Reaktor

p-ISSN 0852 – 0798
e-ISSN 2407 – 5973

Terakreditasi: SK No.: 60/E/KPT/2016
Website : http://ejournal.undip.ac.id/index.php/reaktor/

Reaktor, Vol. 16 No. 4, Desember Tahun 2016, Hal. 212-217

Hydrothermal Carbonization of Biomass Waste by Using a Stirred Reactor: An Initial Experimental Results

Herlian Eriska[1,2,*], Kania Dewi[2], Ari Darmawan Pasek[3], and Enri Damanhuri[2]

[1]Research Unit of Clean Technology, Indonesia Institute of Sciences
Jl. Cisitu/Sangkuriang No. 154/21D Bandung 40135
[2]Faculty of Civil and Environmental Engineering, Institut Teknologi Bandung
Jalan Ganesha No. 10, Bandung 40132
[3]Faculty of Mechanical and Aerospace Engineering, Institut Teknologi Bandung
Jalan Ganesha No. 10, Bandung 40132
[*]Corresponding author: erisbae@gmail.com

Abstract

Hydrothermal carbonization (HTC) is a thermochemical process used for converting wet biomass waste become a coal-like material with higher carbon content called hydrochar. In this study, design and performance test of hydrothermal carbonization prototype reactor was done. Stirred reactor was made of stainless steel 304 with volume of 1 Liter and electric heater as a heating mantle. The HTC reactor was utilized to perform the carbonization of three materials (paper, left-rice, and woodchip) as substrates, in order to study the influence of the temperature conditions on the hydrochar produced. The substrates represented major component in municipal solid waste (MSW). The study showed that chemical and physical properties of several feedstock and hydrochar were vary as a function of reaction temperature. HTC was operated in batch at temperatures of 160, 190 and 220^{o}C, 60 min of reaction time, and 1 MPa initial pressure of nitrogen gas. Three of product were collected from the process with primary material balance. Results indicated that the products was influenced by the temperature elevation. The results suggested that hydrothermal treatment of biomass waste to solid fuel gave high heating value (HHV) with value of 5231.3, 4569.5, and 5422.7 kcal/kg for paper, left-rice, and woodchip respectively after product dried naturally.

Keywords: *biomass waste; hydrochar; hydrothermal carbonization; stirred reactor*

Abstrak

HIDROTERMAL KARBONISASI DARI LIMBAH BIOMASSA MENGGUNAKAN REAKTOR BERPENGADUK: HASIL PENELITIAN AWAL. *Hidrotermal karbonisasi (HTC) adalah proses termokimia yang digunakan untuk mengonversi limbah biomassa basah menjadi material serupa batubara dengan kandungan karbon yang lebih tinggi disebut hydrochar. Dalam studi ini, desain dan uji kinerja prototipe reaktor hidrotermal karbonisasi telah dilakukan. Reaktor berpengaduk ini terbuat dari stainless steel 304 dengan volume 1 Liter dan pemanas listrik sebagai mantel pemanas. Reaktor HTC digunakan untuk melakukan karbonisasi tiga bahan (kertas, sisa makanan/nasi sisa, dan serbuk kayu) sebagai substrat, percobaan ini juga bertujuan untuk mempelajari pengaruh kondisi suhu pada produksi hydrochar. Substrat yang digunakan merupakan wakil komponen utama dalam limbah padat perkotaan. Studi ini menunjukkan bahwa sifat kimia dan fisik beberapa bahan baku dan hydrochar yang dihasilkan bervariasi sebagai fungsi dari suhu reaksi. Proses HTC dioperasikan pada suhu 160, 190 dan 220^{o}C, waktu reaksi 60 menit, dan tekanan awal gas nitrogen 1 MPa. Tiga produk dikumpulkan dari proses dengan neraca bahan utama. Hasil penelitian menunjukkan bahwa produk* *dipengaruhi oleh elevasi suhu. Hasil penelitian menunjukkan bahwa perlakuan hidrotermal limbah biomassa untuk bahan bakar padat memberikan nilai pemanasan tinggi (HHV) dengan nilai 5231,3, 4569,5, dan 5422,7 kkal / kg untuk kertas, sisa makanan (nasi), dan serbuk kayu masing-masing setelah produk dikeringkan secara alami.*

Kata kunci: *limbah biomassa; hydrochar; hidrotermal karbonisasi; reaktor berpengaduk*

