

Thermocatalytic Conversion of Pine and Birch Sawdust over H-ZSM-5 Zeolite Catalyst

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The processing of lignocellulose wastes is one of the urgent tasks in modern society. These wastes can be effectively used for the production of heat, electricity, fuels, and valuable chemicals. Catalytic pyrolysis can be considered the most effective way to convert waste into valuable products. In this work, the investigation of the pyrolysis process of the birch and pine sawdust was carried out in the presence of a zeolite-based catalyst. The synthesised zeolite-based catalyst is characterised by high porosity (the specific surface area of 350 m²/g) and acidity (0.34 mmol/g). The use of the zeolite-based catalyst increases the yield of the gaseous and liquid products of pyrolysis by ca. 5 % in comparison with the non-catalytic one. Despite this increase seems to be negligible, the composition of the products was changed sufficiently because of the higher degree of feedstock decomposition. The addition of pure zeolite into the pyrolysis zone led to an increase in furanes and phenols yield for 3 times while the addition of Fe-ZSM-5 catalyst increased twice the yield of acids/esters, and hydrocarbons.

1. Introduction

Biomass production is about 100×10⁹ t/y (Sheldon, 2014). Biomass is considered to be a potential resource for the production of renewable fuels (Nunes et al., 2020) and chemicals (Ubando et al., 2020). Lignocellulose biomass is a widely available, renewable, biodegradable, and biocompatible resource for the production of heat, electricity, fuel (Zhou et al., 2011), chemicals, and other bioderived products (Taarning et al., 2011). To date, a large amount of lignocellulose waste, which is practically not used, is formed. Current trends require the involvement of all possible resources in the production cycle (Gil, 2021). The recycling of lignocellulose biomass waste is an urgent area of research.

The main components of biomass are cellulose and hemicellulose - macromolecules consisting of sugars - and lignin - an aromatic polymer. Cellulose is a linear polymer consisting of D-glucose subunits bonded by β-1,4-glycoside linkages. The cellobiose molecules form fibrils by forming hydrogen bonds and van der Waals interactions. Hemicellulose, in contrast, does not contain such a number of β-1,4-glycoside bonds as cellulose and has a less regular structure, which leads to less crystallinity and stability. Hemicellulose is a polysaccharide containing D-xylose, D-mannose, D-galactose, D-glucose, L-arabinose, 4-O-methyl glucuronic acid, D-galacturonic acid, and D-glucuronic acid which are linked by β-1,4-glycoside and β-1,3-glycoside bonds. Lignin is an amorphous heteropolymer consisting of phenylpropane units crosslinked by different bonds (Gil, 2021).

Natural lignocellulose materials have low solubility and processibility, which limits their effective practical application. Currently, lignocellulose biomass can be used by direct combustion to generate heat and electricity. However, this approach has a significant problem of low energy efficiency and is also characterised by the emissions of a large amount of carbon dioxide. Considerable attention of researchers is focused on the conversion of biomass into bioenergy through biochemical or thermochemical processes (Chen et al., 2019b). Thermochemical conversion, including pyrolysis (Goyal et al., 2008), gasification, liquefaction (Chen et al., 2019a), etc., receives great attention. Pyrolysis is considered to be one of the prospective methods for lignocellulose biomass conversion. Typically, pyrolysis of biomass is carried out at temperatures from 400 °C

to 800 °C. Fast pyrolysis, slow pyrolysis (Arpia et al., 2021), catalytic pyrolysis, and pyrolysis using microwave approaches (Ong et al., 2019) can be used. Currently, the use of catalysts in the pyrolysis process is one of the promising ways to improve the quality of the resulting liquid and gaseous fractions. Pyrolysis in the presence of catalysts is of great interest worldwide since catalysts contribute to an increase in the conversion efficiency of organic compounds (Huber et al., 2006). Analysis of scientific literature and patent documentation shows that many chemical compounds exhibit a catalytic effect in the processes of thermal decomposition of organogenic feedstock (Badr et al., 2019). These compounds can be divided into the following groups: solid acid catalysts, zeolites (Rahman et al., 2018), and aluminosilicates (Zhang et al., 2013), clays (Putun et al., 2006), solid superacids (Chen et al., 2018), alkali (Takuma et al., 2000) and transition (Ryu et al., 2019) metal oxides, and salts of transition (Eibner et al., 2015) and rare earth metals (Jiang et al., 2015).

