On the role of potassium as a tar and soot inhibitor in biomass gasification.

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Abstract

The work investigates in a drop tube furnace the effect of potassium on carbon conversion for three different types of fuels: an ash lean stemwood, a calcium-rich bark and a silicon-rich straw. The study focuses on an optimal method for impregnating the biomass with potassium. The experiments are conducted for 3 different impregnation methods; wet impregnation, spray impregnation, and dry mixing to investigate different levels of contact between the fuel and the potassium. Potassium is found to catalyse both homogenous and heterogeneous reactions. All the impregnation methods showed a significant effect of potassium on heterogeneous reactions (char conversion). The fact that dry mixing of potassium in the biomass shows an effect reveals the existence of a gas-induced mechanism that supply and distributes potassium on the char particles. Concerning the effect of potassium on homogenous reactions, it is found that potassium in the gas phase leads to much lower yields of C_2 hydrocarbons, heavy tars and soot. The results indicate that potassium reduces the likelihood of light aromatic to progress toward heavier polyaromatic hydrocarbons clusters, thereby inhibiting the formation of soot-like material. A moderate interaction between the added potassium and the inherent ash forming elements is also observed: Potassium has a smaller effect when the fuel is naturally rich in silicon. The combined results are of interest for the design of a gasification process that incorporates recirculation of naturally occurring potassium to improve entrained flow gasification of biomass.

Keywords: Potassium; biomass; gasification; alkali; soot; tar,

1. Introduction

Gasification is a resource-flexible and product-flexible way to upgrade biomass into renewable chemicals. However, the levels of impurities in the syngas are often problematic for operation of the synthesis units downstream of the gasifier[1]. These problems, however, might be reduced to great extent by the utilization of a fuel that contains alkali elements. Alkali compounds have long been shown to catalyse the heterogeneous gasification of char. In 1980's a lot of effort was put into investigating the mechanism by which alkali elements catalysed coal gasification. The different mechanisms were summarized in a comprehensive review by Moulijn et. al. [2]. They realized that there was a general consensus that the alkali compounds act as an oxygen carrier that facilitated the transfer of oxygen into the char. In more recent times, research on alkali has turned towards more factual aspects. Notably, Perander et al. [3] found that the effect of potassium did not depend on whether the potassium was bounded to the organics or as part of inorganic salts (i.e. K_2CO_3). This work also showed that the reactivity of the char was linearly correlated with the loading of potassium up to 2% K. However, most of the published studies on the effect of alkali elements obviate that in biomass gasification, unlike in coal gasification, the most critical technical aspect is not the reactivity of the char but the formation of undesirable gas impurities (e.g. tar and soot). The extensive body of work covering the mechanism through which alkali catalyses the heterogeneous gasification of char (more than 30 publications) contrast with the lack of fundamental knowledge on how alkali affects the formation of gas impurities. Nevertheless, two important studies demonstrated that alkali does have an important effect. Elliott et.al. [4] found that when the biomass was impregnated with K_2CO_3 the yield of light aromatic tar (1 ring) would decrease by approximately 60% whereas that of heavier PAH (3 rings) would do so by a factor of 10. More recently, Postma et. al. [5] confirmed the tar-suppression activity of potassium. In particular, they showed that impregnating a char bed with potassium would increase the tar-suppression activity of the bed whereas adding the potassium directly to the fuel while maintaining the potassium- impregnated bed would further reduce the yield of tar. The benefits of alkali and alkaline elements on tar suppression have also been observed at pilot-scale fluidized bed gasifiers [6–8] and at an entrained flow gasifier [9]. The latter reference, corresponding to a 3 MW_{th} black liquor gasifier showed that the purity of the syngas was so high that the syngas could be upgraded into liquid fuels without complex gas-cleaning units [9]. The experience with black liquor has motivated the expansion of the concept of alkali-catalysed gasification to wider range of biomass. Recently, we proposed a process with a recirculation of the naturally occurring potassium in biomass ashes to enrich the alkali content of the fuel feedstock prior to the gasifier [10,11]. Additionally, impregnating the biomass with potassium lead to other operation benefits as an improved ash flowability as well as in-situ sulphur capture[10]. Nonetheless, alkali metals can corrode process equipment as downstream heat exchangers. The company Chemrec developed a technology intended to gasify alkali rich-fuels (i.e. black liquor), such technology handles alkali by using a special alkali-resistant ceramic lining in the gasifier and avoiding dry heat exchange surfaces in the quench and gas cooling sections after the gasifier[12,13]. Chemrec's design has been validated by more than 28000 operating hours [14]. We assume that the gasification of alkali-impregnated biomass would require a similar technology. In the proposed process, the biomass is impregnated with potassium carbonate. Potassium is the most abundant alkali element in biomass, and therefore it offers the best chances of an efficient recovery and recirculation. Carbonate has been chosen as the anion counterpart because it is in the form in which potassium is predominantly found in the ashes left by gasification conditions. In an earlier study it was found that both hydroxides and carbonates were catalytically active forms of alkali regarding char gasification[15]. Nevertheless, the lack of fundamental knowledge on how alkali influences the formation of gas impurities ultimately leads to practical questions. This work attempts to address some of these questions with the double objective of contributing in the design of a gasification process with alkali recirculation while at the same time improving the fundamental understanding on how alkali reduces tar and soot formation. One fundamental question that is particularly compelling to investigate is how the degree of contact between the added alkali elements and the organic matrix in the biomass influences the activity of alkali. Despite the importance of the issue it has never before been investigated through dedicated experiments. In this work we address the question by means of experiments with varying degrees of contact which arise from different impregnation techniques. Furthermore, due to economic reasons biomass gasification should preferably utilise low-grade biomasses, which are typically ash-rich. Therefore, the effect of potassium should be studied not only in isolation, but also in the presence of other ash-forming elements; particularly calcium, the most abundant inorganic element in forest biomass as well as Si, the most abundant in herbaceous biomass. Silicon has affinity for alkali element, forming molten alkali silicates that are thought to be undesirable both chemically (non-catalytic species)[6,16–18] and physically (a molten layer around the fuel particles might restrict oxygen transfer)[19]. Interestingly, despite the concentration of alkali has almost unanimously found to correlate with char reactivity, in the work by Leteng et al.[20] it was observed that silicon-rich biomass samples showed the opposite trend. The study reported that the reason was likely caused by ash restricting the transfer of gases into the char but did not develop on the issue further. In the present work the effect of alkali has been studied quantitatively as a function of the amount of potassium in the fuel, this is an important consideration as excessive amounts of alkali may be also counterproductive by behaving as a thermal ballast that limits cold gas efficiency of the gasifier.

This work is based on experiments at a laboratory scale drop tube furnace (DTF) that target the effects of: a) the contact between the biomass and potassium as determined by different impregnation methods, b) interactions of the potassium with inherent calcium and silicon in biomass, and c) different alkali levels in the fuel (approx. 2, 4, and 8% on mass basis). The above variables have been studied at a reference temperature of 1000 °C, which is in the range of the temperatures in which alkali-catalysed entrained flow gasification aims at operating. Additionally, a subset of experiments has also been carried out at T=1200 °C to investigate the temperature in which soot formation is most critical but also to provide a basis to interpolate results above 1000°C.

2. Methods

2.1 Sample preparation

Three different biomass feedstocks were used in the experiments: pine bark was selected as a representative of calcium rich forestry residues, wheat straw as a representative of a typical Si-rich agricultural residue and spruce stemwood as a reference of an ash lean fuel. All the raw feedstocks were sieved to select the fraction left within the 200-300µm mesh size. The selected material was divided into representative divisions with a rotary sample generator and the subsequent divisions were impregnated with potassium carbonate through the different methods: dry mixing, spray impregnation and wet impregnation. Additionally, the original non-impregnated samples were also utilised for comparison purposes. Dry mixing consisted of feeding the biomass simultaneously with solid K_2CO_3 particles, thereby limiting any interaction between the two streams to gas-phase reactions. Spray mixing consisted of adding the alkali by spraying a K_2CO_3 solution upon the biomass, thus primarily leading the potassium to being deposited on the external surface of the biomass particles. And wet impregnation consisted of mixing and stirring the biomass in a K_2CO_3 solution.

