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Experimental Research of Heterogeneous Cracking of Pyrolysis Tars

Valentin Kosov, Vladimir Kosov, Victor Zaichenko

Joint Institute for High Temperatures of the Russian Academy of Sciences (JIHT RAS)
Address: Izhorskaya str. 13, 125412 Moscow, Russia
kosov@ihed.ras.ru

Biomass is the largest and the most important renewable energy source in the world. World production of biomass is estimated at 150–200 billion metric tons a year. Currently biomass provides approximately 14% of the total world energy consumption. The most effective way to convert biomass into energy is its conversion into combustible gas. However, the existing gasification technologies have several disadvantages.
One of the most urgent problems of biomass gasification is cleaning the product gas from tar and carbon dioxide. Joint Institute for High Temperatures of the Russian Academy of Sciences suggests the gas cleaning technology based on the heterogeneous cracking of pyrolysis tar on the surface of the charcoal. In this paper the results of experimental determination of hot char filter parameters influencing on the efficiency of heterogeneous of pyrolysis tar cracking are presented.

1. Introduction

There are many methods for biomass conversion into combustible gas (Peres et al., 2013). Air gasification is the easiest method to convert biomass into the gas. However, the resulting gas contains up to 60% nitrogen and 40 % carbon dioxide. The calorific value of the gas is generally around 4 - 5 MJ/m^3, which is too low for efficient use. Overall efficiency of gasification gas power plant is limited to 20 % (Lisý et al., 2008).
Oxygen and steam gasification allow increasing the calorific value of the gas which contains no nitrogen and small amount of carbon dioxide. The maximum gas yield reaches 1.3 m^3 per kg of raw material and its calorific value is about 11 MJ/m^3 (Pengmei et al., 2007). Steam gasification is the widespread process because of its simplicity. The main disadvantage of the process is concerned with necessity of steam generation, which reduces overall effectiveness of power plant. Use of oxygen for the purpose of gasification demands an air separation unit in technological chain that leads to rise in price of end product. It should also be noted that purification of the gas from tar and ash is an urgent problem for all methods of gasification.
For several years, in the Joint Institute for High Temperatures of Russian Academy of Sciences, the two-stage technology of biomass processing has been developing (Kosov et al., 2013). The technology is based on pyrolysis of biomass as the first stage. The second stage is high-temperature conversion of liquid fraction of the pyrolysis on the surface of porous charcoal matrix. Synthesis gas consisted of carbon monoxide and hydrogen is the main products of the technology.
In this method the charcoal is used as catalyst for cracking of liquid fraction of the pyrolysis. Our experiments have shown a significant increase of the volume of gas in the outlet of the reactor due to decomposition of condensable and non-condensable pyrolysis products. In comparison to pyrolysis, the volume of gas increased nearly 10 times at cracking temperature 1,000 °C. At this temperature, the gas consists almost entirely of hydrogen and carbon monoxide in approximately equal parts in the zone of maximum gas release.
For the practical implement of this method it is important to know effectiveness of the charcoal filter for pyrolysis liquid products cracking. There are two cracking processes take place in the cracking chamber:

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homogeneous cracking in volume and heterogeneous cracking on the surface of porous charcoal matrix. The research described in this paper aims to give a good insight into the role of heterogeneous reactions in overall cracking of liquid pyrolysis products.

2. Experimental set-up

The experimental set-up (Figure 1) was similar to one described in our previous paper (Kosov et al., 2009) and 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 two-section furnace with independent heaters for each section. The chambers were 300 mm length each. Raw material was placed into the bottom chamber. Char obtained by pyrolysis of the same raw material was placed in the top chamber. Before experiments the top chamber 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.

Pyrolysis gases passed through the porous carbon bed with the fixed temperature. As a result of homogeneous and heterogeneous chemical reactions in the high-temperature zone a decomposition of torrefaction gases took place. Conversion degree depended both on the temperature in the top chamber and on the residence time in a high-temperature zone. Non-condensable gas came into the volume meter (eudiometer). The samples of the gas were chromatographed. Before each experiment reactor was filled by inert gas (argon). Wood pellets were used as initial raw material.

