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Effect of Pyrolysis Temperature and Residence Time on Bio-char Obtained from Pyrolysis of Shredded Cotton Stalk

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Authors' contributions

This work was carried out in collaboration among all authors. Authors JMM and PNS designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors JMM and PNS managed the analyses of the study. Author PMC managed the literature searches. All authors read and approved the final manuscript.

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ABSTRACT

Bio-char is carbon-rich product generated from biomass through batch type slow pyrolysis. In this study, the effects of pyrolysis temperature and residence time on the yield and properties of bio-chars obtained from shredded cotton stalks were investigated. Safely said that the quality of bio-char of shredded cotton stalk obtained at 500°C temperature and 240 min is best out of the all experimental levels of variables of temperature and residence time. At this temperature and residence time, the quality of bio-char in terms higher heating value (8101.3cal /g or 33.89 MJ/kg), nitrogen (1.56%), Carbon (79.30%), and C/N ratio (50.83) respectively. The quality of bio-char for various applications is discussed along with different quality parameters. The bio-char could be used for the production of activated carbon, in fuel applications, and water purification processes. Average bulk density of whole cotton stalk and shredded cotton stalk was found as 29.90 kg/m^3 and 147.02 kg/m^3 respectively. Thus density was increased by 3.91 times. The value of pH, EC and CEC of shredded cotton stalk biomass was found as 5.59, 0.03 dS/m and 38.84 cmol/kg respectively. Minimum and maximum values pH, EC and CEC of its bio-char was found as 5.85

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to9.86, 0.04 to 0.10 dS/m and 38.02 to 24.39 cmol/kg at 200°C and 60 min and; 500°C and 240 min temperature and residence time respectively. Moisture content, ash content, volatile matter and fixed carbon of shredded cotton stalk biomass were found as, 12.5, 5.27, 80.22, and 14.51 (%, d.b) respectively. The minimum and maximum value of bio-char in terms of ash content, volatile matter and fixed carbon of bio-char were found as 5.5 to 15.56, 48.02 to 79.48 and 15.02 to 36.40 (%, d.b) respectively. Calorific value of cotton stalk biomass was found as 3685.3 cal /g. The minimum and maximum higher heating value of its bio-char was found as 4622.0 cal/ g and 8101.3 cal/g at 200°C and 60 min and; 500˚C and 240 min temperature and residence time.

Keywords: Bio-char; pyrolysis; residence time; temperature; properties.

HIGHLIGHTS

- Bio-char can be used as a fuel.
- Density was increased by 3.91 times and calorific value was increased by 1.19 times.
- High quality bio-char can be produced from shredded cotton biomass by pyrolysis.
- CV, pH, EC, fixed carbon, Nitrogen, C:N Ratio, ash and carbon contents of bio-char increased at 500°C.

1. INTRODUCTION

Biomass can be converted into fuel and chemical feedstock bybiological (fermentation and anaerobic digestion) or thermochemical. Among these conversion processes, pyrolysis allows a high energy recovery and produces fewer pollutants than other options, e.g. incineration. Moreover, this processgene rates a wide spectrum of products (solid, liquid and gas) with numerous applications, thus making pyrolysis treatment self-sufficient in terms of energy usage [1].

Bio-char is a value added product, which can be used for many purposes. It is highly carbonaceous and hence contains high energy content, comparable to high rank coals. Bio-char also has a large microscopic surface area due the micropores developed during pyrolysis, and can be used for the filtration and adsorption of pollutants.

Typically, pyrolysis is divided into three modes: fast, intermediate, and slow. The mode and the conditions of pyrolysis can influence the relative proportions of the three products (gas, liquid and solid) obtained. Slow pyrolysis uses a low heating rate and a long vapor residence time, and it is used to maximize solid product yields [2].

The solid product from pyrolysis contains char, ash and unchanged biomass material and it is known as char or bio-char. Bio-charis carbon-rich and can be used as a fuel in the form of briquettes or a char-oil water slurry [3]. The bio-char can be used in the preparation of active carbon when its pore structure and surface area are appropriate [4]. Bio-char has been attracting growing interest due to its potential in carbon sequestration and in improving soil health [5]. The properties of bio-char are different from those of activated carbon. Generally, bio-char is a not fully carbonized product because pyrolysis is often carried out under low temperatures (<500°C) [6].

Bio-char can be made from various waste biomass sources under different processing conditions. Conditions such as the heat ingrate, temperature and biomass particle size play roles in the structural evolution of bio-char during rearrangement of the solid phase [7,3,6,8]. Also the quality of bio-char for industrial and domestic utilization is often determined by its physicochemical characteristics such as volatile matter, fixed carbon, ash content, % carbon content, and higher heating value (HHV). Moreover, the surface properties of bio-char affect the reactivity and combustion behavior of the bio-char [9].

The present research work is aimed to conduct the pyrolysis of the shredded cotton stalk, as feed stalk, considering more economical for the preparation of raw material, as compared to ground biomass to be used as feed stalk. Keeping the above background in mind, the present study on the development of a small capacity (5 kg) fixed bed reactor pyrolyser for shredded cotton stalk as feed stalk is undertaken.

2. EXPERIMENTAL

2.1 Materials and Sample Preparation

Cotton stalks were collected from Cotton Research Center Junagadh Agricultural University (CRCJAU).The cotton stalks(CS) was air-dried and screened to give a fraction average particle size of un even cotton stalks samples were stored in room temperature under dry conditions(eg. Sundraying).

2.2 Pyrolysis Experiments

Pyrolysis experiments was performed with 5 kg of biomass samples (Shrdded Cotton Stalk) in a pyrolyser at 200, 300, 400 and 500°C and at residence time of 60,120, 180 and 240 min. After each experiment the bio-char yield was obtained from the final weight of the char. The bio-char yields were expressed on a dry ash-free (daf) basis and the average yields from at least six tin experiments are presented. The experimental error was less than <± 15 wt%.

2.3 Characterization of the Bio-chars

Proximate analyses were determined according to the ASTM3174 and ASTM 3175. Fixed carbon content was determined by difference. Ultimate analyses were performed on a CHNS(O) model EA 1108 Elemental Analyzer (Carlo Erba Instruments). Oxygen was determined by difference. pH and electrical conductivity (EC) values were measured by adding bio-char to de-ionized water in a mass ratio of 1:20. The solution was then hand shaken and allowed to stand for 5 min before measuring the pH and EC with a pH meter Hanna Instruments pH 211 (In yang et al., 2010). Cation Exchang capacity (ECE) was determined by difference [10]. Higher heating value (HHV) were determined by GALLENKAMP Auto Adiabatic Bomb Calorimeter according to the ASTM D240.

3. RESULTS AND DISCUSSION

3.1 Bio-char Yields

The effect of pyrolysis temperature and residence time on the bio-char yield is shown in Fig. 1. An increase of pyrolysis temperature and residence time as decrease the yields of bio-char shown in table 1. The decreased in the bio-char yields with increasing temperature could either be due to greater primary decomposition or through secondary decomposition of char residues. The high yield of bio-char at low temperatures indicates that the material has been only partially pyrolysed [11]. The effect of pyrolysis residence time was more important at low temperatures, while at high temperatures, pyrolysis residence time showed a similar trend with respect to bio-char yields. The minimum and maximum value of bio-char was found as 70.20% and 34.0% at 200 C and 60 min and; 500C and 240 min temperature and residence time. Same result also found [12].

3.2 Bio-oil Yield

The by-product in terms of bio-oil was also measured. Bio-oil yield at all the levels of variables of experimental run is shown in Table 1. It can be seen from the Table 1. that the yield of bio-oil was ranged from a minimum of 10.2% at 200°C with 60 min residence time to a maximum of 19.00% at 500°C with 240 min residence time. Graphical representation of variation of bio-oil yield content with temperature at different residence time is shown in Fig. 2. It can be seen from the figure that bio-oil yield increases with increase in temperature. It can also be seen from the figure that bio-oil yield increased with increase in residence time. However, the effect of residence time on bio-oil yield is less compared to temperature.

3.3 Pyro-gas Yield

The other by-product in terms of pyro-gas was calculated by subtracting the yield of bio-char and bio-oil from one hundred. Pyro-gas yield at all the levels of variables of experimental run is also shown in Table 1. It can be seen from the Table 1 that the yield of pyro-gas was ranged from a minimum of 19.6% at 200°C with 60 min residence time to a maximum of 47.8% at 500°C with 240 min residence time. Graphical representation of variation of pyro-gas yield with temperature at different residence time is shown in Fig. 3. It can be seen from the figure that yield of pyro-gas was increased with increase in temperature as well residence time. However, the effect of temperature was more pronounced as compared to residence time.

