

# A GLOBAL ENVIRONMENTAL STRATEGY: FROM SOIL DEPOLLUTION TO MATERIALS VALORISATION WITH SUPERCRITICAL WATER

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## ABSTRACT

Supercritical water is an interesting medium to face the energy problems. Biomass supercritical gasification or liquefaction are both routes towards biomass valorisation. The first process leads to the formation of syn-gas to produce heat or electricity, for instance. The second one can allow to produce biofuel or even more valuable chemicals [1].

Our research works are relevant for the problematic of biomass valorisation in connection with an environmental target.

Regrettably the surface of polluted soils with hazardous metals and metalloids is enormous in Europe. Some researchers have finalised the use of plants which are able to accumulate these metals and/or metalloids in their roots or aerial parts with a high efficiency [2]. The problem is today to treat such plant biomasses, several containing high metal/metalloid concentrations.

Supercritical water is able to react with all of the biomass constituents, *i.e.* cellulose, hemicellulose, and lignin [3,4].

This communication presents results about the behaviour of plant biomass from contaminated sites under phytoremediation in supercritical water either to produce low molecular weight organic polymers (polyholosides, hydrocarbons,...) or some gases with the possibility to recover the inorganic elements. This study will focus on the influence of the operating conditions (p, T ...) on the composition of reaction products (gases, liquids, solids) in order to determine possible routes towards valorisation.

**KEYWORDS:** supercritical water gasification, supercritical water liquefaction, biomass, phytoremediation, soil metal contamination

## INTRODUCTION

European Union and other countries have considerable legacies of soils affected by trace element contamination arising from past land use, industrial activities (mining, smelting, manufacturing emissions), recycling of organic matter (sewage sludges) and diffuse sources (applications of fertilisers, slurries). This often presents a risk to a range of receptors including humans, ecosystems, biodiversity, water quality, and property including crops and animals. Current and future use of the soil may be adversely affected. Uncertainty of such potential risks may inhibit the development or redevelopment of land, and may contribute to long-term dereliction and increasing pressure to develop greenfield land. Technical obstacles as well as potentially large costs mean that it is often neither feasible nor realistic to think in terms of total clean-up of past damage. Instead, the goal is to find solutions that identify and deal with risks from contamination in a sustainable way [5]. The

management of contaminated sites has moved from a cost-centred approach in the mid-1970s, through the technology feasibility studies of the mid-1980s, the risk-based approaches of the mid-1990s and into a new millennium where environmental decisions must be 'socially-robust' within a context of sustainable development [6]. All these efforts were to ensure management and/or remediation is affordable, feasible, effective and latterly sustainable. In response to trace element contaminated soils, a variety of physicochemical remediation methods has been adopted, including solidification, electrokinetics and encapsulation [7]. In many cases, these strategies have resulted in criticisms in regards to their high cost, energy intensiveness, site destructiveness, associated logistical problems and growing degree of public dissatisfaction [8]. The implementation of alternative, gentle strategies that address these concerns is critical in effectively removing trace elements from soil or the risk(s) for receptors.

Phytoremediation is the name given to a set of technologies that use plants (or plant-microbe associations) to remediate contaminated sites. Phytoremediation uses living plants for in situ and ex situ remediation of contaminated soils, sludges, sediments and ground waters through contaminant removal, degradation or stabilization. Phytoremediation can be used to remediate various contaminants including trace elements, pesticides, solvents, explosives, petroleum hydrocarbons, polycyclic aromatic hydrocarbons and landfill leachates [7,9,10,11]. Phytoremediation has been used for point and nonpoint source hazardous waste control. It receives a great deal of attention from regulators, consultants, responsible parties, and stakeholders as it has become an attractive alternative to other clean up technologies due to its relatively low cost potential effectiveness and the inherently aesthetic nature of using plants to clean up contaminated sites. The accumulation of contaminants/waste in the plants however may present a problem with contaminants entering the food chain (e.g. herbivory) or cause the plants to become a waste disposal issue. Consequently the relative concentrations of contaminants in the plant tissue must be determined, and proper harvest and disposal methods must be developed and approved by regulatory agencies. One option is to valorise the plant biomass to face energy and global change problems. Biomass supercritical gasification and liquefaction are both routes for valorising plant biomass. The first process results in the formation of syn-gas to produce *e.g.* heat or electricity. The second allows to produce biofuel or even more valuable chemicals. However the feasibility of such options is still in its infancy. The organic composition and trace element concentrations of the biomass may interact on the processes and these points must be addressed.