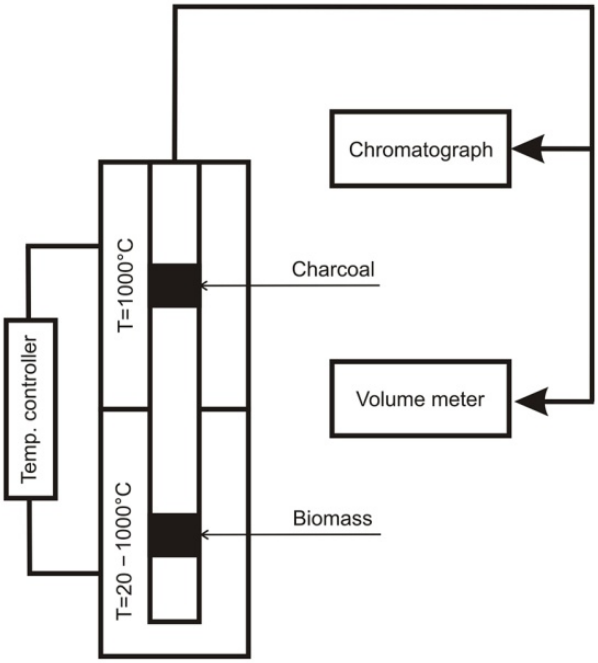

Figure 1: Scheme of the experimental reactor

There were two series of experiments. For first experiment top chamber was leaved empty to explore the process of homogeneous cracking of liquid products. For second experiment top chamber was filled by charcoal. The weight of charcoal was 5 g. The weight of raw material in the bottom chamber was 30 g for both series of experiments.

3. Experimental results and discussion

The data on gas volume (per kg of initial raw materials) obtained in the process of heating of the bottom chamber of the reactor at constant temperature of the top chamber are shown in Figure 2. . As follows from the presented data the volume of the gas produced by homogeneous and heterogeneous cracking reactions is more than the volume of the gas produced by homogeneous reactions only.

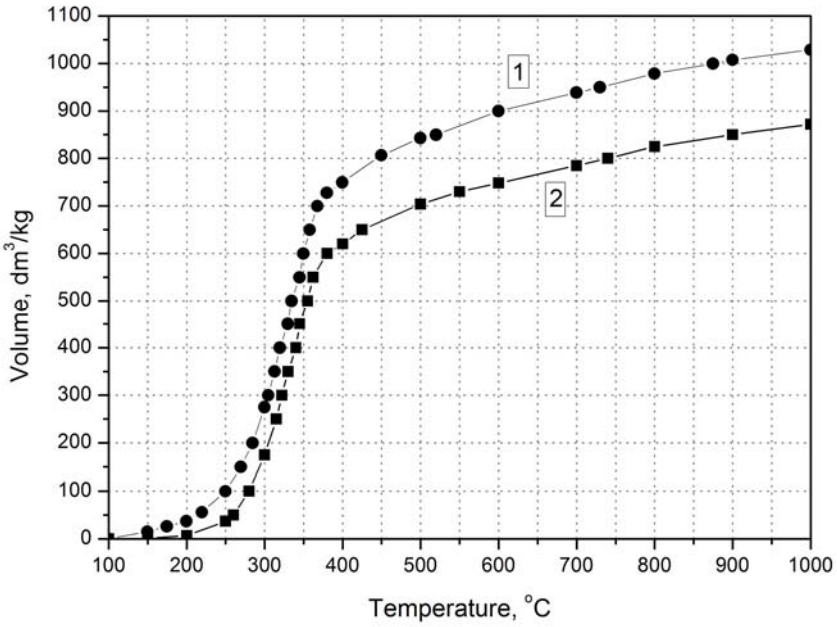

Figure 2: Gas yield per one kg of raw material during pyrolysis of wood pellets. 1 – homogeneous and heterogeneous reactions, 2 – homogeneous reactions only (empty top chamber)

Volume difference (Figure3) shows effect of the char presence in top chamber on the overall volume of output gas. In this case, heterogeneous cracking gave about 14 % by volume of the gas. Our previous research (Kosov et al., 2009) shows that with full decomposition of the pyrolysis products it can be obtained up to 1,400 dm^3 of gas. Thus, the maximum amount of gas generated from the cracking of volatile by heterogeneous reactions is about 36 % of the total gas volume.