3.4 Proximate Analysis

The results of the proximate analysis, pH, EC, CEC, higher heating value (HHV) and bulk density of shredded cotton stalk and its bio-chars produced at different pyrolysis temperatures and residence time are given in Table 2. The volatile matter content of bio-chars was ranged from a minimum of 48.02% (d.b) at 500°C with 240 min residence time to a maximum of 79.48% (d.b) at 200°C with 60 min residence time.Similar results were also found by [13]. They reported that volatile matter of cedar wood, pine wood and cotton stalk bio-char decreased from 37.5 to 18.4%, 37.3 to 17.2% and 32.2 to 15.6% respectively as the temperature increased from 300 to 600°C. [14] also reported that the volatile matter of apple tree branch, oak tree, rice husk and rice straw bio-char decreased from 32.36 to 6.82%, 32.06 to 7.87%, 22.00 to 3.17% and 22.42 to 4.47% as the temperature increased from 400 to 800°C, 400 to 800°C, 400 to 800°C and 400 to 800°C respectively. The reason that as the pyrolysis temperature increases then the reaction of devolatilisation occurs. This resulted in loss of volatile organic compounds hence volatile matter decreases. [15] Also found the balk density, moisture content, volatile matter, fixed carbon and ash per cent of rice husk, rice straw, sugarcane bagasse and cotton stalk.

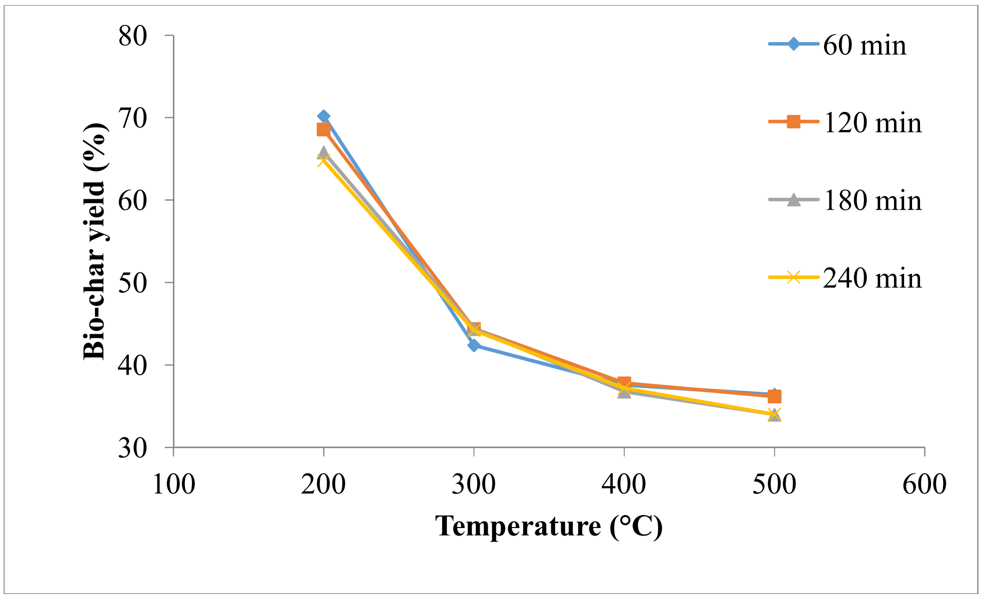

Fig. 1. Effect of different temperature on bio-char yield content during cotton stalk pyrolysis bio-char at different residence time

Table 1. Percentage of Bio-char yield, bio-oil and pro-gas yield at different temperature and residence time

Run No.	Temperature (˚C)	Residence time (min)	Bio-char yield (%)	Bio-oil yield (%)	Pyro- gas yield (%)
1	200*	60	70.2	10.2	19.6
2		120	68.6	10.6	20.8
3		180	65.8	11.4	22.8
4		240	64.8	11.8	23.4
6	300	60	42.4	12.4	45.2
7		120	44.4	13.2	42.4
8		180	44.4	13.8	41.8
9		240	44.2	14.2	41.6
10	400	60	37.6	14.8	47.6
11		120	37.8	15.2	47.0
12		180	36.8	16.0	47.2
13		240	37.2	16.6	46.2
14	500	60	36.4	17.4	46.2
15		120	36.2	17.8	47.0
16		180	34.0	18.2	47.3
17		240	34.0	19.0	47.8

**bio-char yield is considered as torrefied biomass*

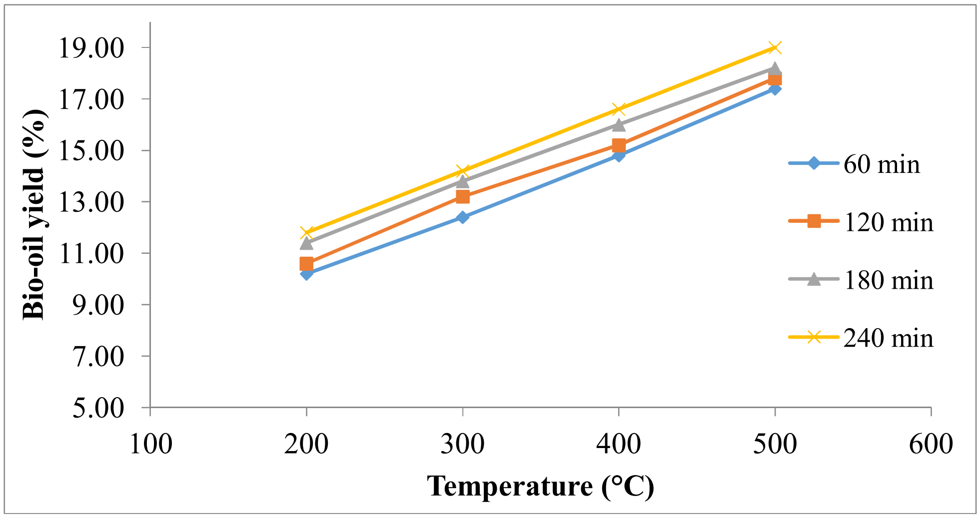

Fig. 2. Effect of different temperature on bio-oil yield content during cotton stalk pyrolysis at different residence time

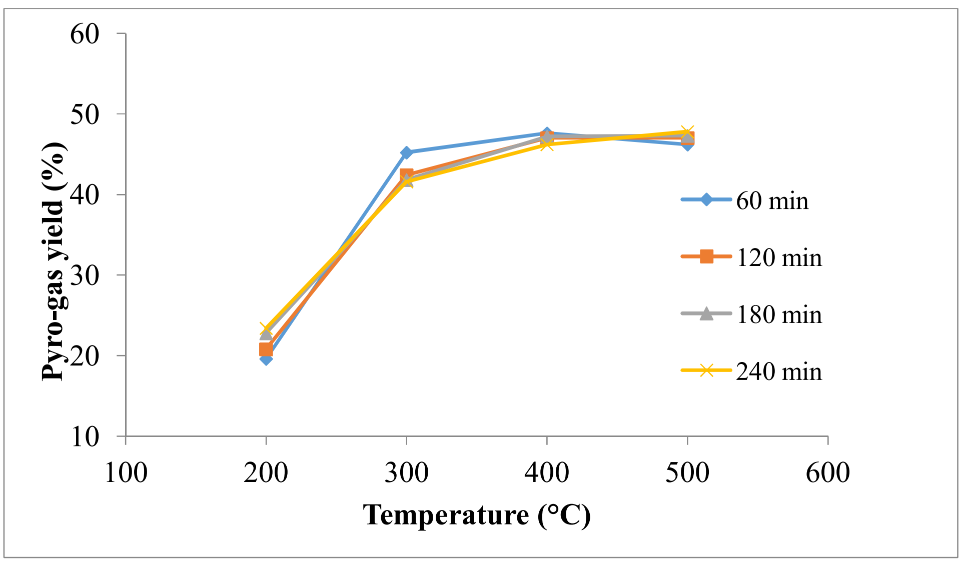

Fig. 3. Effect of different temperature on pyro-gas yield content during cotton stalk pyrolysis at different residence time

The ash content is a measure of the non-volatile matter and non-combustible component of the bio-char. value of ash content of bio-char was ranged from a minimum of 5.5% (d.b.) at 200°C with 60 min residence time to a maximum of 15.56% (d.b.) at 500°C with 240 min residence time is shown in Table 2. Thus, the ash contents of the bio-chars were higher than those of cotton stalk, orange peels, and palm waste bio-chars [16,17,18]. Also similar results were also found by [13]. They reported that ash content of cedar wood, pine wood and cotton stalk bio-char increased from 1.5 to 2.1%, 2.5 to 4.7% and 6.0 to 10.1% respectively as the temperature increased from 300 to 600°C. [19] Was also found the similar behavior for bio-char obtained from different feed stalks like peanut hull, pecan shell, poultry litter and switchgrass. They reported that ash content of peanut hull, pecan shell, poultry litter and switchgrass bio-char was increased from 8.2- 9.3%, 2.4 to 5.2%, 35.9 to 52.4% and 2.6 to 7.8% as the temperature increased from 400 to 500°C, 350 to 700°C, 350 to 700°C and 250 to 500°C respectively. The reason behind that as the temperature increased, more volatiles are driven off which reduced the mass but the mineral components are retained in the solid fraction and therefore the percentage of ash increased.

