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Hazards associated with syngas storage

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Abstract Energy needs of many countries are largely covered by energy obtained from fossil fuels. This in turn involves environmental pollution and greenhouse gas emissions. The growing environmental awareness and the need to prevent climate changes mean that clean energy and alternative energy sources are still a significant research issue. One of the most important technologies for efficient and low-carbon energy generation is the gasification process and synthesis gas production. Worldwide, there are now more than 270 such installations. More installations are under construction. Syngas is a mixture of hydrogen and carbon monoxide. Depending on the feedstock, it can also contain smaller amounts of carbon dioxide, methane and nitrogen. The gasification process consists of four stages: syngas production, storage, transport and utilization, e.g. as fuel. Because syngas is mainly composed of flammable and toxic gases, in the event of an uncontrolled release into the atmosphere these processes may pose a potential hazard to humans and the environment. The paper presents the results of analyses related to hazards resulting from an uncontrolled release of gas at the stage of the gas storage, before it is transported or finally used. Hazard scenarios are presented and the probability of their occurrence as well as the consequences for humans and the environment are determined.

1. Introduction

Energy needs of many countries are covered primarily by energy obtained by firing fossil fuels, which involves environmental pollution and greenhouse gas emissions.

The effect of the growing awareness of the hazards, the stricter requirements concerning the reduction of emissions and the need to protect the environment is that clean energy and alternative energy sources are still a significant research issue. The shortage of conventional energy sources and the advancement in fuel conversion have stimulated interest in research on fuel conversion and gasification technologies as clean, reliable and energy-efficient processes [1,2].

It is assumed that gasification will be one of the main energy sources in future – it will become the tool for the transition from coal-based energy to energy based on hydrogen [1,2].

Syngas is the end product of the gasification process. The term relates to gases being the effect of gasification of different feedstocks, such as coal, biomass, waste, liquid hydrocarbons, etc. The process main gasifying medium is oxygen, steam or air. Synthesis gas is a mixture of carbon monoxide and hydrogen in the first place. It can also contain other gases, e.g. methane, nitrogen or carbon dioxide. The composition depends on the feedstock or the gasifying medium [3,4]. An example composition of syngas is presented in Table 1 [2,5].

Table 1. Syngas example composition

	biomass	brown coal
gasification	fluidized	fluidized

process	bed	bed
CO	20-30	30-50
CO_2	25-40	13-25
H_2	20-30	35-46
CH_4	5-10	1-3
N_2	0-1	-

Syngas can be used as fuel to produce electricity. It can also be used as a semi-finished product in the chemical industry to produce synthetic natural gas, synthetic petroleum, ammonia and methanol. Currently, about 25% of the world◎ ammonia and 30% of the world◎ methanol are produced using the gasification process [6]. Syngas is also used to make biofuels and biomaterials.

The research on the scope of syngas application is therefore centred on the integrated gasification combined cycle (IGCC) technology, alternative internal combustion engines (ICE) and fuel-chemical production [1,4,7]. Such studies are presented e.g. in [2,7]. An analysis of syngas application in a microturbine is conducted in [8]. Syngas with a high content of hydrogen can also be used in high-temperature solid oxide fuel cells (SOFC) or in molten carbonate fuel cells (MCFC) [9].

Regardless of the final method of syngas application and of the technology advancement, each stage of syngas production, storage, transport and use requires additional attention focused on safety issues. Such analyses are presented for example in [4,10]. Safety is an important factor to consider because the presence of flammable and toxic gases in syngas creates potential hazards to humans

and the environment in the event of an installation failure or an uncontrolled gas release. The paper presents an analysis of hazards related to the process of syngas storage in tanks.

2. Synthesis gas production

Many processes are now used to produce synthesis gas. As already mentioned, syngas can be produced from coal, biomass, wood, waste or from natural gas. Gasification plants can be found on every continent, and most of them are located in China [6].

The selection of the syngas production process depends on many factors, such as the availability of raw materials, their cost and, first of all, the final product target composition. The basic parameter that defines syngas composition is the H_2/CO ratio [11].

The gasification dominant feedstock at present, as well as in predictable future, is coal. Biomass and feed waste are also gaining importance and the number of plants gasifying them is on the rise. Last but not least, there are also syngas production plants based on petroleum residues gasification and steam reforming [6].

