Alkali distribution for low temperature gasification

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Preface

This work was conducted as part of the consortium with KEMA and TU Delft. This particular focus is on the distribution of alkalis during low temperature gasification and is part of the larger focus on biomass co-firing in large scale power plants in the framework of the EOS-LT programme, executed by AgentschapNL on behalf of the Dutch Ministry of Economic Affairs.

Abstract

During the 2006-2009 EOS-LT programme on biomass co-firing it became clear that there is potential for biomass to add to the targets set in the Long-Term Energy Research Strategy (EOS-LT) of the Dutch Ministry of Economic Affairs. The strength of indirect co-firing is that it is an efficient technology to produce a combustible gas and it allows for capture of undesired ash components from the gas phase and preventing them from entering the boiler. However, it also became apparent that additional measurements were needed to determine to what extent this is true.

In the 25 kW_{th} lab scale MILENA gasifier at ECN, different fuels were tested to obtain data on the alkali distribution regarding the gas phase and solid phase. Low temperature gasification is a method to prevent alkalis (ash components) to evaporate, as to keep them in the solid phase. The research done during the 2010 EOS-LT period showed that for straw pellets about 10-20 wt.% of the ash related components (potassium, sodium etc.) end up in the gas phase (most of which is fine dust) and will be sent to the boiler. For chlorine the percentage sent to the boiler is about 13%. In case of RDF the amount of biomass ash related components ending up in the gas phase is less. This does not hold for chlorine however. The amount ending up in the gas phase is 18% and is based on a blend of RDF and beech wood. When switching to 100% RDF the total amount that will end up in the boiler can become quite substantial.

Indirect co-firing of difficult fuels shows good potential regarding the effect of capturing alkalis in the solid phase. In case of RDF the amount of chlorine ending up in the boiler will be larger than for straw pellets, but the amount of available potassium is lower. KCl related corrosion issues might therefore be less when RDF is gasified.

Agglomeration was not observed during these ~eight hour tests, but the balance of the gasifier shows an increase of agglomeration related components in the bed material. Eventually these can cause agglomeration, but refreshing of the bed material is a simple measure to prevent this.

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1. Introduction

During the EOS-LT consortium on indirect co-firing of 2006-2009 it became clear that there is potential in using CFB, LT-CFB or indirect gasification as a means of increasing the use of biomass in coal fired power plants. The possibility exists with indirect co-firing to capture a large part of the alkalis in the solid phase and lower the amount of alkalis that end up in the boiler. However, great uncertainties existed on the behaviour of alkalis in the gasification process. For this reason an experimental program was decided upon for the year 2010 to test low temperature gasification of difficult biomass to see the effect on alkali behaviour.

This report will describe the results of a measurement campaign around two types of difficult biomasses. Straw pellets and RDF both contain large quantities of components such as potassium, chlorine, sulphur and others. They are defined as difficult, because these components in the ash of the biomass pose fouling, agglomeration and corrosion problems in downstream processes. To obtain insight in the behaviour of these and other components extensive measurements were performed on biomass, ash, bed material and gas leaving the system.

2. Experimental setup and analysis

For the purpose of this research the MILENA gasifier was used to produce a medium caloric gas suitable for indirect co firing in commercial boilers. Within this research six streams were defined as possible contributors to the alkali distribution. In Figure 2.1 this representation is given.

