

## Investigation of Parametric Effects on Fuel Characteristics of Biochar Obtained from Agricultural Wastes Pyrolysis

Napat Kaewtrakulchai <sup>a</sup>, Masayoshi Fuji <sup>b</sup>, Apiluck Eiad-ua <sup>a,\*</sup>

<sup>a</sup> College of Nanotechnology, King Mongkut's Institute of Technology Ladkrabang, Chalongkrung Rd., Ladkrabang, Bangkok, 10520 Thailand

<sup>b</sup> Advanced Ceramic Research Center, Nagoya Institute of Technology, Tajimi, Gifu, 507-0033 Japan

Received 28 May 2018; Revised 30 August 2018; Accepted 13 September 2018

### Abstract

Development of agricultural waste to biochar is significantly utilized as alternate solid fuel because of its advantages as availability, low cost and eco-friendly material. In this study, we explored the effect of temperature, ramping rate, and feedstock types on the physicochemical properties of biochars. Biochar was produced from corn stalk, cassava cake, and pineapple residue by using pyrolysis at temperatures of 400 and 600 °C with ramping rates of 7 °C min<sup>-1</sup>. The crucial parameters as temperature revealed that the fuel properties were obviously developed under a high temperature condition showing that the HHV of biochar is approximately 27.8 MJ kg<sup>-1</sup>, whereas ramp rate showed insignificant development of biochar fuel characteristics. However, the resulting biochar has a low ash content ranged around 4.7 – 8.9%. This finding indicated that increasing pyrolysis temperature could be developed the fuel properties of biochar.

**KEYWORDS:** GVL; Biochar; Alternate solid fuel; Agricultural wastes; Pyrolysis

\* Corresponding authors; e-mail: apiluck.ei@kmitl.ac.th

### Introduction

Biomass from agricultural sector is increased at this period and most biomass in Thailand comes from agricultural activities and this incident affects the environment as an organic waste. The source of biomass refers to woody biomass (*i.e.* forest residues, fuel wood), non-woody biomass (*i.e.* crop residues, processing residues of agricultural), and organic wastes (*i.e.* animal waste, sewage sludge, and municipal solid waste). For the energy production, biomass is used directly to produce heat via combustion, or indirectly transformed to functional materials or other high beneficial products [1]. Recently, the biomass conversion technologies for biofuel production were a thermochemical or biochemical processes. The types of biofuel were selected by the different conversion technologies to develop a molecular structure which contains high ratio of carbon. Not only producing energy, biomass could also be applied in producing carbon materials, for instance biochar and activated carbon [2 – 3].

Agricultural activity generates a large amount of wastes after harvesting process. These natural wastes can be transformed to a high value-added

product as a biochar by using a thermochemical conversion of carbonaceous material to carbon-enriched char [4]. By the way, biochar is a solid product which commonly utilized into the soil as a soil amender for agronomic [5], or used as an alternative solid fuel in households to provide heat [6]. Moreover, biochar application for solid fuel in large scale heat production has been also reported by several researchers due to some prominences such as eco-friendly material, high availability and carbon sequestration [7]. The most crucial property which is calorific value, chemical ratios, appearance density has obviously been investigated.

Pyrolysis is the thermochemical process occurring in the oxygen limit condition. Pyrolysis can be applied for biomass conversion to various forms of biofuels. In general, the main products in biomass pyrolysis are biochar, bio-oil and gases. The pyrolysis products depend on the conditions and types of conversion technology. The product of pyrolysis is mainly a biochar at low heating rate and low temperature process [8]. This process is widely applied for the chemical industry as the thermochemical conversion in biomass technology, for example, charcoal production, activated carbon production, or other chemical

productions. However, Pyrolysis temperature and feedstock type are considered to be the main factors affecting quality and controlling properties of biochar [9].

