OTTO VON GUERICKE
UNIVERSITÄT
MAGDEBURG

FACULTY FOR SYSTEM- AND PROCESS ENGINEERING

Literature Survey

by

Angshuman Buragohain

PYROLYSIS OF LIGNOCELLULOSIC MATERIALS

Topic: Sustainability Assessment (LCA) for Biofuels

Guide: Dr. Techn. Liisa Rihko-Struckmann

                    Max Planck Institute for Dynamics of
                    Complex Technical Systems

Date: 26.05.2019

1. ABSTRACT

Today, the majority of world energy needs are fulfilled by conventional sources. Fossil fuels rank the highest in terms of current energy source. But the adverse effects of extraction ad utilization of fossil fuels such as ecological degradation, excessive emission of CO_2, global warming as paved way for humanity to look for renewable and green sources of energy. Lignocellulosic biomass serves as a major source of green fuels and many other derived value products. The main step for conversion of biomass to fuels and value products is pyrolysis. Pyrolysis of lignocellulosic biomass yields products with lower life-cycle greenhouse emission than conventional fuels, however, the study of kinetics of the pyrolysis step, its environmental feasibility and economic viability is significant for implementing it and substituting bio products with conventional products.

This article summarizes kinetic models, kinetic parameter optimization for the pyrolysis of biomass and describes a commercially viable, open source pyrolysis reactor. Products obtained from pyrolysis of lignocellulosic materials obatined from various sources are studied and compared. Furthermore, techniques to optimize the pyrolysis step by feed pre-treatment, hydrolysis, catalysis and co-catalysis with low rank coal are also discussed.

2. INTRODUCTION

Lignocellulosic biomass has been increasingly studied in recent years, because its use as energy source does not directly compete with food production [1]. Biomass mainly consists of lignin, cellulose and hemicellulose. Due to their lignocellulosic property, they are mainly composed of alkenes, esters, aromatics, alcohols, and ketones with different oxygen-containing functional groups [1]. These lignocellulosic materials can be obtained from agricultural and forest residues, crops, rice husk or many plant related origins.

The main products of pyrolysis of lignocellulosic materials are carbon-rich solid product, volatile and gaseous products. The volatile and gaseous products can be combusted directly as fuel, or upgraded to higher value bio fuels [2]. The volatile product when condensed forms bio-oil which is a brown organic liquid. Raw bio oil usually has a poor heating value and is required to be refined or blended with ethanol or methanol to increase its efficiency as a fuel. The gaseous product of pyrolysis is mainly composed of hydrogen, methane, carbon monoxide and carbon dioxide. Specifically the yield of pyrolysis depends on many factors viz. source of biomass, conversion process adopted and the rate of pyrolysis. Various pre-treatment of the feed can also alter the yield and composition of pyrolysate. For instance, biomass from corn stover has higher gas yield than liquid yield but rice husk has lower gas yield than liquid yield. Microwave pyrolysis produces more syngas but less polycyclic aromatic hydrocarbons than conventional pyrolysis [3]. Gas and tar are the main products from fast pyrolysis of hemicellulose. CO and CO2 accounts for 80% the gas [4].

3. INVESTIGATION OF PRODUCTS OF PYROLYSIS

Investigation of pyrolysis of lignocellulosic materials for product characterisation and component detection can be done using pyrolysis micro reactor. Luana et al. [1] performed such an investigation on invasive aquatic plants. Invasive aquatic plants, mostly water hyacinths are rich in biomass. These aquatic flora grow like weed mostly on stagnant water bodies which, if kept unchecked causes eutrophication. Chemical and biological means have been adopted to curb this problem in tropical and equatorial regions. However, efficient use of such flora could be its conversion to bio oil by pyrolysis.

