

Research Article

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A study of fast pyrolysis of plant biomass assisted by the conversion of volatile products using Fe(Co, Ni)/ZSM-5 catalysts

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Abstract: This paper discusses the study of plant waste thermocatalytic conversion. The dependence of the conversion of agricultural waste on the pyrolysis temperature, reaction time and feedstock particle size was determined. The optimal temperature of fast pyrolysis providing the highest yield of gaseous products (over 30 wt. %) for all types of waste plant biomass was found to be 700 °C. This temperature allows the lowest tar content in gases to be obtained. Further, ZSM-5 synthetic zeolites modified with iron subgroup metals were studied in the conversion of volatile products obtained by the fast pyrolysis of agricultural waste. It was found that the use of zeolite-based catalysts in the upgrading of gaseous products leads to a decrease in tar content and the increase in the volume concentration of C₁-C₄ hydrocarbons, CO, CO₂, and hydrogen in comparison with the non-catalytic process.

Keywords: fast pyrolysis; pyrolysis gas; tars; metal-containing catalysts; zeolites.

1 Introduction

Currently, the conversion of agricultural waste is an important issue. Methods that can process plant biomass residues allows the share of renewable feedstock in the process of energy generation to be increased, as well

as several environmental problems to be solved. In the Russian Federation [1] about 235 million tons of crop waste is generated annually, which corresponds to more than 80 million tons of fuel equivalent. Today, crop waste is not properly processed. Moreover, only a part of biomass waste (no more than 2 %) is used to generate energy [2].

According to experts, the use of agricultural waste for energy is recognized by Denmark, Sweden, Spain, Germany, Poland, Canada, the USA, China, etc. However, the impact of such feedstock in the total energy generation does not exceed 10 % [3]. In Russia, the collection and disposal of agricultural waste remain the main approach for its utilization. Another way that biomass is used in different countries is through to obtain thermal energy.

Pyrolysis based on the short heating time (no more than 30 seconds) of the feedstock, the so-called “fast” pyrolysis, is considered to be a promising direction of biomass processing [4-10]. The main advantages of fast pyrolysis are low tar content in volatile products due to the low probability of secondary processes; the ability to control the conversion to target products by adjusting the retention time of raw materials in the heating zone; the possibility of creating autonomous closed-loop mobile power plants operating continuously. It should be noted that the low quality of the resulting gaseous and liquid products is one of the main disadvantages of the fast pyrolysis method [11]. Currently, the use of catalysts in the pyrolysis process is one of the promising ways to improve the quality of liquid and gaseous fractions. The pyrolysis in the presence of catalysts causes a significant interest all over the world because the catalysts promote the growth of the effectiveness of organic compound conversion [12, 13]. Two main approaches are applied in this case. The first one is the direct introduction of the catalyst into the pyrolysis zone. Such a technique has problems, e.g. fast catalyst deactivation due to the coke formation on the catalyst surface, problems with the catalyst recycling and regeneration, high impact of the catalyst in the product composition which leads to the impossibility of the process

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Table 1: Characteristics of agricultural waste.

Type of agricultural waste	Moisture, %	Ash content, %	Calorific value Q_{H_2} , MJ / kg
Rye straw	6.48	6.40	16.30
Wheat straw	8.36	4.73	18.04
Oat straw	7.95	7.93	16.74
Corn leaves	4.75	2.21	17.14
Sunflower seed husk	5.14	3.27	18.68
Flax shive	8.05	1.21	17.24

control [14, 15]. The second way for the catalyst application in the pyrolysis is its removal from the pyrolysis zone. In this case, the catalyst is involved in the upgrading of the volatile products obtained by the thermal decomposition of the feedstock. Such an approach allows the pyrolysis product composition and quality to be improved, and the catalyst fast deactivation to be avoided [16,17].

Analysis of scientific literature and patent documentation show that a large number of chemical compounds exhibit a catalytic effect on various processes of conversion of organic raw materials at high temperatures. These compounds can be divided into the following groups: solid acid catalysts (zeolites (n-HZSM-5, HBeta, HMCM-41, HZSM-5, HY) and SiO_2 -aluminosilicates Al_2O_3) [18-20]; mesoporous catalysts (MCM-41, FSM-16, Al-SBA-15) [21, 22]; aluminum-containing clays [23, 24]; nanocrystalline zeolites [25, 26]; solid superacids [27]; gallosilicates [28]; metal oxides [29, 30]; salts of transition and rare earth metals [31-33].