On the contrary, heating rate during biomass pyrolysis also affected the fuel properties of biochar occurred by the volatilization [10]. Recently, some researchers have reported the utilization of briquette biochar for heat production by natural feedstock which had ignition temperatures ranging from 492 – 520 °C. It can be implied that biochar will be effective for the future renewable energy and biomass production and utilization systems [11].

The aim of this study is to show the potential of different agricultural wastes for biochar production in terms of an alternative solid fuel. The selected feedstocks (i.e. corn stalk, cassava cake, and pineapple residue) have been pyrolyzed at temperatures of 400 and 600 °C with different ramping rates of about 7 °C min<sup>-1</sup> for 1 h to investigate the fuel properties by means of proximate analysis follows ASTM D2867-99 for moisture content (ASTM 2014), ASTM D2866-94 for ash analysis (ASTM 2008), and ASTM D2866-94 for volatile substance (ASTM 2011), respectively [12]. Due to comparison of produce biochar to the solid fossil fuels, the produce biochar has been analyzed by Van Krevelen's diagram using a chemical ratios characterized by ultimate analysis [6 – 7, 13].

## Materials and Methods

### Feedstock and biochar production

Corn stalk (CS) and pineapple residue (PR) were collected from a local plantation, Nakhon Ratchasima, Thailand, while cassava cake (CC) was also supplied from post process of starch extraction in a cassava mill, Rayong, Thailand. All feedstocks are quite freshly contained high moisture. It was firstly sundried in open air for five days then, chipped, crushed, and sieved into 0.8 – 1.2 mm. The dried feedstocks were packed in plastic bag for further pyrolysis experiment. The chemical properties of feedstock such as ash, moisture, volatile matter, fixed carbon, carbon, hydrogen, nitrogen were evaluated by using proximate, ultimate analysis, respectively and the chemical composition (i.e. lignin, holocellulose, cellulose) was characterized by Technical Association of the Pulp and Paper Industry (TAPPI) method. Then, Raw materials were directly used for charring process. Each feedstock was loaded inside a rotary horizontal tubular furnace with a diameter of 45 mm and a length of 130 mm. The pyrolysis experiments were conducted by using 10 g of prepared samples at 400 and 600 °C for 1 h in which two independent ramping rate are considered. The two independent ramping rate during process considered in this study is 7 °C min<sup>-1</sup>.

**Table 1** Proximate and ultimate analyses of three feedstock samples.

Biomass source	Proximate analysis (d.b., %wt)			Ultimate analysis (d.a.f., %wt)				Density (kg m <sup>-3</sup> )	Calorific value (d.a.f, MJ kg <sup>-1</sup> )
	VM	FC	Ash	C	H	N	O*		
CS	85.68	10.43	3.89	41.64	6.39	0.63	51.34	89 ± 1.60	14.05
CC	80.71	11.77	7.52	40.28	7.28	0.35	52.09	277 ± 4.70	14.51
PR	87.06	9.63	3.31	41.73	7.61	1.27	49.39	193 ± 1.50	15.75

\* Calculated by different, VM = Volatile Matter, FC = Fixed Carbon

### Characterization

Ultimate or elemental (carbon, hydrogen, nitrogen and sulphur) analysis was analyzed by CHN elemental analyzer according to the procedure provided by the manufacturer difference (Leco Truespec chns-628). The oxygen content (O) was then calculated by difference using the relation. All these parameters were expressed in weight percentage. Moreover,

chemical ratios (H:C, O:C) were evaluated to analyze the biochar fuel properties through the Van Krevelen's diagram [6 – 7]. The heating value of produced biochar was calculated by following Dulong formula below [9], The Lignocellulosic composition such as lignin, hemicellulose and cellulose contents has been explained by previous research [14].

