

CHENGFANG SONG¹, ARTUR PAWŁOWSKI², JIANBING JI³
SHENGDAO SHAN¹, YUCHENG CAO¹

CATALYTIC PYROLYSIS OF RICE STRAW AND PRODUCT ANALYSIS

The effect of addition of NaOH on the pyrolysis of rice straw and properties of its product were investigated. The pyrolysis was examined by means of the thermogravimetric (TG) analysis, and the pyrolysis product was characterized by the elemental analysis, GC and GC-MS. The result showed that addition of NaOH can significantly change TG and DTG peak of the pyrolysis of rice straw. As a result of the catalysis, significant difference in the properties of pyrolysis products was also observed. The addition of the catalyst promoted the increase of the hydrogen content of the gaseous product (from 1.6% to 53.37%), as well as that of the H/C and O/C ratios of solid residue. GC-MS analysis indicated that the liquid product was mainly made up of ketones, phenols and furfural, and NaOH addition did not change the main constitute of the liquid product, but changed their relative content.

1. INTRODUCTION

Development of our civilization greatly depends on supply of energy [1, 2]. Resources of fossil fuels, which nowadays are the most important sources of energy will be exhausted in life time of one generation [3]. A possibility of extraction of shale gas will increase the supply of fossil fuels derived energy for a few decades [4]. Although exhaustion of fossil fuels resources, as energy resources, seems to be the major problem, bigger attention is paid to climate change due to increased emission of CO₂ [5, 6]. To decrease both the exhaustion of fossil fuels and the emission of CO₂, a wide usage of renewable energy sources is recommended [7, 10].

¹School of Environmental and Recourse Science, Zhejiang Agriculture and Forestry University, Hangzhou 311300, China, corresponding author Y. Cao, e-mail: Cao.y@wis.pol.lublin.pl

²Faculty of Environmental Engineering, Lublin University of Technology, ul. Nadbystrzycka 40B, 20-618 Lublin, Poland.

³Research Center of Biomass Energy Engineering, College of Chemical Engineering and Materials Science, Zhejiang University of Technology, 310014 Hangzhou, Zhejiang, China.

One of important resources of renewable energy is biomass. According to EU strategy in 2020, the European Union should use 10% of biofuels for transport [1]. However, according to Pimentel, the use of liquid biofuels will contribute to the increase of the carbon print by about 60%, depending on type of fuel [11]. It means that it does not concern low carbon fuels.

Situation is better when wastes containing biomass are used. One of the most promising methods is production of biogas from wastes using anaerobic fermentation method [12–15] and pyrolysis [17–19].

Pyrolysis is an oxygen-free thermochemical process by which biomass can be decomposed into solid carbon, bio-oil and gases. A number of factors such as addition of catalysts, the type of biomass, water content, inherent minerals, heating rates and reactor patterns have an effect on the process of pyrolysis and properties of its product. It has been widely observed that addition of a catalyst can enhance the pyrolysis reaction for the same ingredients [20], and target product yields or selectivity could be increased by the process of catalytic pyrolysis [21–23]. Therefore, the research of catalytic pyrolysis has been receiving more and more attention.

This process is of great interest to China which produce annually more than 700 million tons of crop straw. Our research group focuses on studying catalytic pyrolysis of a variety of biomass materials by using molten and solid state NaOH as a catalyst. As a part of larger work, this paper was aimed to investigate the effect of inorganic base NaOH on the pyrolysis of rice straw, including the changes of weight loss and the composition of pyrolysis products.

2. MATERIALS AND METHODS

Materials. The rice straw, with a particle size of 100 mesh, used in this study was collected from Zhejiang, China. The samples were dried at 100 °C to a constant weight for subsequent use. NaOH was the analytical reagent available on market. The results of industrial (GB2122008) and elemental (VARIOEL-3) analyses of rice straw are given inn Table 1.