Despite, the catalytic pyrolysis is intensively studied process for organogenic waste utilisation, the catalyst influence on the composition of pyrolysis products is one of the main issues. To develop the proper technology of biomass waste decomposition through the catalytic pyrolysis, comprehensive studies on the catalyst effect on product distribution should be done. In this work, the effect of iron-containing zeolite-based catalysts on the slow pyrolysis of lignocellulosic wastes presented by pine and birch sawdust was investigated for the first time. The comparison of the gaseous, liquid and solid product yields for non-catalytic pyrolysis, and the process in the presence of H-ZSM-5 and Fe-ZSM-5 was carried out. For the first time, the results of the composition of pyrolysis liquid obtained over Fe-ZSM-5 were presented. The correlation between the catalyst acidity and the yield and composition of liquid products was proposed.

2. Experimental

2.1 Materials

Two types of lignocellulose waste were used in this work. The pine sawdust and birch sawdust were collected from the wood processing company of the Tver region of the Russian Federation. The composition of the pine sawdust was presented by the cellulose (52.84 wt. %), hemicelluloses (7.85 wt. %), lignin (27.03 wt. %), extractives (6.72 wt. %). The composition of the birch sawdust was presented by the cellulose (43.38 wt. %), hemicelluloses (33.18 wt. %), lignin (21.23 wt. %), extractives (2.21 wt. %). The humidity of the dried samples was 3.20 wt. % for pine and 2.73 wt. % for birch sawdust. The ash content was 0.36 wt. % and 0.42 wt. %.

2.2 Fe-ZSM-5 catalyst preparation and characterisation

Commercial zeolite H-ZSM-5 (Zeolyst, China) was used for the catalyst synthesis. The catalyst was synthesised as follows: 5 g of H-ZSM-5 was mixed with 10 mL of an aqueous solution containing 1.8 g of iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, c.g., Reachim, Russia). The suspension was continuously stirred for 30 min, filtered, and dried at a temperature of 100 °C. The dried sample was calcined at 500 °C for 5 h in a muffle. The catalyst was analysed by the low-temperature nitrogen physisorption (Beckman Coulter SA 3100 analyser, Coulter Corporation, USA), X-ray photoelectron spectroscopy (ES-2403 spectrometer modified with a PHOIBOS 100 analyser, SPECS, Germany), X-ray fluorescent analysis (Zeiss Jena VRA-30 spectrometer, Carl Zeiss Industrielle Messtechnik GmbH, Germany), and ammonia chemisorption (AutoChem HP, Micrometrics, USA).

2.3 Pyrolysis procedure

The pyrolysis of sawdust was carried out using the experimental setup (Lugovoy et al., 2018). The process was carried out for 50 min at a temperature of 500 °C using 1-2 mm size of the feedstock particles. The feedstock weight was 3 g. The catalyst amount was chosen to be 10 wt. % from the feedstock mass. The composition of pyrolysis gases was determined by gaseous chromatography using the analytical complex based on the Crystallux 4000M chromatograph. The liquid phase was analysed using a gas chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan).

3. Results and discussion

3.1 Fe-ZSM-5 catalyst characterisation

Analysis of the specific surface area by the low-temperature nitrogen physisorption showed that the synthesised zeolite-based catalyst has a mesoporous structure with a bimodal pore distribution with a size of less than 6 nm and 20-80 nm (see Table 1). The Fe deposition practically does not affect the porous structure of the zeolite. It can be associated with the formation of a "shell-type" active phase on the zeolite surface. The specific surface areas of the initial H-ZSM-5 and Fe-ZSM-5 were found to be 560 m²/g and 353 m²/g (see Table 2). A decrease in the specific surface area is probably related to the formation of iron-containing phase particles in the "mouths" of the zeolite pores, leading to their partial blockage. This is confirmed by a slight

change in the forms of nitrogen adsorption-desorption isotherms for the samples of the initial zeolite and catalyst, as well as a change in the shape of the hysteresis loop (see Figure 1).

