

Catalytic Fast Pyrolysis of Cellulose by Integrating Dispersed Nickel Catalyst with HZSM-5 Zeolite

Xiaojuan Lei^{1,a}, Yadong Bi^{1,b}, Wei Zhou^{1,c}, Hui Chen^{1,*}, Jianli Hu^{2,*}

¹Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemical Engineering, Tianjin University of Technology, Tianjin, 300384, China.

²Department of Chemical and Biomedical Engineering, West Virginia University, Morgantown, 26506, USA

*Correspondence: chenhui_410@163.com, jianlijohnhu@hotmail.com

^a1513135311@stud.tjut.edu.cn, ^beasecloud_801@sina.com, ^c563386800@qq.com

Abstract. The effect of integrating dispersed nickel catalyst with HZSM-5 zeolite on upgrading of vapors produced from pyrolysis of lignocellulosic biomass was investigated. The active component nickel nitrate was introduced onto the cellulose substrate by impregnation technique. Based on TGA experimental results, we discovered that nickel nitrate first released crystallization water, and then successively decomposed into nickel oxide which was reduced in-situ to metallic nickel through carbothermal reduction reaction. In-situ generated nickel nanoparticles were found highly dispersed over carbon substrate, which were responsible for catalyzing reforming and cracking of tars. In catalytic fast pyrolysis of cellulose, the addition of nickel nitrate caused more char formation at the expense of the yield of the condensable liquid products. In addition, the selectivity of linear oxygenates was increased whereas the yield of laevoglucose was reduced. Oxygen-containing compounds in pyrolysis vapors were deoxygenated into aromatics using HZSM-5. Moreover, the amount of condensable liquid products was decreased with the addition of HZSM-5.

1. Introduction

Bio-oils derived from lignocellulose pyrolysis are characterized by high oxygen content, high acidity, and high viscosity, which significantly limit its utilization in the existing petrochemical infrastructure [1-3]. Generally, pyrolysis vapors can be upgraded by catalytic conversion over solid acid catalysts such as zeolites to generate products of lower oxygen content [4-6]. HZSM-5 is known to be an effective deoxygenation catalyst which can convert pyrolysis vapors of lignocellulose directly to olefins and aromatics [4].

Due to the difficulty in homogeneous mixing of solid biomass with zeolite catalysts, the mass transfer limitation is usually a challenge in catalytic pyrolysis process, which leading to rapid deactivation caused by coke formation [3]. The introduction of the soluble material, such as inorganic acid, alkali, salt [8-9] and ionic liquid [10], into the lignocellulose substrate by solution impregnation



is a promising approach. As is well known, alkali metal and alkaline earth metal salts are naturally present in lignocellulose, which can effectively change the distribution of pyrolysis products from biomass [8-9].

The effect of adding transition metal salts, especially nickel salts, on the pyrolysis of lignocellulose biomass was studied and reported by a number of researchers in the field [11-16]. Impregnating lignocellulose biomass with nickel salt showed good pyrolysis performance in tar conversion and syngas upgrading. This is largely because the biomass polymer act as adsorption sites for highly dispersed metal cations. In-situ formed Ni^0 nanocrystals is considered as the active phase, which is responsible for hydrogen generation and tar conversion [14].

Supported Ni catalysts, Ni/MCM-41, was used to produce hydrogen and bio-oil with low-carbon deposits through a two-stage pyrolysis-gasification process [17]. In the fast pyrolysis of different kinds of woody biomass, small amounts of high molecular weight phenolic compounds and large amounts of low molecular weight phenols were observed in the presence of Ni supported on ZSM-5 zeolite.

In the literature, products from transition metal catalyzed lignocellulose pyrolysis were usually analyzed after the pyrolysis vapor had been condensed. The disadvantage is that vapor phase products could undergo condensation reaction, affecting the accuracy of the carbon balance. In this study, nickel nitrate was introduced into the cellulose substrate by impregnation technique. The influence of nickel nitrate on cellulose pyrolysis was analyzed on-line by Py-GC/MS instrumentation. The combined effect of impregnated nickel nitrate and HZSM-5 zeolites on catalytic pyrolysis of cellulose was investigated. Our approach is distinctly different from the conventional way of using supported catalyst in biomass pyrolysis. Prior research in biomass pyrolysis or gasification has focused on improving tar conversion and vapor upgrading by nickel catalysts. In contrast, our study is focused on the hypothesis that in-situ generated hydrogen by dispersed catalyst can improve product quality during pyrolysis.

