

TWO-STAGE PYROLYSIS OF HUNGARIAN BROWN COAL TO REDUCE HYDROCARBONS WITHIN SYTHESIS GAS

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During the research, the aim was the expansion of the potential of coal gasification and pyrolysis by the production of synthesis gas that can be used as a chemical raw material. Controlling the process of the pyrolysis experiment can be challenging. The temperature control of the process on its own is not enough to alter the composition of the produced synthesis gas, especially if all reactions take place in a single stage. The main objective of our research is to separate the low temperature and high temperature pyrolysis, and gain additional control over the whole process. Two separate reactors were connected through a still pipe that could allow gas flow between them, and they were inserted in two independent temperature controlled furnaces. Even though synthesis gas produced at low temperatures has high methane quantity, this perhaps can be thermally decomposed by forcing it through the high temperature zone of the experiment setup. The prospects of this setup have been investigated detailing the gasifier setup. The results of experiments will also be discussed in this article.

Keywords: coal gasification, synthesis gas utilisation, two stage gasification

INTRODUCTION

Nowadays, coal is one of the most significant energy sources. This fact is well demonstrated by the world's energy consumption expressed in primary energy sources. The amount of energy obtained from coal alone is almost equal to the energy obtained by all other energy sources combined (*Figure 1*) [1].

The most widespread method for coal-based energy production is combustion. Almost half of the coal used worldwide as primary energy source is used for electric power generation [2], and heat generation for industrial processes is in second place. In recent years, the conversion of coal to gaseous and liquid raw materials (chemical raw material or fuel) is also becoming increasingly important. Coal is a non-renewable fossil fuel, so the supplies are constantly decreasing. According to a 2015 study, the available reserves will last for another 114 years, considering the current rate of consumption [3]. However, the demand has been steadily increasing in last few decades. The utilisation of coal in power generation can be beneficial, having a relatively low cost compared to other fossil-based fuels like natural gas, but it also has many disadvantages. One of the major disadvantages is the SO₂ emission rates of coal combustion. Flue gas can be cleaned but the cost of these processes, especially considering the by-products and the ever-stricter emission regulations, can slowly outweigh the benefits, and the processes will become unsustainable.

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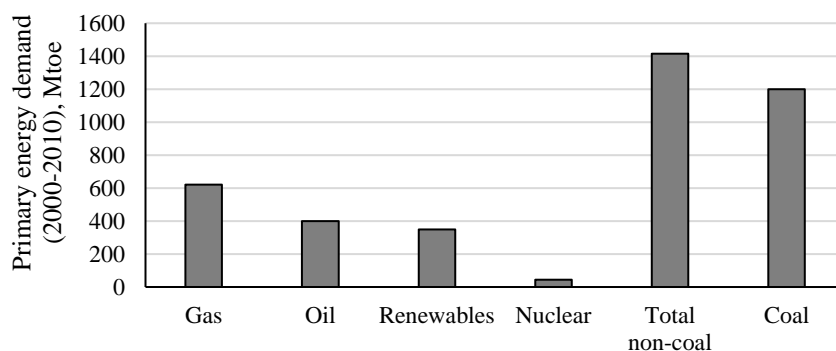


Figure 1

Incremental world primary energy demand by fuel (2000–2010) [1]

One solution could be reductive steam gasification, as the released sulphur in this case is in the form of hydrogen sulphide. This can be cleaned and converted to valuable by-products, as sulphur or sulphuric acid are in high demand by the chemical industry. This could be especially significant in the case of low rank coals that have 2–3% sulphur content within the raw material. The gasification of low rank coals is not as straightforward, in terms of producing synthesis gas with the required H_2/CO ratio for specific chemical industrial applications (Table 1 [4]).

