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Effect of gasifying agents and calcium oxide on gasification of low-rank coal and wastes

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Abstract

The process of gasification is one of the promising technologies of clean combustible gas production from low-grade coals, such as lignite, coal mud and subbituminous LR coals, and from biomass and waste. However, depending on the type of gasification material, the following aspects require investigation and development: the selection of a gasification technology (including parameters and gasifying agents) and the removal of the components constituting a burden and contamination from the raw gas. This paper presents the results of research on the gasification of lignite and sludge with added refuse derived fuel and the gasification of both these substances with added calcium sorbents. Two gasifying agents, water vapour and carbon dioxide, were used in the experiments, which were carried out in a fixed bed reactor at the temperatures of 600, 700, 800, 900, and 1000 °C. The effects of process temperature, the calcium oxide addition and the gasifying agent composition and quantity on fuel conversion and product gas composition have been determined. Higher process temperatures in both atmosphere of gasification (H₂O and CO₂) cause an increase in the volume fraction of hydrogen and carbon monoxide in the resulting gas. The effect of the addition of calcium oxide (CaO) for carbon dioxide gasification of sewage sludge exhibits the positive effect. The increase in the volume of hydrogen and carbon monoxide in the syngas from gasification of sewage was observed. The gasifying agent has a different effect on the composition of the gas depending on the temperature. The gasification process in the atmosphere of water vapour starts faster than in the atmosphere of carbon dioxide and hydrogen formation is significantly higher.

Keywords: Gasification; RDF; Sewage sludge; Lignite; Calcium oxide

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1 Introduction

Gasification is considered to be a clean coal technology minimizing carbon dioxide (CO₂) emission into the atmosphere [1]. Its primary objective is to transform any solid fuel and organic substance into gas. It can be assumed that almost any carbon containing substance can be converted into gas suitable for further use. Gasification can be applied to the following substrates: hard coal, lignite, peat, mixtures of these fuels, biomasses, industrial waste containing organic substances of natural and artificial origin, and municipal waste [2].

Gasification is a complex chemical process consisting of the two main stages: pyrolysis (devolatilization) and char residue gasification. The proper chemical process of gasifying a moisture containing substance is preceded by moisture evaporation. However, at the high temperatures at which the pre-dried organic substance is gasified, evaporation proceeds violently and can occur almost in parallel with pyrolysis. It should be noted that both evaporation and pyrolysis have an effect on the reactivity of the char residue and so on its gasification. The gasification step limits the speed of the whole process. The first stage, i.e., pyrolysis, is based on the decomposition of relatively high-molecular-mass compounds of coal and biomass (e.g., the aromatic C=C ring functional group) in the temperature range of 300–500 °C [3]. Mainly compounds of noncondensing gases, but also condensed hydrocarbons (tar) are produced during the pyrolysis process. The final solid product of pyrolysis amounts to 55–70% of the initial weight of the carbon, depending mainly on the volatiles content in the fuel. In most available solid fuels the pyrolysis process takes place before the temperature typical of gasification reactions begins to predominate. Gasification proceeds at a slower rate than pyrolysis and greatly depends on the pore structure of the sample in the pyrolysis phase [4].

The rate of gasification depends on the gasifying agent, the pressure and the temperature, but also on the composition of the fuel. The resulting gas is combustible and its composition and calorific value largely depend on the gasifying medium. Gasification can be carried out under oxygen, air, steam or carbon dioxide [5]. The gas produced during air gasification has the lowest calorific value than the one obtained from oxygen or steam gasification. This is due to the high levels of nitrogen in the air. Gas with a higher calorific value can be obtained using oxygen as the gasifying agent, but this is economically unviable because the production of pure oxygen is very expensive [6]. The advantage of using steam is that there is an increased amount of hydrogen in the process. By using CO₂ for gasification we contribute to reducing its emissions into the atmosphere [4,11]. In the gasifier the coal particles are heated whereby the moisture contained in

