

Organic Waste Gasification by Steam and Carbon Dioxide

Subjects: Physics, Atomic, Molecular & Chemical

Contributor: Sergey Frolov

The selective studies on environmentally friendly, combustion-free, allothermal, atmospheric-pressure, noncatalytic, direct H₂O/CO₂ gasification of organic feedstocks like biomass, sewage sludge wastes (SSW) and municipal solid wastes (MSW) are considered to demonstrate the pros and cons of the approaches and provide future perspectives. The environmental friendliness of H₂O/CO₂ gasification is well known as it is accompanied by considerably less harmful emissions into the environment as compared to O₂/air gasification. Comparative analysis of the various gasification technologies includes low-temperature H₂O/CO₂ gasification at temperatures up to 1000 °C, high-temperature plasma- and solar-assisted H₂O/CO₂ gasification at temperatures above 1200 °C, and an innovative gasification technology applying ultra-superheated steam (USS) with temperatures above 2000 °C obtained by pulsed or continuous gaseous detonations. Analysis shows that in terms of such characteristics as the carbon conversion efficiency (CCE), tar and char content, and the content of harmful by-products the plasma and detonation USS gasification technologies are most promising. However, as compared with plasma gasification, detonation USS gasification does not need enormous electric power with unnecessary and energy-consuming gas–plasma transition.

Keywords: organic wastes ; allothermal gasification ; atmospheric pressure ; ultra-superheated steam ; carbon dioxide ; solar heating ; plasma heating ; detonation heating ; detonation gun

1. Introduction

Modern society is faced with the problem of clean processing/utilization of organic wastes. Thermal processing of these materials is considered the most suitable solution due to relatively low environmental impact and partial recovery of energy and material resources. Available technologies of thermal processing are based on combustion/incineration, pyrolysis, and gasification, as well as on their combinations. Combustion is the transformation of the matter due to overall exothermic self-accelerating chemical reactions induced by molecular/turbulent mass and energy transport. Pyrolysis and gasification usually involve endothermic thermal degradation of the matter in the absence/presence of gasifying agent, respectively. A mild form of pyrolysis, torrefaction, is another emerging technology aimed at improving the energy density, calorific value, and grindability of feedstocks by their heating in the temperature range of 200–300 °C.

Combustion of wastes results in the formation of airborne gaseous pollutants, like polyaromatic hydrocarbons (PAH), NO_x, SO_x, HCl, furans, dioxins, as well as organic and inorganic aerosol particulate, fly ash, ashes, etc. Thus, biomass consists of lignin, carbohydrates, extractives, and inorganic fractions that are present in different amounts. In the wood smoke, such toxic compounds as PAH, polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs) are detected. Alkalies (potassium, calcium, silicon, etc.) present in the biomass can react with other minerals and cause fouling and slagging. The same relates to SSW. The main groups of organic solids in SSW are carbohydrates, proteins, fats, and oils. During combustion/incineration of SSW, dioxins, and furans, as well as nitrogen, chlorine, and sulfur compounds are released as gaseous pollutants in various forms. As for MSW, it is heterogeneous and contains a variety of materials (paper, wood, yard trimmings, food, plastics, metals, glass, and possibly hazardous materials) with a high fraction of organic compounds (over 70–80%), which implies a possibility of appropriate separation before incineration. Recent studies show that burning biomass, SSW, and MSW with fossil fuels (coal) has a positive impact both on the environment and the economics of power generation. This necessitates cleaning of the flue gas to meet strict emission limits.

Pyrolysis and gasification of wastes can potentially reduce the production of the various pollutants due to the absence or reduced amount of oxygen. However, for providing the required heat for pyrolysis and gasification reactions, the existing autothermal and allothermal technologies usually use the combustion of fossil fuels and/or feedstock or apply air/O₂ as gasifying agents. The use of combustion processes is then again related to harmful pollutants, whereas the use of air/O₂

as gasifying agents promotes the formation of dioxins and furans. In view of it, the use of other substances as gasifying agents, like steam and/or CO_2 looks very attractive, especially when the heat required for gasification is obtained by environmentally clean technologies (solar, microwave (MW), plasma, etc.) different from combustion. Pyrolysis and gasification are usually implemented at temperatures 400–1000 °C and result in production of gases like H_2 , CO , CO_2 , light hydrocarbons, tar, and char. The technologies based on gasification of solids and liquids (coal, lignin, biomass, plastics, crude oil, etc.), especially with steam as a gasifying agent, are used for the production of H_2 , syngas (a mixture of H_2 and CO), olefins, etc. Large-scale coal gasification plants usually use high-pressure O_2 - or air-blown technologies. However, for decentralized gasification of organic wastes atmospheric-pressure $\text{H}_2\text{O}/\text{CO}_2$ gasification is considered as promising alternative. In the small and medium-scale range of gasification plants, atmospheric-pressure $\text{H}_2\text{O}/\text{CO}_2$ gasification of organic wastes provides a significantly higher syngas quality than air-blown gasification. N_2 -free syngas possesses higher heating values and H_2 content over 60%vol. This makes such technologies appropriate for the conversion of biomass, SSW, and MSW into synthetic fuels such as methanol, dimethyl ether, substitute natural gas (SNG), and Fischer–Tropsch (FT) diesel. The conversion efficiency and gas yields are known to significantly increase with the pyrolysis/gasification temperature, whereas the yields of harmful substances are known to significantly decrease in these conditions. When the process temperatures exceed 1200 °C, further conversion steps are not needed anymore as the production of H_2 and CO tends to maximum, and other side by-products do not form at all. Furthermore, the conversion efficiency depends on the availability of catalytically active material, which is in some cases contained in biomass ash, and in other cases is present in gasifier bed material or purposely added to the process. The gasification of wastes with supercritical water (at above 374 °C and 22.1 MPa), despite many potential advantages, requires very high operation pressures, thus making the technology costly. There is also interest in co-gasification of various carbon containing materials (CCMs) with different physical properties, e.g., wood and plastics, MSW and coal, etc., due to synergy effects.

Thus, there is a need for the technologies based on combustion-free, atmospheric pressure $\text{H}_2\text{O}/\text{CO}_2$ gasification of organic wastes with temperatures above 1200 °C. Processing of organic wastes in such an environment will be accompanied by their complete gasification to the syngas of high quality. The target value of the H_2/CO ratio is always possible to adjust. The resultant syngas could be used as a fuel gas for producing heat and/or electricity for other purposes. The S and Cl containing wastes will be transformed to the corresponding liquid acids (after steam condensation), while solid inorganic materials will be transformed to the molten slag consisting of simple oxides and salts, an excellent construction material.

One of the known technological solutions in this respect is atmospheric-pressure plasma-based gasification, in particular steam-blown plasma gasification, known for its capability of treating complex feedstocks such as SSW and MSW while producing syngas of high purity and energy content. In this case, the heat required for gasification reactions comes solely from electricity to produce plasma torches in so-called plasma guns. In plasma gasifiers, tar is thermally decomposed into H_2 and CH_4 and ash is converted into vitrified and inert slag due to high (over 1300 °C) effective temperatures of a heat carrier gas and availability of very chemically active species enhancing gasification reactions. However, for running plasma guns with such high temperatures enormous electricity consumption is required. Other challenges are the need for advanced refractory materials for reactor casing and electrodes.

Another solution is based on using the USS with a temperature above 2000 °C obtained by burning environmentally clean $\text{H}_2\text{--O}_2$ mixture. Combustion of a mixture of syngas with steam and O_2 to obtain such a temperature could be an alternative solution. Due to the wide flammability limits of H_2 , the amount of CO_2 (greenhouse gas, GHG) in the combustion products could be considerably less than in the combustion products of fossil fuel. Such technologies are competitive to the plasma-based technologies as they do not involve energy losses due to unnecessary and energy-consuming transformation of electric energy to the thermal energy of a heat carrier gas through the state of plasma. Such technologies are capable of providing efficient processing of wastes of arbitrary chemical and morphological composition with full utilization of available resources without harmful emissions into water bodies and atmosphere. However, these technologies have not yet been implemented due to problems with the thermal insulation of combustors and gasifiers.

In our patent ^[1], we proposed a new method and devices for obtaining USS with temperatures above 2000 °C at atmospheric pressure, in which the problems of thermal insulation of combustion devices and reactors are solved by substituting conventional combustion by detonation in a pulse- or continuous-detonation steam superheaters (so-called pulsed or continuous USS guns) by means of cyclic or continuously rotating gaseous detonations of ternary fuel gas–oxidizer–steam mixture. Detonation is the transformation of the matter due to overall exothermic self-accelerating chemical reactions induced by volumetric compression and heating in strong self-sustaining shock waves (SWs). So far detonation of high explosives was primarily used for disposal of hazardous wastes like explosives and highly reactive materials (nitrocompounds, organic peroxides, etc.). In patents ^{[2][3]}, the novel gasification technologies based on pulsed

USS guns are applied to USS gasification of CCMs [2] and to fly ash decontamination [3]. The fundamentals of gaseous and spray detonations and the operation principles of pulse-detonation and continuous-detonation combustors for propulsion purposes were reviewed in [4][5]. Syngas, H₂, natural gas, C₃H₈, etc. can be used as fuel gas, while pure air, O₂, or air enriched with O₂ can be used as oxidizer.

In the literature, there are several excellent books on biomass, SSW and MSW management and the fundamentals of incineration, pyrolysis, and gasification technologies, as well as multiple reviews on feedstock pretreatment/aftertreatment, advanced autothermal and allothermal, catalytic and noncatalytic gasifier designs and performances, and downstream technologies and syngas applications. We do not consider these issues herein. Thus, the objective of this review is to consider the selective studies on environmentally friendly, combustion-free, allothermal, atmospheric-pressure, noncatalytic, direct H₂O/CO₂ gasification of organic feedstocks like biomass, SSW, and MSW, and demonstrate the pros and cons of the approaches and provide future perspectives. The main issue addressed is the effect of gasification temperature and H₂O/CO₂-to-feedstock ratio on the gasification efficiency, syngas quality and yield, as well as the feasibility of in-situ control of syngas composition. These objectives and issues are the novel and distinctive features of the present review.

2. Definitions

This section briefly provides the definitions of main terms and indices used in the paper, as well as the literature search approach and methodology limitations.

