Hindawi
International Journal of Chemical Engineering
Volume 2019, Article ID 7135235, 10 pages
https://doi.org/10.1155/2019/7135235

Research Article

Effect of Metal Chlorides on the Pyrolysis of Wheat Straw

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Received 30 November 2018; Revised 25 January 2019; Accepted 11 February 2019; Published 10 March 2019

Guest Editor: Hu Li

In this paper, the results of the study on the influence of the addition of 10 wt.% of $FeCl_3$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $SnCl_2$, and $CuCl_2$ on the wheat straw pyrolysis process are presented. The studied chlorides were found to affect the pyrolysis process; however, the highest activity was observed while using $CuCl_2$. The presence of the copper chloride led to the decrease in the temperature of the initial destruction of hemicellulose fraction of wheat straw by 64°C. Besides, the use of $CuCl_2$ allowed increasing the yield of liquid and solid pyrolysis products as well as decreasing the molecular weight distribution of the volatiles. Moreover, the increase in the hydrogen and decrease in carbon dioxide concentration were also observed in the presence of copper chloride. The analysis of the solid residue obtained in the wheat straw pyrolysis in the presence of $CuCl_2$ showed the increase in the specific surface area of the carbon residue from 24 up to 63.5 m^2/g in comparison with that obtained for the noncatalytic process.

1. Introduction

The limitation of natural fuels and the environmental problems rised during their use increase the interest in the processing of biomass in order to produce transportation fuels, energy sources, and chemicals [1]. The advantages of biomass application compared to fossil fuels are low sulfur and nitrogen content, as well as the absence of the effect on the CO_2 balance in the atmosphere. Agricultural wastes from plants are the available biomass source which is produced annually in large amounts throughout the world [2]. In developing countries, a large amount of agricultural waste is currently used either as a raw material for the paper industry or as a source of animal feed. The collection and disposal of such wastes are complex and expensive processes. Thus, the degree of its rational use remains sufficiently low.

In the Russian Federation, the amount of crop waste, which can be effectively used for energy purposes without concurrence with the agricultural needs, exceeds 50 million tons of fuel equivalent per year [3]. The highest amount of grains produced in the Russian Federation belongs to wheat (more than 55%). Meanwhile, the yield of the straw is in the range from 80 to 130% of wheat grain production [4].

According to history, agricultural plant waste can be used to generate heat and electricity. This is confirmed by a large number of industrial plants in countries such as Denmark, Sweden, Spain, Germany, Poland, Canada, the USA, and China [5]. Thus, the development of the fundamental principles of effective processing methods allowing the use of biomass for energy purposes is an urgent task.

Despite the existence of different methods and approaches to the processing of agricultural plant waste, scientists are currently attracted by various modifications of the pyrolysis methods since traditional pyrolysis is not fully capable of solving the problems of the efficient conversion of plant biomass waste for energy purposes [6]. The composition of the pyrolysis products for the plant biomass strongly depends on the feedstock composition, in particular, the content of cellulose, hemicelluloses, and lignin. First, hemicelluloses undergo thermal destruction at a temperature of 170–260°C; then, the cellulose is decomposed at 240–350°C. At last, the decomposition of lignin takes place at 280–500°C. The highest amount of the gaseous products is formed during the thermal decomposition of polysaccharides. Lignin is the most stable component of biomass because of its aromatic composition and a sufficiently high degree of polymerization [1]. In comparison with the wood biomass, the plant biomass including the agricultural wastes is characterized by the high ash and extractive content. This can lead to the acceleration of the plant biomass pyrolysis as well as promote the formation of carbon-containing residues [2]. The final products of the pyrolysis of plant biomass can be applied as the heat suppliers, gaseous and liquid fuels, and the feedstock for chemicals. For example, during the thermal destruction of cellulose and hemicelluloses, a large number of gaseous hydrocarbons (methane, ethane, ethylene, etc.), hydrogen, and carbon monoxide and dioxide, as well as methanol and acetic acid, are formed. The decomposition of lignin components leads to the formation of phenolic and aromatic compounds. The carbon-containing residue can be applied as the absorbent or filler [1–6]. Moreover, the solid residue containing transition metals can be applied as effective catalysts.

The increase in the efficiency of pyrolysis processes, as well as the quality of the final products obtained, can be reached by the use of catalysis. Therefore, the study of the effect of various compounds on the process of thermal destruction of plant biomass is an important task [7]. The catalyst in the pyrolysis process not only affects the reaction rate but can serve as the heat supplier that leads to the decrease in the process temperature. Besides, the catalyst increases the selectivity to the desired products as well as allows its upgrading. Nowadays, there are numerous studies on the pyrolysis catalysts. Among the different catalysts applied in the biomass pyrolysis process, the soluble salts and oxides of the alkali and transition metals are the most frequently used [8–31]. It is well known that the alkali metal chlorides, particularly K which is present in the plant biomass, increase the rate of the cellulose destruction and promote char formation [8–10]. The presence of NaCl decreases the pyrolysis temperature and increases the yield of low-molecular products [11–14]. The chlorides of alkaline earth metals mainly decrease the pyrolysis temperature [12,15–20]. The treatment of the plant biomass with the solution of $ZnCl_2$ increases the yield of furfural and formic acid. Besides, zinc chloride accelerates the dehydration reactions [21–24]. The chlorides of manganese, iron, nickel, cobalt, and copper increase significantly the formation of carbon-containing residue and decrease the pyrolysis temperature [25, 26]. Moreover, the acid character of the transition metal chlorides significantly accelerates the pyrolysis reactions, leading to the changes in the gaseous product composition [27, 28]. It should be noted that the data on the effect of these compounds are available for the individual components of plant biomass (hemicellulose, cellulose, and lignin). However, the effect of the metal chlorides on the pyrolysis of real feedstock practically was not studied. Thus, the study of the effect of transition metal chlorides ($FeCl_3$, $CoCl_2$, $NiCl_2$, $ZnCl_2$, $SnCl_2$, and $CuCl_2$) on the process of pyrolysis of wheat straw is of theoretical and practical interest.