2. Results

2.1. Thermo Gravimetric Analysis

The TGA/DTG curves of microcrystalline cellulose impregnated with different content of nickel nitrate are shown in Figure 1. According to the different behavior of weight loss in Figure 1, the temperature range during the entire TGA process can be divided into four stages. Table 1 presents the amount of weight loss in each stage.

Table 1. The weight loss of each stage in TG curves of cellulose impregnated with different content of nickel nitrate

Entry	Weight loss fractions (%)			
	RT-150 °C	150-270 °C	270-360 °C	360-700 °C
Cellulose	1.58	0.71	84.84	4.28
Cellulose-1wt.% $\text{Ni}(\text{NO}_3)_2$	1.75	4.39	78.23	9.00
Cellulose-2wt.% $\text{Ni}(\text{NO}_3)_2$	1.98	5.03	74.23	10.00
Cellulose-3wt.% $\text{Ni}(\text{NO}_3)_2$	2.19	6.65	71.68	9.67
Cellulose-4wt.% $\text{Ni}(\text{NO}_3)_2$	2.56	7.31	69.07	10.48
Cellulose-5wt.% $\text{Ni}(\text{NO}_3)_2$	2.53	8.65	67.19	10.95

The first stage, starting from initial temperature to 150 °C, was attributed to the water removal. All samples have shown the similar trends. Due to the release of crystallization water, the weight loss for nickel-containing cellulose increases with nickel content.

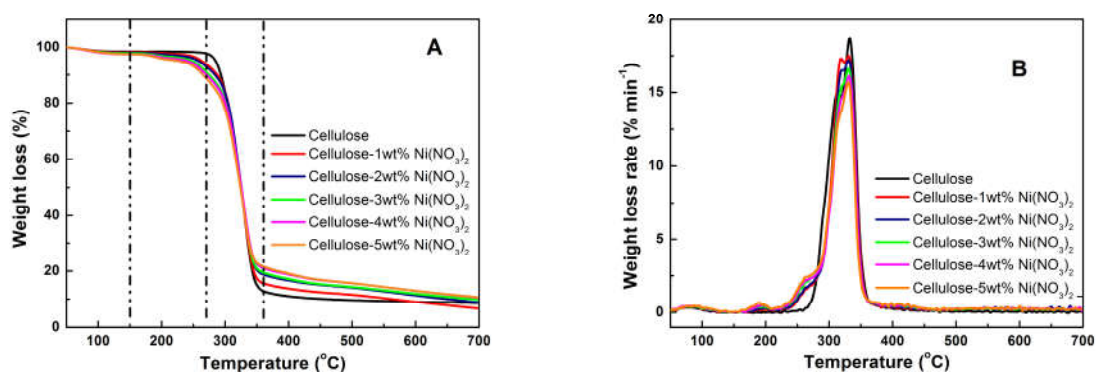


Figure 1. TGA profiles (A) and DTG profiles (B) for cellulose impregnated with different content of nickel nitrate.

In the second stage, which is from 150 to 270 °C, the pristine cellulose basically maintains constant weight. However, with the increase of nickel loading, the cellulose begins to decompose at a lower temperature. For example, from the DTG curve, the decomposition temperature of 5% nickel loading sample centered at 250 °C, with a mass loss of 8.65% at 270 °C. The addition of nickel nitrate leads to a lower onset temperature in the decomposition of cellulose.

During the third stage, which is from 270 to 360 °C, cellulose decomposition occurs resulting in significant weight loss. The peak temperatures of DTG curves are located near 330 °C, while the maximum decomposition rate of the nickel-containing samples is slightly reduced. The weight loss of pristine cellulose is 84.84%, while that of 5% nickel-containing sample is only 67.19%. This indicates that the addition of nickel nitrate causes more char formation at the expense of volatile compounds. As reported by Richardson [11], the impregnation of nickel ions can catalyze the dehydration and decarboxylation reaction of cellulose, which are beneficial to the formation of char.

