HYDROTHERMAL CARBONIZATION & TORREFACTION OF COTTON STALK FOR ENERGY RECOVERY WITH OPTIMUM PROCESS CONDITIONS

Elif Gödekmerdan, Fikret Müge Alptekin, Merve Uyan, Sevim Özgül, Melih Soner Çeliktaş Solar Energy Institute, Ege University, Turkey Corresponding author: Elif Gödekmerdan, e-mail: elifgodekmerdan@hotmail.com

REFERENCE NO	ABSTRACT		
MISC-02	This study aims to compare cotton stalk based biochar obtained using hydrothermal carbonization and torrefaction. Experiments of hydrothermal carbonization (HTC) were carried out by varying temperature (170, 210 and 250 °C), reaction time (30, 45 and 60 min) and particle size (1, 2 and 3 mm). In the experiments of HTC of cotton stalk; temperature, reaction time and particle size effects were optimized via response surface estimation (RSM) with Par Davider of Cotting and determined 210 °C.		
Keywords: Cotton stalk; Biochar;Hydrothermal carbonization; Torrefaction	2mm. Then torrefaction was conducted at the optimum condition. The results of hydrothermal carbonization and torrefaction were compared with considering high calorific value, energy yield, high mass yield, ash yield, carbon yield and energy consumption at the optimum condition.		

1. INTRODUCTION

Owing to the increased world population, the rising energy demand become an important social issue. The consumption of energy resources is the main cause of the depletion in availability of fossil fuels, and deterioration of environmental health and ecological balance. Fossil fuels as non-renewable energy sources serious negative effect have а both environment and alives. For instance, one of the major source of energy production is coal. However, burning of coal has several undesirable results such as smog, soot, acid rain, global warming, and toxic air emissions, which includes the release of heavy metals, such as mercury and arsenic, that are present as trace elements in coal [1]. Searching of alternative energy source is gaining importance when all these negative states are considered. Among all the renewable energy options, biomass which is one of the important being a renewable and sustainable energy feedstock, if properly managed, offers several advantages. In addition, biomass usage significantly mitigate net carbon can emissions when compared to fossil fuels because the carbon dioxide released into atmosphere by using biomass is recovered again by growth of new biomass [2].

In the recent years, the production of biochar from biomass wastes has been of great interest for economic as well as environmental reasons. These wastes constitute an attractive and renewable raw material for biochar production due to their abundances, availability and low cost. Cotton (algodonero Americano), is one of the most abundant lignocellulose-rich agricultural crops. Current estimates for world cotton production are about 25 million tonnes and accounting for 50 million tons of biomass waste [3]. Cotton with approximately an annual production of 2.1 million tons (5.1 tons per hectare) is an important biomass source in Turkey [4]. According to the average of the last 5 production seasons, cotton production in the country accounts for 60% of consumption [5]. Especially cotton wastes exports have 49,8 M in trade volume [6]. Cotton post-harvest residue/cotton stalk is a major agro-residue in Turkey. Annually, the amount of post-harvest residue/cotton stalk is 2,253 MT [7]. Traditionally, cotton is being cultivated for its lint which is used as a textile raw material. However, several studies have examined the use of various cotton-based materials for the production of value-added products such as biochar production. Biochar, the solid material formed during the thermochemical

decomposition of biomass, is defined as a solid material obtained from the carbonization of biomass. As biochar is inexpensive, environment-friendly, and can be used for a variety of purposes, such as soil remediation, waste management, greenhouse gas reduction, and energy production, several studies have been conducted to develop new applications of biomass [Lenmann et al, 2009]

There are several thermochemical techniques to convert biomass to bioenergy [Placido et al, 2013]. Among them is that hydrothermal carbonization (HTC) process which is an environment friendly technology. It thermally converts a variety of biomass feedstocks into high carbon content containing, smokeless solid fuels. HTC of biomass is studied along with water by application of higher temperatures (180-250 °C) at elevated pressure (2-10MPa) for several hours [7]. Torrefaction is a promising pretreatment for biomass upgrading [1]. It is a thermal treatment with a reaction temperature between 200 and 300 °C at atmospheric pressure in the absence of oxygen. This moderate thermal process breaks down the fiber structure of the biomass so that the biomass becomes easier to grind. It can effectively increase biomass density. In addition. energy the hydrophobicity of biomass can be enhanced, which further improves the storage stability [8].

