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# Segmented heating carbonization of biomass: Yields, property and estimation of heating value of chars

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A B S T R A C T

To provide preferable operating conditions for biomass carbonization, the carbonization properties of maize straw, cotton stalk and poplar wood were investigated in nitrogen atmosphere by segmented heating process at different final temperatures of 300–800 °C for 1 h. Segmented heating carbonization contributes to higher ratio of mass and energy yields than a constant temperature/linear heating process with final temperature of around 300 °C. The fuel properties and characteristics of raw and carbonized biomass were analysed systematically. Increasing carbonization temperature, the fuel ratios of the obtained chars rise exponentially, and the profile of atomic H/C ratio versus atomic O/C ratio approximately decreases linearly. There are small changes of sulphur and nitrogen content in the chars. To provide an estimation method for higher heating value for torrefied/carbonized biomass, a new correlation is proposed based on ultimate analysis. The correlation is $HHV = 19.9579 + 0.1284C + 0.3355H - 0.1209O - 1.3836N - 5.4680S$, which is validated through experimental data. The correlation has a low level of errors, that the correlation efficient, mean absolute error, average absolute error and average bias error are 0.971, $-6.75 \times 10^{-6}$MJ, 1.2% and 0.02% respectively. This work will make a contribution to the biomass pretreatment process.



## 1. Introduction

Biomass is a unique $CO_2$-neutral fuel and has the potential to play a significant role in energy composition of China. Biomass can be divided into various types, such as woody plants, herbaceous plants, aquatic plants, manures, municipal solid waste and organic waste [1–3]. Generally, biomass can be converted into three main types of products, i.e. electrical/heat energy, transport fuel and chemical feedstock [4–8]. Increased using of biomass energy for replacing coal can reduce $CO_2$ emission, support sustainable development and regeneration [9].

In China, as reported by China's thirteenth Five-Year-Plan for biomass energy development, the ratio of renewable energy consumption to the total energy consumption was 11.64%, and biomass energy took into account only 8.00% of total renewable energy in the year of 2016 [1,10,11]. China now is trying to enhance the biomass energy utility to 57 million tons of standard coal in the end of thirteenth Five-Year-Plan [10]. It is almost doubling the present amount of the biomass utilization till the end of 2020. What's more, the “Belt and Road” project will promote the utilization of biomass energy world wide [12]. There is a huge potential for biomass utilization while a number of obstacles need to be overcome to achieve extensive utilization and higher efficiency. Therefore it is urgent to develop technologies for upgrading and pre-treating of multifarious biomass resource in China.

On account of the diversity of raw biomass and bio-fuel, there are many ways to improve biomass fuel quality and achieve extensive utilization and higher efficiency [13]. Such like the thermo-chemical upgrading of biomass fuel, which includes torrefaction, carbonization, pyrolysis, gasification and liquefaction [14–16]. Torrefaction, also called low temperature (230–300 °C) carbonization in an inert atmosphere, can remove moisture and low weight organic volatile components in biomass. It can also depolymerize the long polysaccharide chains, produce a hydrophobic solid product with an increased energy density and grindability [17–19]. Products form torrefaction have high porosity, greater reactivity during combustion and gasification [20]. Carbonization is a process that occurs at temperatures of

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**Nomenclature**

| | |
|---|---|
| A | Ash, [%] |
| *AAE* | Average absolute error, [%] |
| *ABE* | Average bias error, [%] |
| $e_i$ | Error of *i*th biomass sample, [MJ kg$^{-1}$] |
| $E_i$ | Estimated higher heating value, [MJ kg$^{-1}$] |
| M | Moisture, [%] |
| $M_i$ | Measured higher heating value, [MJ kg$^{-1}$] |
| *MAE* | Mean absolute error, [MJ kg$^{-1}$] |
| MS | Maize straw |
| CS | Cotton stalk |
| EMCI | Energy-Mass co-benefit index |
| FC | Fixed carbon, [%] |
| HHV | Higher heating values, [MJ kg$^{-1}$] |
| PW | Poplar wood |
| $R_e$ | Ratio of energy yield, [%] |
| $R_f$ | Fuel ratio |
| $R_{my}$ | Ratio of mass yield, [%] |
| $T_f$ | Final temperature, [°C] |
| V | Volatile, [%] |

300–500 °C with an inert atmosphere to obtain solid matter [21]. Pyrolysis is a thermal process that heats and decomposes biomass at high temperature (300–1000 °C) [22] in an inert environment. Gasification is a promising method to produce "product gas" at lower temperatures (below 1000 °C) and "syngas" with high temperatures (above 1200 °C) [23]. Among these processes, torrefied or carbonized biomass potentially shows better performance during combustion or co-combustion with coal [24–26]. Both of them have higher energy density, good grindability and combustion characteristics [27].