3

3.1 Microreactor system and method

The biomass was comminuted and then placed in the borosilicate glass tube for pyrolysis as shown in Figure 1. Before placing, the tube was purged with N_2 gas. The products absorbed in the activated carbon was analyzed by gas chromatography mass spectroscopy and the relative composition of pyrolysate was determined by gas chromatography flame ionization detection.
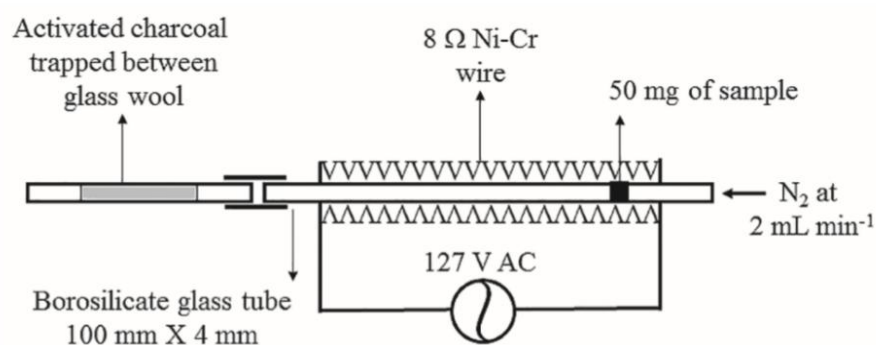

Figure 1: Microreactor system [1]

3.2 Characterisation of the biomass feed

Three species of invasive aquatic plants, Eichhornia crassipes, Eichhornia azura and Nymphaea spp. were analyzed and the Ultimate analysis showed the results tabulated in Table 1.

Table 1: Ultimate analysis of invasive aquatic plants [1]

Element/Property	Eichhornia crassipes	Eichhornia azura	Nymphaea spp.
N (w/w %)	2.8	2.0	2.1
C (w/w %)	34.5	40.6	38.3
H (w/w %)	4.9	4.5	3.9
S (w/w %)	0	0	0
O (w/w %)	45.7	47.1	42.5
HHV (MJ kg^{-1})	11.5	13.0	12.1

3.3 Products of pyrolysis

Various products of pyrolysis absorbed in the activated carbon trap was recovered using various solvents among which Tetrahydrofuran had the best bio-oil recovering property. The three different biomasses yield bio-oil having similar composition. The main components of the derived bio-oil obtained by thermal decomposition of cellulose and subsequent pyrolysis of cellulose and hemicellulose are glycerol, o-benzenediol, p-benzenediol, arabinoic acid, levuglucosan, and hexadecanoic acid. A common component, Levoglucosan (1,6-anhydro-β-D-glucopyranose), formed during the fast pyrolysis of lignocellulosic biomass, can potentially be used to produce biofuels such as ethanol and butanol [1].

EDX analysis of the ashes showed high levels of macronutrients and micronutrients, which would be included in biochars, indicating the potential application of these materials in soil management [1].

4. PYROLYSIS TECHNIQUES

Adopting different pyrolysis techniques yield different specific chemicals. The choice of technique is limited by the biomass feed for pyrolysis as well. Biomass consisting of high amount of water needs to be dried first to make the pyrolysis step energy efficient. This adds to the process economy of conversion. Demineralization of lignocellulosic biomass prior to pyrolysis increased the bio oil yield, significantly influenced its organic composition and suppressed char production compared to raw biomass [5]. Microwave pyrolysis, catalytic pyrolysis, co-catalysis with other materials, combination of hydrolysis and catalytic pyrolysis are some of the modifications that can be done to conventional pyrolysis for obtaining specific products or to increase the efficiency of pyrolysis step as per the biomass feed.

4.1 Microwave pyrolysis of lignocellulosic biomass

Microwave pyrolysis unlike conventional pyrolysis involves heat supply using microwave radiation. This method has certain advantages over conventional pyrolysis in terms of

process efficiency. Some of the advantages as suggested by Yu et al. [6] are: (1) non-contact heating; (2) energy transfer rather than heat transfer; (3) higher heating rate; (4) material selective heating; (5) volumetric heating; (6) quick start-up and stopping; (7) heating from interior of the material body.

