

Production of Tomato Stalk Biochar and its Usage in Hydroponic Agriculture

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Abstract: Tomato stalk is a waste remained after harvesting in agricultural productions. These wastes can be utilized as biochar for various purposes such as fuel, absorbent and soil improver. In this study, in order to waste utilization, biochar production from tomato stalk under different experimental conditions was carried out and effect of temperature, nitrogen gas flow and heating rate on yield of biochar was investigated. Characterization of biochar was performed with FTIR, TGA and SEM analysis. The highest biochar yield was obtained at the temperature of 773 K, heating rate of 5 K/min and inert gas flowrate of 500 ml/min. The highest yielded tomato stalk biochar was used as a supporting material for the tomato seedling planted in the hydroponic system of greenhouse. The tomato stalks obtained as a waste after harvesting in greenhouse were used for biochar production and biochars were applied as supporting material in greenhouse again, so, zero waste idea for a greenhouse was carried out. It has been observed that the supporting material provided a little more growth in the tomato seedling because of water and nutrient holding capacity.

Keywords: Biochar, biomass, carbonization, tomato stalk.

1. INTRODUCTION

Biochar can change the physical, chemical and biological properties of soil and improve nutrient and water holding capacity and plant growth [1-4]. Acidity of soil causes toxicity of aluminum and manganese, and reduces the availability of calcium, magnesium, phosphorus and molybdenum, and affects plant growth negatively. On the other hand, biochar generally has alkaline properties and when it is applied to the soil, it neutralizes acidity of soil and increase the pH [5]. Yuan et al. reported that alkaline properties of biochar and pH were increased with the increasing temperature [5]. It was determined that, inorganic carbonate which is formed after carbonization process, is the main component which gives alkaline property to biochar. Presence of organic anions and carbonates provided alkaline properties. Biomass composition is also affect pH level of biochar. Biochar which has high mineral ash content has high pH levels [6]. Biochar which contain high amounts of N shows alkaline properties. Therefore, pH level of biochar can vary according to compounds of biomass and carbonization conditions [7]. Biochar application on soil improves nutrient availability in soil and nutrient holding capacity of soil [8]. Biochar has higher cation exchange capacity (CEC) than soil due to its wide surface area, negative surface charge and charge density [6]. Lots of cations in ash of wood coal are not related to electrostatic forces and in the form of melted salt, so plant can use them directly.

Biochar also can be utilized as fertilizer with its properties [9]. Stable structure of organic material provides slow nutrient release and cation holding in soil [8]. Biochar is a porous material and has the properties of oxidation, water absorption and water holding capacity [10]. Bulk density of biochar is less than minerals in soil [11]. Density of biochar decreases due to macro- and micropores which hold water and air. This changes bulk density of soil because of potential effects of soil-water relation, rooting and soil fauna [6].

Physical differences between biochar and soil, arrange the tensile strength of the soil, hydrodynamics and the soil-biochar gas exchange. Mechanical strength is the main factor which determines root growth and spread. Decreases in tensile strength of soil can provide easier germination of seeds as well as easier development of roots. Also, decreases in tensile strength can facilitate circulation of invertebrates [6]. Diversity of microbial population in soil is very critic in the case of soil function and ecosystem due to its effect on soil structure, stability, nutrient cycle, aeration, water use efficiency and carbon holding capacity [6]. Porous structure of biochar and ability to holding soluble organic carbon creates a habitat for microorganisms which feed on organic carbon and are protected from grazers. This is the reason of increase in microbial biomass and activity [12]. Biochar application alters nitrogen dynamics of soil [13]. Biochar increases the availability of N via absorbing N (NH_4^+) and improves agricultural efficiency by supporting plant growth [14]. Biochar, contributes indirectly to soil productivity by affecting nutrient availability and water holding capacity

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of soil and microbial Biochar helps ventilation of soil, increases oxygen content of soil and prevents denitrification reactions and N_2O emissions by adsorbing NH_4^+ and NO_3^- [13]. In the literature, it is reported that carbonization conditions affect N dynamic of soil [15]. Carbon content of biochar obtained via slow and fast pyrolysis shows differences. While biochar obtained via slow pyrolysis has more stable carbon structure, biochar which obtained via fast pyrolysis has more fragile carbon structure. Biochar also decreases availability of heavy metal and other organic contaminants [16]. Biochar can bind metal ions to its surface and decrease availability of metal ions in soil [12]. In our country, tomato production was approximately 12 million tons in the year of 2014, and for this production 319109 ha cultivated area was used. Aegean, Marmara and Mediterranean Regions in Turkey have carried out the production of 78%. As for the production amounts in the World, China is the leader with the production amount of 52 million ton and Turkey is the fourth biggest tomato producer after India and America (*Food and Agriculture Organization of the United Nations, Statistical Databases, FAO 2017*). When this production amounts considered, utilization potentials of this product can be seen clearly.