The aim of this study is that to convert cotton stalk to biochar with applying HTC and torrefaction technology. HTC experiments were carried out by using Design Expert software (version 7.0) program with selecting independent factor different temperature, detention time and particle size. According to optimum conditions which are obtained from HTC experiment results, torrefaction process was applied. Biochar obtained by applying HTC and torrefaction technologies at the same conditions were compared with as their high heating value, energy consumption, carbon content %, ash content %, yield of energy %.

2. MATERIALS AND METHODS

2.1. Materials

Cotton stalk was obtained from a field in İzmir which is in the west of Turkey. The volume of cotton stalk was minimized to store biomass under dry and room temperature using a cutting mill. Cotton stalks were separated in 1-2, 2-3.35, and 3.35-5 mm particle size by sieve. Sieved samples were used for the HTC and torrefaction processes.

2.2. Methods

2.2.1 Hydrothermal carbonization (HTC)

HTC of cotton stalk was carried out using 100 ml cylindrical stainless-steel reactor. Effecting factors of experiments are determined based on researched studies (Kambo H. and Dutta A., 2015). The experiments were performed at 170 °C, 210 °C, and 250 °C, with the residence time of 30, 45 and 60 minutes and fixed solid load 7.5:1 (75 gr water, 10 gr cotton stalk). Pressure which into reactor ranged from 1-30 MPa. The experiments was arranged by using Design Expert software program. All conditions were obtained from result of experiment set which was randomly arranged.

The weight of 10 gr cotton stalk is imbedded in reactor with 75 ml deionized water. The reactor was then sealed and heated desired temperature with an PLC electric furnace. When this temperature was achieved, the reaction was maintained for 30, 45 and 60 minutes. After experiment done, the heater was closed down and the reactor was kept into the water sink at the room temperature for 10 minutes to be cool down. The product of reaction was taken from reactor then, the product was put on filter paper and washed with deionized water 3 times. It was separated to as char and liquid phase. The char was kept 24 hours into drying-oven for drying. The liquid phase and chars were weighed and stored in plastic containers until analysis.

2.2.2 Torrefaction

Torrefaction experiments of cotton stalk were carried out in a stainless steel tube reactor with a diameter of 50,8 mm and a height of 800 mm heated by electric heaters of 2.5 KW externally. For each experiment, 160 g of cotton stalk was placed inside the reactor. The reactor was heated to 210 °C and 250 °C with the heating rate of 5 °C /min. After reach desired temperature it was held for 1h. At the end of the residence time, the reactor was cooled down to room temperature. The reactor was opened to collect and the torrified cotton stalk was held inside plastic bag until analysis.

2.2.3. Product characterization

2.2.3.1. HPLC analysis of liquid phase

The liquid phases of HTC were kept in Falcon tubes in refrigerator at 4 °C. The liquids phases were transferred to Eppendorf tubes. The samples had been centrifuged with Hettich ZENTRIFUGEN MIKRO 22 at 1500 rpm for 15 minutes. The centrifuged samples were filtered by 0,25 µm filter to Eppendorf tubes. Sugar concentrations which are glucose and xylose, ethanol, and other fermentation inhibitors which are furfural. 5hydroxymethylfurfural (5- HMF), levulinic acid, formic acid, and acetic acid in the liquid hydrolysates were determined using an Agilent 1260 Infinity high performance liquid chromatograph (HPLC) with an Aminex Biorad HPX-87H column based on NREL standard [11].

2.2.3.2. Determination of the moisture content About 1 g of dried char was weighted out for moisture content by XM 60 Precisa with two replicates. The moisture content determinations were obtained for all dried chars. On the other hand, raw material was weighted about 1 gr and moisture content was determined with the same method.

