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Catalytic Pyrolysis of Volatile Tars Contained in Gaseous Products of Fast Pyrolysis of Agricultural Waste

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The gases produced by fast pyrolysis method can be used as an alternative to fossil fuels. In order to use gaseous products of flash pyrolysis of carbon-containing biomass wastes effectively there is required its purification from resins. One of the promising ways of such purification is thermocatalytic conversion of tars with the production of volatile hydrocarbons. In current work thermocatalytic treatment of tar-containing gases obtained via biomass waste flash pyrolysis was studied. It was found that the use of zeolite catalysts on the base of iron subgroup metals leads to the decrease of tars content in the gaseous product of biomass fast pyrolysis as well as to the increase in C_1-C_4 hydrocarbons, hydrogen and carbon monoxide (II) concentration.

1. Introduction

Year after year the problem of biomass processing is becoming more urgent due to the competitive struggle for the conventional energy sources (Balat et al., 2009). It is noteworthy that the complexity and variability of the composition of one type of biomass do not allow solving the problems of effective complex processing of biomass (Huber et al., 2006).

The problems of biomass processing for energy production still have no solution on a full scale that is connected with the variety of biomass composition. The difficulties of biomass processing are also determined by the differences in physical chemical characteristics of biomass of different origin. The primary biomass sources are wood, vestures and marsh plants. The raw material composition can change depending on the parts of plants (bark, roots, and branches, stock), storage conditions and biomass harvesting methods. These factors can affect the initial humidity, ash content and as the result heat-generation.

The technologies of fast pyrolysis are applied to pyrofuel production, however taking into account its low operating ability (high oxygen content and corrosion activity) it is necessary to search for the new technological solutions. The most important advantages of the fast pyrolysis are: continuous cycle of the process, automation and high level of the process management, high yields of gaseous and liquid products, and low probability of the secondary processes that decrease the quality of the obtained fuels.

The use of catalysts in the organic source conversion process allows increasing of liquid and gaseous products yield as well as increasing of concentration of aromatic compounds and branched hydrocarbons in liquid pyrolysis fraction. Catalytic pyrolysis causes a significant interest all over the world because the use of catalysts promotes the growth of the effectiveness of organic compounds processing (Huber et al., 2006).

Products obtained by catalytic pyrolysis have much more narrow range of the molecular mass distribution in comparison with non-catalytic process. So these products carry the higher quality and can be used as the transportation fuels, it is an important benefit of catalysts application in the waste pyrolysis process.

To generate electrical energy from plant-based biomass waste the fast pyrolysis technologies focused on the increase of the conversion of the initial raw material to the combustible gases with high heat value and low resin content are more preferable (Dickerson et al., 2013).

Thermocatalytic refining of gaseous products of pyrolysis is one of the technological methods focused on the decrease of the content of high-boiling fractions and tars. The gaseous products of the pyrolysis flow through

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the catalyst layer that result in the thermal destruction of high-boiling components and tars. The significant amount of gaseous hydrocarbons form in the thermocatalytic destruction of pyrolysis gases tars. They increase the “working” combustion heat of the pyrolysis gaseous products.

The disadvantages of most catalysts of gaseous products thermal refining from the tars are their high cost and fast activity loss due to the carbon formed on their surface (Milne et al., 1998). So it is necessary to develop cheap and effective catalysts for the thermal refining of pyrolysis gaseous products. Therefore the study of the fast pyrolysis process including the stage of thermocatalytic refining of pyrolysis gaseous products can help solve the problems of renewable feedstock processing with the energy generation followed. Therefore the study of the fast pyrolysis process including the stage of thermocatalytic refining of pyrolysis gaseous products can help solve the problems of renewable feedstock processing with the energy generation followed.

2. Experimental

Biomass waste such as flax shive, husks of sunflower seeds and hazelnut shell were chosen as substrates for fast pyrolysis process investigation. To study the influence of biomass particle size on the process rate and gaseous product composition the grading fractions 0.1, 0.5, 1, 1.5 and 2 mm were used.