Table 1: Pore-size distribution for the H-ZSM-5 and Fe-ZSM-5

Pore diameter, nm	H-ZSM-5		Fe-ZSM-5	
	Pore volume, cm ³ /g	%	Pore volume, cm ³ /g	%
< 6	0.02402	27.24	0.01464	21.99
6-8	0.01105	12.54	0.00684	10.27
8-10	0.00581	5.81	0.00386	5.79
10-12	0.00413	4.69	0.00418	6.28
12-16	0.00636	7.21	0.00496	7.45
16-20	0.00633	7.18	0.00523	7.86
20-80	0.02405	27.28	0.02105	31.62
> 80	0.00710	8.05	0.00582	8.74
Total pore volume, cm ³ /g	0.08817		0.06657	

Table 2: Characterization results for H-ZSM-5 and Fe-ZSM-5

Sample	S _{BET} , m ² /g	Si/Al	Acidity, mmol/g	Fe concentration, wt. %
H-ZSM5	560	57	0.41	-
Fe-ZSM-5	353	64	0.34	4.18

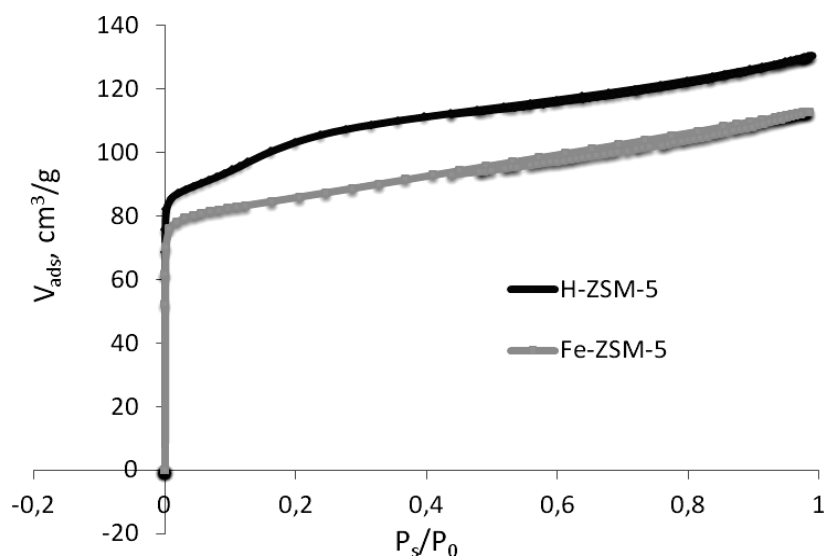


Figure 1: Nitrogen adsorption-desorption isotherms for H-ZSM-5 and Fe-ZSM-5

The study of the surface composition of the catalyst by X-ray photoelectron spectroscopy (Figure 2) showed that oxygen, aluminum, silicon, and carbon are present on the surface of the initial H-ZSM-5 zeolite and synthesized catalyst samples. For the catalyst, the presence of iron is also noted. When iron was deposited to zeolite, an increase in the Si/Al ratio, as well as a decrease in the acidity was observed (see Table 2). This indicates that during the impregnation, the partial leaching of aluminium from the zeolite surface takes place. The surface Fe concentration was 7 wt.%, whereas the total Fe concentration according to XFA was 4.5 wt.%. This indicates the coordination of Fe on the surface of the zeolite and the formation of a shell-type catalyst.

