Comparison of Charcoal, Ceramics and Dolomite as a Bed Material in Two-Stage Pyrolytic Processing of Wood Waste into the Synthesis Gas

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This document explains the advantages and disadvantages of three types of bed materials used in two-stage pyrolytic processing of wood waste into the synthesis gas. The process combines pyrolysis and subsequent high-temperature heterogeneous cracking of volatiles in the carbon residue fixed bed (obtained by raw material pyrolysis), the inert material (aluminum oxide ceramics) or dolomite. Experimental data characterising the dependence of the gas yield, its chemical composition, the calculated lower heating value and tar content on the process parameters are presented. The optimisation of parameters and the bed material mostly depends on the process purpose: a large-volume inert material bed is preferable for using in burners in the cracking zone, it allows to obtain the most calorific gas with a lower calorific value up to 13 MJ / m^3; whereas a carbon residue at a temperature of above 1,010 °C is a preferable bed material in gas engines (when the tar content is less than 50 mg/m^3); and a carbon residue at a temperature less than 1,000 °C is the best for the synthesis of liquid fuels (H$_2$ to CO ratio reaching its maximum). Using dolomite turned up to be impractical because of its thermal instability and high amount of both CO$_2$ and H$_2$O in the gas product.

1. Introduction

Pulp and paper industry is the source of a huge amount of wood waste. According to the Federal State Statistics Service, the amount of waste from pulp and paper production was up to 5,545.6 kt in the Russian Federation over 2017 year and its processing is not carried out completely (Formation …, 2019). In the worst case, the waste is simply dumped near the factory forming piles of bark and wood chips. Due to the exothermic processes in the layer of moist biomass, fires are frequent and accompanied by release and emission of pollutants into the environment. Meanwhile, the wood waste energy potential can be transformed into the thermal and electric energy, as well as liquid products such as methanol, dimethyl ether (DME), biofuels, aromatic hydrocarbons, etc. Paper factories show their interest in development of the biomass processing devices providing additional financial benefit from efficiently and environmentally safe recycling. This is another step towards the climate change problem solving, and making a cost-effective changeover from fossil fuels to the local renewables such a wood waste.

We can distinguish two main groups of methods used for wood waste energy recycling. The first is based on the combination of the waste incineration followed by the Rankine cycle with water or an organic fluid (ORC). The second is based on the thermochemical processing of waste into a liquid or gaseous energy carrier, which is further used in power generation units. Gasification can be considered a better solution for the electricity production comparing with the ORC technology, because it offers notably higher power-to-heat ratio, in spite of higher technology-related cost (Rentizelas et al., 2009). The gasification appears to be the most commercially attractive and viable technology for the production of a fuel suitable for spark ignition gas engines (McKendry, 2002). Syngas, produced via using air as a gasifier agent, contains a large amount of nitrogen, that leads to reduction in its lower heating value (LHV) down to 3–6.5 MJ/m^3 (Basu, 2010). The use of such a low-calorific gas leads to decreasing of nominal power capacity and efficiency of internal combustion engines. Syngas also

contains a significant amount (about 50 to 500 mg/m^3) of tar (Martinez et al., 2012). Tar content in gaseous fuels used in internal combustion engines must be strictly limited to a value of 10 to 100 mg/m^3 (Thapa et al., 2017). High cost of gas cleaning is the main impediment to the widespread introduction of gasification technologies (Singh et al., 2014).

The main disadvantage of the traditional slow biomass pyrolysis is a low energy conversion degree of raw material into gas due to formation of a liquid fraction. An increasing of the pyrolytic processing efficiency can be achieved by conversion of a liquid fraction into additional amount of gas for which both catalytic and non-catalytic methods are applied (Makwana et al., 2018). Among such devices the special air-steam gasifiers with a pre-pyrolysis such as "Viking" (Heidenreich, 2015) can be mentioned; they provide very low tar content, but syngas remains low-calorific. The two-stage pyrolytic conversion method, that combines pyrolysis and subsequent high-temperature cracking of volatiles in a fixed charcoal bed, provides a high degree of the raw material energy conversion into synthesis gas with LHV of 10–12 MJ/m^3 and at least 90 vol. % of hydrogen and carbon monoxide in a ratio of 1:1 to 2:1, depending on the raw material type and process parameters (Lavrenov et al., 2016). It can also be used for methanol, DME and biofuels catalytic synthesis (Kachalov et al., 2016). Another advantage of the process is its cheapness comparing with oxygen or steam gasification.

