydrogen can be obtained from digester and sewage gas. In both cases there is economic interest to energy production from such hydrogen or its introduction into natural gas pipelines. Technical potential of such hydrogen source in Russia has been briefly estimated in case of fuel cells usage. Resource potential visualization maps have been created.

1. Introduction

During last 2 years the new wave of interest in hydrogen energy has arisen. It is assumed that wide application of hydrogen, especially in transport and energy will slow down climate changes due to significant CO_2 emission reduction. European Union developed strategy to stimulate increase of hydrogen usage and production share in different branches of industry. Renewable energy based power plant output stability increase also gives chance for hydrogen energy technologies application. The main problem is that hydrogen is not a fossil fuel as a natural gas or widely available sort of renewable energy as solar one. Hydrogen must be produced using fossil fuels with corresponding carbon trace or using water and energy through electrolysis. Philippov et al [1] reported, that coal gasification can be prospective alternative to natural gas as a fossil source of hydrogen in the nearest future, especially for countries, possessing large amounts of coal, because coal is usually cheaper, coal mining is a great social factor for involved regions and coal is in less need for energy and industry than natural gas. Natural gas steam reforming is the main source of hydrogen today due to relatively cheap and well-designed industrial process. CO removal from reformate is also well-known technology using mainly pressure swing adsorption and other approaches [2]. But the carbon trace for fossil fuels utilization is the issue and risk for the whole approach, based on greenhouse gases decrease mentioned by European authorities [3].

From this point of view water electrolysis using traditional alkaline, relatively small-scale polymer-electrolyte membrane and novel solid oxide electrolyzers seems to be more ecologically friendly. Coupled with renewables and using electricity and water it also can be used for electric grid parameters stabilization. But capital costs for electrolyzers are the main issue. Some hope is concerned with prices decrease due to scaling effect in case of wide industrial electrolyzer production.

Methane pyrolysis is also discussed as a way to produce hydrogen with minimal carbon trace. Risks are concerned with further increase of prices for natural gas price and possible political limitations, influencing export and import operations.

Several branches of industry can also produce hydrogen, hydrogen-containing or calorific gases as by-products. Their amount is usually small in sight of future hydrogen demand, but they can be used to solve local problems. In addition, energy utilization of such calorific gaseous wastes leads to decrease of fossil fuels utilization or direct emissions of such wastes into atmosphere, making contribution into the whole picture of industry carbon trace.

The purpose of this research is to estimate numerically possible role of such gaseous wastes utilization as a mean to mitigate gaseous pollution from different industry branches.

2.Calorific gases generation as a by-product: volumes estimation

International waste management and ecology policy experience in the field of calorific waste gases has been taken into account to evaluate possible gaseous waste sources. Industrial calorific gases and products of wastes digestion in landfills or sewage sites are usually considered as valuable fuel resource, especially in case of traditional fuels shortage [4]. CH_4, H_2, CO or their mixtures are the most widespread sorts of such kind non-traditional fuels for energy and transportation. The present research task is to estimate amount of hydrogen and potential for its conversion into electric energy for Russian Federation.

First step involves amount of produced waste gases estimation for each source. According to literature data, landfills and sewage fields give the significant amount of biogas, having about 50 vol. % CH_4 as a component [5]. Metallurgy for the first time also has been considered as a source of hydrogen and CO, but detailed analysis revealed that the most part of produced gases usually is consumed as a part of technology process inside the factories, usually for heat production.

Chlorine and caustic soda production generates significant amount of hydrogen as by-product [6]. This amount can be estimated according to [6] as 0.03 kg. of hydrogen per kg of chlorine. Caustic soda, also produced during NaCl aqueous solution electrolysis, has about 0,025 kg of by-product hydrogen per kg of NaOH. A significant portion of by-product hydrogen comes from sodium chlorate production. Sodium chlorate is usually used for municipal water treatment and in bleaching wood pulp production, an important ingredient of paper.

Production sites in the second case are usually located in wooded areas, remote from other chemical industries that could use the byproduct hydrogen. This demand effective ways for its on-site utilization. According to experiments, performed in [7] about 0,15 kg (1,7 m^3) of hydrogen can be obtained from the process of sodium chlorate production as a by product. These experiments also showed that about 1 vol% CO is present in such hydrogen, opposite to higher purity in case of chlorine production.

Further steps involved statistical data analysis to estimate quantity of produced gases. For landfill gas its production rate can be roughly estimated through the amount of solid wastes delivered to landfills every year. According to data from Moscow region landfills [8], about 0.086 m^3 of methane from landfill gas is generated per 1 kg of solid municipal wastes. It has been assumed that landfill site is operated in stable mode (after 3-5 years after the operation has begun). Total amount of methane, generated in large-scale landfill sites of Russia, can be estimated as $4.12*10^9$ m^3/year, according to statistical data from Russian Ministry for natural Resources on delivered to landfills solid wastes in 2019 ($47.9*10^6$ tons for the whole country).