Proximate analysis of feedstock and biochar fuel (*i.e.* ash (ASTM D1102-84), moisture (ASTM E871-82), volatile matter (ASTM E872-82) and fixed carbon) was determined via thermogravimetric analysis (PerkinElmer Pyris 1) which obtained at

the temperature range 30 – 900 °C using a constant heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere from 30 – 900 °C, and then oxygen was switched into the TG system due to pyrolysis and combustion, respectively.

$$\text{Heating value} = 338.2C + 1442.8 (H - O/8) + 94.2S \quad (\text{kJ kg}^{-1}) \quad (1)$$

Surface morphology of biochar samples was scanned by scanning electron microscopy using a 20 kV (Zeiss evo 50, Germany). Before the

investigation, biochar samples were stained on a carbon tape attached to a stub, then coated with gold layer by sputtering.

**Table 2** Chemical composition of raw materials analyzed by the TAPPI method.

Biomass source	Lignocellulosic composition (d.a.f., % wt)		
	Hemicellulose	Cellulose	Lignin
CS	38.32	38.14	23.54
CC	61.12	26.04	12.84
PR	57.23	29.06	13.71

## Results and Discussion

### *Biomass properties and pyrolysis products*

The results of chemical and elemental analysis are displayed in Table 3. The chemical composition reported in dry basis that consists of volatile matter, fixed carbon, and ash. The results revealed that corn stalk, cassava cake, and pineapple residue contain 3.9%, 7.5% and 3.3% of ash content, respectively. Ash content is lower in corn stalk and pineapple waste because it is not a residue from extracting process as cassava cake. Fixed carbon of raw materials is approximately between 9.65 – 11.82%. In addition, the elemental composition also depends on different type of biomass. The carbon content of raw materials has resulted as 40.28 – 41.73%. The oxygen and hydrogen contents of all the samples ranged in 49.39 – 52.09% for O, 6.39 – 7.61% for H, and contained a small amount of nitrogen (0.3 – 1.2%) as shown in Table 1.

### *Fuel properties of biochars*

The produced biochars derived from each raw material were observed on chemical composition that is volatile matter, fixed carbon and ash, (Table 3). The pyrolytic temperature was increased from 400 – 600 °C with heating rates of 7 °C min<sup>-1</sup>. The results found that high temperature pyrolysis essentially affected a biochar because of high rate of devolatilization.

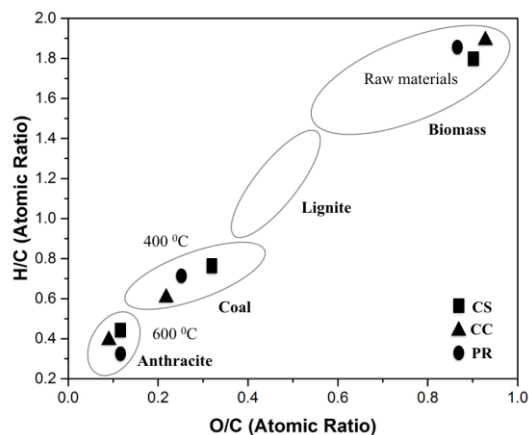
Fixed carbon and ash content are suddenly increased, only volatile matter was gradually decreased. Biochar quality is determined from the percentage of fixed carbon and ash, therefore quality biochar should have high fixed carbon and low ash content. In addition, biochar produced from corn stalk has higher fixed carbon content of 57.56 – 74.21 %wt compared to a biochar derived from cassava cake and pineapple residue which ranged from 45.91 – 66.20 %wt, and the percentage of ash in cassava biochar is quite high; 5.81 – 15.94 %wt when pyrolyzed at 600 °C.

The elemental compositions of biochar samples were also reported on moisture-ash-free basis. It was presented the C composition was noted about 67.51 – 81.36 %wt for CS biochar, 73.97 – 80.81 %wt for CC biochar and 69.30 – 79.48 %wt for PR biochar. Furthermore, the high heating value of produced biochar was significantly different via pyrolytic temperature. Consequently, high-temperature pyrolysis causes higher HHV due to the dehydration of biochar structure such as dehydration and decarboxylation reaction as shown in Table 2.