the coal evaporates. The further heating of the particles leads to the emission of volatile gases. The quality of the produced gas depends on the characteristics of the fuel, the gasifier design and the amount of the agents introduced into the system. The quality of the gas is determined primarily by the quantity of light gases (such as hydrogen, methane, carbon monoxide and carbon dioxide) in the gas stream. The higher the content of volatiles in the fuel, the greater the amount of heat obtained from the gaseous products. The gaseous products can have a low, medium or high calorific value [7–9]. Gasification aimed at utilizing the energy of low-rank fuels and wastes, which contain harmful impurities (inter alia: sulphur, chlorine and ash), results in low-energy gas, but after purification the gas (alone or together with natural gas) is suitable for electricity production [2].

Calcium oxide (CaO) has been used in liquefaction residue (LR) coal and biomass gasification processes in order to improve the composition of the raw gas obtained from gasification [10,12–13]. CaO can act as a sorbent in CO₂ adsorption to form CaCO₃. Another way of affecting the composition of the raw gas consists in exploiting the catalytic effect of CaO in the tar cracking process [14–16]. However, CaO has been used as a catalyst to improve the composition of the product gas obtained from wastes gasification in relatively few studies [17–20].

In this study, gasification with calcium oxide as an additive was carried out in a fixed bed using lignite, a blend of sludge and refuse derived fuel (RDF), and steam and carbon dioxide as the gasifying agents with the aim of examining the effect of the calcium oxide addition and temperature on the raw gas composition and the rate of fuel conversion. The gasification tests were carried out at the temperatures of 600, 700, 800, 900, and 1000 °C.

This technique has a potential to become an interesting alternative to other innovative techniques developed for utilization of low rank coals, such as combustion in oxygen-enriched O₂/CO₂ atmospheres in a circulating fluidized bed boiler [21].

1.1 Chemical process of gasification

Gasification takes place under reducing conditions. The gasification process is complicated from the chemical point of view. The main reactions in this process are shown in Tab. 1. Gasification reactions (1) and (2) are endothermic reactions. Most of the energy is provided by exothermic oxidation reactions (5) and (9). The oxidation reactions can occur very quickly, fully utilizing the oxygen from the gasifier, whereby they proceed under reducing conditions. In reaction (6) vapour is converted into hydrogen. The production of methane (4) is an exothermic reaction. Approximately 70% of the product gas calorific value comes from carbon

monoxide and hydrogen. This value can be higher depending on the type of gasified fuel and process condition. Besides the above described reactions, there are more, controlling final gas composition. In the initial stage of gasification, as the temperature increases, moisture begins to evaporate and the weak chemical bonds disintegrate forming gases, tars, oils, hydrocarbons and phenols. These products usually react further to form hydrogen, carbon monoxide and carbon dioxide. After degassing the solid residue reacts with oxygen, water vapour, carbon dioxide and hydrogen [7].

Table 1: Basic reactions in gasification process [9].

Serial no.	Reactions		ΔH , kJ/mole	Eq. no.
A	Primary reactions			
R1	Water gas reaction	$C + H_2O \leftrightarrow CO + H_2$	117.9	(1)
R2	Boudouard reaction	$C + CO_2 \leftrightarrow 2CO$	160.0	(2)
R3	Partial oxidation	$C + 2H_2O \leftrightarrow CO_2 + 2 H_2$	75.8	(3)
R4	Hydro-gasification reaction	$C + 2H_2 \leftrightarrow CH_4$	-87.1	(4)
R5.	Incomplete combustion	$C + \frac{1}{2}O_2 \leftrightarrow CO$	-122.1	(5)
B	Secondary reactions			
R6	Conversion of carbon monoxide with steam	$CO + H_2O \leftrightarrow CO_2 + H_2$	-40.8	(6)
R7	Methanation	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$	-205.0	(7)
R8		$CO_2 + 4H_2 \leftrightarrow CH_4 + 2 H_2O$	-163.0	(8)
C	Combustion reactions			
R9	Coke combustion	$C + O_2 \rightarrow CO_2$	-397.7	(9)
R10	Combustion of carbon monoxide	$CO + \frac{1}{2}O_2 \rightarrow CO_2$	-282.1	(10)
R11	The combustion of hydrogen:	$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	-240.1	(11)

The rate of various gasification reactions depends on the local conditions, i.e., the pressure, the temperature, the gas composition and the heating rate which determines the final gas composition. This study examined in particular the effects of temperature on the gasification of lignite, a mixture of sludge and RDF, and each of these fuels with a calcium oxide addition.