The investigation of the thermal stability of biomass samples was carried out by thermogravimetric analysis method. Thermogravimetric analysis was performed on the thermoanalyser NETZSCH 2000. The samples were heated at a constant rate (10 ºC/min) under nitrogen in the temperature range 50 - 600 °C.

The study of the biomass fast pyrolysis involving the choice of the most active metal-containing aluminosilicate catalyst of thermal refining of gases from the tars was conducted using the laboratory - scale plant shown in Figure 1.

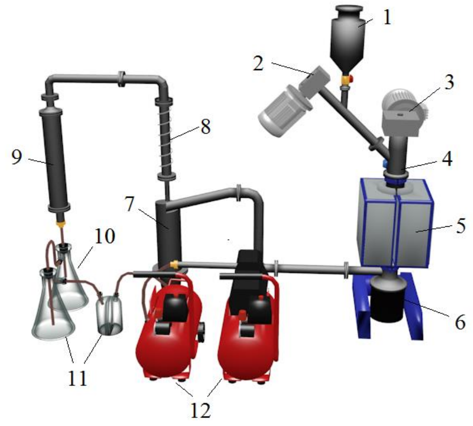

Figure 1: Experimental setup for the biomass waste fast pyrolysis process

The biomass waste was loaded into the batch hopper 1. The feedstock supply and its residence time in the hot region of the reactor 4 were controlled by feeding warm 2 and 3. The residence time of the feedstock in the hot region of the reactor was less than 5 seconds. The temperature of the electric furnace 5 that heated the reactor of fast pyrolysis varied in the range 450 - 650 °C.

The biomass fast pyrolysis process was carried out under inert atmosphere (nitrogen). The solid carbon residue of fast pyrolysis accumulated in discharge hopper 6. The formed gaseous products were purified from the dust in cyclone 7 and refined from the resins and high-boiling fractions in the catalytic column 8. To estimate the catalytic activity the sample collection was conducted before and after catalytic column 8. Then the volatile products passed through condenser 9 and the condensed liquid fraction of pyrolysis products was collected in flask 10. After that the gaseous products passed through refining system 11. The refined gases were collected in the gas collection system 12.

The feedstock mass loaded into the reactor was 500 g. The total time of the experiment was 30 min.

To estimate the rate of thermodestruction of initial source in the presence of the catalysts the rate of gaseous products evolution was controlled during the experiment.

The gaseous products analysis was performed by the gas chromatography method. The analysis of the fast pyrolysis gaseous products consisted of C_1-C_4 hydrocarbon, carbon oxides and hydrogen content definition, as well as the express analysis of the lower specific heat value. The chromatographic analysis of the gaseous products was performed on the base of chromatograph “Kristallux” 4000M and modified chromatograph “Gasochrom 2000”.

3. Results and Discussion

The various parameters affect the conversion of the feedstock. The temperature setting of the process is one of the most important ones. The thermal stability of the biomass samples were studied by the differential thermal analysis (Figure 2).

In Figure 2 it is shown that for the studied samples there is a weight loss peak in the temperature range 80 - 180 °C, which characterizes the dehydration process. The low-resolute peaks with the significant weight loss in the temperature range 210 - 450 °C account for the thermal destruction of biomass components – hemicellulose, cellulose and lignin respectively (Wild et al., 2011).