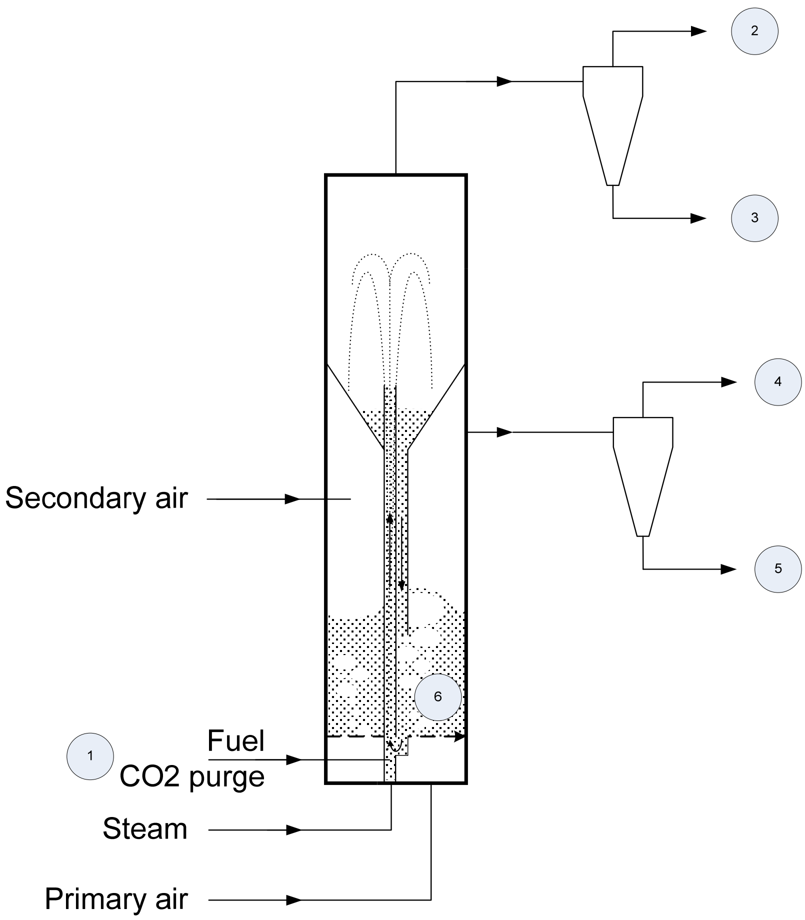

Figure 2.1 *Schematic representation of the gasifier and points identified as possible contributors to the alkali balance*

A short outline is given on what is measured at the different defined points. The two streams relevant for the application of indirect co-firing are stream 2 and 4, since these two streams will end up in the boiler.

1. The fuel was analysed with ICP at the analysis department of ECN. The ICP analyses results in a list of alkalis that are present in the ash of the fuel. The full list is given in Appendix I. Also the proximate and ultimate analyses were done on the different fuels and amongst others this results in the amount of chlorine in the biomass.[1]
2. The producer gas is analysed for dust after the cyclone at high temperature in combination with a wash bottle to capture chlorine[2]. The dust is captured with a filter which is analysed for chlorine and alkalis. The wash bottle is analysed for chlorine and alkalis as well.
3. The ash obtained in the producer gas cyclone (char) is analysed for alkalis with ICP.

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[1] More on the analysis methods referred to in the text can be found on the ECN website: http://www.ecn.nl/units/es/products-services/materials-testing-consultancy/materials-testing

[2] Demineralized water is used for this purpose.

4. The flue gas from the combustor is analysed for alkalis and chlorine by using a wash bottle to capture these components.
5. The ash obtained from the flue gas cyclone (ash) is analysed with ICP.
6. The bed material was analysed with ICP for the amount of alkalis present in the bed before and after the test.

After each gasification test the bed was emptied and refilled with fresh sand.

2.1 Fuels

The gasification of straw pellets followed after unsuccessful gasification of non-pelletized straw. Non pelletized straw was milled and it turned out to be impossible to feed this material. Therefore straw pellets were purchased, which were easier to grind an subsequent easier to feed. The pellets were purchased at Equi'n Motion V.O.F. in St. Michielsgestel, the Netherlands.

The gasification of RDF also started with some problems. Feeding enough RDF to get the circulation going in the gasifier turned out to be impossible. Bridging in the feeding line was the main cause that resulted in abandoning pure RDF feeding. The amount of RDF fed to the gasifier was decreased and beech wood was added to the mix to produce enough gas for solids circulation in the gasifier. The mixture of 60 w.% RDF and 40 w.% beech wood resulted in good gasification properties. The beech wood is purchased from the Rettenmaier company. RDF was obtained through NIHOT recycling in Utrecht.

2.2 Experimental settings

The gasification took part in the lab scale MILENA gasifier at ECN. This gasifier is normally used for high temperature gasification tests (750 °C – 850 °C), but as it is also possible to operate it at lower temperatures (600 °C – 700 °C). The feeding of different mediums to the gasifier is depicted in Figure 2.1. The settings for the three test that are described in this report are given in Table 2.1.

