Characterization of biochar and bio-oil from cocoa pod husks thermal treatment under reactive and inert atmospheres

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Abstract

→ This work aimed to analyze the properties of biochar that could be "in situ" easily obtained at cocoa-growing farms and provide preliminary information of carbon sequestration when using this biochar in soil.

Methods

→ The thermal treatment of cocoa pod husks (CPH) under reactive (RA) and inert atmosphere (IA) was analyzed. Proximate and elemental analysis of CPH was performed to characterize the raw material obtained from a local farm in Moraspungo, Ecuador. A lab-scale reactor was set to three different temperatures (150°C, 350°C and 500°C) for each reaction atmosphere. The nomenclature used to identify samples was: two letters to identify the atmosphere and a number to identify the reaction temperature (example: IA-350). First, biochar yield and its physical-chemical properties were determined, in terms of pH, electrical conductivity, surface area, elemental analysis, and metal content. Later, bio-oil from reactor experiments was condensed and characterized by GCMS. Finally, TG-GC-MS (inert and reactive atmosphere) and EGA/Py (inert atmosphere) analysis were used to compare results obtained from the reactor.

Results and Discussion

CPH and biochar characterization

After characterization of CPH and biochar obtained at different reaction atmospheres and temperatures, IA-500 was determined as the best biochar to use as soil ammendment due to its properties.

Table 1. Summary of CPH and biochar IA-500 characterization

Variable	Unit	CPH	IA-500 Biochar
Initial moisture	%	29.9 ± 6.3	31.9±2.9
Final moisture (dry material)	%	10.5±0.2	7.2±1.7
Volatiles	%	59.4±1.2	20.0±3.4
Fixed Carbon	%	21.4±0.4	**53.3±4.0**
Ash	%	8.8±0.2	19.6±0.4
Surface area	m^2/g	0.24±0.01	4.93±0.09
C	%	41.5±1.0	**69.8±1.3**
N	%	1.69±0.11	1.22±0.12
H	%	6.2±0.2	2.4±0.2
O	%	41.6±1.0	6.7±1.3
S	%	0.20±0.04	0.26±0.03
Empiric formula	-	$CH_{1.79}N_{0.03}O_{0.75}$	$CH_{0.41}N_{0.01}O_{0.07}$
H/C molar		1.79±0.07	**0.41±0.04**
O/C molar		0.75±0.03	**0.07±0.01**
Higher heating value*	MJ/kg	17.3±0.4	26.06±0.54
Hemicellulose**	%	21.2±0.4	12.3±0.03
Celullose**	%	23.2±0.5	13.53±0.76
Lignin**	%	15.0±0.3	31.9±2.9
pH	-	5.7±0.1	7.2±1.7
Conductivity	mS	6.7±0.2	20.0±3.4

* Obtained using Gaur – Reed equation ** Products of thermal decomposition

Metal content and leaching analysis

Metal content was determined using ICP-MS (Fig 1). Leaching analysis with water was performed to determine the amount of metals that can leach to water from biochar. The amount of metals that leach into water is almost nil, being potassium the only metal whose yield decreases after leaching (from 2.8 to 2.3%).