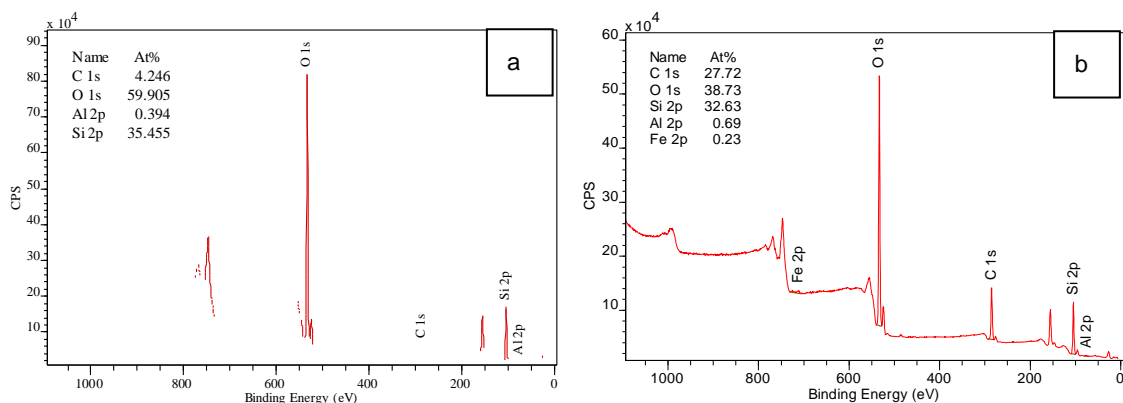


Figure 2: Survey XP spectra of H-ZSM-5 (a) and Fe-ZSM-5 (b)

3.2 Sawdust pyrolysis

The results of the non-catalytic process and pyrolysis in the presence of zeolite and synthesized catalyst were compared (Figure 3).