As the pyrolysis temperature increased from 200 to 500°C and residence time 60 to 240 min, the average values of fixed carbon of shredded cotton stalk bio-char for all the experimental run at different temperature and residence time is shown in Table 1. The value of fixed carbon of bio-char was ranged from a minimum of 15.02% (d.b) at 200°C with 60 min residence time to a maximum of 36.40% (d.b) at 500°C with 240 min residence time in this study. In similar studies with increasing temperature, fixed carbon content for rapeseed cake and palm stones was increased from 57.08% to 73.05%, 52.44% to84.19% and 31.0% to 85.10%, respectively [20,16,21].Similar results were also found by [13]. They reported that fixed carbon of cedar wood, pine wood and cotton stalk bio-char increased from 61.1 to 79.5%, 60.2 to 78.1% and 61.8 to 74.2% respectively as the temperature increased from 300 to 600°C [22]. Also reported that the fixed carbon of cotton stalk bio-char increased from 58.7 to 71.0% as the temperature increased from 350 to 500°C. Perhaps the reason behind may be due to increase in temperature the volatile matter being driven off during the pyrolysis process, resulting in the formation of more stable carbon known as fixed carbon.

Table 2. Characteristics of cotton stalksbio-chars produced at different pyrolysis temperatures and residence time

	Residence time (min)				**Shredded cotton stalk**
	60	**120**	**180**	**240**	
Pyrolysis temperature (200°C)					
Volatile matter (%)	79.48	78.73	77.73	75.71	80.22
Ash (%)	5.5	5.95	6.32	6.85	5.27
Fixed carbon (%)	15.02	15.32	16.33	17.44	14.51
pH	5.88	5.97	5.85	5.96	5.59
EC (dS/m)	0.04	0.04	0.04	0.04	0.03
CEC (cmol/kg)	38.02	37.89	37.78	37.61	38.84
Bulk density (kg/m^3)	184.09	178.40	179.54	173.86	147.02
HHV (cal/g)	4622.0	4687.0	4738.0	5632.6	3685.3
Pyrolysis temperature (300°C)					
Volatile matter (%)	72.68	70.62	67.49	65.23	-
Ash (%)	7.09	8.02	8.95	9.35	-
Fixed carbon (%)	20.23	21.36	23.56	25.42	-
pH	8.83	8.34	8.41	8.55	-
EC (dS/m)	0.04	0.05	0.05	0.06	-
CEC (cmol/kg)	37.42	36.79	36.33	35.70	-
Bulk density (kg/m^3)	177.27	165.90	161.36	168.18	-
HHV (cal/g)	5473.1	5747.6	6093.4	6099.6	-
Pyrolysis temperature (400°C)					
Volatile matter (%)	63.16	60.94	58.85	56.87	-
Ash (%)	9.98	10.53	11.23	12.02	-
Fixed carbon (%)	26.86	28.53	29.92	31.11	-
pH	9.33	9.42	8.35	9.36	-
EC (dS/m)	0.08	0.09	0.07	0.07	-
CEC (cmol/kg)	34.23	33.10	29.38	27.77	-
Bulk density (kg/m^3)	160.22	156.81	163.18	163.18	-
HHV (cal/g)	6463.5	6587.6	7974.3	7983.1	-
Pyrolysis temperature (500°C)					
Volatile matter (%)	54.54	52.13	49.88	48.02	-
Ash (%)	13.04	13.91	14.86	15.56	-
Fixed carbon (%)	32.42	33.96	35.26	36.40	-
Ph	9.68	9.70	9.61	9.86	-
EC (dS/m)	0.09	0.08	0.09	0.10	-
CEC (cmol/kg)	26.23	25.57	25.03	24.39	-
Bulk density (kg/m^3)	151.54	151.13	150.90	151.59	-
HHV (cal/g)	8013.0	8018.9	8042.1	8101.3	-

The fixed carbon, volatile matter and ash content were found as 14.51, 80.22, and 5.27 (%, d.b) respectively for cotton stalk as shown in Table 1. The results of proximate analysis of cotton stalk in the present study were in accordance with the results presented by [23] as fixed carbon, volatile matter and ash content of 15.30, 81.40 and 3.30 (% d.b) respectively for cotton stick. Similarly for other biomass, [24] also found that the fixed carbon, volatile matter and ash content as 24.99, 71.04 and 3.97 (%, d.b.) respectively for jatropha seed husk [25]. Also reported that fixed carbon, volatile matter and ash content as 14.9, 77.4, and 7.7 (%, d.b.) respectively for sugarcane leaves.

3.5 Higher Heating Value of Shredded Cotton Stalk Biomass and its Bio-char

The calorific value of shredded cotton stalk was found 15.42 MJ/kg. The graphical representation of CV is shown the Fig. 4. The results of calorific value of cotton stalk in the present study were in accordance with the results presented by [23] as LHV and HHV of cotton stick as 16 and 17.40 MJ/kg respectively [24]. Also determined the lower calorific value of jatropha seed husk as 16.92 MJ/kg [26]. Analyzed 20 different biomass samples and determined net calorific value in the range of 15.41-19.52 MJ/kg.

Higher heating value indicates the bio-chars potential to be used as fuel. The higher heating value of shredded cotton stalk bio-char for all the experimental run at different temperature and residence time is shown in Table 1. The calorific value of bio-char was ranged from a minimum of 4622.0 cal /g (19.34 MJ/kg) at 200°C with 60 min residence time to a maximum of 8101.3 cal /g (33.89 MJ/kg) at 500°C with 240 min residence time. Similar results were also found by [13]. They reported that of cedar wood, pine wood and cotton stalk bio-char increased from 25.1 to 29.5MJ/ kg, 25.6 to 28.8 MJ/ kg and 25.7 to 27.6 MJ/ kg respectively as the temperature increased from 300 to 600°C [27]. Also reported that the calorific value of food waste containing grain, vegetables or meat ranged from 23.7 to 29.7 KJ/g as the temperature increased from 200 to 400°C. The higher heating values of the bio-chars were similar in comparison with that of other bio-chars such as those derived from beechtrunk bark, cotton stalk, Cynaracar dunculus L. [28,16,29]. The HHVs of the bio-chars were comparable with those of solid fuels ranging from lignite to anthracite [30], suggesting the bio-chars have potential usage as solid fuels.

3.6 pH Values

The pH value of the shredded cotton stalk and its bio-chars obtained under different pyrolysis temperature and heating rate are given in Table 2. The value of bio-char was ranged from a minimum of 5.88 at 200°C with 60 min residence time to a maximum of 9.86 at 500°C with 240 min residence time. Shown the graphical representation is Fig. 5.

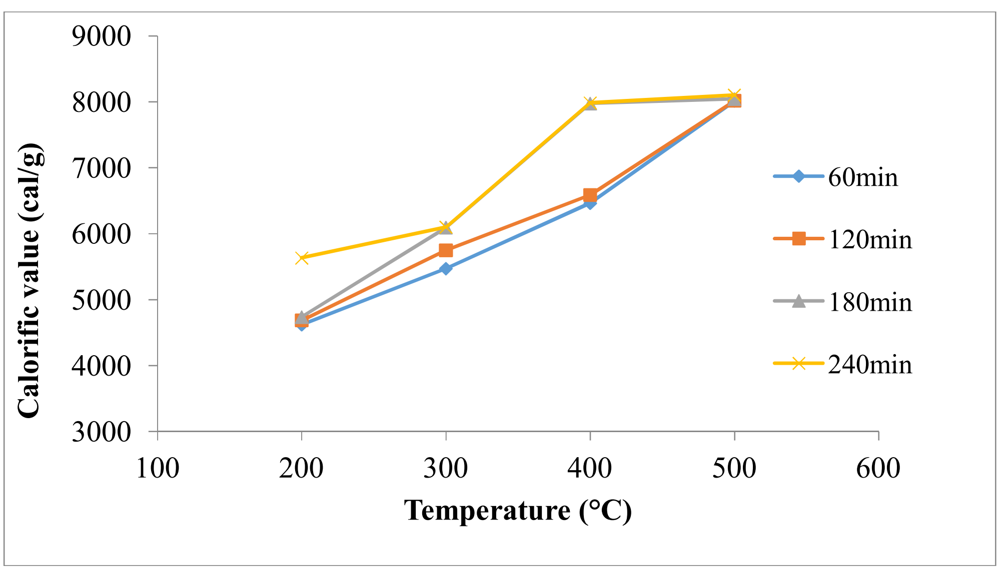

Fig. 4. Effect of different temperature and residence time on calorific value of cotton stalk bio-char