Table 1

Results of industrial and elemental analyses of rice straw [wt. %]

Industrial analysis				Elemental analysis/				
Mad	Ad	Vd	FCd	C	H	O	N	S
14.17	14.93	66.33	4.57	40.79	7.66	49.89	1.17	0.49

Thermogravimetry. Thermogravimetric investigation of rice straw samples was performed using a thermogravimetric analyzer (TGA, type TG 209 F3 Tarsus, instru-

ment accuracy 1 μg). The initial weight all samples investigated was close to 10 mg. The samples were heated up to 700 $^{\circ}\text{C}$ with the heating rate of 10/30/50 deg/min under nitrogen atmosphere (100 cm^3/min).

Pyrolysis. The experiments were conducted in a cylindrical fixed bed reactor made of stainless steel. In each test, the reactor was charged with 120 g of rice straw and sealed. The nitrogen (1000 cm^3/min) was introduced into the reactor to purge air and carry gaseous product. The reactor was heated to 550 $^{\circ}\text{C}$ at 7–10 deg/min until constant temperature was maintained for 20 min with less than ± 10 K variation. After the treatment, the reactor was cooled in a natural way to the room temperature. The gaseous product was removed by nitrogen from the reactor and condensed in a multistage glass spherical condensing tube, and then liquid bio-oil and non-condensable gas were obtained. The gas fraction was sampled after drying and the bio-oil was extracted with carrene. The solid product was characterized by the elemental analysis.

Composition of products. The main composition of gas and bio-oil was analyzed by using gas chromatograph (GC 9790SD) and GC-MS (GC7890A-MS5975C), respectively. The elemental composition of biochar was determined by the elemental analysis (VARIOEL-3).

3. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependence of weight loss (TG) and weight loss rate (DTG) of rice straw at three various heating rates. The data on pyrolysis of rice straw were listed in Table 2.

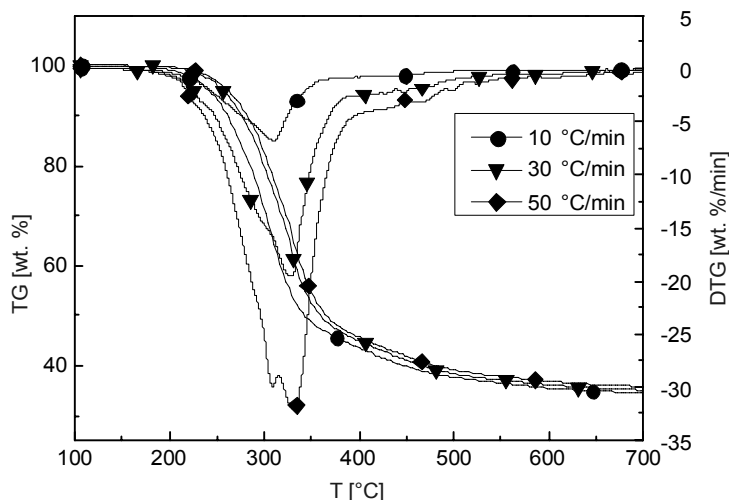


Fig. 1. TG and DTG curves of pyrolysis of rice straw at various heating rates

Table 2

Parameters of pyrolysis of rice straw at various heating rates

Heating rate [°C/min]	Temperature range [°C]	T_p^{DTG} [°C]	$\left(\frac{dw}{dt}\right)_{max}$ [wt. %/min]	Weight loss [%]
10	261.3–352.7	312.0	7.52	69.37
30	269.3–362.0	325.5	20.01	65.93
50	272.6–366.8	330.0	32.24	65.26

As is visible in Fig. 1, the shapes of TG curves at various heating rates are almost the same. When heating rates increase from 10 deg/min to 50 deg/min, the temperature ranges of pyrolysis do not increase significantly but the maximum weight loss rate and the corresponding temperature increase from 7.52 wt. %/min and 312 °C to 32.24 wt. %/min and 330 °C, respectively, and the peaks of DTG curve became sharper. These changes were closely related to biomass particle heat transfer and mass transfer.