However, there are still problems related to biomass torrefaction and carbonization, such as the higher expenses of inert atmosphere and quality of obtained char. Although the cost of heating conditions could potentially be reduced if the air or hot flue gas is used as a carrier gas instead of inert atmospheres, the energy and mass yields, and quality of solid fuel are reduced simultaneously [28]. In the meantime, the combustible volatile released into the carrier gas is difficult to deal with or used. Thus it is important to carry on a research about the properties of obtained chars.

Reviewing literature concerning torrefaction and low temperature carbonization, the influence of process parameters and conditions on the char quality parameters were further explored, which included heating rate, staying time, final temperature, atmospheres, pressure, raw material particle size [28–31], etc. Qi et al. has also studied the effect of three additives on the residual contents of alkali metal elements and $SO_2$, $NO_x$ emission [1]. The parameters related to char quality include the properties of solid fuel (solid yields, energy yield, higher heating values) and the heating conditions. These are essentially important in analysing the quality of biomass char obtained from torrefaction and low temperature carbonization.

In consideration of the influences of heating rate and stay time on the quality of chars, and further reduction of heating cost during the process, a new three-step carbonization process was developed with the characteristics of self-heating by burning the pyrolysis gas and initial heating by an external supply of oil or gas [32]. Detailed description of three-step carbonization equipment is discussed in Sec.2.2. It indicates that the heating process of segmented design contributes to higher mass and energy yields than linear heating and/or constant temperature heating.

For industrial application, it is usually use correlations to estimate the higher heating values (HHVs) of the fuel. There are many available correlations about biomass and coal in the literature [33–37], most of which are reported with a high accuracy applied to the investigators own database, mainly biomass and coal. However, an extrapolation to obtained bio-solid fuel from torrefaction and carbonization leads to considerable differences between the calculated results of the correlations and experiments. Most studies provide the proximate, elemental (ultimate), calorific analysis of raw biomass samples, but few studies offer analysis of the solid fuel. Thus a correlation for the prediction of HHVs for obtained biomass char is needed for further industrial application. What's more, according to Sheng's research [33], that the correlations based on ultimate analysis are the most accurate. Thus in this study, based on analysis of fuel properties of the obtained chars, a correlation of estimating higher heating values for biomass chars was proposed.

According to the previous discussion, the scope of this paper is raised up as 1) to evaluate the potential of carbonization by segmented heating and properties of biomass chars precisely, 2) to discuss the quality of obtained chars and 3) to proposed a new correlation for estimation of higher heating values.

Work presented in this paper reports on fundamental investigations into carbonization, which including the comparison of heating values of the obtained chars for biomass (cotton stalk) torrefaction and carbonization, the mass and energy yields, and the property of chars obtained from typical biomass carbonization at different final temperatures. The remainder of this paper is organized in the following structure: Sec.2 will report the methodology of three-segment carbonization technology and the simulation and experimental methods, Sec.3 will discuss the effect of final temperatures on the yield of solid fuels and the fuel properties of chars. Finally the correlation to predict the higher heating values is proposed and validated.

The results from this paper will contribute to optimizing the carbonization process and upgrading the quality of chars. The energy efficiency, economic analysis and pollution control are beyond the scope of this paper.

## 2. Materials and methods

### 2.1. Raw biomass samples

Two agricultural crops and a fast-growing tree residue, namely maize straw (MS), cotton stalk (CS), and poplar wood (PW) which grown in rural areas in DeZhou, Shandong Province, China are selected as test samples, for that these types of herbaceous, lignocellulose, and woody biomass materials are cheap and convenient to acquire. They are also widely used for biomass moulding fuel, household heating and cooking, and power generation in northern China.

These samples were first dried with hot air, then torrefied and carbonized for subsequent analysis of the solid residues. Proximate analysis, ultimate (elemental) analysis and calorific values estimation were carried on for all available samples. The proximate analysis was performed in accordance with the standard procedure of the American Society for Testing and Materials American Society for Testing and Materials standard, E870-82 (2013) [38]. The ultimate analysis was carried out using an ultimate analyser (Leco TruSpec CHN) and sulphur analyser (Leco S144DR). The volatile content of the samples was analysed with an auto volatile analyser (CKIC 5E-MAG6600). The higher heating values (HHV) of the samples were measured by a bomb calorimeter (CKIC 5E-AC8018).