Table 1

Synthesized final products and the required H_2/CO ratios for the synthesis [4]

Product	Basic chemical reactions	H_2/CO ratio
FT liquid fuels	$2n H_2 + n CO \rightarrow C_n H_{2n} + n H_2O$	2.0
	$(2n+1) H_2 + n CO \rightarrow C_n H_{2n+1} + n H_2O$	2.1
Methanol	$2 H_2 + CO \rightarrow CH_3OH$	2.0
Ethanol	$2 CO + 4 H_2 \rightarrow C_2H_5OH + H_2O$	2.0
Higher alcohols	$n CO + 2n H_2 \rightarrow C_n H_{2n+1}OH + (n-1) H_2O$	2.0
Dimethyl ether	$2 CO + 4 H_2 \rightarrow CH_3OCH_3 + H_2O$	2.0
Acetic acid	$2 CO + 2 H_2 \rightarrow CH_3COOH$	1.0
Ethylene	$2 CO + 4 H_2 \rightarrow C_2H_4 + 2 H_2O$	2.0
Ethylene glycol	$2 CO + 3 H_2 \rightarrow C_2H_6O_2$	1.5
Acetic anhydride	$4 CO + 4 H_2 \rightarrow (CH_3CO)_2O + H_2O$	1.0
Ethyl acetate	$4 CO + 6 H_2 \rightarrow CH_3COOC_2H_5 + 2 H_2O$	1.5
Vinyl acetate	$4 CO + 5 H_2 \rightarrow CH_3COOCHCH_2 + 2 H_2O$	1.25

Synthesis gas or syngas is produced via the gasification or pyrolysis of coal. The main components are carbon monoxide and hydrogen. The gasification setups can be rather different regarding the application of the produced syngas, the base material used and if the synthesis gas represents the main product of the gasification. Hydrocarbon rich synthesis gas is mainly utilised by the energy industry. Synthesis gas that is mainly composed of hydrogen and carbon monoxide is chiefly used by the chemical industry. Within the chemical industry, the required ratio of these two components, as represented in Table 1, is determined by the final product of the chemical synthesis.

A single stage setup is used in most gasifier systems (Lurgi, Shell, GE Energy, U-Gas etc.) [5], where the raw-material is introduced in a step-by-step fashion. However, two-stage setups are less widely used. One example is coke production where pyrolysis takes place at a low temperature, then the produced hydrocarbon rich syngas is used in coking process for heat generation [6].

The used method is different, in terms of setup. The synthesis gas produced in the low temperature pyrolysis is forced through the high temperature pyrolysis zone in a closed system. The final syngas is expected to have reduced hydrocarbon ratio and increased quantities of H_2 and CO .

1. MATERIALS AND METHODS

The low rank brown coal used in the gasification experiment is from the North-East brown coal basin in Hungary.

The flow route of the syngas produced in the experiment is presented in the *Figure 2*.

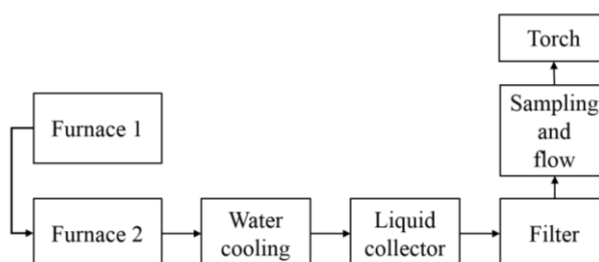


Figure 2

The flow route of the synthesis gas produced during the experiment

Two series of experiments were conducted in this research, all with different setups:

- In the first series of experiments, both reactors in the furnaces were filled with previously dried brown coal. Both furnaces were set to 450 °C final temperature, with a maximum heating rate.
- In the second series of experiments, the two furnaces were set to different temperatures, with coals from the different stages of pyrolysis. The reactor in the bottom furnace (*Figure 2, Furnace 2*) was filled with brown coal from the previous series of low temperature pyrolysis experiments and set to a final temperature of 900 °C. The high temperature pyrolysis was started and when the gas flow rate decreased below 2 l/h, the furnace on the top (*Figure 2, Furnace 1*) was turned on. The reactor in the top furnace was filled with pre-dried brown coal and the temperature was set to 450 °C. The produced syngas in the top reactor, following the gas flow path, must flow through the bottom side reactor where the temperature is set to 900 °C. The hydrocarbons in the syngas of the low temperature pyrolysis (450 °C) are expected to break down to carbon monoxide and hydrogen while flowing through the high temperature zone of the gasification setup. This way, synthesis gas with low ration of hydrocarbons and with hydrogen and carbon monoxide as main components can be produced, which is the aim of the experiments.