Table 2.1 *Gasification settings for the low temperature tests*

	Unit	*Test 1*	*Test 2*	*Test 3*
Biomass		Straw pellets	Straw Pellets	RDF and Beech
Gasification temperature	°C	690	660	680
Combustion temperature	°C	730	700	720
Fuel feed	gram/h	5580	5100	3060 (RDF)
				2340 (Beech)
Steam	gram/h	1081	1082	1190
Primairy air	Nl/min	119	99	100
Secundairy air	Nl/min	20	20	23
CO_2	Nl/min	3	5	12

3. Results and discussion

For keeping the results clear, the discussion about the analysis part of the different sample points will be done first.

3.1 Discussion

After the experiments were finished the bed material was taken from the reactor and analysed with ICP. The sample taken from the bed material was not representing the fully mixed bed but was taken from the top after it was completely emptied. Since not all bed material will partake in the solids circulation (< 5 w.% will be in stagnant zones) an error will be introduced when the total amount of bed material is used in the calculation. This could have been avoided by completely mixing the bed material after it was taken from the reactor.

A second uncertainty is the char obtained from the cyclone. The mass flow, as it turned out during the experiments, was not always as stable as would be desired for a good measurement. During the RDF test, char obtained in the cyclone was 40 gram/h in the first 5 hours and 200 gram/hour after it was emptied and cleaned because it was assumed to not operate well. These two show quite a big difference and this was observed during other tests as well. The low temperatures and smaller gas flows might be the cause of this problem. The results of the ICP are greatly affected by a fivefold increase in char production. However, the results are included, since they will only lead to an underestimation of the different alkalis.

The second gasification test with straw pellets resulted in a char production twelve times less than the first straw pellets gasification test. This will greatly affect the alkali distribution as well. Furthermore during this test the high temperature dust filter after the cyclone got miss placed and is not analysed. Therefore no reference could be made with the first test to see the difference in dust captured on the high temperature filter.

Some chlorine measurements were not done because the focus was on the alkalis. Chlorine was measured in the gas phase and in the dust from the filter and not in the solid phases.

3.2 Results

3.2.1 Straw pellets gasification at 690°C

The gasification of straw pellets at 690°C went well. The distribution of the different components over the different phases is given in Table 3.1. The first column is a reference to the stream numbers in Figure 2.1. The first row gives information on the amount of alkalis and chlorine that enters the gasifier via the biomass in absolute numbers. All five possible end points (number 2 - 6 in Figure 2.1) for these components are given as a percentage of the total amount that was fed to the gasifier. It turns out that most of the calcium, potassium and phosphorous end up in the solid phase, either in the flue gas stream or in the producer gas stream. Sulphur will also end up in the gas phase as H_2S and COS in the producer gas and as SO_x in the flue gas. These components will not completely be captured in the wash bottles, because the solvent used is acidic. Especially the H_2S and COS will represent rather big losses on the overall balance. Chlorine was not measured in all phases but from the balance it shows that very little ends up in the gas phase. In case of the producer gas roughly 13% will end up in the gas (either as dust or gas phase components) and the flue gas will contain virtually no chlorine. This means that for indirect co-firing about 13% of the chlorine will end up in the boiler.

Table 3.1 *Alkali balance for straw pellet gasification at 690°C*

			Ca	K	Na	P	S	Cl	
1	Straw pellets @ 690°C		18461	59728	632	9093	3404	15989	mg/h
4	Flue gas	Wash bottle	0.0%	0.0%	6.9%	0.1%	0.0%	0.0%	
5	Flue ash	Cyclone	21.6%	29.4%	38.2%	25.8%	3.5%	ND	
2	Producer gas	Wash bottle	0.0%	0.0%	0.1%	0.0%	5.6%	1.4%	
2	Producer dust	Dust filter	17.6%	7.9%	9.1%	17.0%	4.3%	11.1%	
3	Producer char	Cyclone	23.0%	28.3%	32.1%	25.3%	3.5%	ND	
6	Bed material	Sand	32.1%	29.9%	-51.4%[3]	29.2%	1.6%	ND	
Missing from the overall balance			5.8%	4.5%	65.0%	2.6%	81.2%	87.5%	

In case of indirect co-firing, streams 2 and 4 will end up in the boiler. In that case this would mean a reduction of chlorine to the boiler of about 88% and for difficult alkali components such as potassium it would mean a reduction of about 92%. The bed material shows an accumulation of calcium and potassium, which might lead to agglomeration. This has not been observed during testing and can easily be avoided by refreshing with new bed material.