2.1. Feedstocks

Biomass comprises a variety of CCMs with different properties consisting predominantly of C, H, and O elements. It is derived from biological objects using photosynthesis to transform solar energy into carbohydrates. Agricultural and forestry wastes comprise wood sawdust (WS), crop waste products; and foliage which are often uneconomical to transport. Wet biomass sources include food wastes, SSW, animal slurry, etc.

SSW is a heterogeneous by-product of municipal or industrial wastewater treatment with high moisture content (up to 80%) and with a range of organic contaminants.

MSW is a heterogeneous feedstock containing materials with widely varying compositions, sizes, and shapes. MSW of typical composition is represented by 47%wt paper and cardboard, 21%wt food waste, 12%wt glass, 3%wt iron and its oxides, 5%wt plastics, 5%wt wood, 3%wt rubber and leather, 2%wt textiles, 2%wt calcium carbonate, i.e., CCMs constitute over 80%.

Refuse derived fuel (RDF) is a processed form of MSW. Conversion of MSW into RDF includes several operations like shredding, screening, sorting, drying, and pelletization to improve the homogeneity of the material and its handling characteristics. The RDF possesses a significantly higher energy density than MSW.

Hazardous wastes (HW) are classified according to the form in which they appear and according to the hazardous material content. A list of waste materials includes hazardous liquids and gases (PCB-containing oils, chlorinated fluorocarbons (CFCs) and various widely used solvents); hospital solid wastes (HSW); contaminated soils; low level radioactive wastes; and other wastes (military, asbestos materials, etc.).

Coal is a solid fossil fuel with high C content and various fractions of H, O, N, and S. Coals are differentiated into categories in terms of the descending LHV, composition, content of volatiles and moisture, namely, anthracite, bituminous, sub-bituminous, and lignite. ***This review deals mainly with biomass, SSW and MSW, despite some technologies include co-gasification with coal.***

2.2. Processing Technologies

Incineration is full oxidative combustion converting CCMs in an O₂-rich environment, typically at temperatures above 800 °C, to a flue gas composed primarily of CO₂ and H₂O with harmful by-products. Inorganic materials are converted to ash. This is the most common and well-proven thermal process using a variety of combustible materials.

Pyrolysis is thermal decomposition of CCM due to the use of an external heat source, typically at temperatures 400–900 °C, in the absence or at small amount of free oxygen. During pyrolysis, volatile portions of CCMs are driven off, resulting in the production of syngas composed mainly of H₂, CO, CO₂, CH₄, as well as higher hydrocarbons and harmful by-products. The condensed residue of the CCMs is left as tar and char. Inorganic materials form bottom ash.

Gasification is the thermal process of converting CCMs to syngas which can then be used for producing heat, electricity, and valuable products, such as H_2 , motor fuels, SNG, and chemicals. During gasification, partial oxidation reactions of all hydrocarbons with the aid of externally fed gasifying agent containing either free or bound oxygen (O_2 , air, H_2O , CO_2) producing syngas. The maximum conversion efficiency of feedstock to syngas is achieved if all carbon is oxidized to CO . A feedstock itself can contain enough bound oxygen needed for converting all carbon to syngas.

Plasma-based gasification is the high-temperature gasification process with plasma used as an external heat source for heating and converting CCMs into syngas in an O_2 -lean environment. The main element of the process is a plasma gun, containing two electrodes with an intense electric arc in the gap between them or an MW gun. The gasifying agent passing through the gun is heated up to temperatures above $5000\text{ }^\circ\text{C}$, but in the region where it contacts with the feedstock stream, the temperature is much lower ($1500\text{--}2000\text{ }^\circ\text{C}$). Plasma technologies require large electricity consumption. Plasma arc electrodes are sensitive to a gasifying medium. The use of electrodes can be avoided by using MW energy for plasma production. During MW heating the energy is delivered directly inside CCM creating multiple spots of microplasma in the interior of material and causing the material to sustain a high temperature.

Detonation-based gasification is the novel high-temperature detonation-assisted gasification process converting CCMs into syngas in an O_2 -free environment, patented in [1][2][3]. The main element of the process is the USS detonation gun producing the H_2O/CO_2 gas by detonating a part of CCM gasification products (syngas) in a triple mixture with O_2 and steam. The temperature of the gasifying agent exceeds $2000\text{ }^\circ\text{C}$, i.e., it is comparable with the temperature of plasma-based technologies, but detonation is not accompanied by energy loss inherent in electric energy conversion to plasma.

Combined processes are the combinations of the various thermochemical processes listed above. For example, two types of pyrolysis–gasification combination can be considered, namely subsequent and directly connected processes, both implying the preparation of char during pyrolysis followed by char gasification in the presence of a gasifying agent.

The choice of the most suitable processing technology for a given feedstock depends on the properties of the feedstock such as physical structure, moisture, metals, and ash content, which determine feedstock reactivity. ***This review deals solely with direct gasification of feedstock.***

2.3. Gasifying Agents

Superheated steam is water vapor heated above the saturation temperature. The main driving force for choosing superheated steam as gasifying agent is its ability to gasify solid waste and produce no negative effects to the environment. The gasifying agent is composed only of H and O atoms thus no other gases dilute the produced syngas. Due to the high enthalpy of steam, a lower amount of agent is needed for energy supply into a gasifier. Currently, steam-gasification of organics wastes is considered as an economically viable and competitive technology for the near future, in particular for H_2 production.

Ultra-superheated steam (USS) is the steam superheated to temperatures above $1200\text{ }^\circ\text{C}$. High steam temperatures prevent the production of tar, dioxins, furans, etc., which facilitates gas cleaning operations. Such steam can hardly be produced in boilers with heat exchangers because of the need for highly thermal-resistant (refractory) materials. There are several methods for producing USS. The method patented in [6] involves mixing the saturated or superheated steam with O_2 in a ratio up to 60%vol O_2 and continuously burning this blend with a fuel gas at a near stoichiometric composition to yield a product gas composed predominantly of H_2O and CO_2 . Another method patented in [4] involves admixing of saturated or superheated steam to a fuel gas–oxygen mixture in a ratio up to 40 to 60%vol and intermittently or continuously detonating this blend to yield a gas mixture composed predominantly of H_2O (up to 80%vol) and CO_2 (up to 20%vol). One more approach for producing USS is plasma heating of steam. The main problem of steam as a plasma gas follows from high electrode erosion rates in arc guns.

Carbon dioxide is the promising gasifying agent capable of enhancing the gasification of CCMs. It is composed only of C and O atoms; thus, no other gases dilute the produced syngas. As CO_2 has high enthalpy a lower amount of agent is needed for energy supply into a gasifier. CO_2 can be used directly or together with steam or O_2 . The addition of CO_2 in a blended H_2O/CO_2 gasifying agent allows manipulating the composition of syngas. The use of CO_2 , one of the main GHG, as gasifying agent can help decrease the GHG emissions which is a major cause of global warming. As CO_2 is a pollutant from almost every industry, CO_2 -assisted gasification can be coupled with a power plant to use up the flue gas CO_2 . Additionally, the incentives for reducing the carbon footprint can make this process attractive for energy producers. CO_2 can be also used as plasma gas, but energy efficiency is reduced as additional energy is needed for CO_2 dissociation.

Oxygen is the gasification agent currently used in most gasification systems. Oxygen of 95–99% purity is usually generated using proven cryogenic technology. Oxygen gasification exhibits high energy efficiency as partial oxidation of CCM produces additional energy. Energy for O₂ production is estimated as 1.1 MJ/kg O₂ produced. The problem of oxygen as a plasma gas follows from high electrode erosion rates in arc guns.

Air is a mixture of O₂ (21%vol) and N₂ (79%vol). It is often used as a gasifying agent, but the syngas is diluted by N₂ and possesses low LHV and H₂ content (8–14%vol). Air plasma is the cheapest option, but the gas produced is also diluted by a high amount of N₂. Moreover, N₂ presence can also contribute to the formation of NO_x in output gases.

Nitrogen is used as a feedstock purging gas and as plasma gas because it provides higher arc voltages, which increase the plasma jet power.

Argon is used as plasma gas providing long electrode life. However, the low specific heat of Ar results in relatively low plasma gun power. Furthermore, reactive species such as O atoms are generated only indirectly through energy transfer from Ar to O₂ with low energy transfer rates.

This review deals solely with H₂O/CO₂-assisted gasification of feedstock.

2.4. Gasification Products

Syngas is a mixture of H₂ and CO, which is one of the most important intermediates to produce various chemicals and motor fuels. At present, syngas is mainly produced from natural gas, coal, or by-products from refineries. The syngas composition is highly dependent on the reaction conditions and gasification technologies used. Thus, in the bubbling fluidized bed (BFB) gasifiers syngas composition depends even on the point of feedstock injection, in-bed or above-bed. When superheated steam is used as gasifying agent, the syngas produced contains much more H₂ as compared to conventional air-assisted gasification. As a result, the syngas in superheated steam and USS gasification is more energy dense. Syngas is also a good and environmentally friendly fuel exhibiting an LHV of 15–17 MJ/kg (12–16 MJ/nm³). The LHVs of its combustible constituents are 10.8 MJ/nm³ (H₂), 12.6 MJ/nm³ (CO), and 35.8 MJ/nm³ (CH₄). The syngas quality depends on the molar H₂/CO and CO₂/CO ratios. Depending on the level of H₂/CO ratio, the syngas can be suitable for different applications. H₂-rich syngas with large values of the H₂/CO ratio can be used for NH₃ synthesis or for producing pure H₂. Syngas with the H₂/CO ratio in the range of 1–2 is highly desirable for producing methanol and transportation fuels. The CO₂/CO ratio is a measure of the contamination and should be kept preferable as low as possible. Currently, the usage of syngas is about 50% to NH₃, 25% to H₂, and the rest is methanol, FT products, etc. The most valuable component of syngas is H₂. The amount of H₂ in syngas depends on the molecular structure of feedstock, gasifying agent, system losses, etc. However, based on the feedstock elemental composition and on the gasification reaction pathway, one can readily estimate a theoretical maximum yield of H₂. For example, wood biomass is sometimes represented as CH_{1.5}O_{0.7}, volume basis (vb). If steam is used as an oxidizer, then the theoretical maximum yield of 165 g H₂/kg of feedstock is obtained. This value is a factor of ~3 higher than 60 g H₂/kg of feedstock potentially available from the biomass alone. H₂ exhibits very wide flammability limits in mixtures with air, so that combustion of H₂-lean mixtures is accompanied by no harmful emissions. H₂-rich syngas–air mixtures also exhibit wide flammability limits therefore their combustion produces no harmful pollutants and emits essentially reduced amounts of CO₂.