2.2.3.3. Determination of the ash content

To determine the ash content for each samples approximately 1 g of cotton stalk dry samples, from both, treated and untreated, was burned in a muffle furnace set at 250 °C for 1 h then, at 550 °C for 2 h with three replications according to EN 15403:2011 European Standard. The ashes were then cooled in a

desiccator for 15 min and reweighed. The relative ash content (%) was calculated for untreated and treated cotton stalk as following: one based on original untreated cotton stalk and one based on after the weight loss due to heating (treated cotton stalk). The relative ash content value was calculated according to equation 1.

% Relative ash content= [(M1-M2)/m] * 100 (1)

M1: Mass of untreated cotton stalk M2: Mass of treated cotton stalk m: Mass of raw material

2.2.3.4. Determination of the high heating value (HHV)

The higher heating values of raw and solid samples from HTC and torrefaction were determined using a Parr 6300 calorimeter. Obtained char was made pellet for all run with two replicates.

2.2.3.5. Instrumental characterization

The carbon, hydrogen and nitrogen content of samples were measured by Elemental Analyzer Leco TruSpec CHN. Complete combustion and superior recovery of the elements of interest were conducted under pure oxygen in a furnace to determine of elemental C, H, and N instrument by Leco TruSpec CHN. To determine sulphur content by using analyzer Leco TruSpec CHN. In order to determine the carbon and sulphur content in a wide variety of organic materials as well as some inorganic materials by combustion with nondispersive infrared detection via the analyzer.

2.2.3.6. Design of Experiment

Design Expert software (version 7.0) was used in this study to design the experiment and optimize the reaction conditions. The experimental design employed in this work via response surface estimation (RSM) with Box-Benhken including 15 experiments. Temperature, A, detention time, B, particle size, C were selected as independent factors for the optimization study. The responses chosen were the HHV, carbon %, ash content %, mass %, energy yield %.

2.2.3.7. Mass and Energy Yield

The mass yield (MY) and energy yield (EY) of

solid products were calculated as follows:

 $M_y (\%) = m_{SP} / m_{RW} X 100$

(2)

 E_y (%)= M_y X HHV_{SP} / HHV_{RW}

Where m_{SP} and HHV_{SP} are the mass and high heating value of solid products, m_{RW} and HHV_{RW} are the mass and calorific value of cotton stalk samples, and HHV_{SP} / HHV_{RW} is energy density of the solid products.

3. RESULTS AND DISCUSSIONS

3.1. Characterization of HPLC

The optimum condition of HTC process was determined by Design Expert Software program which was explained on related section. Four experiments were carried out at optimum condition; 210 °C, 2 mm and 1,2,3,4 h. The samples of liquid phase of experiment were analyzed by using HPLC. The content of liquid phase was represented on Table 1.

Table 1. The content of liquid phase

Sampl	Cellob	Gluko	Xylose	Glyser	Acetic
e	iose	se	(mg/m	ol	Acid
	(mg/m	(mg/m	1)	(mg/m	(mg/m
	1)	1)		1)	1)
HTC_	1.12	1.05	1.06	0.04	0.52
210_1					
HTC_	1.12	0.95	1.04	0.05	0.57
210_2					
HTC_	1.12	0.97	1.08	0.07	0.63
210_3					
HTC_	1.11	0.95	1.05	0.05	0.55
210_4					

3.2. Characterization of the moisture content

At the beginning of experiments, the moisture content of raw material was found as 8.03 %. The results of moisture content were carried out all of dried chars. The results are suggested that the moisture content is decreased by drying.

3.3. Characterization of energy consumption on HTC

HTC was carried out based on reaction parameters and energy consumptions of each

experiment was noticed. The energy consumptions are shown below in Table 2.

According to Table 2 the minimum energy consumption is that 0,16 kWh at 170 °C and 60 min.