Compared to conventional pyrolysis, microwave pyrolysis yields more solid and gaseous products but less liquid products. Maximum conversion of biomass into permanent gases such as H_2, CH_4, CO and CO_2 can be achieved by microwave pyrolysis and can serve as an excellent method for biomass gasification. The comparative yield of solid, liquid and gas from microwave pyrolysis and conventional pyrolysis is shown in Figure 2.
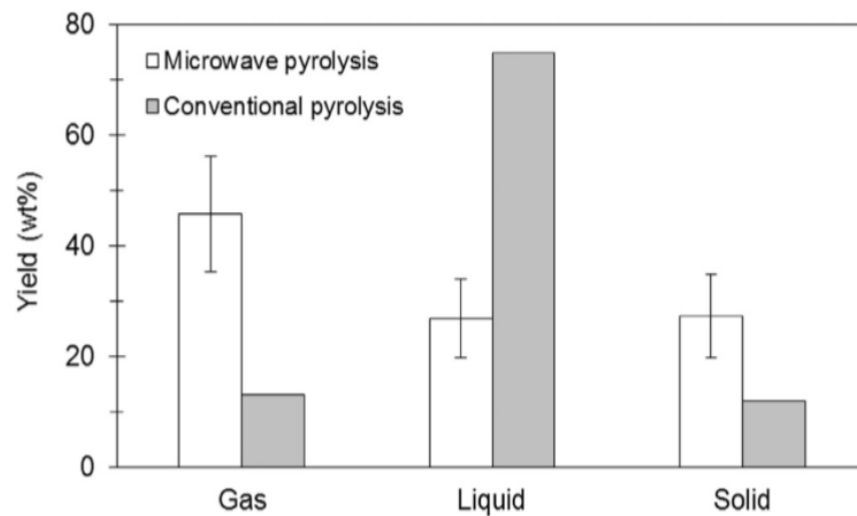

Figure 2: Product distribution of conventional and microwave pyrolysis [6]

4.1.1 Solid product

The solid product of microwave pyrolysis had larger surface area with uniform orderly pores with open structure due to the release of volatile matter. Microwave pyrolysis also increases the heating value of the biomass owing to the devolatilization of hemicellulose and cellulose. Lignin has more thermal resistance. However, when the microwave power level is higher, the devolatilization of lignin would be substantial, leading to the production of char with lower heating values [6].

4.1.2 Liquid product

The liquid yield is the volatile condensable fraction of the pyrolysis product. The liquid yield is lower than that for conventional pyrolysis, however, as reported by Yu et al. [3], microwave pyrolysis produced bio-oil with higher carbon content, higher heating value and lower oxygen content. Blending with ethanol or methanol would improve the stability of the bio-oils.

4.1.3 Gaseous product

The gaseous product of microwave pyrolysis yield primarily H_2, CH_4, CO and CO_2. The rest of the products contribute to a very minute percentage of the gaseous product. Microwave pyrolysis yields more H_2 and CO but less CH_4 and CO_2 as compared to conventional pyrolysis, Figure 3.
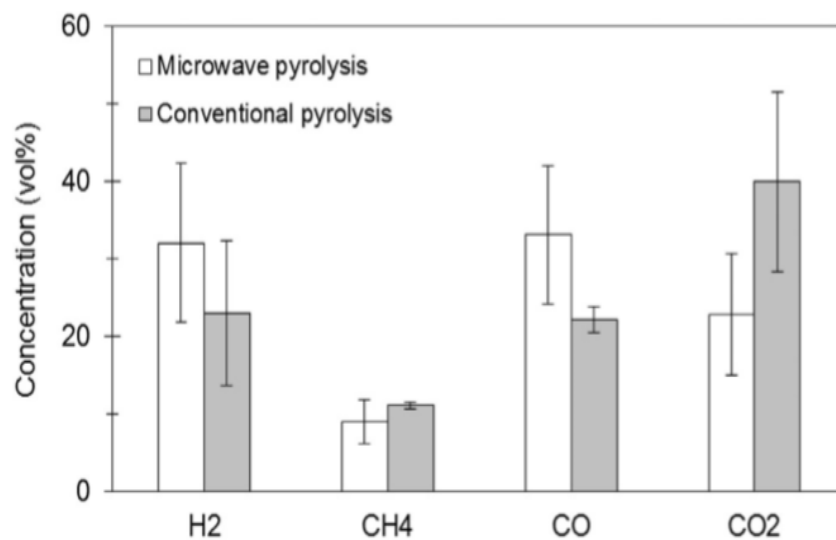