Slag is a glass-like nonhazardous by-product of most solid and liquid feed gasifiers, which can be used in roadbed construction, as roofing material, etc.

Tar is a hazardous by-product of pyrolysis and gasification, which includes condensable aromatic organic species heavier than benzene, formed during thermal treatment of organic wastes. It is a major concern for CCM gasification due to its negative effect on downstream equipment and the environment. Syngas tar is also considered as an energy loss. The LHV of tar is 13–18 MJ/kg wet basis (wb). Tar reduction approaches can be in-situ and ex-situ. The in-situ reduction is achieved by adjusting a gasifier design and operation process, as well as by using additives and catalysts during operation. The ex-situ tar reduction does not affect the gasification process as tar is removed from the product syngas. The tar yield strongly depends on gasification conditions and therefore, very different results are obtained depending on the technology used.

Char is the remaining devolatilized residue of organic wastes. It is composed primarily of carbon (~85%), can contain some oxygen and hydrogen, and contains very little inorganic ash. The LHV of biomass char is about 32 MJ/kg, which is considerably higher than that of the original feedstock or its tar. Char surface is characterized by a large porosity and surface area. The char yields reported in the literature differ considerably depending on the technology used and feedstocks applied.

Other harmful by-products include smoke, NO_x and SO_x, NH₃, H₂S, dioxins, furans, hydrocarbons, etc.

2.5. Gasification Reactions

The general objective of gasification is to reach complete conversion of carbon contained in the feedstock. Before gasification, the solid/liquid feedstock is usually homogenized by means of fine granulation/fragmentation. The gasification process starts from feedstock drying at temperatures up to ~200 °C and is followed by pyrolysis at temperatures up to ~900 °C, and thermal cracking and partial oxidation of produced gases, tar, and char at higher temperatures, leading to the formation of syngas. The composition, amounts, and characteristics of the syngas depend on the composition and structure of the feedstock, gasifying agent, and multiple process parameters. The gasification process of CCMs includes many heterogeneous and homogeneous endothermic and exothermic reactions between active radicals, atoms, and molecules, as well as electronically excited and ionized species in case of plasma gasification. The absence of oxidizing environment eliminates necessary steps of the dioxin synthesis mechanism and strongly reduces or completely avoids PCDD and PCDF formation. The reaction rates depend on the local temperature and reactant concentrations. Heterogeneous reactions between gas and char can be kinetically or diffusion controlled depending on char particle size, porosity, temperature, and the intensity of interphase heat and mass transfer. The latter is mainly determined by the local velocity slip between gas and particles. Besides chemical transformations, particle properties may be a factor causing slagging and fouling phenomena in gasifiers. In general, the final composition of gasification products is determined by the rates of reactions and by catalytic effects important for overall tar decomposition reactions $pC_xH_y = qC_nH_m + rH_2$ and $C_nH_m = nC + m/2H_2$. Nevertheless, thermodynamic calculations, implying chemical equilibrium after an infinite time, provide some important trends. In general, the equilibrium calculations of CCM gasification show that (i) at temperatures ~600 °C, carbon, and oxygen exist as CO₂, tar and char, i.e., tar and char conversion is low; (ii) at temperatures above ~900 °C, in presence of carbon, CO₂ breaks down to CO and available oxygen mostly reacts with carbon to form CO and CO₂ rather than with H₂ to form water; and (iii) at temperatures above ~1500 °C tar and char are completely transformed to syngas composed mainly of H₂ and CO. It is worth noting that equilibrium calculations may generally provide the trends rather than actual values of temperature and species concentrations. The differences between calculations and experiments are usually attributed to thermal losses, imperfect mixing of components, and finite rates of heat and mass transfer, and chemical transformations. This should be kept in mind when using the equilibrium data for design considerations. As compared to O₂/air gasification, H₂O/CO₂ gasification provides lower reactivity. Moreover, due to reaction endothermicity, the local gasification temperatures are lower than the inlet temperature of the gasifying agent. Therefore, various approaches to accelerate gasification reactions by supplying additional heat to the reaction zone are implemented. Obviously, higher H₂O/CO₂ temperatures will result in higher rates of reactions. In fluidized bed gasifiers, a bed material or char are often used as solid heat carriers. The rates of gasification reactions can be also enhanced relative to the competing reactions by increasing the concentration of a gasifying agent. One of the major advantages of using H₂O as the gasifying agent is the availability of more H atoms to produce H₂ gas through overall reaction $CO + H_2O = CO_2 + H_2$. This reaction is facilitated by the carbon input in the form of CO because it is the limiting factor as hydrogen and oxygen can be produced from steam. As a result, this reaction would be promoted with more available carbon resulting in higher H₂ production. Thus, for the production of more H₂, there is a need for both more C-content feedstock and more H atoms from steam.

2.6. Gasification Process Parameters

Feedstock composition and physical properties. The gasification process is affected by feedstock properties: elemental composition, LHV or higher heating value (HHV), ash content and composition, moisture, volatile matter content, other contaminants like N, S, Cl, alkalis, etc., bulk density and size. For example, ultimate analysis of wood wastes yields a typical mass composition of 49%wt C, 44%wt O, and 6%wt H with the balance comprised of traces of N, S, and mineral species.

Gasifying agent and gasification temperature play a major role to determine the syngas composition and LHV. According to the Le Chatelier principle, increased temperature favors the products of endothermic reactions and favors the reactants in exothermic reactions. In view of it, H₂O and CO₂ have their own advantages in gasification. Steam promotes overall endothermic reactions $C + H_2O = CO + H_2$, $pC_xH_y = qC_nH_m + rH_2$, and $C_nH_m = nC + m/2H_2$ of char and tar, as well as overall exothermic reaction $CO + H_2O = CO_2 + H_2$. CO₂ promotes overall endothermic reaction $C + CO_2 = 2CO$ to produce CO. In general, higher gasification temperatures favor H₂ production and syngas yield.

Gasification pressure. According to available literature, with increasing pressure at a constant gasification temperature of 1000 °C the mole fractions of H₂ and CO in the syngas decrease, while those of CO₂ and CH₄ increase. The reason is that overall reaction $C + 2H_2 = CH_4$ has a low rate except for high pressures, while the rate of overall reaction $CO + H_2O = CO_2 + H_2$ does not change much with pressure. A similar trend exists at temperatures above 1500 °C but the differences

in product yield look negligible. ***In this review, we concentrate on atmospheric pressure gasification implying that atmospheric pressure provides the maximum yield of H₂ and CO in syngas.***

Oxygen-to-Steam Ratio, O/S. A blend of steam with O₂ or air is often used as a gasifying agent. The O/S ratio affects the resultant concentrations of H₂, CO, and CH₄ in syngas tending to a higher degree of their oxidation. However, the availability of free oxygen promotes the formation of harmful by-products like dioxins, furans, etc. ***In this review, we focus on O₂-free gasification of organic feedstocks, i.e., O/S = 0.***

Oxygen-to-Fuel equivalence ratio (ER) is the ratio between the free O₂ content in the gasifying agent and that required for stoichiometric combustion. A zero value of ER corresponds to pyrolysis conditions, i.e., combustion is entirely avoided. The value equal to 1 corresponds to stoichiometric combustion conditions. The values of ER less than 1 leave unconverted char and higher tar content, whereas the values of ER greater than 1 lead to the oxidation of part of syngas and the reduction of syngas LHV. ***In this review, we focus on combustion-free gasification of organic feedstocks, i.e., ER = 0.***

Steam-to-Carbon Ratio, S/C, or Steam-to-Feedstock Ratio, S/F is defined either on vb or mass basis (mb). Increasing the S/C or S/F ratios increases the yields of H₂ and CO₂ and decreases the yield of CO. This is attributed to overall reactions $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$ and $\text{C}_n\text{H}_m + n\text{H}_2\text{O} = n\text{CO} + (n + m/2)\text{H}_2$, which lead to a decrease in CH₄ content with the S/C or S/F ratio. The feedstock C-content is used to estimate the S/C or S/F ratio required for complete gasification of feedstock without formation of solid carbon. The condition, at which the amount of gasifying agent is exactly sufficient for complete carbon conversion is referred to as the Carbon Boundary Point (CBP). Available studies show that the CBP is the optimum operation point with respect to exergy-based-efficiency for both gasification with air and steam. As the temperature increases, the CBP is reached at a lower S/F value. For example, while the S/F value is 0.9 at 600 °C, it reduces to 0.2 when the steam gasification temperature of rice husk is 900 °C. The S/F values above 1.2–1.5 are not recommended because the major part of steam is not used in the syngas. The most appropriate range for S/F is between 0.40 and 1.0.

CO₂-to-Carbon Ratio, CO₂/C, or CO₂-to-Feedstock Ratio, CO₂/F is the analog of S/C and S/F ratio for the case when CO₂ is used as gasifying agent. It can be defined either on vb or mb. The gasification conditions corresponding to the CBP are also optimal for CO₂-assisted gasification. Like the S/C ratio, the optimal CO₂/C ratio decreases with gasification temperature attaining large values on the level of ~5 at 600 °C and a nearly constant value below 0.5 at temperatures above 800 °C.

Residence time (RT) of feedstock and gases is the characteristic time the CCM is flowing through the gasifier reaction zone. It defines the completeness of gasification and depends on reactor type, design, and dimensions, as well as on the arrangement of the operation process. The RT of granulated/fragmented feedstock can be varied from fractions of seconds to hours. A required RT is usually estimated based on the assumption that the slowest gasification reaction is char conversion. Strictly speaking, one should consider RT distribution (RTD) rather than a single value, which is caused by the complexity of gasifier designs with spatially nonuniform velocity fields and with feedstock particle size distribution.

Cold gas efficiency (CGE) is defined as the ratio of LHVs or HHVs of syngas and feedstock. It is referred to as cold efficiency since it includes only the potential chemical energy of syngas. The CGE describes the efficiency of a gasification process for further power applications of syngas.

Hot gas efficiency (HGE) is defined as the ratio between the sum of chemical energy and sensible heat of the produced syngas, on the one hand, and the sum of chemical energy and sensible heat of the feedstock fed to the plant, on the other hand. The hot-gas efficiency assumes that the heating of the unconverted char is a loss.