In the fourth stage, which is from 360 to 700 °C, the pristine cellulose basically maintains constant weight, while the nickel-containing cellulose continues to lose weight. This is probably because that, in this temperature range, Ni^{2+} was reduced to Ni^0 through carbothermal reduction reaction $\text{NiO} + \text{C} \leftrightarrow \text{Ni} + \text{CO}$. Literature reported that nickel oxides can be reduced to metal nickel by the amorphous carbon atoms in 500 to 400 °C [11, 14]. In-situ generated nickel nanoparticles are highly dispersed over carbon substrate, which are effective in catalyzing reforming and cracking of tars. Therefore, the TGA curve shows continued weight loss due to tar conversion. Essentially, on raising temperature in TGA experiments, nickel nitrate first loss the crystallization water, then successively decomposed into nickel oxide, which are reduced to metallic nickel through carbothermal reduction reaction.

As shown in Table 1, at 1.0 wt% of nickel nitrate loading, the weight loss during the decomposition of cellulose is significantly affected. However, when nickel nitrate loading is further increased to 5.0 wt%, the impact on cellulose decomposition doesn't seem to increase. In the fourth stage (360–700 °C), the weight loss is $10.00 \pm 1\%$ for all nickel-containing cellulose. It was reported that when the concentration of nickel nitrate in the impregnating solution was 0.1 M, the final saturated adsorption capacity could be 0.07 moles per kg of wood [11], which is equivalent to 2.0 wt% nickel nitrate. The specific surface area of cellulose is very low and the number of oxygen-containing functional groups on the surface for adsorption of nickel ion is limited. With the increase of Ni loading, the poorly dispersed Ni nanoparticles deteriorate the catalytic activity. Therefore, the reforming/cracking conversion of the tar was not significantly improved. In addition, the catalytic activity of metallic nickel may also be inhibited by carbon deposition, because of the increase of char production during cellulose decomposition process for high nickel loading samples.

2.2. Cellulose Pyrolysis

2.2.1. Catalytic Pyrolysis of Cellulose by Impregnated Nickel Nitrate, the products from cellulose pyrolysis are very complex. It becomes very difficult to measure individual component. As a result, Dauenhauer [3] divided condensable liquid products into the 5 categories: Anhydrosugars, Linear oxygenates (small molecular oxygen-containing compounds), Furans (furan ring like oxygenated compounds), Cyclopentanes (five carbon ring oxide) and Undefined. The retention time and the characteristic ion fragments of each compound in the total ion current chromatogram. The yield of the condensable liquid product during Py-GC/MS experiments is represented by the sum of the absolute peak area of the total ion chromatogram peak (calibrated with the precise cellulose sample weight), while the selectivity of a certain category of compound is represented by the percentage of peak area measured in total area. Light gas, mainly CO₂, CO and other non-condensable gas, is not included in the sum of the absolute peak areas of condensable liquid products.

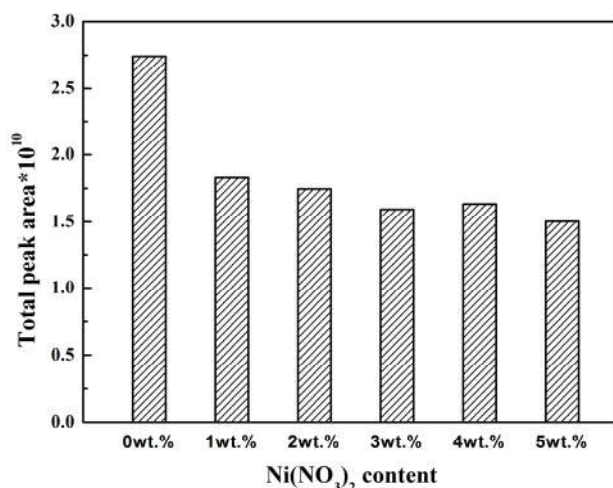


Figure 2. The total yield of condensable liquid products from fast pyrolysis of nickel-impregnating cellulose

The yield of the condensable liquid products from fast pyrolysis of nickel-containing cellulose at 600 °C is shown in Figure 2. It can be seen that the yield of the condensable liquid products decreases with the increase of nickel nitrate content. Collard has shown that nickel nitrate inhibits the thermal depolymerization of cellulose and thus reduces the yield of liquid products [13]. Consistent with the results of the thermogravimetric experiment, the yields of the liquid product is reduced, whereas gas and solid products are increased.