Pyrolysis in the presence of zeolites can proceed through the deoxygenation caused by the simultaneous dehydration, decarboxylation, and decarbonylation. Thus, synthetic zeolites can be used for the conversion of oxidized organic compounds into hydrocarbons [18-24, 34]. Transition metals in the pyrolysis catalyze the dehydrogenation reactions as well as the cracking of the organic compounds [29-33]. Besides, the presence of the catalysts leads to the decrease in the apparent activation energies of the feedstock decomposition and, hence, to the decrease in the pyrolysis temperature.

As both the catalysts containing metals of the iron subgroup and the aluminosilicates exhibit high activity in the thermal degradation but have different catalytic behavior, their combination is of significant scientific and practical interest [35-39]. Such catalysts contain two different active sites and can significantly improve the

quality of the pyrolysis products. Therefore, in the current work, the influence of ZSM-5 synthetic zeolites modified with iron subgroup metals was studied in the conversion of volatile products obtained by the fast pyrolysis of agricultural waste of plant origin. Thus, the main goal of this work is the study of the zeolite-based catalyst influence on the process of fast pyrolysis of different agricultural wastes aimed at the production of highly purified gases for electrical (or thermal) energy generation.

2 Equipment and materials

2.1 Feedstock

Various types of plant biomass waste were used in this experimental work: flax shive, wheat straw, rye straw, oats straw, sunflower seed husk, and corn stalks. The initial characteristics of agricultural waste of plant origin are presented in Table 1. For the study, three fractions of agricultural waste particles (0.1-2 mm) were selected. In the work, the dependencies of the conversion of the studied agricultural waste types on the pyrolysis temperature, reaction time and feedstock particle size were determined in the process of fast pyrolysis in a laboratory setup in the temperature range of 500 – 750 °C. The retention time of the feedstock in the heating zone was varied from 1 to 20 seconds.

Studies of the comprehensive composition of agricultural waste of plant origin were performed according to the methods described in detail in [33]. The data of component and elemental composition of the selected waste is presented in Table 2.

2.2 Catalyst synthesis

Synthetic zeolites ZSM-5 modified with iron subgroup metals with a metal content of 1 to 10 wt. % were used as catalysts for the upgrad of pyrolysis volatile products. The catalysts were synthesized by the incipient impregnation of H-ZSM-5 zeolite (Sorbis Group, Hong Kong) with the aqueous solution of iron subgroup metal nitrates ($Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$, chemically grade, Reakhim, Russia) with the following calcination at 500 °C for five hours. Characteristics of the initial zeolite are presented in Table 3.

Table 2: The component and elemental composition of the selected types of biomass.

	Rye straw	Wheat straw	Oat straw	Corn leaves	Sunflower seed husk	Flax shive
Component composition, % (wt.)						
Hemicellulose	40.1	41.1	37.1	33.6	28.5	15.2
Cellulose	31.8	31.6	27.0	36.3	28.2	38.1
Lignin	10.5	9.8	15.4	16.9	29.6	27.7
Extractives	4.7	4.5	4.6	6.2	5.3	9.9
Elemental composition, % (wt.)						
C	44.1	41.6	43.7	45.6	45.8	46.9
H	5.0	4.8	5.3	5.6	4.5	5.7
N	0.4	0.6	0.5	0.5	0.5	0.6
O	37.5	39.7	34.6	41.3	40.7	37.5
S	0.1	0.2	0.1	0.0	0.1	0.1

Table 3: Characteristics of zeolite ZSM-5.

Indicators	Values
Type of particles	crystals
Particle size	1-10 μm
Crystallinity	85%
Specific surface area	560 m^2/g
Na_2O content	0.1%
$\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio	125

2.3 Experiments on the fast pyrolysis

In the investigation, the influence of pyrolysis temperature, the residence time of the feedstock particles in the heating zone, and the type of agricultural waste on the conversion and composition of gaseous products were studied. These experiments were performed using a laboratory setup which is shown in the image (see Figure 1).

