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Two-stage Gasification of Untreated and Torrefied Wood

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The major methods of biomass thermal conversion are combustion in excess oxygen, gasification in reduced oxygen, and pyrolysis in the absence of oxygen. The end products of these methods are heat, gas, liquid and solid fuels. From the point of view of energy production, none of these methods can be considered optimal.
Two-stage gasification of biomass proposed by JIHT RAS is pyrolysis of biomass, as the first stage, and cracking of the pyrolysis products as the second stage. This method can be considered optimal for energy production, because it allows obtaining synthesis gas consisting of hydrogen and carbon monoxide and not containing liquid or solid particles. Since no byproducts are formed, there is no need for complicated cleaning methods of the gas.
In this study we investigated the effectiveness of heterogeneous cracking of pyrolysis products on the surface of charcoal in comparison with the homogeneous cracking. The effect of preliminary torrefaction of biomass on secondary cracking process and composition of the resulting synthesis gas was investigated. It is shown that the use of torrefied biomass allows obtaining a high-calorific gas even by homogeneous cracking of pyrolysis products.

1. Introduction

Biomass gasification is a complex thermo-chemical process involving numerous different reactions (Dupont, 2007) and can be divided into two parts: pyrolysis and gasification itself. Pyrolysis of biomass occurs through heat transfer processes inside the gasifier. Thermal degradation of biomass during pyrolysis leads to the formation of mainly solid and 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).
Biomass gasification is a complex combination of secondary oxidation reaction of the biomass pyrolysis products. Depending on the type of gasification, the oxidizing agent may be air, oxygen, steam or a combination thereof. The end product of biomass gasification is synthesis gas consisting mainly of hydrogen and carbon monoxide, which are formed due to the reaction of carbon with oxygen or steam as shown at Eq(1) and Eq(2).

$$C_{(s)} + H_2O \rightarrow CO + H_2 \quad (1)$$

$$2C_{(s)} + O_2 \rightarrow 2CO \quad (2)$$

Pyrolysis of biomass and subsequent gasification of the pyrolysis products occur in the same reactor volume, which creates technical difficulties related to the uniformity of oxidant distribution. Therefore there is also reaction of carbon complete oxidation to carbon dioxide (Eq(3)).

$$C_{(s)} + O_2 \rightarrow CO_2 \quad (3)$$

In the case of steam gasification an excess of steam results in its incomplete reaction with carbon and unreacted water vapor come out of the reactor together with the synthesis gas (Eq(4)).

$$C_{(s)} + 2H_2O \rightarrow CO + H_2 + H_2O \quad (4)$$

In addition, the water-gas shift reaction (Eq(5)) can increase of carbon dioxide amount in synthesis gas.

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$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (5)$$

The Boudouard reaction (Eq(6)) allows converting carbon dioxide into carbon monoxide. However, at temperatures below 1000°C, this reaction is in equilibrium and the carbon dioxide remains in the synthesis gas.

$$C_{(s)} + CO_2 \leftrightarrow 2CO \quad (6)$$

The known gasification methods can produce synthesis gas consisted of combustible components (H_2, CO, CH_4) and non-combustible gases and vapors (CO_2, N_2, H_2O) in various proportions. The presence of non-combustible gas significantly reduces the overall efficiency of the technology by reducing the heating value of the synthesis gas. Furthermore, the tar formation in all types of gasification processes makes it impossible direct use of the product gas in the power generating units. Dividing of pyrolysis and gasification processes and the use of cracking instead of oxidation allows obtaining syngas that does not contain non-combustible components.

Such a scheme is offered by JIHT RAS (Kosov et al., 2013). The two-stage process is pyrolysis of biomass, as the first stage, and cracking of the pyrolysis products on surface of charcoal as the second stage. This method allows obtaining synthesis gas consisting of hydrogen and carbon monoxide and not containing liquid or solid particles. Since no byproducts are formed, there is no need for complicated cleaning methods of the gas.

Cracking reaction may be homogeneous and heterogeneous. Homogeneous cracking occurs in the volume of the reactor, the heterogeneous occurs on the reactor walls and on the surface of coal. For the practical application of the method it is necessary to investigate the processes of homogeneous and heterogeneous volatile pyrolysis products cracking, as well as to estimate the effectiveness of both cracking processes.

Some of these studies have been performed previously ((Kosovo et al., 2014) and (Kosov et al., 2015)). It has been suggested that the heterogeneous cracking process decomposes volatiles formed upon pyrolysis temperatures of 200-300°C. This paper describes a series of experiments with torrefied wood, confirmed earlier assumptions made about the nature of the reactions of heterogeneous cracking of the pyrolysis products on the surface of charcoal.

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.