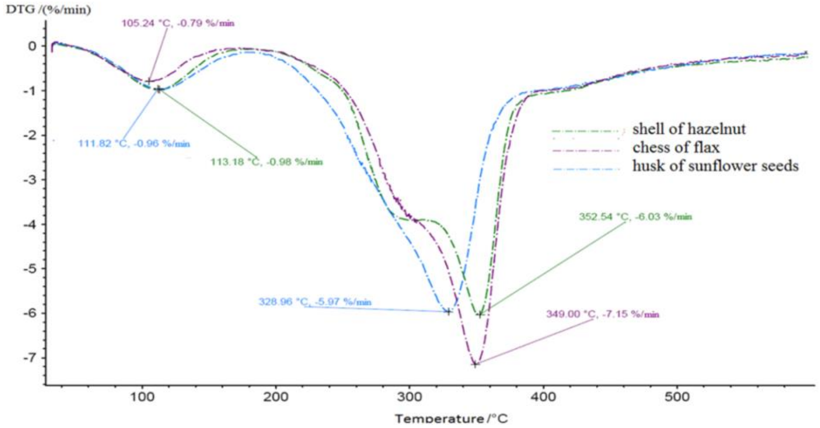

Figure 2: DTG data of the samples of the plant waste in the temperature range 50 - 600 °C

As the heating time of the feedstock in the fast pyrolysis process is short, the higher temperature range 450 - 650 °C was chosen for the study to reach the higher conversion of the feedstock.

The temperature range of the process is one of the major parameter determinative the mass distribution of the pyrolysis products. The increase of temperature leads the increase of gaseous and liquid products mass. However while temperature is increasing the cost of the process is also increasing, that leads the increase of prime cost of the final product.

The influence of the fast pyrolysis temperature on the biomass waste conversion was studied using the experimental set-up in the range 450-650 °C with the 1 mm feedstock fraction.

Beside the temperature such factors as residence time of the feedstock in the hot region of the reactor and the particle size of the processed material affect the feedstock conversion during the fast pyrolysis (Figures 3, 4).

According to Figure 4 the increase in the substrate heating time over 2 seconds is unfavorable. It leads to the increase in the energy costs of the feedstock processing and promotes the secondary reaction flow negatively affecting the energy supplies quality. The optimal feedstock particle size for the studied types of biomass is about 1 mm due to the increase of energy demand for the process conduction at higher disruption.

The dependence of flax shive conversion on the fast pyrolysis temperature is shown on Figure 5.

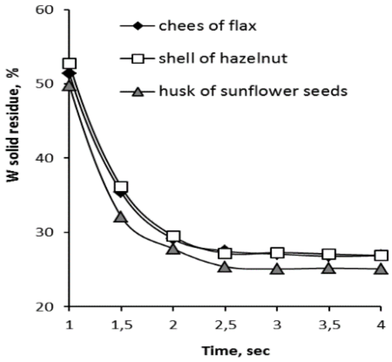

Figure 3: The solid residue weight percentage dependence on the residence time in the fast pyrolysis reactor (d~0.5 mm)

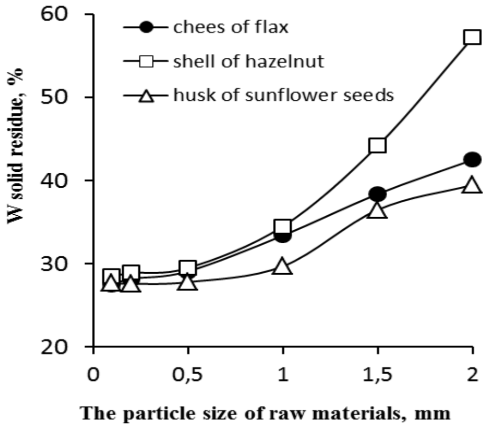

Figure 4: The solid residue weight percentage dependence on a particle size (T = 600 ºC; t = 2 s.)

