

Thermocatalytic Refining of Gaseous Products Produced by Fast Pyrolysis of Waste Plant Biomass

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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. 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 to solve the problems of renewable feedstock processing with the energy generation followed. 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 C₁-C₄ hydrocarbons, hydrogen and carbon monoxide (II) concentration.

1. Introduction

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 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 technologies of fast pyrolysis are applied to pyro fuel 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. (Tsai et al., 2007). The most important advantages of the fast pyrolysis are a 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.

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 tars content are more preferable. 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). 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 (Kosov and Zaichenko, 2014). Products obtained by catalytic pyrolysis have a much narrower range of the molecular mass distribution in comparison with the 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 (Balat et al., 2009).

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 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 (Dickerson and Soria, 2013). 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.

2. Experimental

The thermogravimetric analysis of feedstock of waste plant biomass (flax shive) and inorganic compositions of metals of Fe-subgroup was carrying out in the first stage of this study. The flax shive obtained after flax scutching was used as the raw material for the thermal destruction process. The flax shive samples were crushed with an electric mill and the fraction with drop size in the range of 0.045-0.1 mm was chosen. The initial humidity of flax shive was 5.48 % and the ash content was 4.16 %. To study the influence of iron subgroup metals chlorides on flax shive thermal destruction process the samples with 10% content of mineral compounds were prepared by trituration. The study of flax shive pyrolysis process kinetics was carried out using [thermoscales TG 209 F1](#) (NETZSCH) with different heating rate (5, 10, 15, 20 °C/min). The samples mass used in the thermogravimetric analysis was about 5 mg. The analysis conditions were the following: sample heating from 30 up to 600 °C with heating rate 5, 10, 15 or 20 °C/min and further holding up for 30 min at 600 °C. The analyses were carried out in argon at a gas rate of 20 mL/min.

The research of the thermocatalytic refining of gaseous products produced by fast pyrolysis was conducted using the laboratory-scale plant shown in Figure 1 (Kosivtsov et al., 2015).

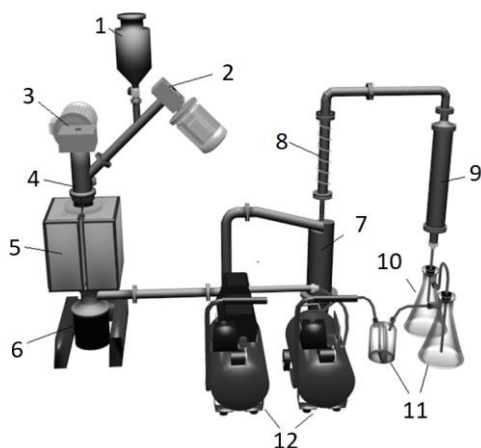


Figure 1: Experimental setup for the thermocatalytic refining of gaseous products

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 tars 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 biomass fast pyrolysis process was carried out under inert atmosphere (nitrogen). The feedstock mass loaded into the reactor was 500 g. The total time of the experiment was 30 min. To estimate the rate of thermal destruction of the 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 C₁-C₄ 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" 4000 M and modified chromatograph "Gasochrom 2000". The use of metal-containing aluminosilicate catalyst in the pyrolysis gas refining from the tars results in the change of the gas volume and heat value.

3. Results and discussion

To estimate the influence of iron subgroup metal chlorides on the flax shive thermal destruction process, thermogravimetric analysis of the individual mineral compounds was done (Figure 2). At a temperature of 500 °C, the decomposition of metal chlorides takes place that is proved by the significant weight loss of the samples. According to the thermal stability, the studied metal chlorides can be ranked in descending order: $\text{CoCl}_2 > \text{NiCl}_2 > \text{FeCl}_2$.

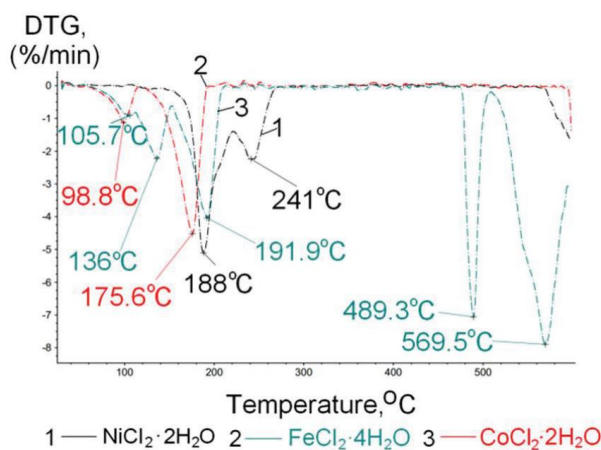


Figure 2: DTG curves of thermal decomposition of iron subgroup metal chlorides

The influence of iron subgroup metal chlorides on the flax shive thermal destruction process is shown in Figure 3.

