



Full Length Article

Influence of pressure and temperature on key physicochemical properties of corn stover-derived biochar



Manuel Azuara ^{a,*}, Bárbara Baguer ^b, José I. Villacampa ^a, Niklas Hedin ^c, Joan J. Manyà ^d

^a Institute of Nanoscience of Aragón (INA), University of Zaragoza, Spain

^b Technological College of Huesca, University of Zaragoza, Spain

^c Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, Sweden

^d Aragón Institute of Engineering Research (I3A), University of Zaragoza, Spain

HIGHLIGHTS

- As-received corn stover was pyrolyzed as a means to avoid pre-treatment costs.
- The effect of pressure was studied keeping the gas residence time constant.
- Increasing the pressure led to a higher gas production at the expense of water.
- The pressure had only a minor influence on the properties and yield of the biochar.

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ABSTRACT

This study focuses on analyzing the effect of both the peak temperature and pressure on the properties of biochar produced through slow pyrolysis of corn stover, which is a common agricultural waste that currently has little or no value. The pyrolysis experiments were carried out in a fixed-bed reactor at different peak temperatures (400, 525 and 650 °C) and absolute pressures (0.1, 0.85 and 1.6 MPa). The inert mass flow rate (at NTP conditions) was adjusted in each test to keep the gas residence time constant within the reactor. The as-received corn stover was pyrolyzed into a biochar without any physical pre-treatment as a way to reduce the operating costs. The properties of biochars showed that high peak temperature led to high fixed-carbon contents, high aromaticity and low molar H:C and O:C ratios; whereas a high pressure only resulted in a further decrease in the O:C ratio and a further increase in the fixed-carbon content. Increasing the operating pressure also resulted in a higher production of pyrolysis gas at the expense of water formation.

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1. Introduction

Global warming is of worldwide concern and related to the anthropogenically enhanced concentrations of CO₂ and other greenhouse gases in the atmosphere. Previous studies have highlighted the positive effect of adding biochar to soil in terms of reducing such emissions to the atmosphere [1,2]. Biochar can be produced by several thermochemical processes as conventional or slow pyrolysis which has been used to generate charcoal for many years [3,4].

The production of biochar from corn stover appears to be a very promising alternative to integrate carbon sequestration measures and renewable energy generation into conventional agricultural

production. Corn stover is the waste remaining in the field following the harvest of the grains. The corn production in Spain is about 4700 thousand tons per year [5]. Considering a waste yield of 0.65 (dry basis) and an average moisture content of 20 wt.% [6,7], around 2440 thousand tons of corn stover are harvested per year in Spain.

Despite the fact that pyrolysis of biomass from agricultural or forest residues has been widely studied [3,8], further research is strongly needed to fill the knowledge gaps related to how the operating conditions and feedstock affect the properties of biochar [9]. Typical operating conditions are the peak temperature, pressure, gas residence time, heating rate, atmosphere type, etc.

So far, very few studies have investigated how the operating conditions of pyrolysis influence the physicochemical properties of the corn stover-derived biochar. Fuertes et al. [10] reported that the biochar from corn stover pyrolysis at a peak temperature of

* Corresponding author.

E-mail address: mazuara@unizar.es (M. Azuara).

Nomenclature

C_{char}	carbon content of biochar in a daf basis
C_{raw}	carbon content of feedstock in a daf basis
d_{avg}	average pore diameter (nm)
%FC	fixed-carbon content in a daf basis
m_{char}	mass of produced char (g)
m_{raw}	dry mass of raw material (g)
R^2_{adj}	adjusted coefficient of determination
S_{BET}	Brunauer–Emmet–Teller specific surface area ($m^2 g^{-1}$)
T_{peak}	pyrolysis peak temperature ($^{\circ}C$)
V_t	total volume pore ($cm^3 g^{-1}$)
x_1	coded variable for peak temperature
x_2	coded variable for absolute pressure
y_{char}	biochar yield ($kg kg^{-1}$ of biomass in a daf basis)
y_{gas}	gas yield in a dry basis ($kg kg^{-1}$ of biomass in a dry ash and N_2 -free basis)
y_{tar}	yield of producer gas ($kg kg^{-1}$ of biomass in a daf basis)
y_{water}	yield of producer gas ($kg kg^{-1}$ of biomass in a daf basis)

Greek symbols

β_0	regression coefficient for the intercept term
β_1	regression coefficient for the linear effect of peak temperature
β_2	regression coefficient for the linear effect of absolute pressure
β_{12}	regression coefficient for the interaction term