The quantity of the gas produced in the gasification experiment was measured with Medingen type rotameters (3–30 and 20–260 l/h). As the amount of coal fed to the furnace was not always the same, to be able to compare the l/h values, they were converted to 1 kg base material. The gas compositions were determined with an Agilent 490 Micro GC, using a COX column channel. Using the COX column, the MicroGC can detect the main components of the synthesis gas (CO, CO₂, H₂, CH₄) with a sampling rate of 2 minutes.

The adiabatic flame temperatures (T_{\max}) were calculated for every gas sample taken using an iterative method, taking into consideration the calculated LHV [7], the specific heat capacities found in the literature [8] and the combustion theory equations [9].

2. RESULTS

2.1. Single stage experiment

To produce a starting material with high energy density for the high temperature pyrolysis, both reactors were filled with previously dried low rank brown coal in the first stage. The temperatures were set to 450 °C with a heating rate of 20 °C/min. Even though both furnaces were set up to the same temperatures and heating rates, there were observable differences in the actual heating rates (*Figure 3*) as a result of the differences in their nominal power output. The evolution of the produced syngas in relation to time is also presented on *Figure 3*. Observable synthesis gas flow is first detected at the 300 °C which steadily increases to 120 l/kg at 450 °C. After this point, the gas flow stabilises until the volatiles, which can be released at this low temperature, are discharged. The experiments were concluded after the gas flow decreased to 2 ml/h.

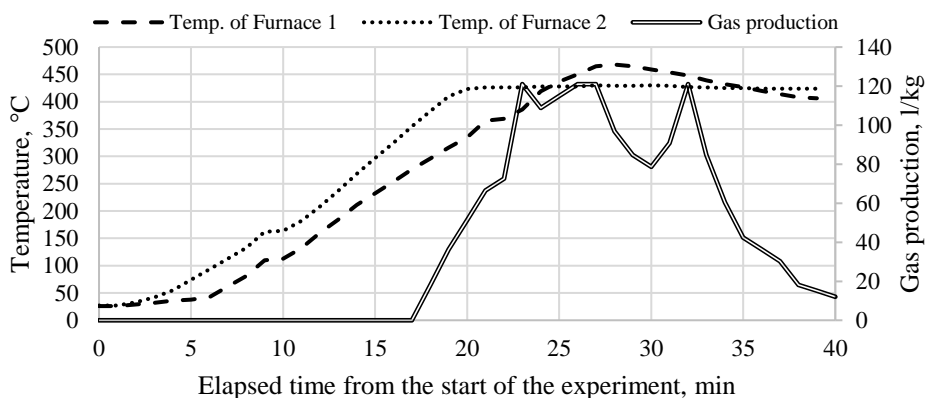


Figure 3

The evolution of temperatures and gas flow in relation to time in the two reactors (Single stage experiment)

Based on the composition of the produced synthesis gas (*Figure 4*), it can be stated that the initial temperature, where the volatiles release starts, is sufficient for the volatiles to react with the oxygen trapped within the reactor and combust. This is analysed in depth along with the results obtained with the use of a derivatograph detailed in the in the article “*Analysis of*

Solid and Liquid Phase Products of the Two-Stage Pyrolysis” also published in the current issue. At the beginning of the gas flow, as it can be seen on the *Figure 4*, the oxygen quantity is declining while the ratio of the carbon dioxide is increasing. The ratio of carbon dioxide is peaking at 50% V/V. With the declining oxygen ratio, there is not enough oxidizer left for combustion reactions. Therefore, the amount of carbon monoxide, methane and other hydrocarbon compounds start to increase within the produced synthesis gas. Previous experiments showed that the amount of other hydrocarbons within the synthesis gas can be accounted for the 20% V/V of the total amount of the methane produced. The methane production of the pyrolysis experiment shows an increasing trend throughout the process, peaking at 12% V/V of the syngas produced.