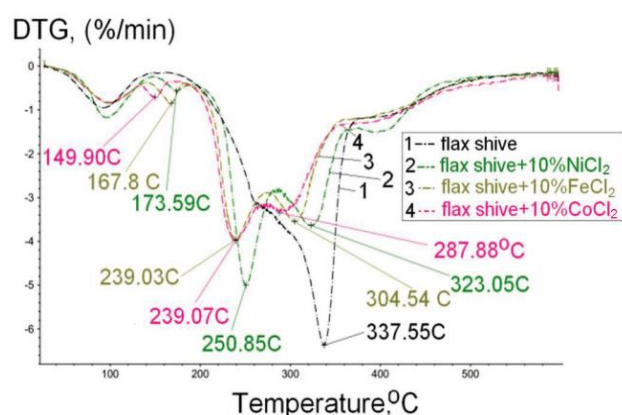


Figure 3: DTG curves of pure flax shive and the samples with the addition of iron subgroup metal chlorides

A higher destruction temperature was observed while using nickel chloride, but it is important to note the higher rate of the sample weight loss in comparison with the use of iron and cobalt chlorides. According to the influence on cellulose destruction temperature the studied metal chlorides can be ranged as follows: $\text{CoCl}_2 > \text{FeCl}_2 > \text{NiCl}_2$. Besides in spite of the decrease in the temperature of the flax shive cellulosic compound decomposition the use of iron subgroup metal chlorides led to the slight decrease in the destruction rate mainly due to the decrease in hemicelluloses decomposition temperature. According to the curves presented in Figure 3, it also can be noted the negligible decrease of destruction temperature of lignin which is a compound of flax shive while using both nickel and cobalt chloride. In the case of use of nickel chloride also the increase of lignin destruction rate was observed. As shown, results obtained in this study the Fe-subgroup metal influence on the pyrolysis process of flax shive, but the stage of recovery used salts from carbon residue increases cost of processing. As shown the obtained in this study dates the Fe-subgroup metals influence on the pyrolysis process of flax shive and decrease thermal stability of all components of waste biomass. Stage of recovery used salts from solid carbon residue increases the cost of processing, therefore in this study were used catalysts applied to avoid direct contact with the catalysts and used feedstock. Produced catalysts contact with volatile products

of fast pyrolysis of flax shive at high temperature and result in the rise of yield and heat of combustion of pyrolysis gas.

The technology of synthesis of zeolite catalyst includes impregnation of structure ZSM-5 by Fe-subgroup metals with next calcinations (Kosivtsov et al., 2016). ZSM-5 metal-containing catalysts used in present study depicted in Figure 4.

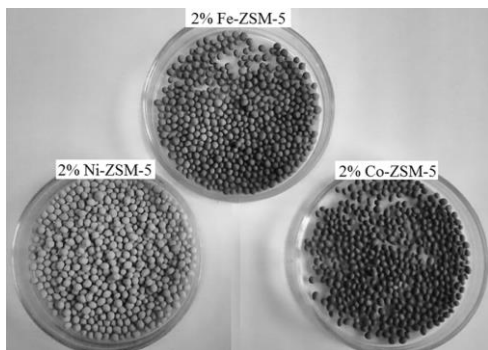


Figure 4: Samples of synthesized catalysts for thermocatalytic refining of gaseous products

The gaseous product heat value is determined by methane and ethane content (Figure 5), 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 the thermocatalytic method. To do this the pyrolysis gases flowed through the heated layer of aluminosilicate catalyst impregnated by iron subgroup metal of various concentrations. The dependence of the pyrolysis gas tars amount on the iron subgroup metal supported on zeolite H-ZSM-5 is shown in Figure 6.

As it is shown in Figure 6, 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 the Co-containing catalyst. It was found that catalyst-substrate mass ratio, granules size, and surface metal concentration affect the catalyst activity.

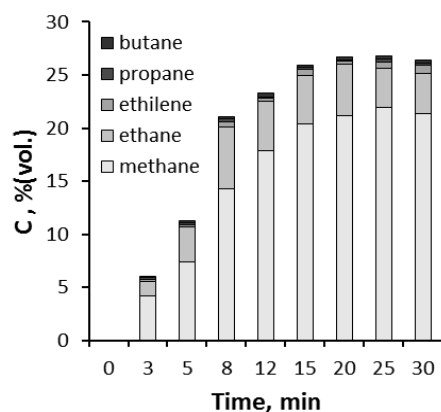


Figure 5: C_1 - C_4 gaseous hydrocarbons content dependence on the process time ($T=600$ °C, flax shive, $t=2$ s, $d\sim 1$ mm)

The experiments showed that for the full removal of the tars from a combustible gas the mass ratio of aluminosilicate 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.