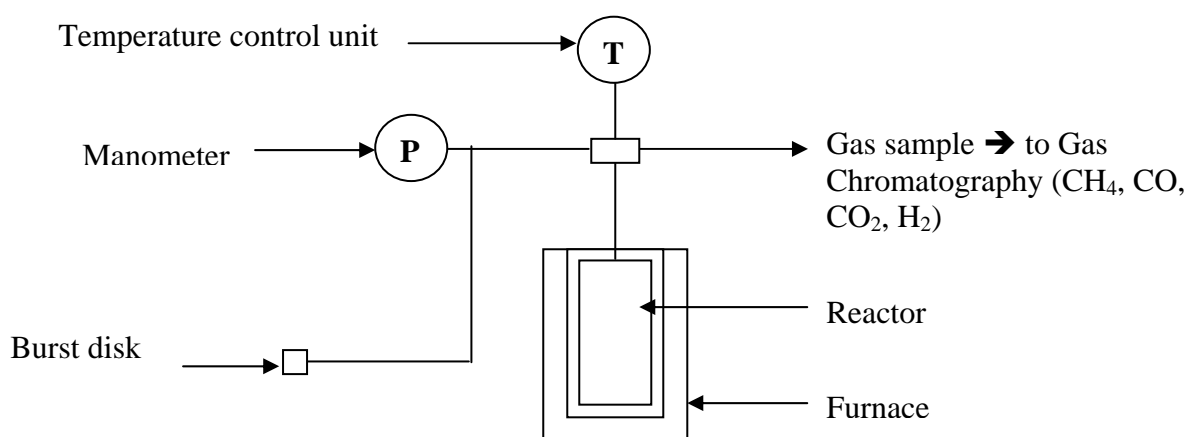
Our paper concerns the valorisation of such plant biomass, some being contaminated in case of hyperaccumulators, in supercritical water. First we focus on initial characterisation of biomass in order to understand its behaviour regarding operating conditions. Secondly, we give details about the supercritical process. Experimental and analytical results on the biomass degradation will be communicated during the oral presentation, particularly the behaviour of the biomass during the process and the identification of final products.

## **MATERIALS AND METHODS**

### **1. Experimental Setup**

Experiments were carried out in a titanium based batch autoclave (inner volume of 270 mL), with an outer diameter of 85 mm and an inner diameter of 51 mm (Figure 1).

For each experiment, biomass and water in different proportions were loaded in the reactor. Argon gas was used to remove the residual air in the autoclave. Then the reactor was heated to the wanted temperature. At the end, the reactor was cooled to room temperature under atmospheric conditions. After cooling, the amount of gases was measured and the separation of liquid and solid phases by filtration was made. Samples of the gaseous, liquid and solid products were analyzed.



**Figure 1: Schematic diagram of the experimental setup.**

## 2. Material

Real biomass used in this work is the fern *Pteris vittata* L. which is extremely efficient in extracting arsenic from soils and translocating it into its above-ground biomass. This plant has many attributes that recommend it for use in the remediation of arsenic-contaminated soils [7,28].

## 3. Analysis

### *Biomass and solid phase*

The elemental analysis and particle size of initial biomass were investigated with a CHNS-O Analyzer model 2400 from PerkinElmer and a laser Malvern 2000S respectively.

The thermogravimetric behaviour of biomass was studied in a TAG 2400 Setaram thermobalance which was coupled to a thermostar Balzers quadrupole mass spectrometer. The ion source was operated at 70 eV. To avoid heat and mass transfer limitations, sample masses between 5 and 10 mg were used, an argon flow of 2 L h<sup>-1</sup> and a low heating rate of 5 °C min<sup>-1</sup>. The samples were heated from room temperature up to 700 °C, where they remained for 30 min. Mass loss and rate were continuously recorded under these conditions.

Trace element concentrations in initial biomass and solid phase were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis.

Particulate Organic Carbon (POC) content was performed on a LECO CS 125 analyzer. The filters were decarbonated with HCl 2 N and dried for 24 h. ICP-AES analysis was carried out on a Varian 720-ES instrument. Concentrated nitric acid (10 mL) was added to an amount of 10 mg of solid sample, the solutions were heated to 110 °C for 1 hour. After the solution had cooled, hydrogen peroxide (2 mL) was added, and the solution again was heated to 110°C. Samples were cooled to room temperature, transferred to 100 mL volumetric flasks, and made up to the mark with distilled water. The digests were then filtered through 200 µm stainless railing.

### *Gas phase*

Analyses of the N<sub>2</sub>, CO, CO<sub>2</sub>, CH<sub>4</sub> and light hydrocarbons were accomplished with a Varian model STAR 3600 CX gas chromatograph with thermal conductivity detectors. The carrier gas was helium and carrier gas pressure was 80 psi. To determine the hydrogen content, a Varian model CP-4900 micro gas chromatograph.