Std	Run	Temp	Detenti	Partic	Energy
		eratu	on	le	Consu
		re	time	size	mption
		(°C)	(min)	(mm)	(kWh)
14	1	210	45	2	0.33
4	2	250	60	2	0.75
2	3	250	30	2	0.56
11	4	210	30	3	0.21
3	5	170	60	2	0.16
13	6	210	45	2	0.27
7	7	170	45	3	0.15
1	8	170	30	2	0.16
15	9	210	45	2	0.30
8	10	250	45	3	0.75
6	11	250	45	1	0.60
5	12	170	45	1	0.18
9	13	210	30	1	0.25
12	14	210	60	3	0.33
10	15	210	60	1	0.29

Table 2. Energy consumption on HTC

However, the maximum energy consumption is observed that 0,754 kWh at 250 °C and 45 min. As results are compared with each other, it is easily to see that the energy consumption is related with temperature of process. Also, the energy consumption is related with reactor usage frequency. Evaluation of effects on energy consumption is figured out that detention time has less impact on energy consumption. When the energy consumption of run 13 and run 15 compare each other, it is clearly to see that the values are very close.

3.4. Characterization of the ash content

The ANOVA results showed that the quadratic model is suitable to analysis the experimental data. The model in terms of the coded values of the process parameters is given by: Ash content = $+2.54 + 0.35 * A + 0.48 * B + 0.34* C+0.62 * A * B-0.10 * A * C-0.20 * B * C+0.040 * A^2+0.18 * B^2+0.40 * C^2$ (3)

According to analysis, although effect of reaction time on ash content is the most effective factor, temperature was effected slightly than other factors. The interaction of factors on ash content is shown in Figure 1.



Figure 1. The interaction of factors on ash content

3.5. Mass yield

The maximum weight loss between the observed cotton stalk is due to degradation of its basic organic components such as hemicellulose, cellulose, and lignin. Mass loss occurs due to a release of CO2, CH4 and H2O, and the gases formed during the decomposition of hemicellulose (190–320 °C), cellulose (280–400 °C) and lignin (320–450 °C) [8]. The result of analysis of variance is given in Table 3. The ANOVA results showed that the quadratic model is suitable to analysis the experimental data. The model in terms of the coded values of the process parameters is given by:

mass yield = $73.19 - 9.09 \times A - 2.52 \times B + 2.13 \times C$ (4)

The Model F-value of 42.92 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. The analysis shows that effect of temperature on mass yield is most effective factor while the detention time has less effect.

Based on results, the minimum mass loss is occurred at 170 °C, 45 min and 3 mm particle size with 83.17 %. The maximum mass loss is occurred at 250 °C, 30 min and 2 mm with 61.68 %. The interaction of factors on mass yield is shown in Figure 2.



Figure 2. The interaction of factors on mass yield

3.6. Characterization of the high heating value (HHV)

The ANOVA results showed that the quadratic model is suitable to analysis the experimental data. The model in terms of the coded values of the process parameters is given by:

HHV= $+4581.68 + 189.98 * A + 48.67 * B - 18.95 * C + 10.26 * A * B - 16.09 * A * C + 4.95 * B * C + 49.48 * A^2 + 49.56 * B^2 - 96.66 * C^2$ (5) The Model E value of 21.07 implies the

The Model F-value of 21.97 implies the model is significant. There is only a 0.17% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, B, C^2 are significant model terms. The interaction of factors on HHV is shown in Figure 3.



Figure 3. The interaction of factors on mass yield

The result of analyses show that the minimum HHV is that 4348,15 cal/g at 170 °C, 45 min

and 1 mm. The maximum HHV is that 4922,81 cal/g at 250 °C, 60 min and 2 mm.

3.7. Atomic H/C and O/C ratios

The calorific value of materials is strictly related to the atomic H/C and O/C ratios [12]. The weight percentages of C, H, O, and N in the hydrothermal carbonization materials are given Table 6. The decarbonization, dehydration and deoxygenation mechanism occur while the thermal degradation of biomass proceeds. The dehydration and deoxygenation reactions are more important compared to the decarbonization reaction, so, the HTC temperature or duration is raised when both the atomic H/C and O/C ratios decrease. Within the investigated ranges of HTC temperature, duration, and particle size, the atomic H/C and O/C ratios are in the of 0.12-0.15 and 0.86-1.15, ranges respectively.