The article covers the two-stage pyrolytic processing of pulp and paper industry waste (wood chips and bark) into the synthesis gas. Three types of bed material were selected for comparison: carbon residue of raw material, an inert material (aluminum oxide ceramics) and dolomite. Carbon residue was selected because it is formed by quantities during the pyrolysis of raw materials as a by-product and its further use as a bed material seems obvious from a technological and economic points of view. It has a relatively large surface area which increases reaction velocity. Carbon residue works as both a reagent and a catalyst. Carbon, which forms its main part, actively interacts with water vapor and carbon dioxide. The inert material, used as a baseline to be compared with a carbon residue, works only as a catalyst. The use of inert material would lead to a sharp increase in the proportion of carbon dioxide, because the Boudouard reaction ($C + CO_2 = 2CO$) does not proceed in the absence of free carbon. Dolomite as a bed material was chosen in order to reduce the amount of CO_2 by another mechanism comparing with the Boudouard reaction. Dolomite was subjected to decarbonisation before the experiment. During the experiment the reverse process was expected, accompanied by the partial CO_2 absorption in a reaction of the calcium carbonate formation $CaO + CO_2 = CaCO_3$. A number of articles consider this process; although they discuss different types of biomass, only one type of bed material for cracking zone was used – charcoal (carbon residue of raw material). The novelty of this work is a close comparison of the three widely available bed materials. Close comparison of the gas characteristics (gas yield, its composition, calculated LHV and a tar content) is made for the same process parameters, which allows to get a clear picture of the feasibility of using each of these materials for a specific purpose. The practical value of the article is a recommendation for the bed material and temperature choice in the design of wood waste processing devices.

2. Experimental setup and materials

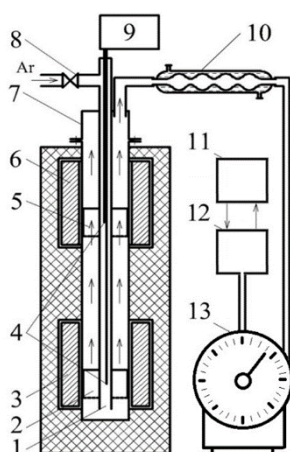The experiments performed in an experimental setup are presented in Figure 1.

Figure 1: Experimental setup (1 – tube, 2, 5 – perforated bowls, 3, 6 – electric furnaces, 4 – thermocouples, 7 – retort, 8 – valve, 9 – thermometer, 10 – condenser, 11 – gas analyser, 12 – gas holder, 13 – volume meter)

The upper and lower parts of the cylindrical retort 7 were equipped with electric furnaces 3 and 6. Retort is the steel tube with an inside diameter of 37 mm. Two bowls with a perforated bottom were placed on the tube 1 inside the retort before the experiment, the bowl 2 (pyrolysis zone) was filled with the raw material and the bowl 5 (cracking zone) was filled with the carbon residue of raw material, inert material (ceramics) or dolomite. Then, the retort was blown with argon through the tube 1. After that the valve 8 was closed. Then the cracking zone was heated to the temperature of 950, 1,000 or 1,050 °C, which remained stable during the experiment. After that the pyrolysis zone was heated up to a rate of 10 °C/min up to a temperature of 700 °C. The temperature in the bowls was measured by two chromel-alumel thermocouples 4, placed on a thermometer 9. The volatiles from the pyrolysis zone moved through the cracking zone. Then the gaseous products left the retort 7 and entered the condenser 10. After separating the condensing fraction (at 0 °C), the amount of non-condensable gases was measured by a gas meter 13 ("RG7000"). Non-condensable gases entered the gas holder 12, and their chemical composition was measured by a flow gas analyser 11 ("MRU Vario Industrial "Syngas").