2. Materials and Methods

The wheat straw used in the current work as a feedstock was collected in July 2017 in the Bologoe district of Tver region, Russia. As the composition of the raw material plays an important role in the pyrolysis process, the determination of moisture and ash content was carried out. Moreover, the content of the main components of wheat straw—extractives, hemicellulose, cellulose, and lignin—was estimated by extraction according to the methods described in [32].

In order to estimate the moisture content in the wheat straw, a weighed portion of the feedstock particles with the mean size of 0.45 mm was dried at 150°C for 1.5 h till the constant mass in a calcinatory. The cooled samples were weighed, and the moisture content (W) was calculated as the relative differences in the weight of initial and dried samples:

$$W = \frac{(m - m_1) \cdot 100}{m}, \tag{1}$$

where m is the feedstock weight in g and m_1 is the feedstock weight after drying in g.

The ash content was measured as the following: a weighed portion of the feedstock particles with the mean size of 0.45 mm was placed in a calcinatory; then, the calcinatory was covered by a cone of the ash-free filter and placed in a muffle furnace at a temperature 550–650°C for 1 h. The ash content (X) was calculated according to

$$X = \frac{m_1 \cdot 100 \cdot 100}{m_2 \cdot (100 - W)}, \tag{2}$$

where m_1 is the ash weight in g, m_2 is the feedstock weight in g, and W is the moisture content in %.

For the measurement of the content of the extractives, a weighed portion of the feedstock particles with the mean size of 0.45 mm was boiled in 50 mL of 70% ethanol for 2 h using reflux condenser; then, the mixture was cooled to the room temperature and filtered. The obtained filtrate was evaporated, and the dried residue was weighed. The extractive content (E) was calculated using

$$E = \frac{m \cdot 200 \cdot 100}{m_1 \cdot (100 - W)}, \tag{3}$$

where m is the weight of the dried residue in g, m_1 is the feedstock weight in g, and W is the moisture content in %.

In order to estimate the effect of transition metal salts on the pyrolysis process of wheat straw, the following compounds were selected: $ZnCl_2·6H_2O$, $SnCl_2·4H_2O$, $CuCl_2·2H_2O$, $NiCl_2·6H_2O$, $CoCl_2·6H_2O$, and $FeCl_3·6H_2O$. The salts were used in dry form by direct application into the samples of wheat straw. The salt concentration in the sample varied from 1 to 10 wt.% according to the preliminary experiments and literature data. The influence of the $CuCl_2$ concentration on the pyrolysis process was studied. In order to estimate the activity of a copper ion in the wheat straw pyrolysis, the thermogravimetric study of the influence of copper salts ($CuSO_4·5H_2O$, $Cu_2OH_2CO_3$) was performed.

The pyrolysis process of samples containing the inorganic salts and the sample without additives was studied using a NETZSCH TG 209 F1 thermal analyzer. The conditions of thermogravimetric analysis were similar for all samples. The process was carried out in an inert argon atmosphere in the temperature range from 50 to 600°C with a heating rate of 5°C/min. The composition of the volatile products obtained in the thermal destruction process was studied using the NETZSCH QMS 403 D MS device for a sample containing 10 wt.% of $CuCl_2$ and the wheat straw without additives.

Based on the preliminary results, copper chloride was also chosen for the experiments in a laboratory pyrolysis unit. The experimental setup (Figure 1) consists of the periodic steel reactor (length 150 mm, diameter 30 mm, and wall thickness 3 mm) with a fixed substrate layer, electric furnace, sealing trap, and eudiometer [32]. The pyrolysis process was carried out at a temperature of 550°C for one hour in a nitrogen atmosphere. The solid and liquid product masses were calculated via differences between the reactor and the liquid trap masses, respectively. The relative error of the mass measurements of pyrolysis products was 0.5 wt.%.

The composition of the gaseous pyrolysis products formed in the thermal decomposition of the wheat straw samples with 10 wt.% $CuCl_2$, as well as the sample without additives, was studied by the chromatographic determination using a unique analytical complex including gas chromatographs (Crystallux 4000M, GAZOKHROM 2000) and a specially developed analyzer of the specific heat of combustion on the base of a flame-temperature detector. The chromatographic analysis of hydrocarbons in the gaseous mixture was carried out on the chromatograph Crystallux 4000M under the following conditions: the consumption of gas carrier (nitrogen) 120 mL/min; gas-carrier pressure 1.5 kgs/sm^3; duration of the analysis 30 min; sample volume 1 mL; carrier silica gel 0.4 mm; column length 1 m; column temperature 50°C; detector temperature 100°C. Volume concentrations of nitrogen, carbon oxide, and methane were analyzed on the chromatograph GAZOKHROM 2000. The flow rate of the gas carrier (helium) was 30 cm^3/min, sample volume of the gas was 0.5 cm^3, and thermostat temperature was 40°C [33].