In the typical experiment, a sample of feedstock was loaded into the loading device (1) with an electric low-speed mixer, which prevents the formation of bridging and ensures a uniform supply of biomass particles to the screw feeder. The speed of rotation of the screw feeder is controlled by a frequency controller connected to the gear motor (2). The rotational speed of the screw feeder determines the residence time of the raw material in the heating zone. The screw feeder is located inside the tubular pyrolysis reactor (3), which is heated using an induction furnace coil (4). Feedstock particles having been passed the heating zone enter the discharge hopper (5). Volatile pyrolysis products pass through a furnace for thermocatalytic cleaning (6) in which they interact with a

heated catalyst. Volatile products are collected in a flask (7) connected to a reflux condenser (8). Further, gaseous products pass through a water trap (9) and are collected in a eudiometer (10), where the volume of gaseous products of thermal destruction of agricultural waste is determined by the displaced volume of water. The experiment time was 30 minutes, with a sample weight of agricultural waste of 10 g.

The composition of the gaseous products of thermal degradation of agricultural waste was investigated using a complex of laboratory analytical support tools, which consists of the following devices: 1) chromatographic analyzer of the concentration of gaseous hydrocarbons in the gaseous medium, implemented on the basis of the Crystallux 4000M chromatograph; 2) analyzer of the lowest volume-specific heat of combustion of gaseous media; 3) analyzer of volumetric concentration of hydrogen in the gaseous medium; 4) chromatographic analyzer of the concentration of carbon oxides in the gaseous medium, implemented on the basis of the modified gas chromatograph Gasochrome 2000.

3 Results and discussions

The experiments on fast pyrolysis productivity were performed using different types of plant biomass waste. First, the influence of the feedstock particle size on the conversion of biomass and the yield of pyrolysis products was studied. The results of the experiments are presented in Table 4. The optimal feedstock size for the studied biomass (flax shive and sunflower seed husk)

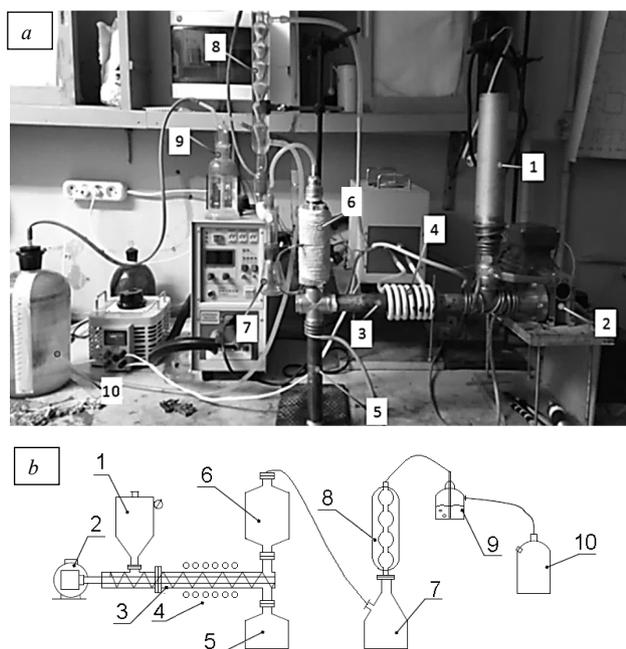


Figure 1: Laboratory installation (a) and the scheme of laboratory installation (b) for the study of thermal processing of agricultural waste of plant origin (1 – loading device; 2 – gear motor; 3 – tubular pyrolysis reactor; 4 – induction furnace coil; 5 – discharge hopper; 6 – furnace for thermocatalytic cleaning of volatile products of fast pyrolysis; 7–flask; 8–reflux condenser; 9– water trap; 10–eudiometer).

Table 4: Influence of feedstock particle size on the yield of the solid residue of fast pyrolysis (temperature - 700 °C, contact time - 4.4 s, particle fraction < 1 mm).

Particle size, mm	Solid residue yield, wt. %	
	Flax shive	Sunflower seed husk
0.1	27.5	27.7
0.2	28.2	27.6
0.5	29.1	27.8
1.0	33.4	29.7
1.5	38.4	36.5
2.0	42.5	39.5

was found to be below 1 mm. An increase in the size of the biomass fraction over 1 mm leads to an increase in the yield of pyrolysis solid residue and, hence, to the decrease in the feedstock conversion degree. This is due to the low thermal conductivity of the biomass and, thus, the complicated heat transfer from the surface of the particle to its center. When the biomass particle size was below 1 mm, no sufficient difference in the solid residue yield was

observed (in particular, for the sunflower seed husk, see Table 4).

To estimate the influence of plant biomass type on the fast pyrolysis productivity, the experiments were performed using rye straw, wheat straw, oat straw, flax shive, corn leaves, and sunflower seed husk with particle fraction below 1 mm at a temperature of 700 °C and retention time in the heating zone of 4.4 s. The results of the study are presented in Figure 2.