Figure 3: Gaseous composition of microwave and conventional pyrolysis [6]

 Thus, the heating value of gaseous product of microwave pyrolysis is higher than that of conventional pyrolysis. Microwave pyrolysis allows high temperature of reaction and H_2 and CO composition increases and CO_2 composition decreases with increase in temperature. The composition of CH_4 does not change significantly. This is due to the self gasification reaction of char given by Equation (1).

$$C + CO_2 \leftrightarrow CO \qquad\qquad (1)$$

Equation (1) is called the Boudouard reaction and is one of the most important reactions in biomass gasification [6]. The high H_2 component of the gaseous product is due to the water gas reaction as in Equation (2).

$$C + H_2O \leftrightarrow CO + H_2 \qquad\qquad (2)$$

4.2 Demineralization and catalytic pyrolysis

Demineralization of lignocellulosic materials is done to reduce the ash content of biomass without reducing its volatile matter. The effect of ash removal pretreatment on the yield and quality of bio oil obtained from softwood sawdust was studied by Persson et al. [5]. Acid leaching with 2L 10% (w/w) of acetic acid and de-ionized water pre-heated to $85^{\circ}C$ is the leaching agent used for 100g of pre-dried biomass. HZSM-5 catalyst was used for the heterogeneous pyrolysis reactions.

4.2.1 Characterization of raw and pre-treated biomass

The ultimate analysis of raw and pre treated softwood sawdust revealed that pre-treatment reduced the ash content in a significant amount while keeping the other properties almost identical, Table 2.

Table 2: Characterisation of raw and pretreated biomass [5]

Property	Raw	Pretreated
Ash content (w/w %)	0.21	0.05
Volatile matter (w/w %)	84.4	86.3
C (w/w %)	50.7	50.9
H (w/w %)	6.0	6.5
N (w/w %)	<0.1	<0.1
O (w/w %)	43.0	42.5

The volatile matter showed a slight increased which would in turn be a positive precursor to the formation of volatile and gaseous products of pyrolysis in terms of yield.

4.2.2 Change in product composition and yield due to demineralization

Pre-treated biomass produced higher organic liquid yield than raw biomass at higher temperatures of around 600°C. Pyrolysis of pre-treated biomass at 600°C increases the organic liquid yield by 33 % compared to raw biomass, where also the yield of gas and water was reduced [5]. At the same temperature the char yield of the pre treated biomass reduced by 20% relative to the raw biomass.

Pre-treated biomass yields lower amount of acetic acid and a higher enhanced concentration of levoglucosan with increasing temperature. As reported by Persson et al. [5] there was a decrease in 17% of acetic acid against an increase in 339% of levoglucosan. Increase in the levoglucosan yield is directly related to the bio-oil yield as discussed in section 3.3.

Increase in temperature increased the gas yield of pyrolysis for both the cases of raw and pre treated biomass. However, the production of CO is suppressed in demineralized feed by 31%.