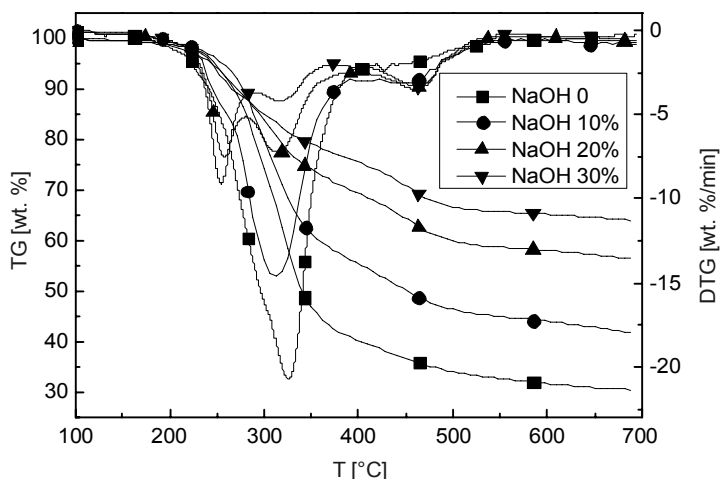


Fig. 2. TG and DTG curves of pyrolysis of rice straw with various additions of NaOH

In Figure 2, only one peak on the DTG curve is present at the heating rate of 10 deg/min but a shoulder peak gradually appeared upon increasing heating rate. This is due to the fact that gradient of temperature of a particle and distribution of temperature are smaller and at low heating rates, whereas pyrolysis peaks of hemicellulose and cellulose are overlapping. The peak at lower temperature refers to the decomposition of hemicellulose, and that at higher temperature – to cellulose [24].

The TG and DTG curves of rice straw changed apparently after adding NaOH. The temperature range of pyrolysis was broader, the one peak on DTG curves visible during pyrolysis of pure rice straw split into two peaks clearly as a result of 10%

NaOH addition, and further into three peaks as the content of NaOH increased. Pyrolysis of semicellulose and cellulose occurs at 220–315 °C and 315–400 °C, respectively. Above 400 °C, mainly slow pyrolysis of lignin occurs [25]. Thus it may be concluded that three peaks originated from pyrolysis of hemicellulose, cellulose and lignin. For pure rice straw pyrolysis, the weight loss of hemicellulose and cellulose was significant and their peaks overlapped, whereas lignin pyrolysis was slow and the peak was not obvious. After adding NaOH, the lignin weight losses intensified and its peaks were much sharper. The peaks assigned to hemicellulose and cellulose were separated from each other upon increasing content of NaOH. Since the temperature of the maximum weight loss rate of cellulose was relatively stable, the separation of the peaks was due to decrease of the temperature of the semicellulose pyrolysis. Summing up, the catalysis by NaOH promoted pyrolysis of lignin in rice straw and decreased the temperature of hemicellulose pyrolysis. This result shows that catalytic pyrolysis of rice straw with NaOH may lead to different products at various temperatures. Under the assumption that the nitrogen volume is constant, the contents of the main components of the gas products were calculated by the external standard method (Table 3).

Table 3

Gas composition depending on the presence of NaOH [%]

Material	H ₂	CO	CH ₄	CO ₂	Other
Rice straw	1.60	0.66	54.45	31.09	12.20
Rice straw + 15% NaOH	53.37	0.20	32.70	12.09	1.64

Table 3 shows that NaOH has a great influence on the gas composition of the products of rice straw pyrolysis. After adding NaOH, the content of H₂ increased from 1.60% to 53.37%, and the total content of 29.56% of flammable gases (H₂, CO and CH₄) was obtained. NaOH can promote the generation of hydrogen, and catalytic pyrolysis of rice straw with NaOH can be a method of preparation of hydrogen. It seems that NaOH might play a special role in obtaining hydrogen energy, exploitation and utilization of biomass [26]. Composition of the solid product depending on the presence of NaOH is presented in Table 4.

Table 4

Composition of the solid product depending on the presence of NaOH [%]

Material	N	C	H	S	O	H/C	O/C
Rice straw	1.61	59.43	2.35	0.39	33.85	0.04	0.57
Rice straw + 15% NaOH	1.32	51.4	2.12	0.35	41.06	0.041	0.799

Table 4 summarizes the main elements of biochar, and that it was mainly composed of carbon. It was also found that the effect of NaOH catalyst on the content of

carbon and oxygen was remarkable, the content of carbon decreased from 59.43% to 51.4%, while the content of oxygen increased from 33.85% to 41.06%.