Solid pyrolysis residues were analyzed by X-ray fluorescence analysis (XFA), X-ray photoelectron spectroscopy (XPS), and low-temperature nitrogen adsorption. XFA was used for the study of catalyst metal migration into the solid carbon residue. The metal content in the solid pyrolysis product was analyzed using a Spectroscan-Maks-GF1E spectrometer (Spectron, St-Petersburg, Russia) equipped with Mo anode, LiF crystal analyzer, and SZ detector. The analysis was based on the Co Ka line. XPS was used to analyze the surface chemical compositions of the solid carbon-containing pyrolysis product. The spectra were obtained with a spectrometer (ES 2403 M-Y IAI RAS). Characteristic MgKa radiation ($h\nu = 1253.6$ eV) was used. The radiation power was 100 W. The spectra were recorded at pressures below 10^{-9} Torr. The specific surface area of the solid pyrolysis product was measured using a Coulter SA 3100 Series Surface Area and Pore Size Analyzers (Beckman Coulter Company). The analysis was conducted for four hours at 200°C, a pressure of 10^{-5} to 10^{-6} Pa, and under constant nitrogen flow at a rate of 1 mL·min^{-1} [32].

3. Results and Discussion

The composition of the wheat straw varies depending on the habitat and growth conditions as well as the season of collection. Difference between the compositions of the feedstock can be significant. Thus, we provided experiments on the estimation of the moisture, ash, extractive content, and the composition of main biomass compounds (Table 1). The experimental data obtained in the current work are in accordance with the literature data [34–38]. The moisture and ash content of wheat straw was found to be 7.2 ± 0.1 and 4.7 ± 0.1 wt.%, respectively. The content of extractives in the wheat straw was estimated as 5.6 ± 0.1 wt.%. The amount of hemicellulose in the raw material, which was calculated as the difference between the weight of the sample before and after the extraction of the sample, was equal to 41.1 ± 0.1 wt.%. The cellulose content was determined by the weight difference of the biomass components and the initial wheat straw weight. Thus, the cellulose content in the wheat straw was found to be 31.7 ± 0.1 wt.%. The total lignin content (9.8 ± 0.1 wt.%) was determined to be the sum of acid-insoluble lignin and acid-soluble lignin.

The mechanism of the metal chloride impact in the thermal destruction process can be described by the formation of carbocations according to the scheme presented in Figure 2 [33]. The studied metal salts are the aprotonic acid centres with the medium strength which are characterized by the relatively high activity and high selectivity in the processes of thermal destruction of hydrocarbon materials [38]. The difference between the influences of the studied chlorides on the wheat straw pyrolysis process consists of the difference in the electronic structure of the metals used which determines the difference in the catalytic properties.

According to the scheme presented in [39, 40], the possible mechanism of the catalytic effect of the aprotonic acid sites of metal chlorides can be described by the scheme (Figure 3).

In order to account for the previously presented mechanisms, the activation of the surface cellulose molecule by metal chlorides should include both solid-state hydrolysis and the glycosidic bond cleavage [41].

In order to estimate the influence of metal chlorides on the wheat straw pyrolysis, the preliminary thermogravimetric experiments of the feedstock without catalysts and with 10 wt.% of salts were performed. As shown by the experimental data (Figure 4), all the studied metal chlorides differently influenced the pyrolysis process of wheat straw. Basically, the presence of metal chlorides had the highest effect on the shift towards lower temperatures of the hemicellulose destruction and the lowest impact on the cellulose destruction temperature. Thus, based on the shift of the hemicellulose destruction temperature peaks towards lower temperatures, the studied transition metal chlorides can be ranked in order of decreasing effects: $CuCl_2 > SnCl_2 > ZnCl_2 > FeCl_3 > CoCl_2 > NiCl_2$. In terms of the effect on the shift of the cellulose destruction temperature peak towards lower temperatures, the studied transition metal chlorides can be arranged in a row slightly different from the above-presented: $CuCl_2 > FeCl_3 > ZnCl_2 > SnCl_2 > NiCl_2 > CoCl_2$.

It should be noted that in the case of using $FeCl_3$ and $ZnCl_2$, besides the shift of the hemicellulose weight loss peak towards lower temperatures, a broadening of the peak was observed. This may be due to the nonselective effect of these

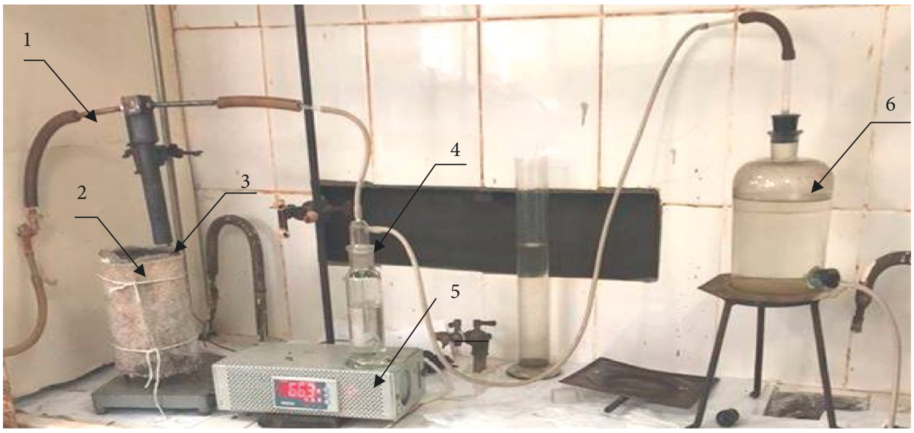


Figure 1: Laboratory equipment for the pyrolysis process: (1) nitrogen purging; (2) electric furnace; (3) reactor; (4) sealing trap; (5) temperature controller; and (6) eudiometer.

