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Investigation of a Two-stage Process of Biomass Gasification

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The two-stage gasification of biomass proposed by JIHT RAS is a pyrolysis of biomass, followed by cracking the condensable pyrolysis products on the surface of charcoal to produce synthesis gas. The paper presents the results of experiments designed to produce synthesis gas by the two-stage gasification of wood. The processes of homogeneous and heterogeneous cracking of pyrolysis products on the surface of coal were studied, the optimal parameters of the carbon catalyst for this type of biomass were determined.

1. Introduction

The pyrolysis process, especially fast pyrolysis, aimed at obtaining liquid products. The composition and quantity of these products and the possibility of their use as a fuel have now been well studied (Bridgwater, 2012). However, pyrolysis can be used to produce synthesis gas by a secondary cracking of liquid products. The advantage of this two-stage process in comparison with air gasification is the high calorific value of gas produced due to the absence of nonflammable nitrogen in its composition. Another advantage of the process is its cheapness in comparison with other gasification methods, such as oxygen or steam gasification.
The decomposition of the liquid fraction of the pyrolysis products can be carried out by known methods used for gas cleaning from tars. Typically, it is a partial oxidation or catalytic cracking methods. Also, the decomposition of the liquid fraction can be carried out by heterogeneous cracking on the surface of charcoal. In this case, the charcoal acts as a catalyst and a reagent simultaneously. Such a scheme with the partial oxidation and heterogeneous cracking of tars was used in two-stage gasifier developed by the Technical University of Denmark (Henriksen et al., 2003). The gasifier called “Viking” gives almost complete tar conversion (< 15 mg/Nm^3). The high tar removal of this gasifier is related to passing the volatiles through a partial oxidation zone followed by a char bed.
The two-stage method of biomass gasification offered by JIHT RAS (Kosov et al., 2013) differs from the Viking gasifier scheme in absence of partial oxidation; thereby it is possible to obtain the synthesis gas with the maximum calorific value. For the practical application of the method it is necessary to investigate the processes of homogeneous and heterogeneous volatile pyrolysis products cracking in the reactor volume and on the surface of charcoal, as well as to estimate the effectiveness of both cracking processes.

2. Experimental set-up

The experimental set-up (Figure 1) consisted of a high-temperature two-chamber fixed-bed reactor and a system of extraction and analysis of gas and vapor forming as a result of heating an initial raw material.
The reactor was a stainless steel tube with an inside diameter of about 37 mm, which was placed within a two-section furnace with independent heaters for each section. The chambers were 300 mm length each. Raw material was placed into the chamber 1. There were series of experiments with different amount of char placed and different temperatures in the chamber 2. Pyrolysis process was explored when chamber 2 was empty and its temperature was 20 °C.
To explore homogeneous and heterogeneous cracking, the chamber 1 was heated up to temperature 1 000 °C that was held further at the constant level. After that the temperature of the bottom chamber was

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raised at the rate 10 °C/min. Process of homogeneous cracking was explored with empty chamber 2. To explore heterogeneous cracking, char obtained by pyrolysis of the same raw material was placed in the chamber 2 and heated up to 1 000 °C.

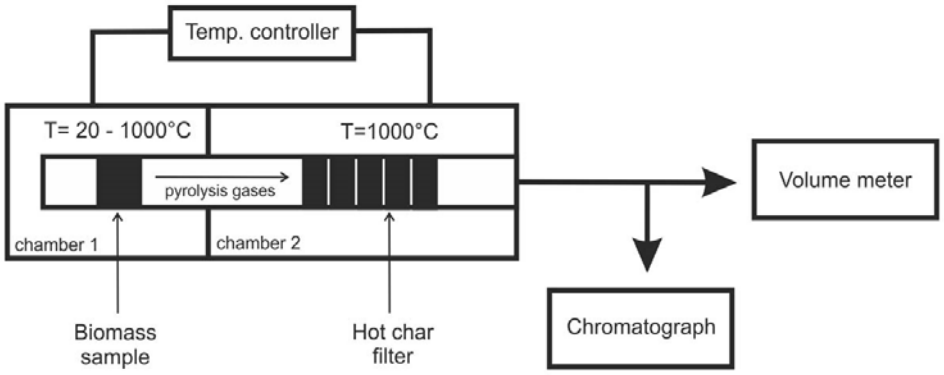

Figure 1: Scheme of the experimental reactor

Gases formed during pyrolysis of initial raw material passed through the porous carbon bed in the chamber 2. As a result of homogeneous and heterogeneous chemical reactions in the high-temperature zone, the pyrolysis gases decomposed into synthesis gas, which came into the volume meter (eudiometer). The samples of the gas were chromatographed. Softwood pellets were used as a raw material for pyrolysis. Carbonized softwood pellets were used as the hot char filter.