3.2.2 Straw pellets gasification at 660°C

The test with straw pellets gasification at 660°C had some problems regarding the filter used for capturing dust and the amount of char obtained in the cyclone was also far below what could be expected as explained before. Therefore, there are no results on the producer dust and the results for the producer char can easily be off by a factor twelve. The results are given in Table 3.2. Based on the measured phases most of the components (except sulphur) end up in the solid phase. The chlorine in this case is below the detection limit for the flue gas and for the producer gas the amount measured in the gas phase only represents 1% of the total chlorine content. Although data in this test is limited the general outline of the results is similar as gasification of straw pellets at 690°C.

Table 3.2 *Alkali balance for straw pellet gasification at 660°C*

			Ca	K	Na	P	S	Cl	
1	Straw pellets @ 660°C		16873	54590	578	8311	3111	14614	mg/h
4	Flue gas	Wash bottle	0.0%	0.0%	6.6%	0.1%	-0.1%	0.0%	
5	Flue ash	Cyclone	15.6%	22.6%	27.7%	19.0%	3.3%	ND	
2	Producer gas	Wash bottle	0.0%	0.0%	0.4%	0.0%	8.4%	0.9%	
2	Producer dust[4]	Dust filter	ND	ND	ND	ND	ND	ND	
3	Producer char[5]	Cyclone	2.2%	2.5%	3.0%	2.3%	0.3%	ND	
6	Bed material	Sand	36.7%	36.9%	-72.3%[3]	33.9%	2.4%	ND	
Missing from the overall balance			45.5%	38.0%	134.7%	44.7%	85.6%	99.1%	

3.2.3 Co-gasification of RDF and beech wood at 680°C

As mentioned before the RDF gasification test did not go according to schedule and to obtain good gasification behaviour the material was co-gasified with beech wood. The results for the alkali balance is given in Table 3.3. These values show remarkable differences with the straw gasification. First of all the amount of alkalis is different as can be seen when comparing the values in Table 3.1 to Table 3.3.

[3] Sodium is a volatile component and some the sodium in the bed material will evaporate, hence the negative number.
[4] No results due to a misplacement of the filter
[5] The amount of char is about a factor 12 off and therefore these results are much lower compared to the first test on straw pellets

Table 3.3 *Alkali balance for RDF and beech wood gasification at 680°C*

			Ca	K	Na	P	S	Cl	
1	RDF and beech wood @ 680°C		86172	7288	9128	1096	16545	32215	mg/h
4	Flue gas	Wash bottle	0.0%	0.0%	0.0%	0.1%	0.0%	5.5%	
5	Flue ash	Cyclone	23.2%	26.3%	11.5%	19.6%	15.6%	ND	
2	Producer gas	Wash bottle	0.0%	0.0%	0.0%	0.0%	0.0%	10.3%	
2	Producer dust	Dust filter	2.3%	1.3%	0.5%	3.3%	2.9%	1.8%	
3	Producer char	Cyclone	34.3%	40.3%	21.3%	32.4%	27.8%	ND	
6	Bed material	Sand	26.9%	23.3%	63.0%	17.9%	11.7%	ND	
Missing from the overall balance			13.3%	8.8%	3.6%	26.8%	42.0%	82.4%	

The flue gas in this case does not contain a lot of alkali components but is only rich in chlorine. Based on the large amount of this present in the fuel it is not surprising that there is an increase in the gas phase as well. Also in the producer gas the amount is large, however in total only 12% of the chlorine is accounted for. This is similar to the straw pellets gasification test at 690°C. But the total load of chlorine to the boiler in case of indirect co-firing would be about 17.5%, which is large but not surprising since in this case there is already 100% more chlorine to start with. The positive side is that the amount of potassium in the fuel is low compared to straw pellets and it ends up in the cyclone ashes for the most part.