The variation of pH values of cotton stalk bio-char with temperature at different residence time also presented in Fig. 5. It can be seen from the figure that the pH value of cotton stalk bio-char was increased with increase in temperature. The results are in accordance with the results presented by [22]. They reported that the pH value of cotton stalk bio-char increased from 8.9 to 9.3 as the temperature increased from 350 to 500°C [31]. Also reported that the pH value of cotton stalk bio-char ranged from 8.9 to 9.0 as the temperature increased from 450 to 500°C. [14] also reported that the pH of apple tree branch, oak tree, rice husk and rice straw bio-char increased from 7.02 to 10.02, 6.43 to 9.68, 6.84 to 9.62 and 8.62 to 10.47 as the temperature increased from 400 to 800°C respectively [19]. Found the similar behavior for bio-char obtained from different feed stocks like peanut hull, pecan shell, poultry litter and switchgrass. They reported that pH of peanut hull, pecan shell, poultry litter and switchgrass bio-char was increased from 7.9 to 8.6, 5.9 to 7.2, 8.7 to 10.3 and 5.4 to 8.0 as the temperature increased from 400 to 500°C, 350 to 700°C, 350 to 700°C and 250 to 500°C respectively. However, no significant change or behavior was observed with respect to increase in residence time.

Higher temperature during the conversion process had the strongest influence on the bio-char pH suggesting that higher temperature may have attributed to higher degree of volatilization, decomposition of surface oxygen groups and dehydroxylation. Substantial increases in pH occurred at the higher temperatures may be due to the concentration of non pyrolyzed inorganic elements in the bio-char.

3.7 EC and CEC Values

The electrical conductivity (EC) and cation exchange capacity (CEC) values of the shredded cotton stalk and its bio-chars obtained under different pyrolysis temperature and residencs time are given in Table 2, graphical representation shown Fig. 6 and Fig. 7. EC value of the shredded cotton stalk was found as 0.03 dS/m. It can also be seen from the table that the salinity of all the cotton stalk bio-char had low EC value and from a minimum of 0.04 dS/m at 200°C with 60 min residence time to a maximum of 0.10 dS /m at 500°C with 240 min residence time. The CEC value of the cotton stalk was found as 38.84 cmol/ kg. It can be seen from the Table 2. that the value of CEC of bio-char was ranged from a minimum of 24.39 cmol/ kg at 500°C with 240 min residence time to a maximum of 38.02 cmol / kg at 200°C with 60 min residence time.

The variation of EC and CEC values of cotton stalk bio-char with temperature at different residence time also presented in Fig. 6 and Fig. 7. It can be seen from the figure that the EC value of cotton stalk bio-char was increased with increase in temperature and CEC value

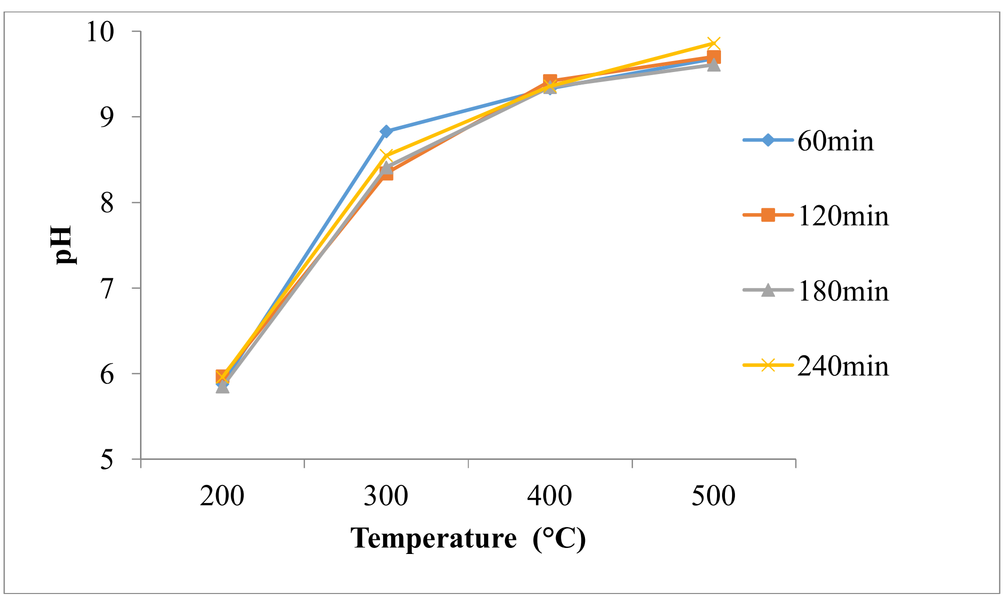

Fig. 5. Effect of different temperature on pH of cotton stalk bio-char at different residence time

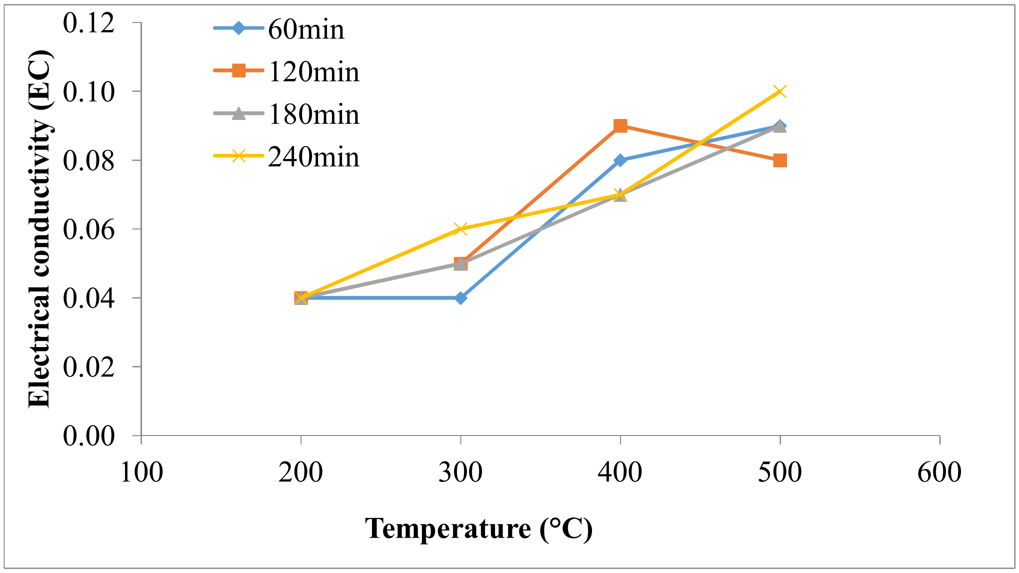

Fig. 6. Effect of different temperature on EC of cotton stalk bio-char at different residence time

decreased with increased in temperature. Similar results were also found by [22] and reported that the EC and CEC value of cotton stalk bio-char increased from 0.05 to 0.11 dS/m and 51.3 to 11.7 cmol / kg as the temperature increased from 350 to 500°C [32]. Reported that the EC and CEC value of castor bean stalk bio-char increased from 0.01 to 0.05 dS/m and 40.8 to 16.4 cmol / kg as the temperature increased from 350 to 500°C. However, no significant change in EC and CEC values of the cotton stalk bio-char was observed at all the levels of experimental levels.

