Experimental investigations of the two-stage pyrolytic processing of pulp and paper industry wood waste

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Abstract. The article presents results of experimental investigations of the two-stage pyrolytic processing of pulp and paper industry wood waste into gas, which combines pyrolysis of raw material and subsequent high-temperature heterogeneous cracking of volatile pyrolysis products in a fixed bed of the coke residue of raw material. Dependence of specific gas yield, chemical composition, heating value and specific tar content on the cracking temperature are obtained. In different conversion modes the following gas characteristics were obtained: specific yield up to 1.5 m$^3$/kg, volumetric fraction of combustible components more than 92%, lower heating value 10.8–12.5 MJ/m$^3$, specific tar content 10–100 mg/m$^3$. The data obtained form the basis for calculating the energy and mass balance of pilot unit of the two-stage pyrolytic conversion of pulp and paper industry wood waste into gas.

1. Introduction
Interest in the use of biomass for energy purposes is caused by problems related to global climate change and the reduction of conventional fossil fuels reserves [1]. Wood and wood waste is one of the promising CO$_2$-neutral renewable energy sources. According to the Federal State Statistics Service in the Russian Federation over 2015 year the volume of waste from wood processing, production of wood products, pulp and paper production from publishing and printing activities gave 11.3 million tons. On the part of many woodworking, pulp and paper industry enterprises, there is a considerable interest in the implementation of ready technical solutions to produce energy-efficient utilization of both newly formed and accumulated in the dumps and storages wood waste. In the production of electricity by the wood biomass conversion into gaseous fuel for power generating units based on a gas piston internal combustion engine, the most effective and commercially viable method is gasification [2]. However, this technology has a number of significant drawbacks. Syngas obtained using air as a gasifier contains a large amount of nitrogen, which leads to a significant reduction in its lower heating value (LHV) to 3–6 MJ/m$^3$ and also contains a significant amount (0.1–100 g/m$^3$) of condensable organic compounds (so-called tars) [3]. Since there are rather stringent restrictions on the content of tars in gaseous fuels intended for use in internal combustion engines (10–100 mg/m$^3$), the need for gas cleaning and its high cost are the main obstacle to the widespread introduction of gasification technologies [4,5].

One of the methods for obtaining a relatively clean mid-calorific gas from wood biomass is a two-stage conversion combining pyrolysis and subsequent high-temperature heterogeneous
cracking of volatile products in a fixed bed of the coke residue of biomass. For the first time this method has been considered in [6]. The LHV of the resulting gas, consisting of not less than 90 vol % of hydrogen and carbon monoxide, is 10–12 MJ/m$^3$, and the efficiency of energy conversion of raw materials into gas reaches 86% [7]. The specific tar content does not exceed 50 mg/m$^3$ [8]. Gas does not contain condensable products (under normal conditions) and can be used without cleaning from tars both as fuel for internal combustion engines and burners [9] and as a raw material for the synthesis of liquid hydrocarbons [10, 11]. Compared with traditional pyrolysis of different types of biomass, the two-stage pyrolytic process is characterized by a much higher conversion efficiency of raw material into gaseous fuels [12].

2. Experimental setup
An experimental setup (figure 1) similar to that one from [13] was used. The upper and lower parts of the cylindrical retort 7 are independently heated by two electric furnaces 3 and 6 in the temperature range from room temperature to 1300 °C. The heating rate is set and controlled by a programmable electronic control system. A sample of the raw material is placed in bowl 2 (pyrolysis zone). Coke residue of raw material, ceramics or dolomite are placed in bowl 5 (cracking zone). The temperatures in the pyrolysis and cracking zones are measured by two chromel-alumel thermocouples 4 output to a digital electronic thermometer 9. Both bowls have a perforated bottom and are fixed to pipe 1, through which the retort is purged with argon before the start of the experiment, after which the tap 8 is closed. Gas, leaving the retort, enter the condenser 10. The liquid fraction is condensed, and the volume of non-condensing gases is measured by the gas volume meter 11.

The mass of the raw material subjected to pyrolysis in the lower bowl and mass of coke residue in the cracking zone in all experiments was 10 g. Moisture content of raw material in all experiments was 10 wt %. The temperature in the cracking zone was maintained constant throughout each experiment and was equal to 950, 1000 or 1050 °C. The coke residue of the raw materials was previously obtained at a temperature of 950, 1000 or 1050 °C respectively to cracking zone temperature.

Two types of wood waste were used in the experiments: birchwood chips and bark shown in figures 2(a) and 3(a) respectively, which characteristics are detailed in table 1. The chips particles have a length up to 30 mm, a width and a height up to 6 mm. The bark basically has
Figure 2. Wood chips (a) and its coke residue before (b) and after (c) the experiment.

Figure 3. Bark (a) and its coke residue before (b) and after (c) the experiment.