How to Cite This Article: Eriska, H., Dewi, K., Pasek, A.D., and Damanhuri, E., (2016), Hydrothermal Carbonization of Biomass Waste by Using a Stirred Reactor: An Initial Experimental Results, Reaktor, 16(4), 212-217, http://dx.doi.org/10.14710/reaktor.16.4.212-217

INTRODUCTION

Hydrothermal Carbonization (HTC), originated by Friedrich Bergius in 1913, is a thermochemical conversion technique which uses water as a reaction medium for conversion of wet biomass. Subcritical water, typically ranging from 180 to 350°C, is utilized in order to heat feedstock at temperature (Lu *et al*., 2012), even though carbonization itself can be achieved under temperature below 300°C (Hwang *et al.,* 2012). HTC process generally comprises a series of hydrolysis, condensation, decarboxylation and dehydration reactions according to several researchers (Titirici *et al,* 2007*;* Sevilla and Fuertes, 2009; Funke and Ziegler, 2010). As non-combustion process, HTC considered as one of recommended technology for municipal solid waste (MSW) treatment (Lu *et al*., 2011). As we know, most of undeveloped and developing countries have serious problem with the management of waste. Poor treatment, lack of recycling, inadequate collection, and uncontrolled disposal of waste are major challenges that should be faced. If not solved, they will lead to severe human health and environmental disaster.

Compared to landfilled and biological approaches which produced greenhouse gas emission, HTC of biomass waste has various advantages. During HTC process, solid and liquid phases are formed (Wang *et al.,* 2013). The other advantages of this technique include large volume reduction of the wastes in shortly time, odorless, and no need biomass moisture removal unlike incineration and gasification. Furthermore, the using of high pressures is able to eliminate pathogens and making the products sterile and hygiene (Libra *et al*., 2011).

Although HTC seems to be a potential technology to treat biomass waste like sewage sludge, MSW, and industrial waste, unfortunately, facts about the chemistry of HTC is fully complicated and highly feedstock dependent (Wiedner *et al*., 2013). So that, the implementation are still in laboratory and pilot plant scale. Due to high cost, this technology seems to be restricted and suitable for developed countries. Of course, this could be a big challenge for developing countries as well.

In this research, design, construction, and preliminary performance test of hydrothermal carbonization prototype reactor is done. HTC operated under low temperature condition to produce solid fuel from artificial biomass waste. Paper, left-rice, woodchip, and plastic were prepared as the main components of municipal solid waste. Decomposition characteristics of each component and yield and composition of obtained char were investigated.

MATERIALS AND METHODS

Design Requirements of Reactor

This section outlines several possible options for reactor design. The reactor should be matched to condition in developing countries. Reactor should has a simple design and low-tech component. A lab scale reactor is usually smaller than 3 Liters. A HTC experimental apparatus consists of a stainless steel (SS-304) cylindrical reactor with internal volume 1 Liter. Reactor has stirrer to fasten heat transfer through medium from the bottom surface to upper reactor. Batch process was used in this system. This process has low complexity, simple and easy process control. However, it require bigger reactor for the same production.

Electric mantle was utilized for the heating system. Although has energy losses problem, electric mantle was selected due to cheap and simple to use. It preferred to use rather than oil mantle and steam heater. Oil mantle is complex and expensive. The steam heater also have problems with high operating cost and security risks factor because of additional need for pressurized unit.

Table 1. Evaluation table of different criteria

	Process		Heating System		
	Continuous	Batch	Oil	Steam	Electric
Cost	2	4	3	2	3
Material Availability	2	4	3	2	4
Durability	3	4	4	2	4
Security	3	3	4	1	4
Handling	3	4	3	1	4
Level of Technology	2	4	4	2	4
Total	15	23	21	10	23

(1= not fulfilled, 5=fulfilled; the criteria with most point will be considered as the most appropriate)