Table 3. Elemental analysis of hydrothermalcarbonized cotton stalk at selected operating conditionsof HTC

Tempe ra ture (°C)	Reacti on time (min)	Partic le size (mm)	C %	H %	0%	N %
250	45	3	47.2 7	6.0 6	45.5	1.1 7
210	60	1	46.2 8	6.0 6	46.6	1.0 6
170	30	3	44.1 7	6.2 6	48.6 8	0.8 9
210	60	3	45.7 5	6.2	47.0 6	0.9 9
250	60	2	48.9 9	5.9 9	43.9	1.1 2
170	60	2	45.1	6.3	47.7 5	0.8 5
170	45	1	44.4 2	6.3 5	48.8 6	0.8 7
250	45	1	47.8 2	6.1 8	43.4 2	2.5 8

170	45	3	43.1	6.2	49.6	0.9
			9	9	2	
210	30	3	43.8	6.2	48.8	1.0
	20	0	2	6	3	9
210	45	2	44.7	6.3	48.0	0.9
			3	3	3	1
210	45	2	44.3	6.2	48.4	0.9
			4	5	7	4
210	45	2	11.8	62	17.0	0.0
210	45	2	44.0 6	0.2	47.9	3
			0	/	+	5
250	30	2	47.4	6.2	45.2	1.1
			1	4	4	1
210	30	1	44.3	6.3	48.5	0.8
			5	3	1	1
210	60	2	11.5	62	10 1	1.0
210	00	2	3	0.2	40.1	1.0
			5	-	,	-
210	120	2	49.8	6.0	43.0	1.1
				4	2	4
210	180	2	49.7	6.0	43.2	1.0
			4	1	1	4
210	240	2	50.1	58	42.8	10
210	210	_	8	5	8	9
			Ĵ	5	Ĵ	Í

Based on the optimum condition of torrefaction, its C%, H%, O% and N% values are 48.92, 5.84, 44.08, and 1.16, respectively. Within the investigated condition of 210 °C, 60 min, and 2 mm-particle size, the atomic H/C and O/C ratios are 0.12 and 0.91, respectively.

Elemental analysis shows that while detention time were increasing, carbon content is increased at optimum condition (210 °C, 2mm-particle size). On the other hand, torrified cotton stalk has higher carbon content than hydrochar at optimum condition.

3.7. Experiments of optimum condition

To determine optimum condition; response surface estimation (RSM) is used. Optimum condition was given 210°C, 60 min and 2 mm particle size from selected range by ANOVA. When graph columns were investigated reaction time is more important effect than others. In this sense, it was decided to do new experiments for HTC on optimum conditions which the same temperature and particle size with different reaction times. The experiments were carried out for 1, 2, 3, and 4 hours on optimum condition. For torrefaction method, optimum condition experiment carried out for 1 hour.

Comparing both of two experiments of method based on 1-hour results, higher heating values of two method at optimum condition which are 4920.4 cal/g and 4858.8 cal/g respectively. It shows that the result of torrefaction is nearly close to result of HTC. For this reason, the experiment of torrefaction was carried out only for 1 hour.

Accordingly seeking an compatible HTC operation for producting biochar fuel temperature (190, 225 and 260°C), reaction time (5, 15 and 30 min) and feedstock to water ratio (1:6 and 1:12) are three most common and important parameters were examined (Kambo and Dutta, 2015). The results of experiments suggested that increasing reaction time enhances higher heating values.

Another recent study was performed for optimizing torrefaction method for producting biochar fuel. The study suggested that increasing higher heating values of torrified biomass could be achieved at a higher temperature along with longer duration (Chen at all, 2017).