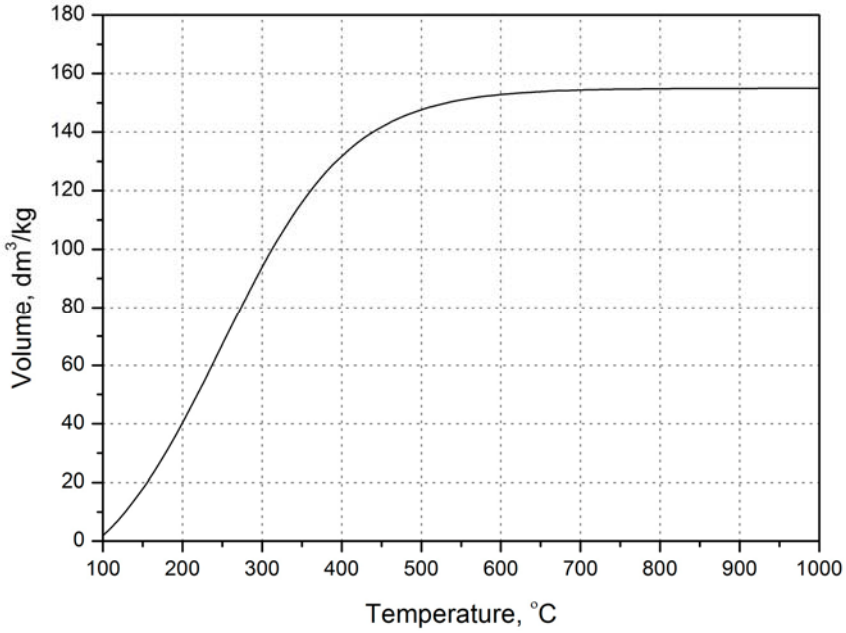

Figure 3: Gas yield by heterogeneous reactions of the pyrolysis products cracking

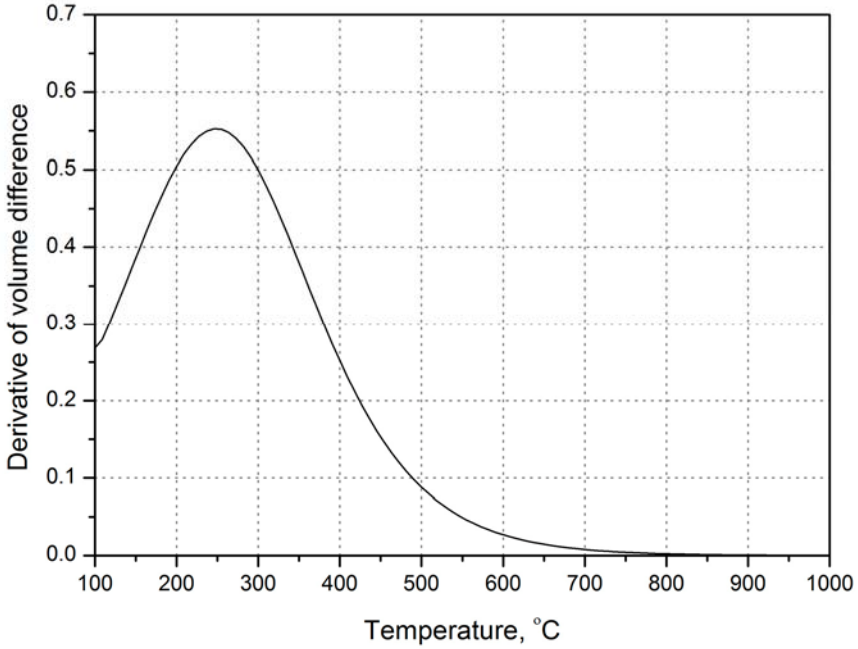

Figure 4: Derivative of the gas volume by heterogeneous reactions

Derivative of volume difference (Figure 4) shows that maximum effectiveness of char filter lies in the temperature range of 200-300 °C. At the same time, the maximum rate of the volatiles decomposition in volume falls on the temperature range 300-370°C (Figure 5). Thus, it can be assumed that due to the heterogeneous reaction on the surface of charcoal it takes place decomposition of volatiles which homogeneous reaction speed is low.