The selectivity of various categories of liquid products is shown in Figure 3. It can be seen that with the increase of nickel nitrate content from 1 wt% to 5 wt%, the selectivity of hydraugers decreases from 77.06% to 61.51%. Meanwhile, selectivity to linear oxygenates increases from 5.81% to 8%, selectivity to furans and cyclopentanes increase slightly.

In the pyrolysis reaction, cellulose is first melted, then depolymerized and decomposed. The decomposition reaction follows two pathways. One directly leads to low molecular weight products such as furan, laevoglucose, glycolaldehyde, and hydroxyl acetone, whereas the other pathway results in low-degree oligomers. The low-degree oligomers can further break down to form furan, light oxygenates, char, permanent gases, and laevoglucose [1].

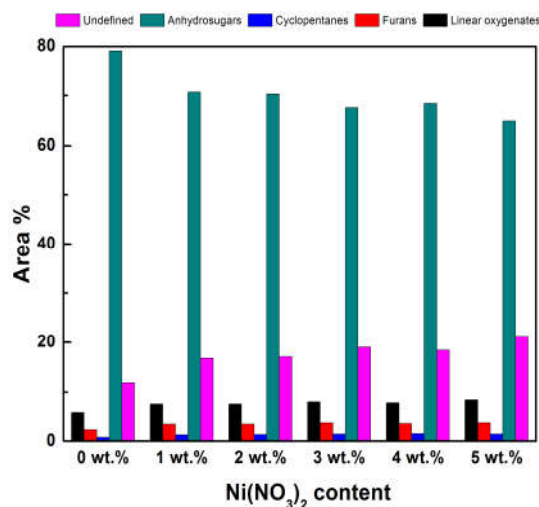


Figure 3. The selectivity of various condensable liquid products from fast pyrolysis of nickel-impregnating cellulose

The decrease in the selectivity of anhydrosugars indicates that nickel nitrate can inhibit the depolymerization of cellulose into laevoglucose. Laevoglucose can undergo condensed-phase secondary pyrolysis to form light oxygenates. Dehydration and isomerization of laevoglucose lead to the formation of other anhydro-monosaccharides. The secondary reaction of primary pyrolysis products was found to increase the yield to char. Re-polymerization and secondary pyrolysis of laevoglucose were found to be an important pathway for char formation [1].

As for the primary pyrolysis reaction products, laevoglucose and light molecular weight oxygenates are formed by competitive pyrolysis reactions rather than sequential pyrolysis reactions [7]. It has been reported that for cellulose pyrolysis, glycosidic bond cleavage and furan are directly produced from cellulose without passing through low molecular weight (e.g., glucose) intermediates [3], thus the selectivity of linear oxygenates has increased, while the yield of laevoglucose is reduced.

Nickel nitrate is a potential deoxygenation catalyst in pyrolysis process, which can catalyze decarboxylation reaction to generate large amounts of CO₂ [15]. The zero-valent nickel species formed by in-situ reduction can catalyze the water-gas shift reaction, CO disproportionation reaction, tar pyrolysis and reforming reaction, and therefore the amount of CO₂ increase. It can be observed that with the increase of impregnated nickel nitrate, the amount of liquid product did not change significantly, which is consistent with the results of thermogravimetric experiments.

2.2.2. Catalytic Pyrolysis of Cellulose using Impregnated Nickel Nitrate with HZSM-5, In this work, we present the catalytic pyrolysis of cellulose, employing impregnated nickel nitrate and HZSM-5 catalysts. Different from ordinary supported transition metal catalyst, the active component Ni²⁺ was introduced into the biomass matrix prior to the reaction by impregnating cellulose with nickel nitrate aqueous solutions, followed by mixing with HZSM-5. The yield of the condensable liquid products from fast pyrolysis of nickel-containing cellulose by Py-GC/MS at 600 °C is shown in Figure 4. It can be seen that the amount of liquid product decreases further with the addition of HZSM-5.