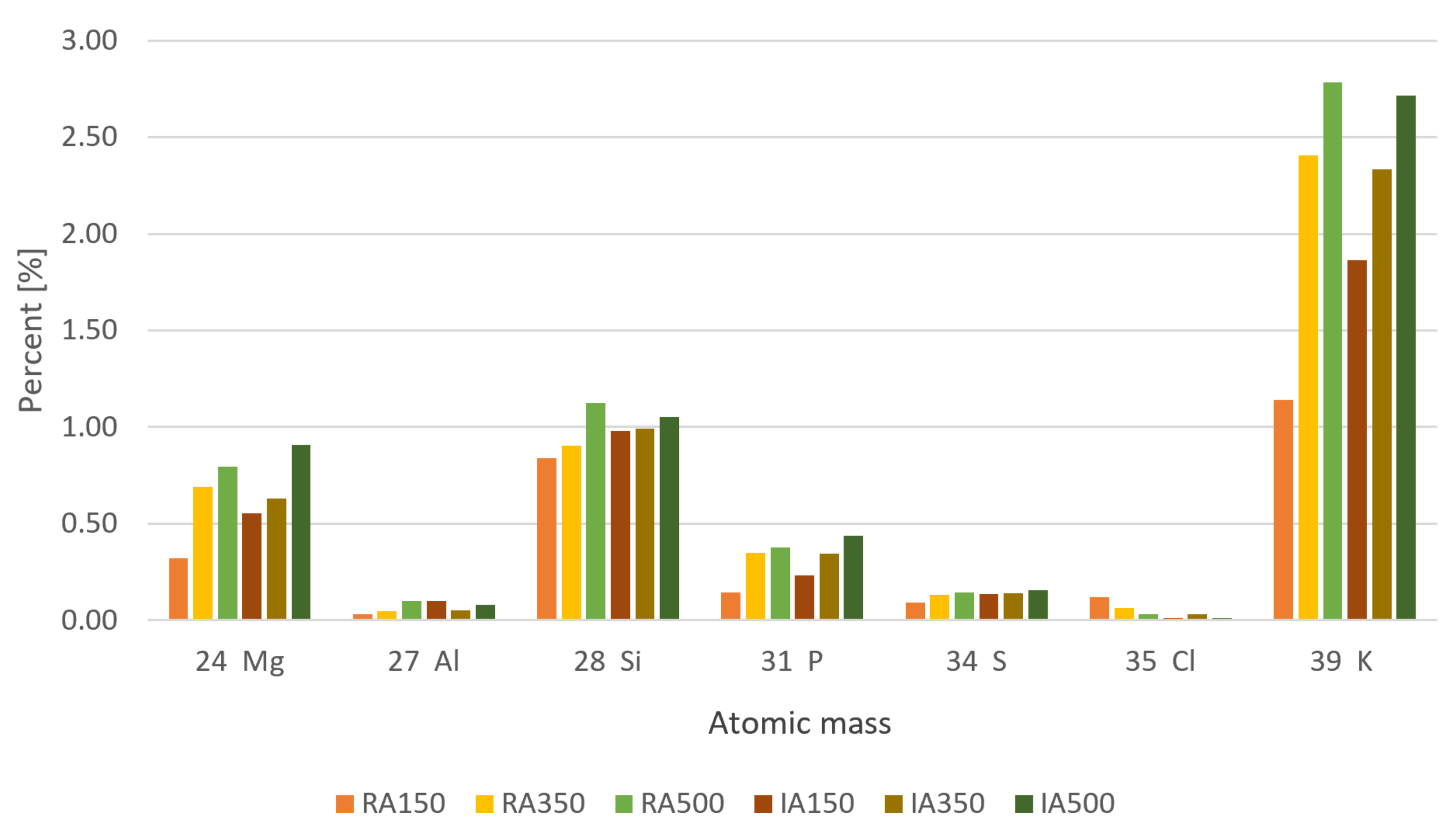
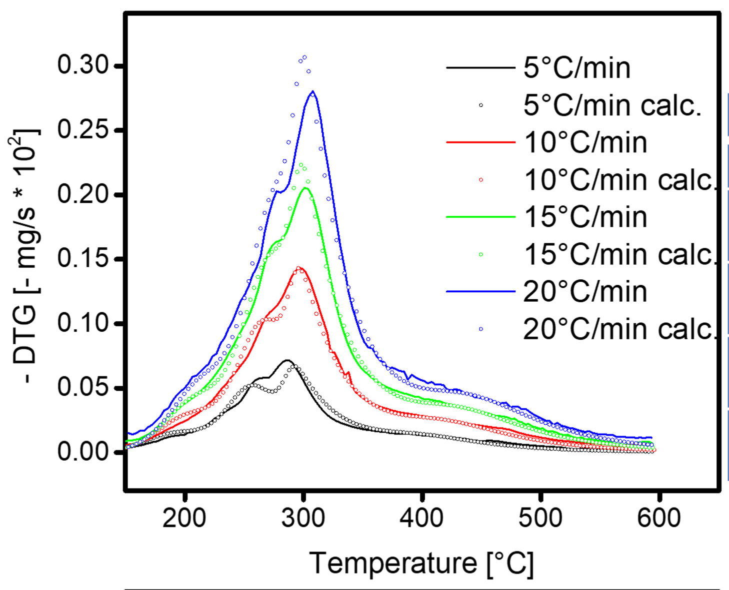