1.2 Factors affecting gasification process

Depending on the process pressure and temperature and the gasifying agent, the gasification of a solid fuel usually takes place in two stages: 1) one-step degassing and 2) the pyrolysis and gasification of the coke residue wherein these effects may overlap or happen consecutively. The presence of oxygen, hydrogen, water vapour, carbon monoxide and other compounds in the atmosphere during the pyrolysis reaction can support or slow down many reactions with carbon. The amount and chemical composition of the products depend on the prevailing conditions, such as the temperature, the pressure, the heating rate and the residence time, but also the type and quality of the raw material are important. In order to obtain high-calorific gas it is necessary to increase the methane content in it. The reactions of methane production are exothermic, i.e., the enthalpy reaction is less than zero ($\Delta H < 0$) and the reaction rate is relatively slow. Therefore, in order to accelerate the reaction, it is essential to use a catalyst. The gas product of gasification usually contains significant amounts of carbon monoxide and hydrogen and minor amounts of other gases. The carbon monoxide and the hydrogen (at the ratio of 1:3) can be reacted in the presence of a catalyst to produce methane. Hydrogen-rich gas can be obtained using vapour. Significant amounts of methane are formed directly in the gasifier and the heat released by methane formation at a sufficiently high temperature is used in the vapour-carbon reaction to produce hydrogen, whereby less oxygen is used for heat production in vapour-carbon reactions. As a result, the heat loss during methanation at a lower temperature (the second stage of gasification) is lower, which leads to an improvement in the overall process efficiency. Catalysts are commonly used in the chemical industry in order to enhance the reaction rate. They can also be used in gasification. Thanks to the use of suitable catalysts, not only the temperature of the reactions can be reduced, but also the rate of gasification can be increased. In addition, the catalysts reduce the risk of tar formation [7].

2 Experimental part

2.1 Materials preparation and characterization

The samples used in this study were as follows:

- lignite bearing the Sieniawa symbol,
- Sieniawa lignite with an addition of calcium oxide,
- sludge (60%) with RDF (40%),

- sludge (60%) with RDF (40%) and calcium oxide.

The lignite and the waste – a blend of sludge (60% of the mass) and RDF (40% mass fraction) – are presented in Figs. 1a and 1b. The lignite particle size was in the range of 3.15–6.30 mm. The weight of the sample subjected to coal gasification was 15 g. The weight of the sludge sample with the RDF addition was also 15 g. The addition of calcium oxide in each sample replaced 5% of its initial weight. The results of proximate and ultimate analyses of the tested materials are presented in Tab. 2.

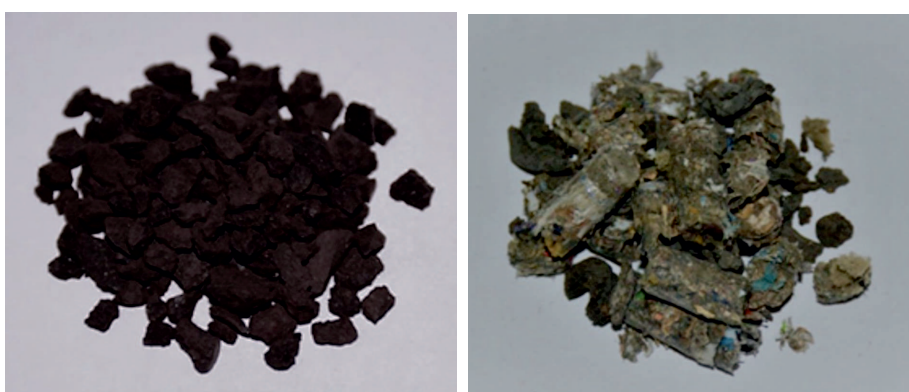


Figure 1: a) lignite sample, b) sewage sludge (60% by wt.) + RDF (40%) sample.

