Willow as fuel from arable land with high cadmium content

Susanne Paulrud[1], Anders Hjörnhede[1], Magnus Svensson, Fredrik Axby[2]

[1]*SP Technical Research Institute of Sweden*
[2]*Grontmij*

Introduction

Cadmium is a major health problem (Naturvårdsverket, 2013). We ingest cadmium when we eat, and it increases the risk of osteoporosis and various types of fractures that are estimated to cost the Swedish society 4 billion per year according to a report from the Swedish Chemicals Agency. To reduce the intake of cadmium via food, the supply to arable land must be strangled or removed. Fertilizers, mineral and organic nutrient products (manure, bio-fertilizers, sewage sludge, etc.) will always contain certain amounts of cadmium. Also the deposition of cadmium from the air pollution will not completely cease. In the current situation there is a balance between contributions and exit of cadmium in the soil, so that cadmium levels are no longer rising, at the same time the stored amount of cadmium in the soil is very large, (Naturvårdsverket, 2013).

Previous studies show that willow cultivation is an effective method to clean arable land from cadmium. A well-maintained willow cultivation accounts for an annual uptake that is 20 to 50 times higher than for cereals (Hasselgren, 2014). If the willow is grown before the wheat, the cadmium content will be reduced in wheat. If the willow will serve as a crop in order to both produce energy and clean arable land from heavy metals more knowledge is needed how the cadmium should be handled at the heating plant. With increased use of willow chips from cadmium-rich land there may be a risk that the cadmium concentration increases in the condensate since the willow has significantly higher levels than forest fuel, average 5-10 times higher levels. The goal of the project was to perform full-scale experiments with fuel mixes of wood chips and willow chips in a 2x10 MW biomass plant at Ystad Energy and to propose measures to reduce possible problems with cadmium in ash and condensate.

Material and Methods

The heating plant consists of two boilers per 10 MW, supplier Weiss (Denmark), 3 MW condensation after each boiler. The boilers are equipped with a moving grate, staircase, divided into three sections. The boilers went into operation in 2007. The fuel is primarily wood chips, pine-wood/forest residues and hardwood chips and a smaller portion of willow. The flue gas cleaning is composed of a cyclone and then a scrubber (Venturi) and the last is the gas flue condensation tower. It is a flue gas cleaning equipment for each boiler. Purification of the condensate is made through a sand- and lamella filter.

During the combustion tests, a mixture of 50% by volume of willow chips and 50% by volume of hardwood chips, was used. To find a willow cultivation with a high content of cadmium, two samples for analysis, were taken in two different cultivations in two areas that were judged to lie on cadmium-rich land in southern Sweden. Two different experiments with a mix of willow chips (leafy and non-leafy) and hardwood chips, was performed during three days and which measurements were carried out day three, ie the boiler was used with willow chips at least two days before measurement. Before experiments with willow chips were carried out, experiments and measurements with 100% hardwood chips (reference fuel), was performed. The flue gases NO_x, CO, SO_2, CO_2, och O_2 were continuously analyzed during the trial period, and sampling of total dust were carried out simultaneously three times per sample, before the cyclone, after cyclone and after the venturi. Sampling of condensate were made on six different occasions, three of these were so-called total analysis which includes all the elements. Fuel sample, fly ash sample and bottom ash sample was collected on three occasions during each measurement period for each fuel.

Results

The willow fuel mix showed no major differences in fuel properties of the main elements in comparison with the reference fuel. The greatest difference showed the trace elements zinc and cadmium with about 5-6 times higher cadmium content in the willow fuel mix (figure 1). For the willow variety used in the experiment the cadmium content did not increase in willow chips with leaves (sample from the month of May) in comparison with willow without leaves (March).

