

FATE OF ALKALI METALS DURING CO-COMBUSTION OF BIODIESEL RESIDUES WITH COAL IN A SEMI-INDUSTRIAL CFB BOILER

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Abstract – The use of biodiesel, especially of Rapeseed Methyl Ester (RME), has recently increased in the European countries. This gives rise to an increasing amount of after production residues. Rapeseed cake is the main residue of the RME production process, and may become available in large amounts for energy recovery. Since rapeseed cake contains high levels of alkali metals, it may cause bed agglomeration, deposit formation and corrosion upon combustion in fluidized beds.

This paper presents the fate of alkali metals formed during co-combustion of coal and up to 25% of rapeseed cake pellets in a 12 MW Circulating Fluidized Bed Boiler at Chalmers University of Technology (Sweden). Standard fuel analyses combined with sequential leaching and SEM/EDX, showed the alkali entering the boiler. Gaseous emissions, bed samples, fly ash and deposits were analyzed in order to monitor the alkali metals distribution. Gaseous alkali chlorides were measured upstream from the convective pass at a flue gas temperature of 800 °C using an In-situ Alkali Chloride Monitor (IACM). In the same location, deposits were collected on a deposit probe fitted with rings for SEM/EDX analysis. Re-circulated bed material was analyzed as well.

Two-day tests showed successful co-firing of up to 25% rapeseed cake on energy basis in the semi-industrial fluidized-bed boiler. Alkali metals were enriched in fly ash. No significant difference could be noticed in the distribution of alkali metals when increasing the share of rapeseed cake from 15% to 25% on energy basis. In the near future, further studies will be carried out to determine the influence of limestone on the performed tests.

INTRODUCTION

In the EU-25 biodiesel, which production is stimulated by the European Union politics, is mainly produced from rapeseed [1]. Its use for biodiesel production was estimated at 4.6 million tons in 2004, which is an increase of ~70% compared with year 2002. As a result, the demand for biodiesel has become a major factor influencing the rapeseed and rapeseed oil markets [2].

During Rapeseed Methyl Ester production about two-third of the feedstock becomes rapeseed cake residue [3]. Its potential as a biomass source for energy recovery was investigated by Esin Çulcuoğlu et al. [4] where it was stated that rapeseed cake may be utilized by direct combustion or by other energy conversion processes, which was proved by Kandefer et al. [5] during co-firing of 15% of rapeseed cake with coal in a grate furnace.

This paper presents the fate of alkali metals formed during co-combustion of up to 25% rapeseed cake pellets with coal in a 12 MW Circulating Fluidized Bed (CFB) Boiler. Fuel standard analyses and fractionation results are presented. Ash and deposit samples collected during the campaign were analyzed by SEM/EDX. Gaseous alkali chlorides were measured before the convective pass at a flue gas temperature of 800 °C using an In-situ Alkali Chloride Monitor (IACM).

EXPERIMENTAL SET-UP

Boiler

A 12 MWth CFB boiler was used for the tests. It is presented in Fig. 1. The boiler is large enough to be representative for a semi-industrial CFB boiler and is described in detail elsewhere [6-7].

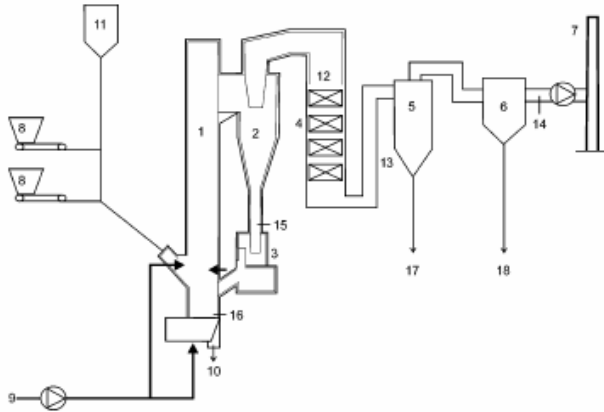


Figure 1 Schematic of the boiler [7].

