SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

The STSM applicant submits this report for approval to the STSM coordinator

Action number: CM1404
STSM title: Organization meeting for the activity on the production of biofuels through pyrolysis
STSM start and end date: 18/04/2018 to 24/04/2018
Grantee name: Paola Giudicianni

PURPOSE OF THE STSM/

The mission will be focused on the planning of the future experimental activity on biomass pyrolysis. The work relates to a research program aimed at studying the pyrolysis as eco-sustainable process for the combined production of a solid residue (char) and gaseous-liquid combustible fractions, embedded in the gas carrier flow, to be directly burned in a MILD combustion burner (hence in highly diluted and pre-heated conditions) for energy recovery.

The process raises some concerns when biomass from phytoremediation is used as feedstock, since it could contain potential toxic elements (PTEs). Pyrolysis could represent an environmentally sustainable strategy capable to reduce the volume and weight of contaminated matter with respect to the original biomass; concentrate the PTEs in the solid product and produce a vapor phase heavy metal free energy carrier. The choice of the proper operating conditions should take into account both the release of the PTEs during the pyrolysis process and the physico-chemical properties of the residual char including also the stability of PTEs retained in the char.

The activity is motivated by the need of a more fundamental understanding of the transformations of the solid matrix occurring during the pyrolysis process with a special focus on the inorganic matrix (inherent or deriving from soil contamination). The knowledge of the fate of heavy metals deriving from soil contamination is important in the application of the vapor phase as fuel because heavy metals belong to PTEs classification and pose environmental concerns. At the same time, the chemical form and the mobility of these elements in the char is fundamental for the identification of possible application fields.

Trough STSM, the visit of the modern laboratory equipment for the detailed physical, chemical and morphological characterization of inorganic materials available at the hosting institute will be performed with the aim of defining a detailed plan of the future experimental activity on the lab scale pyrolyser available at Istituto di Ricerche sulla Combustione in Naples.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The first 2 days of the STSM were dedicated to the visit of the experimental facilities available at the host institution. In particular the attention was focused on a lab scale reactor devoted to the catalytic fast pyrolysis tests for the screening of new catalysts to be used in the pilot scale pyrolyser. The reactor allows to perform fast pyrolysis tests with in-situ catalysis and to collect at the end a bio-oil with improved characteristics (lower oxygen content, lower viscosity). The laboratory is equipped with analytical instruments for the characterization of the biomass and of the pyrolysis products, namely char, gas and liquid, such as CHNSO analyser, ICP/EOS, XRD, FTIR spectrometer, gaschromatograph coupled with mass spectrometer. In particular, during the stay ICP/MS and XRD analyses were performed on:

- 4 biomasses (Branches and leaves from Populus nigra and culms and rhyzomes from Arundo donax) from phytoremediation of soils contaminated with heavy metals, namely Pb, Zn, Cu and Cd.

- Chars previously produced at different pyrolysis temperatures in the pyrolyser available at IRC-CNR.

In the two next days a discussion with the prof. George Skevis and his co-workers, followed aiming at identifying possible collaboration routes among the research groups involved in biomass pyrolysis studies for bio-oil and bio-char production.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

The ICP/EOS analyses provided information on the initial contamination of the biomass and on the amounts of heavy metals retained in the chars produced at different final temperatures. This characterization allowed to identify the maximum pyrolysis temperature at which the biomass can be processed without the release of heavy metals in the vapour phase and, consequently, in the bio-oil. In tables 1 and 2 the results of ICP/EOS analyses are reported. By considering the yields of chars and calculating the ratios between the amounts of each heavy metal retrieved in the chars and the amount in the corresponding feedstock, it can be argued that the devolatilization of Cd started al temperatures higher than 653 K and is completed at 873 K. On the contrary, Pb, Zn and Cu are more stable and their recovery at 873 K is about 0.8.