The elemental ratios of H/C and O/C explain the degree of aromaticity, maturation and bonding arrangement of the biochar samples [15]. Both H/C and O/C ratios increased from 0.04% and 0.57% to 0.041% and 0.799%, respectively, in the presence of NaOH, which indicated more H and O elements in the solid residue. This means that the rate of carbonization of rice straw decreased. It was noted that in the biochar obtained ratios H/C were very low (ca. 0.04%), what points to its high stability [27].

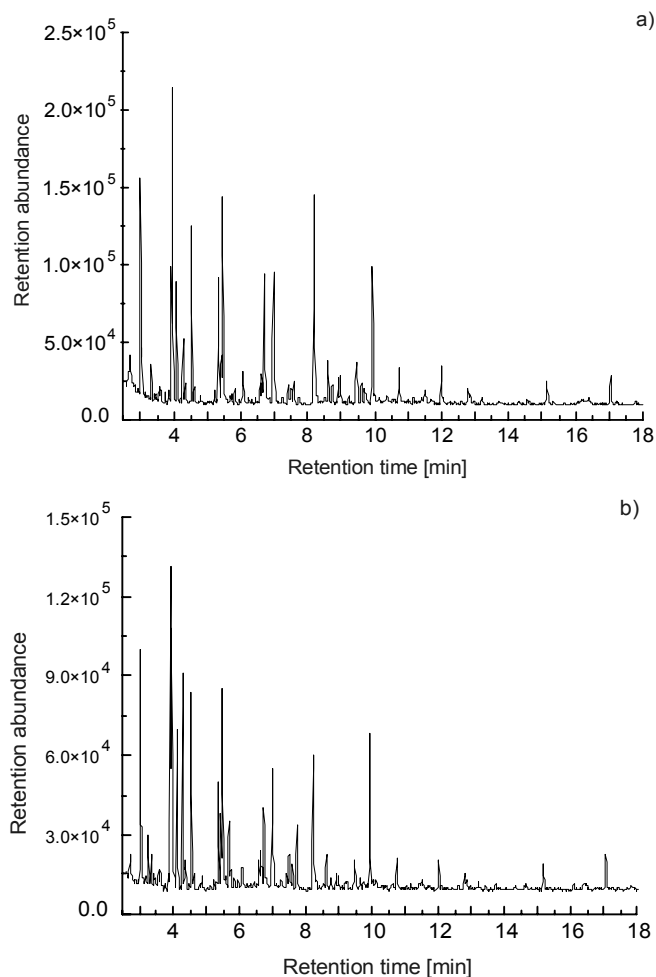


Fig. 3. Total ion current diagrams of liquid product of rice straw pyrolysis: a) rice straw, b) rice straw + 15% NaOH

Effect of sodium hydroxide on the bio-oil composition was studied. Acetone was used as an extractant to give bio-oil of high purity according to the mass ratio of 2:1. Figure 3 is the total ion chromatogram of bio-oil. Table 5 presents the main compounds in the bio-oil obtained from acetone extract. By the peak area normalization method, the relative contents of 11 main components have been calculated. The retention time of 11 compounds was concentrated between 3 and 12 min.

Table 5

Composition of bio-oil depending on the presence of NaOH

No.	Molecular formula	Compound	Rice straw [%]	Rice straw +15% NaOH [%]
1	C ₄ H ₈ O ₂	1-hydroxy-2-butanone	9.48	11.89
2	C ₅ H ₄ O ₂	furfural	7.42	8.59
3	C ₅ H ₆ O	2-cyclopenten-1-one	13.35	12.32
4	C ₆ H ₁₂ O ₂	4-hydroxy-4-methyl-2-pentanone	4.83	7.47
5	C ₅ H ₈ O ₃	1-acetoxy-2-propanone	6.27	8.65
6	C ₆ H ₈ O	2-methyl-2-cyclopenten-1-one	4.94	4.23
7	C ₅ H ₈ O	cyclopentanone	11.70	10.79
8	C ₅ H ₆ O ₂	1,2-cyclopentanedione	0.07	3.47
9	C ₆ H ₈ O	3-methyl-2-cyclopenten-1-one	7.08	4.88
10	C ₆ H ₆ O	phenol	8.20	6.80
11	C ₆ H ₈ O ₂	3-methyl-1,2-cyclopentanedione	12.70	8.61

As is seen from Table 5, the bio-oil was mainly composed of ketones, phenols and furfural. These polar compounds contain oxygen, thus the bio-oil has a high oxygen and hydrophilic content. The addition of NaOH to rice straw did not change main components in the bio-oil but changed their relative content.