Table 2: Proximate and ultimate analysis of Sieniawa lignite.

Tested material	Moisture M^{ar} , %	Ash Ash^d , %	Volatiles VM^d , %	Heat of combustion HHV^{ar} ; $MJ\ kg^{-1}$	Calorific value LHV^{ar} ; $MJ\ kg^{-1}$	C^d , %	H^d , %	N^d , %	S^d , %	O^d , %
Sieniawa lignite	42.7	11.0	66.7	13.16	11.59	57.0	4.2	0.9	0.8	26.5
Blend of RDF and sludge	4.3	25.1	70	12						

ar – as received (operating conditions), d – dry composition

2.2 Experimental apparatus and procedure

The gasification of sludge + RDF and that of lignite with and without an addition of CaO bulk particles (held in a mesh basket 60 mm in height and 60 mm in diameter) were carried out in a lab-scale apparatus using electric heating. Figure 2 shows a schematic of this apparatus. For each of the samples the tests were carried out at five different temperatures. The tests would begin at the temperature of 600 °C and were continued up to 1000 °C. The tests were performed at every 100 °C. Two gasifying agents were used in the experiments: carbon dioxide and water vapour. During the gasification process the concentration of combustibles was continuously measured by a SERVOMEX gas analyser.

A three-stage tubular reactor was used in the experiment (Fig. 2). A fixed bed test sample in a mesh basket was placed in the reactor and subjected to gasification. The basket was suspended from a thermocouple attached to scales placed on a gantry. The position was fully fixed, thereby allowing the control of the process parameters, i.e., time, the temperature of each section and the amounts of the gasifying agent and the raw gas. All the signals from the sensors were continuously transmitted to a computer and recorded.

The experiment consisted of three stages. The first one lasted 5 minutes. The test sample was placed in the reactor's lower part (heating zone 3) where the temperature amounted to 20 °C ± 2 °C. Then the reactor chamber was closed and the gasification gas intake of 1 × 10⁻³ m³/s was turned on in order to flush the air atmosphere from the chamber. Subsequently, the sample was placed in the reactor's upper zone (heating zone 1), where the temperature was suitable for gasification, and kept there for 1800 s. The tests were carried out at the temperature ranging from 600 °C to 1000 °C. During the gasification process the derived gas flowed through a nozzle located in the reactor's upper part to the gas analyser. In the final step, the sample was cooled under nitrogen in the reactor's lower part at 20 °C ± 2 °C for 300 s without air to prevent the combustion of the sample. After the process the sample residues were weighed to determine the conversion of the fuel.

2.3 Results of experimental studies

The degree of conversion is the ratio of the substrate mass loss to the mass of the substrate at the beginning of the process