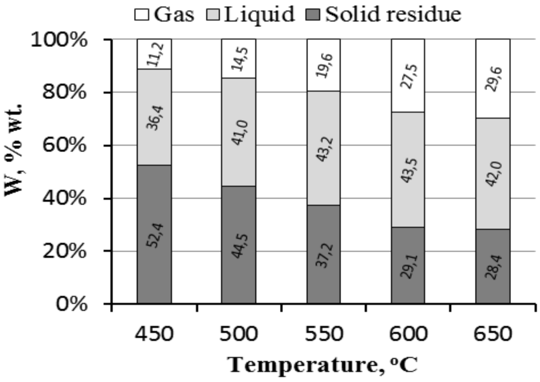

Figure 5: The flax shive conversion dependence on the fast pyrolysis temperature (2 s)

The optimal temperature of fast pyrolysis was 600 °C. The further temperature rise does not lead to the increase of the gaseous and liquid products yield and decreases the heat value of the obtained combustible gas due to the increase of the yield of low molecular weight gases – hydrogen and carbon monoxide (II).

The similar dependence of the feedstock conversion on the process temperature was obtained in the case of hazelnut shell and sunflower seed husk.

Table 1 shows the dependence of the heat value of the gases obtained on flax shives pyrolysis process temperature. The experiments showed that the highest heat of combustion (17.14 MJ/m^3) was reached at 600 °C.

Table 1: Influence of pyrolysis temperature on heat of combustion of gaseous mixture

Temperature, °C	450	500	550	600	650
Heat of combustion, MJ/m^3	15.07	15.78	16.43	17.14	15.82

C_1-C_4 hydrocarbons content of the gaseous products obtained in the pyrolysis of flax shive is shown on Figure 6. The gaseous product heat value is determined by methane and ethane content (Figure 6), therefore the form and the character of the curves of C_1-C_4 hydrocarbons concentration change agree well with the data on the kinetics of the gaseous product heat value. However it is noteworthy that the pyrolysis gases contain a considerable amount of resins that interfere with the effective use of such gases as a source of energy.

The tars content much depends on the process conditions and the reactor construction, type and moisture of the feedstock, as well as on the refining system of the pyrolysis gases. In this research the gas refining from the resins was carried out by thermocatalytic method. To do this the pyrolysis gases flowed through the heated layer of alumosilicate catalyst impregnated by iron subgroup metal of various concentrations. The dependence of the pyrolysis gas resins amount on the iron subgroup metal supported on zeolite H-ZSM-5 is shown in Figure 7.

As it is shown in Figure 7, the use of zeolite catalysts leads to the decrease in the tars amount in a pyrolysis gas. The most active catalyst of the tars degradation in a pyrolysis gas for all the types of the studied feedstock is Co-containing catalyst. It was found that catalyst-substrate mass ratio, granules size and surface metal concentration affect the catalyst activity.

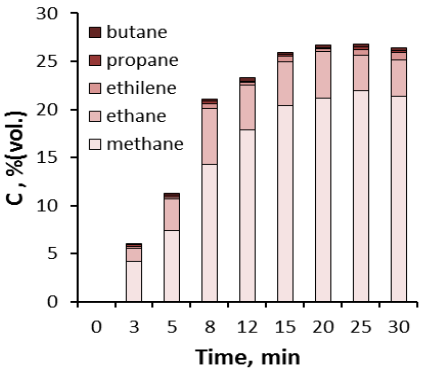

Figure 6: C_1-C_4 gaseous hydrocarbons content dependence on the process time (T=600 °C, flax shive, t=2 s, d~1 mm)

The experiments showed that for the full removal of the tars from a combustible gas the mass ratio of alumosilicate catalyst-feedstock must be more than 1:20 by weight. The optimal catalyst granule size is chosen depending on the unit capacity according to the gaseous product formation and the system pressure. In the present research the optimal granule size was 1 mm.

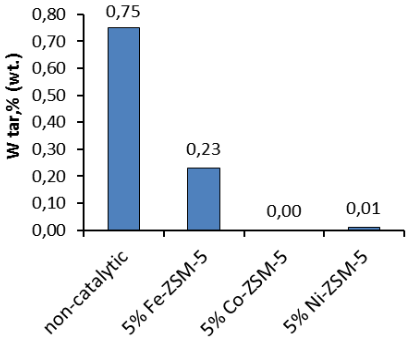

Figure 7: The concentration of the resins in the gas for different zeolite catalysts

The use of metal-containing alumosilicate catalyst in the pyrolysis gas refining from the tars results in the change of the gas volume and heat value. The use of the studied zeolite catalysts containing the iron subgroup metals leads to the change in the concentration of hydrogen, C_1-C_4 hydrocarbons and carbon oxides.