3. Results and Discussion

The results of measurements of the volume gas produced per 1 kg of softwood pellets during pyrolysis and two types of tars cracking are shown in Fig. 2.

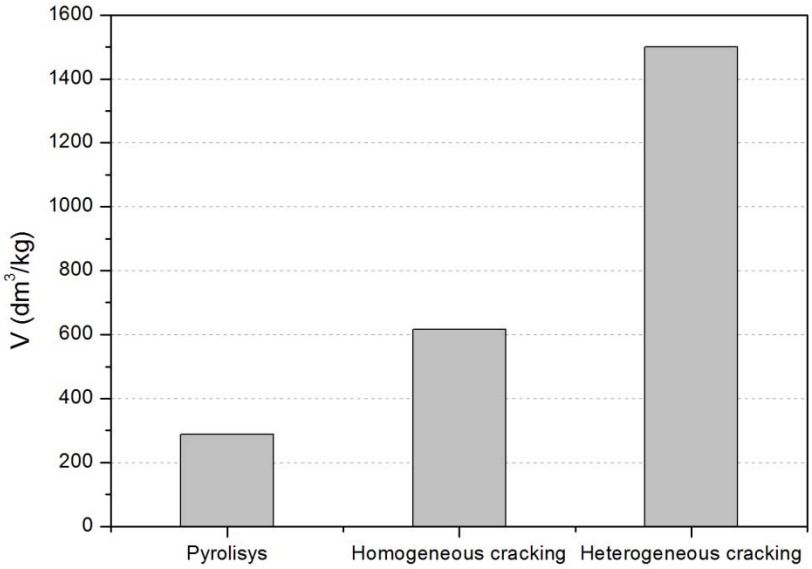

Figure 2: Gas yield per one kg of raw material during pyrolysis of softwood pellets and two types of tars cracking

From these data it follows that heterogeneous cracking of pyrolysis tars on the surface of charcoal is more effective than homogeneous cracking in volume of the reactor and allows receiving the maximum volume of synthesis gas in the same reactor.

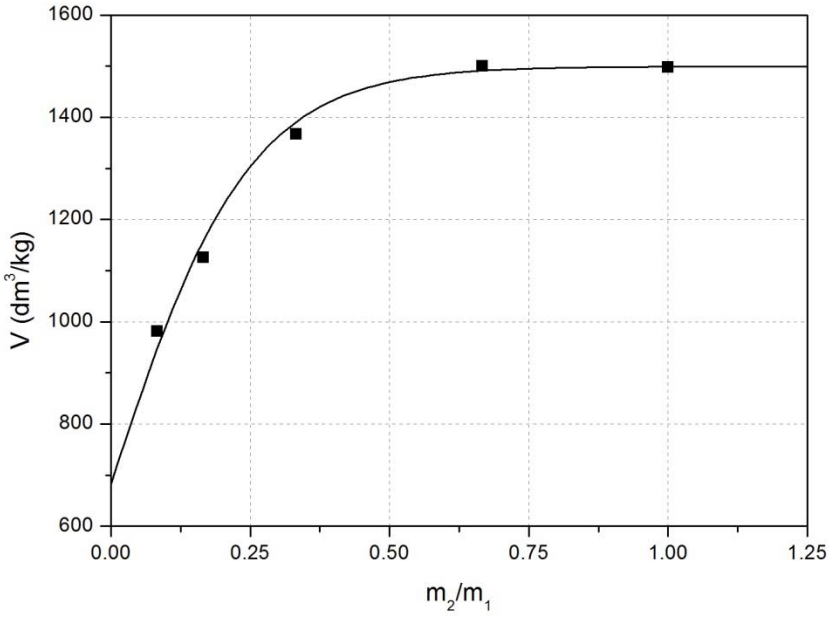

Figure 3: Gas yield per one kg of raw material during pyrolysis and subsequent cracking of tars at different mass ratio

During the experiments, the optimal ratio of the mass of the initial biomass (m_1) and mass of the coal in chamber 2 (m_2) was determined. The results are presented in Figure 3.
From these data it follows that at a mass of coal in the chamber 2 at half the weight of processed biomass, the amount of the product gas becomes close to the maximum, indicating the complete decomposition of pyrolysis tars. This is confirmed by the data on the composition of the synthesis gas produced at different quantities of coal in the chamber 2, as it is shown in Table 1.