Ash composition *mg/kg db*									
Populus nigra									
	branches					*leaves*			
	Feedstock	**613**	**653**	**753**	**873**	*Feedstock*	**653**	**753**	**873**
Na	206	415	882	351	634	573	1223	1912	2023
Al	248	271	179	448	379	1854	2081	2582	4654
P	468	885	974	1822	3074	1088	1899	2300	2614
K	4477	12069	9844	16155	21935	3596	6966	8343	9487
Mg	836	2201	2305	3694	4407	2325	4439	5256	5627
Ca	9407	25410	26985	42195	44000	37500	71795	99605	102760
Si	132	112	-	152	362	783	715	983	952
Fe	58	230	280	624	868	39	603	1096	952
Cd	2	6	6	1	0.4	10	16	1	0.3
Cu	8	22	15	28	37	63	7	101	132
Pb	60	174	207	403	192	423	520	779	857
Zn	50	75	98	204	155	118	173	240	272

Table 1: Ash composition of branches and leaves of Populus nigra and of the corresponding chars obtained at 613, 653, 753, and 873 K.

Ash composition *mg/kg db*								
Arundo donax								
	rhizomes				*culms*			
	Feedstock	**703**	**753**	**873**	*Feedstock*	**703**	**753**	**873**
Na	266	911	1013	1803	258	557	628	635
Al	2317	2575	6480	9268	28	72	91	94
P	3458	7019	8673	10010	3182	6590	7957	8514
K	13566	28635	17350	38900	9052	16660	20257	20870
Mg	1194	2202	2605	3292	818	1597	1985	2003
Ca	1440	3602	4953	7322	540	1434	1504	1482
Si	-	798	-	-	43	-	596	492
Fe	2289	1907	2375	3682	87	97	106	121
Cd	0.3	0.5	0.17	0.05	0.15	0.44	1	0.2
Cu	8	18	18	28	4.32	11	13	15
Pb	17	26	26	38	0.4	1	1	1
Zn	140	255	323	406	87	187	234	247

Table 2: Ash composition of rhizomes and culms and of the corresponding chars obtained at 703, 753, and 873 K.

XRD analyses were performed in order to monitor possible chemical transformations involving heavy metals during pyrolysis. Unfortunately, the concentrations of heavy metals in the biomasses and in the chars were lower than the detection limit of the instrument. XRF analyses are needed to shed light on this aspect.

FUTURE COLLABORATIONS (if applicable)

On the basis of the information acquired during the visit of the experimental facilities and the further discussion, the activities that could be conducted in the next future were planned.

An interesting topic of investigation could be the comparison between slow and fast pyrolysis of both clean and contaminated biomasses in order to study the effect of heating rate on bio-oil and biochar characteristics, and on heavy metal devolatilization.

CENTRE FOR RESEARCH AND TECHNOLOGY HELLAS
CHEMICAL PROCESS AND ENERGY RESOURCES INSTITUTE
6th km Charilaou-Thermi Rd • 570 01 Thermi, Thessaloniki
Tel: 2310 498 112 • Fax: 2310 498 130
web: http://www.cperi.certh.gr • E-mail: cperi@cperi.certh.gr

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To Whom It May Concern

I hereby confirm that Dr. Paola Giudicianni, Institute of Research on Combustion - CNR, Naples, Italy, has spent 6 days (from 18-04-2018 to 24-04-2018) at the Chemical Process & Energy Resources Institute (CPERI) of the Centre for Research & Technology Hellas (CERTH) within the framework of a Short Term Scientific Mission (STSM) under the SMARTCATs COST Action CM1404.

Some of the analytical tools available at CPERI, namely ICP/EOS and XRD, where used for the investigation of heavy metals behavior during pyrolysis of contaminated biomasses for bio-oil and biochar production. Moreover, an interesting topic of investigation was identified coupling the potentialities of the different experimental facilities present at the two reference institutes. A possible topic of investigation could be the comparison between slow and fast pyrolysis of both clean and contaminated biomasses in order to study the effect of heating rate on bio-oil and biochar characteristics, and on heavy metal devolatilization.
I approve the scientific report of the STSM.

I believe that there are plenty of opportunities to promote the collaboration between the two institutes also on other topics concerning biofuel production and utilization.

George Skevis PhD DIC
Principal Researcher
CPERI/CERTH