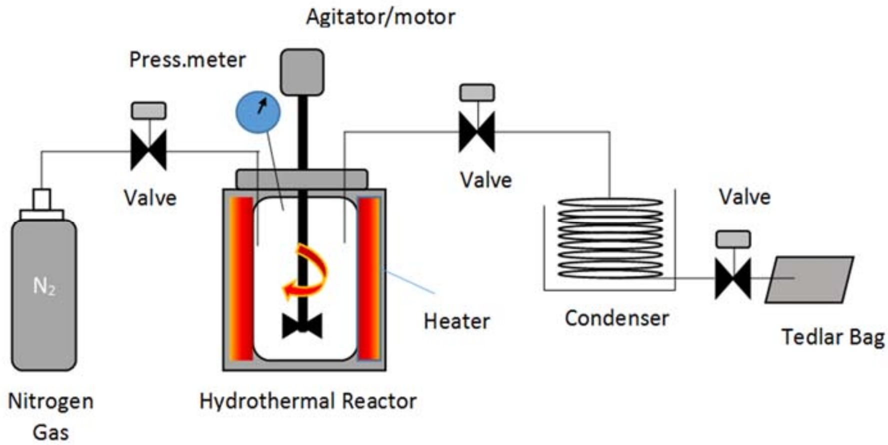


Figure 1. Experimental apparatus setup

From reasoning above, some criteria have been chosen to help selecting an option that is adapted to conditions in developing countries. Table 1 showed that batch process and electric mantle option were the best criteria.

Water Test

The reactor was filled with 700 mL of water, closed, and heated at different set temperatures. The aim of this test is to get information and data related with the elevation of pressure which influenced by the present of external temperature.

Initial Experimental Procedure

Several individual feedstock that represent major fractions of municipal solid waste were evaluated in this study: office paper, food residue, woodchips, and plastic. Before use, the paper and plastic were shredded manually. Food residue was comprised of left-rice. The experiments presented in this work were aimed at obtaining information on both the mass yield and the elemental (carbon, hydrogen, oxygen, nitrogen, sulfur) content of the hydrochar produced, by varying the temperature of the HTC process.

250 gram of sample was loaded into reactor in every single run. Samples were mixed with deionized water with same amount to ensure complete soaking (feed/water ratio = 1). Before reactor heated up, nitrogen gas was passed through the reactor for 5-10 min to guarantee oxygen free in the system. Reactor was heated up in 10-20 min and maintained at desired temperature for 60 minutes. Temperature was set 160, 190, 220°C due to cellulose and hemicellulose start to decompose at 150 and 180°C (Bobleter, 1994). The residence time was predicted to complete the process of conversion of cellulose and hemicellulose until homogeneous.

Once the inside temperature of reactor dropped to room temperature, the pressure valve was released under fume hood to discharge gaseous products. Solid and liquid product were separated using Whatman™ filter paper (diameter 125 mm). Both gas and liquid were collected without further evaluation. Solid fuel (hydrochar) were dried naturally before analysis. The experimental system is shown in Figure 1.

RESULTS AND DISCUSSION

Test with Water

When electrical heater is set with increasing temperature gradually, the pressure rises as well (see Figure 2). Experimental test resulted the pressure increased exponentially along equation y = 4.6881e0.2172x, with R^2 = 0.9987. There were no significant differences between actual pressure from experimental with steam table by Spirax-Sarco, 2015, a leading manufacturer of steam management system, which equation y = 4.3305e0.2348x and R^2 = 0.9956.

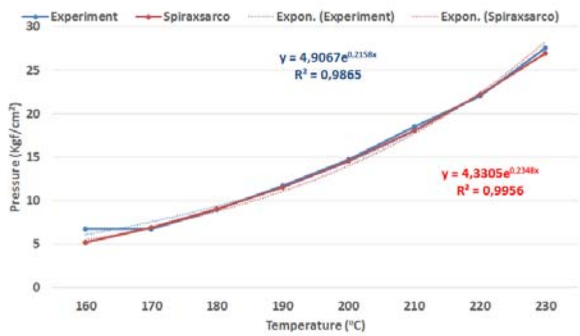


Figure 2. Saturated steam curve

This experimental result test gave that there was no significantly difference between performance showed by constructed reactor and commercially reactor.

The Effect of Operating Condition

Table 2 showed the experimental design in this study. Three different reaction temperature 160, 190, and 220°C with reaction temperature 60 minutes, and feed/water ratio equal to 1, were used during HTC process and their effect on calorific properties of each

Table 2. Experimental design for hydrochar

Parameter Analysis	Biomass Component	Operating Condition (60 minutes, feed/water ratio=1)		
		160°C	190 °C	220 °C
Mass yield (%)	Left-rice	70.7	68.9	66.9
	Paper	51.7	51.2	50.3
	Woodchip	71.2	69.2	67.4
	Plastic*	99.2	99.1	99.2
Heat Heating Value** (kkal/kg)	Left-rice	4617.8	5055.8	5231.3
	Paper	3733.7	4271.2	4569.5
	Woodchip	4403.5	4943.9	5422.7
	Plastic*	6474.2	6474	6476.7
Energy Yield	Left-rice	75.88	80.96	83.54
	Paper	55.70	63.11	81.34
	Woodchip	71.66	78.19	83.54
	Plastic*	99.13	99.1	99.24

