CONSIGLIO NAZIONALE DELLE RICERCHE

ISTITUTO DI RICERCHE SULLA COMBUSTIONE

to:
Management Committee Members
SMARTCATs COST Action
CM1404

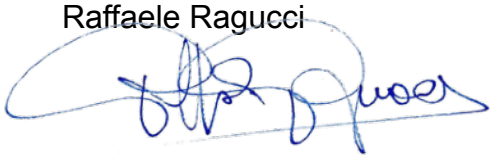
Object : Support Letter for a STSM application presented by Corinna Maria Grottola

Dear Management Committee Members,

As scientific supervisor of Dr Corinna Maria Grottola at the Institute of Research on Combustion of the Italian National Research Committee (IRC-CNR), Naples, Italy, I express my full support to the application she has presented for a Short Term Scientific Mission (STSM) in the framework of COST ACTION CM 1404 - Chemistry of Smart Energy Carriers and Technologies (SMARTCATS). The scientific mission programmed, from 15th April to 21st April 2018, at the Centre for Research and Technology Hellas – CERTH, Thessaloniki, Greece, under the supervision of Dr George Skevis, will be focused on “Investigation on the formation of inorganic polluntants from contaminated biomass pyrolysis”. In my opinion the scientific program, attached to the grant application, is well in line with the aims of the Action and the timing are fully compatible with the current commitment of Corinna at IRC-CNR.

Naples, April 10th, 2018

sincerely,
Raffaele Ragucci



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SMARTCATs Management Committee
c/o Istituto di Ricerche sulla Combustione
Consiglio Nazionale delle Ricerche
P.le Tecchio n°80, 80125, Napoli
Italy

Thessaloniki, 09 April 2018

Re: Confirmation to host Dr Corinna Maria Grottola, Institute for Research on Combustion-CNR, within the SMARTCATs STSM

Dear Management Committee,

I hereby confirm our full support to host Dr Corinna Maria Grottola, Institute for Research on Combustion – CNR, Italy, for a scientific visit at the Chemical Process and Energy Resources Institute of the Centre for Research and Technology Hellas – CERTH, Thessaloniki, Greece within the framework of a Short Term Scientific Mission under the SMARTCATs COST Action CM1404. During her stay, we will collaborate on the research activity dealing with the production of inorganic contaminants during biomass torrefaction and pyrolysis.

Dr Grottola will have access to the CPERI/CERTH experimental infrastructures necessary to successsfully carry out her work. Both groups will benefit from this visit that will strengthen our scientific collaboration.

Yours sincerely,

George Skevis PhD DIC
Principal Researcher

SHORT TERM SCIENTIFIC MISSION (STSM) – SCIENTIFIC REPORT

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

Action number: CM1404
STSM title: Investigation on the formation of inorganic pollutants from contaminated biomass pyrolysis
STSM start and end date: 15/04/2018 to 21/04/2018
Grantee name: Corinna Maria Grottola

PURPOSE OF THE STSM/

Phytoremediation is a viable technique for the restoration of contaminated soils. To implement phytoremediation properly, a plan for the safe disposal of the contaminated plant material after harvesting is required. Composting and compaction have been proposed as post-processing treatments, as both are capable of greatly reducing the volume of the harvested biomass. Nevertheless, the high solubility of heavy metals in the leachate from these processes warrants additional treatments to ensure their appropriate collection and disposal. A more appealing approach consists of utilizing of the contaminated plant material as feedstock in a bio-based energy and/or material supply chain. Pyrolysis can be explored as a possible thermal treatment capable of producing, in the absence of molecular oxygen, a solid residue (char) suitable for application in several fields (as a fertilizer, activated carbon, etc.) and a liquid (bio-oil) and gaseous products that can be exploited for energy applications.

The activity that will be conducted during the STSM 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 severe 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.

The mission will be focused on the characterization of the behaviour of the inorganics contained in the contaminated biomasses during pyrolysis, with a special focus on specific heavy metals. The chemical transformations of some heavy metals during pyrolysis will be monitored by analysing chars produced from different biomasses and at different temperatures in a lab scale pyrolyzer available at the home institution. The analysis will be performed using the modern laboratory equipment for the detailed physical, chemical and morphological characterization of inorganic materials available at the host institution.

The aim is to correlate the pyrolysis operating conditions to the chemical transformations of these PTEs and to their release in the vapour phase. This study is of great importance in defining the operating conditions of an integrated pyrolysis/combustion system in which the biomass is processed for the combined production of a material (char) and of a vapour phase fuel for energy production.