4.2.3 Catalytic pyrolysis

Heterogeneous catalysis was done over HZSM-5 for upgrading the bio-oil obtained from non-catalytic pyrolysis in a bench scale, fixed bed setup. In bed catalytic upgrading done over HZSM-5 in Py-GC/MS is relatively inefficient as the kinetic diameter of livoglucosan is larger and the catalyst pores are narrow. This limitation can be overcome by adopting ex-bed catalytic pyrolysis on a bench scale setup which produced higher yields of aromatic hydrocarbons when performed at higher temperatures [5]. Hence, demineralized biomass feed when pyrolzed, gives a better volatile yield than raw biomass feed, which can be further upgraded over HZSM-5 catalyst in an ex-bed bench scale setup to boost the production of aromatic hydrocarbons.

5. KINETIC STUDY OF PYROLYSIS OF BIOMASS

The study of kinetics of pyrolysis is important for optimising major parameters such as pyrolysis temperature, residence time, and heating rate. Although substantial contributions have been made on kinetic modeling as reported by Gao et al. [7], estimation and comparison of the optimum values of the important kinetic parameters affecting the pyrolysis process for numerous lignocellulosic materials are still lacking in the literature so far [8].

5.1 Two-step kinetic model simulation

The kinetic model used by Hamayoun et al. [8] is a two-step model for lignocellulosic biomass pyrolysis reaction. This model is based on an experimental setup involving a tubular reactor placed vertically in an electrically heated tubular furnace. Simulation of kinetics of pyrolysis of lignocellulosic materials using this model was done by Hamayoun et al. [8] with various lignocellulosic materials like wood sawdust, bagasse, peanut hull, fir bark and rice husk which gave results close to that in existing literature. The model describes thermal degradation of virgin biomass (B) into primary volatile, gases (G_1) and solid char (C_1) with reaction order n_1. The evolution of secondary volatile, gases (G_2) and char (C_2) from primary products (G_1 and C_1) and unreacted biomass (B) follows a reaction order $n_2 = 1.5$. The reaction of primary char is of the order $n_3 = 1.5$. The kinetic equations for the above mentioned model is as follows (Equations 3-7).

$$\frac{dC_B}{dt} = -k_1 C_B^{n_1} - k_2 C_B^{n_2} \tag{3}$$

$$\frac{dC_{G_1}}{dt} = -k_1 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{4}$$

$$\frac{dC_{C_1}}{dt} = k_2 C_B^{n_1} - k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{5}$$

$$\frac{dC_{G_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{6}$$

$$\frac{dC_{C_2}}{dt} = k_3 C_{G_1}^{n_2} C_{C_1}^{n_3} \tag{7}$$

The model was simulated in Matlab-7 using Runge Kutta Method considering both isothermal and non-isothermal condition. Experiments on optimization of the reaction parameters viz. pyrolysis temperature, residence time, and heating rate revealed that maximum pyrolysis rate for different biomass occurs at the same heating rate and temperature under non-isothermal and isothermal conditions, respectively, which proves that these two quantities are independent of reaction order of virgin biomass, n_1 [8]. The optimum pyrolysis rate depends on the biomass feed. Among all the biomass feeds, wood sawdust had the fastest optimum pyrolysis rate with minimum reaction order, $n_1=1$.

5.2 Experimental investigation for a suitable model

The modeling of pyrolysis reactions of lignocellulosic materials is a difficult task due to the numerous intermediates formed during thermal decomposition of cellulose and hemicellulose. The model might even vary depending upon the biomass feed for pyrolysis. Through the combination of thermogravimetric analysis data with experimental data from FTIR, Py-GC/MS and NMR reflecting the compositional and structural changes of the decomposed material and evolved products, should provide valuable assistance in the selection of a suitable reaction mechanism [9].