Wet impregnation was carried out by mixing the biomass with an aqueous solution of K_2CO_3 at a ratio of 15ml solution per 1 g of biomass. The concentration of the impregnating solution was 0.2M for stemwood and 0.1M for bark and straw. These concentrations were determined, on the basis of a pre-study, to target a 4% K in the biomass (on the mass basis) in the impregnated samples. The resulting slurry was stirred for 30 min at 80°C, and afterwards, vacuum-filtered to remove as much of the impregnating solution as possible before drying. However, some of the K_2CO_3 solution still remained in the biomass, precipitating upon drying. In this way, the potassium on the wet-impregnated samples would ultimately exist both as ionically-bonded to the biomass as well as precipitated as crystals on the surface of the biomass particles. This split of potassium was measured and the results are provided in the appended material. In general, ionically-exchanged potassium accounted for 60-70% of the potassium.

Spray impregnation was carried out by spraying a calculated amount of K_2CO_3 solution (0.4M) into the biomass under continuous stirring. This method targeted concentrations of potassium in the biomass samples (i.e. impregnation levels) of 2, 4 and 8% on mass basis. After spraying, the samples were dried overnight at 105 °C. The same procedure was followed for all of the 3 original fuels (wood, bark or straw).

The prepared impregnated materials were further divided into representative samples for the chemical analyses and for each of the planned experiments. Table 1 shows the ultimate analyses and the concentration of the major ash-forming elements for each of the samples that were utilised in the experiments.

Table 1 Elemental analysis of the different fuels used in the experiments.
a: Ultimate analysis at our lab.
b: By ICP-MS at a commercial lab
n.a.: Not analysed
bdl: Below detection limit/level

Fuel	Imp. Method	C (wt.%)[a]	H (wt.%)[a]	O (wt.%)[a]	Si (mg/kg)[b]	Al (mg/kg)[b]	Ca (mg/kg)[b]	Fe (mg/kg)[b]	K (mg/kg)[b]	Mg (mg/kg)[b]	Na (mg/kg)[b]
Spruce stemwood	none	47.6	6.1	42.5	n.a.	8.29	815	16.7	580	89.6	bdl
	spray-2%	48.3	6.0	n.a.	81.3	23.8	602	24	16300	87	bdl
	spray-4%	46.6	5.8	41.8	bdl	14.5	755	18.3	35100	97	bdl
	spray-8%	44.7	5.3	n.a.	231	13.9	714	16.1	73700	91.2	167
	wet-4%	46.3	5.9	41.1	bdl	10.9	628	18.1	31200	46.9	82.3
Pine Bark	none	49.8	5.9	42.7	n.a.	530	4280	141	1990	420	93.6
	spray-2%	49.6	5.7	n.a.	523	657	3130	130	18700	412	107
	spray-4%	48.4	5.6	38.6	520	777	3770	154	38700	460	190
	spray-8%	45.1	4.9	n.a.	685	723	3020	123	86000	411	221
	wet-4%	46.8	5.5	39.5	416	783	3730	128	43300	448	198
Wheat straw	none	40.4	5.6	40.6	n.a.	18.6	3240	35.8	7330	1030	bdl
	spray-2%	42.4	5.4	n.a.	6400	25.1	2770	38.2	25700	994	59.3
	spray-4%	40.5	5.4	38.8	7630	30.3	3050	33.9	42900	1110	94.9
	spray-8%	37.5	4.9	n.a.	6610	23.6	2520	36.6	89900	915	126
	wet-4%	40.0	5.3	38.6	5250	25.2	2710	30.8	45100	1120	153

2.2 Experimental configuration

All the experiments were conducted in an atmospheric laminar drop tube furnace (DTF) as sketched in figure 1. The reactor consists of an alumina tube (internal diameter: 54 mm, heated length: 2.3 m) inside split tube furnaces. The gas flow rate into the reactor is regulated by mass flow controllers (Bronkhorst: EL-FLOW series). The biomass is fed by a vertically-arranged syringe pump that continuously displaces the bed of particles upwards. In the centre line of the bed, an 8 mm tube leads the fuel to fall into the reactor. Vibration is applied to the feeding unit to improve the consistency of the fuel flow. The fuel particles fall into the high temperature zone in the reactor through a water-cooled probe, thus ensuring a high heating rate, characteristic of entrained flow gasifiers (ca.10000 °C/s).

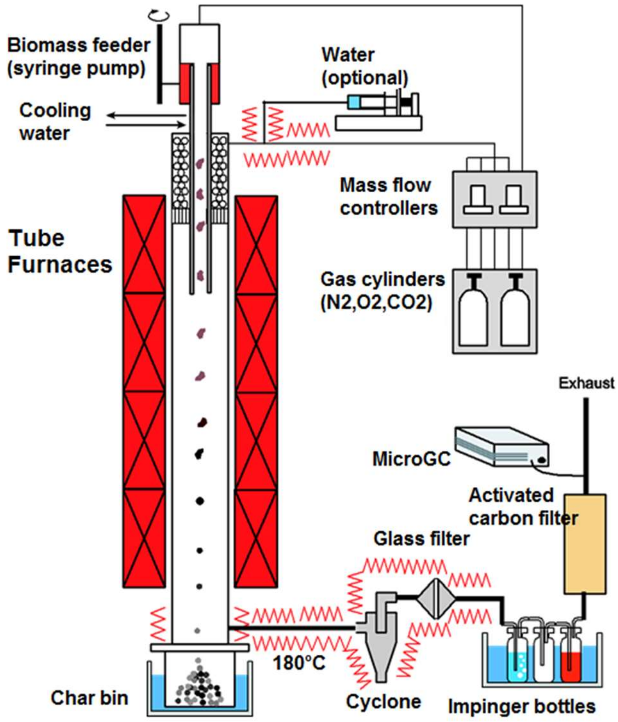

Figure 1 Configuration of the reactor used in the experiments. The rector is also called drop tube furnace or laminar entrained flow reactor. It is composed by a ceramic tube heated by 6 pairs of electrical furnaces. The biomass and the gas flow are fed from the top

The temperature of the reactor was set to 1000 °C for the majority of the experiments, but a subset of experiments was performed at 1200°C. Upon reaching a steady state both in temperature and gas environment, biomass was fed into the reactor at a rate of approximately 6 g/h. A primary flow of gas (160 ml/min of N_2) was injected through the central tube together with the fuel. A secondary flow (4.64 l/min of N_2 and 0.258 l/min of CO_2) was concentrically supplied to set the gas composition of the reactor at approximately 5% of CO_2 on the volume basis. Low partial pressures of CO_2 promote the release of gaseous alkali species, thus allowing us to examine the activity of alkali through homogenous gas-phase reactions. This low concentration of CO_2 was also chosen to ensure a good closure of the carbon balance. All the gas volumes are given at the reference conditions of T=0°C and P=101.3kPa. The feeding was maintained for 25 min but the experiment was not considered completed until the reactor recovered the initial gas composition. The solid residue from the gasification (char + ashes) was collected in a char bin at the bottom of the reactor. The particles suspended in the gas were captured first through a cyclone (URG corporation: URG-2000-30ENS-1; nominal cut size 2.5 µm) and subsequently through a glass filter (Whatman GF/A 50mm; particle retention 1.6 µm). Based on SEM images of previous work, we estimate that this type of filter was able to capture particles as small as 0.8 µm. The exhaust gas line was heated to T=180 °C to avoid the condensation of heavy tars before its sampling point. As shown in the appended material the partial pressure of heavy tars in exhaust gas was well below the saturation pressure at 180 °C. The condensable compounds (tar and water) were collected by bubbling the gas through methanol-filled washing bottles kept in a cold bath at -50°C. Finally, a microGC (Agilent 490 equipped with PoraPLOT U and MolSieve 5A columns) continuously measured gaseous species with a sampling interval of 120 sec. The detected species were H_2, N_2, CO, CO_2, CH_4, C_2H_2, C_2H_4. The detection limit for H_2, CO, CH_4, C_2H_2, C_2H_4 was 0.01, 0.15, 0.02, 0.0001 and 0.0005 vol.%, respectively. After the completion of each experiment, we conducted a burnout routine by passing a flow of oxygen (5% of O_2 diluted in N_2) through the reactor to combust any carbon that deposited on the walls of the tube. The exhaust gas arising from this burnout routine was collected in a gas-sampling bag and subsequently analysed in the microGC device. The CO_2 formed under this process was assumed to arise from the combustion of carbon-rich material that deposited on the walls of the reactor, this product is referred as “deposited carbon”. It is worth noting that the existence of deposited carbon is due to the nature of the laboratory setup (i.e. high wall surface to biomass feed rate ratio and low gas velocity). Nevertheless, it is of interest because it is associated with the concentration of intermediate precursors of soot. Table 2 summarizes the different types of undesired products, which will be evaluated throughout this paper in terms of carbon mass. The main gas species are presented in the appended material.