The concentration of metal on the surface of the alumosilicate catalyst strongly affects the catalyst activity in the thermodestruction process of a pyrolysis gas tars. The gaseous product composition in dependence to the type and concentration of the metal on the catalyst surface is shown in Figures 7 and 8. In comparison with a non-catalytic process the volume concentration of C_1-C_4 hydrocarbons increases by 1.39; 1.66 and 1.52 times using Fe-containing, Co-containing and Ni-containing alumosilicate catalysts respectively (Figure 8).

The use of the catalysts also results in the increase in hydrogen concentration; moreover the growth of hydrogen concentration in a gaseous product increases from Fe to Ni. The increase in alumosilicate catalyst metal content also leads to the increase in hydrogen concentration that is caused by the dehydration reaction of pyrolysis organic products in the presence of iron subgroup metals. The growth of hydrogen concentration in a pyrolysis gas is accomponied by the increase in coke-formation on the catalyst surface, so the use of the catalysts with higher metal content is economically unfavorable.

The considerable effect of the studied catalysts on the pyrolysis gas composition can be explained both by the catalyst high activity in the thermodestruction process and thermal decomposition of high-boiling fractions of pyrolysis liquid products. According to the data on the gaseous product composition (Figure 9) the optimal Co content in the zeolite catalyst is 2 %wt.

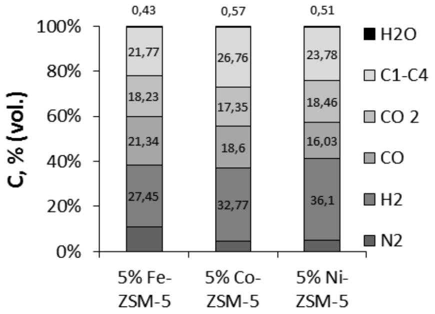

Figure 8: The pyrolysis gas composition dependence on the metal supported on H-ZSM-5

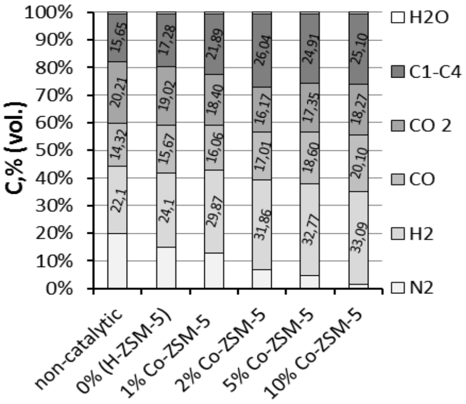

Figure 9: The dependence of pyrolysis gas composition on the metal concentration on the surface of ZSM-5

Such metal content in the catalyst allows increasing C_1-C_4 hydrocarbons concentration and removing the tars from the combustible gas of the fast pyrolysis of the studied types of biomass.

4. Summary

According to the data received the following conclusions can be made:

- The optimal temperature for the fast thermolysis treatment of flax shive, hazelnut shell, sunflower seed husk was about 600 °C;
- The optimal feedstock size was 1 mm at the residence time inside the reactor about 2 seconds;
- 2 % Co-ZSM-5 had the highest activity at the catalyst-substrate mass ratio 1:20;
- The use of zeolite catalysts on the base of iron subgroup metals leaded to the decrease of tars content in the thermolysis gas as well as to the increase C_1-C_4 hydrocarbons amount, hydrogen and carbon monoxide (II) concentration compared to non-catalytic process.

Acknowledgement

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