By the GC-MS analysis it was found that content of 2-cyclopenten-1-one was highest and it was followed by 3-methyl-1,2-cyclopentanedione, cyclopentanone, 1-hydroxy-2-butanone. These were 4 compounds accounting for more than 40% of the total amount of compounds. At the same time biphenyl, anthracene with larger molecular weight and aromatics were also found in greater than 15 min retention time, which may be generated by lignin pyrolysis. The composition of the liquid fraction suggests its further exploitation as a liquid fuel or chemical feedstock.

4. CONCLUSIONS

The present study showed that NaOH can promote reaction of pyrolysis of lignin in rice straw and decrease the temperature of pyrolysis of hemicellulose. The catalyst also significantly increased the content of hydrogen in gas from pyrolysis of biomass.

The biochar obtained had very low H/C ratios (ca. 0.04%), the carbon content decreased and both H/C and O/C ratios of biochar were increased as well. The bio-oil is mainly composed of polar ketones, phenols and furfural containing oxygen. NaOH does not change main components of the liquid product but only affects their relative content. Therefore, this study can provide the method for the treatment and comprehensive utilization of rice straw by catalytic pyrolysis technology.

ACKNOWLEDGEMENTS

This research was financially supported by the Public Service Project of the Department of Science and Technology in Zhejiang Province (2012C32006) and the Priority Theme of Great Agriculture Project (2010C12001) of the Department of Science and Technology in Zhejiang Province.

REFERENCES

- [1] HOEDL E., *Europe 2020 Strategy and European Recovery*, Problemy Ekorozwoju, 2011, 6 (2), 11.
- [2] WALL G., *Exergy, Life and Sustainable Development*, Problemy Ekorozwoju, 2013, 8 (1), 27.
- [3] PAWŁOWSKI L., *Do the Liberal Capitalism and globalization Enable the Implementation of Sustainable Development Strategy?*, Problemy Ekorozwoju, 2012, 7 (2), 7.
- [4] SIEMEK S., NAGY S., SIEMEK P., *Challenges for Sustainable Development: The Case of Shale Gas Exploitation in Poland*, Problemy Ekorozwoju, 2013, 8 (1), 91.
- [5] PAWŁOWSKI L., *Is Development of Nowadays world Sustainable?*, Problemy Ekorozwoju, 2010, 5 (2), 9.
- [6] LINDZEN R.S., *Global Warming: The Origin and Nature of the Alleged Scientific Consensus*, Problemy Ekorozwoju, 2010, 5 (2), 13.
- [7] DASGUPTA P., TENEJA N., *Low Carbon Growth: an Indian Perspective on Sustainability and Technology Transfer*, Problemy Ekorozwoju, 2011, 6 (1), 65.
- [8] SHAN S., BI X., *Low Carbon Development of China's Yangtze River Delta Region*, Problemy Ekorozwoju, 2012, 7 (2), 33.
- [9] LEBIOCKA M., MONTUSIEWICZ A., PAWŁOWSKA M., *Variability of Heavy Metal Concentrations in the Co-Digestion Proceedings of EURASIA Waste Symposium*, Istanbul, 2011.11.14–17.
- [10] PAWŁOWSKA M., SIEPAK J., *Współfermentacja odpadów komunalnych i osadów ściekowych na składowisku odpadów*, [w:] *Polska inżynieria środowiska pięć lat po wstąpieniu do Unii Europejskiej*, t. 3, M. Dudzińska, L. Pawłowski (red.), Monografie Komitetu Inżynierii Środowiska, 2009, 60, 191–198.
- [11] PIEMENTEL D., *Energy production from Maize*, Problemy Ekorozwoju, 2012, 7 (2), 15.
- [12] PAWŁOWSKI L., PAWŁOWSKA M., DADEJ W., *Method and device for methane recovery from biogas with low content of methane*, Patent No. EP08169065.3, 2008.11.13.
- [13] PAWŁOWSKI L., PAWŁOWSKA M., DADEJ W., *Method and device for enrichment of biogas with methane from purified municipal waste*, Patent No. EP08169066.1, 2008.11.13.
- [14] PAWŁOWSKI L., PAWŁOWSKA M., *Method for utilisation of sewage sludge integrated with energy recovery*, Patent No. EP08173045.9, 2008.12.29.
- [15] MONTUSIEWICZ A., PAWŁOWSKI L., OZONEK J., PAWŁOWSKA M., LEBIOCKA M., *Method and device for intensification of biomass production from communal sewage sludge*, Patent No. EP08173043.4, 2008.12.29.
- [16] PAWŁOWSKI L., MONTUSIEWICZ A., POLESZAK A., DUKLEWSKI W., JAŚKOWSKI R., *Method for producing biogas from sewage sludge*, Patent No. EP10197094.5, 2009.12.27.