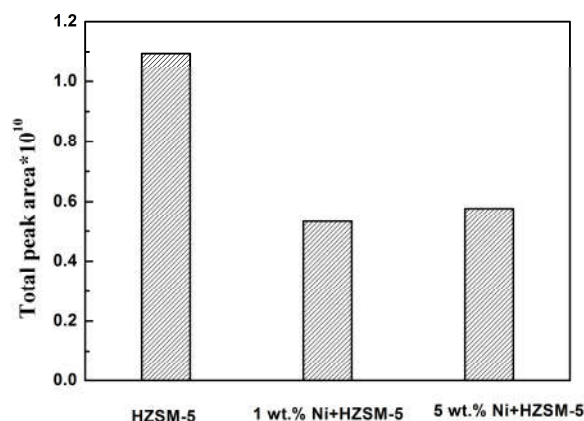


Figure 4. The total yield of condensable liquid products from fast pyrolysis of nickel-impregnating cellulose before and after adding HZSM-5

The selectivity of various categories of products is shown in Figure 5. The presence of HZSM-5 catalyst leads to improved deoxygenation of the high oxygen-containing compounds into aromatics. The liquid product consisting of mainly polycyclic aromatic hydrocarbon (PAH), monocyclic aromatics (BTX) and low molecular weight compounds (LMW, mainly furan or phenols), as well as a small amount undefined compounds. The retention time and the characteristic ion fragments of each compound in the total ion current chromatogram are shown in Table S2. There was no significant change in product selectivity after addition of metallic nickel. The introduction of Ni^{2+} results in the selectivities of BTX and PAH being 46.2% and 36.5%, respectively.

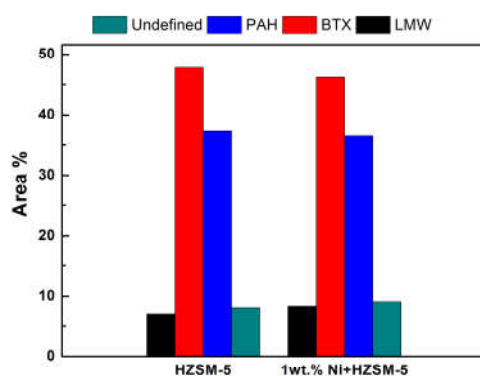


Figure 5. The selectivity of various condensable liquid products from fast pyrolysis of nickel-impregnating cellulose before and after adding HZSM-5

It is clear that Ni^{2+} inhibits cellulose depolymerization and levoglucosan production. With the combined effect of dispersed Ni^{2+} and HZSM-5 zeolite, the pyrolysis vapors of cellulose can be upgraded via complex reaction pathways, including acid-catalyzed dehydration, decarboxylation, alkylation, and reforming reaction, which leads to decrease in PAH and BTX aromatics.

3. Materials and Methods

3.1. Catalyst Preparation and Feedstock Pretreatment

Microcrystalline cellulose, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and HZSM-5 with Si/Al ratio of 50 were purchased commercially. Prior to the experiments, the HZSM-5 zeolite was crushed and sieved to 80-100 mesh and calcined at 550 °C in air for 5 h before use.

Hydrochloric acid treatment of cellulose was performed by heating 10 g of sample in 50 ml of 2.0 M HCl at 60 °C for 6 h to remove the impurities. The sample was filtered, and then washed using de-ionized water until a stable conductivity was reached (normally 30-40 μS).

To obtain 1-5 wt% nickel nitrate loading on cellulose, the appropriate amount of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 10 ml deionized water and the solution was then added to 2 g of cellulose and stirred to obtain well-mixed slurry. The sample was dried at 60 °C for 8 h to obtain the pretreated samples.

3.2. Thermo Gravimetric Analysis (TGA)

The nickel-impregnated cellulose samples were analyzed using a TGA analyzer (TG 209 F1 NETZSCH, Germany). For each test, a typical sample mass of 5 mg was used. TGA measurement was carried out under temperature of 40-700 °C with ramping rate of 10 °C/min under N_2 flow rate of 60 ml/min. The first derivative of the TGA curve (the DTG curve) may plotted to determine inflection points useful for in-depth interpretations.