*plastic was carbonized at reaction time 30 minutes
**HHV feedstock, paper 3465.3 kkal/kg, rice 4302,5 kkal/kg, woodchip 4375,2 kkal/kg, plastic 6474.2 kkal/kg

Table 3. Proximate and ultimate analysis feedstock and product after HTC

Feedstock	Process	Proximate (dry basis)			Ultimate (wt,%), dry ash free					Calorific Value (kkal/kg)
		Volatile Matter	Fixed Carbon	Ash	Carbon	Hydrogen	Nitrogen	Oxygen	Sulphur	
Paper	Raw	76.8	10.4	12.8	39.7	5.2	0.1	54.9	0.1	3465.3
	HTC-160	71.2	15.3	13.5	41.9	5.7	0.1	52.2	0.1	3733.7
	HTC-190	57.2	26.1	16.7	47.2	5.3	ND	47.5	ND	4271.2
	HTC-220	56.1	26.3	17.6	53.9	5.4	ND	40.7	ND	4569.5
Left-rice	Raw	88.6	10.2	2.2	47.6	6.8	3.5	42.0	0.1	4302.5
	HTC-160	57.4	29.7	12.9	56.8	8.6	10.4	16.2	ND	4617.8
	HTC-190	50.1	33.2	16.7	69.1	6.9	7.5	10.5	ND	5055.8
	HTC-220	51.5	33.1	15.4	72.8	8.0	7.2	10.0	ND	5231.3
Woodchip	Raw	83.2	13.6	3.2	52.5	6.0	0.2	42.3	ND	4375.2
	HTC-160	80.7	16.9	4.4	54.3	6.3	0.1	39.2	0.1	4403.5
	HTC-190	75.5	20.1	4.4	59.9	6.4	0.1	33.5	0.1	4943.9
	HTC-220	69.5	22.4	8.1	68.6	6.3	0.1	24.9	0.1	5422.7

paper, rice, woodchip, and plastic was determined. The results are presented in Table 2, it was shown that except plastic, the properties of biomass are influenced by reaction temperature. Plastic did not degrade in low temperature due to its high densities. Plastic was not added in the input waste, because it will disturb the form of char due to lack of process temperature.

The results suggest that even mass yield decreased, both energy yield and heat heating value increased along temperature rises. Biomass which contain cellulose and hemicellulose were easier to decompose than lignin during hydrothermal carbonization. It also explains the reason of the calorific value and carbon content increase of the most of feedstock after the hydrothermal treatment whose major component is cellulose (Table 3).

More than 90% hemicellulose starts to decompose in the temperature range 180-220°C. Temperature of biomass hydrolysis starts at 180°C (Bobleter, 1994). Lignin behavior is different, less than 10% of lignin decomposed at below 250°C (Bobleter, 1994; Yuliansyah *et al.*, 2010). At temperature process 160°C, biomass only experienced drying process, and hydrochar was not formed.

Figure 3 shows the effect of temperature on the mass yield of different feedstock during HTC. As expected, the mass yield less reduces with an increase in the temperature. Paper was the only one feedstock that showed the lowest mass yield. Paper is one of biomass with high cellulose and hemicellulose content. Because of low thermal stability, paper tend to loss its mass easily (Garrote *et al.*, 1999).

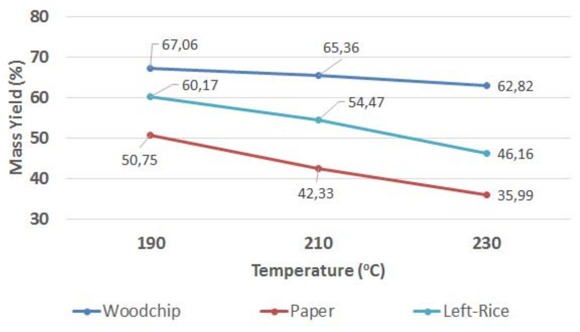
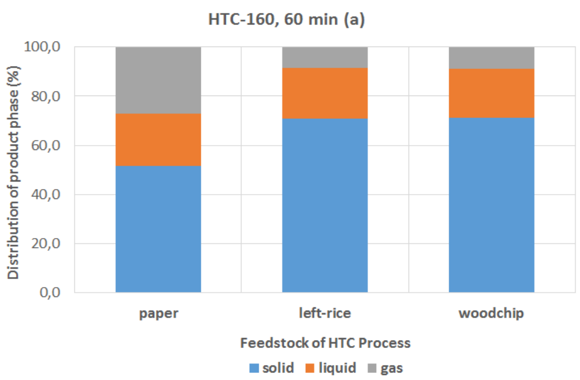


