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STUDY OF THE FORMATION OF DIOXINS, FURANS AND PCBS IN THE PRODUCTION OF BIOCHAR AND BIOOIL FROM AGRICULTURAL WASTE

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Introduction

Our modern society generates lot of waste in the form of municipal solid waste or agricultural and forestry residues. Most of them are burned or crushed for their use as a constituent element of roads, parks, sport fields, or filling tree pits in cities. One way to handle this waste is by thermal degradation processes in non-oxidizing atmosphere such as pyrolysis or gasification, which, unlike the combustion, yields higher value fuel with a broader spectrum of use. Pyrolysis is the thermal decomposition of organic matter in the absence of oxygen or with less than the amount needed for a combustion. The aim of the pyrolysis is to obtain a liquid (biooil) from biomass although the process also yields a solid fraction (biochar) and a gas. Variables influencing the pyrolysis of organic matter are final reaction temperature, temperature gradient at which the biomass is transformed, gas flow and reaction time [1]. Depending on the thermal gradient which the sample is subjected to, higher amounts of one or the other phase (biooil and biochar) can be obtained and it determines the type of pyrolysis that is being developed. The main use of biooil is in the energy field. However, it can also be interesting as a raw material for the production of higher value-added products [2,3]. Biochar is the solid carbonaceous residue that remains inside the reactor at the end of the process. It is a very rich solid carbon, which has a broad spectrum of applications ranging from fuel to material for electrodes, through fertilizers and wastewater treatment [4-6]. Due to its high porosity, carbon has a retention capacity of water and nutrients. Moreover, the pyrolysis process, as most thermal processes, can also lead to the formation of pollutants, including polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons [7]. Present work has focused on the possible formation of PCDD/Fs and PCBs in the pyrolytic process.

Materials and methods

Pyrolysis experiments

Four pyrolysis experiments were carried out with hazelnut shells and with the same material spiked with possible precursors of PCDD/Fs and PCBs.

The experiments were performed in a tubular pyrolyzer (27 cm long and 25 mm internal diameter). Nitrogen stream was provided into the reactor to keep it free of oxygen in order to avoid combustion processes. Gases produced during the pyrolysis were evacuated from the reactor and passed through a condenser. Condensed substances were collected in a round flask, while those not condensed were emitted to the atmosphere.

Three fractions were collected in each experiment: (1) solid fraction remaining in the pyrolyzer (biochar), (2) liquid fraction collected from the condensation (biooil), (3) effluent gas passed through XAD-2 resin to evaluate the pollutants in the effluent gas. All the fractions and the raw material used for the experiment were analyzed for PCDD/Fs and PCBs.

The conditions of the experiments were the following:

- Experiment 1: Raw material was dried hazelnut shells. Pyrolysis was performed at 450ºC.
- Experiment 2: Raw material was hazelnut shells spiked with PCB (a mixture of Aroclors). Pyrolysis was performed at 450ºC.
- Experiment 3: Raw material was hazelnut shells spiked with a mixture of chlorophenols and chlorobenzenes with different chlorination degree. Pyrolysis was performed at 450ºC.

- Experiment 4: This experiment was carried out with the same raw material as the experiment 3, but the pyrolysis temperature was 600ºC.

Sample analysis

The main steps of the analytical methodology were the following: (1) addition of $^{13}C_{12}$ labelled internal standards, (2) extraction, (3) clean-up in a multilayer silica column, (4) fractionation in SPE carbon tubes to obtain PCDD/F fraction and PCB fraction, (5) separation of dl-PCBs from the bulk of PCBs by HPLC equipped with a pyrenyl column, (6) concentration of the fractions, (7) instrumental determination by GC-HRMS and (8) quantitation by the isotopic dilution method. Biooil was liquid-liquid extracted with hexane and solid matrixes (raw material, biochar and XAD-2 resin) were extracted with toluene in a Soxhlet equipment.

Results and discussion

The amount of PCDD/Fs and dl-PCBs in the samples obtained in the four experiments are shown in Table 1 (experiment 1 and experiment 2) and in Table 3 (experiment 3 and experiment 4). All the results are expressed as pg in the sample in order to make easy the mass balance.

In all the experiments, biochar samples showed low concentrations of PCDD/Fs and dl-PCBs. Most congeners were below the detection limit. Even in the experiment 2, where PCBs were added to the raw material, less than 0.01% of PCB were remaining in biochar after the pyrolysis. In the same experiment, less than 3% of PCDD/Fs were still in biochar after the process.