### *Liquid phase*

The residual Total Organic Carbon (TOC) was measured by a Shimadzu 5050A instrument. TOC and ICP-AES analyses were performed on liquid products too. Moreover, GC-MS will be used in order to detect and to quantify the presence of different products in the liquid phase such as sugars, furfurals and phenols, which were identified in further studies on supercritical treatment of model

molecules (cellulose, glucose, lignin) [12,13,14,15,16] and real biomass [17,18,19]. Trace elements were quantified by ICP analysis in the aqueous phase.

## RESULTS AND OBJECTIVES

### 1. Initial characterization of biomass

This initial characterisation of biomass materials is necessary in order to evaluate their suitability as chemical feedstock in different valorisation processes. This explains why we present analyses on the studied biomass, the fern *P. vittata*. The elemental analysis is particularly important in evaluating the feedstock in terms of heating value and of potential technical problems like reactor slagging and potential pollution problems. Moreover the heteroatom quantification should be an evaluation of the efficiency of the phytoremediation process with the amount of arsenic particularly and will be also necessary to study the behaviour of trace elements during the supercritical process.

#### *C,H,N,S-O determination and metal concentrations*

Table 1 gives the elemental analysis of the fern *P. vittata*. The granulometric analysis shows a relative homogeneous particle size distribution at around 300  $\mu\text{m}$ . The high ash content is probably due to the fast growing of this fern sample [20]. The results confirm the arsenic hyperaccumulation behaviour of *Pteris vittata* fern corresponding to 0.12 wt.% of dry biomass (Table 2) [21]. Fern fronds frequently contain only 0.03 wt.% of arsenic species.

**Table 1: Biomass characteristics.**

Granulometry Volume (%)	Residual moisture (wt.%)	Ash (wt.%)	C	H	N	S	O (from difference) (dry, wt. %)
294-310 $\mu\text{m}$	1.4	33.5	43.8	5.6	1.4	1.3	43.4

**Table 2: Element concentrations in dry biomass.**

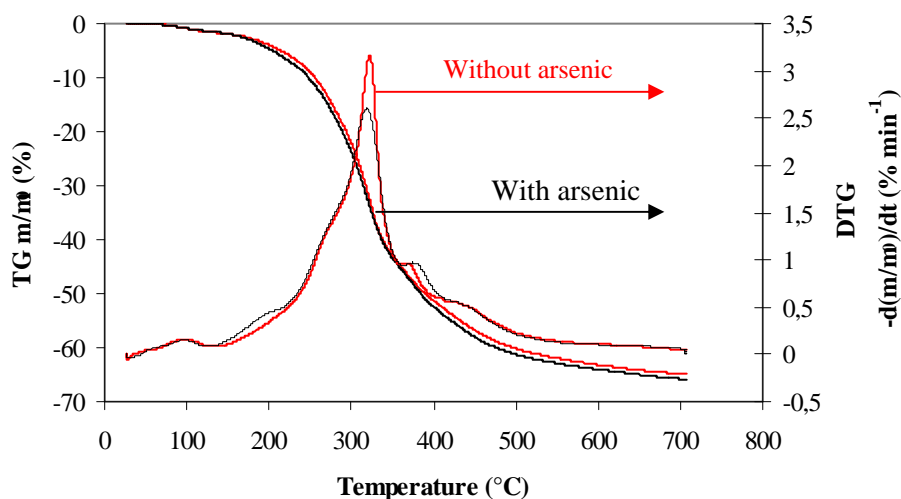
Elements	As	Cd	Ca	K	Mg	P	Fe
Amount (dry, $\text{mg kg}^{-1}$ )	1173	368	15907	13361	5813	7372	657
Amount (dry, wt. %)	0.12	0.04	1.61	1.36	0.59	0.75	0.07