Table 2 Description of the different sources of carbon as part of the undesired products

Source	Description
Char	Mass of carbon in the solid residue (Char + ashes) (including C as $CO3^{-2}$)
Soot	Mass of carbon in the filter (excluding C as $CO3^{-2}$)
Deposited carbon	Mass of C recovered by passing O_2 through the tube after each experiment
C_2 gases	Mass of C as C_2H_2 and C_2H_4. C_2H_6 was always below the detection limit
Tar	Mass of C in tar. Further subdivided by number of aromatic rings

Another aspect that is important is the chronological order in which the experiments were carried out. As it was learnt from previous work with the same experimental equipment, alkali elements interact with the alumina walls of the tube. The alumina wall can either accumulate or release alkali elements depending on the thermodynamic conditions, in other words the tube has some chemical inertia. For this reason, we conducted the experiments of all the sample without alkali impregnation at the beginning. Then, the experiments using the fuel with the same amount of alkali elements (for example, 4% of K) were grouped together and the order of experiments within that group was randomized. Before moving to the next group of experiments (for example experiments with the fuel containing 8% of K), a stabilization run was conducted. Stabilization runs were carried out with the same configuration that the ordinary experiments but for longer time and without measuring any of the products.

2.3 Chemical analysis

The ultimate analyses were carried out with EuroEA3000 by Eurovector srl. These analyses were conducted for the biomass samples, char bin material and filter material. The inorganic composition of the fuel samples was measured in a commercial laboratory through ICP-MS following the *SS EN ISO 17294-1, 2* for ICP and the *EPA-method 200.8* for the MS. Methanol-dissolved tar species were measured with a GC-FID analyser (Agilent 7820A with DB-EUPAH column, length: 60 m; internal diameter: 0.25 mm; film thickness: 0.25 μm). The temperature of the oven was increased from 57 °C to 97 °C at a heating rate of 4 °C/min and then to the final temperature of 280 °C at 10°C/min. Temperature was then maintained for 12 minutes.

SEM-EDS analyses were conducted for a selection of fuels and chars. The model used was a JEOL JSM-IT300, using a shadow back-scattered electron detector for the morphological study and an Oxford instrument block for the EDS analysis.

2.4 Thermodynamic equilibrium calculations

The equilibrium of the major gas compounds and the speciation of potassium under experimental conditions were calculated utilising the commercial software "FactSage 7.0" with the databases FactPS 7.0. We also included the solution packages; FT Oxid-SLAGA and FT Pulp- MeltA for liquid solutions and FTpulp-Hexa for solid mixtures[21].

3. Results and discussion

3.1 The effect of the impregnation methods

As described in the section above, different impregnation methods were utilised to recreate different degrees of contact between the alkali and the biomass. Fig. 2 and Fig. 3 shows the yields of undesired products for each of the impregnation cases. All the above-mentioned yields are calculated on the carbon basis. As it can be seen in both figures the addition of potassium into the biomass led to a strong and significant reduction of undesired products in general (the analysis of the statistical significance of the studied effects is provided in the appended material).

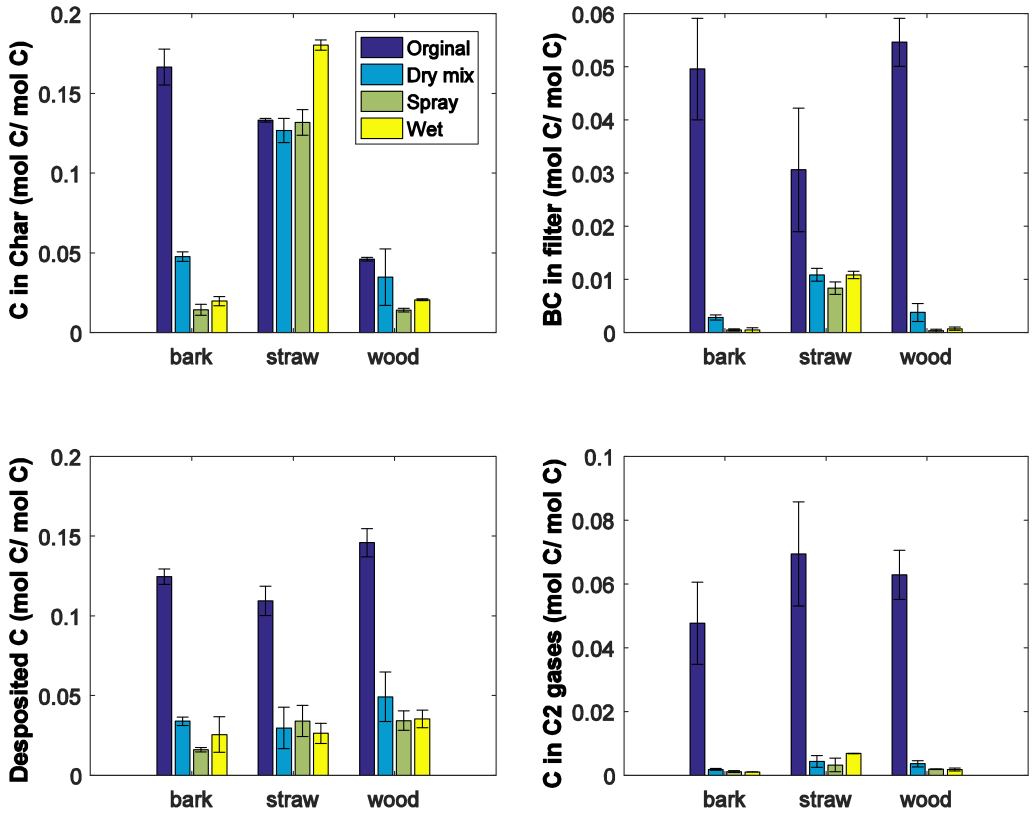

Figure 2 Yield of undesired products expressed as a carbon balance. The impregnation level is 4% K and the temperature 1000°C.The error bars shows one standard deviation with a sample size of N=3.

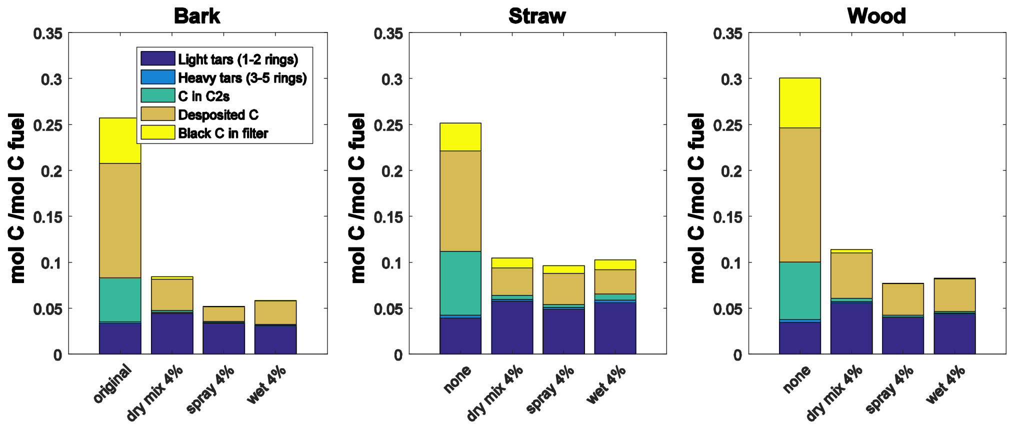

Figure 3 Combined yield of soot-relevant undesired products. The impregnation level is 4% K and the temperature 1000°C. The data has been stacked to facilitate the comparison between the different products.