Carbon conversion efficiency (CCE) is defined as the ratio of the carbon in the syngas to carbon fed to the reactor with feedstock. The CCE is the unconverted carbon indicator and provides a measure of chemical efficiency of the gasification process.

Net process efficiency (NPE) is the ratio of the produced syngas LHV, on the one hand, to the feedstock LHV and the external energy needed for syngas production, on the other hand. Contrary to CGE, the NPE considers the energy needed for obtaining a high-temperature gasifying agent in the energy balance.

2.7. Gasification Technologies

Depending on the heat source for gasification and the level of gasification temperature, all gasification technologies can be categorized into allothermal/autothermal and low/high-temperature technologies.

Allothermal technology implies that heat for gasification is introduced from an external source such as heat exchangers, heat carriers, electric heaters, plasma guns, detonation guns, etc. A well-known example of allothermal technology is a dual fluidized-bed (DFB) steam gasifier.

Autothermal technology implies that the heat for gasification is produced within a gasifier, usually by adding air or O₂ for partial combustion of the feedstock. The part of the feedstock to be burned at the combustion stage can be significant. A well-known example is a classical moving bed gasifier.

Low-temperature gasification is typically performed at temperatures below 1000 °C and along with syngas produces nonhazardous and harmful by-products (slag, char, tar, etc.). Low-temperature steam gasification of CCMs produces a syngas with a 30–60 vol.% H₂ content.

High-temperature gasification is performed at temperatures above 1200 °C, where the organic part of wastes is converted mainly into H₂ and CO. High-temperature steam gasification of CCMs produces a syngas gas with a 50–60 vol.% H₂ content.

3. Low-Temperature H₂O/CO₂-Assisted Allothermal Gasification

The thorough literature review [2] indicates that the main bottlenecks of existing allothermal, atmospheric pressure, noncatalytic, direct low-temperature H₂O/CO₂ gasification technologies of CCMs consist in

- *low-quality syngas due to high content of tar (up to 27%wt. db) and CO₂ (up to 30%vol. db),*
- *low gasification efficiencies due to high char residues (up to 40%wt. db),*
- *difficult in-situ gas quality control due to the need in long RTs of feedstock in the reaction zone (up to 100 min), and*
- *low yields of syngas due to low gas yields (below 90%wt. db), high tar and char contents and partial use of syngas (together with product char) for the production of heat required for gasification in the existing DFB gasifiers.*

The current R&D efforts are mainly directed on feedstock preprocessing (e.g., biomass torrefaction) and postprocessing (reforming) of produced syngas, as well as improving feedstock reactivity by adding various catalysts. Despite some improvements in the CCE and other performance indices, all these activities lead obviously to the increase in the syngas production costs. As for the positive effect of catalysts on carbon conversion at 800–900 °C, it indicates that the feedstock conversion is kinetically controlled, i.e., heat and mass transfer is, in general, faster than chemical transformations. This kinetically controlled gasification is provided even by small fluidization velocities and low turbulence intensities in fluidized bed gasifiers on the level of 1 m/s. The increase in the gasification temperature other conditions being equal (e.g., at fixed flow rate of steam) results in the increase of both, the reaction rate and the intensity of heat and mass transfer, and by the decrease in the gas RT in a gasifier. The latter is due to the increase in the flow velocity of the gasifying agent caused by its density decrease with temperature. If the process is still kinetically controlled then all observed improvements in syngas quality detected in the experiments discussed above are mainly due to higher mixing intensity and trade-of between enhanced reactivity and reduced RT.

These considerations imply that for improving the process performance the kinetically controlled mode must be replaced by the diffusion-controlled mode when the chemistry is fast compared with heat and mass transfer processes. This can be attained only by increasing both the gasification temperature and velocity slip between phases (gasifying agent and feedstock particles). With increasing the gasification temperature and velocity slip between phases the rates of chemical reactions will increase drastically only if interphase and intraphase transport processes ensure the availability of hot reactants due to turbulent and molecular heat and mass transfer in both phases.

The optimal conditions for diffusion-controlled gasification could be obtained by applying the modern CFD approaches, which allow the optimization of gasifier design to ensure a required RT for gases and solids. Despite significant progress in understanding the various hydrodynamic and thermal processes in gasifiers and successfully simulating their overall performance, the existing approaches fail to adequately represent the gasification chemistry, one of the most important aspects of the process. Firstly, the chemistry used in the CFD studies is based on overall molecular reactions between valence-saturated molecules with high apparent activation energies. As a matter of fact, chemical reactions proceed through active intermediates like atoms and radicals via different reaction channels, and the corresponding reactions possess zero activation energies. Secondly, the reaction rates in the CFD studies are calculated based on the mean

temperature and species concentrations. In reality, reaction rates are governed by local instantaneous temperatures and species concentrations, which could differ considerably from their mean values, in particular, at the presence of intense turbulent transport.

4. High-Temperature H₂O/CO₂-Assisted Allothermal Gasification

The thorough literature review [2] indicates that the main advantages of existing allothermal, atmospheric pressure, noncatalytic, direct plasma and solar high-temperature H₂O/CO₂ gasification technologies of CCMs consist in

- *high-quality syngas due to negligible or low content of tar (less than 1 g/nm³) and CO₂ (less than 6%vol. db),*
- *high gasification efficiencies with CCE attaining 100% due to negligible or small tar and char residues,*
- *easy in-situ gas quality control due to relatively short RTs of feedstock (less than 5–10 min) in the reaction zone, and*
- *high yields of syngas due to the use of electric or solar energy for the production of heat required for gasification.*

The conventional heating systems with the operation temperatures up to 1400 °C could be considered as exception, because the lab-scale experiments with fixed bed and drop tube reactors show relatively low CCEs (77–84%) due to different reasons (residual char in locally cold zones, short RT, etc.).

The highest CCEs are attained in arc plasma systems evidently due to availability of high temperature and high velocity (up to ~1 km/s) gasifying agent. The presence of ions, electrons, excited molecules, and photons in the arc plasma jet enhances chemical transformations.

MW plasma is also efficient due to a specific heating mechanism of a feedstock. When a CCM is exposed to electromagnetic field, delocalized p-electrons start to move through broad regions of the material inducing its heating due to electrical resistance and formation of multiple localized hot spots (“microplasma”) with temperatures above 5000 °C. Chemical transformations in these hot spots are enhanced by the high-velocity microjets of plasma gases facilitating heat and mass transfer with the material. As for solar gasification of CCMs it can be considered as a means of storing solar energy in feedstock gasification products in a controlled form.

Despite many advantages, high-temperature plasma and solar gasification technologies have certain drawbacks which limit their widespread applications. Due to high operating temperatures water-cooling systems and or special construction materials and refractory liners are required for gasifier walls. Industrial scale arc and MW plasma technologies require enormous electric power. Moreover, the efficiency of plasma guns is at most 70–80%, and the lifetime of arc electrodes amounts hundreds of hours only. Despite very high plasma temperatures in the arc-jet (above 10,000 °C) and MW “microplasma,” the typical working temperatures in plasma gasifiers are only 1300–1700 °C to keep the reactor wall temperatures at an acceptable level dictated by refractory material of the wall. The question then arises what is the energy-consuming gas–plasma transition needed for if most of the feedstock is gasified at such a relatively low working temperature? As for the MW plasma, in addition to electric energy requirements its gasification efficiency highly depends on feedstock properties, which requires sorting operations. Also, there is often a need in mixing a feedstock with special materials possessing appropriate polarization properties in electromagnetic field, i.e., an additional operation which requires optimization is introduced. The main drawback of solar gasification is its intermittent character depending on time of day and weather conditions. Also, there is always a need in keeping a reactor window clean and providing uniform heating of feedstock.

In addition, plasma and solar gasification plant optimization requires highly sophisticated CFD software providing a solution of a coupled hydrodynamic (Navier–Stokes) and electrodynamic (Maxwell) equations complicated by chemical transformations and turbulent/molecular transport in a multicomponent environment. There are actually no publications on detailed numerical simulations of H₂O/CO₂ gasification of CCMs in plasma or solar gasifiers aimed at optimizing their operation conditions.

5. High-Temperature H₂O/CO₂-Assisted Allothermal Detonation-Based Gasification

5.1. Preliminary Remarks

In existing steam generators, superheated steam is usually obtained by heat transfer from the hot combustion products of some fuel: heat is first supplied for heating feed water to saturation temperature and its vaporization, and then to saturated water vapor. As a result, superheated steam of a given temperature is obtained at the outlet of steam generator, which cannot exceed the adiabatic combustion temperature of the fuel (for example, for a mixture of CH_4 with air it is about 1950°C) and is determined by the heat resistance of the material of heat exchanger walls. Even if the wall of heat exchanger is made of heat-resistant steel, its maximum temperature usually does not exceed $\sim 1000^\circ\text{C}$. Therefore, the production of USS, i.e., steam with a very high temperature (above 2000°C) is a problem that has not yet been resolved. To solve this problem, a new method was proposed in [1] for generating USS using its shock or detonation compression and heating in a cyclic or continuous operation process based on pulse-detonation [4] or continuous-detonation [5] burning of fuel. First, in this method, instead of a relatively slow heat transfer through heat exchanger walls, a fast process of shock compression and heating of steam in a traveling shock wave (SW) or detonation wave (DW) is used, which increases the pressure and temperature by factors 25–30 and 8–10, respectively, within few microseconds. Secondly, in terms of energy efficiency detonation of fuel is more efficient than deflagration [4]. In [1] several options of producing USS are considered. The first option implies that USS is obtained by compression and heating of a detonable premixed fuel gas–oxidizer–steam mixture in propagating DWs. In the second option, USS is obtained through compression and heating of steam by propagating SWs generated by detonation of a fuel gas–oxidizer mixture. In both options, USS is additionally obtained as a product of detonation of fuel gas. The walls and internal elements of USS guns are heated to low temperature due to periodic filling of cool gas mixture, i.e., a USS gun can be made of conventional construction materials.