$$\alpha_i = \frac{m_{oi} - m_i}{m_{oi}}, \quad (1)$$

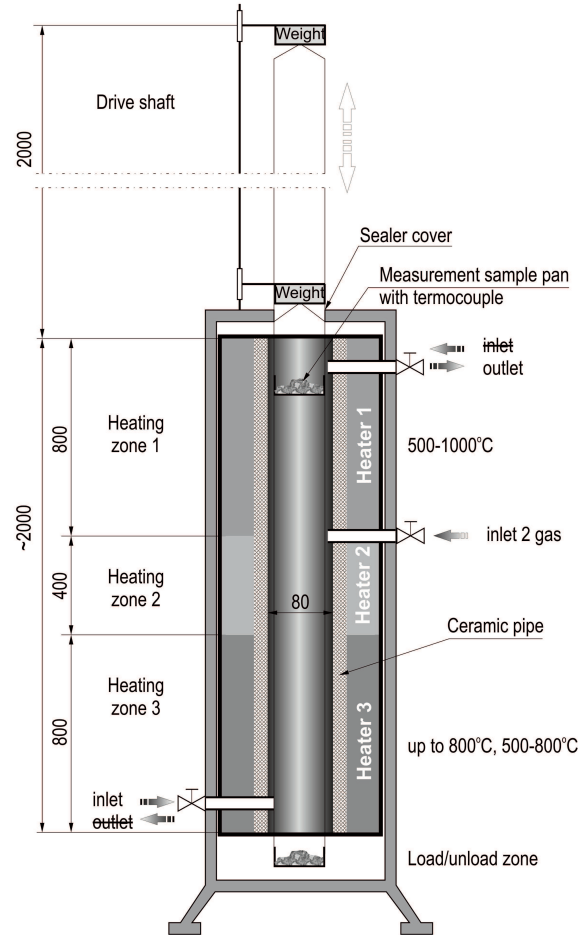


Figure 2: Testing site – three-tube reactor.

where α_i is the conversion stage, m_{oi} is the initial mass of the substrate, m_i is the final mass of the substrate.

Figures 3a–3e show the values of the conversion ratio for each of the process temperatures and gasifying agents. One can see that for both gasifying agent the degree of conversion of lignite significantly increased with temperature. The addition of CaO to Sieniawa lignite had practically no effect on the degree of conversion. For sludge with RDF the conversion rate increases with temperature, but the addition of CaO has a far greater influence on the increase in the conversion degree. The degree of conversion for Sieniawa gasification with water vapour is