1: furnace, 2: primary cyclone, 3: particle seal, 4: convection pass, 5: secondary cyclone, 6: bag-house filter, 7: stack, 8: fuel bunkers, 9: air, 10: bottom material removal, 11: bed sand, 12: measurement spot before convection pass, 13: measurement spot after convection pass, 14: measurement spot after bag-house filter (stack), 15: cyclone leg material sampling spot, 16: bed material sampling spot, 17: secondary cyclone ash sampling, 18: bag-house filter ash sampling.

Combustion experiments

The experimental plan consisted of three tests listed in Table 1. The varied parameters were the rapeseed cake ratio and the addition of limestone (CaCO_3) to the bed consisting of silica sand. During the tests coal was used as a base fuel. The first test of co-firing 15% of rapeseed cake pellets and coal with limestone addition (L15) lasted for 12.5h. During the two other tests a ratio of 25% of rapeseed cake was used. In the last test limestone was not added. The duration of the second (L25) and third (NL25) test was approx. 22h and 23h, respectively. The limestone was taken from Ignaberga in south Sweden. The operational conditions were chosen to represent a typical case of an industrial CFB boiler with a bottom bed temperature of 850 °C and an excess air ratio of 1.2

Sampling and analyses

Fuel samples (coal and rapeseed cake used during the tests) were analyzed using standard fuel analysis and chemical fractionation. Chemical fractionation is a method based on selective consecutive leaching by water (H_2O), 1M ammonium acetate (NH_4Ac) and 1M hydrochloric acid (HCl) [8-12]. The increasingly aggressive solvents leach samples into a series of four fractions (including the unleached residue) for analysis. The untreated samples, liquid fractions and the remaining solids were analyzed. All chemical analyses were carried out by an external laboratory. Dry matter was determined at 105 °C. Carbon, hydrogen and nitrogen analysis was carried out according to Swedish standards. For determination of the main ash forming elements samples were molten with LiBO_2 and dissolved in HNO_3 . Analysis took place either with ICP-AES or ICP-SFMS. Also samples from all outgoing solid material streams (secondary cyclone and bag filter) as well as from the bed and the return leg were collected. Sampling spots of cyclone leg material, bed material, secondary cyclone ash and bag-house filter ash are shown in Figure 1. Samples were analyzed semi quantitatively using SEM/EDXA. The results are presented in wt-% of oxide of all analyzed elements in the sample.

Table 1 Rapeseed cake and coal co-combustion tests.

test name	test duration	fuel load [kg ds/h]		rapeseed cake ratio % _{en}	limestone addition [kg/h]	bed regeneration [kg silica sand/h]	Temperatures [°C]			
		r. cake *	coal				bed	before convective pass	secondary cyclone	bag house filter
L15	12h 25min	197.35	687.00	15 %	96.12	2.14	850	800	150	150
L25	22h 16min	324.91	650.23	25 %	92.81	1.62	850	800	150	150
NL25	22h 53min	300.96	666.67	25 %	0.00	102.72	850	800	150	150

* r. cake – rapeseed cake

%_{en} – % on energy basis

Deposit samples were collected on steel rings which were fitted on an air-cooling probe situated in the middle of the flue-gas stream before the convective pass. The surface temperature of the steel rings was set to 480 °C to simulate a superheater tube. The flue gas temperature was maintained at about 800 °C in all tests. Samples of the deposit from windward (0°) side and leeward (180°) side of the ring were analyzed with SEM/EDXA.

At the same position in the flue gas duct, gaseous alkali chlorides and sulphur dioxide were measured continuously using the IACM developed by Vattenfall. The instrument has a sampling time of 5-10 seconds. The detection limit at a 5 meter measuring length (width of the flue gas channel) is 1 ppm for KCl and NaCl and 4 ppm for SO₂ [13].

RESULTS AND DISCUSSION

Standard fuel analyses

The standard fuel analyses are given in Table 2. Compared to coal rapeseed cake pellets contain 9 times more potassium (12300 mg/kg db) and 7 times more sodium (4660 mg/kg db). A chlorine content of 2600 mg/kg db adds to a high risk of deposit formation in the boiler when firing rapeseed cake. Moisture content of the fuels was between 7-12% when introduced to the boiler.