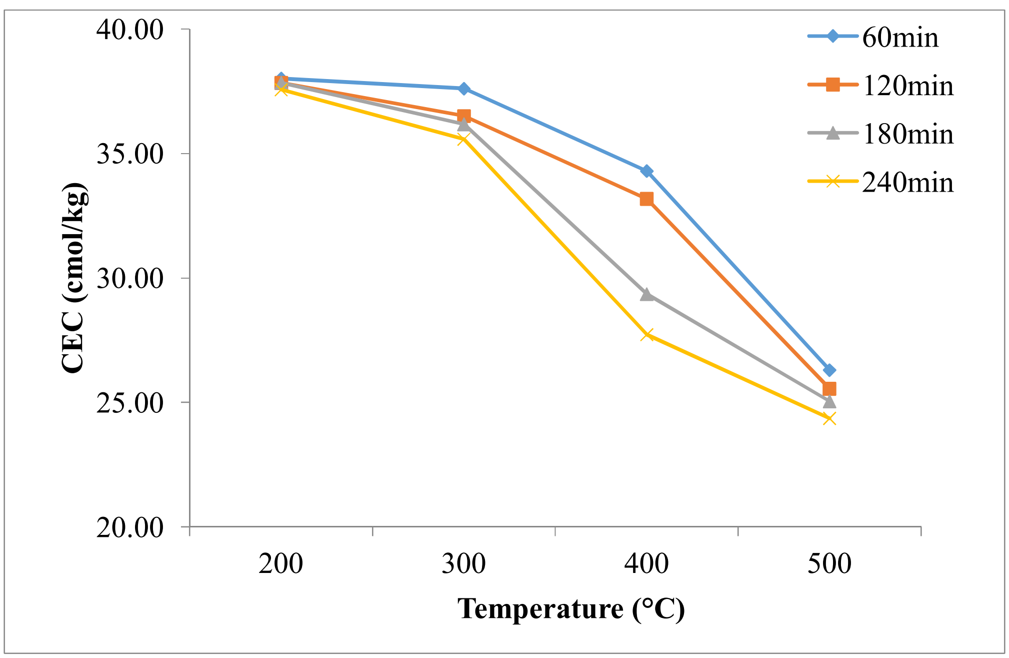

Fig. 7. Effect of different temperature on CEC of cotton stalk bio-char at different residence Time

Table 3. Elemental analyses of cotton stalks bio-chars produced at different pyrolysis temperatures and residence time

	Shredded cotton stalk	Residence time(min)			
		60	120	180	240
Pyrolysis temperature (200°C)					
C (wt. %)	47.90	49.01	52.21	53.32	54.01
H (wt. %)	5.59	5.46	4.52	4.09	3.43
N (wt. %)	1.29	1.31	1.34	1.35	1.36
O (wt. %)	39.36	43.19	40.87	40.17	40.12
S (wt. %)	1.20	1.03	1.06	1.07	1.08
C/N (wt. %)	37.13	37.41	38.96	39.50	39.71
H/C (wt. %)	0.12	0.11	0.09	0.08	0.06
O/C (wt. %)	0.82	0.88	0.78	0.75	0.74
Pyrolysis temperature (300°C)					
C (wt. %)	-	55.12	55.78	57.66	60.86
H (wt. %)	-	3.67	3.27	2.70	2.61
N (wt. %)	-	1.38	1.40	1.41	1.43
O (wt. %)	-	38.75	38.47	37.14	34.01
S (wt. %)	-	1.08	1.08	1.09	1.09
C/N (wt. %)	-	39.94	39.84	40.89	42.56
H/C (wt. %)	-	0.07	0.06	0.05	0.04
O/C (wt. %)	-	0.70	0.69	0.64	0.56
Pyrolysis temperature (400°C)					
C (wt. %)	-	62.85	62.64	64.79	68.62
H (wt. %)	-	2.49	2.18	2.16	2.13
N (wt. %)	-	1.45	1.47	1.48	1.49
O (wt. %)	-	32.12	32.61	30.47	26.65
S (wt. %)	-	1.09	1.10	1.10	1.11
C/N (wt. %)	-	43.34	42.61	43.78	46.05
H/C (wt. %)	-	0.04	0.03	0.03	0.03
O/C (wt. %)	-	0.51	0.52	0.47	0.39
Pyrolysis temperature (500°C)					
C (wt. %)	-	69.21	74.02	75.04	79.30
H (wt. %)	-	1.98	1.84	1.53	1.12
N (wt. %)	-	1.51	1.53	1.55	1.56
O (wt. %)	-	26.16	21.44	20.71	16.83
S (wt. %)	-	1.14	1.17	1.17	1.19
C/N (wt. %)	-	45.83	48.38	48.41	50.83
H/C (wt. %)	-	0.03	0.02	0.02	0.01
O/C (wt. %)	-	0.38	0.29	0.28	0.21

3.8 Ultimate Analysis

The results of the elemental analysis of shredded cotton stalks and its bio-chars obtained at various pyrolysis temperatures and residence time are shown in Table 3. The residence time did not have a significant effect on the elemental composition of the bio-chars. With an increase in the pyrolysis temperature from 200,300,400 and 500°C, the carbon content ofthe shredded cotton stalk biomass was found as 47.9% andvalue of carbon per cent of cotton stalk bio-char was ranged from a minimum of 49.01% at 200°C with 60 min residence time to a maximum of 79.30% at 500°C with 240 min residence time.

The values of C/N ratio of shredded cotton stalk biomass and its bio-char at all the experimental run is shown in Table 3. The C/N ratio of shredded cotton stalk biomass was found as 37.13. Value of C/N ratio of bio-char was ranged from a minimum of 37.41 at 200°C with 60 min residence time to a maximum of 50.83% at 500°C with 240 min residence time. As the temperature rose, H/C and O/C atomic ratios gradually decreased, implying that the bio-chars became increasingly more aromatic and carbonaceous [33]. The values of H/C ratio and O/C ratio of shredded cotton stalk biomass and its bio-char at all the experimental run is shown in Table 3. The H/C ratio and O/C ratio of shredded cotton stalk biomass was found as 0.12 and 0.82. Value of H/C ratio and O/C ratio of bio-char was ranged from a minimum of 0.01 and 0.21 at 500°C with 240 min residence time to a maximum of 0.11 and 0.88 at 200°C with 60 min residence time. The graphical representations shown Figs. 8,9 &10.

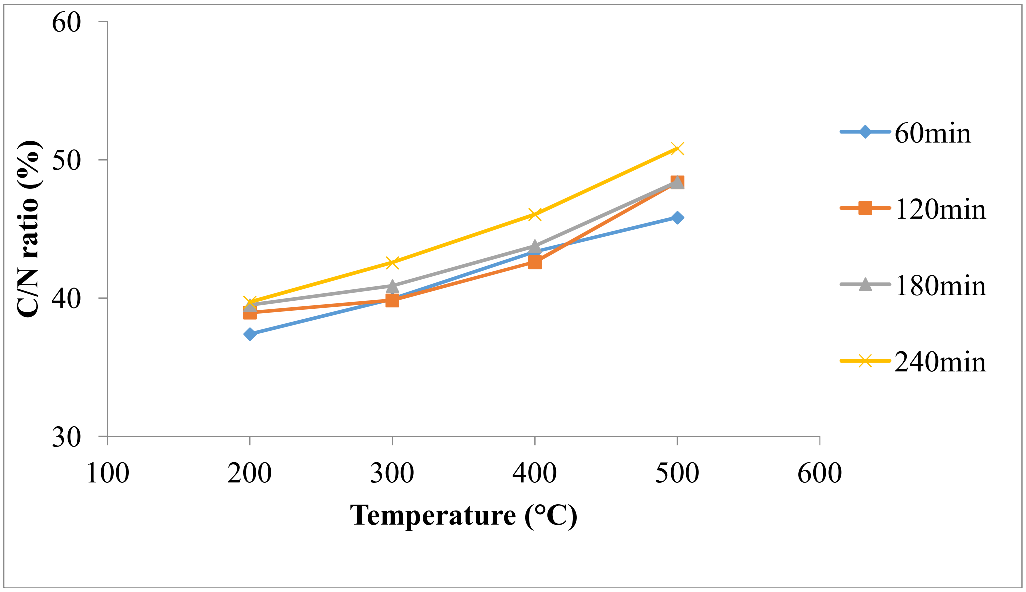

Fig. 8. Effect of different temperature on C/N ratio content of cotton stalk bio-char at different residence time

