

# FATE OF BIOMASS-DERIVED RADIOCAESIUM AND RADIOSTRONTIUM IN DOWNDRAFT FIXED-BED GASIFICATION PROCESS: A TEST RIG APPROACH

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**ABSTRACT** : This study was performed to assess the adequacy of the downdraft fixed bed gasification process in burning radioactively contaminated biomass. A gasification test was carried out in a realistic process unit rig in order to characterise the possible radiocaesium and radiostrontium particulate removal and redistribution into ash and effluents. In our experimental conditions, the biomass conversion rate was 94.5 %. A particulates mass equivalent to 0.2 % of initial biomass escaped with gaseous effluents. Most of the residual matter was recovered in the gasifier reduction zone as bed materials (84.5 % of recovered dried mass) and with ashes (7.61 % of recovered dried mass). After vaporisation, the compounds Cs is likely to form during subsequent reaction are however less stable than those of Sr. Compared to Sr, the higher mobility of Cs is shown by lower enrichment factor values characterising bed materials and increasing values in next compartments. 5.74 % of Cs escaped from the installation while only 0.007 % of Sr is loosed with gaseous effluents. This is partly due to a prevalent Cs condensation on finest particles which contributes to its dissemination with gas stream.

## 1. Introduction

In Chernobyl-affected lands of CIS, alternative management have to be defined aiming at an economical and durable management of vast contaminated agricultural area. Among different options, production of biomass on waste farm lands and its conversion for renewable energy production could be promoted on a wider scale. Indeed, bioenergy is a renewable and domestic resource showing increasing general concern for future energy supply. A promising industrial procedure to simplify the valorization of contaminated wood-derived fuels could be obtained at gasification of woody biomass. Gasification is one of the "emerging technologies" allowing to convert into heat or electricity various low grade fuels and to some extent willow from short rotation coppice proposed as a tool for contaminated site valorization. Among several technologies, fixed bed gasification is particularly attractive for decentralized power production close to the biofuels sources and energy needs. In the gasification diesel power plant for electricity production, a particular attention is also paid to the flue gas cleaning. Indeed, wood gas contains particulates and tars which have to be removed to avoid damages to engines. Such advanced gas cleaning systems seem particularly suitable in case of radioactive contaminated wood.

The special features of the gasification technology open up new questions, which have to be solved especially when contaminated biomass is considered. This study concentrates on downdraft fixed bed gasification process. A gasification test was carried out in a realistic process unit rig in order to characterize the possible radiocaesium and radiostrontium particulate removal and redistribution into ash and effluents.

## 2. Materials and Methods

In the frame of the RECOVER project [1], SCK-CEN collaborated with UCL-TERM (*Groupe Energie Biomasse*) who has developed a 100 kWt benchmark downdraft fixed bed gasifier. The facilities includes gasifier, cyclone, water scrubber for gas cleaning and impingement filter for gas sampling. Technical data characterizing the nominal conditions of UCL test rig are presented in Table I.

**Table I:** Nominal conditions of the UCL downdraft gasifier

| Design parameter        | Specification          |
|-------------------------|------------------------|
| Fuel feedrate (maximum) | 35 kg/h                |
| Thermal input (maximum) | 180 kW                 |
| Gasification agents     | Atmospheric air        |
| Air flowrate            | 40 Nm <sup>3</sup> /h  |
| Product gas flow rate   | 65 Nm <sup>3</sup> /h  |
| Product gas temperature | 400 °C                 |
| Product gas LHV         | 5-6 MJ/Nm <sup>3</sup> |

The feedstock was of willow (*Salix viminalis L.*) biomass originating from short rotation coppice, regarded as a possible source of bioenergy in several countries. The 3-years old willow sample was harvested from test culture area located in the central part of Belgium. After harvest, the stem were later to dry in the field during one year. After chipping, a final drying of the biofuel was performed in the laboratory to reduce the biomass moisture below 20%. To simulate a wood contamination in <sup>137</sup>Cs and <sup>90</sup>Sr respectively, the chipped biomass was previously treated with water spray containing stable Cs and Sr. The sampling and analysis of fuel and ash was conducted to allow the determination of mass redistribution in unit rig key-compartments during biomass processing and the calculation of balance on

primordial elements (Ca, Fe, Si, Al, Fe, Ca, Mg, K, Na, Zn, Mn) with emphasis on Cs and Sr. The element content were measured in fuel, in residual bed material (gasifier reactor), in ash products (bottom ash from the ashpot and fly ash from the cyclone) and in samples from liquid (water scrubber) and gaseous effluents. The different elemental analysis was carried out by AAS (Atomic Absorption Spectrometry) and ICP (Inductively coupled plasma-atomic emission spectrometry) after samples treatment and mineralization following the borate fusion method.