Birch chips and bark taken from the pulp and paper mill (Perm, Russia) was used as the raw material. Chips were the shredded stem wood. The wood chips had a length of up to 30 mm, a width and a height of up to 6 mm. The bark, also birch, mainly had the form of spirally twisted strips. Bark particles had a length and a width of 30 mm, a height of 15 mm. The moisture content of the raw material samples was controlled by the "Ohaus MB45" moisture analyser and was at average 10 wt. % in all the experiments. The weight of the sample was 10 g in all the experiments. Table 1 describes the characteristics of dry-weighed raw materials. The ash and volatile content measurements were carried out on a thermogravimetric analyser "TA Instruments SDT Q600", the elemental analysis was carried out on the "Elementar Vario MACRO Cube" element analyser (the oxygen mass fraction was calculated as a residue), the LHV was calculated using the Mendeleyev formula:

$$Q_i^r = 4.18 \cdot 10^{-3} \cdot [81 \cdot x_C^r + 246 \cdot x_H^r - 26 \cdot (x_O^r + x_S^r)] \tag{1}$$

where x_C^r, x_H^r, x_O^r, and x_S^r are the content of carbon, hydrogen, oxygen, and sulfur in the raw material expressed as wt. %, Q_i^r is expressed as MJ/kg.

Table 1: Dry-weighed raw materials characteristics

Raw material type	Ash, wt. %	Volatiles, wt. %	LHV, MJ/kg	Element composition, wt. %				
				C^d	H^d	N^d	S^d	O^d
Chips	1.00	80.83	19.0	50.16	6.24	0.09	0.85	41.66
Bark	0.38	93.48	32.5	71.46	9.95	0.05	0.00	18.16

Carbon residue of raw material (CR), aluminum oxide ceramics (Cer.) and dolomite (Dol.) were used as bed materials. Carbon residue was preliminary produced by the raw material pyrolysis at a temperature of 950, 1,000 or 1,050 °C. The ceramic particles had the form of beads, with the particle size of 5 mm. Dolomite particle size was at average 0.1–0.2 mm. The total percentage of calcium and magnesium carbonates ($CaCO_3$ and $MgCO_3$) was not less than 80 wt. %. Dolomite preliminary preparation contained its decarbonisation by heating in argon at a temperature of 1,000 °C and subsequent screening of the dust fraction produced during heating. Volatiles conversion degree reaches its maximum when weight ratio of CR to raw material is 0.5–0.6 or more (Kosov et al., 2015). The CR weight was 10 g in all experiments which is equal to raw material weight. The weight of ceramics and dolomite was the same, except two experiments with ceramics. The temperature in the cracking zone remained stable to 950, 1,000 or 1,050 °C for the CR and 1,000 °C for both ceramics and dolomite.

3. Results and discussion

During the decomposition of high molecular organic compounds in the cracking process, pyrocarbon was precipitated on the surface of bed material. It increased noteworthy when bark was used as a raw material. This led to a significant decrease in the surface area of open pores, which was 272 and 31 m^2/g for CR of chips and bark before the experiment, and after the experiment – 14 and 13 m^2/g respectively. Measurements of the specific surface were made on the "Sorbi-M" analyser. On the contrary, a pyrocarbon covering the surface of the ceramic beads and the dolomite particles made it capable of interacting with water vapor and carbon dioxide. Figure 2 shows the specific gas yield dependence on the pyrolysis and cracking temperatures and the bed material type. The specific yield of non-condensable gases increased with a temperature rising in the pyrolysis and cracking zones. Two carbon reactions had a great influence on the gas yield increasing:

- the gasification of carbon with steam: $C + H_2O = CO + H_2$,
- the Boudouard reaction: $C + CO_2 = 2CO$.