The material that accumulated more PCDD/Fs and PCBs was biooil in all the experiments. Probably the reason is that PCDD/Fs and PCBs are semivolatile compounds and, at the pyrolysis temperatures, they are desorbed from the solid material (raw material, biochar), condensed and collected with the other compounds that form biooil. This liquid fraction accumulated between 76% and 97% of total PCDD/Fs detected in the three fractions (solid+liquid+gas), while for PCBs these values ranged between 72% and 89%.

In the experiment n. 2, where a technical mixture of PCB was added, the total amount recovered in the three fractions was 69% of the amount of dl-PCB detected in the spiked raw material. Some losses of PCB could have occurred due to degradation. The other possibility is that XAD-2 resin would not retain completely the pollutants from the effluent gas. For PCDD/Fs, no formation was observed in this experiment.

In the experiment n. 3, a mixture of chlorophenols and chlorobenzenes was added to hazelnut shells. These compounds have been reported to be precursors of PCDD/F formation. An increase of PCDD, especially penta-, hexa- and heptachlorinated congeners, was observed, from 99.8 pg in the raw material to 436 pg in biooil fraction. However, for PCDF no increase was detected. The amount of dl-PCB was also increased, from 224 pg in the raw material to 382 in the biooil. It seems that the presence of chlorophenols and chlorobenzenes is related to the formation of PCDD, although the process performed is not a combustion, but a pyrolytic process.

In the experiment n. 4, the raw material was the same as for the experiment n. 3. The difference between these two experiments was the pyrolysis temperature: in n. 3 maximum temperature was 450ºC, while in n. 4 temperature rose until 600ºC. The formation of dioxins was similar (407 pg in the biooil fraction), while for dl-PCB was less than in experiment n.3.

References

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Table 1. Amount (pg) of PCDD/Fs and dl-PCB detected in the experiments 1 and 2.

	Experiment 1				Experiment 2			
Congener	**Raw material (pg)**	**Biochar (pg)**	**Biooil (pg)**	**XAD-2 (pg)**	**Raw material (pg)**	**Biochar (pg)**	**Biooil (pg)**	**XAD-2 (pg)**
2,3,7,8-TCDF	8,06	0,49	6,23	0,35	9,25	0,42	7,28	0,84
1,2,3,7,8-PeCDF	1,29	<LOD	1,14	0,30	1,67	<LOD	2,04	0,37
2,3,4,7,8-PeCDF	3,49	<LOD	1,46	<LOD	5,53	<LOD	4,13	0,48
1,2,3,4,7,8-HxCDF	4,76	0,23	1,73	0,16	12,8	0,33	8,04	0,75
1,2,3,6,7,8-HxCDF	2,40	<LOD	0,75	<LOD	3,43	<LOD	3,57	0,35
2,3,4,6,7,8-HxCDF	2,99	<LOD	0,77	<LOD	4,23	<LOD	2,55	<LOD
1,2,3,7,8,9-HxCDF	<LOD	<LOD	<LOD	0,37	1,79	0,48	1,13	0,50
1,2,3,4,6,7,8-HpCDF	6,44	0,40	1,54	0,36	13,1	0,34	11,3	1,77
1,2,3,4,7,8,9-HpCDF	0,92	<LOD	<LOD	<LOD	3,26	<LOD	1,08	<LOD
OCDF	2,17	<LOD	<LOD	<LOD	21,8	<LOD	6,09	2,66
2,3,7,8-TCDD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
1,2,3,7,8-PeCDD	0,59	<LOD	<LOD	<LOD	0,66	<LOD	<LOD	<LOD
1,2,3,4,7,8-HxCDD	0,42	<LOD	<LOD	<LOD	0,54	<LOD	<LOD	<LOD
1,2,3,6,7,8-HxCDD	0,93	<LOD	0,47	<LOD	0,99	<LOD	<LOD	<LOD
1,2,3,7,8,9-HxCDD	0,71	<LOD	0,64	<LOD	1,07	<LOD	<LOD	<LOD
1,2,3,4,6,7,8-HpCDD	4,94	0,58	2,69	0,62	4,26	<LOD	3,06	1,01
OCDD	11,6	1,24	5,77	2,11	18,7	1,44	7,71	2,81
Total furans	32,5	1,12	13,6	1,54	76,8	1,6	47,2	7,7
Total dioxins	19,2	1,81	9,56	2,73	26,2	1,4	10,8	3,8
Total PCDD/F	51,7	2,93	23,2	4,27	103	3,0	57,9	11,5
PCB 81	<LOD	<LOD	5,30	<LOD	6615	<LOD	4895	802
PCB 77	11,2	2,71	21,5	2,45	16743	<LOD	10275	1107
PCB 123	<LOD	<LOD	4,98	<LOD	10823	<LOD	8442	1343
PCB 118	107	37,6	152	33,3	252968	20.6	149293	18708
PCB 114	<LOD	<LOD	<LOD	<LOD	8251	<LOD	4881	557
PCB 105	49,7	13,5	68,6	11,3	118576	8.45	66514	7039
PCB 126	3,49	<LOD	<LOD	<LOD	962	<LOD	553	83,1
PCB 167	8,10	2,80	8,01	<LOD	18472	2,20	10391	1120
PCB 156	19,3	5,03	19,2	3,35	47391	6,56	28543	2823
PCB 157	4,17	<LOD	2,75	<LOD	7340	<LOD	4279	382
PCB 169	2,21	<LOD	<LOD	<LOD	15,8	<LOD	38,2	3,59
PCB 189	4,17	0,78	2,59	0,64	7376	3,61	4186	345
Total dlPCB	210	62,5	285	51,0	495533	41,4	292292	34313