In this study, firstly biochar production from tomato stalk under different experimental conditions was targeted and parameters which have effect on biochar yield were investigated. In addition to this, after the characterization of biochar, utilization of it as supporting solid media material for hydroponic system was investigated for zero waste management.

2. EXPERIMENTAL STUDY

2.1. Materials and Methods

In the experimental study, tomato stalk (*Solanum lycopersicum*) remained after harvesting in greenhouse located in Yildiz Technical University Davutpasa Campus was utilized for biochar production (Figure 1). Tomato stalks were cut and prepared to be in uniform size. Samples were dried in an oven at the temperature of $105^\circ C$ for 24 h. After drying process, samples were stored in air-tight containers.

In order to investigate the experimental conditions, experiments were conducted under different conditions as different temperature ($500^\circ C$ and $600^\circ C$), heating rate ($5^\circ C/min$ and $20^\circ C/min$) and nitrogen gas flowrate ($50 ml/min$ and $1000 ml/min$). The carbonization experiments were performed in "Protherm" model split type reactor which is a horizontal flow pipe type reactor with an inner diameter of 10 cm. Weighed samples were loaded in a ceramic boat and placed into reactor. Before heating, the system was swept with nitrogen gas for 15 min. to provide an inert media. Nitrogen gas was continuously supplied during carbonization. When temperature of inside reactor reached the final temperature, reactor was kept at final temperature for 10 min and after that, reactor was allowed to cool. At the end of carbonization, samples were collected from the system and weighed in assay balance to calculate the yield of biochar.

Tomato seedlings were planted in hydroponic plant growth system. Some of these seedlings were placed directly in the hydroponic growth medium without any



Figure 1: Tomato stalks after harvesting in hydroponic greenhouse and dried, chopped tomato stalks.

supporting solid media material, and some of them were placed in the hydroponic growth medium by the addition of biochar as solid support material and their growth was examined.

3. RESULTS

3.1. Evaluation of Experimental Results

The influence of parameter effects, and interactions of the parameters on the yield of biochar were investigated using the factorial design technique. Experimental results, obtained from carbonization process were given in Table 1, were used to statistically evaluate carbonization parameters on biochar yield. The carbonization experiments were conducted according to a 2^3 factorial design. The experimental variables and their levels were given as below:

T: Temperature (K); 873 (superior level), 773 (inferior level), 823 (central level).

I: Heating rate (K/min.); 20 (superior level), 5 (inferior level), 12.5 (central level).

N: Nitrogen gas flow (ml/min.); 750 (superior level), 500 (inferior level), 625 (central level).

In order to examine experimental parameters that affect biochar yield, a regression equation was acquired. X_T , X_I and X_N are the normalized values that are used for obtaining the regression equation. Analysis of variance (ANOVA) was carried out to examine the design matrix and to quantitatively evaluate the main effects. As a consequence, regression Equation 1 was obtained for predicting the biochar yield values of tomato stalk:

$$Y_{\text{tomato}} = 35.5 - 0.264 \cdot X_T - 0.073 \cdot X_I - 1.26 \cdot X_N \quad (1)$$

Correlation coefficient was found as $R^2 = 92.2\%$ for Equation 1.

It was seen from ANOVA results (Table 2) that R^2 are high and p value is low which indicates that regression equations found above was well calculated statistically. According to Equation 1, it can be indicated that the coefficient of X_N is the highest among all the variables and it can be reported that its effect is the strongest. Respectively, after the nitrogen gas flow, temperature and the heating rate affects the biochar yield. Negative coefficients defines that there is an inverse proportion between this parameter and biochar yield.