Table 1: Composition of the synthesis gas produced at different coal/biomass mass ratio

m_2/m_1	H_2	CO	CO_2	CH_4	N_2
pyrolysis	32.6 %	22.4 %	24.1 %	16.3 %	4.6 %
0.00	43.7 %	36.2 %	10.3 %	7.9 %	1.9 %
0.08	46.8 %	38.7 %	6.6 %	6.1 %	1.8 %
0.17	49.4 %	40.7 %	4.9 %	4.1 %	0.9 %
0.33	50.2 %	42.4 %	3.1 %	2.5 %	1.8 %
0.67	53.2 %	43.6 %	0.9 %	1.2 %	1.1 %
1.00	54.4 %	43.6 %	0.3 %	0.9 %	0.8 %

For the mass ratio greater than 0.5 synthesis gas composition becomes constant, that indicating complete tar decomposition. Thus, using the charcoal filter is equal to one half of initial weight of the biomass may be considered as optimal to achieve the maximum degree of decomposition of the pyrolysis products. Further increase in coal mass filter does not increase the degree of decomposition and volume of the gas.

In our previous research (Kosov et al., 2014) it was shown, that the maximum gas yield speed for reactions of heterogeneous cracking is in the temperature range from 200 °C to 300 °C, whereas the maximum gas yield speed for reactions of homogeneous cracking is in the temperature range from 300 °C to 400 °C (Figure 4), which corresponds with the pyrolysis temperature range in which the pellets mass loss occurs at the maximum speed (Figure 5).

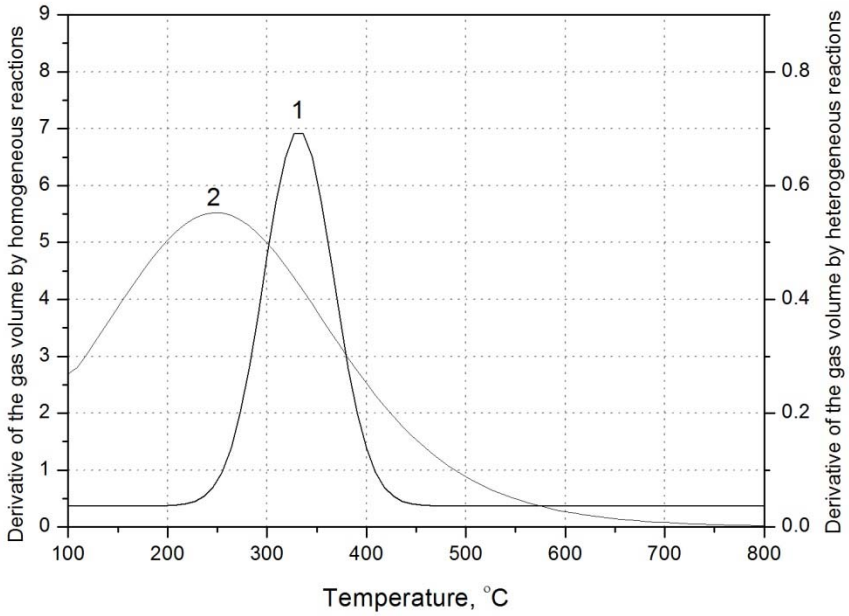

Figure 4: Derivative of the gas volume by homogeneous (1) and heterogeneous (2) reactions