#### *Thermogravimetry analysis:*

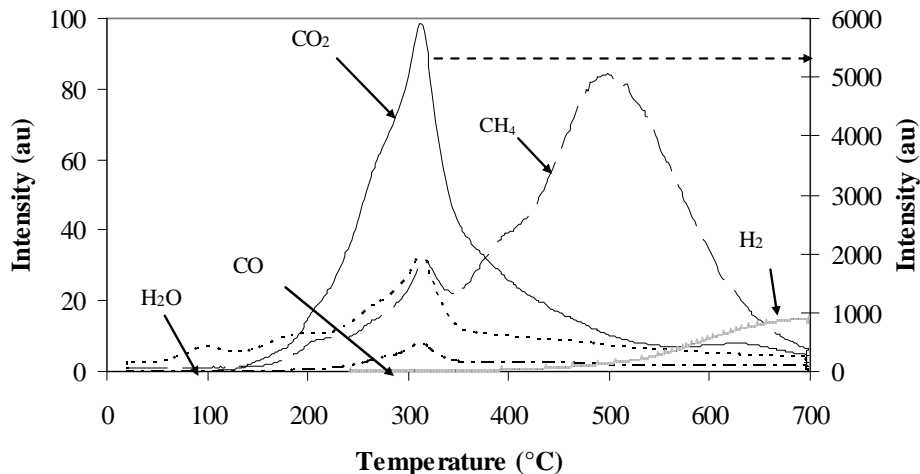
From a chemical point of view, most plant materials can be regarded in the first approximation as a mixture of 40-80 wt.% of cellulose, 15-30 wt.% of hemicellulose and 10-25 wt.% of lignin on the average. These compounds are completely different in a chemical point of view. Cellulose is a biopolymer of glucose units connected with an ether bond. Hemicellulose is an amorphous polysaccharide, and lignin is a high reticulated polymer of phenylpropane units [1,3]. Biomass decomposition in supercritical water proceeds through a series of complex reaction pathways which are logically different for each component [1]. So it is necessary to quantify each constituent in order to have an idea of the global behaviour during the supercritical process.

In order to know the amount of lignin, cellulose and hemicellulose in the biomass and to predict their behaviour during supercritical water treatment TGA was used [22]. We carried out in the lab TGA analyses. Studying the DTG curve in presence of arsenic (Figure 2) four overlapping peaks and a flat tailing section are observed. The overlapping peaks produce a single DTG peak with two shoulders located on the left. It has been debated [23,24,25] that the lower temperature shoulder represents the decomposition of hemicellulose and the higher temperature peak the decomposition of cellulose. Lignin is known to decompose slowly over a broad temperature range, providing thus the flat tailing section of the DTG curve.

The shape of the DTG curves is strongly influenced by the presence of trace elements. For example a shoulder disappeared on the left of without arsenic DTG curve. We can assess that the three compounds are present: hemicellulose, cellulose and lignin. Concerning the identification of the products' lost thanks the mass spectra, H<sub>2</sub>O, CO, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub> were observed (Figure 3). The water evolution which proceeds along the increase in temperature indicates the presence of different bonds between water and biomass. At higher temperatures, the slow charring of the residue released further amounts of CH<sub>4</sub> and H<sub>2</sub>. At the moment, the determination of the quantities of each compound is in progress in the laboratory with various analytical techniques.



**Figure 2: Comparison of TG and DTG of biomass at 5 °C min<sup>-1</sup>.**



**Figure 3: Ion intensity curves (in arbitrary units) of *Pteris vittata* biomass with arsenic.**

## 2. Supercritical water process

This work aims to study the effects of various parameters on biomass gasification and/or liquefaction in supercritical water. These parameters include temperature, pressure, residence time, solution concentration and catalysts.

First, the solution concentration and the pressure were fixed. An amount of 5 wt.% of biomass in water was loaded in the reactor for each experiment. The amount of water was determined by a preliminary test so that a partial pressure of water of 30 MPa was reached. The biomass should be

treated by supercritical water in a range between 300-500 °C at 30 MPa. These conditions allow to prevent the plugging problem and to have a satisfactory gasification conversion [17, 19].

The aim is to liquefy and/or gasify the biomass. The most relevant way of valorisation for biomass should be chosen only if the process is well described and well understood. A very precise analytical procedure is necessary and therefore it will be conducted. This is the only way for us to be able to describe in details the behaviour of this contaminated biomass in supercritical water. Gas phase, liquid phase, and solid phase will be analysed carefully. The results will be analysed as a function of experimental conditions. The essential carbon balance will be also carried out in order to access to the best understanding of the supercritical process. Results of this supercritical water process should then permit us to try to optimise the process and for instance to direct our choice of catalysts which improve the gasification yield [26].

## CONCLUSIONS

Supercritical water is a new method to valorise biomass. Two objectives can be followed: the first one is the supercritical water gasification process, where biomass can be gasified into gases, such as CO, H<sub>2</sub>, CH<sub>4</sub>. These gases can then be used in different processes, some of which were described elsewhere [1,27]. The second one consists in the supercritical water liquefaction process, where the relevant experimental conditions are selected to carry out the desired chemical reaction(s) leading to liquid products. In view of the complex structure of biomass and therefore of the numerous possible chemical reactions in supercritical water, we proposed rigorous analytical and experimental procedures to study these supercritical water processes on the contaminated fern. This aims to propose optimum operating conditions for these supercritical water processes.

After this process optimization the recovery of trace elements such as As and metals is then imperative and will obviously be studied. Most As in biomass are in As(III) and As(V) inorganic forms, which are relatively toxic [28]. But their behaviour in supercritical water hasn't been yet studied.

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