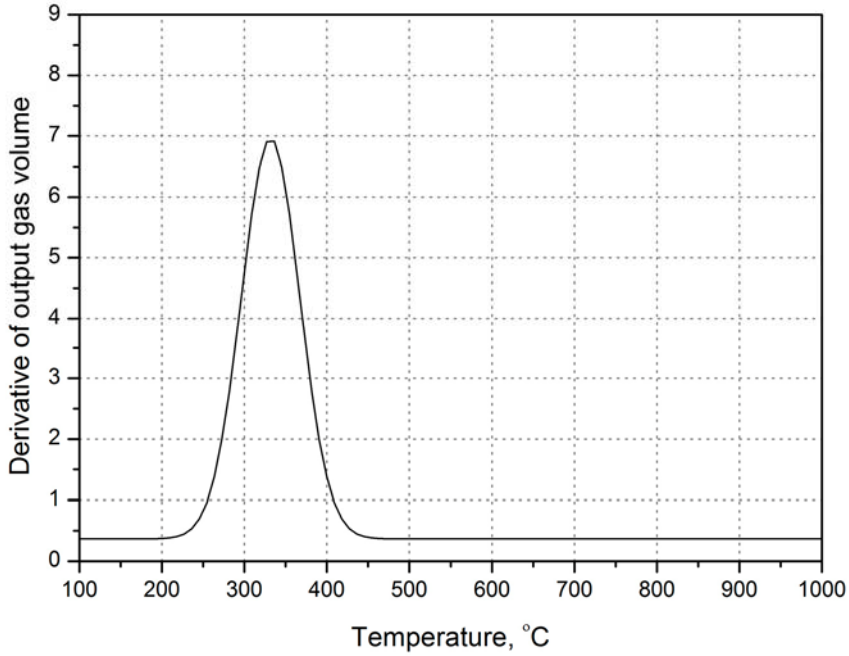

Figure 5: Derivative of output gas volume by homogeneous reactions

The pyrolysis volatiles consist of a condensable fraction and a noncondensable fraction. Chromatographic analysis shows that in the temperature range of 200-300 °C noncondensable fraction consists of a small amount of CO and CO_2 (Figure 6). Thus, it can be argued that due to heterogeneous reactions it takes place decomposition of mainly condensing fraction of the pyrolysis products.

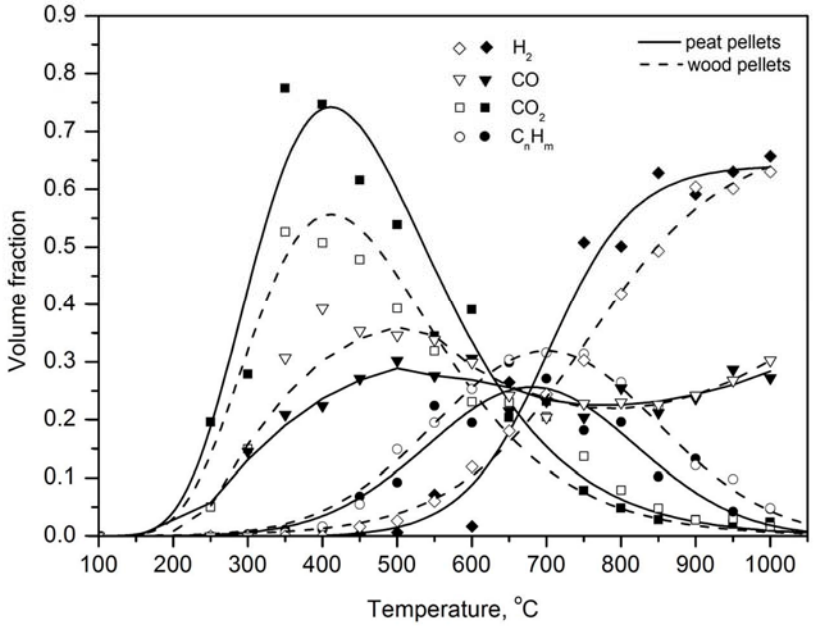

Figure 6: Noncondensable pyrolysis products yield for different kinds of biomass

Condensable products of pyrolysis 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). Water is the most stable component of the condensable fraction. We can therefore say that the main volume of gas generated by heterogeneous reactions in this case, was formed by the decomposition of water contained in the biomass.

4. Conclusions and future work

Due to homogenous and heterogeneous reactions of cracking the condensable and non-condensable pyrolysis products can be converted into gas.

In a case where mass of the charcoal filter is substantially less than the mass of the original biomass, pyrolysis tars heterogeneous cracking hardly occurs. Increase in volume of the gas obtained occurs by the heterogeneous cracking of low-temperature pyrolysis volatile products, in the first place, water.

Future work will be aimed at the study of the processes of heterogeneous cracking volatile with increased weight charcoal filter. There will be determine the optimum ratio of the amount of processed biomass and charcoal filter size for the complete decomposition of the pyrolysis products into synthesis gas.

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