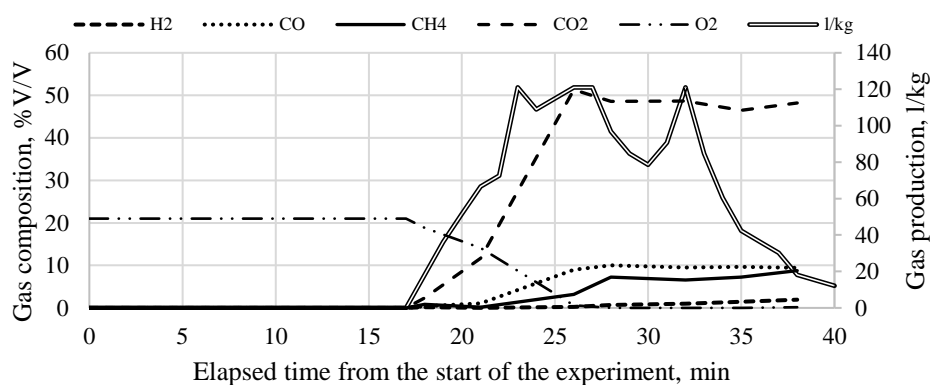


Figure 4

The evolution of the synthesis gas composition in time (Single stage experiment)

For the produced synthesis gas to be utilised in the chemical industry, it would require at least a H_2/CO ratio of 1 (*Table 1*). However, the ration of the syngas from low temperature pyrolysis is well below this (*Figure 5*). The use of this synthesis gas case would require a large amount of hydrogen addition. Furthermore, the high ratio of other gas compounds, like hydrocarbons, would require a separation which would further increase the cost.

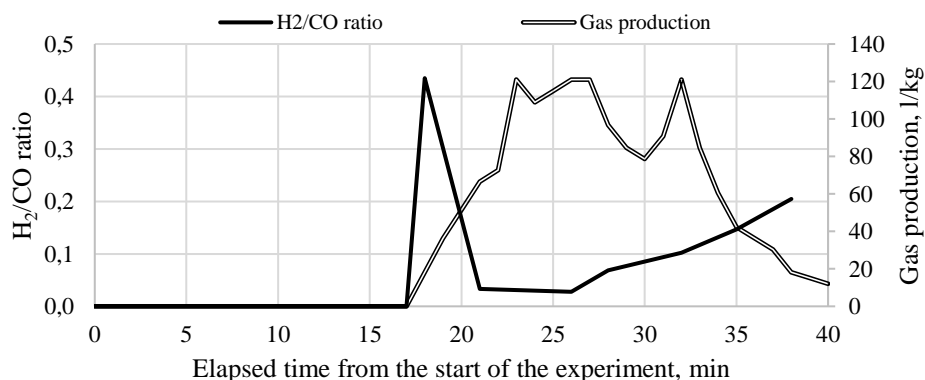


Figure 5

The evolution of H_2/CO ratio throughout the experiment (Single stage experiment)

The calculated adiabatic temperature is increasing in time, due to the increasing ratio of combustible compounds within the synthesis gas. The calculated flame temperature using the data acquired from the DSO-Tigáz Ltd – with 90–95% V/V methane, 3–5% V/V other hydrocarbons and 1–3% V/V non-combustible compounds [10] – is just below 1500 °C at its peak. However, it is still well below the 2000 °C of adiabatic flame temperature measured in the case of the natural gas (*Figure 6*).