3.3. Py-GC/MS Test

Pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) study was performed at a series of temperature using a micro-furnace system (PY-3030D, Frontier Laboratories, Japan) installed with a gas chromatograph (GC) (7890A, Agilent Technologies, USA). A mass spectrometer (MS) (5975C, Agilent Technologies, USA) was used to analyze the products. The injector temperature was kept at 300 °C with a carrier gas flow rate of 1.0 ml/min and a 1:100 split ratio. The GC oven temperature program began with 35 °C (3 min) to 130 °C with the heating rate of 5 °C /min and then to 250 °C at 20 °C/min. The final temperature was held for 2 min. The temperature of the GC/MS interface was held at 300 °C, and the mass spectrometer was operated in EI mode at 70 eV. The mass range from m/z 29 to 350 was scanned at 4.37 scans/s. Pyrolysis products were identified according to the NIST MS library and the literature data of bio-oils. In each experiment, about 0.3 mg sample (and 3 mg HZSM-5 for catalytic pyrolysis) were placed in a sample cup, and for each sample, experiments were conducted at least three times to confirm the reproducibility of the reported procedures.

4. Conclusion

Bio-oils derived from lignocellulose pyrolysis are characterized by high oxygen content, which significantly limit its utilization as transportation fuels and petrochemical replacement. HZSM-5 is known to be an effective deoxygenation catalyst which can upgrade pyrolysis vapors. The main disadvantages for zeolite catalyzed pyrolysis process are the rapid deactivation due to coke formation and mass transfer limitation between biomass powder and zeolite catalysts. In this work, as a promising solution to the main disadvantage, the soluble active component nickel nitrate is introduced into the cellulose substrate by impregnation method. The addition of nickel nitrate is very effective in cellulose pyrolysis based on TGA analysis. Through carbothermal reduction reaction in 400 to 500 °C, the nickel oxides can be reduced in-situ to metallic nickel nanoparticles which are highly dispersed over carbon substrate. The addition of 1 wt. % dispersed nickel catalyst significantly affected change the distribution of products of cellulose pyrolysis, based on the measurement by on-line Py-GC/MS technique. Experimental results have shown that the yield of the condensable liquid products decreases due to the combined effect of impregnated nickel nitrate and HZSM-5 zeolites. However, further increase nickel loading did not seem to have strong impact on biomass decomposition. The poorly dispersed nickel nanoparticles or the coke deposition could deteriorate the catalytic activity. To certain extent, the dispersion of nickel appeared to be more effective than nickel content in biomass pyrolysis.