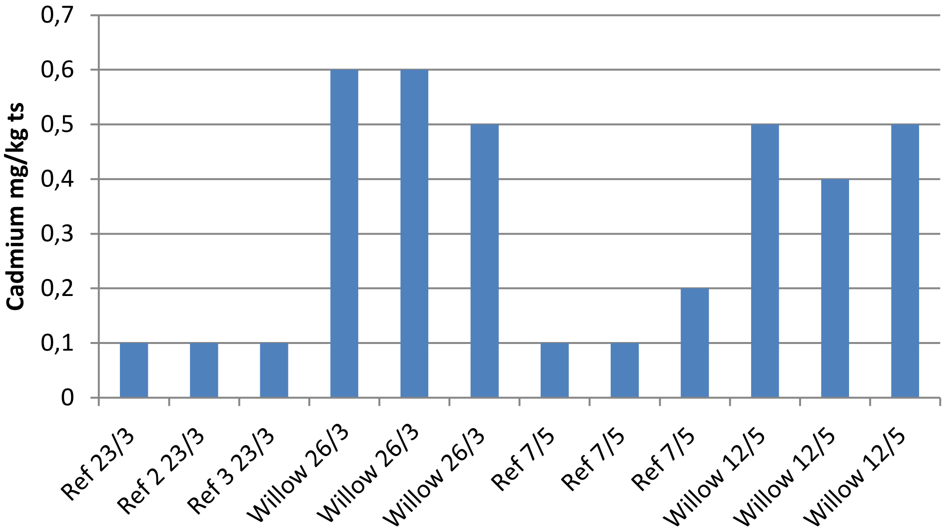

Figure 1. Difference in the cadmium content between 100% hardwood chips (ref) and a willow fuelmix consisting of 50 volume% willow chips and 50 volume% hardwood chips.

Table 1 shows the mean (approximately four hours of measurement) of the measured gas concentrations in flue gas. Combustion of the willow fuel mix increases NO_x emissions slightly due higher nitrogen content in willow. The mixing of the willow fuel also increases the dust content in the raw gas. The higher CO content when using willow mix (March) does not depend on the fuel. According to operating staff at the heating plant, the boiler sometimes independent of the fuel ends up in an irregular combustion" causing high CO. At the second trial in May the boiler load was lower (<50%) in the willow experiment in comparison with the other trials which resulted in lower flue gas temperature, lower NO_x content and lower dust content in the raw gas before purification.

Table 1. Average values of the measured gas concentrations in flue gas. Total dust shows the mean of three samples. Reference fuel is 100% hardwood chips and willow mix consists of 50% by volume willow chips and 50% by volume of hardwood chips.

		Temp	**NO_x**	**CO**	**$O_{2\text{-real value}}$**	**Dust Before cleaning**	**Dust After cyclone**	**Dust After Venturi**
Date	Fuel	^oC	mg/nm^3 6% O_2	mg/nm^3 6% O_2	%	mg/nm^3 6% O_2	mg/nm^3 6% O_2	mg/nm^3 6% O_2
2015-03-23	Ref.	186	149	152	3,5	173	92	13
2015-03-26	Willow mix	179	168	511	5,7	347	125	21
2015-05-07	Ref.	181	183	58	4,2	188	104	27
2015-05-12	Willow mix	159	159	51	5,5	238	131	27

*SO2 ended up under detection limit for most of the measurements and are not reported.

After combustion the majority of the cadmium was found in the fly ash and in which the cadmium content was about 75-100% higher in the fly ash from willow mix in comparison with the reference fuel (figure 2). The cadmium content of bottom ash shows a low level in all samples. The majority (> 85%) of the cadmium ended up in the cyclone ash during combustion in the tested plant while the increase in the condensate was marginal when using willow (figure 3).