In 2019 the total amount of produced caustic soda in Russian Federation was estimated as $1291*10^6$ kg [9]. Yearly average sodium chlorate production in Russia can be estimated as $87*10^6$ kg/year.

In this case total amount of produced hydrogen can be estimated as $426*10^6$ m^3/ year of relatively pure hydrogen (from chlorine and caustic soda production), $148*10^6 m^3$/ year of CO-containing (1-2 vol. %) hydrogen, which needs additional purification to fulfil ISO 14687-3:2014or ISO 14687-2:2012 and $4.12*10^9 m^3$/ year of landfill methane. Regarding sodium chlorate low chemical stability, some relatively municipal water-treatment facilities prefer its production on-site, using available sodium chloride, water and electricity. Such production is not included into estimation, because statistical data deals only with chlorine industry in this case. So amount of such hydrogen can be even higher.

3. Possibilities for calorific gases conversion into electric energy.

Though estimated amount of produced hydrogen and methane seems to be enormous, it is worth mention that it is no deal with one giant gas field. These resources are distributed between about 100 industrial enterprises and landfill sites from St. Petersburg to Siberia (Figure 1).

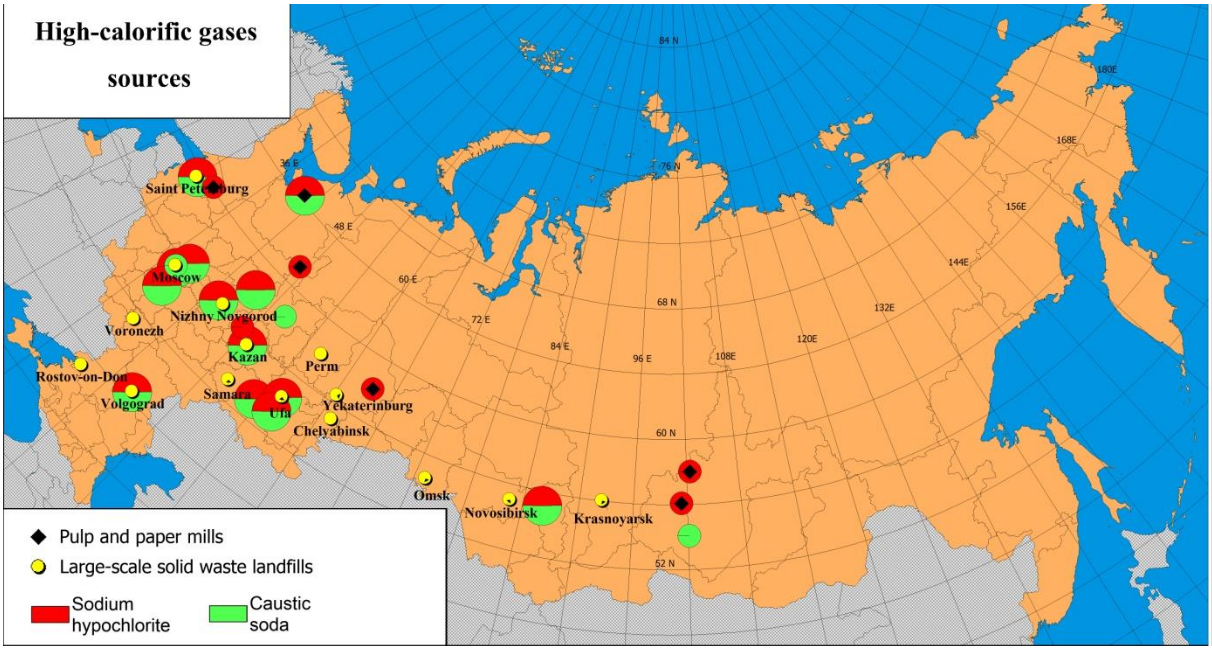

Figure 1. Spatial distribution estimation of calorific waste gases sources for Russia.

Some of these objects are situated quite far from industrial and transport infrastructure, as wooden industry enterprises. This circumstance makes hydrogen shipment for chemistry or energy purposes into urbanized areas less effective and attractive. But in this case utilization of these gases on-site leads to less resources consumption, decreasing fossil fuel or electric energy amount delivered to such enterprises. For chlorine industry there’s no problems for transport infrastructure, they are usually situated close to cities, receiving necessary for electrolysis energy from city power plants. The problems in this case are concerned with additional capital and operational expenses for hydrogen conditioning and transportation and with large electric energy consumption for electrolysis (usually 3-4 kWh/m^3 of chlorine). Explosion and fire danger coming from hydrogen are also additional arguments against hydrogen collecting and transportation, so now the most part of this gas is vented into atmosphere, preliminary diluted to safe concentration. But this can be the key to energy economy, using hydrogen and fuel cells for electrolysis energy consumption. In [6] Nedstack Fuel Cell Technologies B.V. specialists estimate possibility of such recuperation as 15% of consumed for electrolysis energy.