Table 1: Wheat straw composition according to the literature and experimental data.

Parameter	Experimental results	Literature data			
		[34]	[35]	[36]	[37]
Moisture content (wt.%)	7.2 ± 0.1	—	—	10.23	8.30
Ash content (wt.%)	4.7 ± 0.1	12.78	8.0	6.99	4.77
Calorific value (MJ/kg)	18.04 ± 0.01	17.10	—	17.38	17.73
Extractives (wt.%)	4.5 ± 0.1	—	5.4	—	—
Hemicelluloses (wt.%)	41.1 ± 0.1	—	23.60	—	26.30
Cellulose (wt.%)	31.6 ± 0.1	—	32.30	—	45.2
Lignin (wt.%)	9.8 ± 0.1	—	17.10	—	10.90
Elemental composition (wt.%)					
C	41.6 ± 0.1	42.49	—	45.48	47.12
H	4.8 ± 0.1	5.12	—	6.12	5.78
N	0.6 ± 0.1	0.68	—	0.52	0.47
O	39.7 ± 0.1	36.52	—	39.96	40.20
S	0.2 ± 0.05	0.39	—	0.13	0.19

substances on the various components of hemicellulose, which ultimately led to a “blurring” of the destruction process for this component and, accordingly, reduced the maximum rate of destruction.

In the presence of $ZnCl_2$, $CoCl_2$, and $NiCl_2$, a decrease in the mass of the solid carbon residue of wheat straw pyrolysis by 14.2 ± 0.05, 5.7 ± 0.03, and 2.8 ± 0.02 %, respectively, was observed. In the case of using $CuCl_2$, $FeCl_3$, and $SnCl_2$, the weight of the solid residue, in contrast, increased by 15.2 ± 0.05, 14.4 ± 0.05, and 4.7 ± 0.02%, respectively. This calculation took into account the weight loss of the chlorides used during heating under conditions similar to the experiment.

As copper ion has the highest impact in the wheat straw destruction temperature, it was chosen for the further experiments. According to the data described in [40], based on the decrease in the biomass thermal destruction temperature and the apparent activation energy, inorganic salts can be ranked as the following: $CuSO_4 > NaOH > Na_2CO_3 > NiCl_2 > ZnCl_2 > NaCl$. This data confirms the high activity of copper compounds in the plant biomass pyrolysis. The experiments on the influence of the copper salts on the wheat straw pyrolysis process (Figure 5) allowed ranking the Cu-containing catalysts as follows: $CuCl_2 > CuSO_4 > Cu_2OH_2CO_3$.

As it is seen in Figure 5, among the studied compounds, copper chloride has the highest activity in the wheat straw pyrolysis process. This can be explained by the higher strength of the acid aprotonic center of Cu^{2+} in the copper chloride [33, 42].

As it was shown by the results of mass spectrometry study of volatile products of wheat straw pyrolysis in the presence of $CuCl_2$, a decrease in the molecular weight distribution and a decrease in the molecular weight of volatile products were observed. It may be of practical interest in purifying volatile products from the resins (Figure 6).

The catalyst content strongly influences the pyrolysis process. In order to estimate the effect of copper chloride content on the wheat straw thermal destruction, the concentration range of 1–10 wt.% was chosen according to the literature [43]. The thermogravimetric study (Figure 7) showed that 10 wt.% of $CuCl_2$ was optimal for the wheat straw pyrolysis using laboratory setup.

As $CuCl_2$ had the highest effect on the process of wheat straw destruction, this chloride with the concentration of

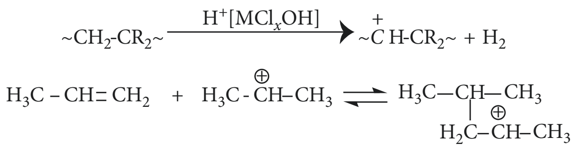


Figure 2: Scheme of the pyrolysis mechanism in the presence of metal chlorides.

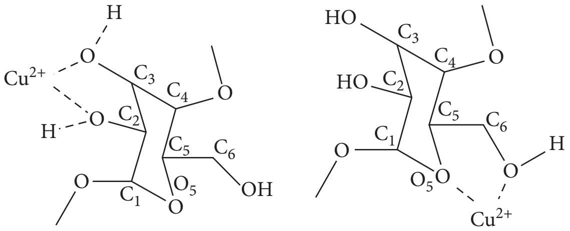


Figure 3: Scheme of the pyrolysis mechanism in the presence aprotonic acid centers.