Acronyms

BET	Brunauer Emmett Teller
CP MAS ^{13}C NMR	Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance
DP ^{13}C NMR	Direct Polarization Carbon-13 Nuclear Magnetic Resonance
XRF	X-ray fluorescence

550 $^{\circ}C$ was highly aromatic and had low H:C and O:C molar ratios (0.3 and 0.1, respectively). It was also reported by Enders et al. that both the H:C and O:C molar ratios decreased (from 0.9 to 0.4 and from 0.3 to 0.1, respectively) as the peak temperature was increased from 300 to 600 $^{\circ}C$ [11]. Furthermore, and as observed for other types of biomass, the efficiency of carbonization was improved for large particles as compared with small, which led to charcoals with higher fixed-carbon contents [12]. This trend was related to the major role of the secondary charring reactions that occurred at the intra-particle level, which is highly relevant to industrial processes as it can contribute to saving costs in milling.

Previous investigations focused on producing charcoal from different lignocellulosic biomass have shown benefits of increasing the pressure used when it comes to both the charcoal and fixed-carbon yields [13–16]. The authors of those studies attributed this pressure effect to the enhanced kinetics of the secondary reactions of repolymerization and recondensation of the volatile matter during its contact with the solid matrix. However, this improvement in carbonization efficiency, as previously was stated by Manyà et al. [17], can also be related to an increase in the gas residence time within the pyrolysis reactor. In other words, the intrinsic effect of the pressure should be evaluated keeping constant the gas residence time of the inert carrier gas within the reactor.

The major goal of this study is to provide evidence on how the stability-related properties of the corn stover-derived biochars depend on both the temperature (pyrolysis peak temperature) and absolute pressure at a constant gas residence time. The effect on additional process variables, as for example the product distribution and the pyrolysis gas composition, was also investigated.

2. Materials and methods

2.1. Materials

The used corn stover (CS) contained corncob (15.5 wt.%), leaf (4.3 wt.%) and stalk (80.2 wt.%) that remained in the field following the harvest of cereal grain. It was supplied by a local farm located in the Spanish region of Aragón. The as-received CS was pyrolyzed without any previous crushing and sieving step. In this way, the thermochemical conversion of this agricultural waste can be performed in a more cost-effective manner. The ranges of particle size for each fraction were: 1.5–10.0 cm long (stalk); 0.5–5.0 cm long (leaf); and 1.2–2.0 cm diameter and 2.0–5.0 cm long (corncob).

Proximate analyses were performed in quadruplicate according to ASTM standards (D3173 for moisture, D3174 for ash, and D3175 for volatile matter), whereas elemental analyses were carried out using a Leco TruSpec Micro CHNS analyzer (Leco Corporation, USA). Moreover, an ADVANT'XP+ XRF spectrometer (Thermo ARL, Switzerland) was used to measure the ash composition on the basis of the weight fractions of the equivalent oxides (according to ASTM standard D4326-04). Table 1 lists the results from the above-mentioned analyses.

2.2. Experimental system and procedure

The fixed-bed pyrolysis system consists of a cylindrical and vertical tube (140 mm inner diameter; 465 mm long) made of Sandvik

Table 1
Proximate, elemental and XRF analyses of corn stover.

Proximate (wt.%)	
Ash	2.50 \pm 0.20
Moisture	7.27 \pm 0.31
Volatile matter	80.3 \pm 0.11
Fixed carbon	9.93 \pm 0.49
Elemental (wt.%, daf basis)	
C	44.4 \pm 0.31
H	5.60 \pm 0.04
N	0.43 \pm 0.01
S	0.45 \pm 0.05
Inorganic matter (wt.% of ash)	
SiO ₂	31.41 \pm 0.23
CaO	30.71 \pm 0.23
K ₂ O	9.85 \pm 0.15
Fe ₂ O ₃	6.49 \pm 0.12
Al ₂ O ₃	4.85 \pm 0.12
P ₂ O ₅	4.13 \pm 0.10
MgO	3.45 \pm 0.17
PbO	2.50 \pm 0.08
S	1.94 \pm 0.07
Cl	0.594 \pm 0.030
TiO ₂	0.586 \pm 0.029
MnO	0.526 \pm 0.026
SnO ₂	0.450 \pm 0.034
ZnO	0.240 \pm 0.021
SrO	0.199 \pm 0.021
Cr ₂ O ₃	0.178 \pm 0.023
CuO	0.081 \pm 0.024

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