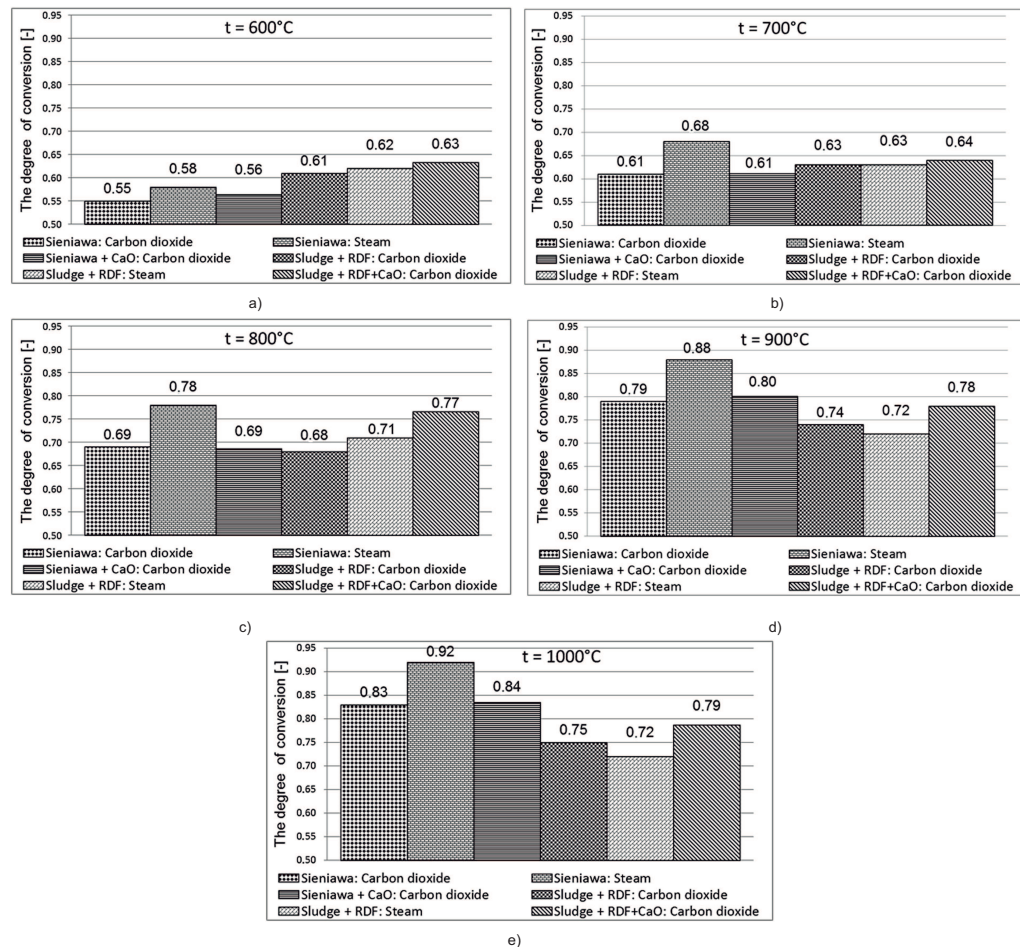


Figure 3: Values of conversion ratio for each of process temperatures and gasifying agents.

the highest for all the investigated cases. The effect of the gasification agent, i.e., CO_2 or steam, on the degree of conversion of sludge + RDF is negligible at all the tested temperatures. The conversion rate of the blend of sludge and RDF at the temperatures of 600 °C and 700 °C is the same for the two gasifying agents and the calcium oxide addition. The effect of the CaO addition is noticeable at higher temperatures, i.e., 800, 900, and 1000 °C (at which the highest conversion of the blend with CaO occurs).

Figure 4 shows the effect of temperature on some of the combustibles produced during gasification for the different fuels with additives. The average volume mix-

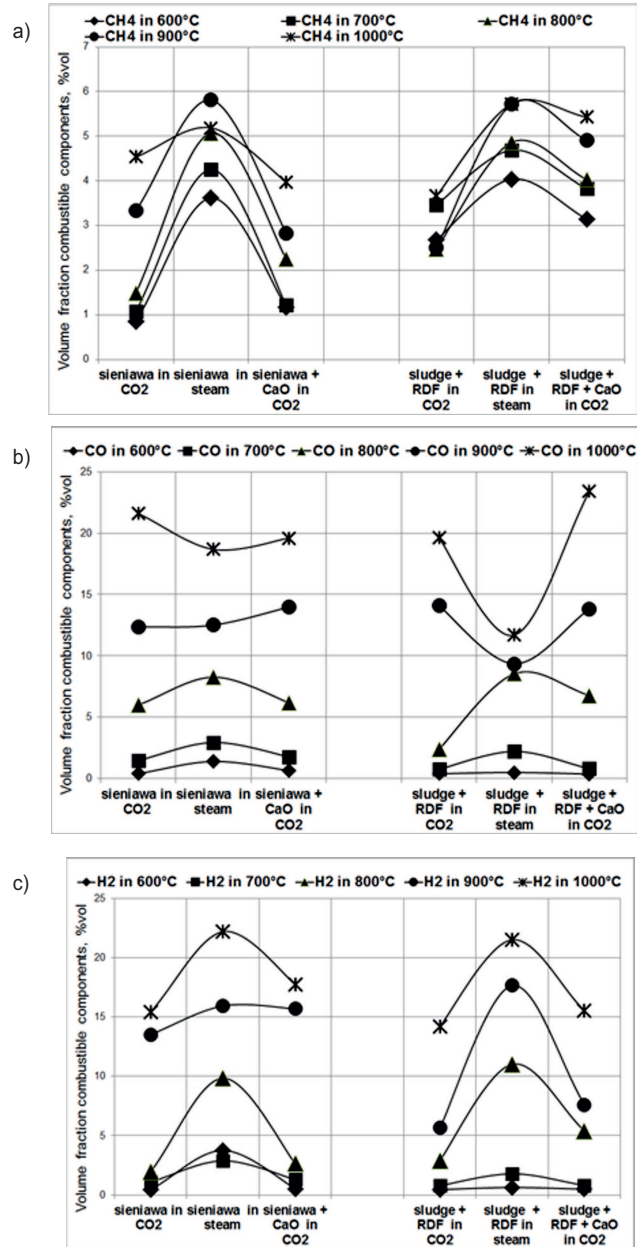


Figure 4: Average volume fraction of individual combustible components: a) methane, b) carbon monoxide, and c) hydrogen for each process temperature.

ture composition of the combustible products (Figs. 4a–4c) in the gasification process is calculated as the area under the curve (the graph generated by the exhaust gas analyser on the basis of the gasification process progression), related to the total surface area at a given time. Data collection time for each trial was the same, amounting to 900 s and beginning at the start of the first gasification reaction.