To get an insight on the parameters and composition of detonation products Figure 1 shows the results of thermodynamic calculations for H_2O -diluted (40%vol.) stoichiometric oxygen mixtures of syngas with the H_2/CO ratios of 1 (Figure 1a) and 2 (Figure 1b), as well as CH_4 (Figure 1c), and C_3H_8 (Figure 1d). The curves show the equilibrium product gas composition at different temperatures and atmospheric pressure (P – T problem). Closed circles in the plots correspond to the temperature and composition of detonation products in the Chapman-Jouguet (CJ) point, while open circles correspond to the temperature and composition of detonation products after their isentropic expansion to 1 bar. As seen, the expanded detonation products of syngas have a temperature of 2300 – 2400°C and contain 70–80% H_2O , 15–20% CO_2 , up to 7% CO , 1–2% H_2 , and trace amounts of other species, including O_2 . The expanded detonation products of CH_4 and C_3H_8 have a temperature of 2500 – 2600°C and contain 60–70% H_2O , 15–20% CO_2 , 4–7% CO , 2–3% H_2 , 2–3% O_2 and trace amounts of other species.

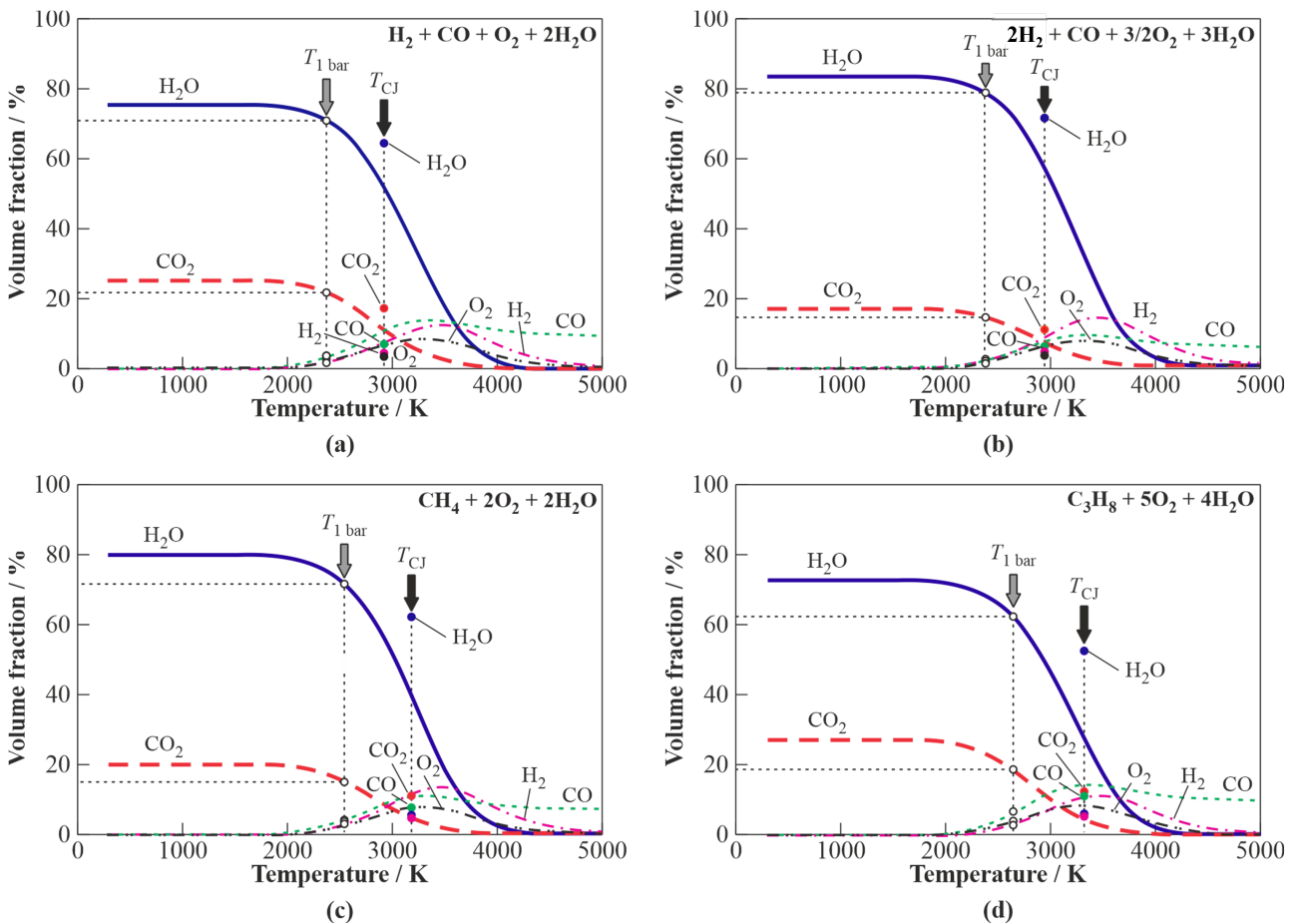


Figure 1. Equilibrium composition of detonation products for the steam-diluted (40%) stoichiometric fuel gas–O₂–steam mixtures. Closed circles correspond to temperature and composition at the CJ point; open circles correspond to temperature and composition of detonation products isentropically expanded to 1 bar; (a) syngas (H₂/CO = 1); (b) syngas (H₂/CO = 2); (c) CH₄; and (d) C₃H₈.

Thus, the syngas with the H₂/CO ratios of 1 and 2 could be considered as fuel gas for obtaining a gasifying agent for organic feedstocks with the H₂O/CO₂ ratio of 4–5. As for CH₄ and C₃H₈, these gases could be considered as good starting fuels for gasifiers operating on the USS obtained by gaseous detonations. The literature contains only few publications on the effect of H₂O on the properties of gaseous detonations. The latter deal mainly with H₂–O₂ or H₂–air mixtures as well as with CO–O₂ or CO–air mixtures and H₂/CO blends and are mostly related to the explosion safety of nuclear power plants rather than to the production of USS.

5.2. USS Detonation Guns

The invention [4] relates to methods and devices for producing USS for use in various technological installations including those for processing and disposal of biomass, SSW, MSW and other wastes using O₂-free technologies. Figure 2 shows a schematic of the first version of the USS detonation gun. The main element of the device is a pulse-detonation tube (PDT) referred to as the pulsed USS gun. The inlet of the gun is connected with a steam manifold equipped with a valve. The gun and steam manifold are placed in the steam supply tank with a feed water level sensor and a temperature sensor. The device also includes a spark ignition, oxidizer and fuel supply, and control systems. The gun and the supply lines of the oxidizer and fuel are immersed in the feed water, and the steam manifold with a valve located in the upper part of the supply tank, which is filled with steam.

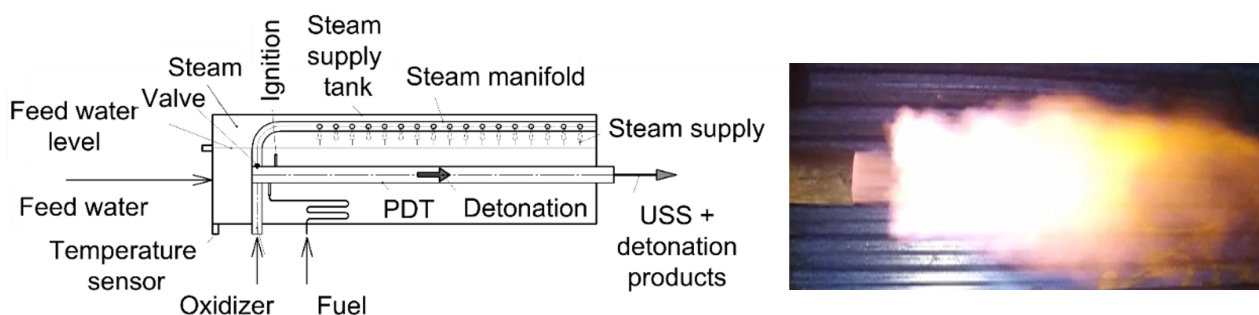


Figure 2. Pulsed detonation steam superheater (left) and its pulsed USS exhaust plume (right).

Figure 3 shows a schematic of the second version of the device. In contrast to the first version, the main element of the device is a continuous-detonation combustor referred to as the continuous USS gun equipped with a forced cooling system. All other systems are the same as in Figure 2. Note that the USS is issued from the gun at the velocity over 1 km/s and temperature above 2000 °C, as seen from the images of the exhaust plumes in Figures 2 and 3. Moreover, the issuing USS possesses the density, which is a factor of ~2 higher than the initial density of the low-temperature saturated steam. The ignition energy of pulsed and continuous detonations is negligible as compared to plasma torches.

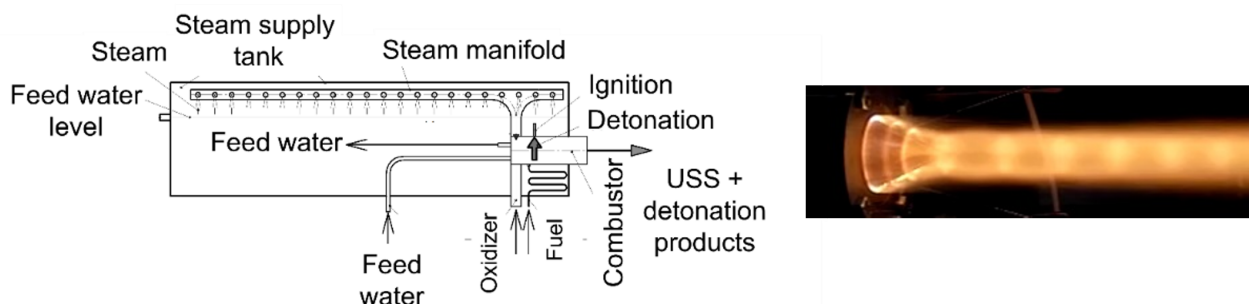


Figure 3. Continuous detonation steam superheater (left) and its continuous USS exhaust plume (right).