Hrablay et al. [9] performed experimental analysis of various reaction schemes for pyrolysis of beech sawdust to determine the suitable kinetic approach to determine optimum kinetic parameters. Several mechanisms were investigated as shown in Figure (4).
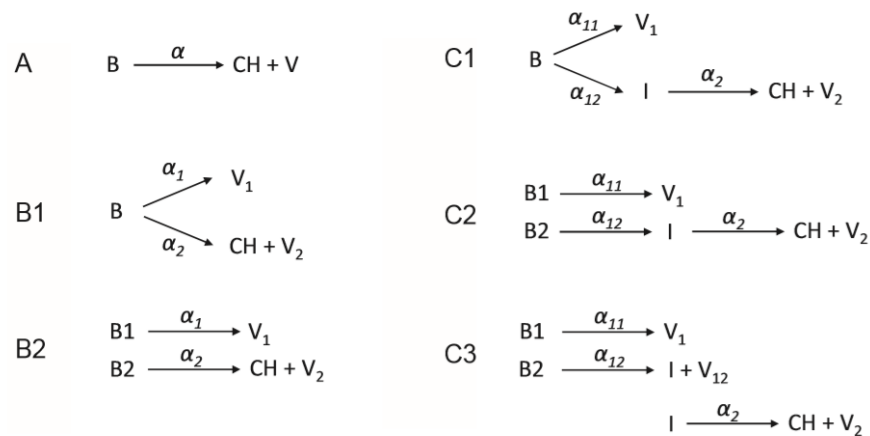

Figure 4: Mechanisms selected for experimental model fitting procedure [9]

11

Mechanism A is a one step mechanism with conversion of biomass to char and volatiles. Mechanisms B1 and B2 are two and three-step mechanisms with parallel and competitive parallel reactions respectively. Mechanisms C are three-step mechanisms including an intermediate step with or without the production of volatiles. Mechanisms C2 and C3 are modifications of mechanism B2 involving intermediate formation.

The experimental results showed that C2 provided a better fit to experimental data followed by B2 which means that intermediate formation step has some significance for kinetic modeling. The evolution of intermediates was supported by NMR experiments and can be linked to the lignin structure starting with the process of lignin demethoxylation [9].

6. LARGE SCALE PYROLYSIS REACTORS

Pyrolysis of lignocellulosic materials to obtain bio energy and other potent chemicals is a noble process for a sustainable future. However, the efficiency of the process, its impact on the environment, the economic feasibility and availability of affordable technology are the determining factors for up-scaling the process to a commercial level. A thermally integrated efficient pyrolysis equipment that is a net producer rather than consumer of biofuels, is needed.

Woolf et al. [2] proposed such a pyrolysis reactor which is not only energy efficient but also safe, affordable and can be fabricated locally. The reactor is made of three sections for: (i) drying, (ii) torrefaction and pyrolysis, and (iii) combustion of the pyrolysis gases and volatiles. The schematic diagram of the reactor is shown in Figure 5.
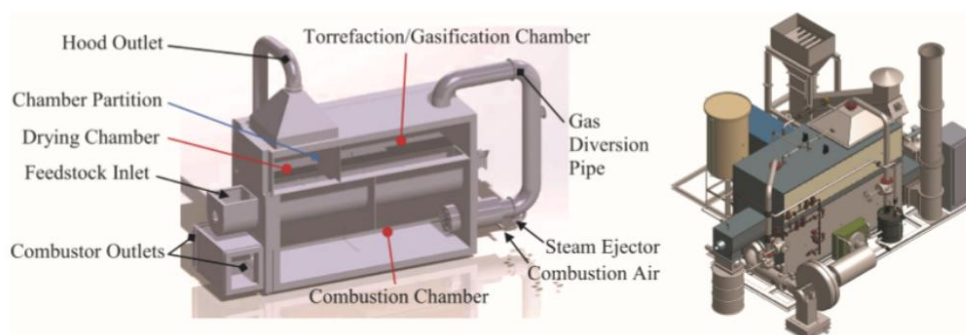

Figure 5. Schematic diagram of an open source pyrolysis reactor [2]

12

The pyrolysis retort was designed to process biomass with a moisture content up to 30% at temperatures ranging from 450°C up to 600°C [2]. Conventional kilns are labor intensive, polluting and leads to inefficient reaction and inconsistent products. The reactor shown above is a retort which combusts the pyrolysis gases and volatiles before venting them out and is, thus, less polluting and more energy efficient.