The char yield from bark and wood decreased significantly by adding potassium in the biomass. This observation is consistent with the understanding that alkali promotes char conversion rate. Indeed, the catalytic effect of alkali elements on char gasification has repeatedly been reported in literature [3,16,22] and it is not the focus of this paper. However, there are a few observations that should be drawn from the results. First, the apparent rates of char conversion were at least affected by kinetics, although we cannot conclude that the char conversion was controlled by the reaction kinetics. Second, the behaviour of impregnated straw was very different to those of impregnated stemwood and bark, thus showing that there is a mixed effect between the fuel type and the presence of alkali. This observation centres the discussion in the next chapter. Finally, it can be seen that char conversion improved even when potassium was added through the dry mixing method. This last observation is also observed for the rest of the products shown in the Figure 2. It indicates that the catalytic effect of potassium is a gas-phase induced phenomenon. Thus, it is not necessary that there exists an initial contact at a molecular level between the biomass and the alkali salts. Notably, the gas-phase induced effect of alkali element is not exclusive to products from a gas-phase origin (e.g. tar, C_2H_2, soot) but also to the heterogeneously-reacting char. It implies that there exists a pathway to transport potassium from K_2CO_3 particles to the char through the gas phase. Such a pathway has recently been presented on the basis of experimental work relevant for fluidized bed gasifiers [23]. In particular, it was shown that potassium volatilized from the ash-covered bed material (olivine particles with a layer of Ca and K on the surface) and re-condensed on the char particles to catalyse char gasification[23]. The possibility of this gas-induced mobility of potassium should be, however, evaluated from a thermodynamic perspective under the conditions relevant to our experiments.

In our reactor, there are two scales where relevant phenomena take place: the global reactor scale and the particle scale. The global scale captures the environment that causes potassium to be released from the K_2CO_3 solid particles (in the dry mixing case). The local particle scale, captures the environment around the biomass particle, which is where recondensation of gaseous potassium onto char particles would occur. It assumes that the out-going pyrolysis gases form a boundary layer around the biomass particle, acting as a diffusion barrier that causes that the gas composition around the char particles differs from that of the overall reactor. Note, that the out-going pyrolysis gases of a 250 μm biomass particle occupy a volume approximately 360 times bigger than that of the initial biomass particle. The results from these thermodynamic calculations are illustrated in Fig. 4. They show that, under the global equilibrium, all the potassium is expected to be released to the gas phase, demonstrating the thermodynamic likelihood of potassium to migrate from the condensate (K_2CO_3 solid particles in the dry mixing method) to gaseous phase. Thereafter, and once the devolatilization is over, part of the gaseous alkali may diffuse into surroundings of the char particles. Our calculations indicate that although most of the potassium that reaches the surroundings of the char particles remains in the gas phase, re-condensation may take place to some extent. Note that, because char gasification is endothermic, the temperature in the vicinities of the char surface must be lower than that of the reactor. However, thermodynamic modelling does not capture the chemical and physical complexity of the phenomena that take place in the local regions and therefore the above results should be interpreted only as an indication of the likelihood for the gas-induced mobility of alkali rather than as a proof.

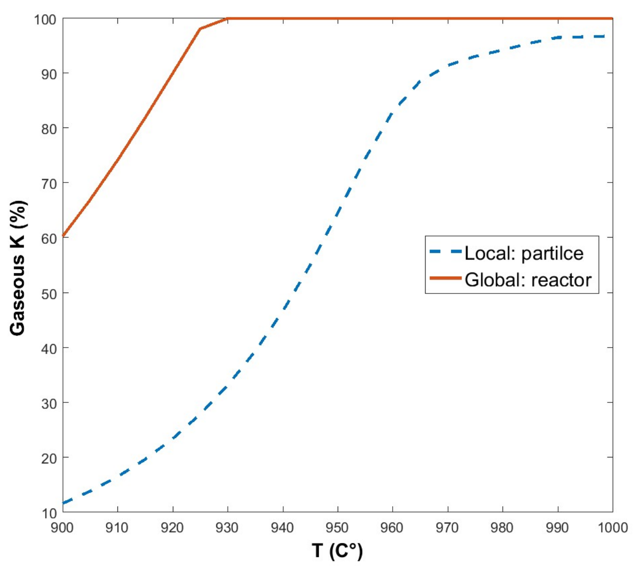

Figure 4 Potassium in the gas phase as predicted by the thermodynamic equilibrium. Conditions simulating the experiments in the DTF: T=1000°C, CO_2=5 %. The simulated case corresponds to stemwood with a content of 4% K.

In general, dry mixing is slightly less effective than wet and spray impregnation methods. This difference is probably because only a part of the potassium has time to be released from the K_2CO_3 particles before exiting the reactor, thus the amount of potassium that is active in dry mixing is smaller than in the other methods.

The results have important implications for the design of an alkali-catalysed biomass gasification process. Because the alkali element does not require be tightly bonded to the biomass, the impregnation unit could be greatly simplified by adopting a large scale version of the spray impregnation method. The spraying method is also preferable over the wet impregnation, among other reasons, because it requires a smaller energy consumption to dry the impregnated fuels while at the same time avoiding the carbon –leaching effects associated with wet impregnation of biomass[15].

3.2 Interactions of potassium with silicon

Fig 2 showed that for all the impregnation methods, potassium had a much weaker effect in straw than in bark and stemwood. This was especially obvious regarding the residual carbon left in the char but it was also visible in the rest of undesired products. There was therefore a combined effect between the addition of potassium and the type of biomass. This combined effect was identified through an analysis of variance with the following factors a) fuel type (3 categories) and b) added K (0% vs spray- 4%). The results of the analysis are provided in the appended material. They showed that indeed the mixed effect between the fuel type and the added potassium is significant with the p-values of the mixed effect being well below 0.05with the exception of C in the C_2 gases. Straw contains much more silicon than bark and wood (see table 1), and thus the factor "fuel type" implicitly carries the effect of the silicon content in the fuel. Therefore, given the affinity of silicon for potassium to form inert K-silicates, the combined statistical effect between the fuel type and the added potassium should be interpreted as an interaction between the added potassium and the inherent silicon in the fuel.

The distribution of potassium as expected from thermodynamic equilibrium is shown in Fig. 5. The results showed that a noticeable amount of the potassium was captured by silicon in the condensate phase, essentially as potassium silicates. The formation of K_2SiO_3 limited the amount of gaseous potassium, which is active as a gas-phase homogenous catalyst. This may be the reason why straw yielded higher quantities of soot-related products. On the other hand, at 1000 °C, K_2SiO_3 is a viscous liquid with a tendency to stick on particles. This behaviour is undesirable in char gasification as it tends to encapsulate char particles and increase resistance to mass transfer.