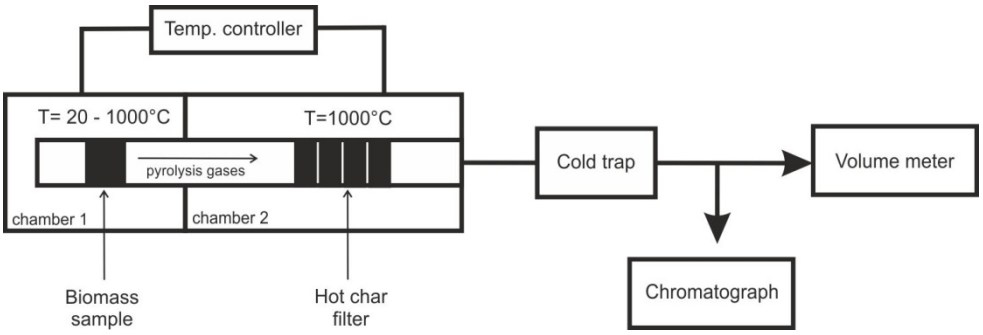

Figure 1: Scheme of the experimental reactor

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 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.

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. The properties of the pellets are shown in Table 1.

Table 1: Properties of softwood pellets

Moisture (wt%)	Dry material (wt%)						LHV, MJ/kg
	Ash	Volatiles	C	H	N	O	
4.7	0.8	82.5	50.3	6.0	0.4	43.3	20.6

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. The results indicate that the heterogeneous cracking is much more effective than homogeneous and allows obtaining the maximum volume of the gas in the same reactor. This gas volume is up to 1.5 m^3 per 1 kg of wood biomass.

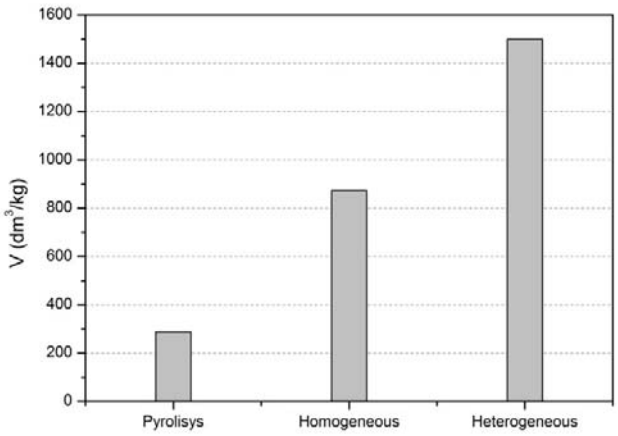

Figure 2: Gas yield per one kg of raw material during pyrolysis of softwood pellets and two types of tars cracking

The mass balance of the pyrolysis process and the two types of secondary cracking is shown in Figure 3. The pyrolysis process, especially fast pyrolysis, aimed at obtaining liquid products. The proposed two-stage scheme of gasification uses a slow pyrolysis (biomass heating rate of 10 degrees per minute). The pyrolysis products consist of solid (18% by weight), liquid (58% by weight) and a gaseous fraction (24% by weight). As can be seen, homogeneous cracking of the liquid and gaseous pyrolysis products at the temperature of 1000 °C causes a significant change in the mass balance. After homogeneous cracking the gaseous fraction of is already 82% by weight and the liquid fraction is only 10%. Heterogeneous cracking allows decomposing the liquid fraction completely. As a result, 82% of the weight of the raw material converts into the gas.
Figure 2 shows that as a result of heterogeneous cracking reactions, the gas volume increases almost double in comparison with homogeneous cracking. Heterogeneous cracking of the liquid fraction remaining after the homogeneous cracking the pyrolysis products and consisting mainly of water, cannot provide such a significant increase in the product gas. Therefore, increasing the volume of the product gas occurs due to decomposition of gaseous components of the synthesis gas obtained after the homogeneous cracking of liquid products of pyrolysis. Analysis of composition of the synthesis gas obtained by cracking of homogeneous and heterogeneous confirms this hypothesis (Table 2).

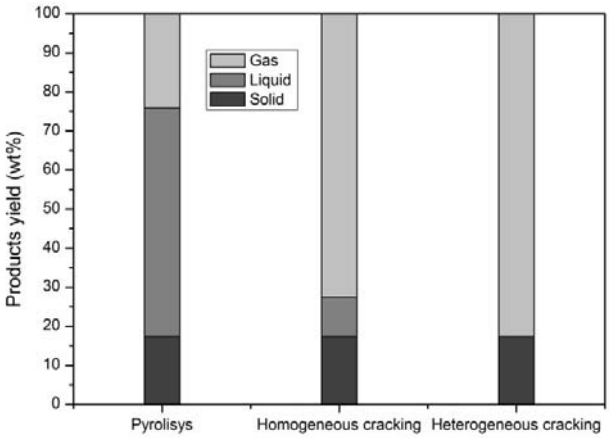

Figure 3: Mass balance of untreated wood pyrolysis and the two types of secondary cracking

Table 2: Composition of the synthesis gas for two types of untreated wood pyrolysis products cracking

Component	Homogeneous cracking	Heterogeneous cracking
CO	36.8%	54.2%
H_2	47.1%	46.5%
CO_2	11.4%	-
CH_4	14.4%	-
N_2	0.3%	0.3%

Synthesis gas produced by homogeneous cracking of the pyrolysis products contains about 25% of relatively heavy gases - methane and carbon dioxide. The decomposition of these gases to carbon monoxide and hydrogen doubles the volume of synthesis gas while their mass fraction remains constant.