In the process of steam-methane reforming, the heated mixture of steam and methane flows through a nickel catalyst. In such conditions methane undergoes a strong endothermic process referred to as steam reforming, which makes it possible to obtain hydrogen-rich synthesis gas with the typical H_2/CO ratio of 3:1 to 5:1 [6].

The next method – coal gasification – is one of the most developed technologies of the gasification process. Considering the type of the feedstock bed, gasification technologies can be divided into processes taking place in a fixed bed, fluidized bed or entrained-flow bed reactor. In the fixed bed technology the coal grain size is included in the range of 5-80 mm. Coal is on the fuel bed and the gasifying medium, i.e. air and/or steam, is fed from below (updraft gasification). In fluidized bed gasification the coal grain size is up to 10 mm. The processes occurring in this case are similar to combustion processes typical of a fluidized bed boiler, and gasification proceeds under atmospheric pressure. In entrained-flow reactors, pulverized fuel (<0.1 mm) is fed into the reaction zone in a jet of steam and oxygen. The fluidized layer is created as coal dust is lifted by gasifying mediums [1,3,12].

Biomass is usually gasified using air in fixed bed (con- and countercurrent) reactors or fluidized bed reactors. In concurrent reactors, the feedstock and the gasifying medium are transported in the same direction, whereas in countercurrent gasifiers – in opposite ones. Such systems are characterized by a number of requirements concerning the degree of biomass comminution, and their main disadvantages are low efficiency and the tar content. Two bed types are used in the fixed bed technology of biomass gasification: the circulating fluidized bed and the bubbling fluidized bed. Good-quality gas is obtained.

Many different kinds of reactors can be used for waste gasification. They differ in size and the feedstock type. Some are intended for solid municipal waste gasification, others – for gasification of construction and demolition debris. Many of them often require the feedstock pretreatment, e.g. breaking up or drying, or removal of non-organic materials that cannot be gasified [2,8,9].

3. Synthesis gas storage

Syngas storage is not currently a common practice. This is due to the fact that synthesis gas is usually fed directly for use. However, there is an extra potential in syngas storage compared to its immediate use. Storage enables wider applications, additional supplies and - ultimately - economic advantages to both producers and end consumers. For example, stored synthesis gas can be used to produce electricity in peak-demand periods. It can be a method to improve productivity, reliability and availability of IGCC power plants by increasing syngas availability during scheduled and unscheduled downtimes [7,13].

However, it has to be remembered that syngas storage involves technical difficulties because it contains hydrogen enhancing metal embrittlement. It is also necessary to consider specific safety issues in case of an uncontrolled release or corrosion. Therefore, the technical feasibility and economic attractiveness of syngas storage lie first of all in the gas properties, such as energy density or composition. Low energy density of synthesis gas, which varies from about a sixth to a third of that of natural gas, means that more syngas has to be produced to generate the same amount of electricity. This in turn makes it necessary to design large storage tanks with a high working pressure. Syngas can be stored in low- and high-pressure ground tanks, in existing pipelines or in underground sites [13].

The most essential large-scale stationary syngas storage system is compressed gas storage. This is a simple way to store syngas which generally needs only a pressure tank and a compressor. The costs are therefore lower compared to condensing, for example [13].

4. Hazards related to synthesis gas use

Syngas composition and the physicochemical properties arising therefrom have a substantial impact on the safety of the gas utilization. The analysis of the risk and hazards created by the process of syngas production, transport and storage should take account of the properties of the two basic components: hydrogen and carbon monoxide. Due to the content of the two gases, released synthesis gas can pose a fire hazard or explosion risk. The presence of a toxic gas can also present a toxic hazard.

The consequences of an uncontrolled failure-related release of syngas depend on the course of the event, i.e. whether the release is prompted by complete or partial damage to the pipeline (rupture or puncture) and whether ignition of the gas occurs. The consequences of the failure will also depend on the installation type and operating parameters, such as the tank pressure for example.

If there is a failure of a synthesis gas installation and immediate or delayed ignition of the mixture occurs, a number of dangerous events may follow, such as:
• jet fire - caused due to a release and ignition of gas flowing through the hole (puncture) under high pressure; it is characterized by a long and stable flame;
• flash fire - the cloud of released gas moves and ignites suddenly, sometimes far from the failure site;
• BLEVE - a violent phenomenon related to a release of liquid vapours to the environment with a temperature exceeding the boiling point; it is most often caused by flames washing the storage tank, which results in an increase in the tank inside temperature, the tank rupture and a violent release of the tank contents; if the failure involves a volatile flammable substance, the BLEVE phenomenon is usually accompanied by a fireball;
• explosion - i.e. a violent oxidation or decomposition reaction causing a rise in pressure and/or temperature [3,4,10,11].