References

- [1] Liu, C.J.; Wang, H.M.; Karim, A.M.; Sun, J.M.; Wang, Y. Catalytic fast pyrolysis of lignocellulosic biomass. *Chem. Soc. Rev.* 2014, *43*, 7594-7623, DOI: 10.1039/c3cs60414d.
- [2] Vispute, T.P.; Zhang, H.Y.; Sanna, A.; Xiao, R.; Huber, G.W. Renewable Chemical Commodity Feedstocks from Integrated Catalytic Processing of Pyrolysis Oils. *Science* 2010, *330*, 1222-1227, DOI: 10.1126/science.1194218.
- [3] Mettler, M.S.; Mushrif, S.H.; Paulsen, A.D.; Javadekar, A.D.; Vlachosa, D.G.; Dauenhauer, P.J. Revealing pyrolysis chemistry for biofuels production: Conversion of cellulose to furans and small oxygenates. *Energy Environ. Sci.* 2012, *5*, 5414-5424, DOI: 10.1039/c1ee02743c.
- [4] Wang, K.G.; Johnston, P.A.; Brown, R.C. Comparison of in-situ and ex-situ catalytic pyrolysis in a micro-reactor system. *Bioresource Technology* 2014, *173*, 124-131, DOI: 10.1016/j.biortech.2014.09.097.
- [5] Wang, Z.; Lu, Q.; Zhu, X.F.; Zhang, Y. Catalytic Fast Pyrolysis of Cellulose to Prepare Levoglucosenone Using Sulfated Zirconia. *ChemSusChem* 2011, *4*, 79-84, DOI: 10.1002/cssc.201000210.
- [6] Mettler, M.S.; Paulsen, A.D.; Vlachosa, D.G.; Dauenhauer, P.J. Tuning Cellulose Pyrolysis Chemistry: Selective Decarbonylation via Catalyst-Impregnated Pyrolysis. *Catal. Sci. Technol.* 2014, *4*, 3822-3825, DOI: 10.1039/c4cy00676c.
- [7] Patwardhan, P.R.; Satrio, J.A.; Brown, R.C.; Shanks, B.H. Product distribution from fast pyrolysis of glucose-based carbohydrates. *J. Anal. Appl. Pyrolysis* 2009, *86*, 323-330, DOI: 10.1016/j.jaap.2009.08.007.
- [8] Patwardhan, P.R.; Satrio, J.A.; Brown, R.C.; Shanks, B.H. Influence of inorganic salts on the primary pyrolysis products of cellulose. *Bioresource Technology* 2010, *101*, 4646-4655, DOI: 10.1016/j.biortech.2010.01.112.
- [9] Wang, K.G.; Zhang, J.; Shanks, B.H.; Brown, R.C. The deleterious effect of inorganic salts on hydrocarbon yields from catalytic pyrolysis of lignocellulosic biomass and its mitigation. *Applied Energy* 2015, *148*, 115-120, DOI: 10.1016/j.apenergy.2015.03.034.
- [10] Kudo, S.J.; Zhou, Z.W.; Norinaga, K.; Hayashia, J.I. Efficient levoglucosenone production by catalytic pyrolysis of cellulose mixed with ionic liquid. *Green Chem.* 2011, *13*, 3306-3311, DOI: 10.1039/c1gc15975e.
- [11] Richardson, Y.; Motuzas, J.; Julbe, A.; Volle, G.; Blin, J. Catalytic Investigation of in Situ Generated Ni Metal Nanoparticles for Tar Conversion during Biomass Pyrolysis. *J. Phys. Chem. C* 2013, *117*, 23812-23831, DOI: 10.1021/jp408191p.
- [12] Bru, K.; Blin, J.; Julbe, A.; Volle, G. Pyrolysis of metal impregnated biomass: An innovative catalytic way to produce gas fuel. *J. Anal. Appl. Pyrolysis* 2007, *78*, 291-300, DOI: 10.1016/j.jaap.2006.08.006.
- [13] Collarda, F.X.; Blin, J.; Bensakhria, A.; Valette, J. Influence of impregnated metal on the pyrolysis conversion of biomass constituents. *J. Anal. Appl. Pyrolysis* 2012, *95*, 213-226, DOI: 10.1016/j.jaap.2012.02.009.
- [14] Richardson, Y.; Blin, J.; Volle, G.; Motuzas, J.; Julbe, A. In situ generation of Ni metal nanoparticles as catalyst for H₂-rich syngas production from biomass gasification. *Applied Catalysis A: General* 2010, *382*, 220-230, DOI: 10.1016/j.apcata.2010.04.047.
- [15] Eibner, S.; Broust, F.; Blin, J.; Julbe, A. Catalytic effect of metal nitrate salts during pyrolysis of impregnated biomass. *J. Anal. Appl. Pyrolysis* 2015, *113*, 143-152, DOI: 10.1016/j.jaap.2014.11.024.
- [16] Shen, Y.F.; Yoshikawa, K. Tar Conversion and Vapor Upgrading via *in Situ* Catalysis Using Silica-Based Nickel Nanoparticles Embedded in Rice Husk Char for Biomass Pyrolysis/Gasification. *Ind. Eng. Chem. Res.* 2014, *53*, 10929-10942, DOI: 10.1021/ie501843y.
- [17] Wu, C.F.; Wang, L.Z.; Williams, P.T.; Shi, J.; Huang, J. Hydrogen production from biomass gasification with Ni/MCM-41 catalysts: Influence of Ni content. *Applied Catalysis B: Environ.* 2015, *168*, 102-110, DOI: 10.1016/j.apcatb.2015.05.015.

Environmental 2011, 108-109, 6-13, DOI: 10.1016/j.apcatb.2011.07.023.