DESCRIPTION OF WORK CARRIED OUT DURING THE STSMS

The characterization and the determination of the inorganic fraction in the solid produced is fundamental for understanding the correlation between the effect of the pyrolysis temperature on the volatilization of the inorganic species and their transformation after the treatment. The content of major inorganic elements in the biomass and in the chars produced at different pyrolysis temperatures was determined by dissolving the samples via microwave-assisted acid digestion based on US-EPA Methods 3051 and 3052. A representative sample was dissolved in 10 ml 65% nitric acid and 1.5 ml H2O2. The vessel was sealed and heated in the microwave unit at 140 °C for 10 min, then 180 °C for 30 min. After they were cooled, the digested samples were analysed by inductively coupled plasma mass spectrometry (ICP/ MS) using an Agilent 7500CE instrument. XRD analysis for the identification of surface elements of the biomass and chars, was performed with the Siemens D-500 x-ray diffractometer with the scanning angle (2ϴ) varying from 10 ° to 80°.

DESCRIPTION OF THE MAIN RESULTS OBTAINED

In Table 1 reports the concentrations of the major inorganic elements in the *Populus nigra* leaves and chars produced at different pyrolysis temperatures. The leaves were characterized by the high concentration of contaminants as well as the other detected inorganics. The most abundant species detected was the Ca followed by K, Al, and Mg. It should be noted that the pyrolysis temperature affected the metal accumulation in the chars except for the Cd. The highest Cd concentration was obtained at 653 K, above this temperature, the amount was strongly decreased in the chars. Meanwhile, for the others metal the concentration increase with the temperature.

A great amount of Ca was observed in the char obtained at T= 873 K, which concentration increased approximately threefold in comparison with the feedstock. This accumulation was also observed for K and P.

Ash composition

mg/kg db

Populus nigra: leaves				
	biomass	***char***		
	PL	**PL653**	**PL753**	**PL873**
Na	573	1223	1912	2023
Al	1854	2081	2582	4654
P	1088	1899	2300	2614
K	3596	6966	8343	9487
Mg	2325	4439	5256	5627
Ca	37500	71795	99605	102760
Si	783	715	983	952
Fe	39	603	1096	952
Cd	10	16	1	0.3
Cu	63	7	101	132
Pb	423	520	779	857
Zn	118	173	240	272

Tab.1: Ash composition of leaves and corresponding chars produced at different temperatures

However, this metal was also detected from the patterns obtained from the XRD analysis. The comparison of X-ray diffraction spectra of the feedstock and chars produced at different is shown in Figure 1 and Figure 2.

Although all the chars had analogous diffractogram patterns, some differences were noted among the samples. The broad peak situated at approximately 20° and 45° represents the main carbon compound bands, as reported in Figure 1.

Calcium Oxalate Monohydrate ($C_2CaO_4•H_2O/CaC_2O_4•H_2O$) was the relevant species present in the raw material and in the char produced at low temperature. The effect of the temperature on chars was clearly evident on chars produced at a higher pyrolysis temperature, as shown in Figure 2. The temperature led to a decomposition of the $C_2CaO_4•H_2O/CaC_2O_4•H_2O$ compound in Calcite ($CaCO_3$), which broad peaks were situated in the angle range ❨❩= 25°-55 °, and minor approximately ❨❩ = 55°-75°.