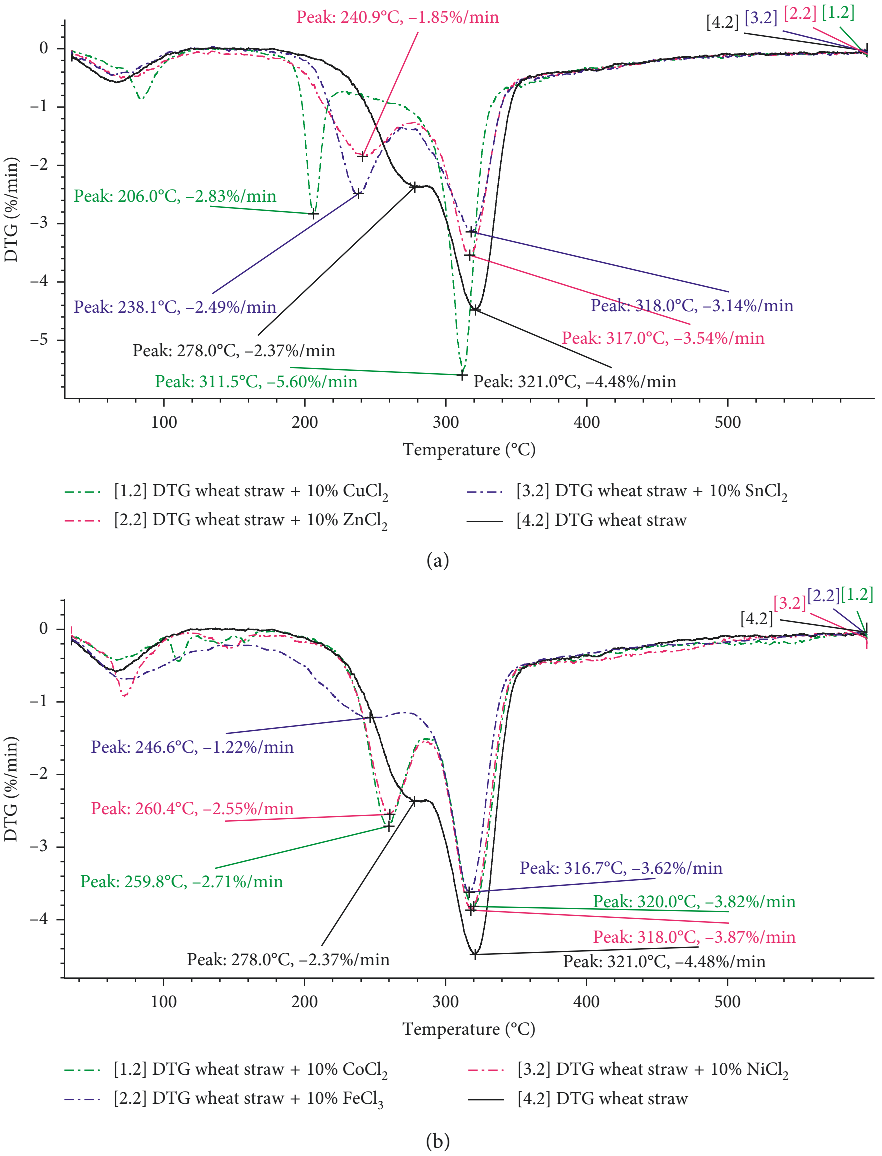


Figure 4: DTG curves obtained as a result of pyrolysis of wheat straw in the presence of copper, tin, and zinc chlorides (a); iron, cobalt, and nickel chlorides (b); and a sample of straw without additives.

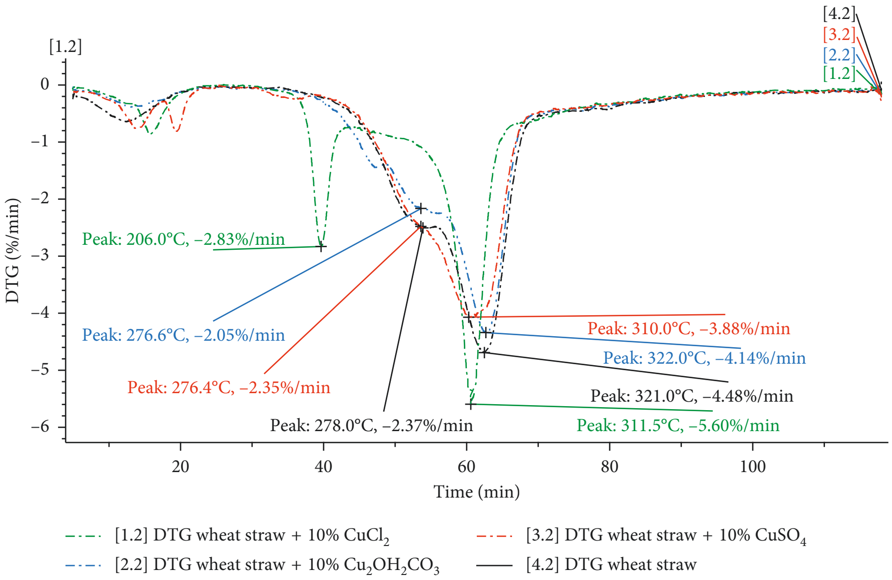
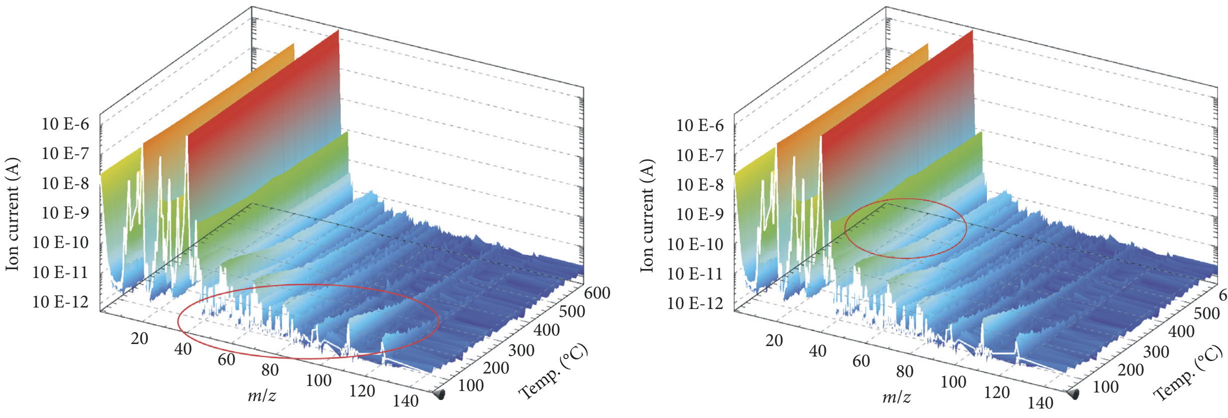