### 3. Results

#### 3.1. Operational data and mass balance

The characteristics of the chipped feedstock used in the gasification experiment are given in Table II. The elemental composition of the fuel ashes prepared by ashing at 550°C is shown in Fig. 1.

**Table II :** Willow feedstock analysis

| Biomass characterization and analyses       |            |
|---|------------|
| <i>Pellet size (mm)</i>                     |            |
| + Mean diameter (std)                       | 7.3 (5.0)  |
| + Mean length (std)                         | 29.4 (6.8) |
| <i>Bulk density (kg/m<sup>3</sup>)</i>      | 154        |
| <i>Proximate analysis (wt %, dry basis)</i> |            |
| + Moisture                                  | 12.42      |
| + Ash                                       | 2.19       |

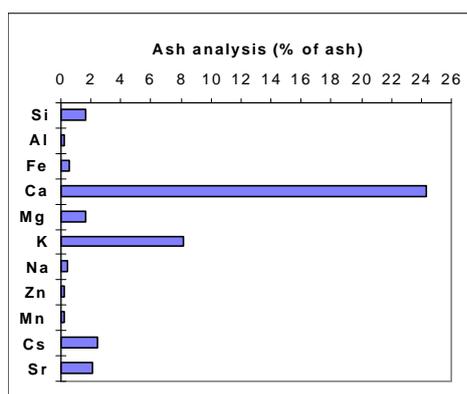


Figure 1: Ash composition of willow feedstock

The willow ashes were dominated by calcium and potassium with levels which are consistent with other wood-derived fuels ashes such as whole tree or forest residues. Compared to other forest woody fuels, the relatively low silicium and aluminium contents may be due to their low concentration in willow bark. Indeed bark of forest stem contain generally high level of silicium and aluminium and contribute mainly to the average stem content in these elements. The level of

cesium and strontium were exceptionally high because of the artificial enrichment of the feedstock.

A total amount of 78.712 kg (d.m.) of wood chips was gasified in a single test run. The ash and residual particulates sampling was conducted in such a way that a mass balance could be estimated, inferring that the missing mass was released under energetic gaseous form. General pattern of mass recovered in total residual ashes and effluents after biomass processing is shown in Table III.

**Table III :** Distribution of recovered particulates in produced ashes and effluents

| Samples         | Recovered Dried Mass (g) | % of Initial Biomass |
|-----------------|--------------------------|----------------------|
| Total ashes (1) | 3769.5                   | 4.8                  |
| Liquid Effl.    | 401.7                    | 0.5                  |
| Gaseous Effl.   | 148.7                    | 0.2                  |
| <b>TOTAL</b>    | <b>4319.8</b>            | <b>5.5</b>           |

(1) Residual bed material + bottom ash + fly ash

From measurement of total recovered materials, it is deduced that an equivalent biomass to 94.5% of the initial feedstock was converted into energetic gaseous effluents and released from the installation. The residual particulates were mainly recovered in ashes (total of 4.8 % of initial biomass). Tar and fine particles removal with liquid effluents corresponded to 0.5 % of initial biomass and a particulates mass equivalent to 0.2 % of initial biomass was measured in gaseous effluents escaping from the installation.

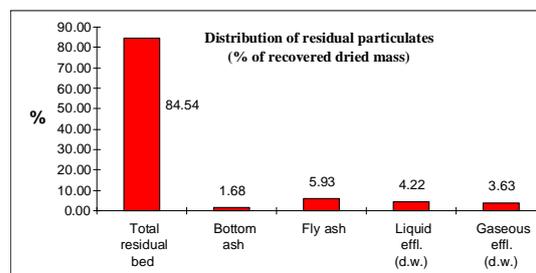


Figure 2: Fraction of the total amount of residual particulates recovered in different compartments of the unit rig.

In more details, Fig.2 presents the percentage of particulates distribution in ashes and effluents as observed from various key-compartment of the test rig. In our experimental conditions, the fuel gasification was carried out with a single fuel feeding and in one test run. Accordingly, the material balance rely to an intermediary operational phase with most of the recovered ashes remaining as bed materials (84.5 % of recovered dried mass). In these conditions, bottom ash and fly ash represent only 1.68 and 5.93 % of recovered dried mass respectively. Liquid effluents removed 4.22 % of particulates and 3.63 % were contained in final gaseous output. With successive fuel feedings and gasification runs, more residual bed materials are expected to be

transferred to immediate ash accumulation compartments (bottom and fly ash). Ash recovery in liquid and gaseous effluents could be also higher.