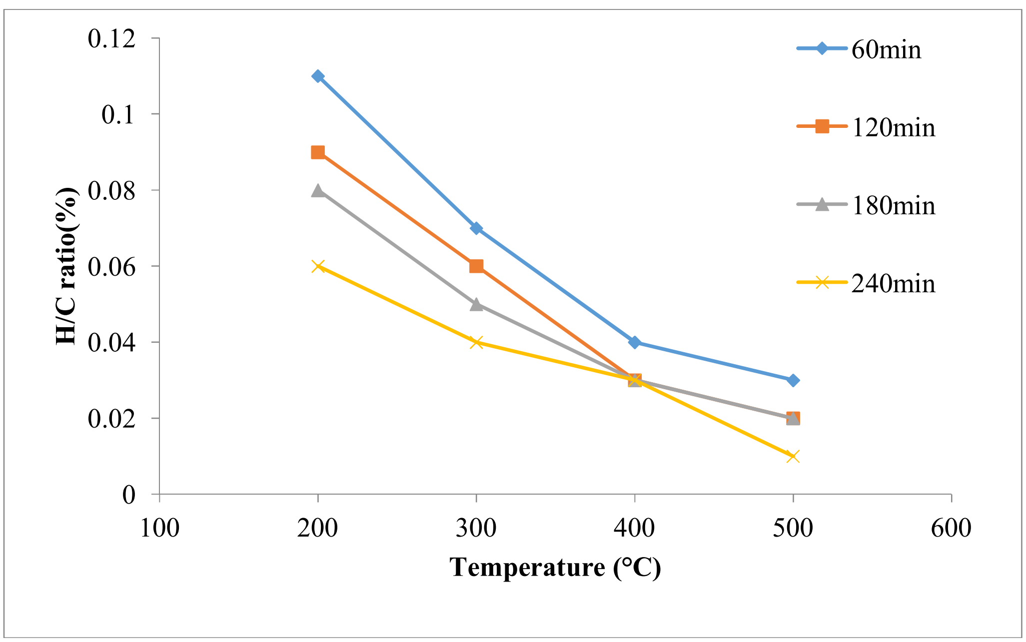

Fig. 9. Effect of different temperature on H/C ratio content of cotton stalk bio-char at different residence time

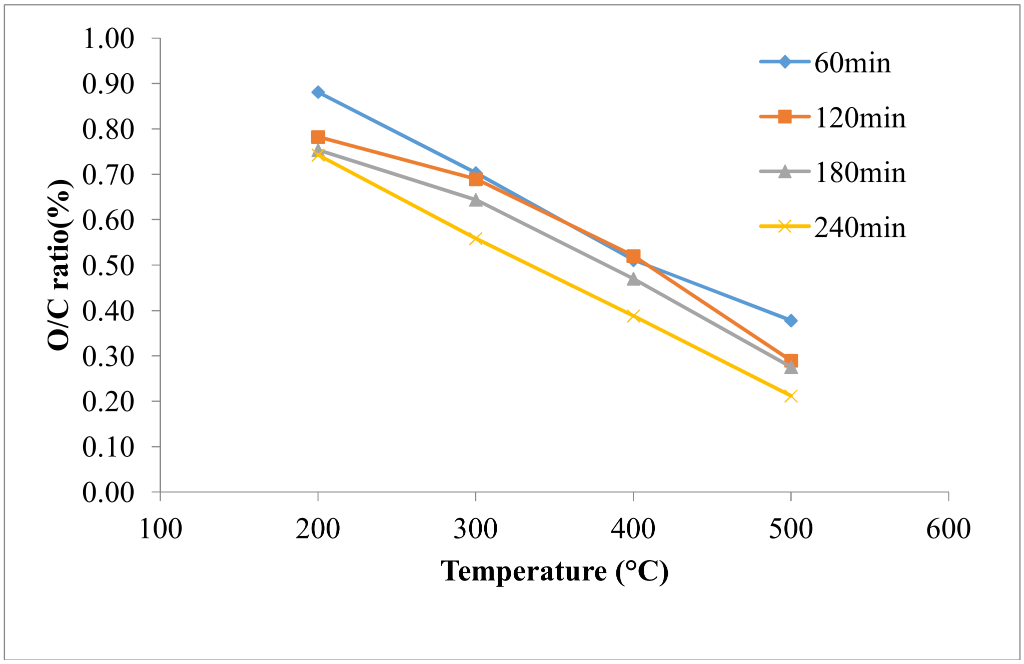

Fig. 10. Effect of different temperature on O/C ratio content of cotton stalk bio-char at different residence time

The C/N ratio increased with increase in temperature. Similar results were also observed by [22,32] and reported that the C/N ratio of cotton stalk bio-char and castor bean stalk increased from 40.8 to 61.9% and 43.2 to 52.2% respectively as the temperature increased from 350 to 500°C. The ratio of C/N provide as important information on the function groups present, the extent of carbonisation, as well as the preferred ratio levels and properties which determine how beneficial the bio-char will be as a soil amendment.

The H/C and O/C ratio decreased with increase in temperature. Similar results were also found by [19] for bio-char obtained from different feed stocks like peanut hull, pecan shell, poultry litter and switchgrass. They reported that H/C ratio and O/C ratio of peanut hull, pecan shell, poultry litter and switchgrass bio-char were decreased from 0.72 to 0.42, 0.98 to 0.19, 0.96 to 0.08 and 1.29 to 0.39 and 0.01 to 0.03, 0.32 to 0.01, 0.14 to <0.01 and 0.48 to 0.04 as the temperature increased from 400 to 500°C, 350 to 700°C, 350 to 700°C and 250 to 500°C respectively. The H/C ratio and O/C ratio of bio-char was also decreased with residence time. However, the effect of residence time on H/C ratio and O/C ratio of bio-char was less as compared to temperature.

The value of carbon per cent of shredded cotton stalk biomass and its bio-char at all experimental run is shown in Table 3. Carbon per cent of shredded cotton stalk biomass was found as 47.9% and Carbon per cent cotton stalk bio-char was ranged from minimum of 49.01% at 200°C with 60 min residence time to a maximum of 79.30% at 500°C with 240 min residence time.

In general, high nitrogen content of bio-char can provide nutrientsto soil and improve crop productivity [34]. The values of nitrogen per cent of shredded cotton stalk biomass and its bio-char at all the experimental run is shown in Table 3. Nitrogen per cent of shredded cotton stalk biomass was found as 1.29%. Value of nitrogen content of cotton stalk bio-char was ranged from a minimum of 1.31% at 200°C with 60 min residence time to a maximum of 1.56% at 500°C with 240 min residence time. The graphical representation of C, N, H, O and S shown Figs. 11-15.

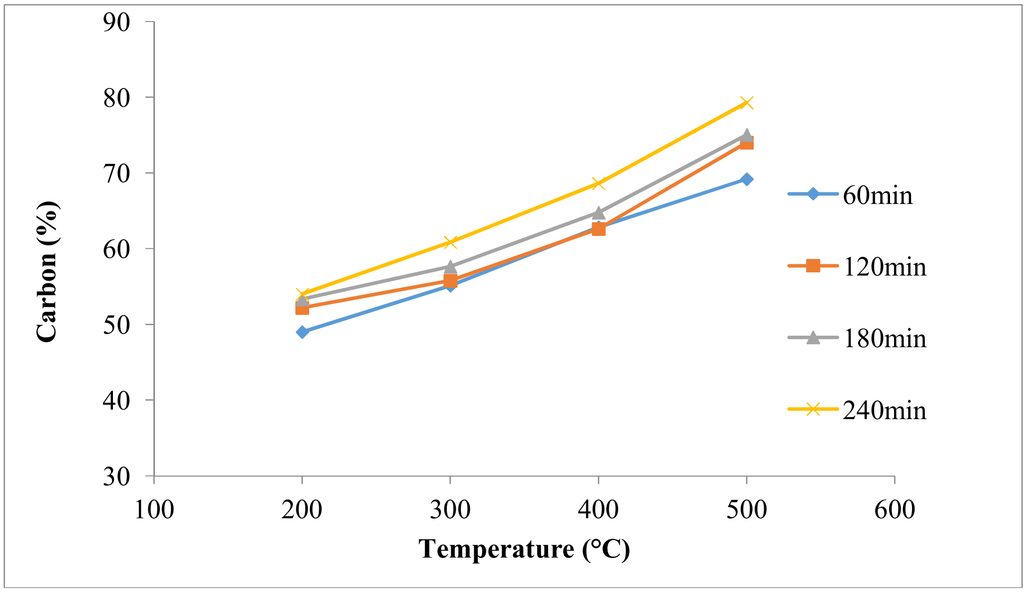

Fig. 11. Effect of different temperature on carbon content of cotton stalk bio-char at different residence time