Figure 5: DTG curves obtained as a result of pyrolysis of wheat straw in the presence of copper salts.



(a)

(b)

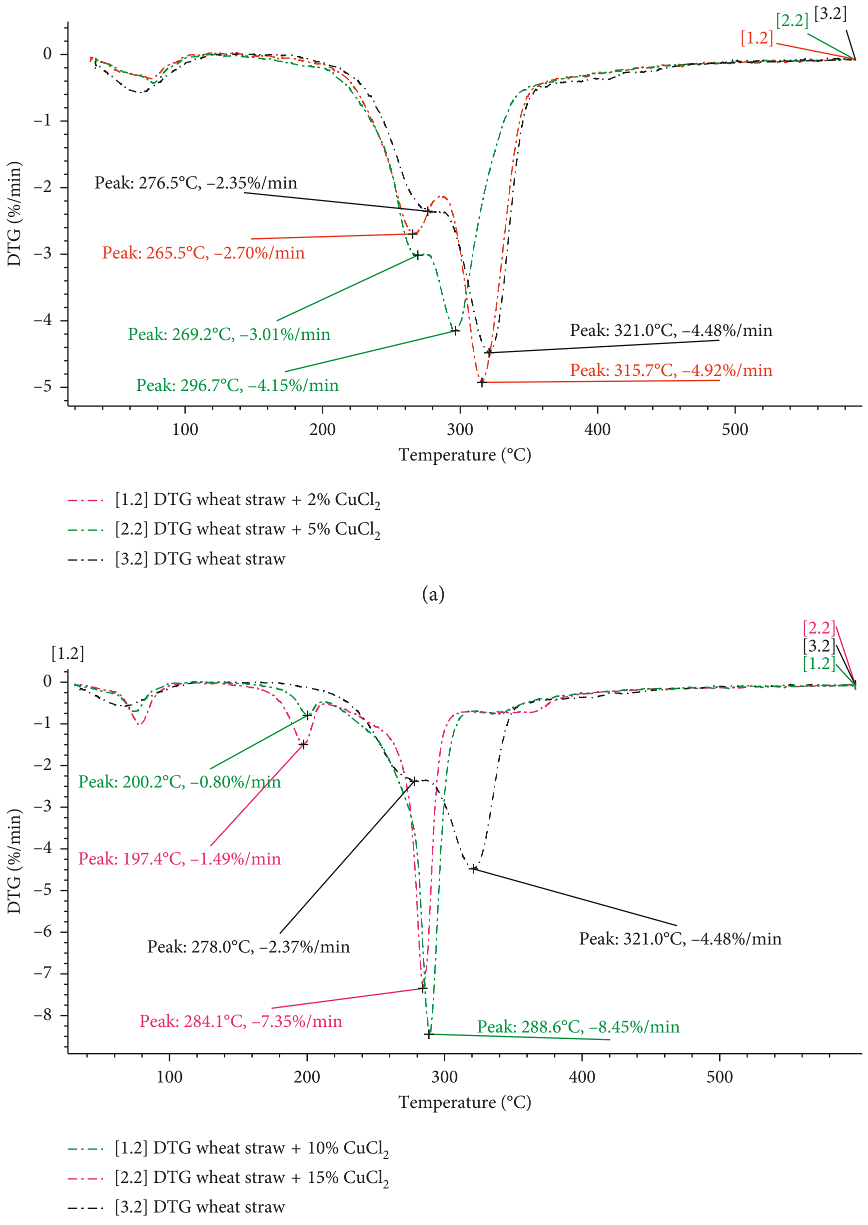
Figure 6: Mass spectrometric study of volatile products of wheat straw pyrolysis without additives (a) and with 10 wt.% CuCl$_2$ (b).

10 wt.% was used in the study at the laboratory pyrolysis unit. It should be noted that in the case of a noncatalytic pyrolysis process, the weights of gaseous, liquid, and solid products were found to be 35.9, 26.1, and 38.0 wt.%, respectively. The use of copper chloride (10 wt.%) led to an increase in the weight of liquid and solid products by the factor of 1.35 and 1.11, respectively, by reducing the weight of gaseous products by the factor of 1.36. It is noteworthy that no decrease in the volume of gaseous products was observed. This should logically lead to a decrease in the average molecular weight of the pyrolysis gas, which is confirmed by chromatographic analysis of gaseous products. In the presence of CuCl$_2$, the hydrogen content during the process increases from 5 to 20 vol. %; meanwhile, the total CO$_2$ content in the gaseous products decreases from 11.5 to 0.3 vol.%.