Sulphur during this test is five times larger than for straw pellets. Roughly 50% ends up in the ash and char. The rest most likely will be present as H_2S and COS. Based on a mass and energy balance for RDF and beech gasification the amount of sulphur going to H_2S and COS is roughly 1400 mg/h (8.5%). More accurate measurements on these components as well as the SO_x can provide insight in the accuracy of this balance. For the other components, large amounts are captured in the solid phases (bed, ash and char).

With straw pellets the amount of sodium in the biomass is relatively low and it can be observed that the bed material releases sodium. In case of RDF gasification the amount of sodium in the feed is high and in this case the bed accumulates this component. The exact interaction of this components and others (calcium and potassium) is unknown, however it can be assumed that agglomeration related issues might occur here as well as is assumed for the straw pellets. Refreshing of the bed material from time to time can avoid this.

The effect of 100% RDF gasification is difficult to predict. The origin of the material determines the ash composition and the ash composition can affect agglomeration and corrosion properties. Therefore careful selection of RDF can already help prevent agglomeration or corrosion.

4. Conclusions

From these tests it became clear that at low temperature gasification a lot of difficult alkali components end up in the solid phases, either in the cyclones or in the bed material.

With regard to RDF and beech gasification there is still a significant amount of chlorine present in the gas phase. If RDF is gasified 100% beech free, the amount of chlorine ending up in the gas phase will increase even more. Compared to straw pellets the amount of potassium in RDF is low so the effect of KCl related corrosion is limited.

There are strong indications that in case of straw pellets 10-20 wt.% of the biomass ash related components end up in the gas phase and will be sent to the boiler. For RDF this fraction is somewhat lower (up to 3.5%). However for chlorine the amount is much higher and since RDF also contains more chlorine (four times more) gasifying pure RDF for indirect co-firing will cause an increased load of chlorine to the boiler.

Agglomeration problems with the bed material were not observed during the tests. However, the balance shows an increase in typical agglomerated components in the bed material. Over time the particles can form agglomerates, but this can be prevented by refreshing the bed material.

From an alkali load to the boiler point of view, the best route for applying these two fuels is indirect co-firing at low temperatures instead of direct firing in a boiler.

Appendix A Proximate, ultimate and ICP results for the fuels

	BEECH	*STRAW PELLETS*	*RDF*	
Ash	1.1	6.7	15.1	wt.% ar
Water	8.9	7.8	7.7	wt.% ar
Volatiles	73.7	67.5	64.1	wt.% ar
C	43.3	41.1	41.4	wt.% ar
H	5.8	5.6	5.4	wt.% ar
O	44.5	41.2	28.2	wt.% ar
N	0.2	0.4	1.1	wt.% ar
S	0.0	0.1	0.5	wt.% ar
Cl	0.005	0.264	1.049	wt.% ar
F	0.000	0.002	0.007	wt.% ar
HHV	17521	16492	18088	kJ/kg ar
LHV	16036	15076	16712	kJ/kg ar
Al	26	398	6702	mg/kg dry
As	0	1	9	mg/kg dry
B	5	5	82	mg/kg dry
Ba	25	53	541	mg/kg dry
Ca	2964	3309	25895	mg/kg dry
Cd	0	0	3	mg/kg dry
Co	1	3	7	mg/kg dry
Cr	2	3	429	mg/kg dry
Cu	3	3	610	mg/kg dry
Fe	99	291	4689	mg/kg dry
K	1331	10704	1364	mg/kg dry
Li	0	0	4	mg/kg dry
Mg	503	701	1966	mg/kg dry
Mn	94	29	126	mg/kg dry
Mo	0	1	17	mg/kg dry
Na	36	113	2955	mg/kg dry
Ni	2	1	266	mg/kg dry
P	104	1630	279	mg/kg dry
Pb	0	3	260	mg/kg dry
S	203	610	5252	mg/kg dry
Sb	0	1	61	mg/kg dry
Se	0	0	0	mg/kg dry
Si	242	16479	26903	mg/kg dry
Sn	0	0	17	mg/kg dry
Sr	6	11	143	mg/kg dry
Ti	4	17	1654	mg/kg dry
V	0	1	7	mg/kg dry
W	18	33	37	mg/kg dry
Zn	3	5	393	mg/kg dry