- [17] SKOULOU V., ZABANIOTOU A., *Fe catalysis for lignocellulosic biomass conversion to fuels and materials via thermochemical processes*, Catal. Today, 2012, 196 (1), 56.
- [18] SADDAWI A., JONES J.M., WILLIAMS A., LE COEUR C., *Commodity fuels from biomass through pre-treatment and torrefaction: Effects of mineral content on torrefied fuel characteristics and quality Saddawi*, Energy Fuels, 2012, 26, 6466.
- [19] LORICERA C.V., CASTAÑO P., INFANTES-MOLINA A., HITA I., GUTIÉRREZ A., ARANDES J.M., FIERRO J.L.G., PAWELEC B., *Designing supported ZnNi catalysts for the removal of oxygen from bio-liquids and aromatics from diesel*, Green Chem., 2012, 14 (10), 2759.
- [20] CHATTOPADHYAY J., KIM C., KIM R., PAK D., *Thermogravimetric study on pyrolysis of biomass with Cu/Al₂O₃ catalysts*, J. Ind. Eng. Chem., 2009, 15 (1), 145.
- [21] HAN J., KIM H., *The reduction and control technology of tar during biomass gasification/pyrolysis. An overview*, Renew. Sust. Energ. Rev., 2008, 12 (2), 397.
- [22] REN Q.Q., ZHAO C.S., WUA X., LIANG C., CHEN X.P., SHEN J.Z., TANG G.Y., WANG Z., *Effect of Mineral Matter on the Formation of NO_x Precursors during Biomass Pyrolysis*, J. Anal. Appl. Pyrolysis, 2008, 85 (1–2), 447.
- [23] MEDRANO J.A., OLIVA M., RUIZ J., GARCÍA ARAUZO J., *Catalytic steam reforming of model compounds of biomass pyrolysis liquids in fluidized bed reactor with modified Ni/Al catalysts*, J. Anal. Appl. Pyrolysis, 2009, 85 (1–2), 214.
- [24] ANTAL M.J., VARHEGYI G., *Cellulose Pyrolysis Kinetics: The Current State of Knowledge*, Ind. Eng. Chem. Res., 1995, 34 (3), 703.
- [25] RAVEENDRAN K., GANESH A., KHILAR K.C., *Pyrolysis characteristics of biomass and biomass components*, Fuel, 1996, 75 (8), 987.
- [26] LIU W.W., HU C.W., YANG Y., TONG D.M., *Study on the effect of metal types in (Me)-Al-MCM-41 on the mesoporous structure and catalytic behavior during the vapor-catalyzed co-pyrolysis of pubescens and LDPE*, Appl. Phys. B: Environmental, 2013, 129 (17), 202.
- [27] GHANI ABDUL K.W.A.W., MOHD G.D.S.A., BACHMANN R.T., TAUFIQ-YAP Y.H., RASHID U., AL-MUHTASEB ALA'A H., *Biochar production from waste rubber-wood-sawdust and its potential use in C sequestration: Chemical and physical characterization*, Ind. Crop. Prod., 2013, 44, 18.