The negative effects of the scenarios presented above are the fire-generated heat flux affecting humans and the environment (cf. Table 2) and the explosion-generated pressure wave (cf. Table 3) [14]. The effect of a release of syngas without ignition is the toxic hazard related to the toxicity of carbon monoxide contained in the mixture.

Table 2. Effects of the heat flux on humans and facilities

heat flux [kW/m²]	effects
35-37.5	100% death rate within 1 min; destruction of buildings
25-32	deformation of steel
23	100% death rate within 1 min; serious injuries within 10 s
12.5	1% death rate within 1 min; first-degree burns within 10 s
4.7	pain if exposure time exceeds 20 s
4	glass cracking after 30 min of exposure
2.5	threshold value causing pain if exposure time exceeds 1 min

Table 3. Effects of explosion-related overpressure on humans and facilities

overpressure [kPa]	effects
500 – 800	100% death rate
350 – 500	50% death rate
199.8	99% death rate due to lung damage
34.4	lung damage
20.7	minor damage to heavy machinery and equipment
17.2	demolition of 50% of brick buildings
4.8	damage to the structure of buildings
0.21	cracking of large window panes

|	
	(ordinary glass)
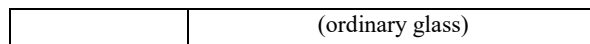
5. Consequences of a syngas tank failure

The potential hazards related to failures of syngas storage installations were analysed using the PHAST software [15].

Depending on the production process, synthesis gas composition may vary. This in turn has an impact on different properties creating fire-, explosion- or toxicity-related hazards. The following composition of the gas mixture is adopted for the purposes of the analysis:
• CO - 19%, CO_2 - 12%, H_2 - 19%, CH_4 - 2%, N_2 - 48% (mixture I)
• CO - 23%, CO_2 - 29%, H_2 - 38%, CH_4 - 9.5%, N_2 - 0.5% (mixture II).

The mixtures are obtained by gasifying biomass and coal, respectively. Fig. 1 and Fig. 2 present hazard zones within which humans feel pain if they happen to be there (heat flux exceeding 4.7 KW/m²). The analysis assumes a catastrophic complete rupture of a 10 m³ tank and syngas pressure of 25 bar. Due to the gas release and ignition, a fireball is created (BLEVE). The wind speed is 1.5 m/s.
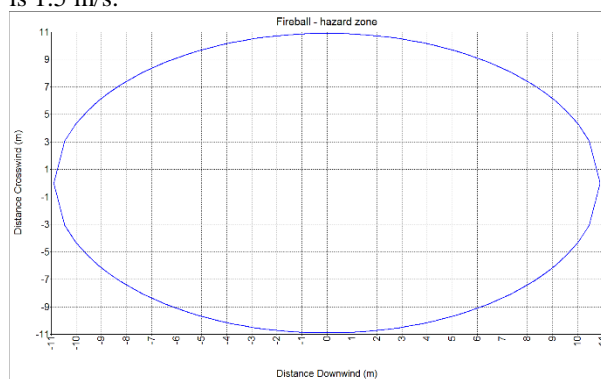
**Fig. 1.** Fireball hazard zone (mixture I)
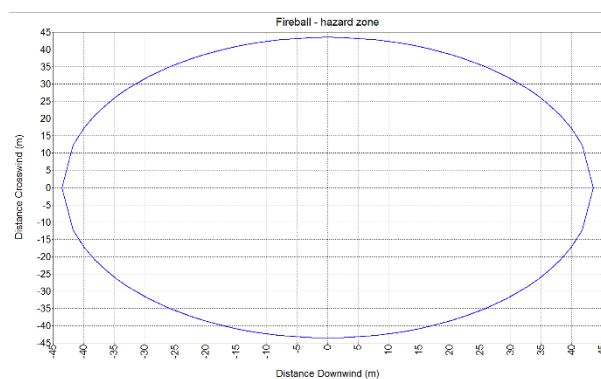
**Fig. 2.** Fireball hazard zone (mixture II)

The charts presented above indicate that a change in the content of flammable gases in the syngas mixture has a substantial impact on the level of the hazard related to a tank failure. If the hydrogen content is doubled, the hazard zone gets longer by about 35 metres.