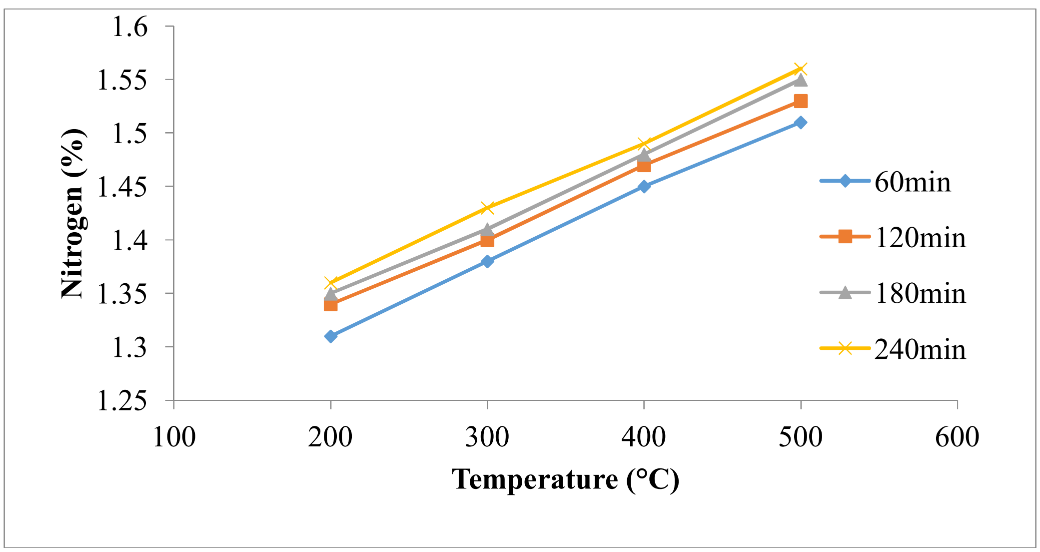

Fig. 12. Effect of different temperature on nitrogen content of cotton stalk bio-char at different residence time

Similar results were also found by [19] for bio-char obtained from different feed stocks like peanut hull, pecan shell, poultry litter and switchgrass. They reported that nitrogen content of peanut hull, pecan shell, poultry litter and switchgrass bio-char was increased from 2.6 to 2.7%, 0.26 to 0.51%, 4.9 to 2.8% and 0.43 to 1.07 as the temperature increased from 400 to 500°C, 350 to 700°C, 350 to 700°C and 250 to 500°C respectively. [22,32] also reported that the nitrogen content of cotton stalk bio-char and castor bean stalk increased from 1.03 to 1.74% and 0.95 to 1.42% as the temperature increased from 350 to 500°C respectively. Percentage of nitrogen content increased with increase in temperature because, as the temperature increases, volatiles are driven off resulting in an overall decrease in mass. It can be seen from the table that the nitrogen content of the bio-char was increased with increase in residence time. However, no definite pattern was observed at all the levels of temperature.

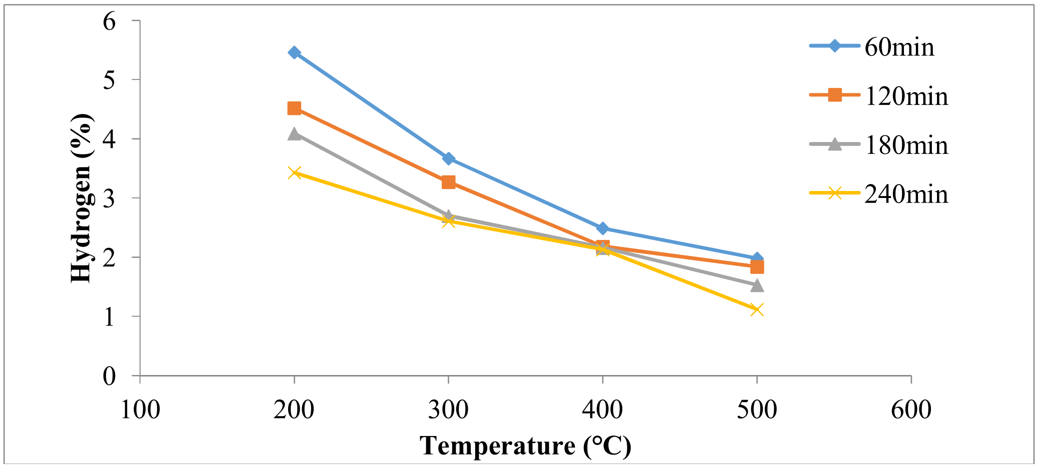

Fig. 13. Effect of different temperature on hydrogen content of cotton stalk bio-char at different residence time

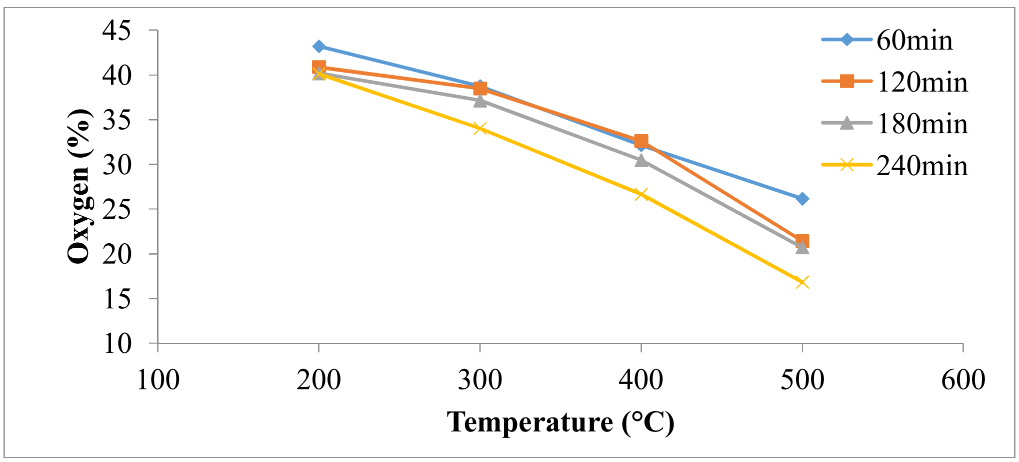

Fig. 14. Effect of different temperature on oxygen content of cotton stalk bio-char at different residence time

Hydrogen per cent of shredded cotton stalk biomass and its bio-char at all the experimental run is shown in Table 3. The hydrogen per cent of shredded cotton stalk biomass was found as 5.59% and value of hydrogen per cent of bio-char was ranged from a minimum of 1.12% at 500°C with 240 min residence time to a maximum of 5.46% at 200°C with 60 min residence time.

The decrease in hydrogen content with increase in temperature may be due to the reason that, as the temperature increases, reactions occurs which change the structure of carbon and number of active sites decreases which results in a loss of reactivity. This loss in reactivity is weaker bonds breaking and results in the decrease of hydrogen [35,36,37]. The hydrogen content of bio-char was also decreased with residence time. However, the effect of residence time on hydrogen content of bio-char was less as compared to temperature.

The values of oxygen per cent of shredded cotton stalk biomass and its bio-char at all the experimental run is shown in Table 3. Oxygen content of shredded cotton stalk biomass was found as 39.36% and value of oxygen content of cotton stalk bio-char was ranged from a minimum of 16.83% at 500°C with 240 min residence time to a maximum of 38.52% at 200°C with 60 min residence time. Oxygen content decreased with increase in temperature. Similar results were also observed by [19] for bio-char obtained from different feed stocks like peanut hull, pecan shell, poultry litter and switchgrass. The reason may be that feed stock loses surface functional –OH groups and loses C-bond O and H atoms due to structural core degradation at higher temperature. The oxygen content of bio-char was also decreased with residence time. However, the effect of residence time on oxygen content of bio-char was less as compared to temperature.

The values of sulphur per cent of shredded cotton stalk biomass and its bio-char at all the experimental run is shown in Table 3. Sulphur content of shredded cotton stalk biomass was found as 1.2% and value of sulphur content of cotton stalk bio-char was ranged from a minimum of 1.03% at 200°C with 60 min residence time to a maximum of 1.19% at 500°C with 240 min residence time. Sulphur content increased with increase in temperature. Similar results were also observed by [19]. The sulphur content of bio-char was also increased with residence time. However, the effect of both temperature and residence time on variation of sulphur content of bio-char was less.

The elemental content of the cotton stalks bio-chars were similar to those of bio-char produced from other biomass samples such as orange peels, wheat grains, pinewood sawdust, maize stalk, rice and cottonstraw [17,34,38,33]. Since the sulfur content of cotton stalk was below the detection limit,the bio-char could be used in fuel applications and activated carbon production. Figs. 16 to 19 is a deferent temperature and residence time, Produced bio-car.