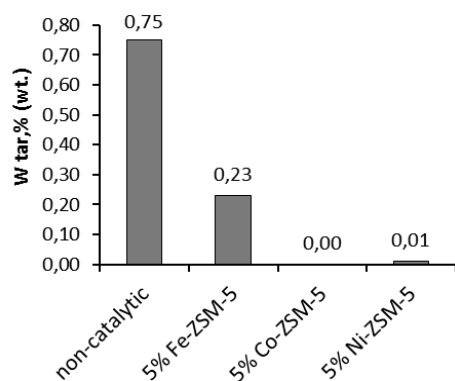


Figure 6: The concentration of the resins in the gas for different zeolite catalysts

The use of metal-containing aluminosilicate 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, C₁-C₄ hydrocarbons and carbon oxides.

Figure 7 shows the effect of metal type on the distribution of gaseous products. The concentration of C₁-C₄ hydrocarbons increases by 1.39; 1.66 and 1.52 times when using 5 % Fe-ZSM, 5 % Co-ZSM and 5 % Ni-ZSM catalysts respectively compared to a non-catalytic process. Hydrogen concentration also grows from Fe to Ni catalysts compared to a non-catalytic process.

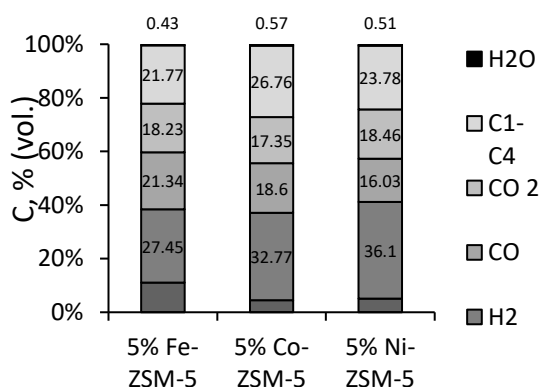


Figure 7: Influence of metal H-ZSM-5 supported catalysts on gas composition

The increase in aluminosilicate 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 accompanied 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 thermal destruction process and thermal decomposition of high-boiling fractions of pyrolysis liquid products.

The considerable effect of the studied catalysts on the pyrolysis gas composition can be explained both by the catalyst high activity in the thermal destruction process and thermal decomposition of high-boiling fractions of pyrolysis liquid products. According to the data on the gaseous product composition, the optimal Co content in the zeolite catalyst is 2 % (wt.). Such metal content in the catalyst allows increasing C₁-C₄ hydrocarbons concentration and removing the tars from the combustible gas of the fast pyrolysis of the studied types of biomass. The increase in aluminosilicate 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 accompanied by the increase in coke-formation on the catalyst surface, so the use of the catalysts with higher metal content is economically unfavorable.

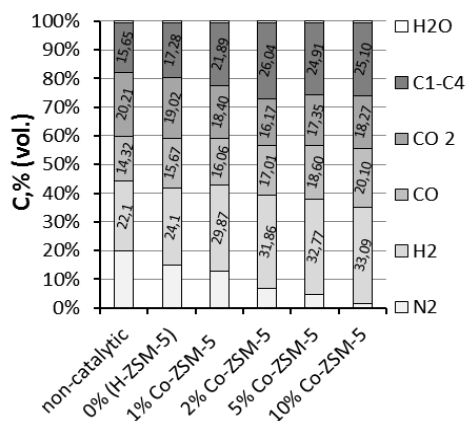


Figure 8: The dependence of pyrolysis gas composition on the metal concentration on the surface of ZSM-5

The influence of the studied catalysts on fast pyrolysis gas composition can be explained by the catalyst high activity during the high-temperature destruction processes and thermal decomposition of tars and high-boiling fractions of the pyrolysis liquid products. The catalysts studied also affect the carbon oxides (II) and (IV) yields. The use of zeolite catalysts on the base of iron subgroup metals led to the decrease in tars content in the pyrolysis gas as well as to the increase in C₁-C₄ hydrocarbons amount, hydrogen and carbon monoxide (II) concentration compared to non-catalytic process.

4. Summary

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

- the flax shive samples containing iron subgroup metal chlorides showed lower thermal stability;
- iron subgroup metal chlorides lead to the decrease in thermal stability of all the flax shive components (hemicelluloses, cellulose, and lignin);
- according to the influence on cellulose destruction temperature, the studied metal chlorides can be ranged as follows: CoCl₂ > FeCl₂ > NiCl₂;
- 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 led to the decrease of tars content in the -fast pyrolysis gas as well as to the increase C₁-C₄ hydrocarbons amount, hydrogen and carbon monoxide (II) concentration compared to non-catalytic process.

Acknowledgment

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