Another important parameter that affects the range of hazard zones related to a fire and the generated heat flux is syngas pressure in the storage tank. Fig. 3 presents

heat flux values depending on the distance from the site of the tank failure, assuming different values of syngas pressure.
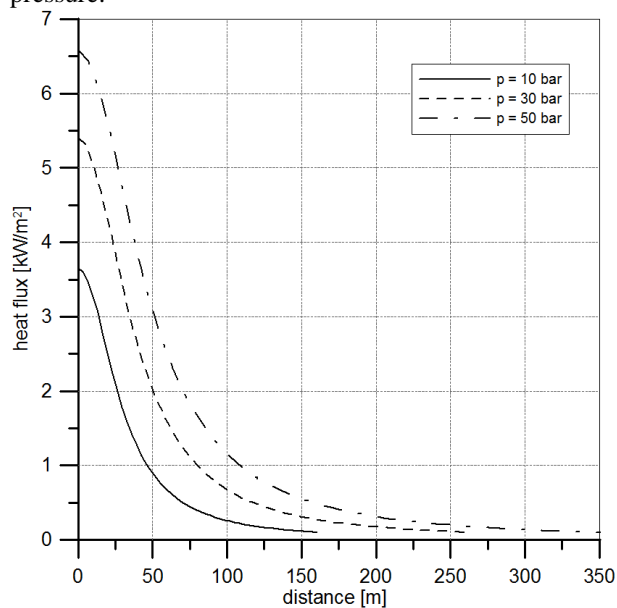

Fig. 3. Heat flux depending on the distance from the tank failure site (mixture I)
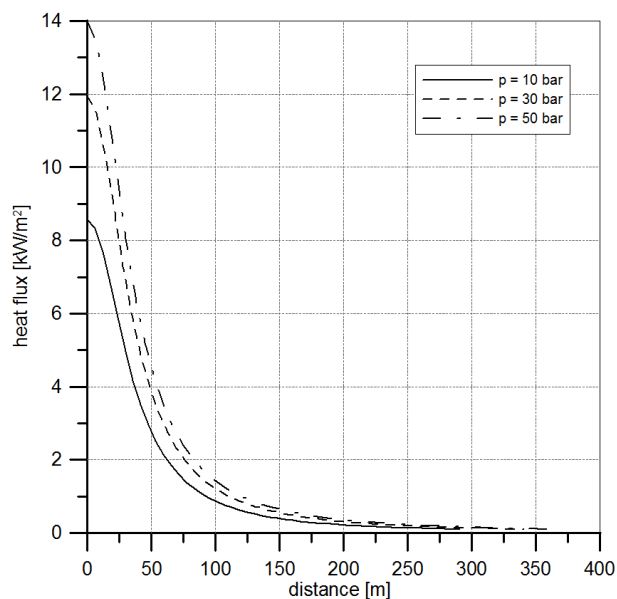

Fig. 4. Heat flux depending on the distance from the tank failure site (mixture II)

The tank immediate and complete rupture, in the case of delayed ignition, may also pose an explosion hazard. The next two figures present hazard zones related to an explosion of released synthesis gas. The parameters of the gas and of the storage tank assumed for the analysis are the same as in the analysis of the fireball hazard. The hazard zone corresponds to the explosion-generated pressure wave at the level of 34.4 kPa and higher, which causes damage to human lungs.
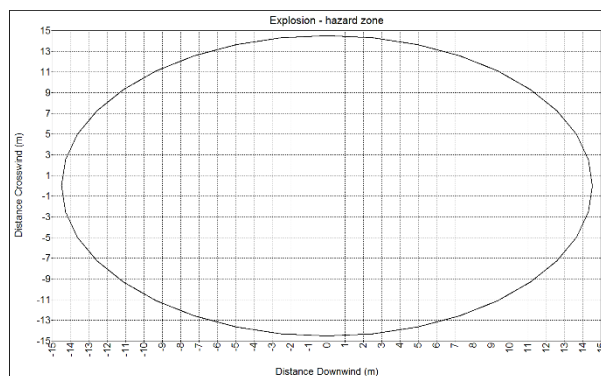