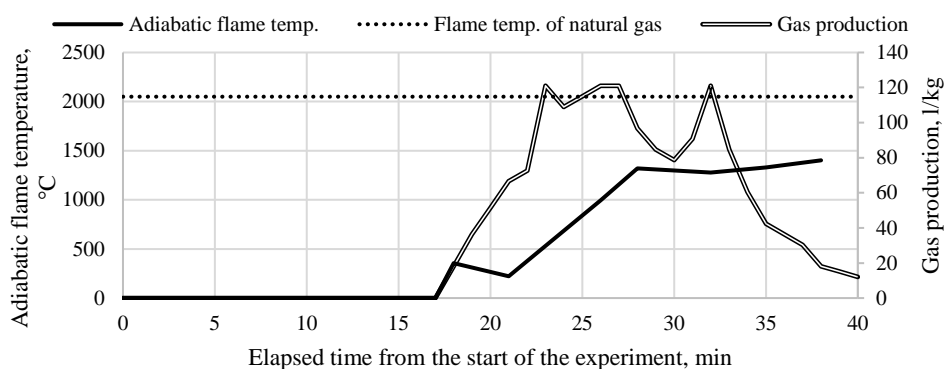


Figure 6

The evolution of adiabatic flame temperature in the one stage experiment

2.2. Two stage experiment

In this series of experiments the two furnaces were started with a time shift between the stages. First, the furnace marked as *Furnace 2* was turned on (*Figure 7*). The furnace was set to 900 °C final temperature with a heating rate of 20 °C/min. After the gas flow decreased to 2 l/h, the other furnace marked with *Furnace 1* was turned on and set to 450 °C, with a heat rate of 20 °C/min. *Furnace 2* was held at 900 °C. The aim of the experiment was to investigate the possibility of hydrocarbon ratio reduction during the low temperature pyrolysis, by forcing the gas through a high temperature zone (*Furnace 1*). *Figure 7* also shows the synthesis gas flow rate throughout the experiment. It is apparent, that in the case of *Furnace 2*, syngas production starts around 450 °C, where the low temperature pyrolysis was finished in the first stage of the experiment.

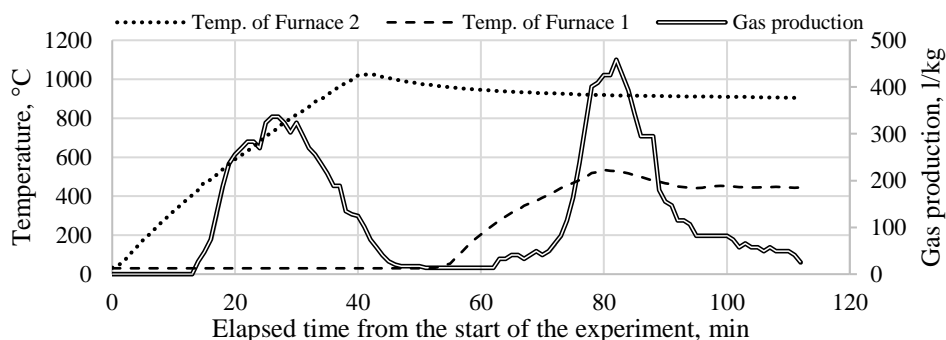


Figure 7

The evolution of the temperatures and the gas flow of the two-stage experiment

Separating the two stages of the gasification, it is obvious that the low temperature pyrolysis (450 °C) has lower synthesis gas yield than the higher temperature (450–900 °C) pyrolysis (Figure 8). The flow rates of the single- and two-stage gasification are also different, comparing the low temperature pyrolysis with and without passing through the high temperature zone (900 °C). In case of the latter, the flow rate is noticeably higher. This effect is mostly caused by the decomposition of hydrocarbons in the gas phase and the volatiles in the vapour phase that would otherwise condense. At this higher temperature gasification also takes place, using oxygen and water vapour from the decomposed hydrocarbons (detailed in the in the article *Analysis of Solid and Liquid Phase Products of the Two-Stage Pyrolysis* also published in the current issue).

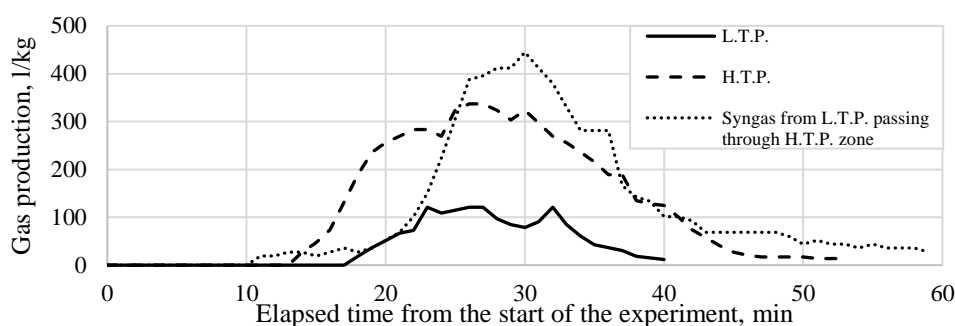


Figure 8

The flow rate comparison of the synthesis gas in the case of the two stage gasification at different temperature ranges and stages

Similarities between the composition of the syngas from high and low temperature pyrolysis can also be observed (Figure 9). First of all, both the carbon dioxide and oxygen ratios were high at the beginning of the experiment. This is the result of the similar start up conditions, namely the non-inert filling of the gasifier with brown coal.