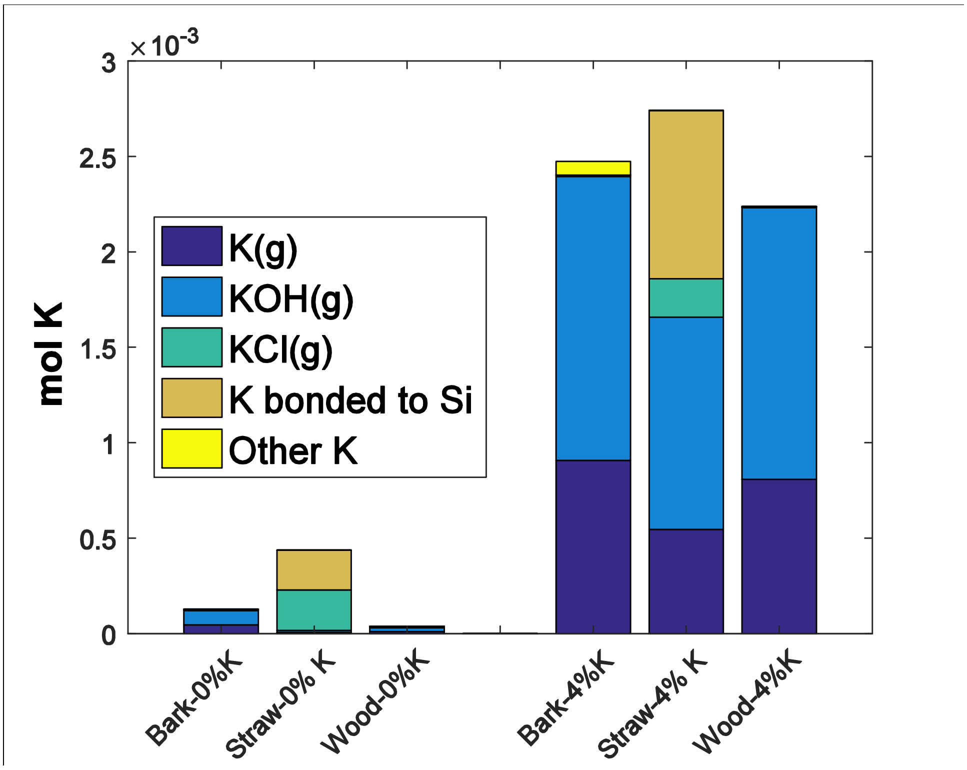

Figure 5 Speciation of K as predicted by the thermodynamic equilibrium at the experiment conditions T=1000°C, CO_2=5%. K=0%/4%.

To investigate the encapsulation event, we conducted SEM imaging and EDS mapping for gasification residues originated from straw. Fig 6 shows the residue left by the experiments with wet-impregnated (top images) and spray-impregnated straw (bottom images). The left images feature a large domain of the sample, picked randomly, providing an idea of the overall morphology of the gasification residue. The right images refer to a magnified region that was further analysed with EDS mapping. The mapped area was carefully selected to include both singular features such as external surfaces and internal sections of the material but also material that was representative of the majority of the sample.

The elemental maps in the Fig. 7 and Fig. 8 show that considerable amounts of silicon existed on the external surface of large particles (i.e. unconverted char particles). Besides the signal of silicon was aligned with those of oxygen and potassium, giving evidence of the formation of K-Si-O- rich compounds. The fact that these elements were found predominantly on unconverted particles should be understood as that the depositions of these elements constrained the conversion rate of char. This observation, in combination with the results on char conversion shown in Fig. 2, suggests that adding potassium in silicon- rich biomass may be counterproductive as it may lead to the formation of a layer of molten ash, encapsulating the char particles and thereby limiting char conversion by restricting the supply of oxidant gases to the reacting char.

On the other hand, the SEM pictures visualized that spray-impregnated straw (bottom images) underwent a higher degree of conversion than wet-impregnated straw (top images). This observation is also consistent with the yields of residual carbon reported in Fig. 2. Although Si-rich compounds were found on the surfaces of larger char particles similarly from spray and wet- impregnated straws, wet impregnation yielded a much larger number of these unconverted particles. It seems that the encapsulation event in Si-rich fuels is more severe if the potassium is added through wet impregnation than through spray impregnation. Perhaps this circumstance is because of the lower degree of contact between the potassium and the biomass arising from spray impregnation, precluding an exhaustive chemistry between the potassium and the silicon inherent in the biomass.

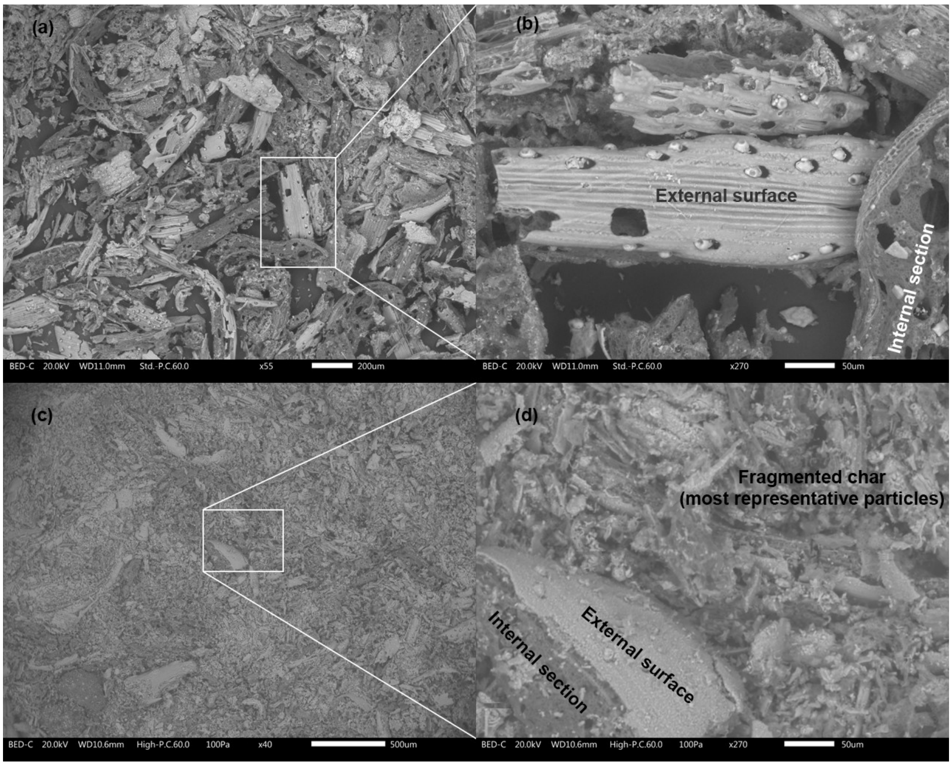

Figure 6 Appearance of the gasification residues arising from wet-impregnated straw (top images) and spray-impregnated straw (bottom images). The magnified areas were mapped with EDS and are they are shown in figures 7 and 8. The magnified regions includes singular features such as external surfaces and internal sections of char particles but also material representative of the majority of the char.