Chemical fractionation

Results from the chemical fractionation of the two fuels are shown in Figure 2. The main ash forming elements in the leachates and the final solid residue expressed as mg/kg dry fuel are presented. Crosses show the amount of the specified elements present in the untreated fuels. A white bar represents the amount leached with water, a light grey bar the amount leached with NH₄Ac and a dark grey bar the amount leached with hydrochloric acid. A black bar represents the amount remaining in the rest fraction. Alkali metals in the rapeseed cake pellets are mainly leached by water and acetate. Usually, components leached out by water are believed to be alkali sulphates, carbonates, chlorides and phosphates. Elements leached out by ammonium acetate are mostly organically associated metals [14]. Compared to rapeseed cake, alkali metals in coal are less soluble in water or acetate. In coal the major part of the alkali metals was found not dissolved at all, indicating an association with insoluble silicates.

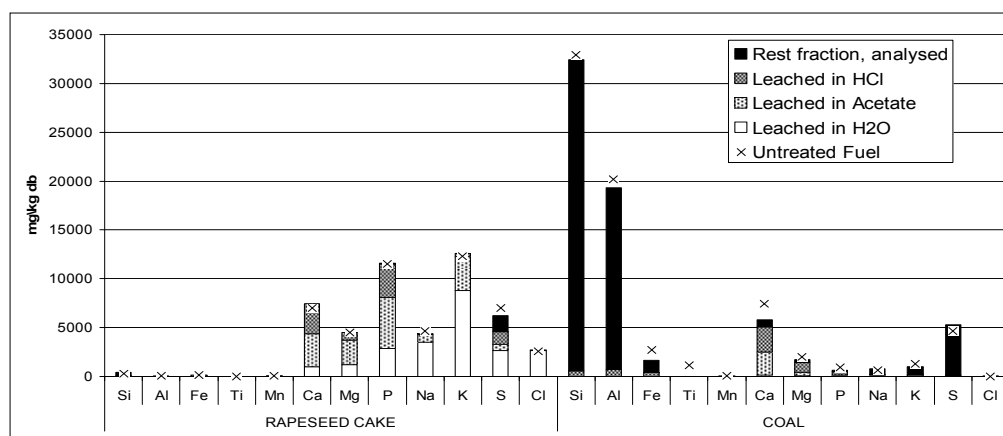


Figure 2 Results of chemical fractionation of rapeseed cake and coal used during tests.

Table 2 Properties of fuels.

Fuel		Rapeseed cake pellets	Coal
Ash	[% db]	7,5**	14,0* 40,3**
HHV	[MJ/kg db]	22,157	28,029
LHV	[MJ/kg db]	20,672	27,089
C	[% db]	49,9	69,3
H	[% db]	6,9	4,4
N	[% db]	5,1	1,8
O (by difference)	[% db]	29,9	10,01
S	[% db]	0,72	0,47
Si	[mg/kg db]	261	32900
Al	[mg/kg db]	43,4	20200
Fe	[mg/kg db]	152	2690
Ti	[mg/kg db]	3,60	1180
Mn	[mg/kg db]	59,70	57,50
Ca	[mg/kg db]	7040	7470
Mg	[mg/kg db]	4500	2030
P	[mg/kg db]	11500	915
Na	[mg/kg db]	4660	637
K	[mg/kg db]	12300	1310
Cl	[mg/kg db]	2600	below detection (<500)

* ashed at 1000^oC; ** ashed at 550^oC;
ar – as received; db – on dry basis

Bottom ash

Figure 3 presents the SEM/EDX surface analyses results of alkali metals found in the cyclone leg samples. To facilitate proper comparison between different shares of rapeseed cake co-fired with coal, cyclone leg samples collected after 11.5h of both L15 and L25 were used.

For comparison between tests L25 and NL25, samples taken after 22.5h were used. In Figure 3, white bars represent samples taken before tests. Since there was only a one hour break between tests L25 and NL25 (black bars), it is assumed that reference values for the beginning of the test NL25 are presented by the values of L25 after 22h. Bed material surface analysis results show similarities with cyclone leg particles surface analysis, with the difference that bed material samples contain also partly unburned fuels.