The gasification agent has a significant effect on the composition of the gas – especially higher concentrations of CH_4 and H_2 were observed for all the tested substances at each of the temperatures during steam gasification. The concentrations were higher at higher temperatures, as shown in Figs. 4a–4c. The concentration of CO behaves differently: a higher concentration than in the case of steam occurs for the CO_2 gasifying agent, but especially for the sludge-RDF blend. Moreover, the CaO has a visible effect on CO concentration for the sludge-RDF blend, greater at higher gasification temperatures.

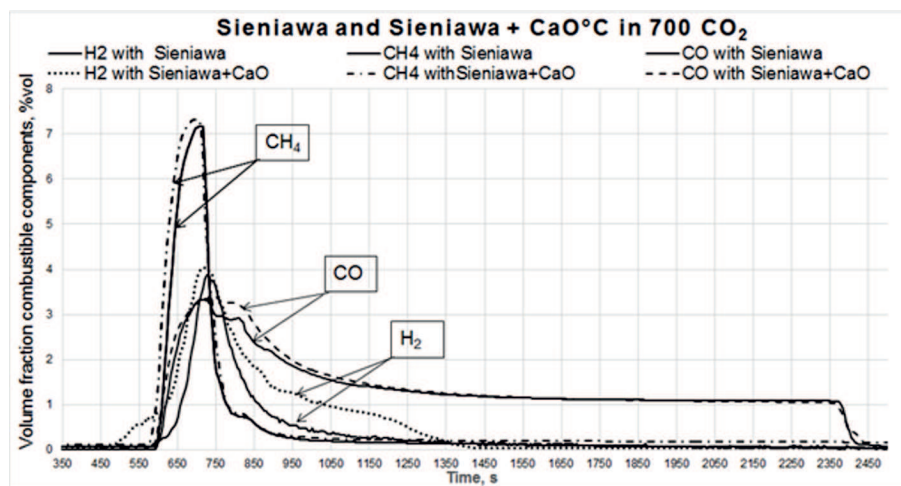


Figure 5: Comparison of volume fraction of combustible components in gas obtained during gasification of lignite and lignite with calcium oxide addition under carbon dioxide at temperature of $700\text{ }^{\circ}\text{C}$.

In the case of Sieniawa lignite steam gasification, the concentration of H_2 increases with gasification temperature, starting from $800\text{ }^{\circ}\text{C}$, while the maximum concentration of CH_4 occurs at $900\text{ }^{\circ}\text{C}$ and decreases at $1000\text{ }^{\circ}\text{C}$. In the case of the CO_2 gasification of Sieniawa lignite and the blend of sludge and RDF, CO is generated for the entire duration of the experiment. As regards the other combustible gases, their production usually ends in a very short time from the