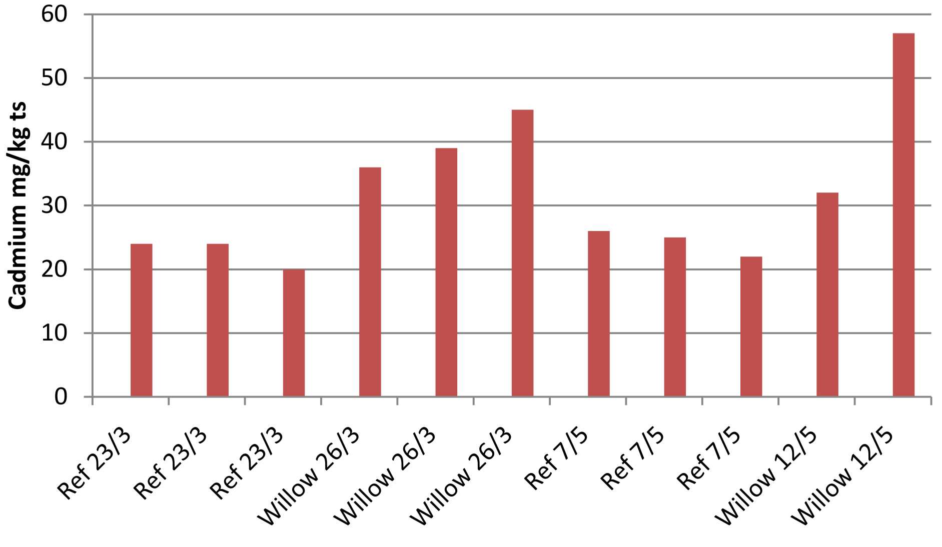

Figure 2. Cadmium content in the fly ash, the comparison between all trials. Reference fuel is 100% hardwood chips and willow mix consists of 50% by volume willow chips and 50% by volume of hardwood chips.

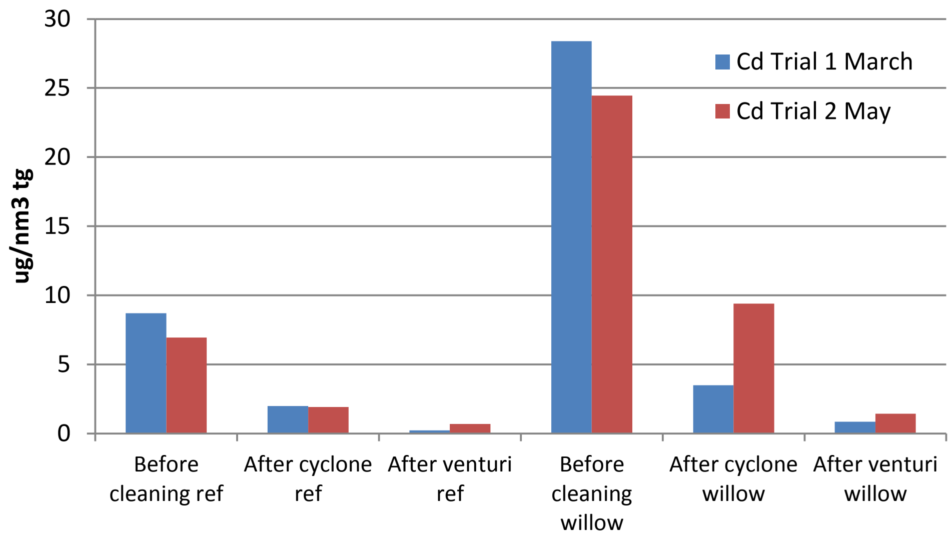

Figure 3. Cadmium content of the particles after and before purification of flue gases. Reference fuel is 100% hardwood chips and willow mix consists of 50% by volume willow chips and 50% by volume of hardwood chips.

The results from the measurements of metals in the condensate showed that the concentrations of lead, chromium, nickel, and thallium reduced with the mixing of willow while the concentrations of cadmium and particularly zinc increase. The increase of cadmium corresponded to about 20%. In order to assess the need for purification efforts of the condensate, samples were filtered to investigate the respective metal's distribution as particle-bound or loose (Table 2). Table 3 shows levels after filtration. Significant amounts of arsenic, lead, cadmium, copper, nickel and zinc is present as particle-bound, which means that good purification can be achieved only through a particle-removing step. The heating plant in Ystad has both sand- and lamella filter which provide an outlet water with normally low levels of heavy metals.