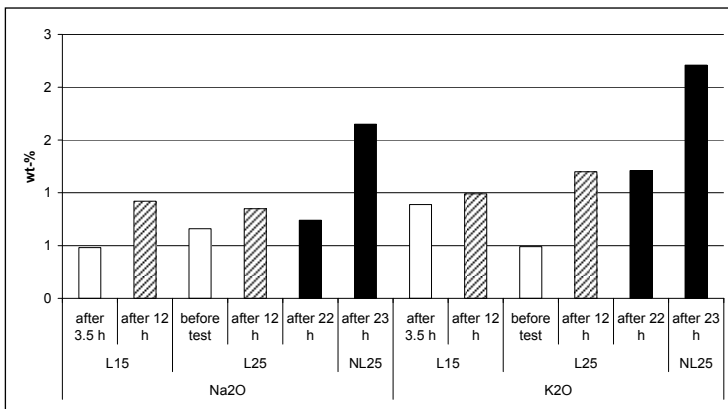


Figure 3 SEM/EDX surface analyses of alkali in cyclone leg samples; presented in oxide form (wt-% of total amount elements).

The results show that an increase in rapeseed cake share from 15 to 25% (striped bars) during the co-combustion tests did not have a significant influence on the alkali concentration in the cyclone leg samples. During the test without limestone - NL25, a decrease of sulphur in the re-circulated bed material could be noticed, compared to the test with limestone - L25. This can indicate that probably at the test NL25, more sulphur is bound as alkali sulphates, leaving the furnace as fly ash.

SEM/EDX point analyses show that reaction between alkali metals, silicon, and aluminum may have taken place (Figure 4). In Figure 5 the spot analysis of a cyclone leg particle is presented. The composition showed that alkali from coal could not be responsible alone for the alkali found in the particle. This means that aluminium-silicates from the coal reacted with rapeseed cake's potassium as well. Probably rapeseed's cake potassium also reacted with bed material forming potassium silicates.

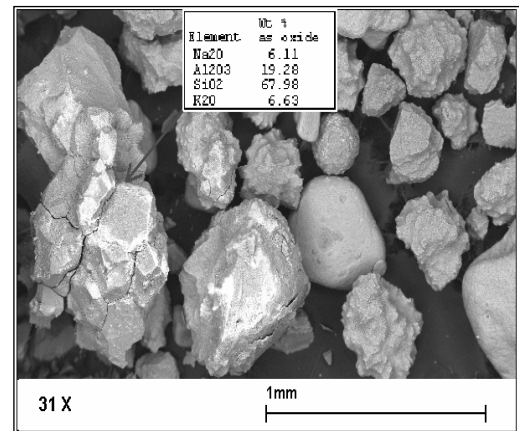


Figure 4 Point analysis on particle found in bed material sample after 7.5 h of co-firing 25% of rapeseed cake with no lime addition. Picture taken at WD of 11 mm and EHT = 20 kV.

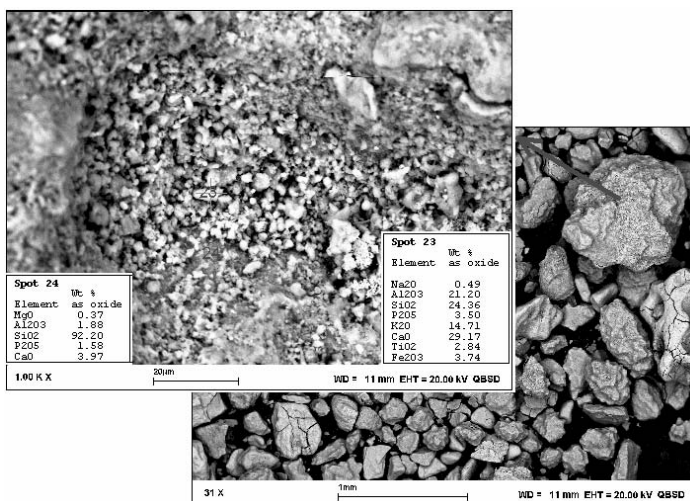


Figure 5 Cyclone leg sample after 7.5 h of co-firing 25% of rapeseed cake and coal with lime addition.