Table 2. Amount (pg) of PCDD/Fs and dl-PCB detected in the experiments 3 and 4.

	Experiment 3				Experiment 4			
Congener	**Raw material (pg)**	**Biochar (pg)**	**Biooil (pg)**	**XAD-2 (pg)**	**Raw material (pg)**	**Biochar (pg)**	**Biooil (pg)**	**XAD-2 (pg)**
2,3,7,8-TCDF	7,63	0,57	6,60	<LOD	7,63	<LOD	2,70	<LOD
1,2,3,7,8-PeCDF	1,34	<LOD	2,29	<LOD	1,34	<LOD	1,71	0,25
2,3,4,7,8-PeCDF	2,29	0,40	2,05	<LOD	2,29	<LOD	0,92	<LOD
1,2,3,4,7,8-HxCDF	3,57	0,51	2,66	<LOD	3,57	<LOD	1,34	<LOD
1,2,3,6,7,8-HxCDF	2,46	<LOD	1,69	<LOD	2,46	<LOD	1,17	<LOD
2,3,4,6,7,8-HxCDF	2,06	<LOD	4,80	<LOD	2,06	<LOD	4,16	<LOD
1,2,3,7,8,9-HxCDF	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
1,2,3,4,6,7,8-HpCDF	11,2	<LOD	16,9	0,85	11,2	<LOD	16,6	0,52
1,2,3,4,7,8,9-HpCDF	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
OCDF	69,4	<LOD	16,3	<LOD	69,4	<LOD	10,3	<LOD
2,3,7,8-TCDD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	4,29	<LOD
1,2,3,7,8-PeCDD	<LOD	<LOD	15,6	<LOD	<LOD	<LOD	26,2	0,47
1,2,3,4,7,8-HxCDD	<LOD	<LOD	24,2	1,27	<LOD	<LOD	26,7	0,47
1,2,3,6,7,8-HxCDD	7,05	<LOD	76,2	4,16	7,05	<LOD	74,8	1,19
1,2,3,7,8,9-HxCDD	1,17	<LOD	62,3	1,97	1,17	<LOD	50,0	0,88
1,2,3,4,6,7,8-HpCDD	13,8	<LOD	224	9,65	13,8	0,23	201	4,51
OCDD	77,8	1,30	32,8	2,40	77,8	<LOD	24,5	3,97
Total furans	99,9	1,48	53,3	0,85	99,9	<LOD	38,8	0,77
Total dioxins	99,8	1,30	436	19,5	99,8	0,23	407	11,5
Total PCDD/F	200	2,78	489	20,3	200	0,23	446	12,3
PCB 81	2,70	<LOD	6,30	<LOD	2,70	<LOD	3,28	<LOD
PCB 77	18,2	<LOD	26,4	3,60	18,2	<LOD	13,8	<LOD
PCB 123	1,39	<LOD	3,77	<LOD	1,39	<LOD	<LOD	<LOD
PCB 118	91,2	9,71	182	32,8	91,2	10,3	94,6	21,0
PCB 114	2,31	<LOD	4,59	<LOD	2,31	<LOD	6,05	<LOD
PCB 105	39,9	3,54	83,6	12,5	39,9	3,36	42,1	7,97
PCB 126	5,76	<LOD	5,21	<LOD	5,76	<LOD	<LOD	<LOD
PCB 167	7,56	<LOD	12,9	2,15	7,56	<LOD	6,79	<LOD
PCB 156	15,6	<LOD	27,9	4,61	15,6	<LOD	15,9	2,64
PCB 157	32,7	<LOD	23,0	2,05	32,7	<LOD	15,8	<LOD
PCB 169	3,19	<LOD	2,22	<LOD	3,19	<LOD	<LOD	<LOD
PCB 189	3,20	<LOD	4,02	0,6	3,20	<LOD	2,38	<LOD
Total dlPCB	224	13,3	382	58,4	224	13,6	201	31,6