The proposed devices operate as follows. The device of Figure 2 operates cyclically at a frequency set by the control system. The operation cycle begins with filling the gun with a detonable mixture diluted by steam. The oxidant and fuel are fed into the gun through the corresponding supply lines. Steam is fed into the gun through a steam manifold with a valve from the upper part of the steam supply tank. The control system can provide several modes of device operation. In mode I, the oxidizer, fuel, and steam are fed into the gun simultaneously until it is completely or partly filled. In mode II, only steam is initially supplied to the gun, and then, in addition to steam, oxidizer and fuel are simultaneously supplied until the gun is filled with steam, and partly filled with the detonable mixture. In mode III, only steam is first supplied to the gun, and

then the supply of steam is stopped and at the same time only the oxidizer and fuel begin to be supplied, and the filling of the gun continues until it is filled with such a stratified mixture in whole or in part. Upon reaching a given degree of gun fill, the supply of oxidizer and fuel stops. The filling of the gun with a combustible mixture ends when, at the command of the control system, the detonation process is initiated in the gun using the ignition system. The detonation process is carried out in accordance with the principle set forth in [4]. When the operation mode I is implemented, the USS is obtained because of its compression in a DW traveling through the fuel–oxidizer–steam mixture. When the operation modes II and III are realized, the USS is mainly obtained because of steam compression in a strong traveling SW. In all considered operation modes of the device, the resulting mixture of USS with an admixture of detonation products, e.g., CO_2 , is sent to a gasifier through the gun outlet section until the control system gives a signal to start the next operation cycle with filling the gun by a fresh portion of the WF.

In the device of Figure 3 the continuous-detonation operation process is supported in accordance with the principle set forth in [5]. Here, the USS is obtained because of its compression in a DW continuously rotating in the USS gun, filled with the fuel–oxidizer–steam mixture. Detonation of the fuel–oxidizer mixture produces an additional amount of USS, if fuel contains hydrogen. The resulting mixture of USS with an admixture of detonation products, e.g., CO_2 , is continuously injected in a gasifier through the gun outlet.

Figure 4 shows the 3D model and photographs of the pulsed USS detonation gun. For its operation, C_3H_8 and CH_4 were used as starting fuels, and O_2 as oxidizer.

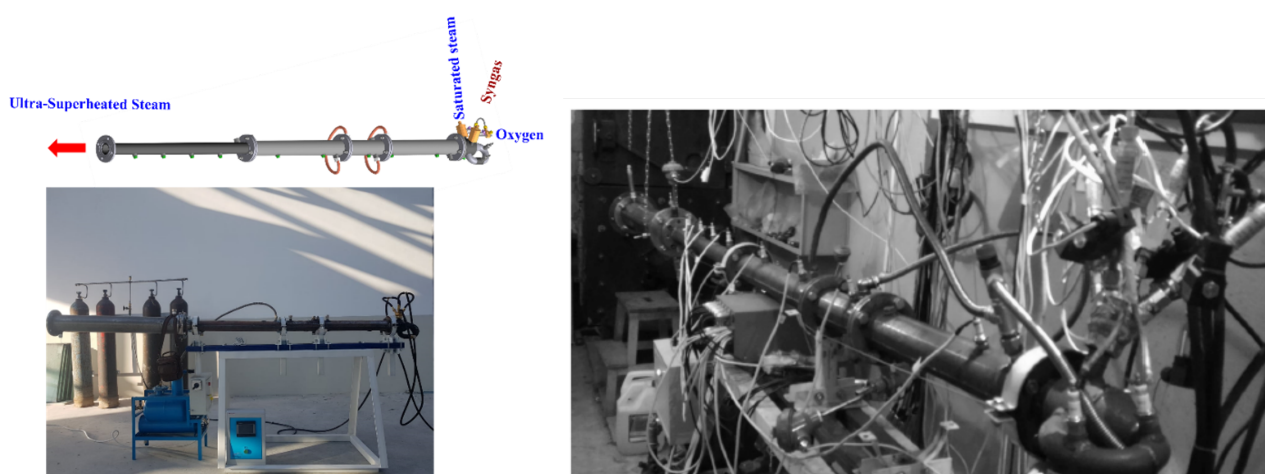


Figure 4. 3D model and photograph of the 50-mm i.d. USS gun (**left**) and USS gun at test firing (**right**).

The gun was a round tube 2.7 m long and 50 mm in diameter with one closed and one open end. The closed end was equipped with the ports for fuel gas and O_2 supply. Downstream the ports, two standard spark plugs with the ignition energy of 100 mJ were mounted. A Shchelkin spiral made of steel wire with a diameter of 6 mm, pitch of 50 mm, and length of 1.5 m was inserted into the gun to ensure reliable detonation initiation. The gun was equipped with water cooling jacket. An electrically heated water boiler of adjustable capacity was a source of low-temperature steam for the USS gun. The boiler delivered steam with a temperature of 102 °C to the gun through a thermally insulated line under a small overpressure of ~8 kPa downstream the spark plugs. The gas feed system was set up to ensure complete fill of the gun with the mixture. In these conditions, DDT occurred at a short run-up distance from the ignition source in a wide range of compositions. The fuel-to-oxygen ER was varied from 0.14 to 1.77 in $\text{C}_3\text{H}_8\text{--O}_2\text{--H}_2\text{O}$ mixtures and from 0.3 to 1.84 in $\text{CH}_4\text{--O}_2\text{--H}_2\text{O}$ mixtures. The volume fraction of H_2O in the mixtures, X , was varied from 0 to 0.7. A set of eight ionization probes (IPs) was used to measure the velocities of reaction fronts including DWs. The velocity of reaction front was determined as the quotient of dividing the distance between the IPs by the time required for the reaction front to pass this distance.

Figure 5 shows the dependences of temperature and composition of isentropically expanded detonation products on steam volume fraction X in the stoichiometric $\text{C}_3\text{H}_8\text{--O}_2\text{--H}_2\text{O}$ (Figure 5a) and $\text{CH}_4\text{--O}_2\text{--H}_2\text{O}$ (Figure 5b) mixtures. The shaded areas show the conditions in which DWs were registered experimentally. The temperature of expanded detonation products is seen to exceed 2000 and 2200 °C, respectively. The detonation products contain mainly USS (80 and 75%vol.) and CO_2 (18 and 15%vol.), respectively. These findings correspond well with Figure 1c,d.

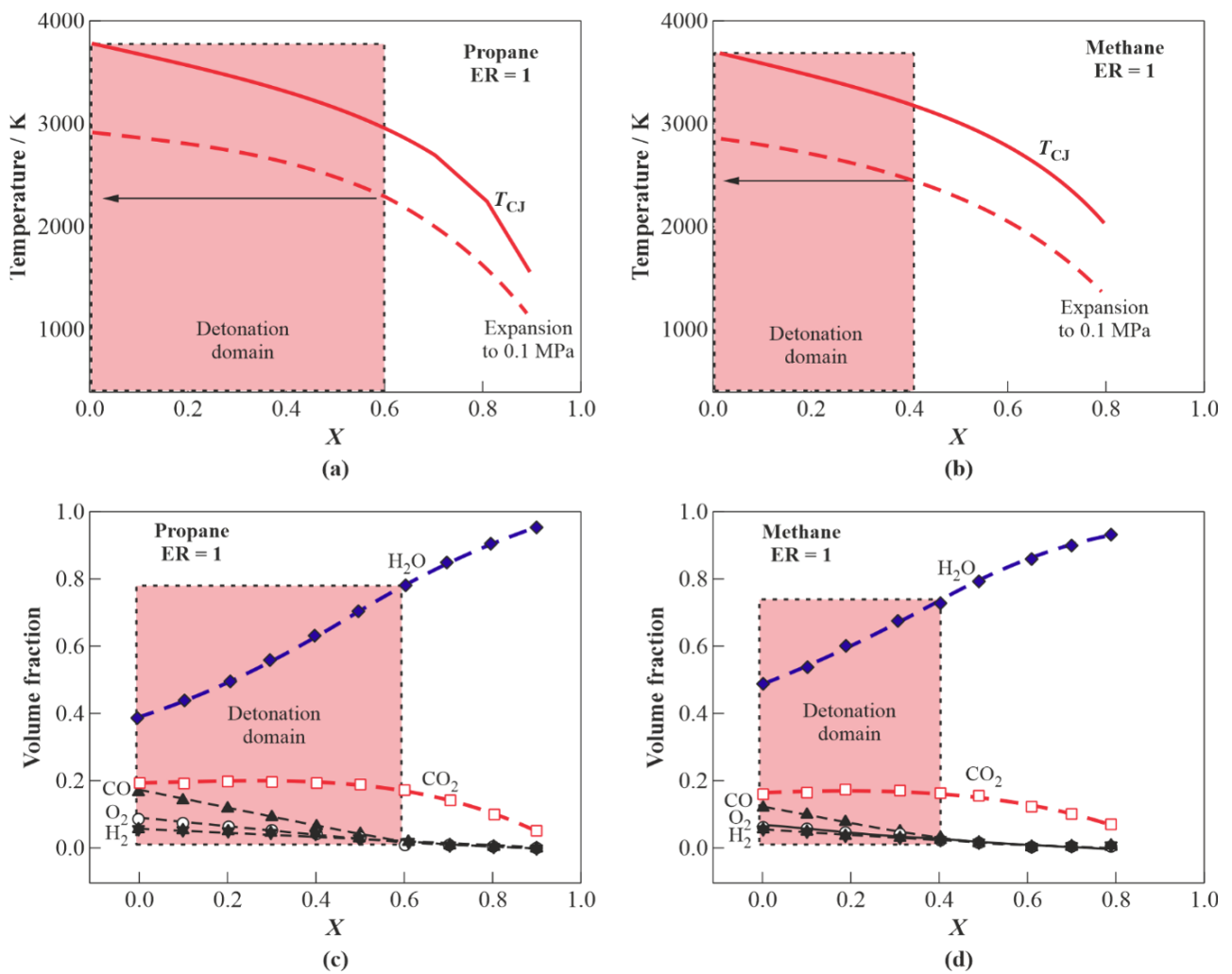


Figure 5. Parameters of detonation products of stoichiometric mixtures $C_3H_8-O_2-H_2O$ and $CH_4-O_2-H_2O$ depending on H_2O volume fraction (X) after isentropic expansion to atmosphere: (a,b) temperature, (c,d) composition. Conditions in which detonation is registered experimentally are indicated by shaded areas.