HAZOP studies on the reactor showed that there are no hazard rating below 3, proving that the reactor is considerably safe. Modification of design and SOPs are provided by Woolf et al. [2] to mitigate any risks involved with this reactor. CFD analysis using ANSYS Fluent software showed stable flow and combustion pattern in the reactor.

7. CONCLUSION

Lignocellulosic materials have a very high potential to be a source of bio energy and other value chemicals. The volatiles of pyrolysis product can be used to produce bio-oil and can be upgraded by adding methanol and ethanol. The gaseous product is mostly permanent gases like H_2, CO, CO_2 and CH_4. Optimizing the production of H_2 and CH_4 will produce a very good gaseous fuel. The solid yield of pyrolysis, char can be gasified using catalyst or can be used as a source of various macronutrients.

Kinetic study is necessary to model reactions and optimize parameters for pyrolysis. Studies employing also TG-GC/MS, 1H NMR, 13C NMR or two-dimensional heteronuclear single quantum coherence (2D-HSQC) NMR, for instance, can shed more light onto the reaction mechanisms [9].

Availability of an open source pyrolysis retort which is affordable, clean and can be fabricated locally should be taken advantage of to produce more and more bio-fuels from lignocellulosic materials. Further research is needed to develop technologies for extraction and utilization of potent chemicals from lignocellulosic materials by pyrolysis.

8. REFERENCES

[1]   Santos, L. O.; Silva, F. F.; Santos, L. C.; Carregosa, I. S. C.; Wisniewski, A., Potential bio-oil production from invasive aquatic plants by microscale pyrolysis studies, *Journal of the Brazilian Chemical Society* **29** (2018) 151-158.

[2]   Woolf, D.; Lehmann, J.; Joseph, S.; Campbell, C.; Christo, F. C.; Angenent, L. T., An open-source biomass pyrolysis reactor, *Biofuels, Bioproducts and Biorefining* **11** (2017) 945-954.

[3]   Lo, S. -L.; Huang, Y. -F.; Chiueh, P. -T., Kuan, W.-H., Microwave Pyrolysis of Lignocellulosic Biomass, *Energy Procedia* **105** (2017) 41-46.

[4]   Wu, Z., Li, Y.; Meng, H.; Yang, W.; Yang, B., On-line analysis on fast pyrolysis of lignocellulosic biomass: Thermal behavior and kinetic analysis of hemicellulose, *Energy Procedia* **152** (2018) 1290-1295.

[5]   Persson, H.; Yang, W., Catalytic pyrolysis of demineralized lignocellulosic biomass, *Fuel* **252** (2019) 200-209.

[6]   Huang, Y. -F.; Chiueh, P. -T.; Lo, S. -L., A review on microwave pyrolysis of lignocellulosic biomass, *Sustainable Environment Research* **26** (2016) 103-109.

[7]   Gao, W., M. R. Farahani, M. Rezaei, A. Q. Baig, M. K. Jamil, M. Imran, and R. Rezaee-Manesh. 2017. Kinetic modeling of biomass gasification in a micro fluidized bed. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects* **39** (2017) 643–48.

[8]   Mahmood, H.; Ramzan, N.; Shakeel, A.; Moniruzzaman, M.; Iqbal, T.; Kazmi, M. A.; Sulaiman, M., Kinetic modeling and optimization of parameters for biomass pyrolysis: A comparison of different lignocellulosic biomass, *Energy Sources, Part A: Recovery, Utilization and Environmental Effects* **41** (2019) 1690-1700.

[9]   Hrablay, I.; Jelemenský, L., Kinetic study of the thermochemical degradation of lignocellulosic materials based on TG-FTIR, Py-GC/MS and 13C NMR experiments, *Chemical and Biochemical Engineering Quarterly* **30** (2016) 359-372.