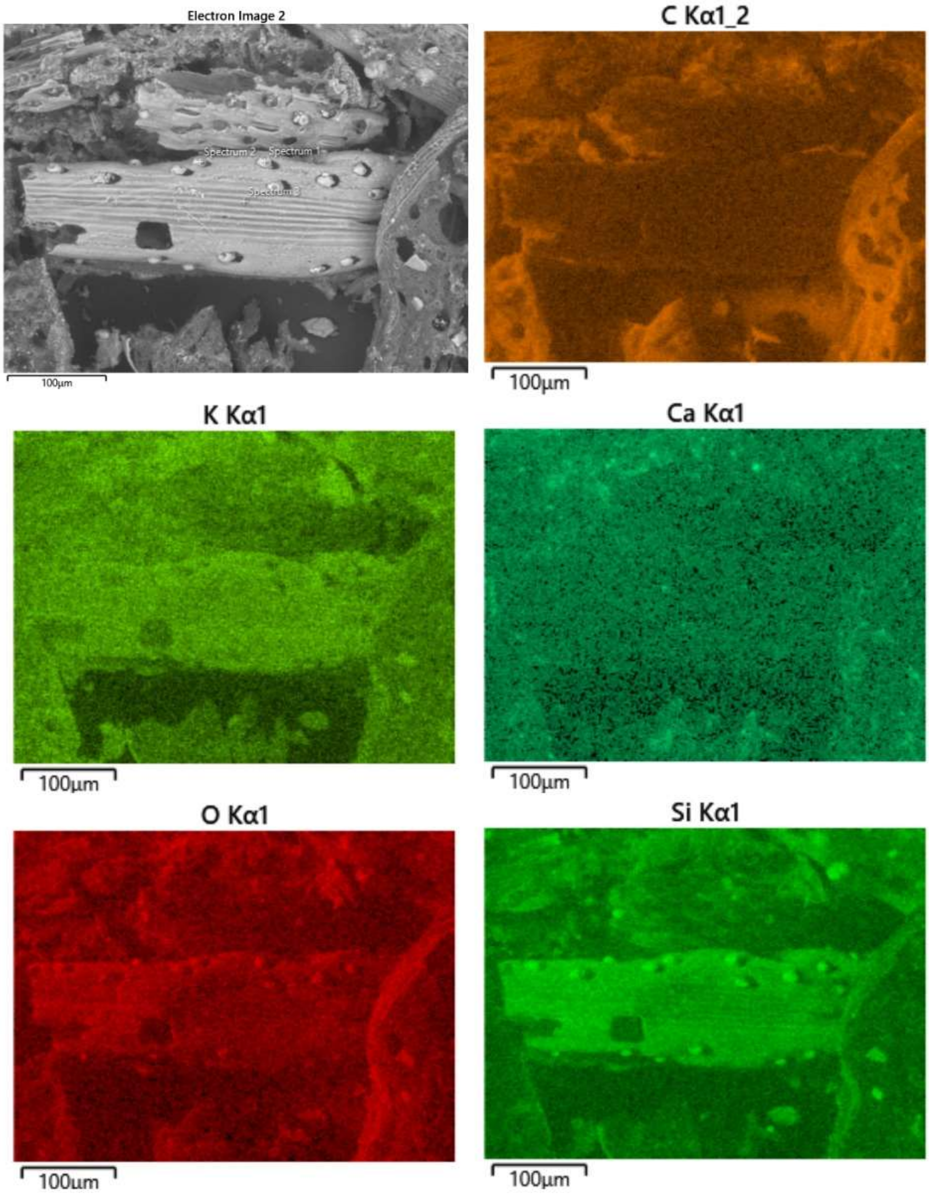

Figure 7 EDS mapping of the region showed in 6b. The sample corresponds to the gasification residue from experiments with wet-impregnated-straw. K=4%, T=1000C.

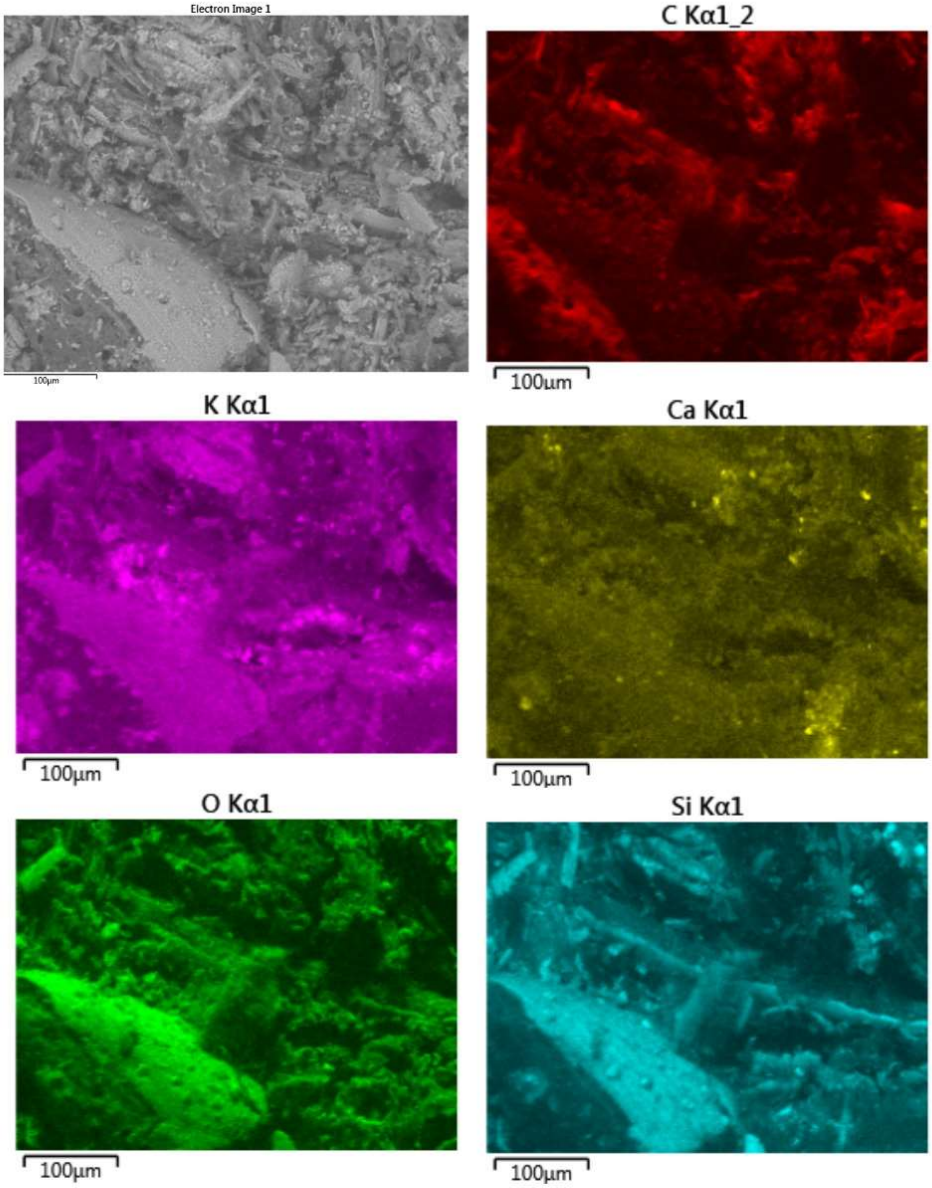

Figure 8 EDS mapping of the region showed in 6d. The sample corresponds to the gasification residue from an experiments with spray- impregnated straw. K=4%, T=1000C

3.3 The effect of the potassium impregnation level

To this point all the results indicate that adding potassium in the biomass through spray impregnation is as effective as through wet impregnation, or even more in the case of straw. Therefore, given that spray impregnation is much more convenient to implement in a full-scale gasifier than wet impregnation, for the remaining of the paper we focus on spray impregnation as the method to add potassium in the biomass.

Figure 9 shows the yield of the various undesired products as a function of the potassium content in the fuel. The figure illustrates that the potassium has a weaker effect in straw than in the other fuels. As discussed earlier this is due to the affinity of the inherent silicon to bond with potassium thereby limiting its availability in a catalytic form. The thermodynamic analysis indicated that the interaction of potassium with silicon in straw dominates the fate of potassium up to content of 1.5% K. Any additional potassium above this threshold remains free and therefore stays active as a catalyst. In fact, Fig 9 illustrates that in straw the yield of residual carbon remaining in the gasification residue peaked around 2% K. Above this value, the added potassium showed a positive effect in reducing unconverted char by probably promoting char conversion in those particles where the encapsulating ash layer was milder.