3.8. SWOT analyses of HTC and torrefaction

In this study, optimum condition was determined by using via response surface estimation with Box-Benhken. Then HTC and torrefaction experiments were carried out at optimum condition. The results of experiments were very closed each other. In this point, qualifications of two methods were determined with using SWOT analysis. The analysis which has strengths, weaknesses, opportunities and threats is shown below. *3.8.1. Strengths*

3.8.1.1.HTC

-Simple and low technology system -Low construction costs -Easy and safe operation -Low energy requirements [14]. -Considerable reduction in the ash content -Eliminates the risk of fouling, scaling, slagging and corrosion during combustion [16].

3.8.1.2. Torrefaction

-Increasing calorific power
-The possibility of use without being packed
-Less biodegradable
-Better efficiency of combustion
-Low moisture content [15].
-Converts biomass into an upgraded solid
[16].

3.8.2. Weaknesses

3.8.2.1. HTC

-Rigorous design and construction requirements
-Requires the use of water if feedstock not sufficiently wet[14].

3.8.2.1. Torrefaction

-An additional operation is required new costs -Mass losses -Non-suitable grind to fine sized particle[15].

3.8.3. Opportunities

3.8.3.1.HTC

-Substitute firewood in developing countries -Reduces GHG emission

-Reduction of waste burden

-Improvement of health and environmental situation[14].

3.8.3.1. Torrefaction

Promising give a solution for climate crisis
Water uptake is minimized
Upgrading the fuel quality
not require post-drying of product [15].

3.8.4. Threats

3.8.4.1. HTC -Post-treatment of process-water

-Building a HTC reactor might not be available

-Requirements in terms of energy supply [14].

3.8.4.1. Torrefaction

-The mass yield during torrefaction decreased rapidly

-The volatiles produced in the torrefaction step

-Process condition requires higher cost [15].

4. FUTURE PERSPECTIVES OF BIOCHAR

produced Biochar both hydrothermal carbonization and torrefaction have surface area and porosity with aromatic surfaces and oxygen functional groups. Depending upon the field of application biochars can be activated to increase their surface area and porosity in order to improve their adsorption capacity. By applying activated process, they are referred to as 'activated carbon' materials. Biochars/activated carbon have the potential to adsorb a variety of organic pollutants and heavy metals from water due to their its high surface-to-volume ratio and strong affinity to nonpolar substances [12].

Supercapacitor are energy storage devices which has long cycle life, fast charge, and high power density [17]. Improving of the high surface area and porosity during biochar process, increasing the conductivity which gives an opportunity to be electrodes for energy storage devices. High conductivity level content gives a chance biochar based active carbon to using in supercapacitor.

Clean energy has become most important topic nowadays. Changing old fashion technologies and materials with clean ones, it is a new approach which is necessary for environment. Quantum Dot (QD) has distinct size-dependent optoelectronic characteristics. Due to its properties, it is a good candidate for solar energy conversion area. Quantum dot sensitized solar cell (QDSSC) is a new technology in the field of solar cell. Photoanode is important for QDSSC due to net photo conversion efficiency. Carbon based materials such as carbon nano tubs, graphene, active carbon and the other complex nanostructures can raise conductivity of active layer and charge transfer rate. Photoanode which have carbon based materials can be more research to upgrading solar energy conversion [18].

COD has enormous wide range of applications. Besides supplying clean energy, it has also bio-application area application such as bio-imaging, cellular-imaging, drug/gene delivery. By improving CQD research, health standarts can be increase and it can be also possible human cloning in the future [19].

With high surface area and porosity of biochar develops soil aeration and supplies an asylum to the beneficial soil organisms like arbuscular mycorrhiza (AM), a type of fungus. These organisms are supported the supply of minerals and water, and guards crops against infections by root pathogens. There are several functional groups which are hydroxyl, keton, ester, aldehyde, amino, nitro, phenolic and carboxyl groups in biochar surface. Hydrophilic/ hydrophobic and acidic/basic properties are exhibited by biochar. Biochar has very few polar functional groups at the surface and highly hydrophobic in nature. Owing to these qualification, the surface of biochar gets oxidized and forms more carboxylic and phenolic groups, when mixed in soil, after exposure to O_2 and water present in the soil. Also, the biochar gets more hydrophilic than before. If the biochar has these groups on the surface, it will enhance the cation exchange capacity (CEC), nutrient retention capacity (NRT) and water holding capacity (WHC) of soil. Soil health and crop productivity can be improved by all these features significantly [20].