Table 1: Factorial Design Matrix and Experimental Results of Tomato Stalk Carbonization

Experimental Number	Temperature (K)	Heating Rate (K/min)	N ₂ flow (ml/min)	X _T	X _I	X _N	Yield of Biochar (%)*
1	773	5	500	-1	-1	-1	37.53
2			750	-1	-1	1	34.57
3		20	500	-1	1	-1	36.47
4			750	-1	1	1	34.76
5	873	5	500	1	-1	-1	36.38
6			750	1	-1	1	34.08
7		20	500	1	1	-1	36.93
8			750	1	1	1	33.82
9	823	12.5	625	0	0	0	34.94

*The average of the two experimental results were taken.

Table 2: ANOVA Results of Statistical Analysis

Sources of variations	Degree of freedom	Sum of squares	Mean squares	f-value	p-value
Regression model	3	13.29	4.43	19.72	0.003
Error	5	1.12	0.22		
Corrected total	8	14.42			

3.2. Effect of Carbonization Temperature on Biochar Yield

Biochar yield obtained under the conditions of heating rate of 5 K/min and nitrogen gas flow of 500 ml/min with different temperatures (T=723 K, 773 K, 823 K, 873 K and 923 K) was showed in Table 1. As can be seen in the Table 1, there was a linear decreasing of biochar yield when temperature increases. The reason of the decrease is primer degradation of biomass or secondary degradation of char residue [17]. Under low carbonization temperatures, primer degradation of biomass occurred. Increasing temperature causes conversion of volatile products to organic compounds and gas products and more volatile products are obtained [18, 19]. In addition to this, when lignin degrades at the temperatures of between 523 and 773 K, hemicellulose degrades at the temperatures of between 590 and 648 K. For this reason, generally high content of lignin provides high yield of biochar [20].

In the literature, it was mentioned that degradation of lignocelluloses biomass starts with moisture output at the temperature of 373 K, yet degradation rate and amount were very low as neglectable up to the temperature of 473 K. Degradation of extractive compounds occurs at the temperature of between 373-523 K and hemicelluloses and a morph part of cellulose occurs at the temperature of between 483-623 K. Volatiles such as methanol, furfural and acetic acid are formed with the degradation of hemicelluloses and cellulose. Thermal degradation of cellulose and lignin compounds are carried out at the temperature of between 623-773 K and flammable gases and condensing liquid tar are formed from these compounds [21]. Results obtained from this study are in agreement in literature studies which carried out by utilizing various biomass feedstock's such as pine sawdust [22], seed [23], rice straw [24], soybean and peanut shell [25], safflower seed press cake [17].

3.3. Effect of Heating Rate on Biochar Yield

Biochar yield of tomato stalks obtained under the conditions of nitrogen gas flow of 500 ml/min and the temperature of 773 K with different heating rates (I=5K/min, 10 K/min, 15 K/min, 20 K/min, 25 K/min) was showed in Table 1. As can be seen that a decrease occurred on biochar yields with increasing heating rate for all tomato stalks samples. Heating rate is a parameter affects formation of volatile compounds from biomass. High heating rate above 400°C causes

rapid formation of volatiles. In this environment, the molecules decomposes rapidly and volatile components are released very quickly [26]. While high heating rate increases bond cleavage reactions which forms volatile products, low heating rate increases char reactions [27]. It was reported that high heating currents in high heating area decreases viscosity of molten biochar and forms volatiles [28]. Results obtained from this investigation are in agreement in literature studies which carried out by utilizing various biomass feedstock's such as safflower seed press [17], rapeseed [29], wheat straw, grass and pine [30].

3.4. Effect of Sweeping Gas Rate on Biochar Yield

Biochar yield of tomato stalks which obtained with experiments carried out under the conditions of heating rate of 5 K/min and the temperature of 773 K with different nitrogen gas flow (N=50 ml/min, 250 ml/min, 500 ml/min, 750 ml/min and 1000 ml/min) was showed in Table 1.

As can be seen that there was a linear decreasing of biochar yield when nitrogen flow increases. Sweeping flow gas minimizes homogeny reactions such as reforming and water-gas conversion and removes volatile compounds from heated area [31]. Yield of biochars increases with secondary reactions such as thermal decomposition, recondensation and repolymerization [32]. In literature, it was indicated that sweeping gas removes volatiles and minimize secondary reactions and causes a decrease in char yield [33]. On the contrary, in cases where there is no or very low sweeping gas entry causes increase in char yield [34]. Results obtained from this experiment are in agreement in literature studies which carried out by utilizing various biomass feedstocks such as pistachio shell [32], safflower seed presscake [35], paddy rice [36], palm fruit [37].