In general, results show that cyclic detonations of ternary $C_3H_8-O_2-H_2O$ and $CH_4-O_2-H_2O$ mixtures allow producing USS with temperatures above 2000 °C at 1 bar. The maximum steam dilution in the mixtures can be as large as 60% for $C_3H_8-O_2-H_2O$ and 40% for $CH_4-O_2-H_2O$ mixtures. The maximum content of USS in the expanded detonation products can attain 80%vol. for $C_3H_8-O_2-H_2O$ and 75%vol. for $CH_4-O_2-H_2O$ mixtures with the rest represented mostly by CO_2 . It can be expected that a USS gun with a larger diameter of detonation tube will exhibit wider detonability limits in terms of the highest possible steam dilution of the initial mixture. This goes from the known dependence of detonability limits on tube diameter: the larger the diameter, the wider the concentration limits. Therefore, the amount of steam in USS guns with larger tubes can be larger. The measured temperature of gun walls in the tests with low operation frequency (below 1 Hz) was below 130 °C due to periodic filling of the USS gun with the cold gas mixture. The operation frequency was readily increased to 5–6 Hz by detechning the flow rates of mixture components.

Processing of organic wastes by such USS is accompanied by their pyrolysis, thermal destruction, and complete gasification. As a result, a high-quality syngas is generated, which can then be partly (estimated as 20% of total syngas yield) used as a fuel gas for the USS gun and for heat/electricity production and/or other downstream applications.

5.3. Gasification Plant 1

The objectives of invention [2] were to create a method and device for steam gasification of CCMs using high-speed USS jets obtained by shock or detonation compression of steam in a cyclic operation process with a pulsed USS detonation gun. Figure 6 shows a schematic of the USS gasifier. The main units of the device are a vortex reactor equipped with a pulsed USS gun and a CCM feeder. The USS gun is installed in the lower part of the vortex reactor and is oriented tangentially, as shown in the cross-section A–A. Inside the vortex reactor, lower and upper screens are provided for bordering the gasification region of CCM particles. The CCM feeder for supplying feedstock particles is made in the form of a metering device that provides the supply of feedstock particles to the USS gun upstream the inlet port of the vortex reactor. The proposed device operates as follows.

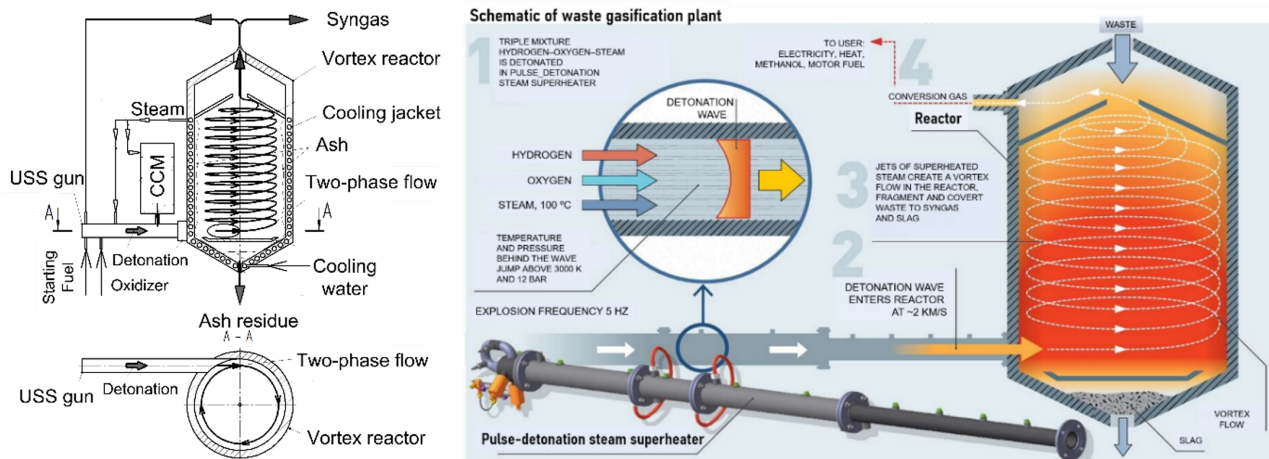


Figure 6. Waste gasification plant: (a) schematic, (b) operation principle.

The two-phase USS–CCM mixture is supplied to the vortex reactor cyclically with the frequency of USS gun operation, whereas production of syngas in the vortex reactor occurs in a continuous mode. The operation of the device includes three stages. Stage I is the start-up stage, at which the USS gun operates on the starting fuel. Stage II is the stage of reaching the operation mode, in which the USS gun gradually switches from the starting fuel to syngas produced in a vortex reactor. Finally, stage III is the working stage, in which the USS gun operates on a part of syngas produced in a vortex reactor, while the remaining part of syngas goes to the downstream equipment.

Feedstock particles are fed from the CCM feeder into a high-speed USS jet. In the USS jet, aerodynamic fragmentation of particle agglomerates and initial thermochemical transformation of a two-phase mixture occur. The two-phase mixture is directed tangentially into a vortex reactor, where, under conditions of a strongly swirling flow, feedstock particles are gasified to produce syngas. The resulting syngas is removed from the gasification zone to feed the USS gun and to go to downstream equipment. The bottom ash formed during feedstock gasification is fed to the bottom ash removal system. To ensure oxygen-free operation, the reactor operates at a slightly elevated pressure with the lowest overpressure on the level of 0.1–0.2 bar. Preliminary CFD calculations showed that the USS temperature in the central parts of the reactor exceeds 2000 °C, whereas the peripheral (near-wall) temperatures depend on the thermal boundary conditions and can attain the level of cooling water temperature. Nevertheless, due to the complex structure of the vortical high-speed flow in the reactor, resembling the flow structure in a reciprocating piston engine, the RT of feedstock particles in the high-temperature zone is sufficient for complete conversion.

Invention [2] is implemented in the lab-scale setup shown in Figure 7. It is based on the pulsed USS detonation gun of Figure 4 and uses natural gas (96% CH₄) as a starting fuel and O₂ as oxidizer. The vortex reactor is made of a standard 40-L gas cylinder. The feedstocks used are the coffee residue, WS, lignin, and water–coal emulsion (WCE). The WCE contained 60%wt. bituminous coal and 40%wt. water. The average size of coal particles in a WCE was 10–15 μm. The WCE was fed to the USS gun as a spray produced by a centrifugal injector with a mean droplet size of about 0.5 mm. The mass flow rate of feedstock in the setup attained 11 kg/h. The maximum wall temperature of the vortex reactor was 700 °C. The overpressure in the reactor was 0.2–0.5 bar. The S/F ratios were 0–3.

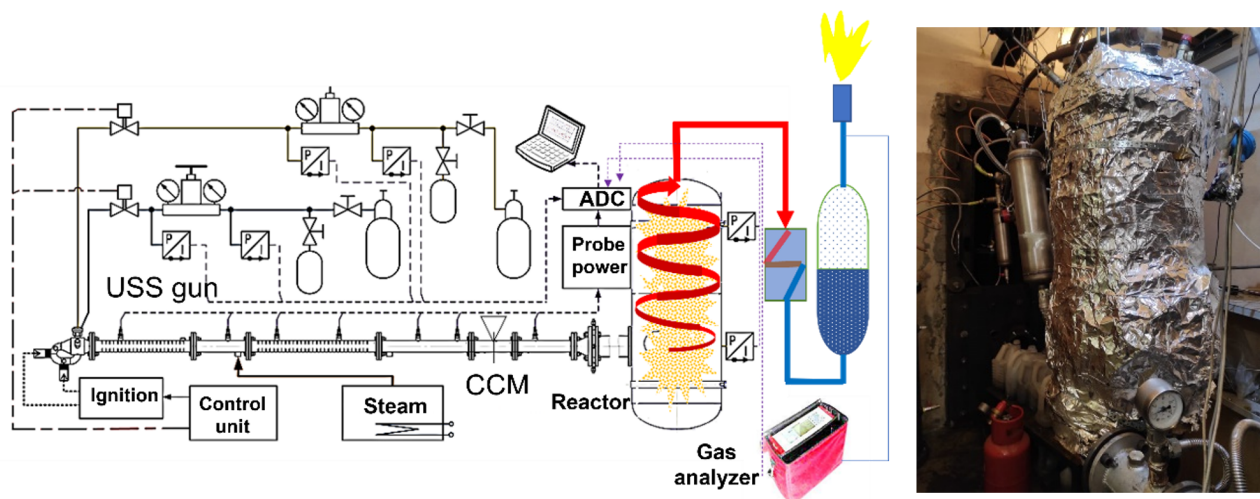


Figure 7. Laboratory scale gasification reactor: (a) schematic, (b) photograph.

The preliminary tests indicated that steam gasification of the feedstocks using the pulsed USS gun was comparable with plasma gasification in terms of syngas composition and conversion efficiency. Syngas composition depended on the feedstock. Thus, syngas produced by WS gasification tended to contain H_2 and CO up to 40–45%vol. daf in proportion about 1:1 with small amounts of CO_2 and CH_4 . The other important finding was that feedstock particles entering the USS gun were subject to extremely high dynamic and thermal stresses, which facilitated chemical transformations even before they entered the vortex reactor. Thus, upon feeding the WCE into the gun, coal particles radiated intensely at the gun exit despite the emulsion contained 40%wt. H_2O . A preliminary gas analysis of the WCE gasification products showed that they mainly contained H_2 and CO in a ratio close to 2:1. The degree of coal conversion depended on the USS gun operation frequency and reached 90% at a frequency of 5 Hz.

5.4. Gasification Plant 2

Invention [3] relates to method and device for neutralizing fly ash generated during incineration of MSW. Chemical compounds (dioxins, furans, etc.) as well as vapors of heavy metals (mainly Pb, Cd, Zn, Cu, Cr) formed during MSW incineration condense on fly ash particles in the economizer part of boilers with decreasing flue gas temperature. Fly ash particles concentrate up to 78% Cd, 43% Pb, and 38% Zn entering a furnace with MSW. The development of methods and devices reducing the toxicity of fly ash is an important task. One of the most effective ways to reduce the toxicity of fly ash in MSW incinerators is its neutralization by treatment with USS, which provides gasification and thermal destruction of toxic chemicals in the absence of O_2 , as well as the conversion of heavy metals into nonhazardous oxides and salts.