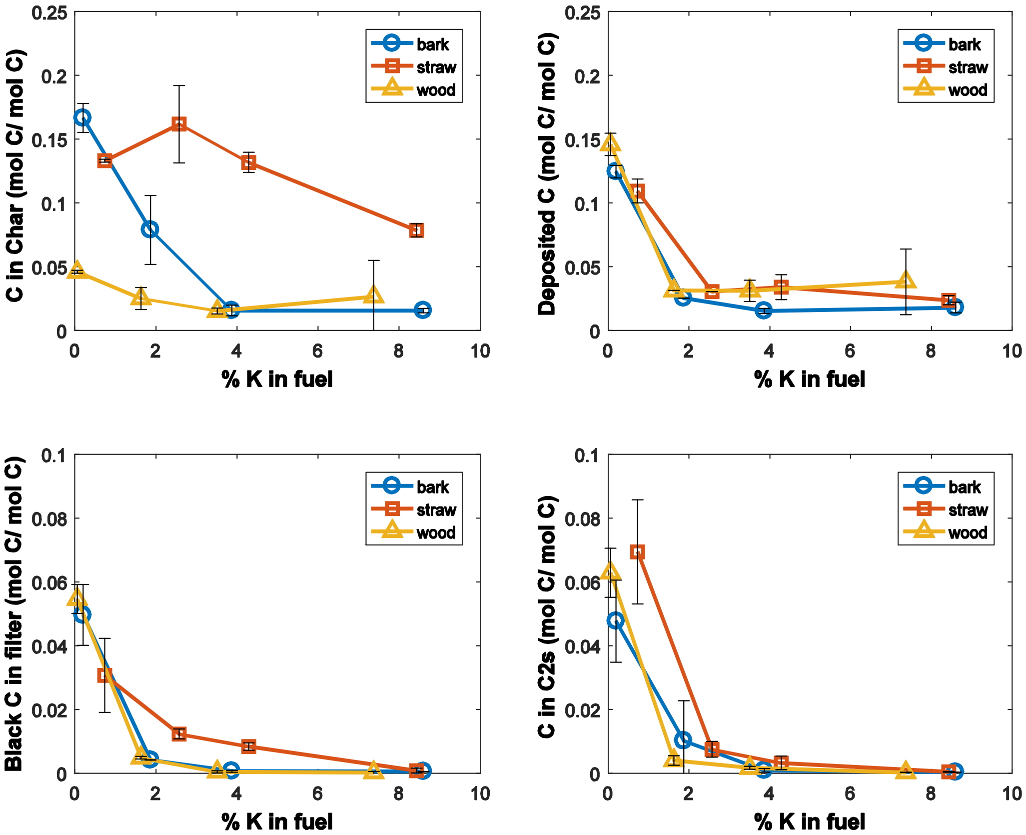

Figure 9 Yields of undesired gasification by-products. Experiments for the spray impregnation method at T=1000 °C and 5 % CO_2. The error bars show 1 standard deviation. N=3 for the K= 0 and 4 % whereas N=2 for K=2 and 8%.

Figure 9, also shows that, the yield of soot-like materials (i.e. black carbon in the filter and deposited carbon) as well as that of soot precursors (i.e. C_2 gases) are very sensitive to K. Soot is the ultimate product of a long and complex sequence of reactions. This sequence is often subdivided in four major steps: homogeneous nucleation of soot particles, particle coagulation, particle surface reactions and particle agglomeration. The nucleation step is arguably the most critical step as it controls the number of inceptive soot particles. The prevailing opinion is that the nucleation step is triggered by the formation and growth of PAH clusters and that these clusters repeatedly experiment collisions with each other ultimately evolving into to 3-D solid particles [24]. The formation and growth of PAH therefore appears as a critical step in the formation of soot. Two main mechanism are responsible for it:

The HACA mechanism holds that the growth of aromatic hydrocarbons proceeds by a continued removal of hydrogen atoms and addition of carbon atoms. One particularly important case of HACA is that which happens in presence of C_2H_2 as formulated by Frenklach[24]

$$R_i + H \Leftrightarrow R_i\text{-} + H_2 \tag{1}$$

$$R_i\text{-} + C_2H_2 \Leftrightarrow R_iC_2H_2 \tag{2}$$

$$R_iC_2H_2 + C_2H_2 \Leftrightarrow R_{i+1}\text{+H} \tag{3}$$

Where R_i is the growing aromatic radical, and i the number of rings.

The availability of C_2H_2 is critical for the HACA pathway. Figures 9 and 11 show that C_2 gases are strongly reduced by adding potassium. This could be interpreted as potassium promoting C_2H_2-consuming reactions (HACA being one of them) or by potassium inhibiting the formation of C_2H_2 at an earlier stage. The fact that the yield of black carbon in the filter (aka soot) is strongly reduced by potassium suggests that the reduction of C_2H_2 is likely driven by the second option. The unavailability of C_2H_2 would, then, limit the growth of PAH through the HACA pathway. It is also interesting that the decrease in C_2's species in presence of potassium is of the same magnitude (in terms of carbon mass) than the increase of CH_4.

Additionally, the growth of PAH takes place also as a result of successive collisions between lighter aromatic, this pathway is also known as the direct combination route[25]. For instance, in benzene-rich environments, as in our experiments, the growth of PAH can be initiated by the formation of biphenyl from benzene [24]. Note that this mechanism can proceed simultaneously with HACA.

Biomass devolatilization generates a wide range of pyrolysis products, often called primary tars. These species undergo secondary and tertiary reactions tending toward more stable compounds. In our experiments; the residence times and temperatures were such that the collected tar species consisted uniquely of relatively stable aromatic hydrocarbons. In Figure 10 the collected tar species has been grouped according the number of aromatic rings. The figure reveals that light (1-2 rings) and heavier tar species (3-5 rings) responded differently to potassium. The heavier compounds are more sensitive to potassium than the lighter species and they decreased moderately already at low concentration of potassium, showing a similar response that those by black carbon in the filter or C_2's. On the other hand, the yield of light tars (i.e. 1-2 aromatic rings) increased at low levels of potassium peaking at around 2% K. The diverging trends exhibited by light and heavier tar species suggest that potassium reduces the likelihood of light tar species to evolve towards heavier PAH and ultimately towards soot. In doing so potassium can lead to an increase in the yield of light species. However, above 4% of K most of the effect of alkali on PAH and soot has already been captured, thus any additional potassium does not divert any more mass from heavier products towards light tars and consequently the yield of light tars above 2-4% K starts to diminish.

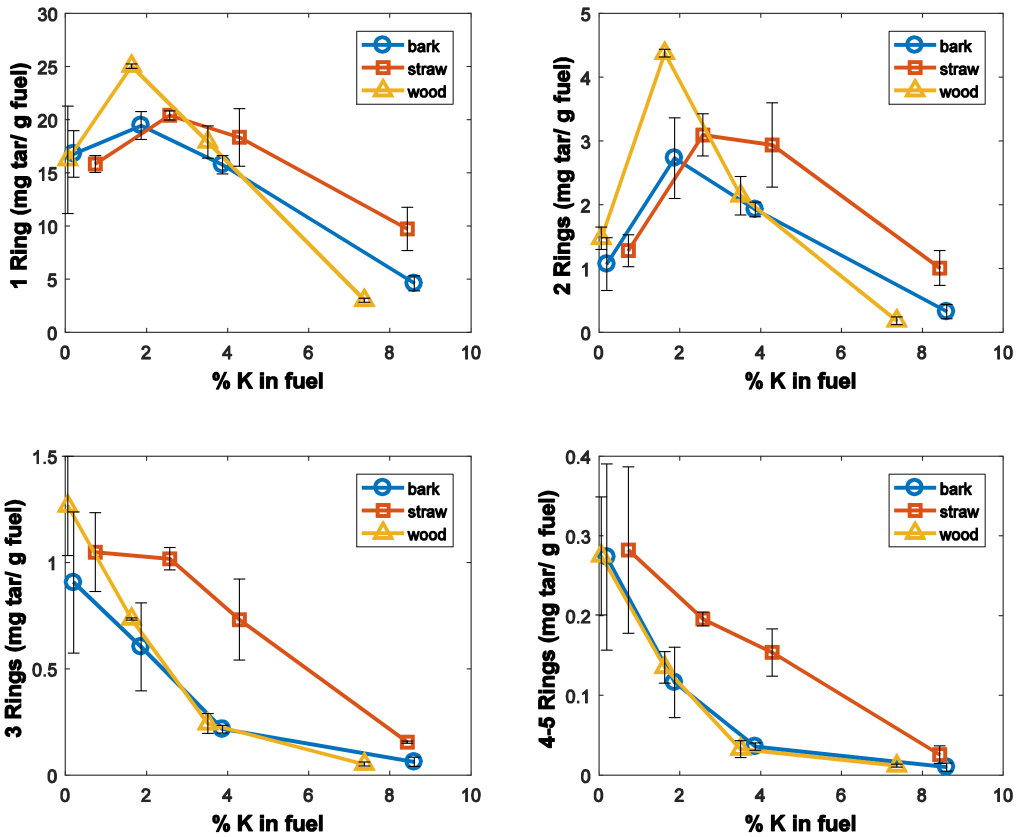

Figure 10 Yields of tars grouped by the number of aromatic rings. Experiments with the spray impregnation method at T=1000 °C and 5 % CO_2. The error bars show 1 standard deviation. N=3 for the K= 0 and 4 % whereas N=2 for K=2 and 8%.