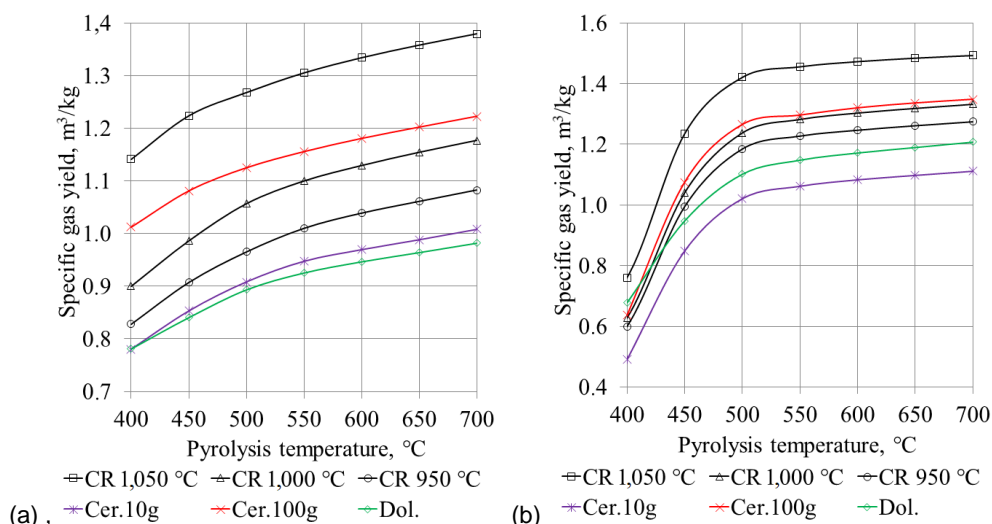The reaction of methane and water vapor ($CH_4 + H_2O = CO + 3H_2$) also increased the amount of gas.

Figure 2: Specific gas yield: a – chips, b – bark

While using ceramics of equal weight (10 g), a noticeable decrease in the specific gas yield was observed. It mainly occurred by two reasons. The first is an absence of the reactions with carbon shown above. The second is a characteristic time breakdown of interactions between volatiles and the bed material in the cracking zone. It occurred because of the bed volume decrease (bulk density of ceramics is about ten times greater than the bulk density of carbon residue of raw material). In order to assess the influence of the interaction time (of volatiles with the bed material in the cracking zone), experiments were carried out when the volume of the inert material was approximately equal to the volume of the carbon residue. In this case ceramics weight was ten times greater and up to 100 g. The experiments showed a recovery (and even a little increment) in the gas specific yield. It indicates that one of the most important parameters affecting the specific gas yield is the characteristic time of interaction of volatiles with the bed material. While using dolomite, low values of the specific gas yield were produced, comparing with the ones while using the inert material of the same weight. It confirmed the necessity of a sufficient time for interaction between volatiles and the bed material.

The data presented in Figure 2 is correlated with the results of the previous research (Lavrenov et al., 2016), obtained for different types of biomass with a charcoal used as a bed material at 1,000 °C in the cracking zone. The specific yield was from 1.0 m^3/kg for sewage sludge up to 1.3 m^3/kg for wood (at the pyrolysis temperature was up to 700 °C).

Elemental analysis of raw material and carbon residue showed that only a small part of the nitrogen passed into the gas fraction during pyrolysis. This part was equivalent to the percentage of the nitrogen fraction of about 0.2 % in the gas. On this premise the chemical gas composition was normalised. Table 2 describes the gas composition dependence on the cracking temperature and the bed material type for pyrolysis temperature of 700 °C. Table 2 also contains data on the specific moisture content.

Table 2: Gas chemical composition for pyrolysis temperature of 700°C

| Raw material type | Cracking temperature, °C | Bed material type | Bed material weight, g | Gas chemical composition, vol. % | | | | Moisture content, g/m^3 |
				H_2	CO	CH_4	CO_2	
Chips	950	Chips CR	10	52.0	43.4	2.8	1.6	7.8
	1,000	Chips CR	10	47.7	48.5	2.3	1.4	2.0
	1,000	Cer.	10	43.7	41.8	7.0	7.2	33.0
	1,000	Cer.	100	40.6	50.9	6.0	2.3	3.4
	1,000	Dol.	10	29.4	47.4	9.0	13.9	51.1
	1,050	Chips CR	10	36.4	60.5	1.8	1.1	0.5
Bark	950	Bark CR	10	59.9	30.7	8.4	0.8	8.5
	1,000	Bark CR	10	57.2	35.2	6.9	0.5	2.7
	1,000	Cer.	10	49.3	34.6	11.3	4.7	46.2
	1,000	Cer.	100	45.7	42.8	9.8	1.5	5.0
	1,000	Dol.	10	44.7	43.5	6.1	5.4	41.4
	1,050	Bark CR	10	48.9	44.9	5.6	0.4	0.7