The analysis of solid carbon residue obtained in the wheat straw pyrolysis experiment in the presence of CuCl$_2$ by the XPS method results in a survey photoelectron spectra shown in Figure 8(a) and high-resolution photoelectron spectra of the Cu 2p sublevel shown in Figure 8(b). Carbon, nitrogen, oxygen, copper, calcium, silicon, phosphorus, chlorine, and potassium were found on the surface of the solid carbon residue. Carbon, oxygen, calcium, silicon, phosphorus, and chlorine were found in a large amount that can be explained by the presence of these elements in the raw material.

The analysis of Cu 2p3/2 high-resolution spectra shows that copper chloride added to a wheat straw as a catalyst was completely transformed into metallic copper (932.4 eV) and copper oxide (933.7 eV), as well as partially oxidized copper (933.0 eV).

The analysis of high-resolution photoelectron spectra for C 1s sublevel (Figure 9) allows concluding that the major amount of carbon on the solid residue surface is presented by the graphite and some aromatics (284.6 eV), as well as the



(a)

(b)

Figure 7: Thermogravimetric study of the $CuCl_2$ concentration effect on the wheat straw pyrolysis: (a) concentration range 2–5 wt.%; (b) concentration range 10–15 wt.%.

alcohol compounds (285.7 eV) and carbonyl and carboxylic groups (286.7 and 289.0 eV).

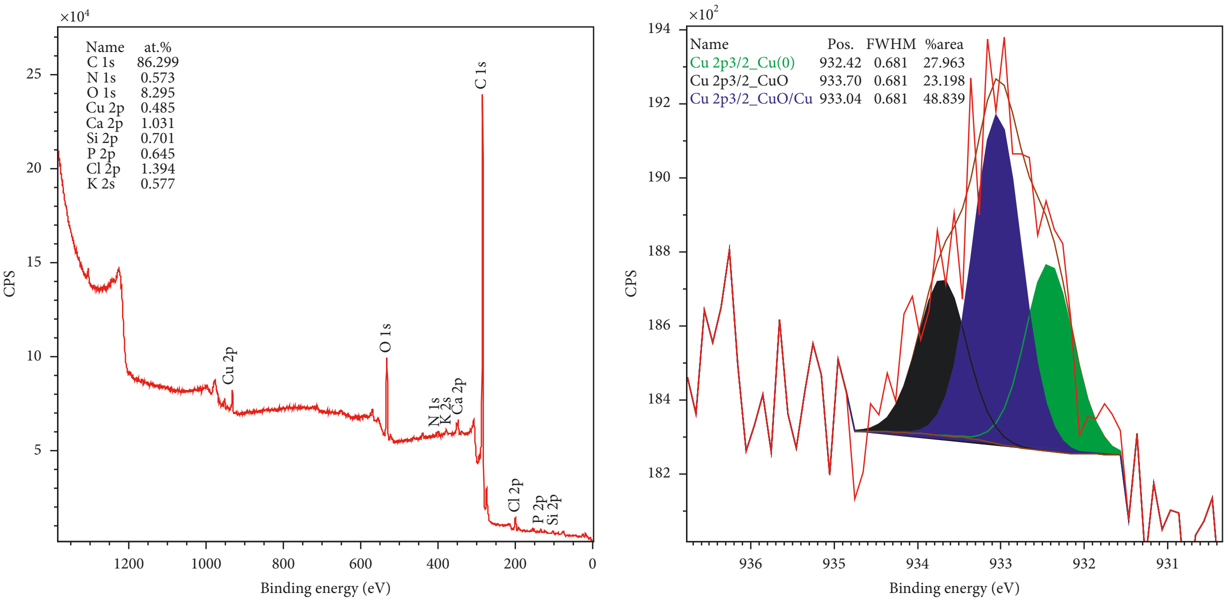
Thus, the solid residue obtained by wheat straw pyrolysis in the presence of copper chloride, the carbonaceous matrix containing graphite, and condensed aromatic rings impregnated by copper phase was produced.

The study of the solid carbon residue of wheat straw pyrolysis using the XFA method showed that the copper content in the solid pyrolysis residue was 0.31 wt.%. It may indicate a slight copper migration into the internals of the carbon residue.

The results of the study of solid residues obtained in the pyrolysis without the catalyst and in the presence of $CuCl_2$ showed that the presence of the catalyst leads to the increase in the specific surface area from 24 ± 0.1 to $63.5 \pm 0.1\ m^2/g$ due to an increase in the total pore volume. The pore size distribution and the surface area of the wheat straw and the carbon-containing residue obtained during noncatalytic and catalytic pyrolysis are presented in Table 2.

4. Conclusions

The studied metal chlorides were found to accelerate the thermal decomposition of the hemicellulosic components of wheat straw in different degrees. $CuCl_2$ had the highest influence on the pyrolysis process of wheat straw. The use of



(a) (b)

Figure 8: Survey photoelectron spectra of wheat straw pyrolysis solid carbon residue in the presence of $CuCl_2$ (a) and high-resolution photoelectron spectra of the Cu 2p3/2 sublevel (b).