Table 2. Part particle-bound metal percent (average). Reference fuel is 100% hardwood chips and willow mix consists of 50% by volume willow chips and 50% by volume of hardwood chips.

	Trial 1		**Trial 2**	
Part of %	**Ref**	**Willow**	**Ref**	**Willow**
Antimony	62	54	51	45
Arsenic	93	80	66	76
Barium	79	82	77	75
Lead	98	90	90	85
Cadmium	86	86	87	84
Cobalt	76	85	85	82
Copper	97	92	88	87
Chromium	67	51	35	27
Mercury	>92	>74	>86	>87
Molybdenum	11	6	6	7
Nickel	73	84	87	86
Vanadium	81	69	77	64
Zinc	88	93	88	87
Selenium	12	-2	14	2
Thallium	-37	-18	-55	-81

Table 3. Metal content after filtration (mean). Reference fuel is 100% hardwood chips and willow mix consists of 50% by volume willow chips and 50% by volume of hardwood chips

	Trial 1		**Trial 2**	
µg/l	**Ref**	**Willow**	**Ref**	**Willow**
Antimony	2,3	1,7	1,7	1,8
Arsenic	0,6	2,2	3,3	1,9
Barium	515	400	265	180
Lead	8,8	27	36	32
Cadmium	22	26	8,3	12
Cobalt	2,1	1,3	0,5	0,6
Copper	10	38	22	21
Chromium	10	12	13	11
Mercury	<0,1	<0,1	<0,1	<0,1
Molybdenum	12	14,5	9,2	14
Nickel	13,5	5,4	2,7	2,2
Vanadium	1,4	1,4	0,9	1,1
Zinc	1950	1350	840	1300
Selenium	7,6	9,8	5,5	6,2
Thallium	11	4,8	9,4	5,8

Conclusions

The use of willow as a purification filter for arable land with high cadmium content is an interesting approach since it is an effective method in a relatively short time and also a cost effective way to reduce the cadmium content in our farmland. Today we have good knowledge of willow as fuel and willow can be used without problems in mix with other wood fuels in most types of combustion plants (Paulrud, 2014). The issue of this study was to investigate the possible problems the heating plants can face when using willow with high levels of cadmium. Conclusions from the project are:

- Ystad heating plant can with good sustained operation at a load around 70-80% of the maximum load, blending up to 50 volume % willow in the fuel base. There is every reason to assume that the operation is not affected either at 100% load.
- The willow fuel mix showed no major differences in fuel properties of the main elements in comparison with the reference fuel. The greatest difference showed the trace elements zinc and cadmium with about 5-6 times higher cadmium content in the willow fuel mix.
- For the willow variety used in the experiment the cadmium content did not increase in willow chips with leaves (sample from the month of May) in comparison with willow without leaves (March).
- After combustion the majority of the cadmium was found in the fly ash and in which the cadmium content was about 75-100% higher in the fly ash from willow mix in comparison with the reference fuel.
- The majority (> 85%) of the cadmium ended up in the cyclone ash during combustion in the tested plant, while the increase in the condensate was marginal when using willow.
- Recommended levels for cadmium in ash for spreading in the forest is 30 mg/kg DM. The fly ash from the trial in Ystad heating plant contained higher levels (36-45 mg/kg DM). Since the bottom ash and fly ash is mixed before ash spreading, the concentrations of cadmium will not be exceeded if the percentage of fly ash is about 30%.
- Actions in the heating plant, that is required when using willow with high cadmium content is controlled by the incorporation rate of willow and cadmium content in the fuel. An admixture of 10-20% willow may allow higher levels of cadmium than 1,5 mg/kg of dry fuel (the result in this study) to not exceed the permissible levels of ash spread in the forest.
- Technically, it is no problem to separate fly ash from bottom ash in a heating plant but there is an additional cost for the heating plant to dispose the fly ash.
- For purification of output levels after the particle separation, an ion exchanger can be an option for Ystad heating plant. An ion exchanger is a relatively cost effective purification method where low output levels can be achieved.

References

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