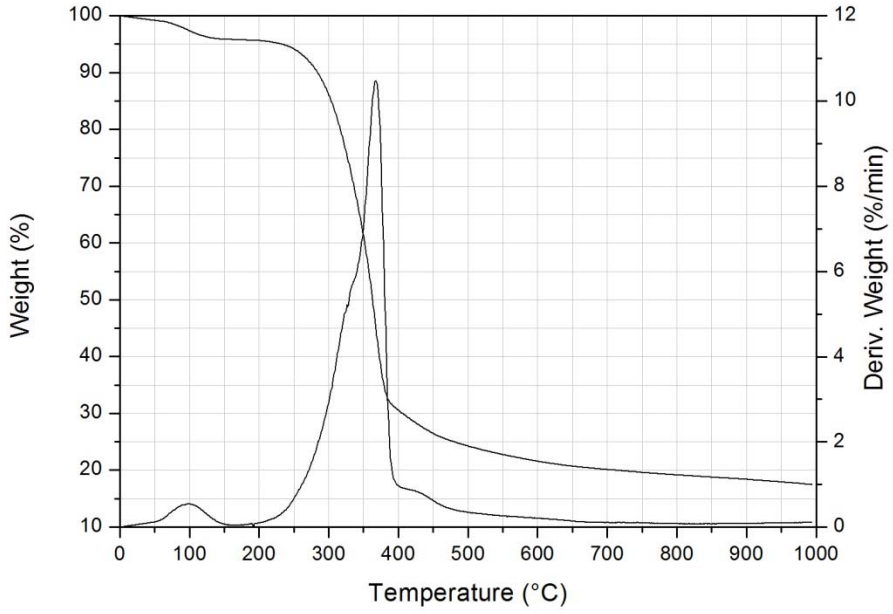

Figure 5: TGA and DTGA of the wood pellets during pyrolysis

Pyrolysis products formed in this temperature range consist of a condensable and non- condensable fraction. Non-condensable fraction consists mainly of carbon dioxide and carbon monoxide (Figure 6). The mass of the non-condensable fraction in the total mass of the pyrolysis products is low and decomposition of carbon dioxide to carbon monoxide cannot provide a substantial increase in the product gas. Thus, it can be argued that due to heterogeneous reactions it takes place decomposition of mainly condensable fraction of the pyrolysis products.

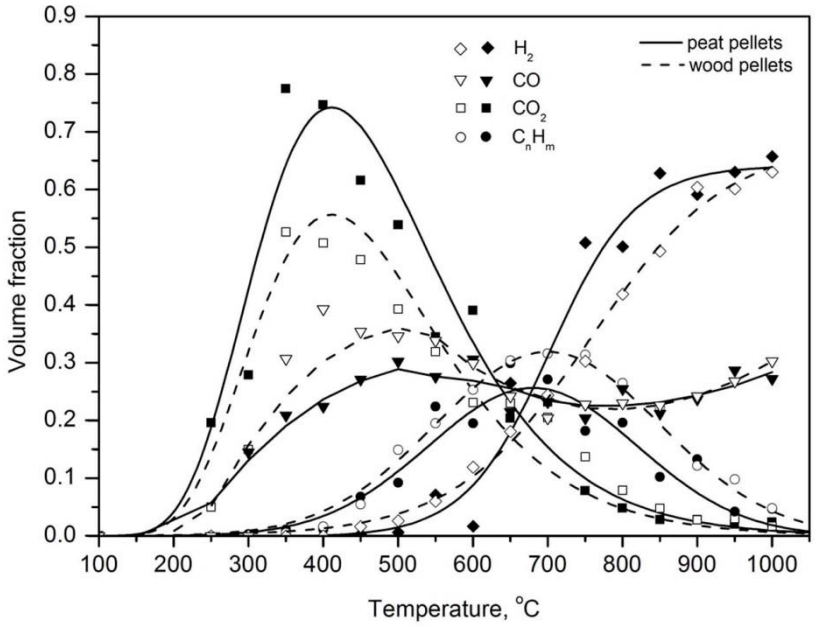

Figure 6: Noncondensable pyrolysis products yield for different kinds of biomass

Condensable fraction of the pyrolysis products for this temperature range consist mainly of acetic acid and water, with smaller quantities of methanol, formic acid, lactic acid, furfural, hydroxyl acetone and traces of phenol (Princs et al., 2006). Thus, the main reactions of heterogeneous cracking are next:

$$H_2O + C \longrightarrow CO + H_2 \quad (1)$$

$$C_2H_4O_2 \longrightarrow 2CO + 2H_2 \quad (2)$$

$$CH_3OH \longrightarrow CO + 2H_2 \quad (3)$$

$$CH_2O_2 + C \longrightarrow 2CO + H_2 \quad (4)$$

$$C_3H_6O_3 \longrightarrow 3CO + 3H_2 \quad (5)$$

$$C_3H_6O \longrightarrow CO + 3H_2 + 2C \quad (6)$$

$$C_5H_4O_2 \longrightarrow 2CO + 2H_2 + 3C \quad (7)$$

As can be seen, in most of these reactions (except for the reaction with water Eq(1) and formic acid Eq(4)), carbon acts as a catalyst. At the same time, by weight water takes up more than half of all the condensable pyrolysis products, so its reaction with carbon gives the greatest increase in the volume of produced synthesis gas.

4. Conclusions

From the data received it follows that heterogeneous cracking of pyrolysis tars on the surface of charcoal is more effective than homogeneous cracking in volume of the reactor and allows receiving the maximum volume of synthesis gas in the same reactor. From the results of measuring the volume of gas produced in

different mass ratios of charcoal and biomass processed, it is clear that it reaches the maximum in the range of the mass ratio m_2/m_1 equal to 0.5 - 0.6.
Analysis of the gas yield speed for two types of cracking shows that the maximum gas yield speed for reactions of heterogeneous cracking is in the temperature range from 200 °C to 300 °C, whereas the maximum gas yield speed for reactions of homogeneous cracking is in the temperature range from 300 °C to 400 °C. It can be argued that due to heterogeneous reactions it takes place decomposition of mainly condensable fraction of the pyrolysis products formed in the pyrolysis temperature range from 200 °C to 300 °C.

Acknowledgements

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