Table 1. Raw materials characteristics by dry state.

| Raw material | Ash (wt %) | Volatiles (wt %) | Heating value (MJ/kg) | Element composition (wt %) |
|--------------|------------|------------------|-----------------------|---------------------------|
|              |            |                  | Higher | Lower | C   | H   | N   | S   | O   |
| Chips        | 0.99       | 80.83            | 20.6   | 19.3  | 50.16| 6.24| 0.09| 0.85| 41.67|
| Bark         | 0.38       | 93.48            | 34.7   | 32.5  | 71.46| 9.95| 0.05| 0.00| 18.16|

the form of spirally twisted strips. The bark particles have a length and width up to 30 mm, a height up to 15 mm. Samples of the coke residue of raw materials shown in figures 2(b) and 3(b) respectively. During the experiments on the surface of coke residue located in the cracking zone pyrocarbon sedimentation occurred, which can be seen in figures 2(c) and 3(c) respectively. During the bark processing much more pyrocarbon is sedimented on the coke residue in the cracking reactor in comparison to wood chips processing because bark has very high volatile yield.

3. Results and discussion
Figure 4 shows dependences of the gas chemical composition (volume fractions of components) obtained from wood chips (a, c, e) and bark (b, d, f) at cracking temperature of 950 (a, b), 1000 (c, d) and 1050 °C (e, f) on the pyrolysis temperature.
Figure 4. Gas chemical composition at different cracking temperatures: (a) chips 950 °C; (b) bark 950 °C; (c) chips 1000 °C; (d) bark 1000 °C; (e) chips 1050 °C; (f) bark 1050 °C.
Figures 5 and 6 show the dependence of the specific gas yield and gas LHV obtained from wood chips (a) and bark (b) at cracking temperature of 950, 1000 and 1050 °C on the pyrolysis temperature. Lower heating value of the gas was calculated according to its chemical composition at a temperature of 20 °C:

\[ Q_{IV} = q_{IVH_2} X_{H_2} + q_{IVCO} X_{CO} + q_{IVCH_4} X_{CH_4}, \]

where \( q_{IVH_2} = 10.05 \text{ MJ/m}^3 \), \( q_{IVCO} = 11.76 \text{ MJ/m}^3 \), \( q_{IVCH_4} = 33.367 \text{ MJ/m}^3 \), \( X_{H_2} \), \( X_{CO} \) and \( X_{CH_4} \) are LHV and volume fractions of hydrogen, carbon monoxide and methane respectively. Figure 7 shows the dependence of the specific tar content in the gas on cracking temperature.
Figure 7. Specific tar content for chips (open squares) and bark (full squares) as a function of cracking temperatures.

In accordance with figure 4, both the CO\(_2\) content and the ratio of the volume fractions of H\(_2\) and CO decrease with the cracking temperature increasing. The specific gas yield increases along with the cracking temperature for both chips and bark, as it shown in figure 5. The most significant increase corresponds to the pyrolysis zone temperature range of 100–300 °C, in which the release of fuel and pyrogenic moisture occurs. A significant contribution to the specific gas yield rising make three reactions:

- the coke residue steam gasification reaction
  \[ C + H_2O = CO + H_2; \]  
  (2)
- the water gas shift reaction
  \[ CO + H_2O = CO_2 + H_2; \]  
  (3)
- the Boudouard’s reaction
  \[ C + CO_2 = 2CO. \]  
  (4)

Considering that reaction (2) is endothermic as well as reaction (3) is exothermic, it can be assumed that with the cracking temperature increasing the role of reaction (2) will increase and reaction (3) decrease. The reaction (4) also contributes to a significant increase of the gas yield with the cracking temperature increasing, because at a cracking temperatures of 950–1050 °C the equilibrium of this reaction is strongly biased towards the formation of carbon monoxide, which should lead to the gas volume doubling. Indirect evidence that reactions (2) and (4) in the cracking zone play an important role in the gas formation is the experimentally observed decrease in the mass of the coke residue in the upper bowl of the reactor.

The gas LHV is nearly constant for wood chips, as it shown in figure 6(a). Figure 6(b) shows that the pyrolysis temperature of above 450 °C is preferable for the bark processing due to producing the significant amount of methane (see figure 4), which contributes highly to the LHV increase in accordance with (1).

The tar content decreases with cracking temperature increasing, as it shown in figure 7, so that a higher cracking temperature is preferable for both wood chips and bark processing.

When comparing wood chips and bark, the bark is characterized by higher values of the volume fractions of H\(_2\) and CH\(_4\) and a lower value of the volume fraction of CO\(_2\) than chips. Proceeding from this, the bark is the more preferred type of raw material from the point of view of obtaining gas for chemical synthesis, for which a large ratio of volume fraction of H\(_2\) to
volume fraction of CO is required, and wood chips are the more preferred type of raw material in terms of producing gaseous fuels for internal combustion engines, for which a large volume fraction of CO is better. Also the gas produced from bark has higher LHV but contains more tar.

4. Conclusions

Experimental data characterizing the dependence of the specific yield of non-condensing gases, their chemical composition, the calculated value of the lower heating value and the specific content of tar on the processing parameters are presented. It is shown that the most optimal cracking temperature for wood chips and bark processing is 1050 °C. The advantages of this mode were observed for all gas characteristics:

- high specific gas yield up to 1.5 m$^3$/kg due to effective conversion of water steam;
- total volume fraction of combustible components more than 98%, low concentration of CO$_2$;
- high LHV up to 12.5 MJ/m$^3$;
- low specific tar content (less than 20 mg/m$^3$).

A brief analysis of changes of the gas characteristics depending upon the two-stage pyrolysis processing parameters is given.

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