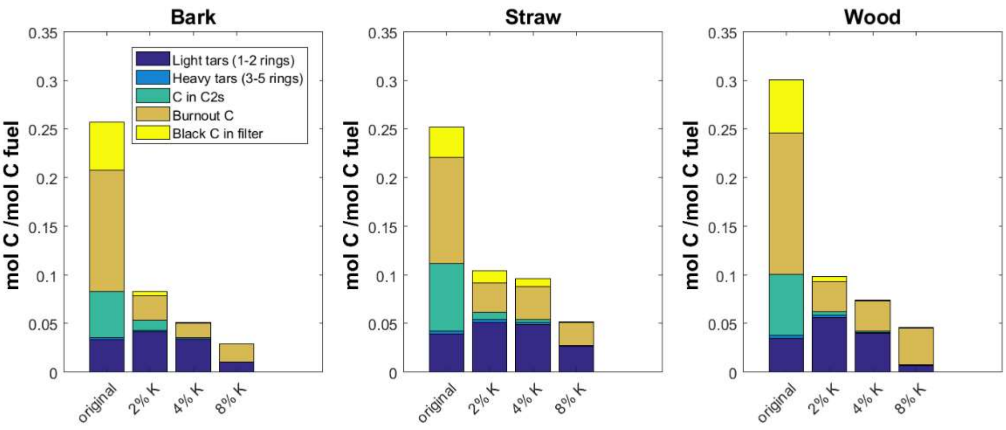

Figure 11 Stacked yields of undesired products. Experiments with the spray impregnation method at T=1000 °C and 5 % CO_2.

In summary, potassium affects more severely the yields of the products that are in a later stage of conversion towards soot (e.g. soot itself) because they capture the accumulated effect of potassium on all the reactions upstream. Nevertheless, given that the experiments were not optimised to investigate reaction mechanisms, we should interpret the above results with care. What appears undisputable is not only that the impregnation the fuel with potassium leads to a decrease in the combined yield of gas impurities (tar+C_2's+ soot) but also that it leads to a reduction in the average molecular size of these products.

3.4 Effect of alkali at higher temperature

Conventional entrained flow biomass gasifiers are operated at a temperature which is high enough to ensure high carbon conversion and low levels of methane and tar and most importantly to ensure that flowability of the ash is good. However, these high temperatures tend to aggravate the problems of soot formation.

The comparison between the yields of unconverted carbon at 1000 °C and 1200 °C provided in Fig. 12 highlights two main results. On the one hand, the benefits of alkali in reducing undesired products (and remarkably soot), discussed in the previous sections on the basis of experiments at T=1000°C, still holds at T=1200°C and therefore we can extrapolate them into higher temperature. In fact, the decrease in soot with potassium impregnation was more accentuated at 1200°C than at 1000°C. On the other hand, the figures also indicate that the impregnation of the fuel with potassium is more advantageous than simply rising the temperature of the reactor. With the exception of straw, the combined yield of carbon in the undesired products from K-impregnated biomass at 1000 °C was lower than that from non-impregnated biomass at 1200 °C. In addition, operation of the reactor at cooler regimes would be also beneficial for cold gas efficiency.

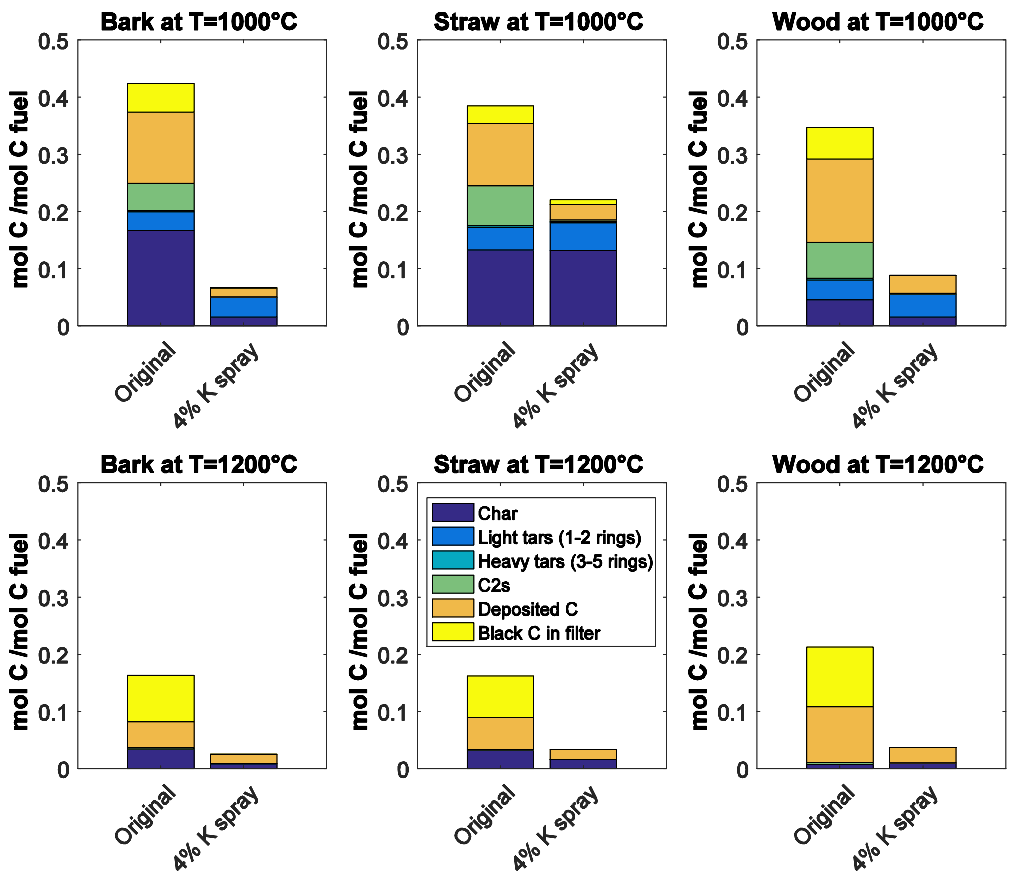

Figure 12 Stacked yields of undesired products (including both C in char as well as gas impurities). Experiments with the spray impregnation method with 5 % CO_2.

4. Conclusions

The effects of potassium on the formation of undesired by-products of gasification have been studied in a laboratory drop tube furnace.

It was found that adding potassium into biomass improved the gasification behaviour of the fuel by significantly reducing the yields of gas impurities as well as the amount of unconverted carbon that was left in the gasification residue.

The degree of contact between potassium and the fuel was found not to be important neither for gas impurities nor for char conversion. This finding suggested that the effect of potassium was a gas-induced phenomenon. Therefore, the impregnation of biomass at a larger scale could be carried out with very simple methods such as spraying. Nevertheless, the benefits of potassium were weaker in straw due to its inherent high content of Si, which led to the formation of non-active potassium silicates. In addition, potassium silicates deposited around the particles (e.g. char encapsulation) thereby impairing char conversion by restricting mass transfer.

The reduction of gas impurities in presence of potassium took place through gas-phase reactions after the devolatilization. The effect of potassium on the undesired products showed two distinct trends: C_2's gases, heavy tar and soot-like material responded very intensively to potassium, with most of the effect of potassium on these products being already captured at 2% K. On the other hand, the effect on lighter tars and char conversion was less intense but did not seem to saturate below 8% K. The diverging effect of potassium on light and heavier tars compounds suggested that potassium reduced the likelihood of light aromatic tars to progress towards polyaromatic hydrocarbons, and thereby to soot.

Finally, from the perspective of minimizing the combined yield of carbon in undesired products impregnating the biomass with potassium was found advantageous over increasing the gasification temperature from 1000 °C to 1200 °C.

In summary, the results presented in this study support the recirculation of K-rich ash into the fuel as a promising process to improve the quality of the syngas. The implementation of such method could lead to improvement in the economic performance of biomass gasification by reducing the need for expensive downstream cleaning stages and reducing the maintenance stops from soot and tar related operational problems.

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Abbreviations

BL: black liquor

DTF: drop tube furnace

EDS: energy dispersive spectroscopy

GC: gas chromatography

HACA hydrogen abstraction carbon addition

ICP: ion coupled plasma

MS: Mass spectroscopy

PAH: polyaromatic hydrocarbons

SEM: scanning electron microscopy

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