Fuel cells, polymer electrolyte membrane-based (PEM) or solid oxide ones (SOFC) have been considered as an apparatus for waste gas utilization due to their high efficiency [10]. PEM fuel cells have been supposed for pure hydrogen utilization in the chlorine industry according to successful Nedstack Fuel Cell Technologies BV experience, described in [6]. SOFCs can be applied in the fields, where fuel gas is supposed to be highly contaminated by CO, CO_2, CH_4. According to literature data one cannot be sure about direct CH_4electrooxidation in SOFC in real tests. Many papers present fast degradation of SOFC operating directly on CH4 at typical modern SOFC operational temperatures of 800-1000°C [11,12]. Ni-containing SOFC anode material in this case serves as a catalyst for the following reaction:

$$\mathrm{CH_4 \rightarrow C + 2H_2} \quad (1)$$

Solid carbon deposits arising from methane catalytic pyrolysis in such conditions are the main problem [13]. Several authors consider small amounts of rare-earth metals additive in anode catalytic layer [14], water vapor increased share in fuel gas [12] and lower operating temperatures [14] to solve the problem. In this case methane steam reforming is necessary to overcome the obstacles, concerned with anode carbon deposition. Steam reforming is a well-established and quite cheap industrial process, described by reaction>

$$\mathrm{CH_4 + H_2O \rightarrow CO + 3H_2} \quad (2)$$

Carbon monoxide and hydrogen mixture produced as a result of reaction (2) is often called reformate. SOFC operation in case of CO application as a fuel gas is described in [15]. So reformate-fuelled SOFC operation can be described as superposition of CO and H_2 oxidation, according to performance curves given in [15].

SOFC can also be operated on pure hydrogen, in this case specific fuel gas consumption is also estimated according to [15]. The data from this paper shows power density of 0.74 W/cm^2 for pure hydrogen and 0.67 W/cm^2 for pure CO at operational current density of 1 A/cm^2. Using Faradaic law for single fuel cell active area of 25 cm^2, one can estimate specific gas consumption of 0.78 m^3/kWh for CO and 0.68 m^3/kWh for H_2. For further estimation, needed to calculate reformate energy output, one must take into account reformate composition: 1 m^3 of methane produces 1 m^3 of CO and 3 m^3 of H_2 according to (2). Competitive processes between H_2 and CO electrooxidation on SOFC anode can be neglected due to large amount of cells in battery – in this case some cells will obtain hydrogen-depleted mixture and will have to utilize CO. So, energy, obtained from reformate (W), can be estimated as:

$$\mathrm{W} = \mu_1 \mathrm{V}\frac{1}{\mathrm{j}_1} + \mu_2 \mathrm{V}\frac{1}{\mathrm{j}_2} \quad (3)$$

Here V is reformate volume, $\mu_{1,2}$ are components shares and $j_{1,2}$ are specific gas consumptions for each component. In this approximation 5.7 kWh can be generated from 1 m^3 of methane. It is also supposed, that heat, needed for reforming, is consumed from SOFC battery due to its high operation temperature [16]. Energy efficiency of the whole process basing on the lowest calorific value for methane, is estimated as 51%.

The main problem of SOFC real life application is their sensitivity to changes in operation current and voltage. Time-consuming procedures are needed for SOFC-based generators due to high operation temperature [14]. But in case of industrial waste gases utilization fuel gas flow and electric load (in case of on-grid operation) are stable due to relative stability of industrial processes. SOFC operation on pure hydrogen can be realized in case of sodium chlorate factories, where small share of CO in waste hydrogen is found, resulting in PEM fuel cells degradation [7].

Estimations for PEM fuel cells, operating on pure hydrogen, are made basing on results from [6]. Specific hydrogen consumption here is much lower due to lower operation temperatures and has value of 0.6 m^3/kWh.

4. Results and discussion

Basing on the made estimations and yearly waste gases production volumes calculated earlier, it is possible to estimate potential energy output in industry and municipal landfills, which can be obtained by fuel cells application. Results for energy output are summarized in Table 1.

Table 1. Technical potential of waste gases from chlorine industry and municipal waste gases estimation results.