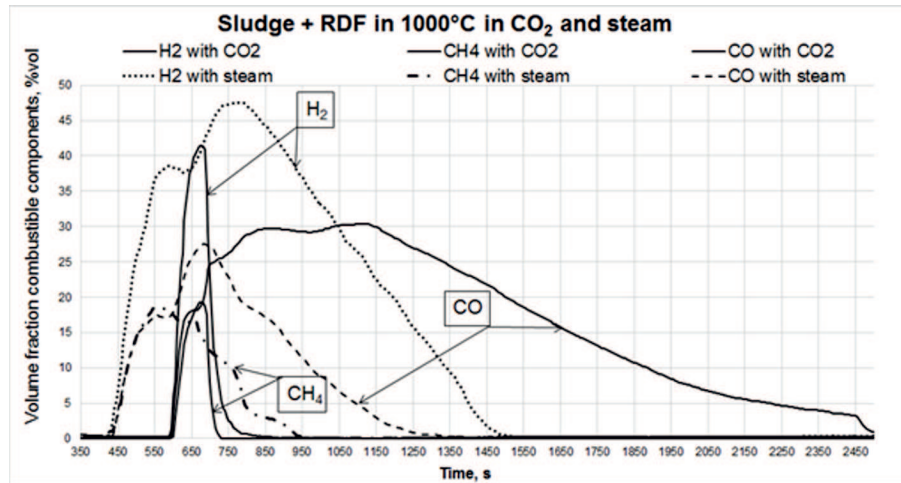


Figure 6: Comparison of volume fraction of combustible components in gas obtained during gasification of sewage sludge with RDF in atmosphere of carbon dioxide and water vapour at 1000 °C.

beginning of the process, as shown in Figs. 5 and 6. Figure 5 shows an example of the lignite gasification process in an atmosphere of CO_2 for lignite and lignite with the addition of calcium oxide. The effect of CaO on the CO_2 gasification of Sieniawa lignite is rather small and only slightly increases as the concentration of H_2 increases at the high temperatures of 900 and 1000 °C. Whereas in the case of the blend, this effect is positive – the concentrations of CH_4 , CO and H_2 increase at above 800 °C (Fig. 6).

In the case of the steam gasification of lignite and sewage sludge with RDF above 800–1000 °C, a significant increase in hydrogen, in comparison with the CO_2 atmosphere gasification, is observed (Figs. 4c and 6). This can be due to the parallel occurrence of the water gas reaction with the Boudouard reaction and subsequently the shift water reaction (R1, R2, and R6).

It should also be noted that steam gasification is characterized by a faster kinetic reaction (1) than carbon dioxide gasification (reaction 2). The faster course of reactions (1) and (2) as the temperature increases and the occurrence of reaction (6) result in a higher concentration of dihydrogen (H_2) in the syngas. There can also occur reactions reforming methane to dihydrogen (Tab. 1, reaction (7)).

3 Conclusion

The composition of the product gas obtained from the gasification of low-grade solid fuels depends on the gasification temperature and the gasifying agent. Two gasifying agents (CO_2 and steam) were used in the experiments. In all the tests, the volume fractions of the combustible components increased with rising process temperature, except the methane fraction which increased only up to 900°C and at 1000°C it was smaller in the case of steam gasification. The experimental results show that the composition of the syngas varies significantly depending on the gasifying agent, whereas the carbon conversion efficiencies vary only slightly. A comparison of the gasification of lignite in the atmosphere of respectively CO_2 and water vapour shows that at all the test temperatures the volume fractions of hydrogen and methane are larger (especially the hydrogen fraction) in the case of steam gasification. As regards the steam gasification of sewage sludge with RDF at 1000°C a significant increase in hydrogen concentration in comparison with the gasification under CO_2 (Fig. 6) is observed. This could be due to the co-occurrence of the water gas reaction and the Boudouard reaction, followed by the shift water reaction: (1), (2), and (6). The concentration of CO from lignite gasification strongly depends on temperature and the gasifying agent effect is weak. The effect of CaO on gas composition and fuel conversion was analysed for the CO_2 gasification of lignite and the blend of sewage and RDF. CaO was found to have a significant catalytic effect on the conversion of the blend of sludge and RDF. This effect was stronger than in the case of the CO_2 gasification without the calcium species at temperature of 1000°C . The concentrations of CO and CH_4 were higher in the case with CaO, which can be explained by the catalytic effect of calcium. The sorption of CO_2 (carbonation) by CaO is rather low at high temperatures, occurring mainly at temperatures below 700°C . The effect of CaO on the gasification of sludge + RDF is promising for the utilization of wastes, but requires more study using other calcium compounds. Also the calcium fraction required to achieve complete conversion to light gas at different temperatures needs to be determined.

The use of a refuse-derived fuel to produce fuel gas seems to be promising. In this paper special attention was given to alternative process technologies such as pyrolysis and gasification.

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