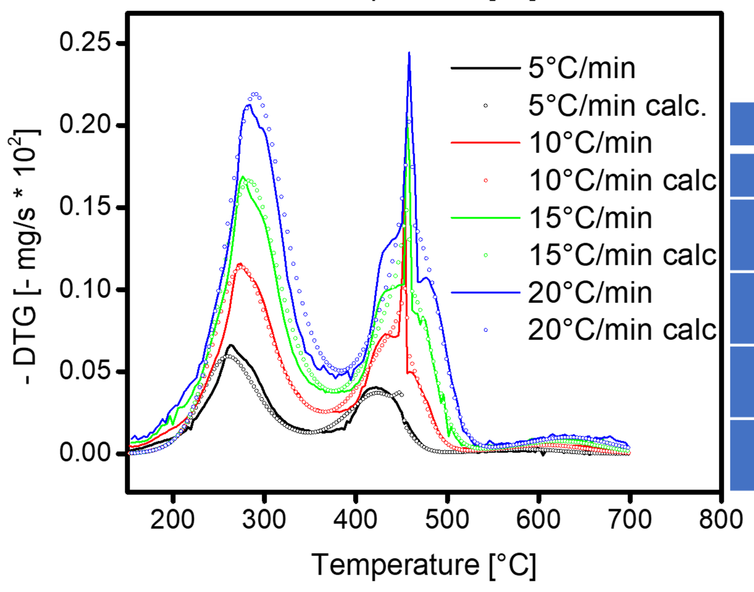
Fig 1. Metal content in biochar samples

Kinetic parameters

TG and DTG curves of the thermal decomposition process at 4 different heating rates were fitted simultaneously by a kinetic model formed by 4 independent reactions. Kinetic parameters of thermal decomposition were calculated using a new fitting strategy. Inflection points were determined using the second derivative of the kinetic equation. Heating rate and temperature range (delimited by inflection points) can be established to ensure better fitness (Fig 2)



Inert Atmosphere				
Parameter	W1	W2	W3	W4
k_0	1.87E+09	2.74E+13	1.41E+40	1.20E+07
E/R	12527.41	19130.53	54889.86	15032.63
n	4.20	2.80	8.40	2.64
w_0	0.18	0.37	0.32	0.14



Oxidative Atmosphere				
Parameter	W1	W2	W3	W4
k_0	2.95E+08	3.29E+07	4.77E+49	9.39E+06
E/R	13333.08	16066.52	85362.67	18950.29
n	2.49	1.13	0.65	1.37
w_0	0.61	0.33	0.02	0.04

Fig 2. DTG fitting using the kinetic parameters determined for each reaction atmosphere

Bio-oil and volatiles analysis

Bio-oil from reactor and volatiles from TG-GC/MS and EGA were characterized. Different molecules with representative functional groups were identified.

Analysis	Reactor condensates		TG-GC/MS		EGA
Atmosphere	Oxidative	Inert	Oxidative	Inert	Inert
Major compounds	Acetic acid*, phenol, p-cresol	Acetic acid*, phenol, p-cresol	2,4 heptadienal, 2,4 decadienal, toluene	acetic acid, toluene	acetic acid, methoxyphenol, toluene
Functional groups**	OA, PD, OO	OA, PD, OO	AL, OO	OA, PD, OO	OA, PD, OO

* Present as major compound in methanol soluble phase of bio-oil

** Other functional groups identified.OA: Organic acids, PD: phenol derivatives, OO: Other oxygenates, AL: Aldehydes.

In TG-GC/MS analysis at oxidative atmosphere, molecules with aldehyde functional group are found, which have no similarity with results in the reactor. Based on this, pyrolysis reactions have been promoted in the reactor even during the oxidative atmosphere. The EGA results are similar to those obtained for the bio-oil produced in the reactor and for the TG-GC/MS at inert atmosphere.

Conclusions

Biochar and bio-oil from thermal treatment of CPH were succesfully characterized. Based on physical properties, the best conditions to obtain biochar were 500°C and inert atmosphere. The biochar does not leach important amounts of metals to water. Based on bio-oil composition, it can be concluded that phenol derivatives and other oxygenates are the main compounds obtained from thermal treatment of CPH.

Acknowledgements

To Chemical Engineering department of University of Alicante and Central University of Ecuador

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