L25 caused by loss of the deposit when removing the probe from the boiler. All the deposit samples contained negligible amounts of chlorine (below the level of 1 wt-% of the total sample composition) which is in agreement with the fact that the concentration of KCl, measured with IACM, was below ppm during all three tests. This indicates that instead of KCl, potassium entered the convective pass as other salts such as K_2SO_4 , K_3PO_4 , and some silicates and that chloride enter the convective pass as HCl.

Solid and gaseous alkali metals entering the convective pass

The deposit probes exposure time was 12h in case of test L15 and the mass gain on the ring was 84 mg. For tests L25 and NL25 the exposure time was 22h in both cases, and the mass gain on the rings was 85 mg and 40 mg, respectively. In Figure 6 the alkali content in the deposits is presented. The highest concentration of alkali appeared on the windward side of the probe. At the same side also the highest concentration of sulphur was noticed. There is no significant difference in the alkali content in the deposits for the tests when 15% or 25% of rapeseed cake was co-fired (L15 and L25). No samples could be taken from the windward side of the probe for the test

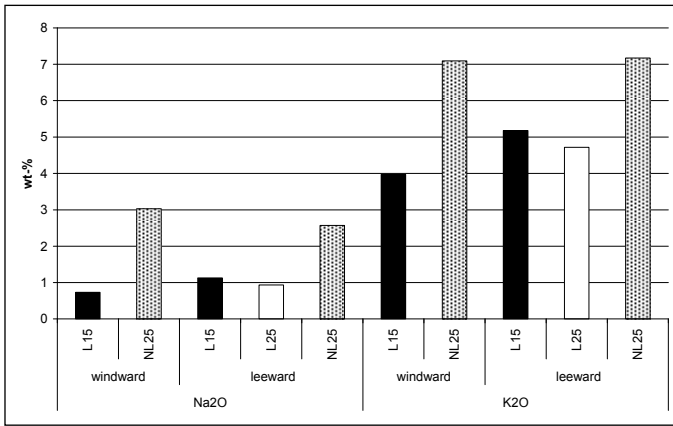


Figure 6 Alkali content in the deposit samples presented in their corresponding oxide form (wt-%) (note: L25 – no deposit retrieved from windward probes).

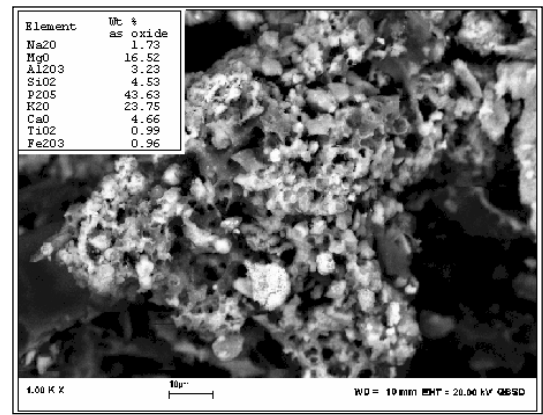


Figure 8 Secondary cyclone ash particle found after 11.5 h of co-firing 15% of rapeseed cake and coal with lime addition.

Fly ash

Results from SEM/EDX analyses of the secondary cyclone and bag filter ash samples are presented in Figure 7. Samples were collected after approx. 12h for each test. Additionally, samples were also taken after approx 23h for test NL25. Black bars correspond to test L15, while white bars represent values for test L25 and dotted ones refer to test NL25. No significant increase in alkali salts could be detected when the share of rapeseed was increased (L15 vs. L25). An increase in alkali for the test when no lime was added can be explained by an increase in formation of small particles as explained above. SEM/EDX point analyses of secondary cyclone ash show that a major part of fly ash consisted of K_3PO_4 (Figure 8).