3.5. Characterization of Biochar

In order to determine the functional groups of biomass samples and biochars obtained after carbonization Thermo scientific Brand Nicolet 6700 FTIR spectrometer was used and absorptions of functional groups which samples include between the range of 650-4000 cm^{-1} were determined. Functional groups of biomass samples and biochar which are defined from spectrums were given in Table 3. According to FTIR results, functional groups which contain O- and H- don't exist in biochar samples. Existence of these groups shows that formation of CO_2 ,

Table 3: Functional Groups of Tomato Stalk Determined with FTIR Analysis

Wave Length (cm ⁻¹)	Functional Groups
3288	-OH stretching
2917	Aliphatic CH stretching vibration
2849	Aliphatic CH stretching vibration
2285	Aromatic carbonyl/carboxyl C=O stretching
2161	Aromatic carbonyl/carboxyl C=O stretching
2050	Aromatic carbonyl/carboxyl C=O stretching
1980	Aromatic carbonyl/carboxyl C=O stretching
1613	Aromatic C=C ring stretching
1516	Aromatic C=C ring stretching
1414	Aromatic C=C ring stretching
1324	Aliphatic CH ₂ deformation
1238	Aromatic CO- stretching
1019	Aliphatic ether C-O and alcohol-C-O stretching
	Biochar Functional Groups
1393	O-H and C-H bending vibration
1255	Aromatic CO- stretching
872	1 adjacent H deformation/ Aromatic CH stretching
834	2 adjacent H deformation/2 adjacent aromatic H in ring
692	3 adjacent H deformation/3 adjacent aromatic H in ring

CH₄ and H₂. Formation of CO₂ is carried out due to degradation and reforming process of C=O bonds; CO, is carried out due to breaking of C-O-C and C-O bonds; H₂ is carried out due to breaking of C-H bonds and formation of H-H bonds [38]. Bands formed at the wavelength of 2917-2849 cm⁻¹ showed that symmetric strength vibration belong to -CH₂ and asymmetric strength vibration belong to C-H due to aliphatic hydrocarbon and saturated aliphatic cyclic hydrocarbons [39]. Also bands are formed in this range due to the presence of methyl and methylene groups [40]. Aliphatic ether C=O and alcohol-C-O strength band is seen wide in the wavelength of 1019 cm⁻¹ for tomato stalk. This can be resulted from extractive materials, which are available in tomato stalk. When it is compared with FTIR results of biochar and raw material, aliphatic transition to aromatic structure with increasing temperature is resulted with formation of aromatic ring and H deformation. During pyrolysis process, while bonds of OH and CH₃ decreased, C=C structures increased [7]. At high temperatures,

functional groups which contain H and O disappeared and more aromatic structures occurred. Band shows aromatic structure between 700-900cm⁻¹ [40]. The presence of hydrogen bonds in the neighboring aromatic is due to the fact that the aromatic structure [39]. Bands between 1500-1600cm⁻¹ are resulted from aromatic C=C ring stretching.

Proximate analysis of biomass samples and biochars were performed with TA Brand Q 5000 thermogravimetric analysis system. According to proximate analysis results, content of volatile compounds, fixed carbon values and ash in biomass samples were found as 47.3%, 29.03%, 23.34%, respectively. After carbonization process, a decrease in volatile substance content and an increase in fixed carbon content were observed and content of volatile compounds, fixed carbon values and ash in biochar samples were found as 20.73%, 48.47%, 30.83%, respectively. This result showed that thermal degradation doesn't occur completely. In the case of ash content, it was seen that after carbonization process there is an increase in ash content. Ash content is a measure of non-volatile and inflammable substance of biochar [17]. Increase in ash content occurred due to removing volatile compounds after carbonization. Results obtained from this analysis are in agreement with literature studies [41].

In order to investigate the effect of carbonization on microstructure, SEM images of biochars obtained from tomato stalk via carbonization were observed with JEOL JSM-T330 SEM and these images were presented in Figure 2. After carbonization process, recess and curved structures were seen in biochar. Tomato stalk has high content of ash. So, there is not seen porous structure in biochar sample. Because high amount of ash content prevents formation of porous structure in biochar morphology [8].