**Fig. 5.** Hazard zone for syngas explosion (mixture I)
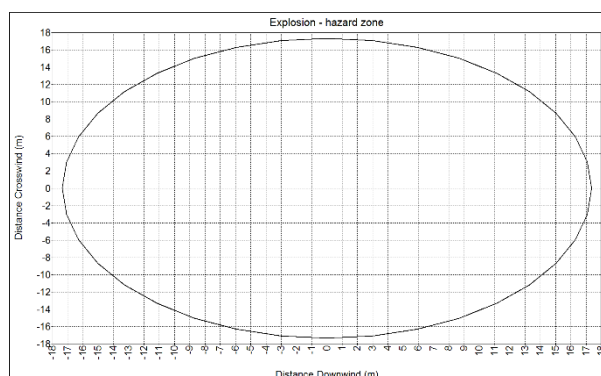
Fig. 6. Hazard zone for syngas explosion (mixture II)

As mentioned above, if the tank is partially damaged (tank puncture), a jet fire may occur. The jet of pressurized gas is ignited immediately, creating a long and stable flame with strong thermal radiation. The figures below illustrate hazard zones related to this failure type for a tank containing 10 m^3 of synthesis gas under the pressure of 25 bar. The assumed diameter of the puncture is 5 cm. The hazard zones correspond to the heat flux of 4.7 and 23 kW/m^2, causing pain and 100% death rate, respectively. If syngas contains a bigger content of hydrogen, an additional zone occurs with a heat flux value causing human death, i.e. the value exceeding 37.5 kW/m^2.
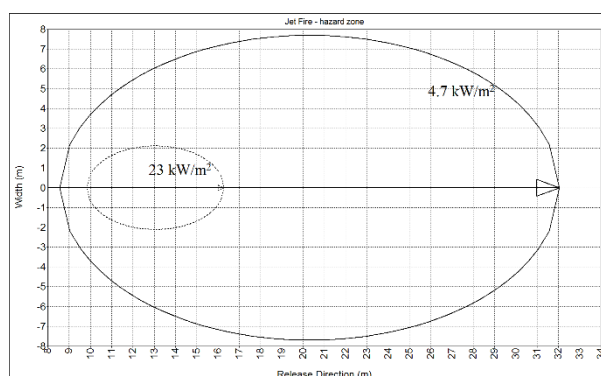

Fig. 7. Jet fire hazard zone (mixture I)
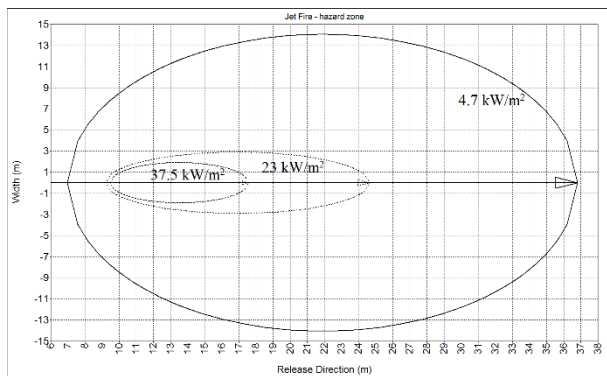
Fig. 8. Jet fire hazard zone (mixture II)

Analysing the figures presented above, it can be noticed that syngas fire hazard zones get bigger if the gas mixture contains bigger contents of flammable constituents.

In the case of a jet fire, the level of the hazard presented to humans and the environment will also be affected by the size of the puncture through which the gas is released. Fig. 9 presents changes in the heat flux generated by the fire of syngas with a higher content of hydrogen depending on the distance from the failure site for three different diameters of the puncture.
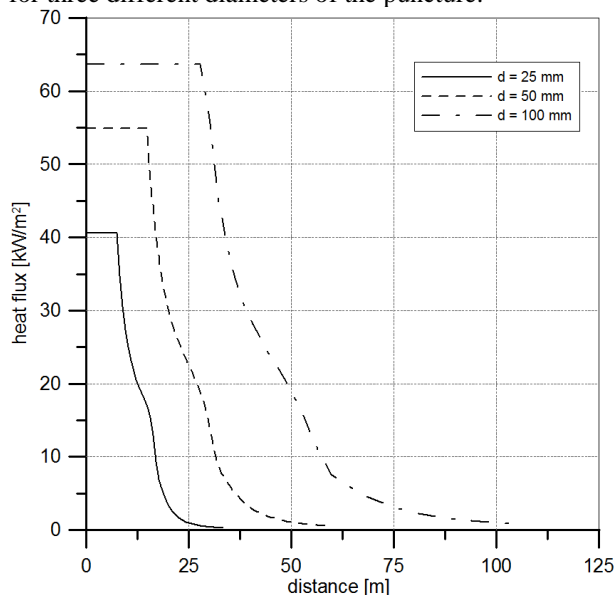
Fig. 9. Heat flux depending on the distance from the tank failure site for three different diameters of the puncture (mixture II)