It should be noted that the studied types of agricultural waste have different thermal stability and, therefore, different yields of pyrolysis products. As it is known, the biomass components have a specified impact on the composition of pyrolysis products [40, 41]. Thus, the fast pyrolysis product distribution depending on the type of agricultural waste can be explained based on the data presented in Tables 1 and 2. It is seen that ash content has the highest impact on the solid residue yield. The highest char productivity (51.8 and 50.2 wt. %) was observed for rye straw and oat straw which have the highest ash content (see Table 2). On the other hand, the ash and char can catalyze the side reactions of vapor product cracking [42, 43], which explains the high yield of gases for these types of waste. A comparatively high amount of char produced by the fast pyrolysis of flax shive can be related to the high lignin content in the feedstock. This waste also showed a high yield of gaseous products which can be connected with the high moisture content that led to the behavior of syn-gas formation by the interaction between water and carbon residue. The feedstock with the high content of cellulose and hemicelluloses (i.e. wheat straw) resulted in the formation of high liquid yields. A significant lignin amount was found to lead to the formation of tars in the gaseous and liquid products due to the lower depolymerization degree. Based on the result analysis, the oat straw, as one of the most heat-resistant wastes, was chosen for further experiments.

The temperature influence on the pyrolysis product yields was studied at a temperature range of 500-750 °C. The temperature dependence of the yield of products of fast pyrolysis of oat straw (particle fraction below 1 mm, retention time in the heating zone of 4.4 s) is presented in Figure 3. According to the experimental data, an increase in the process temperature leads to an understandable increase in the yield of gaseous pyrolysis products, which is associated with an increase in the depth of thermal decomposition. Moreover, the higher pyrolysis temperature causes the side cracking reactions of vapor liquids as well as the acceleration of the water-gas-shift process leading to the highest yield of syn-gas [43]. Meanwhile, the temperature increase leads to an increase

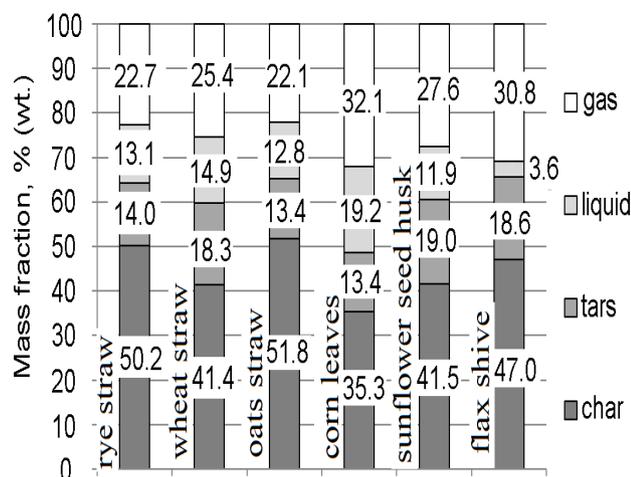


Figure 2: Influence of the agricultural waste type on the productivity of fast pyrolysis (temperature - 700 °C, contact time - 4.4 s, particle fraction < 1 mm).

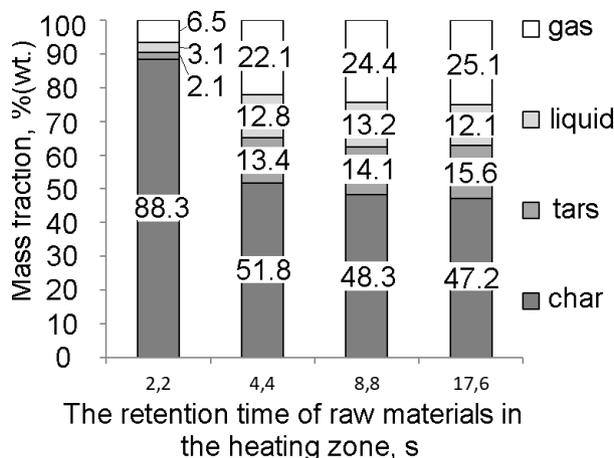


Figure 4: Influence of the retention time in the heating zone on the productivity of fast pyrolysis (temperature - 700 °C, particle fraction < 1 mm).