A comparison biochar derived from the different thermal conversion process and coal is in terms of their elemental composition (O/C and H/C ratios), known as a Van Krevelen diagram shown in Fig. 1. The lower ratios mean the biochar could give more ability to provide heat. The results show that the chemical structure of

biochar is similar to natural coal. The product exhibits lower O/C and H/C ratios than initial product, because of the reduction of H<sub>2</sub>O and CO<sub>2</sub> in the dehydration and decarboxylation reactions. However, O/C and H/C atomic ratio of biochar generally depend on the pyrolytic condition. It can be observed that the elemental ratio from higher pyrolytic temperature, the chemical structure of biochar is more closely the natural coal. For this property, the biochar is possible to generate heat after used as an adsorbent and offer the possibility to eliminate using combustion impurities. The different change among C, H, and O along with increasing charring temperature resulted in a general decrease in atomic ratios of H/C and O/C in biochars. The H/C ratio range of 1.84 to 2.18 for the raw materials was decreased to 0.38 to 0.43 for biochars made at 600 °C, whereas O/C ratio range for these raw materials was decreased from 0.96 – 0.98 to 0.14 – 0.26 for produced biochars as shown in Van Krevelen diagram (Fig. 1). The reduction in H/C ratio implies higher structural stability in biochars due to increased aromatic structures during charring as compared to the uncharred raw materials [8], whereas the

decreased O/C ratio indicates the higher-degree of carbonization due to the elimination of hydrophilic functional groups from the material structures by charring effect [11 – 12, 16].



**Fig. 1** Van Krevelen diagram for raw materials and biochars produced from corn stalk (CS), cassava cake (CC), pineapple residue (PR) at 400 °C, and 600 °C of pyrolysis temperatures, respectively.

**Table 3** Chemical and elemental analyses of produced biochars.

Samples	Proximate analysis (d.b., %wt)			Ultimate analysis (d.a.f., %wt)				Calorific value (MJ kg <sup>-1</sup> )
	VM	FC	Ash	C	H	N	O*	
CS – 400	36.63	57.56	5.81	67.51	4.49	0.72	27.28	24.06
CS – 600	19.12	74.23	6.65	81.36	2.94	0.47	15.23	28.70
CC – 400	38.52	48.40	13.08	73.97	3.76	0.71	21.56	26.23
CC – 600	23.09	60.97	15.94	80.81	2.89	0.58	15.72	28.38
PR – 400	46.34	45.91	7.75	69.30	4.26	1.78	24.66	24.78
PR – 600	23.75	66.20	10.05	79.48	2.53	1.37	16.62	27.25

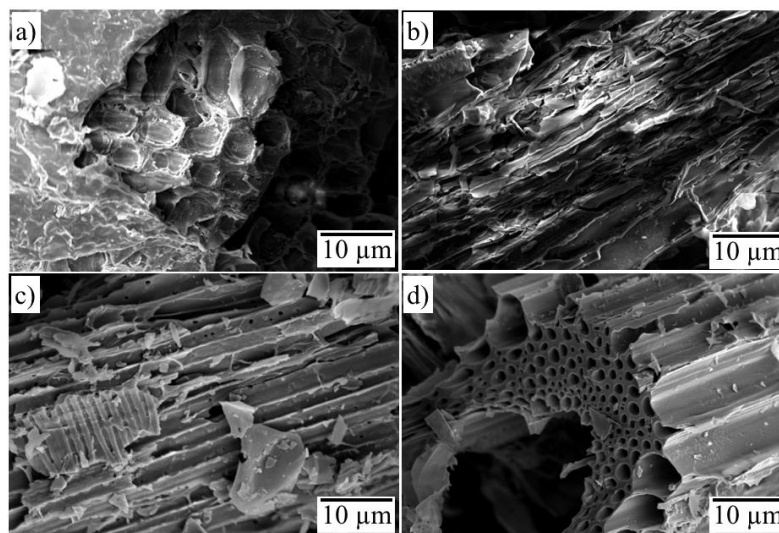
\*calculated by different, VM = Volatile Matter, FC = Fixed Carbon