Waste gas source	Yearly gas volume, mln m^3	Specific gas consumption, m^3/kWh, SOFC	Specific gas consumption, m^3/kWh, PEMFC	Yearly energy output, TWh, SOFC	Yearly energy output, TWh, PEMFC
Caustic soda production	426	0.68	0.6	0.63	0.71
Sodium chlorate production	148	0.68	0.6	0,22	0.25
Municipal solid waste landfill sites	4119 (CH_4) / 2358 (H_2)	0.18	–	23.4	-

Totally 426*10^6 m^3 of relatively pure hydrogen, 148*10^6 m^3 of hydrogen needing simple preatreatment procedures and 12358*10^6 m^3 of hydrogen with high CO additive can be produced from waste gases in Russia. It can be seen, that in case of total application of SOFC in chlorine industry energy efficiency is less, than for PEMFC. But for sodium chlorate production PEMFC application needs some preliminary gas treatment or taking into account fuel cells degradation. Much more complicated pretreatment processes are needed to apply PEMFC in landfills. And here, using SOFC, one can obtain significant amount of energy even i case of landfill gas external reforming. It is worth mentioning that application of fuel cells and reformers for landfill gas utilization will demand complicated pretreatment procedures too, mainly to remove silicon and sulfur-based contaminants [17].

5. Conclusions

Estimations for energy and hydrogen production from waste gases generating by municipal objects and industry were made. Chlorine industry, including bleaching wood pulpproduction and municipal landfills are the main sources of potential fuel gases. The highest potential as methane/hydrogen or energy source among them have municipal landfills. Potential of chlorine industry could be underestimated due to sodium chlorate production directly in water treatment stations, which is not covered by statistical data. Taking into account highly dispersed spatial distribution of calorific waste gases sources energy production on-site can be more attractive than hydrogen collecting and transportation for export or industrial purposes. In this case fuel cells were chosen as efficient and resource converter of chemical energy into electric one. Estimations were made both for solid oxide fuel cells and polymer electrolyte fuel cells as most widespread fuel cell technologies. About 23 TWh of energy per year can be obtained applying SOFC with reformers for landfill gas utilization. Application of PEMFC is not suitable due to high CO content in fuel gas. For chlorine industry this figure is about 0.57 TWh/year. In case of PEMFC application it grows up to 0.96 TWh/year. The issue is small-scale pretreatment for sodium chlorate production plants to delete CO contamination at level 1-2 ppm (vol.). In case of relatively pure hydrogen PEMFC sow better efficiency but for highly contaminated hydrogen SOFC can be better option.

Acknowledgments

This research has been supported by Russian Scientific Foundation, Project No 20-19-00478.

References

[1] Phillipov S and Keiko A 2021 *Therm. Eng*. **68**(3) 45–58
[2] International Renewable Energy Agency. [Electronic resource] Official site. URL: https://www.irena.org/publications/2018/ Sep/Hydrogen-from-renewable-power
[3] Petkov I, Gabrielli P 2020 *Appl. En.* **274** 115197
[4] Sinaps Co [Electronic resource] Official site. URL: http://www.cogeneration.com.ua/ru/analytics/ special-gas/hydrogen-utilization/
[5] Zappini G, Cocca P and Rossi D 2010 *Energy* **35** 5063–9
[6] Verhage A J L, Coolegem J M, Mulder M J J, Yildirim M H and de Bruijn F A 2013 *Int. J. of Hydrogen En*. **38**(11) 4714–24
[7] Ihonen J, Koski P, Pulkkinen V, Kereanen T, Karimeaki H, Auvinen S, Nikiforow K, Kotisaari M, Tuiskula H and Viitakangas J 2017 *Int. J. of Hydrogen En*. **42** 27269-83
[8] Russian Ministry for Emergency Situations (Moscow Regional Department) [Electronic resource] Official site. URL: http://50.mchs.gov.ru/operationalpage/digest/item/8025481/
[9] LLC PTLK. [Electronic resource] Official site. URL: https://ptlc.ru/news/srednyaya-tsena-proizvoditeley-na-kausticheskuyu-sodu-v-2020-godu-sostavila-28-259-0-rub-tys-t/?bxajaxid= 375f9 ad410843e7ec1943c267d8622ed
[10] Staniforth J and Kendall K 2000 *J. Power Sources* **86**:401–3
[11] Girona K, Laurencin J, Fouletier J and Lefebvre-Joud F 2012 *J. of Power Sources* **210** 381–91
[12] Shiratori Y, Oshima T and Sasaki K 2008 *Int. J. of Hydrogen En*. **33** 6316–21
[13] Mohammad A A, Waqas H T, Enas T S and Haj Assad M E 2019 *Renew. and Sust. Energ. Rev.*, **101** 361–375
[14] Reeping K W, Bohn J M and Walker R A 2017 *J. of Power Sources* **372** 188–195
[15] Homel M, Gur T M, Koh J H and Virkar A V 2010 *J. of Power Sources* **195** 6367–72
[16] De Souza T A Z, Coronado C J R, Silveira J L and Pinto G M 2021 *J Cleaner Production* **279** 123814
[17] Kuhn J N, Elwell A C, Elsayed N H and Joseph B 2017 *Waste Management* **63** 246–56