The data presented in Table 2 show an increase of the carbon monoxide fraction and a proportional decrease of the hydrogen fraction with cracking temperature rising. This may be linked to the water gas shift reaction aimed towards the formation of carbon monoxide: $CO_2 + H_2 = CO + H_2O$.

A significant increase in fractions of CO_2 and CH_4 and decrease in the fraction of H_2 while using inert material and dolomite in comparison with the carbon residue is possibly related to both interaction time reduction and minimising the effect of the reactions with carbon. With the use of dolomite, the most significant decrease in the fraction of H_2 is observed, probably due to the disappearance of the mechanism of hydrogen formation from water steam ($C + H_2O = CO + H_2$, $C + CO_2 = 2CO$ and $CH_4 + H_2O = CO + 3H_2$). This was partly confirmed by the amount of moisture collected in the condenser that was much larger during the experiments with dolomite.

If we compare the chips and bark, we will find out that the bark is characterised by higher values of the fractions of H_2 and CH_4 and a lower fraction of CO_2, regardless of the bed material, so bark is more preferable from the viewpoint of using the subsequent synthesis of liquid fuels, as the volumetric ratio of H_2 to CO is increased up to 2. The gas LHV was measured according to its chemical composition using formula:

$$Q_{iV} = Q_{iV_{H_2}} \cdot X_{H_2} + Q_{iV_{CO}} \cdot X_{CO} + Q_{iV_{CH_4}} \cdot X_{CH_4}, \tag{2}$$

where $Q_{iV_{H_2}}$ = 10.05 MJ/m^3, $Q_{iV_{CO}}$ = 11.76 MJ/m^3, $Q_{iV_{CH_4}}$ = 33.367 MJ/m^3, X_{H_2}, X_{CO} and X_{CH_4} are fractions of hydrogen, carbon monoxide and methane respectively.

Figure 3 shows the gas LHV dependence on the pyrolysis and cracking temperatures and the bed material type.
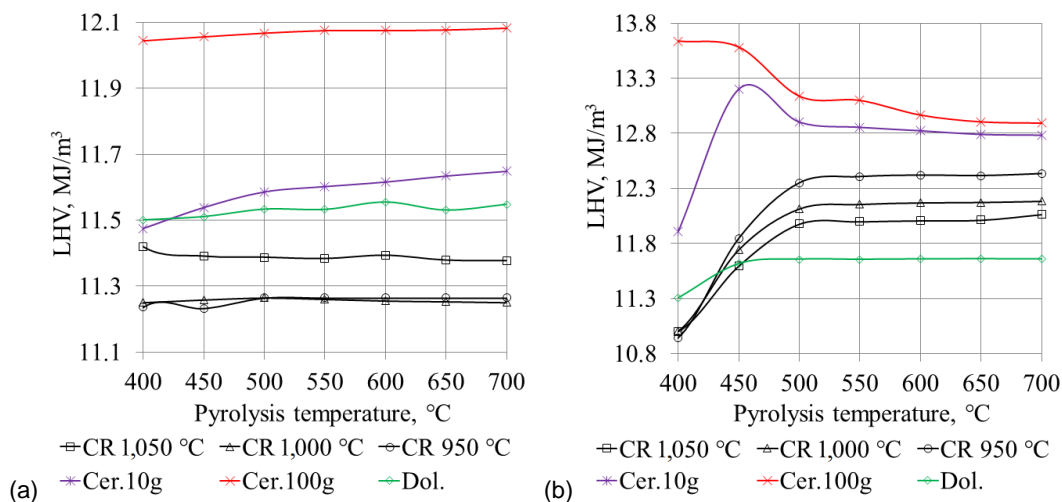

Figure 3: LHV gas: a – chips, b – bark

Figure 3 shows that the gas LHV slightly depends on the pyrolysis temperature in any mode. It is an advantage of the method: when the pyrolysis temperature changes, the gas composition does not. The use of inert material during the bark pyrolysis allows to obtain the highest LHV of about 13 MJ/m^3.