Previous research of output gas speed for homogeneous and heterogeneous cracking processes (Kosov et al., 2015) showed, 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).

Pyrolysis products formed in this temperature range (also known as torrefaction) consist of a condensable and non- condensable fraction. Non-condensable fraction consists mainly of carbon dioxide and carbon monoxide. 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 was argued that due to heterogeneous reactions it takes place decomposition of mainly condensable fraction of the pyrolysis products. 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).

It has been suggested that exactly these substances are decomposed during the heterogeneous cracking on the surface of charcoal, while other pyrolysis products are decomposed in the reactor volume. If this assumption is true, the heterogeneous cracking of torrefied biomass pyrolysis products will not lead increase the volume of the resulting synthesis gas. Comparison of the volume of gas produced by the pyrolysis of untreated and torrefied wood and two types of cracking of the volatile products of pyrolysis is shown in Figure 5.

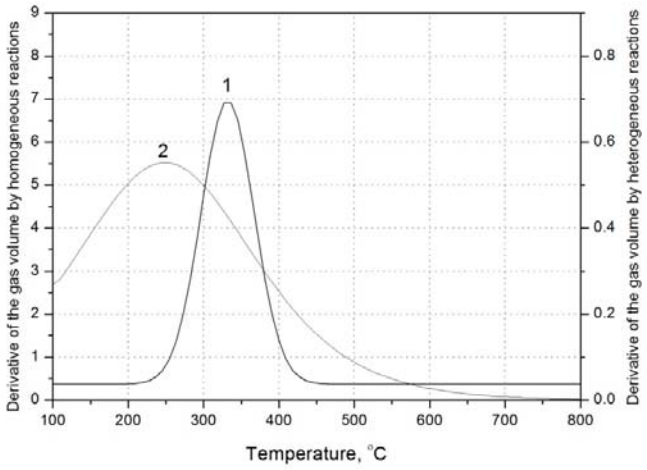

Figure 4: Speed of the gas yield by homogeneous (1) and heterogeneous (2) reactions

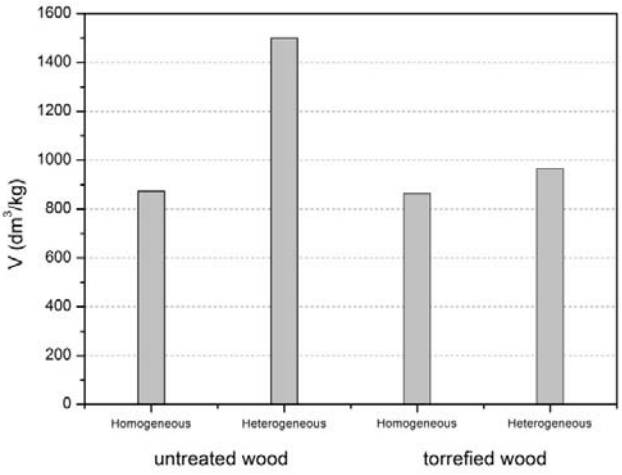

Figure 5: Volume of the gas obtained by homogeneous and heterogeneous cracking of untreated and torrefied wood pyrolysis products.

As shown in Figure 5, in the case of torrefied wood pyrolysis, unlike untreated wood pyrolysis, heterogeneous cracking of volatiles does not lead to a significant increase in the volume of synthesis gas. Consequently, the pyrolysis products of torrefied wood do not contain components that decompose only heterogeneously.
The slight increase in the volume of gas for the heterogeneous cracking can be explained by decomposition of methane and carbon dioxide, which is confirmed by the change of the gas composition (Table 3).

Table 3: Composition of the synthesis gas for two types of torrefied wood pyrolysis products cracking

Component	Homogeneous cracking	Heterogeneous cracking
CO	41.4%	50.5%
H_2	37.5%	43.7%
CO_2	9.1%	-
CH_4	6.1%	-
N_2	1.2%	1.2%

Thus, heterogeneous cracking decomposes pyrolysis products released from the biomass in the temperature range 200-300 °C.

4. Conclusions

From the data received it follows that heterogeneous cracking of volatile pyrolysis products in case of untreated wood is more effective than homogeneous cracking in volume of the reactor and allows receiving the maximum volume of synthesis gas in the same reactor.
Analysis of the gas yield speed for two homogeneous and heterogeneous 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, also known as torrefaction. Comparison the volumes of synthesis gas produced by homogeneous and heterogeneous cracking of torrefied wood pyrolysis products confirmed this hypothesis.
Thus, in the case of using the torrefied wood as a raw material for the two-stage gasification, homogeneous cracking of the volatile products of pyrolysis can be considered the optimal technical solution.

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