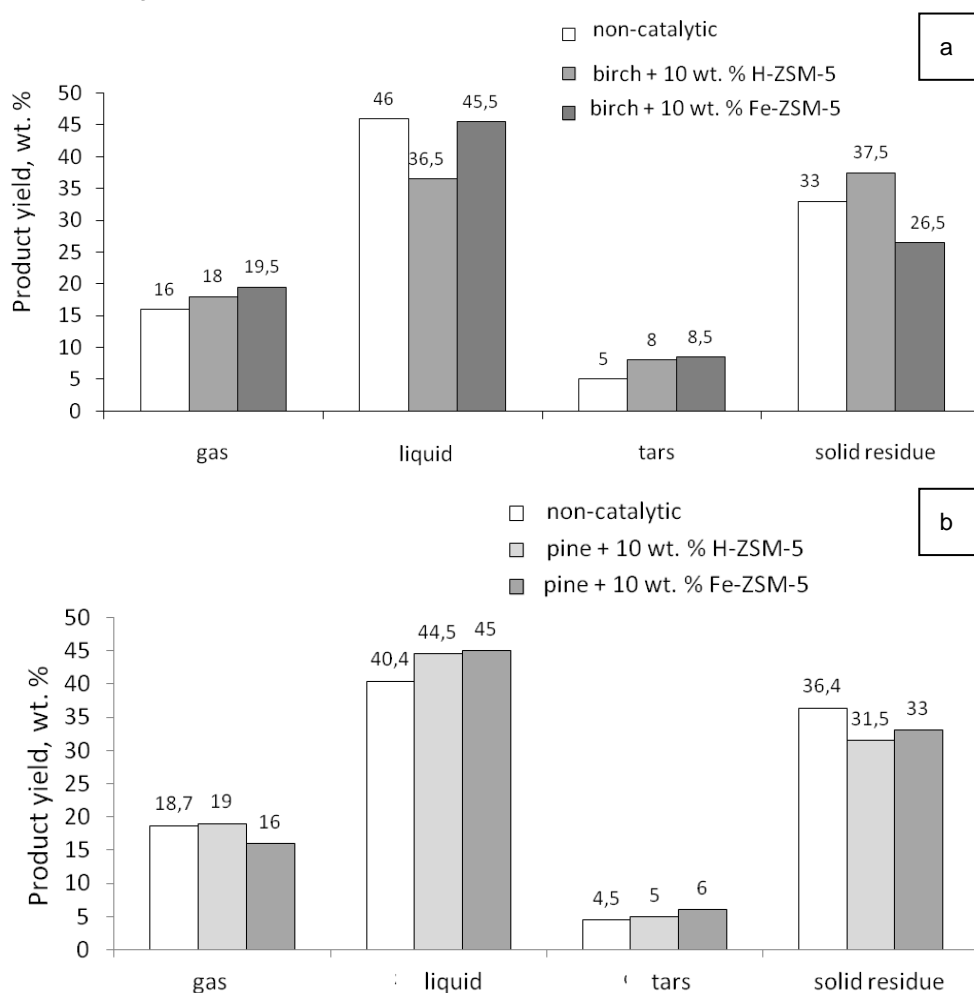


Figure 3: Pyrolysis product yields for birch (a) and pine (b) sawdust

For both pine and birch, the use of zeolite in the pyrolysis leads to an increase in the yield of gaseous products. However, during the pyrolysis of birch sawdust, the presence of pure zeolite significantly reduces

the yield of the liquid fraction of products, increasing the yield of solid residue. This may be due to the processes of condensation of liquid products on the surface of the zeolite, followed by the formation of carbonaceous polyaromatic deposits due to the high acidity of the sample. The use of the Fe-containing catalyst, in contrast, leads to an increase in the yield of liquid products in both cases while the acidity of the catalyst is lower than for the initial zeolite (see Table 2). However, the yield of tars in gaseous products also increases. This result may be related to the contribution of the catalyst to the thermal decomposition of the lignin component in the raw material. Tars in gaseous products affect their properties and reduce the possibility of their use as an energy source. This problem can be solved by additional catalytic conversion of gaseous products with the removal of the catalyst outside the pyrolysis zone.

Evaluation of the effect of the catalyst on the composition of liquid products showed that the use of the catalyst accelerates the processes of thermal degradation of the lignin component of wood, which leads to an increase in the yield of oxygen-containing compounds. The presence of zeolite and synthesized catalyst showed an increase in the content of decomposition products of the lignin component of wood (anisole, guaiacol, ethyl guaiacol, acetoguaiacol, syringol, etc.), as well as low-molecular oxygen-containing products of cellulose and hemicelluloses decomposition (acetic acid and its derivatives, ketones) (Tables 3, 4).

Table 3: Composition of the liquid products of birch sawdust pyrolysis

Compounds	Concentration, wt. %		
	Non-catalytic	H-ZSM-5	Fe-ZSM-5
Acids and ethers	41.6	36.2	55.9
Ketones and aldehydes	39.5	18.3	17.9
Furane derivatives	13.2	31.0	15.1
Alcohols	0.7	3.4	0.8
Phenols	3.2	10.7	7.5
Hydrocarbons	0.8	0.4	2.8

Table 4: Composition of the liquid products of pine sawdust pyrolysis

Compounds	Concentration, wt. %		
	Non-catalytic	H-ZSM-5	Fe-ZSM-5
Acids and ethers	6.2	27.3	48.1
Ketones and aldehydes	31.0	41.1	22.0
Furane derivatives	49.0	21.0	18.3
Alcohols	4.1	1.4	1.2
Phenols	9.7	9.2	9.9
Hydrocarbons	0.0	0.0	0.5

4. Conclusions

In this work, the effect of the addition of a zeolite-based catalyst into the pyrolysis zone on the composition of liquid products of birch and pine sawdust thermal decomposition was studied. Basing on the results obtained the following conclusions can be done:

- 1) Fe-ZSM-5 catalyst has a shell-type structure characterized by a mesoporous structure with the proper acidity;
- 2) the use of the zeolite-based catalyst leads to an increase in both gaseous and liquid product yield of birch and pine sawdust pyrolysis increasing the degree of the feedstock decomposition;
- 3) an increase in the valuable product yield can be correlated to the acidity of the catalyst used;
- 4) a decrease in the catalyst acidity due to the deposition of iron oxide results in deeper decomposition of lignocelluloses waste decreasing the condensation of the phenolic, aromatic and aliphatic products on the catalyst surface.

The future studies are planned to be focus on the kinetic aspects and mechanisms of the pyrolysis process of lignocelluloses waste. The investigation of the influence of the pyrolysis type and method for catalyst preparation on the composition of gaseous and liquid products will be performed.

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