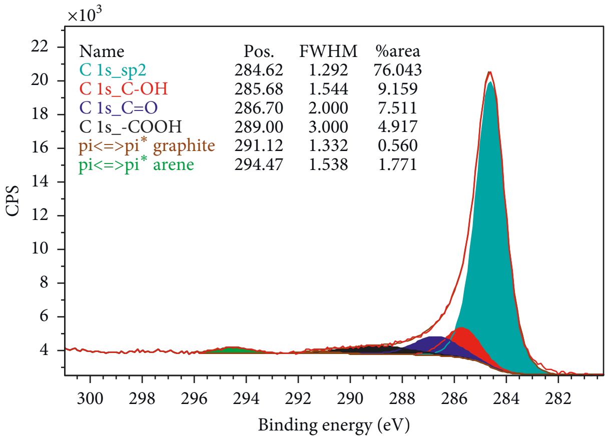


Figure 9: High-resolution photoelectron spectra of the C 1s sublevel.

Table 2: Analysis of the porosity of the initial wheat straw and pyrolysis solid residues.

Sample	Wheat straw		Carbonaceous residue of wheat straw pyrolysis		Carbonaceous residue of wheat straw pyrolysis + $CuCl_2$ 10 wt. %	
Pore diameter range (nm)	Pore volume (mL/g)	(%)	Pore volume (mL/g)	(%)	Pore volume (mL/g)	(%)
Under 6	0.00648	28.94	0.00642	27.41	0.01639	27.80
6–8	0.00311	13.90	0.00305	13.02	0.00844	14.32
8–10	0.00164	7.31	0.00167	7.14	0.00449	7.61
10–12	0.00176	7.87	0.00176	7.51	0.00481	8.16
12–16	0.00172	7.66	0.00188	8.05	0.00541	9.18
16–20	0.00163	7.29	0.00173	7.38	0.00479	8.12
20–80	0.00471	21.05	0.00544	23.23	0.01116	18.93
Over 80	0.00134	5.98	0.00147	6.26	0.00346	5.88
Total	0.02240	100.0	0.02341	100.00	0.05896	100.00
t-Plot surface area (m^2/g)	20.6 ± 0.1		24.0 ± 0.1		63.5 ± 0.1	

copper chloride during the pyrolysis resulted in a decrease in the molecular weight distribution of volatile products, as well as a decrease in the yield of gaseous pyrolysis products due to an increase in the yield of liquid and solid products. The use of copper chloride also led to an increase in the specific surface area of the solid pyrolysis residue, which is probably due to the intense coke formation. XPS data indicate a change in the composition of $CuCl_2$ during the pyrolysis of wheat straw. This indicates the initiating role of this compound in the presented process. The resulting copper-containing carbon residue can potentially be used as a catalyst for the conversion of furfuryl alcohol to 2-methylfuran.

Data Availability

The experimental data used to support the findings of this study are included in the article and in [17].

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

This work was financially supported by the Russian Foundation for Basic Research (grants 18-08-00794 and 17-08-00660). The authors thank Dr. Alexey V. Bykov and Prof. Alexander I. Sidorov for the analysis of the solid residue samples.

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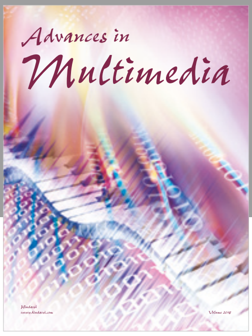
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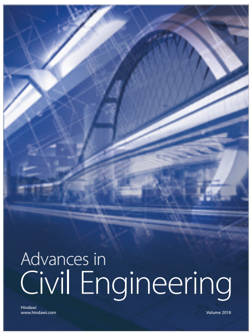
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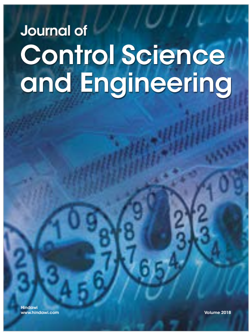
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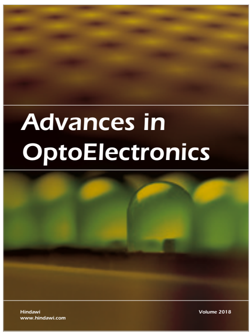
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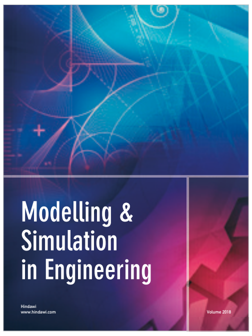
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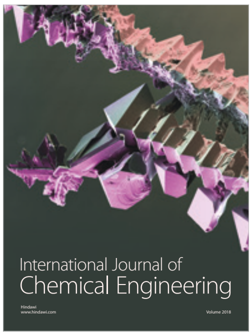
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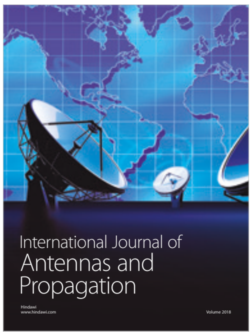
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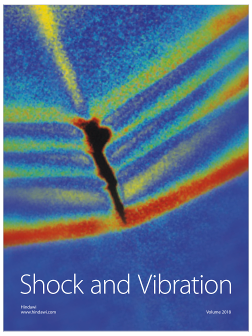
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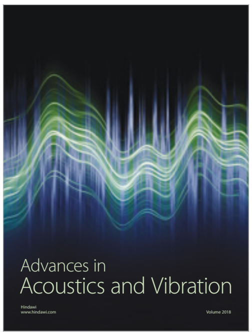
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