Table 4. represents that the pore characteristics of CS, CC and PR biochars from different pyrolytic conditions were characterized by nitrogen adsorption/desorption technique using the BET model. The finding results revealed that specific surface areas suddenly increase in the pyrolytic temperature from 400 to 600 °C. The maximum specific surface areas which found in CS biochar is about 274.71 m<sup>2</sup> g<sup>-1</sup> at 600 °C. In contrast, CC and PR biochars have lower specific surface areas. However, increasing pyrolytic temperature also significantly increased

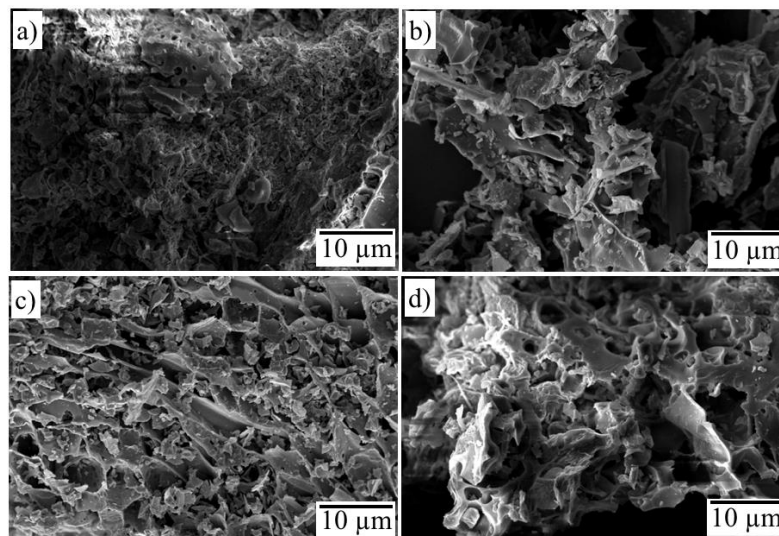
specific surface areas. The measurement of average pore volume was done by N<sub>2</sub> adsorption at relative pressure at 0.99. It was indicated that. It was indicated that maximum average pore volume was 0.17 cm<sup>3</sup> g<sup>-1</sup> for CS biochar at 600 °C. Additionally, the average pore size which approximately 2.04 nm can be described to microporous structure [14 – 15]. However, an increase of biochar porosity is not only influenced by the temperature but also affected by the types of raw materials.

**Table 4** Pore characteristics of biochar produced from CS, CC and PR at different pyrolytic conditions.

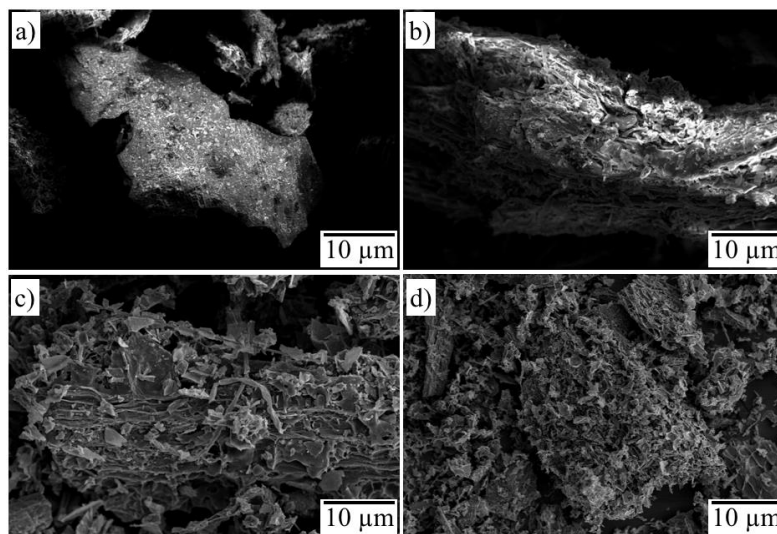
Pyrolytic condition	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Total Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )	Average Pore diameter (nm)
CS400	2.13	0.001	n/a
CS600	274.71	0.17	2.04
CC400	4.82	0.0028	n/a
CC600	34.80	0.008	n/a
PR400	0.95	0.0006	n/a
PR600	5.03	0.004	n/a