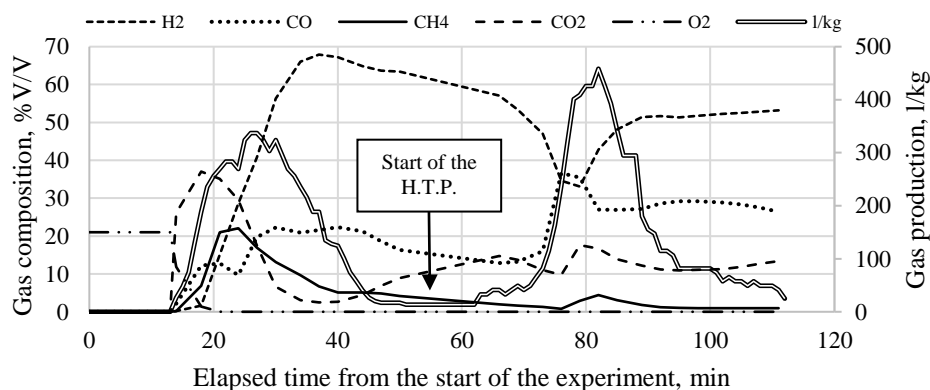
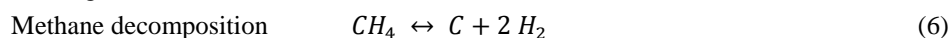
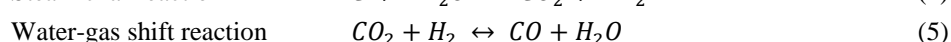
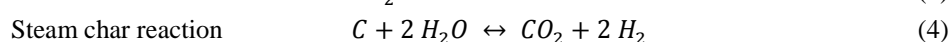
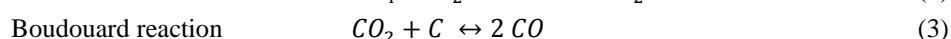
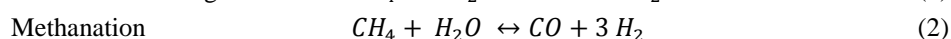
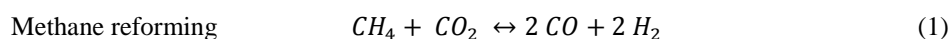


Figure 9

The evolution of the gas composition in the two-stage experiment

The reaction of the oxygen and the char results in high carbon dioxide ratio. After reaching the maximum peak, the ratio of carbon dioxide is starting to drop, while the ratio of methane and hydrogen is rising within the synthesis gas. By the time the flow rate reaches its peak point, the concentration of carbon dioxide is fallen below 20% V/V, and the carbon monoxide and hydrogen ratios are increased above 20% V/V and 40% V/V, respectively, and are steadily increasing. The methane concentration between the temperature range 500–700 °C are steadily above 20% V/V, with its peak concentration of 23% V/V.

The most significant reactions taking place at the high temperature (900 °C) zone of the gasifier are shown below (Equations 1–6). The equilibrium of the reactions presented are shifting to the right, as it can be seen from our results shown in Figure 9. The CO ratio is almost doubled, while the methane ratio is decreased to just a few percent, compared to the single stage gasification experiment. The ratio of CO₂ decreased as well, to nearly half of that in the single stage experiment. The presented results are clear evidence of the advantages of the two-stage gasification compared to the single stage gasification if the aim of the gasification is to produce synthesis gas with increased carbon monoxide and hydrogen ratios and decreased carbon dioxide ratio.



It is apparent from the series of the single and two-stage experiments, that both the higher temperature pyrolysis and the synthesis gas forced to flow through the high temperature zone of the gasifier have increased H₂/CO ratios, compared to the low temperature pyrolysis (Figure 10).