### 3.2. Element distribution and enrichment factor

The fate of primordial elements in gasification, ash removal and gas cooling and filtration was studied by analysing the element contents of the separated residual bed material, bottom and fly ash, particulates from liquid effluent and exhaust gas. Table IV presents the general pattern of distribution of major elements between total ashes, liquid and gaseous effluents.

**Table IV:** Distribution of major elements in produced ashes and effluents (in % of total recovered amount)

| Element | Residual ashes (1) | Liquid effluents | Gaseous effluents |
|---------|--------------------|------------------|-------------------|
| Si      | 98.75              | 0.52             | 0.729             |
| Al      | 99.70              | n.m.             | 0.299             |
| Fe      | 99.32              | 0.18             | 0.497             |
| Ca      | 99.98              | n.m.             | 0.017             |
| Mg      | 99.99              | n.m.             | 0.012             |
| K       | 94.78              | 2.78             | 2.442             |
| Na      | 99.99              | n.m.             | n.m.              |
| Zn      | 50.65              | 25.86            | 23.491            |
| Mn      | 99.97              | n.m.             | 0.025             |
| Cs      | 92.53              | 1.73             | 5.744             |
| Sr      | 99.97              | 0.02             | 0.007             |

(1) Residual bed material + bottom ash + fly ash  
n.m.: not measurable

Except for Zn, most of the elements showed a distribution comparable to the residual particulates mass distribution between ash and effluents (see Fig.2). The particularly high fraction of Zn in liquid (25.86 %) and gaseous effluents (23.49 %) attest of the highly volatile character of this element during gasification. The bulk fraction of most of the other elements was contained in residual ashes with a recovery > 92-99 %. For the former elements, the differences in distribution between residual ashes, liquid and gaseous effluents allowed however to distinguish tree group of elements in terms of mobility:

1. Sr, Ca, Mg and Mn showed the lowest mobilization during gasification as illustrated by the lowest fraction values in gaseous effluents (< 0.02 %) and by the highest content values in residual ashes (> 99.97 %),
2. Si, Al and Fe presented intermediary mobility with gas stream: recovery fraction in ash and gaseous effluent were respectively in the range 98.7-99.7 % and 0.29-0.73 %.
3. Cs and K showed the highest mobility with exhaust gas content representing 2.44-5.74 % of total recovered amount.

The properties of the different elements to accumulate with residual particulates and deposits removed in different compartments of the test rig were evaluated via the determination of enrichment factors. The enrichment

factors listed in Table V were calculated as the quotient of the element concentration in recovered materials and that of dry willow chips. Zn showed increasing enrichment factor values for particulates collected from bed materials to gaseous effluent with maximum values measured for liquid and gaseous effluent. This enrichment pattern confirm the high volatility of Zn with hot gas stream and its tendency to condensate on very fine particles when gas temperature is reduced at below 50-70 °C. To the opposit, Si, Al, Fe, Ca, Mg, Mn and Sr presented maximum values for particulates in the upper part of the bed materials and decreasing values in next compartments. It is assumed that this trends reflect the ability of these elements to react and condense very rapidly on the char in the gasifier reduction zone under calcium-magnesium, calcium-aluminium silicate or various complex oxides and carbonates [2]. Alkali element like Cs and K showed maximum enrichment factor in the lower part of the gasifier char bed and in bottom ash collected under the gasifier reactor. After vaporization, the compounds they are likely to form during subsequent reaction seems thus less stable. Liquid and gaseous effluents exhibit also relatively high values of enrichment factor. The persistent concentration and enrichment of Cs and K on last sampling point of the test rig confirmed that these elements condensate largely on fine particles which contribute mainly to their dissemination.

**Table V.** Enrichment of primordial elements in particulates relative to wood content.

| Element | Bed materials |         | Bottom ash | Fly ash | Liquid effluents | Gaseous effluents |
|---------|---------------|---------|------------|---------|------------------|-------------------|
|         | high bed      | low bed |            |         |                  |                   |
| Si      | 40.36         | 22.12   | 34.18      | 7.92    | 4.44             | 6.2               |
| Al      | 44.34         | 19.91   | 35.27      | 25.08   | n.m.             | 2.75              |
| Fe      | 175.61        | 73.45   | 113.26     | 48.52   | 0.749            | 2.02              |
| Ca      | 28.03         | 15.54   | 17.97      | 5.5     | n.m.             | 0.09              |
| Mg      | 30.51         | 18.76   | 20.94      | 5.53    | n.m.             | 0.08              |
| K       | 14.22         | 21.56   | 23.01      | 7.77    | 11.87            | 10.44             |
| Na      | 16.28         | 17.72   | 18.1       | 7.72    | n.m.             | n.m.              |
| Zn      | 7.13          | 9.05    | 20.37      | 17.6    | 111.01           | 100.78            |
| Mn      | 47.54         | 25.78   | 32.5       | 9.27    | n.m.             | 0.25              |
| Cs      | 17.75         | 40.04   | 35.18      | 10.35   | 11.25            | 37.36             |
| Sr      | 27.3708       | 16.158  | 18.563     | 6.326   | 0.12             | 0.04              |

After vaporization during combustion, most of the vapour-phase elements react and accumulate mainly with bulk ash formed in the gasifier reduction zone. Redistribution of the elements in the product gas line after the gasifier seems thus highly dependent of the size of particles concentrating the elements. Proportion of particles and differences in element enrichment inside the bed materials as a function of the particulates size are showed in Table VI.