The data presented in Table 2 and Figure 3 are also correlated with the previous results (Lavrenov et al., 2016). The hydrogen to carbon monoxide volumetric ratio for woody materials was close to 1 (e.g. for wood chips) whilst for sewage sludge it was about 2 (e.g. for bark). It can be explained by the similarities in the elemental composition of sewage sludge and bark. Gas LHV ranges from 10 to 12 MJ/m^3.

Summarising the obtained results, it can be concluded that the choice of the optimum processing parameters and the bed material depends most on the purpose. For gas burners it is preferable to use a carbon residue or large-volume inert material layer. For gas engines – a carbon residue at high temperature (1,050 °C), inert material or dolomite. For a synthesis of liquid fuels – a carbon residue at low temperature (950 °C).

The tar content is one of the most important indicators characterising the ability of the gas to be used in internal combustion engines. For long-term engine operations the permissible specific tar content is less than 100 mg/m^3, but less than 50 mg/m^3 is more preferable (Thapa et al., 2017). The tar content measurement was carried out using the electronic balance "Mettler Toledo MS105-DU" by measuring the weight of the condenser before and after the experiment and after evaporating the condensed moisture at ambient temperature. Figure 4 shows the dependence of specific tar content on the cracking temperature and the bed material type.

The preferred tar content (less than 50 mg/m^3) is achieved for chips via using any type of bed material at a temperature above 1,000 °C and for bark via using only the carbon residue at a temperature above 1,010 °C.
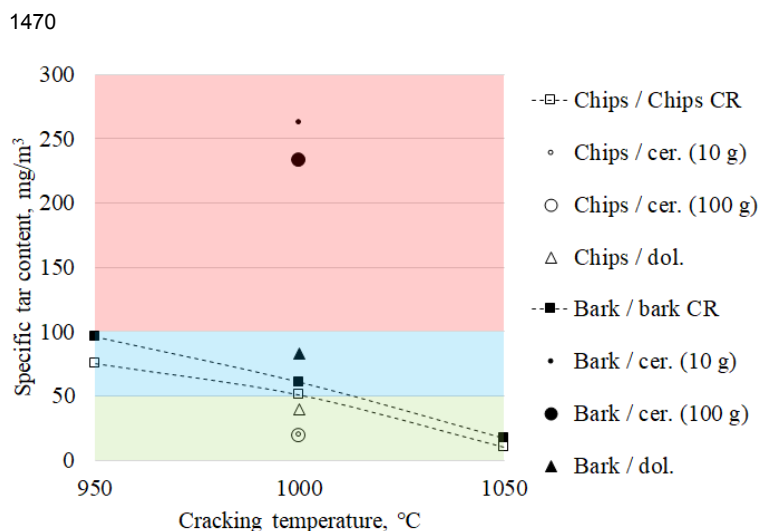
Figure 4: Specific tar content

4. Conclusions

With reference to the experimental data characterising the dependence of the gas specific yield, its chemical composition, the calculated value of the LHV and the specific tar content on the process parameters, it can be concluded that the optimum processing parameters and the bed material choice depend mostly on the purpose: it is preferable to use large-volume inert material for burners (LHV up to 13 MJ/m^3); for gas engines – a carbon residue of raw material at a temperature above 1,010 °C (tar content is less than 50 mg/m^3); for the synthesis of liquid fuels – a carbon residue at a temperature less than 1,000 °C (H_2 to CO ratio reaching its maximum). The use of inert material and dolomite is associated with considerable difficulties, such as thermal instability of dolomite at a temperature above 850 °C, the necessity for regeneration (due to pyrocarbon precipitation), high CO_2 concentration in the gas for inert material and high moisture content for dolomite. The carbon residue is the most convenient bed material considering its constant formation as a by-product during the pyrolysis.

Acknowledgments

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