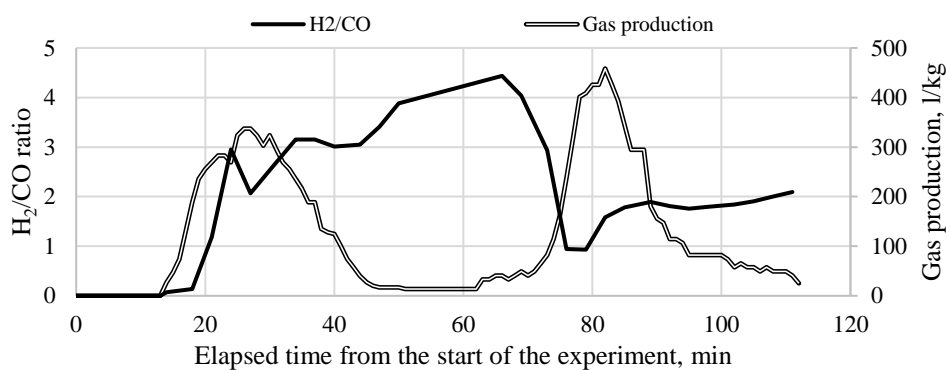


Figure 10

The evolution of the H₂/CO ratio and the gas flow in the two-stage experiment

In the high temperature pyrolysis, the ratio of H₂/CO reached up to 4/1, while the synthesis gas produced via low temperature pyrolysis and forced flow through the high temperature zone, reached up 2/1 ratio. It can be concluded, that with a two-stage setup an increased

hydrogen/carbon monoxide ratio can be accomplished, while the methane concentration can be decreased almost tenfold compared to the low temperature pyrolysis. Furthermore, by mixing the synthesis gas from the low temperature and high temperature zones, the syngas can be steadily held above a H_2/CO ratio that could serve as base material for chemical industrial use in synthetizations (Table 1).

In addition to these results, based on the adiabatic flame temperatures calculated from the samples taken throughout the two-stage experiments it can be concluded that the values are comparable to those of the natural gas (Figure 11). These results demonstrate the viability of this two-stage setup. The produced synthesis gas is a viable option for base material for chemical industrial application while at the same time it can be used in power generation applications.

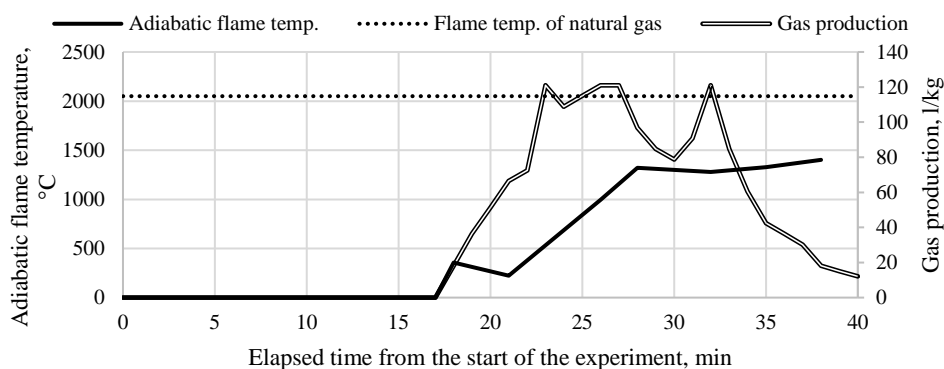


Figure 11

Evolution of the adiabatic flame temperature and flow rate in the two-stage experiment

CONCLUSION

The main goal of this research was to investigate the first step of every gasification, the pyrolysis, focusing on the low temperature pyrolysis, as most of the volatiles are released during this phase of the gasification. Through separating the pyrolysis into two stages, the processes taking place and the composition of the synthesis gas produced could be further investigated. The experiment was setup using two separate furnaces to fine-tune the conditions of the pyrolysis. Therefore, the composition of the produced synthesis gas can be altered. The results clearly show that this setup is a viable solution to reduce the amount of methane and increase the carbon monoxide and hydrogen ratios within the synthesis gas. The results are also encouraging to further investigate this two-stage setup with the inclusion of the redox char gasification in the high temperature zone, while the low temperature zone will be kept with similar setup. This will evaluate the possibilities of the two-stage setup within the whole process and could lead to a “high quality” synthesis gas production from low rank coals which can be used in both, power generation applications and industrial chemical applications.

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