**Fig. 2** SEM micrographs of CS biochars performed at a) 400 °C, 7 °C min<sup>-1</sup>, b) 400 °C, 20 °C min<sup>-1</sup> with steam 2 h., c) 600 °C, 7 °C min<sup>-1</sup> and d) 600 °C, 20 °C min<sup>-1</sup>.



**Fig. 3** SEM micrographs of PR biochars performed at a) 400 °C, 7 °C min<sup>-1</sup>, b) 400 °C, 20 °C min<sup>-1</sup> with steam 2 h., c) 600 °C, 7 °C min<sup>-1</sup> and d) 600 °C, 20 °C min<sup>-1</sup>.



**Fig. 4** SEM micrographs of CC biochars performed at a) 400 °C, 7 °C min<sup>-1</sup>, b) 400 °C, 20 °C min<sup>-1</sup> with steam 2 h., c) 600 °C, 7 °C min<sup>-1</sup> and d) 600 °C, 20 °C min<sup>-1</sup>.

#### Surface morphology of as-prepared biochars

The SEM micrographs of CS, CC and PR biochars are shown in Fig. 2, 3 and 4, respectively. All biochars performed at 400 °C exhibited less porous, compact, and smooth surface morphology (Fig. a). Whereas, Fig. b – c show the development of pore structure by elevated carbonization temperature on the

microstructure of biochars performed at 600 °C. The appearances showed a various pores and cavities at high-pyrolysis temperature causing higher the degradation of volatile substance which effectively affects the formation of pores [15, 17]. However, the pore structure analysis can be assured physical morphology of produced biochars.

## Conclusion

In this study, biochar has successfully been developed from agricultural wastes (*i.e.* corn stalk, cassava cake, pine apple residue). Finding results showed that high pyrolysis temperature causes a high calorific value representing a significance is the high carbon ratio in biochar composition, and these evidences reveal similar fuel properties as compared to natural coals. The calorific value of cassava cake and corn stalk biochar is over 28 MJ kg<sup>-1</sup>. Nonetheless, biofuels were produced and these could be upgraded via using an agricultural waste. The produced biochar also exhibits the potential as an adsorbent which shows better properties such as increased surface area. This preliminary study shows the potential of agricultural wastes as a feedstock for producing pyrolysis based functional materials and biofuels. The further work would focus on more optimization on pyrolysis parameters to enhance performance of biochar production system.

## Acknowledgements

The authors sincerely acknowledge the financial support and facility from the College of Nanotechnology King Mongkut's Institute of Technology Ladkrabang for substantial assistance towards completion of this research work.

## References

- [1] A.R.A. Usman, A. Abduljabbar, M. Vithanage, Y.S. Ok, M. Ahmad, M. Ahmad, J. Elfaki, S.S. Abdulazeem, M.I. Al-Wabel, Biochar production from date palm waste: Charring temperature induced changes in composition and surface chemistry, *J. Anal. Appl. Pyrol.* 115 (2015) 392 – 400.
- [2] B. Zhou, J. Zhou, Q. Zhang, D. Chen, X. Liu, L. Wang, R. Ji, H. Ma, Properties and combustion characteristics of molded solid fuel particles prepared by pyrolytic gasification or sawdust carbonized carbon, *Bioresources.* 10 (2015) 7795 – 7807.