Carbon sequestration or carbon capture and storage occurs when a biomass feedstock is converted to biochar and is then stored in a reservoir (soil). This storage of carbon in soil is the net elimination of carbon from atmosphere. By storage of carbon in soil, the process can result in a carbon-neutral or even carbon-negative environment, so balancing for the effect of anthropogenic CO2 emissions. Thanks to deeply research application of biochar/hydrochar in the soil with improved stability, low GHG emissions, and positive effects on the agricultural productivity [16]. The reaction chemistry of the HTC process gives a wide range of benefits. Formation of intermediate products, that includes, 2-5aldehydes, HMF, and other phenolic compounds occur during HTC thanks to the formation of hydronium ions (from water ionization) catalyzes the breakdown of hemicellulose polysaccharides. This compounds can potentially be used for the manufacture of chemicals and be provided high added value products in the biorefinery industry. The formation and percentage yield of all these chemicals can be made fit by controlling the HTC process condition [16].

Both of Torrefaction and HTC processes can upgrade the fuel quality of cotton stalk. Temperature played an important role in thermochemical treatment of both processes. With increasing temperature, mass yield, energy yield, and volatile content decrease, while calorific value, fixed carbon content and thermal degradation stability increase. Additionally, increasing detention time, fixed carbon content is increasing.

5. CONCLUSION

In this work a study of the optimization of converting cotton stalks to biochar, with applying HTC and torrefaction method, reaction parameters was carried out by response surface methodology (RSM). The process parameters for converting reaction such as: temperature, reaction time and particle size were investigated. The analysis of variance (ANOVA) showed that a satisfactory result was obtained. The experimental results suggested the optimal condition as follows: temperature, 210 °C; reaction time, 60 min; particle size 2mm. Moreover; on optimum condition, increasing reaction time seems to has significant effect. The effect of reaction time (60, 120, 180 and 240 min) on the responses values was investigated using 210 °C and 2 mm for the particle size. And the highest HHV value is determined 5046.4 cal/g for 4 hour. The result suggested that reaction time has significant effect on responses values. The energy consumption of HTC and torrefaction were compared each other based on at 210 °C and 2 mm particle size and 1

hour. Energy consumption at one hour experiment on HTC and torrefaction are 0.351 kWh and 0.378 kWh respectively. Additionally HHV values of two method at optimum condition for one hour which are determined 4920.4 cal/g and 4858.8 cal/g respectively.

It is easily to see that, higher heating values for both of methods are quite close each other. At this point, the energy consumption gets significance to utilize these methods. Based on large scale production, HTC has consumed less energy than torrefaction for continuous reactor.

According to experimental results and SWOT analysis, both of methods are suitable for production. But humidity of raw material and reactor types have an important effect for choosing which technology will be desired.

References

[1] Finkelman, R.B., Orem, W., Castranova, V., Tatu, C.A., Belkin, H.E., Zheng, B., Lerch, H.E., Maharaj, S.V., Bates, A.L., Health Impacts of Coal and Coal Use: Possible Solutions, International Journal of Coal Geology, Vol. 50, No. 10.1016/S0166-5162(02)00125-8, 2002, pp. 425-443.

[2] Tumuluru, J., S., Wright, C., T., Kenny, K., L., Hess, J., R., A Review on Biomass Densification Technologies for Energy Application, *Biofpr*, Vol. 5, No. 10.1002/bbb.324, 2011, pp 683-707.

[3] Hamawand, I., Sandel, G., Pittaway, P., Chakrabarty, S., Yusaf, T., Chen, G., Seneweera, S., Al-Lwayzy, S., Bennet, J., Hopt, J., Bioenergy from Cotton Industry Wastes, *Renewable and Sustainable Energy Reviews*, Vol. 66, No.