Apart from the operating parameters of the installation and the size of the damage, the factors that have an essential impact on the consequences of a potential failure involving synthesis gas are the gas composition and the nature of the properties related thereto. For this reason, any consideration of issues related to the safety of syngas use, transport and storage should take account of the parameter defining the mixture composition, i.e. the H_2/CO ratio. Fig. 10 presents the change in the heat flux generated after a failure resulting in a fireball (BLEVE) and depending on the distance from the failure site for a storage tank with the H_2/CO ratio of 1:1, 2:1 and 3:1.
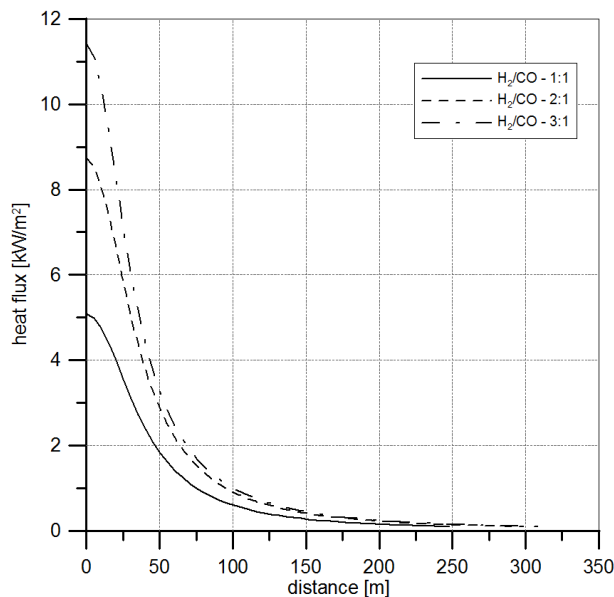
Fig. 10. Fireball-generated heat flux depending on the distance from the failure site for three different H_2/CO ratios

Analysing the chart presented above, it can be seen that a change in the H_2/CO ratio in the syngas mixture causes about twice as high a rise in the generated heat flux in the immediate vicinity of the fire.

6. Summary and conclusions

Undoubtedly, fuel gasification and conversion processes are very important in technologies aiming at a reduction in greenhouse gas emissions and clean energy production. They also play an essential role in the development of the chemical industry.
Synthesis gas can be used as an independent fuel, or it can be processed and utilized as an energy carrier. Any processes related to syngas processing, transport and storage should take account of its low energy density, which may create technical problems. The fact that it contains toxic and flammable gases should also be taken into consideration, as it may pose serious hazards.

The paper focuses on the hazards related to syngas storage. Storage processes may for example be a part of electricity production in IGCC power plants, where stored synthesis gas can be used to improve the power unit productivity or reliability.
A release of syngas may cause a situation with no ignition at all, but it is also possible that immediate or delayed ignition will occur [4].
If the released gas does not ignite, it will disperse in air creating no fire hazard or explosion risk. In the case of immediate ignition, a jet fire will be a potential hazard. If ignition is delayed, an explosion may occur. The level of the hazard presented to humans and the environment will depend on a number of factors, such as the tank geometry, the tank operating parameters and syngas composition. The heat flux generated by a syngas jet fire for the tank damage in the form of a hole with the diameter of 2.5, 5 and 10 cm will vary from about 40 kW/m^2 to 65 kW/m^2 in the immediate vicinity of the tank. Such values pose an essential hazard to human life and structural strength. The hazard zones for humans

arising due to the pressure wave generated during a syngas explosion (and causing lung damage) will reach the range of about 15 metres. In the case of syngas storage installations, the hazard level will also depend on the gas composition and the H_2/CO ratio in the mixture. If the ratio is raised from 1:1 to 3:1, the hazard related to the impact of the heat flux generated by the fire will be about twice as high.

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