- [3] C. Areeprasert, P. Zhao, D. Ma, Y. Shen, K. Yoshikawa, Alternative solid fuel production from paper sludge employing hydrothermal treatment, *Energ. Fuel.* 28 (2014) 1198 – 1206.
- [4] W.A.W.A.K. Ghani, A. Mohd, G. da Silva, R.T. Bachmann, Y.H. TaufiqYap, U. Rashid, A.H. Al-Muhtaseb, Biochar production from waste rubber-wood-sawdust and its potential use in C sequestration: Chemical and physical characterization, *Ind. Crop. Prod.* 44 (2013) 18 – 24.
- [5] A. Amarasekara, F.S. Tanzim, E. Asmatulu, Briquetting and carbonization of naturally grown algae biomass for low-cost fuel and activated carbon production, *Fuel.* 208 (2017) 612 – 617.
- [6] T. Mimmo, P. Panzacchi, M. Baratieri, C.A. Davies, G. Tonon, Effect of pyrolysis temperature on miscanthus (*Miscanthus & Giganteus*) biochar physical, chemical and functional properties, *Biomass Bioenerg.* 62 (2014) 149 – 157.
- [7] A.T. Tag, G. Duman, S. Ucar, J. Yanik, Effects of feedstock type and pyrolysis temperature on potential applications of biochar, *J. Anal. Appl. Pyrol.* 120 (2016) 200 – 206.
- [8] Y. Sun, B. Gao, Y. Yao, J. Fang, M. Zhang, Y. Zhou, H. Chen, L. Yang, Effects of feedstock type, production method, and pyrolysis temperature on biochar and hydrochar properties, *Chem. Eng. J.* 240 (2014) 574 – 578.
- [9] G. Yang, Z. Wang, Q. Xian, F. Shen, C. Sun, Y. Zhang, J. Wu, Effects of pyrolysis temperature on the physicochemical properties of biochar derived from vermicompost and its potential use as an environmental amendment, *RSC Adv.* 5 (2015) 40117 – 40125.
- [10] B. Dutta, Y. Garipey, G.S.V. Raghavan, Effects of process parameters and selective heating on microwave pyrolysis of lignocellulosic biomass for biochar production, *Can. Biosyst. Eng.* 57 (2015) 323 – 332.
- [11] Y. Shen, S. Yu, S. Ge, X. Chen, X. Ge, M. Chen, Hydrothermal carbonization of medical wastes and lignocellulosic biomass for solid fuel production from lab-scale to pilot-scale, *Energy.* 118 (2017) 312 – 323.
- [12] K. Anupam, A.K. Sharma, P.S. Lal, S. Dutta, S. Maity, Preparation, characterization and optimization for upgrading *Leucaena leucocephala* bark to biochar fuel with high energy yielding, *Energy.* 106 (2016) 743 – 756.
- [13] S. Liang, Y. Han, L. Wei, A.G. McDonald, Production and characterization of bio-oil and bio-char from pyrolysis of potato peel wastes, *Biomass Conv. Bioref.* 5 (2015) 237 – 246.
- [14] C. Peng, Y. Zhai, Y. Zhu, B. Xu, T. Wang, C. Li, and G. Zeng, Production of char from sewage sludge employing hydrothermal carbonization: Char properties, combustion behavior and thermal characteristics, *Fuel.* 176 (2016) 110 – 118.
- [15] Z. Liu and G. Han, Production of solid fuel biochar from waste biomass by low temperature pyrolysis, *Fuel.* 158 (2015) 159 – 165.
- [16] H. V. Mulimani, M. C. Navindgi, Production of Solid Fuel by Pyrolysis Process using Neem De-Oiled Seed Cake, *Int. J. Eng. Technol. Sci. Res.* 4 (2017) 2394 – 3386.
- [17] D. Pradhan, R.K. Singh, H. Bendu, R. Mund, Pyrolysis of Mahua seed (*Madhuca indica*) – Production of biofuel and its characterization, *Energ. Convers. Manage.* 108 (2016) 529 – 538.