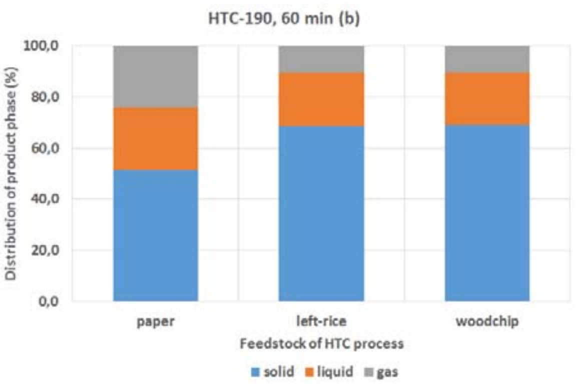
Figure 3. Mass yield during hydrothermal carbonization

Proximate and Ultimate Analysis of Hydrochar

The proximate and ultimate analysis of raw and hydrochar were summarized in Table 2. The proximate analysis is used to determine the quality of coal and other solid fuels. The carbon content of the produced hydrochar ranges from 42-73% (Table 3). Based on many literature (Hwang *et al.*, 2012; Lu *et al.*, 2013; Lu *et al.*, 2014), carbon contents of hydrochar from the carbonization process were vary depend on other compounds. So, it is very hard to compare between carbon-contents measured in this study with reported in other literature. There are so many factors, such as the different of temperature, pressure, reaction time, reactor design, feed/water ratio, water stream, and. Mass balance analyses indicate that carbonization of the feedstock results in a significant fraction of carbon retained within the char (Figure 4). Carbonization of office paper results in the smallest fraction of carbon remaining in the solid-phase.

Hydrothermal process breaks the physical and chemical structure of material into smaller molecules. Biomass feedstock usually have high volatile matter and oxygen content. With the increase of the hydrothermal reaction temperature, the volatile matter and oxygen content decreased while the fixed carbon and high heating value slightly increased that influenced by hydrolysis reaction. The results suggested that the hydrothermal treatment of biomass waste to solid fuel gave a highest heating value of hydrochar recorded were 5231.3, 4569.5, and 5422.7 kcal/kg for paper, rice, woodchip respectively after product dried naturally.





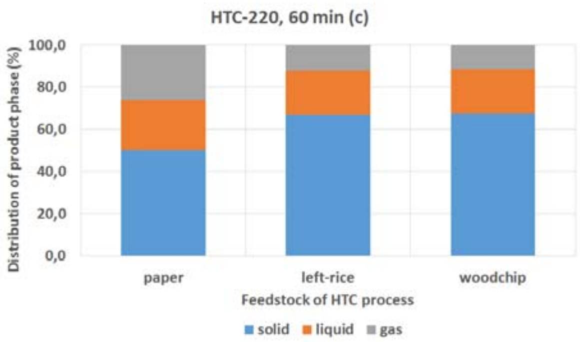


Figure 4. Product phase distribution during hydrothermal carbonization (a) temperature 160°C (b) temperature 190°C dan (c) temperature 220°C

CONCLUSION

In this paper the technical characteristics of a lab-scale batch reactor for HTC of wet biomass waste were described. The HTC reactor was utilized to perform the carbonization of three materials (paper, left-rice, and woodchip), in order to study the influence of the temperature process conditions on the hydrochar produced. The study showed that chemical and physical properties of several feedstock and hydrochar varied as a function of reaction temperature.

The results, both in terms of hydrochar yield and hydrochar chemical and thermal properties, showed that HTC represents an alternative way to obtain a solid product with quite good characteristics as energy path. The resulted showed that increasing reaction temperature and holding time period during hydrothermal carbonization tend to increasing carbon content. Due to there was decreasing polarity and increasing temperature is associated with molecule breaking.

In this perspective, high temperatures increased the heating values of the hydrochar, although the yields resulted lowered. Thus, further experiments are required to assess the optimal values of the process parameters. In particular, a detailed reaction kinetics study could be useful to optimize the process and thus to obtain its maximum performance. Moreover, several parameters such as pure substances usage, variation of ratio feed/water, and catalyst is required in view of an actual assessment of the HTC potentiality for large-scale applications. Characteristic of liquid and gas product should be determined to gain more accurately about process and other carbonization products.