3.6. The Usage of Biochar as Supporting Solid Media Material for Hydroponic Growth System

At this stage of the study, some of tomato seedlings were placed directly in the hydroponic growth medium without any supporting solid media material as control seedlings, and some of tomato seedlings were placed in the hydroponic growth medium supported by biochar as supporting solid material. The development of all tomato seedlings was monitored in the hydroponic system of greenhouse for three months. The biotechnological hydroponic greenhouse view for the first day and 3 months after planting of the tomato

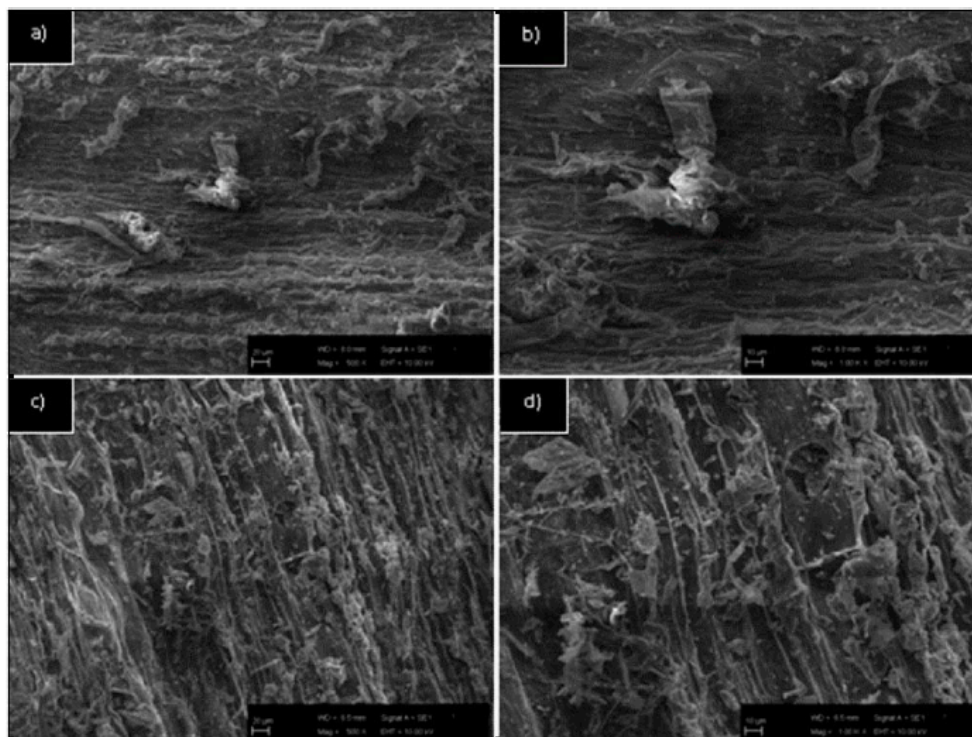


Figure 2: Microstructure images of tomato stalk and biochar; **a)** tomato stalk; (x500); **b)** tomato stalk (x1000); **c)** tomato stalk biochar (x500); **d)** tomato stalk biochar (x1000).



Figure 3: The biotechnological hydroponic greenhouse for the first day and 3 months after planting of the tomato seedling in hydroponic plant growth systems.

seedling in hydroponic plant growth systems was shown in Figure 3. After the planting of the tomato seedlings selected in same size, the water and nutrient requirements of the plants were supplied with the nutrient solution given daily by the nutrient film technique. The effect of the solid media material used

in the hydroponic system on the plant growth was evaluated only in terms of plant height. The tomato seedlings with biochar supporting material were found to be approximately 13% higher than the control seedlings.

4. DISCUSSION

Biochar production from tomato stalk under different conditions was conducted, effect of experimental parameters on biochar yield was investigated, and also characterization of samples was carried out in this study. And, the highest biochar yield was obtained for low temperature, heating rate and nitrogen gas flow rate. FTIR results of biomass and biochar samples were found that biomass samples have more volatile compounds and water content. Similar to FTIR results, TGA results showed that biomass samples have more volatile substances. Biochar supporting material provided a little more growth in the tomato seedlings because of water and nutrient holding capacity. According to these results, biochar obtained from tomato stalk can be suggested as solid media material for innovative soilless agricultural productions within the frame of zero waste management.

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