10.1016/j.rser.2016.08.033, 2016, pp. 435-448.

[4] Turkish Statistical Institute, http://www.turkstat.gov.tr/UstMenu.do?metod =temelist (date accessed 09.10.2017)

[5] Republic of Turkey Ministry of
Customs and Trade, Cotton Report 2015,
http://koop.gtb.gov.tr/data/56e95b3a1a79f5b2
10d9176f/2015%20Pamuk%20Raporu.pdf

[6] The Atlas of Economic Complexity, http://atlas.cid.harvard.edu/explore/?country (date accessed 10.11.2017)

[7] Turkey Renewable Energy Potantial Atlas, <u>http://bepa.yegm.gov.tr/</u>., (date accessed 03.12.2017)

[8] Lehmann, J. and Joseph, S., Biochar for Environmental Management: An Introduction, Biochar for Environmental Management Science and Technology, 2nd Ed, Earthscan, 2009

[9] Plácido J.*, Imam,T., Capareda S., Evaluation of ligninolytic enzymes, ultrasonication and liquid hot water as pretreatments for bioethanol production from cotton gin trash, *Bioresource Technology*, Vol. 139, No. 10.1016/j.biortech.2013.04.012, 2013, pp. 203–208.

[10] Kambo, H., and Dutta, A.,Comparative evaluation of torrefaction and hydrothermal carbonization of lignocellulosic biomass for the production of solid biofuel, *Energy Conversion and Management*, Vol. 105, No. 10.1016/j.enconman.2015.08.031, 2015, pp. 746–755.

[11] National Renewable Energy Laboratory, <u>https://www.nrel.gov/bioenergy/b</u> <u>iomass-compositional-analysis.html</u>, (date accessed 22.10.2017)

[12] Ahmad, M., Rajapaksha, A., U., Lim, J., E., Zhang, M., Bolan, N., Mohan, D.,

Vithanage, M., Lee, S., S., Ok, Y., S., Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere*, Vol. 99, No. 10.1016/ j.chemosphere.2013.10.071, 2014, pp 19-33.

[13] Chen, W., H., Hsu, H., J., Kumar, G., Budzianowski, W., M., Ong, H., C.,

Predictions of biochar production and torrefaction performance from sugarcane bagasse using interpolation and regression analysis, *Bioresource Technology*, Vol. 246, No. 10.1016/j.biortech.2017.07.184, 2017, pp 12-19.

[14] Robbiani Z., Conception and construction of a HTC prototype research unit

for developing countries, Dept. of Mechanical Engineering ETHZ, Zurich, 2013.

[15] Lungulease, A., Spirchez, C., Dobrev,
T., Affects and modelling of sawdust torrefaction, *Bioresources*, Vol. 10, No.3, 2015, pp. 4726-4739.

[16] Kumbo, S., H., and Dutta, A., A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications, *Renewable and sustainable Energy Reviwes*, Vol. 25, pp. 359-378.

[17] Zhang, L., Jiang, J., Holm, N., Minichunk biochar supercapacitor, *Journal of Applied Electrochemistry* Vol. 44, No. 10.1007/s10800-014-0726-7 2014, pp 1145-1151.

[18] Sharma, D., Jha, R., Kumar, S., Quantum dot sensitized solar cell: Recent advances and future perspectives in photoanode, *Solar Energy Materials and Solar Cells*, Vol. 155, No.

10.1016/j.solmat.2016.05.062, 2016, pp. 294-322.

[19] Nmadari, P., Negahdari, B., Eatemadi, A., Synthesis, properties and biomedical applications of carbon-based quantum dots: An updated review,

Biomedicine & Pharmacotheraphy, Vol. 87, No. 10.1016/j.biopha.2016.12.108, 2017, pp. 209-222.

[20] Lehmann J, Gaunt J, Rondon M.,
2006, Bio-char sequestration in terrestrial ecosystems-a review. Mitig Adapt Strateg Glob Change, Vol. 11, No. 10.1007/s11027-005-9006-5, 2006, pp 403-427.