ACKNOWLEDGEMENT

I would like to thank the Research and Development Center of Mineral and Coal Technology (Tekmira) for the support of his research. The author is Indonesia Endowment Fund for Education (LPDP) scholar. The works are financially supported by the Indonesian government through Ministry of Finance, Ministry of Research and Technology and Higher Education, and Bandung Institute of Technology.

REFERENCES

Bobleter, O., (1994), Hydrothermal Degradation of Polymers Derived from Plants, *Progress in Polymer Science*, 19(5), pp. 797–841.

Funke, A. and Ziegler, F., (2010), Hydrothermal Carbonization of Biomass: A Summary and Discussion of Chemical Mechanisms for Process Engineering, *Biofuels Bioproducts & Biorefining-Biofpr*, 4, pp. 160-177.

Garrote, G., Dominguez, H., and Parajo, J., (1999), Hydrothermal Processing of Lignocellulosic Materials, *European Journal of Wood and Wood Products*, 57(3), pp. 191-202.

Hwang, I.H., Aoyama, H., Matsuto, T., Nakagishi, T., and Matsuo, T., (2012), Recovery of Solid Fuel from Municipal Solid Waste by Hydrothermal Treatment Using Subcritical Water, *Waste Management*, 32(3), pp. 410-416.

Libra, J.A., Ro, K.S., Kammann, C., Funked, A., Berge, N.D., Neubauer, Y., Titirici, M.M., Fühner, C., Bens, O., Kern, J., and Emmerich, K.H., (2011), Hydrothermal Carbonization of Biomass Residuals: A Comparative Review of the Chemistry, Processes and Applications of Wet and Dry Pyrolysis, *Biofuels*, 2(1), pp. 71–106.

Lu, L., Namioka, T., and Yoshikawa, K., (2011), Effects of Hydrothermal Treatment on Characteristics and Combustion Behaviors of Municipal Solid Wastes. *Applied Energy*, 88, pp. 3659-3664.

Lu, X., Jordan, B., and Berge, N.D., (2012), Thermal Conversion of Municipal Solid Waste via Hydrothermal Carbonization: Comparison of Carbonization Products to Products from Current Waste Management Techniques, *Waste Management*, 32(7), pp. 1353-1365.

Lu, X., Pellechia, P., Flora, Joseph R. V., and Berge, N.D., (2013), Influence of Reaction Time and Temperature on Product Formation Associated with the Hydrothermal Carbonization of Cellulose, *Bioresource Technology*, 138, pp. 180-190.

Lu, X., Flora, J.R.V., and Berge, N.D., (2014), Influence of Process Water Quality on Hydrothermal Carbonization of Cellulose, *Bioresource Technology*, 154, pp. 229-239.

Sevilla, M. and Fuertes, A.B., (2009a), Chemical and Structural Properties of Carbonaceous Products Obtained by Hydrothermal Carbonization of Saccharides, *Chem. Eur. J.,* 15, pp. 4195-4203.

Sevilla, M. and Fuertes, A.B., (2009b), The Production of Carbon Materials by Hydrothermal Carbonization of Cellulose, *Carbon*, 47, pp. 2281-2289.

Titirici, M.M., Thomas, A., Yu, S.-H., Müller, J.-O., and Antonietti, M., (2007), A Direct Synthesis of Mesoporous Carbons with Bicontinuous Pore Morphology from Crude Plant Material by Hydrothermal Carbonization, *Chemistry of Materials*, 19(17), pp. 4205-4212.

Wang, J.Y., He, C., and Giannis, A., (2013), Conversion of Sewage Sludge to Clean Solid Fuel Using Hydrothermal Carbonization: Hydrochar Fuel Characteristics and Combustion Behavior, *Applied Energy*, 111, pp. 257–266.

Wiedner, K., Naisse, C., Rumpel, C., Pozzi, A., Wieczorek, P., and Glaser, B., (2013), Chemical Modification of Biomass Residues during Hydrothermal Carbonization–What Makes the Difference, Temperature or Feedstock?, *Organic Geochemistry*, 54, pp. 91–100.

Yuliansyah, A.T., Hirajima, T., Kumagai, S., and Sasaki, K., (2010), Production of Solid Biofuel from Agricultural Wastes of the Palm Oil Industry by Hydrothermal Treatment, *Waste and Biomass Valorization*, 1, pp. 395–405.

http://www.spiraxsarco.com/Resources/Pages/Steam-Tables/saturated-water.aspx (accessed on December 12th, 2015