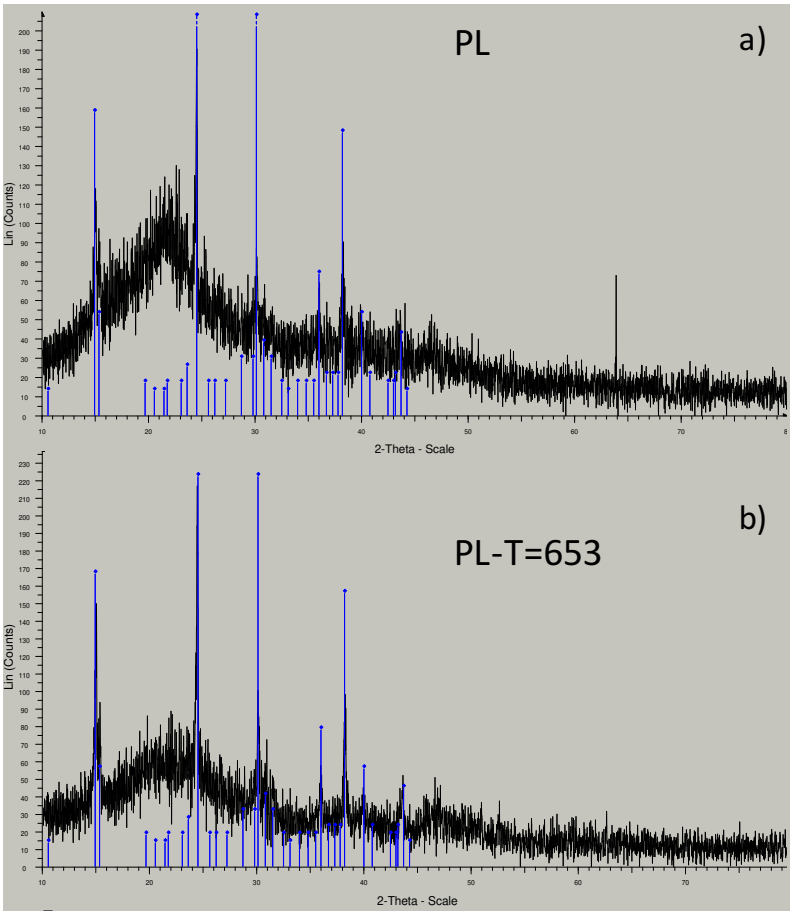

Fig.1: XRD patterns of *Populus leaves* (PL) panel “a” and char produced at T=653 K (PL-653) panel “b”.

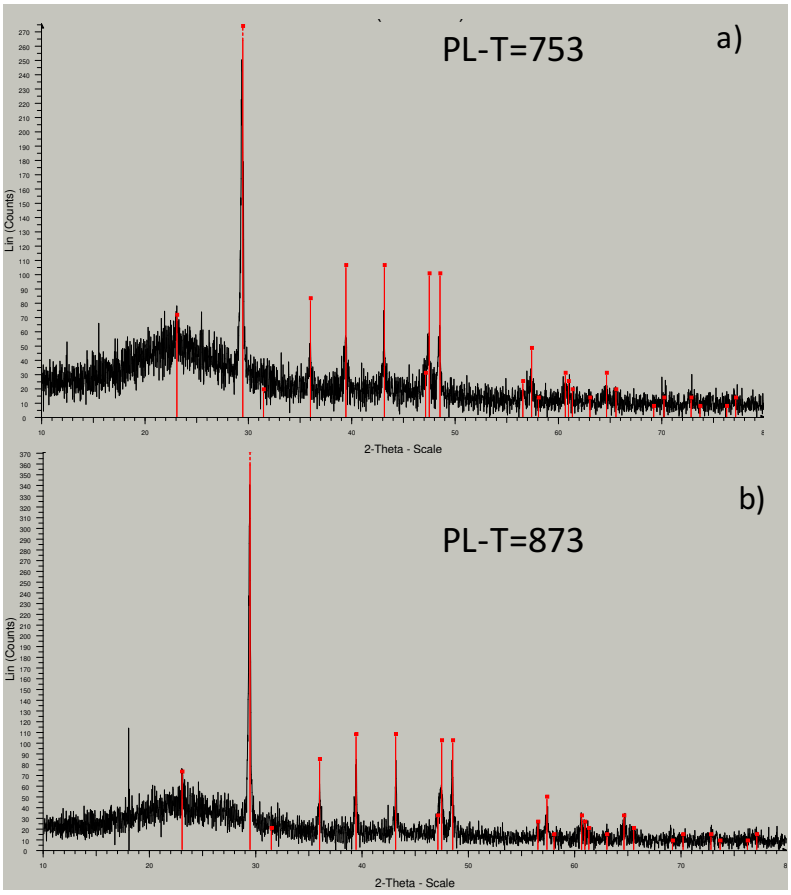

Fig.2: XRD patterns of char produced at T=753 K (PL-T=873 K) panel “a” and char produced at T=873 K (PL-T= 653 K) panel “b”.

This compound was useful to produce stable carbonate compounds. The fraction of Ca in char was clearly affected by the pyrolysis temperature.

FUTURE COLLABORATIONS (if applicable)

The collaboration between the IRC-CNR of Naples and CPERI/CERTH will be a good opportunity to obtain interesting advances and results concerning the application of contaminated chars. Both institutes have a solid background that will enable further study and the possibility of biochar valorization through the pyrolysis process performed in a large-scale reactor.

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Thessaloniki, 29 April 2018

To Whom It May Concern

I hereby confirm that Dr. Corinna Maria Grottola, Institute of Research on Combustion - CNR, Naples, Italy, has spent 5 days (from 16-04-2018 to 20-04-2018) 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.

The content of the visit was directly relevant to the CM1404 action aims. The planned activity was very important for the definition of the potential utlization of biochars. The characterization of the inorganic fraction in the solid matrix is fundamental for understanding the correlation between the operating conditions of the pyrolysis unit and the release of inorganics in the vapor phase with the aim of producing a heavy metal free biofuel and to provide a database for assessing control strategies for the mitigation of inorganic pollutant formation and emission.

The collaboration between the IRC-CNR of Naples and CPERI/CERTH will be a good opportunity to obtain interesting advances and results concerning the application of contaminated chars. Both institutes have a solid background that will enable further study and the possibility of biochar valorization through the pyrolysis process performed in a large-scale reactor.

George Skevis PhD DIC
Principal Researcher
CPERI/CERTH