**Table VI:** Enrichment factor values characterizing the element accumulation with particulates of different sizes in the gasifier reduction zone (residual char bed)

| Particulates size range | Particulates mass distribution (% d.w.) | Element |    |     |    |    |    |    |    |    |    |    |
|-------------------------|---|---------|----|-----|----|----|----|----|----|----|----|----|
|                         |   | Si      | Al | Fe  | Ca | Mg | K  | Na | Zn | Mn | Cs | Sr |
| < 0.2 mm                | 13                                      | 48      | 51 | 239 | 35 | 44 | 21 | 31 | 22 | 80 | 16 | 40 |
| 0.2 - 2 mm              | 32                                      | 72      | 71 | 279 | 42 | 56 | 16 | 22 | 6  | 75 | 10 | 43 |
| > 2 mm                  | 55                                      | 14      | 14 | 90  | 11 | 12 | 11 | 14 | 3  | 18 | 20 | 9  |

Large particles > 2 mm constituted the highest fraction of ashes (55 %). Medium (> 0.2 - 2 mm) and fine (< 0.2 mm) contributes respectively to 32 and 13 % of the total mass of the bed materials. The effect of particulates size on changes in enrichment factors allow to distinguish two groups of elements:

1. Si, Al, Fe, Ca, Mg and Sr concentrate firstly on medium size particles and secondly on fine particles. For these elements, the similar trend in enrichment on particles of different sizes suggests that they are combined in common compounds.

2. K, Na, Zn, Mn and Cs accumulate preferentially on fine particles and to a lesser extend on medium particles. Cs enrichment on larger particles is however comparable to enrichment on fine particles.

Because of its relative important mass and its high concentration in various elements, medium size ashes constitute the main link for most of the elements. Very fine particles which may pass through particulate removal devices can partly contribute to the dissemination of certain elements due to their high concentration.

#### 4. Conclusion

This study focused on the fate of radiocaesium and radiostrontium during willow wood chips gasification using a downdraft fixed-bed pilot rig (100 kWt). The experimental devices allowed the determination of mass and mineralomass redistribution in various compartment of the installation. Most significant trends characterizing residual particulates and element dispersion were as follows:

- In our experimental conditions, the biomass conversion rate was 94.5 %. A particulates mass equivalent to 0.2 % of initial biomass escaped with gaseous effluents. Most of the residual matter was recovered in the gasifier reduction zone as bed materials (84.5 % of recovered dried mass) and with ashes (7.61 % of recovered dried mass).
- Except for Zn, volatilized elements react efficiently with char and condensate mainly in the reduction zone which constitutes the main sink for most of the elements.
- After vaporization, the compounds Cs is likely to form during subsequent reaction are however less stable than those of Sr. Compared to Sr, the higher mobility of Cs is shown by lower enrichment factor values characterizing bed materials and increasing values in next compartments.
- 5.74 % of Cs escaped from the installation while only 0.007 % of Sr is losted with gaseous effluents. This is partly due to a prevalent Cs condensation on finest particles which contributes to its dissemination with gaz stream.
- According to a permissible level of 40 Bq  $^{137}\text{Cs}/\text{m}^3$  in gaseous effluent, and assuming a routine release associated with similar operational conditions than in this experimental test, it was calculated that the maximal  $^{137}\text{Cs}$  content in wood suitable for gasification would be 1240 Bq/Kg d.w.

Depending of the type of biomass and burning process, the amounts, nature and dominant size of ashed produced vary considerably. Moreover differences in prevailing combustion temperature have obvious effects on vaporization rate and subsequent reactions of element with char and ashes. When contaminated biomass is considered, a particularly advantageous operational parameter of the downdraft fixed-bed consists in the subsequent reaction of flue gas stream with char occurring at lower temperature (600-800 °C) prevailing in gasifier reduction zone. After element volatilization, a lowered temperature leads to an efficient condensation on residual particulates. The further removal of radioelement could however be refined with an improved filtration devices for finest particulates in exhaust gas.

#### 5. References

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