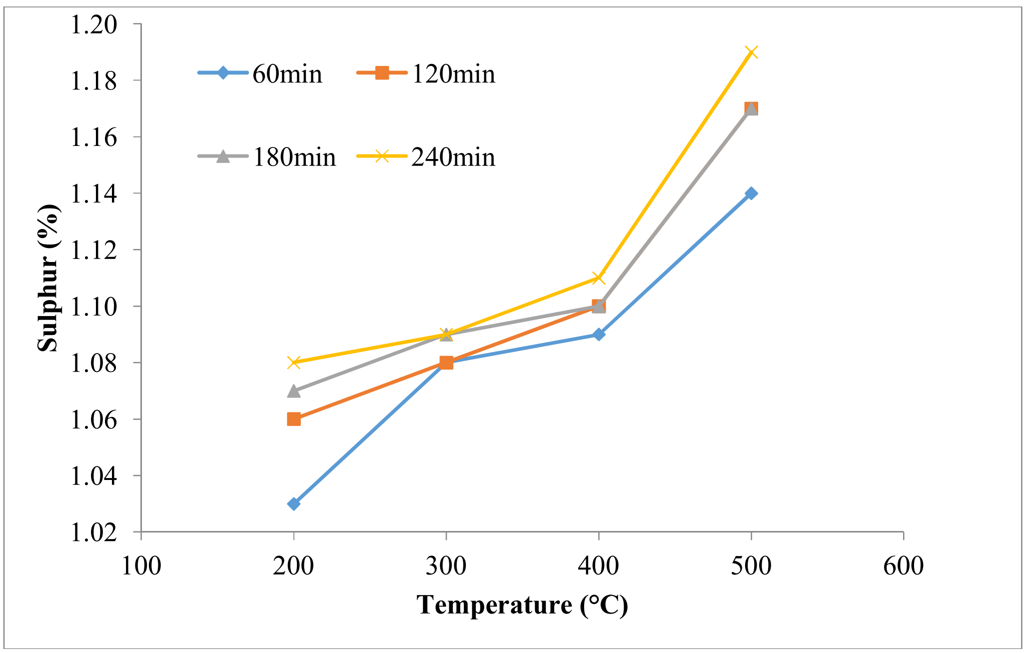

Fig. 15. Effect of different temperature on sulphur content of cotton stalk bio-char at different residence time

Fig. 16. bio-char obtained at 200°C at different residance time

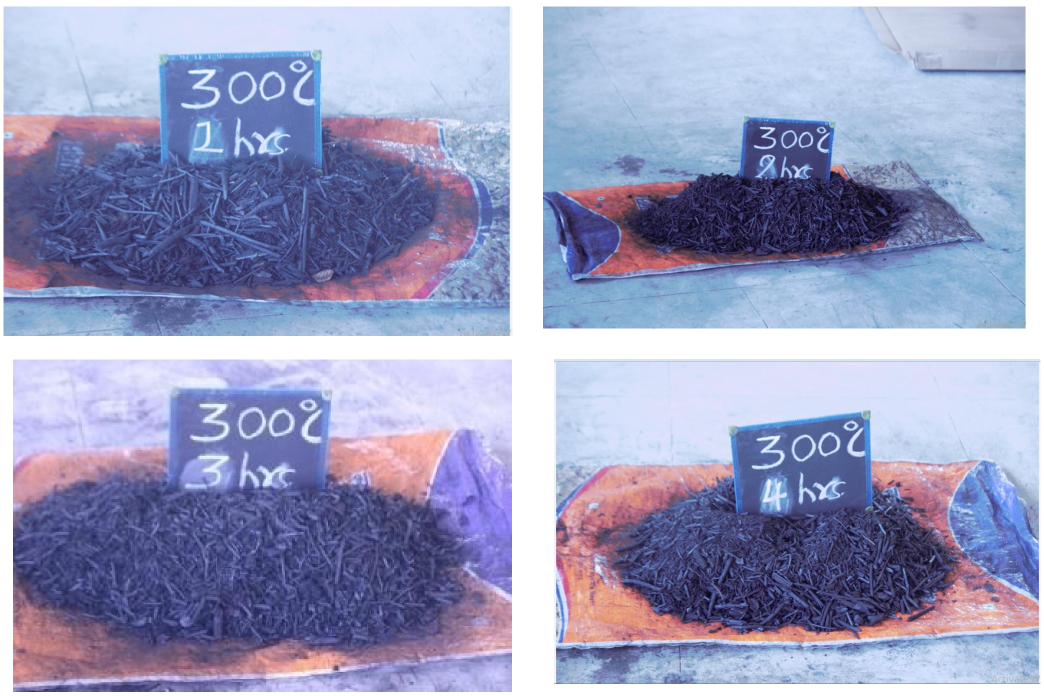

Fig. 17. Bio-char obtained at 300°C at different residance time

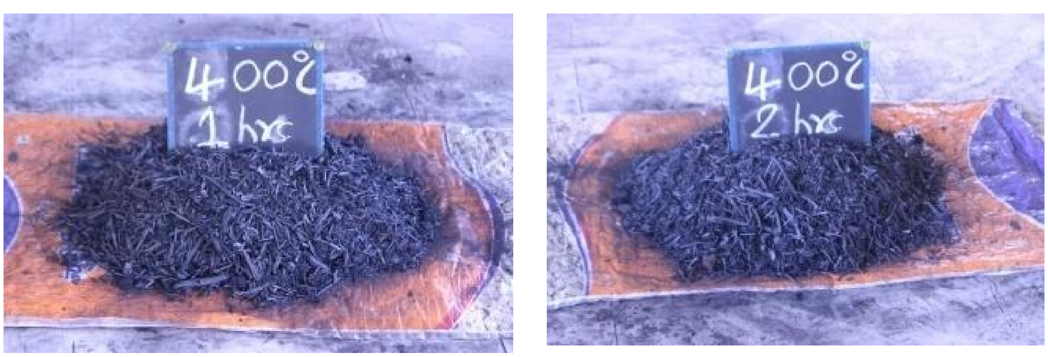

Fig. 18. Bio- char obtained at 400°C at different residance time

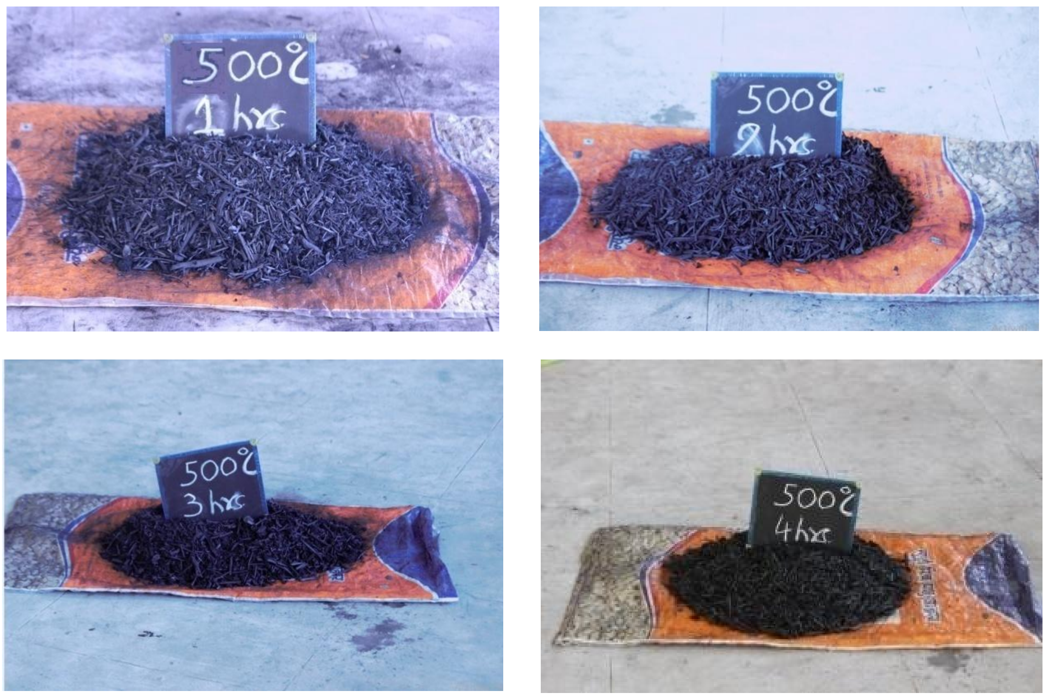

Fig. 19. Bio- char obtained at 500°C at different residance time

4. CONCLUSION

A total number of sixteen experiments were performed on the pyrolysis of shredded cotton stalk at four levels of temperature 200, 300, 400 and 500°C and four residence times of 60, 120, 180 and 240 min respectively. Three main products of pyrolysis of shredded cotton stalk biomass were determined in terms of bio-char, bio-oil and pyro-gas yield. Pyrolysis studies indicated that it can be achieved a more valuable and functional product (bio-char) from cotton stalks. The cotton stalks bio-chars can be effectively used as a raw material for the preparation of activated carbon. Bio-chars obtained at high pyrolysis temperatures (500°C) are suitable for direct use in fuel applications due to their high fixed carbon content, higher calorific value, and low volatile matter content. Bio-chars was also be used as a fuel.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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