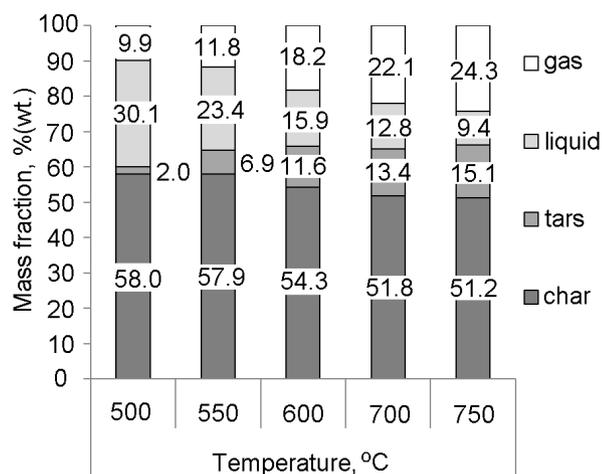


Figure 3: Influence of pyrolysis temperature on the conversion of oat straw (contact time - 4.4 s, particle fraction < 1 mm)

in the tar concentration due to the condensation of organic compounds in a vaped liquid [42].

Process time has a high effect on the composition of the pyrolysis products. Experimental data on the dependence of the oat straw pyrolysis on the retention time in the heating zone (particle fraction below 1 mm, the temperature of 700 °C) are presented in Figure 4. The optimal heating time for oat straw particles was found to be 4-5 seconds. A further increase in the residence time of the feedstock in the heating zone is not economically feasible since this does not lead to a significant increase in the yields of gaseous and liquid products. On the contrary, an increase in the heating time of feedstock leads to an increase in the yield of tars due to the condensation

processes taking place between the vaped organic molecules. The reduction of the pyrolysis time below 4 seconds resulted in the high (over 80 wt. %) yield of the solid residue and, thus, the lower feedstock conversion degree.

To reduce tar content in the gaseous product of fast pyrolysis, the experiments on tar conversion over the zeolite catalysts were performed in a separate furnace directly after the pyrolysis. The dependence of tar concentration in the pyrolysis gas on the type of metal of the iron subgroup deposited on the H-ZSM-5 zeolite is shown in Figure 5. As can be seen, the use of the zeolite catalysts leads to a decrease in the tars content in the pyrolysis gas. Iron-containing catalyst decreases the tar concentration by 3 times, while Ni and Co deposited on H-ZSM-5 provide full removal of tars from the gaseous products of pyrolysis. This is probably connected to the high activity of Co and Ni in the cracking reactions [44].

The use of metal-containing aluminosilicate catalysts in the pyrolysis gas refining from the tars results in the change of the total gas volume and heat value. The use of the studied catalysts leads to the change in the concentration of hydrogen, C₁-C₄ hydrocarbons and carbon oxides in the gaseous pyrolysis products. The gaseous product composition depends on the type and concentration of the metal on the catalyst surface. In comparison with a non-catalytic process the volume concentration of C₁-C₄ hydrocarbons increases by 1.39; 1.66 and 1.52 times using Fe-containing, Co-containing, and Ni-containing aluminosilicate catalysts respectively (see Figure 6). The studied catalysts also influenced the concentration of carbon (II) and (IV) oxides. In the

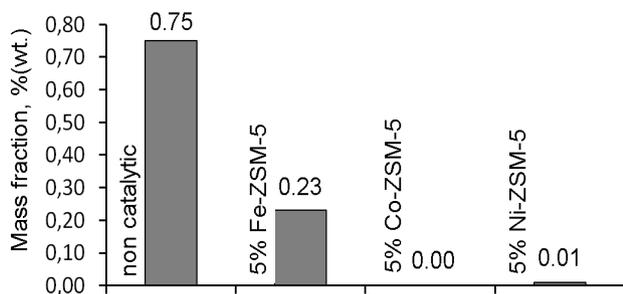


Figure 5: The dependence of the concentration of tars in the gas on the type of metal of the zeolite catalyst (temperature - 700 °C, contact time - 4.4 s, particle fraction < 1 mm).