Figure 8 shows a schematic of the device [3]. The device includes a vortex reactor, a pulsed USS detonation gun split into two branch tubes, a feeder of toxic fly ash, an outlet for removing neutralized fly ash, and reactor cooling and control systems. The device operates as follows. Toxic fly ash in the form of small smoke particles is first separated from flue gases using cyclones and then supplied continuously or cyclically by the ash feeder to the branch tubes. The pulsed USS gun periodically generates supersonic jets of USS supplied through the branch tubes into the vortex reactor. The mass flow rate of toxic fly ash provided by the feeder and the frequency of issuing USS jets must be such as to ensure the injection of the supplied toxic fly ash into the reactor during the time between two successive detonation shots. Toxic fly ash under the action of USS jets enters the vortex reactor and is drawn into the vortex motion formed in the reactor due to the interaction of counter USS jets coming from two opposite branch tubes. The vortex motion in the reactor ensures the formation of stable high-temperature zones in the central region far from the reactor walls, while the wall temperature remains low, but above the steam condensation temperature, which is provided by the reactor cooling system. The stability of the high-temperature zones is maintained by the periodic injection of USS supersonic jets.

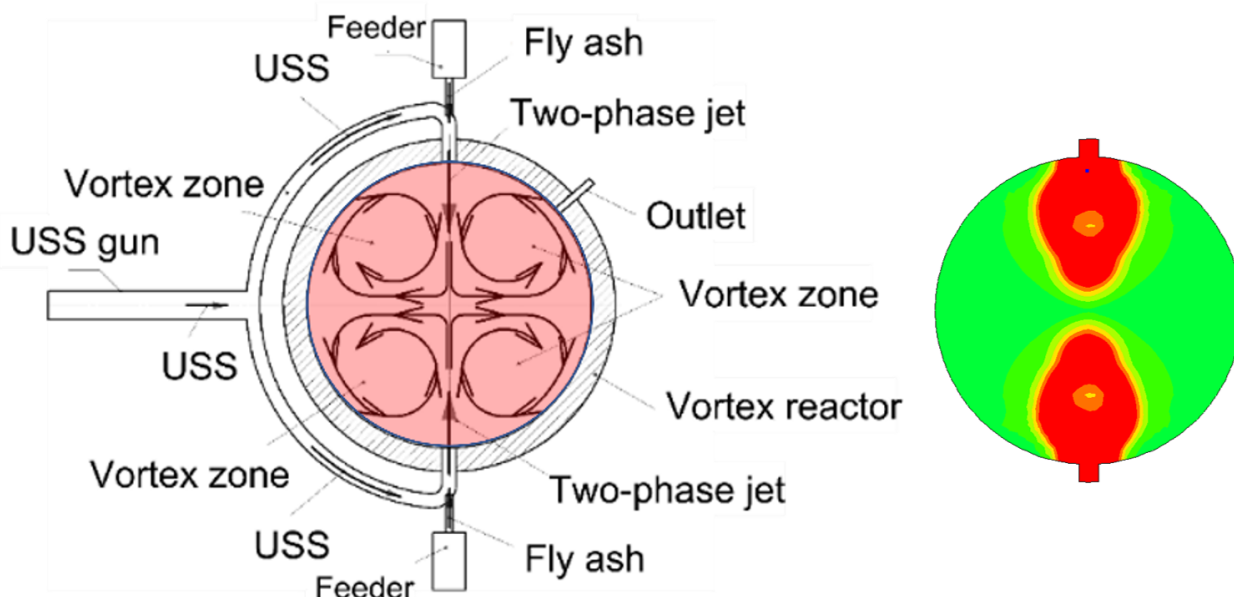


Figure 8. Schematic of fly ash detoxification reactor (left) and injection of USS supersonic jets (right).

Particles of toxic fly ash, involved in the vortex movement, circulate in the reactor, periodically entering the high-temperature zones, where they are rendered harmless under the action of USS in the absence of O_2 . Complex organic compounds adsorbed in fly ash, including dioxins, furans, etc. are thermally decomposed, gasified, and converted into the syngas containing simplest acids HCl, H_2S , etc., while inorganic compounds are converted into the simplest oxides and salts. Periodic intense SWs accompanying the injection of USS supersonic jets prevent the agglomeration of fly ash

particles. The cycle continues until a preset pressure rise in the reactor, e.g., by 30%. Thereafter a mixture of steam with the gasification products of the fly ash and detoxified fly ash itself are taken from the reactor for subsequent condensation of steam to obtain condensed products (acids, oxides and salts) and further disposal of neutralized fly ash.

3D CFD calculations demonstrating the method and device were performed in [3]. The calculation considered a spherical flow-type reactor with a volume of 110 L with two sections for supplying pulsed counter jets of USS (with a temperature above 2000 °C). Toxic fly ash was modeled by a set of spherical particles of constant diameter (0.1 or 1 mm), initially located in the region near the outlet of each of two branch tubes of the USS gun. The frequency of pulsed USS jets was set at 5 Hz. The following variables depending on time (t) were specified at the reactor inlets: the mass flow rate $m_{g,in}(t)$ and temperature $T_{g,in}(t)$ of the detonation products of the stoichiometric ternary mixture 60% H_2 + 30% O_2 + 10% H_2O , and also the mass flow rate $m_{p,in}(t)$ of particles. The dependences $m_{g,in}(t)$ and $T_{g,in}(t)$ were obtained by a preliminary 3D calculation for a PDT of length $L = 2$ m attached to the reactor. The detonation velocity of such a mixture was $D \approx 2800$ m/s. Calculations indicated that, once the DWs entered the reactor, most of the particles (97%) were surrounded by USS at 1700–2100 K. In 0.6 ms after the detonation shot, about 93% of particles were in contact with the USS flow at 1900–3500 K, and in ~100 ms after the shot, nearly all particles were in the USS flow with temperatures 1900–2300 K. Immediately before the next shot, only 3% of the particles were contacted by the USS at 1400–1500 K. The maximum calculated RT of particles in the reactor was 10–15 s, and their median mean RT was about 2 s. Estimates showed that more than 80% of the particles were contacted by USS with a temperature above 2000 K for at least 1 s. Under these conditions, the particles could be completely gasified. For example, the evaporation times of droplets of rapeseed and sunflower oil methyl ester ($C_{18}H_{34}O_2$) with diameters of $d_p = 0.1$ and 1 mm even at 1000 K were less than 10 ms and 1 s, respectively. It is easy to show, that at temperatures above 2000 K the rates of gas-phase oxidation of organic substances and soot by H_2O and CO_2 are extremely high; therefore, the rate of the overall gasification reaction is limited by the rate of particle thermal destruction or evaporation. Finally, Figure 9 shows the USS gasification plant designed based on the concept of [3]. The plant is designed for the mass flow rate of MSW/biomass up to 100 kg/h.



Figure 9. (a) Gasification plant based on pulsed USS gun and (b) thermal radiation of the uncooled USS gun during operation.

6. Conclusions

A selective literature review on atmospheric-pressure, combustion-free, allothermal, noncatalytic, direct H_2O/CO_2 gasification of organic feedstocks like biomass, SSW, MSW, etc. is presented, which demonstrates the pros and cons of the various approaches and provides future perspectives. In the review, three groups of gasification technologies are considered, namely low-temperature (500–1000 °C), high-temperature (above 1200 °C), and promising high-temperature detonation technology. The most important findings are given below:

- The existing low-temperature gasification technologies are mainly based on kinetically controlled feedstock conversion when gasification chemistry is slower than transport processes. Therefore, the **low-temperature gasification technologies are characterized by relatively low-quality syngas, low gasification efficiencies, difficult in-situ gas quality control, and low yields of syngas.**
- The existing **high-temperature plasma and solar gasification technologies provide high-quality syngas, gasification efficiencies up to 100%, easy in-situ gas quality control, and high yields of syngas.** However, despite these advantages, they have certain drawbacks which limit their widespread applications. Firstly, industrial scale arc and MW plasma technologies require enormous electric power, and the efficiency of plasma guns is at most 70–80%, whereas solar gasification depends on time of day and weather conditions. Secondly, in view that most of feedstock in plasma guns is gasified at relatively low temperatures (1300–2000 °C), the gas–plasma transition appears

an unnecessary energy-consuming stage. Thirdly, in addition to water-cooling systems they require special construction materials and refractory liners for gasifier walls.

- ***As a more efficient alternative to high-temperature plasma guns, a novel environmentally friendly USS detonation gun technology for gasification of organic wastes is proposed and demonstrated.*** Such a technology has several attractive features. Firstly, in a USS gun, high gasification temperatures (above 2000 °C) are attained by detonating a part of produced syngas (about 20%), while the energy consumption for detonation ignition is negligible. Secondly, the corresponding gasification plant can be made from conventional structural materials. Thirdly, such a plant can be readily scaled-up from small to large scale by applying multiple USS guns of the same power or guns of high power, keeping in mind that detonation phenomenon can be readily scaled up. Moreover, such a plant can be implemented as a mobile version, e.g., in the form of a trailer to a car or onboard ship. Nevertheless, for further progress in this direction there is a need in a thorough economic analysis of organic waste H₂O/CO₂ gasification using the USS detonation gun technology.

References

1. Frolov, S.M.; Smetanyuk, V.A.; Avdeev, K.A.; Nabatnikov, S.A. Method for Obtaining Highly Overheated Steam and Detonation Steam Generator Device (Options). Patent of Russian Federation No. 2686138, 24 April 2019. Priority dated 26 February 2018.
2. Frolov, S.M.; Smetanyuk, V.A.; Nabatnikov, S.A. Method of Gasification of Coal in a Highly Overheated Water Vapor and Device for Its Implementation. Patent of Russian Federation No. 2683751, 1 April 2019. Priority dated 24 May 2018 (WO2019/226074 A1 dated 28 November 2019).
3. Frolov, S.M.; Nabatnikov, S.A.; Diesperov, K.V.; Achildiev, E.R. Method for Decontamination of a Fly Ash Formed during Burning of Wastes and a Device for Its Implementation. Patent of Russian Federation No. 2739241, 22 December 2020, priority dated 11 June 2020.
4. Roy, G.D.; Frolov, S.M.; Borisov, A.A.; Netzer, D.W. Pulse detonation propulsion: Challenges, current status, and future perspective. *Prog. Energ. Combust. Sci.* 2004, 30, 545–672.
5. Bykovskii, F.A.; Zhdan, S.A. Continuous Spinning Detonation; Lavrentiev Institute of Hydrodynamics Publ.: Novosibirsk, Russia, 2013.
6. Lewis, F.M. Generation of an Ultra-Superheated Steam Composition and Gasification Therewith. U.S. Patent US20030233788A1, 2007.
7. Frolov, S.M. Organic Waste Gasification: A Selective Review. *Fuels* 2021, 2, 556-650. <https://doi.org/10.3390/fuels2040033>