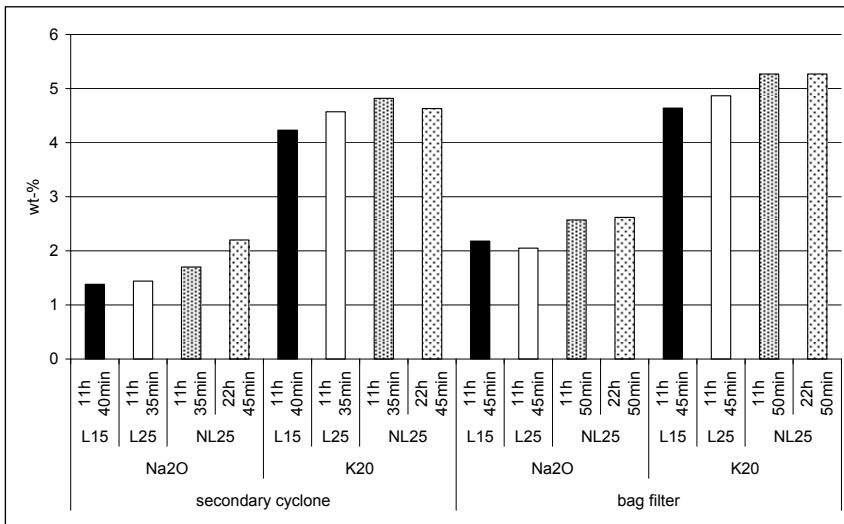


Figure 7 Alkali content in the secondary and bag filter ash.

Alkali distribution

The distribution of K and Na over different particle fractions is shown in Figure 9. This figure shows the distribution of alkali over the fine fly ash, course fly ash and bed material fraction. Figure 9 shows that some 85% of alkali was present in the fly ash fraction. This is in agreement with Lind [15] who stated that up to 20% of alkali may become trapped in the bed. No significant difference could be detected between L15 and L25. When comparing L25 with NL25, more alkali seemed to become enriched in the bed in NL25. However, it

was expected that lime addition would shift the alkali distribution to the bed material when compared to no lime addition (less sulphur available for fly ash formation). The trend was found to be opposite. This unexpected result could be explained by the fact that the NL25 test was carried out with the same bed material directly after L25 and alkali was already present in coatings on the bed and coal ash particles.

CONCLUSIONS

The co-combustion tests were carried out in a 12 MWth scale boiler for 48 h successfully. Since rapeseed cake has high concentration of alkali metals, focus of this paper is put on their behavior during the experiments. Chemical fractionation showed that alkali present in the tested fuel are easily soluble indicating their reactive form. In all three tests alkali metals are found enriched in the fly ash fraction. It is assumed that alkali compounds were released from the combustion chamber as entrained aluminosilicates, phosphates, or volatilized K_2SO_4 . A small amount of KCl was formed as well. About 20% of alkali were trapped in the bed. However, no obvious heavy bed sintering or deposits were noticed.

In this study two shares of rapeseed cake pellets were used. No significant difference in the distribution of alkali compounds could be noticed. Alkali distribution results of the tests with lime addition (L25) and no lime addition (NL25) showed that the history of bed material may have dominated the test results. Alkali enriched in L25 became enriched even more in NL25.

These mid-term tests proved successful co-combustion of up to 25%_{en} rapeseed cake with coal in a semi-industrial CFB boiler with and without limestone injection. However, longer term effects on boilers' operation need to be studied.

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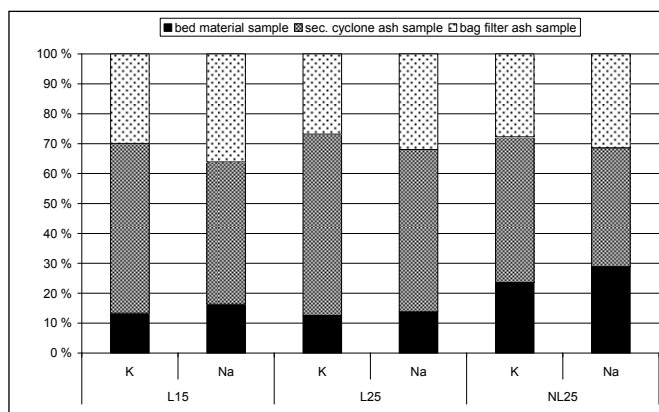


Figure 9 Alkali metals distribution based on SEM/EDXA of samples collected after 11.5 hours for