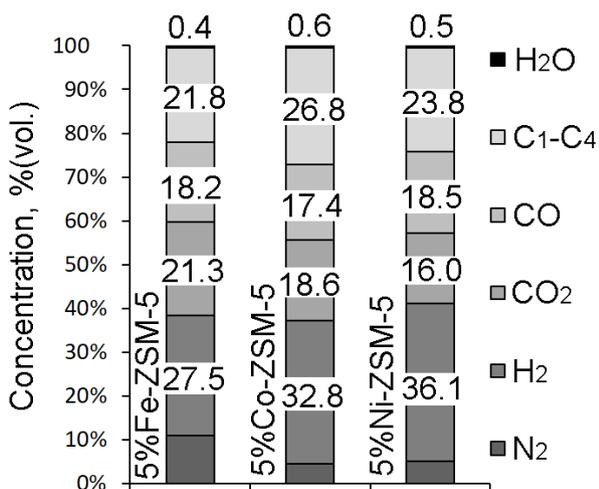


Figure 6: Dependence of the composition of the pyrolysis gas on the type of metal in the zeolite-based catalyst (temperature - 700 °C, contact time - 4.4 s, particle fraction < 1 mm).

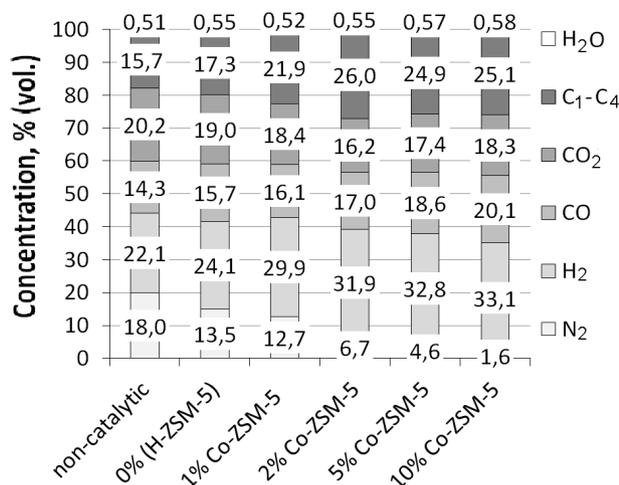


Figure 7: Dependence of the gas composition on the concentration of metal in Co-ZSM-5 (temperature - 700 °C, contact time - 4.4 s, particle fraction < 1 mm).

presence of zeolite-based catalysts, there is a slight decrease in the concentration of CO₂ and an increase in the concentration of CO, according to the interaction of carbon dioxide with carbon species formed on the catalyst surface during the tar decomposition. The use of the catalysts also increases hydrogen concentration. Moreover, the growth of hydrogen concentration in a gaseous product increases from Fe to Ni. This is due to the increase in the dehydrogenation activity of metal in the row Fe-Co-Ni. The growth of hydrogen concentration in a pyrolysis gas is accompanied by the increase in coke-formation on the catalyst surface that leads to an increase of CO formation.

Metal concentration on the catalyst surface also strongly affects the catalyst activity in the thermal decomposition of tars in a pyrolysis gas (see Figure 7). An increase in the Co content leads to an increase in the yield of carbon monoxide (II). It is well known, that Co tends to surface carbonization during the cracking processes [44]. Thus, the increase in CO yield can be also explained by the Boudouard reaction behavior. According to the data on the composition of the gaseous products presented in Figure 7, the optimal cobalt content in the zeolite catalyst was found to be 2 wt. %. This catalyst provides the highest yield of C₁-C₄ hydrocarbons in the gaseous products. It should be noted that some researchers also indicate a high activity of cobalt in the thermal decomposition processes [44-46].

4 Conclusions

This work discussed, the fast pyrolysis of agricultural waste assisted by the ex-situ upgrading of gaseous products. The influence of the biomass type, process temperature and feedstock residence time on the yield of pyrolysis product was investigated. The following refining of gaseous pyrolysis products from tars over the zeolite-based catalysts containing iron subgroup metals was studied. The results of the study are as follows: The optimal temperature of fast pyrolysis for all types of waste plant biomass was found to be 700 °C. This temperature provides the highest yield of gaseous products.

1. The optimal residence time of the feedstock in a heated zone was 4-5 seconds resulting in the highest yields of gases and liquids and the minimum of tar content in the gaseous products.
2. The use of zeolite-based catalysts in the following upgrading of gaseous products leads to a decrease in tar content. Iron subgroup metal activity in the conversion of tars can be ranged as following: Co > Ni > Fe.

3. The use of zeolite-based catalysts in the upgrading of gaseous products increases the volume concentration of C_1 - C_4 hydrocarbons, CO , CO_2 , and hydrogen in comparison with the non-catalytic process.
4. The highest concentration of C_1 - C_4 hydrocarbons in pyrolysis gases after upgrading was obtained in the presence of 2% Co-ZSM-5.

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