ALKALI CATALYZED GASIFICATION OF SOLID BIOMASS – INFLUENCE ON FUEL CONVERSION AND TAR/SOOT REDUCTION

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ABSTRACT: Based on char gasification experiments in an isothermal thermogravimetric analyzer, a suitable concentration of alkali salt (K_2CO_3) was chosen for impregnation due to almost five-fold increase in gasification reactivity and relatively low amount of carbon leaching during impregnation. Furthermore, an optimum method for wet alkali impregnation was proposed based on the several tests performed by varying temperature and time. To study the catalytic effect on tar and soot yield, untreated and impregnated woody biomass were gasified under entrained flow condition between 900 ^{o}C and 1200 ^{o}C. Impregnation leads to 70% lower tar yield from gasification around 1000 ^{o}C and 1100 ^{o}C. The lowest amount of soot was detected for the same temperature range whereas the soot yield was one order of magnitude higher for untreated biomass. For tar, this influence became insignificant at a higher temperature (1200 ^{o}C). This defines the suitable temperature range for alkali catalyzed gasification without the loss of catalytic activity.
Keywords: biomass, gasification, alkali, catalysis, tar, soot.

1 INTRODUCTION

Inherent presence of alkali in solid fuels shows significant influence during gasification [1]. To further benefit from this, researchers studied the effects of by impregnating a controlled amount of alkali [2]–[4] for gasification of biomass. These studies indicate the possibility of having significant improvement in gasification, mainly, by having efficient fuel conversion. However, there are other factors which define an efficient gasification process such as – the gas conditioning necessary due to the presence of tar and soot. Decreasing the amount of tar and soot will contribute to a more efficient and cost-effective gasification process.

To make it more applicable in a larger scale, the catalyst recovery is another important consideration. In the past decade, one technology that showed promising outcome in pilot scale is the black liquor gasification [5], [6]. Due to the pre-processing in the pulp mill it contains significant amount of alkali (~20% Na) from the beginning. This allows the gasifier to be operated at a lower temperature (1050 ^{o}C) with 99% carbon conversion efficiency with very low amount of tar and almost no soot [7]. At the same time, with this technology fuel alkali content is recovered as an aqueous solution at bottom of the quench. As it is possible to recover the added alkali catalyst using the same method, alkali catalyzed gasification of solid fuels might also benefit from this technology.

This indicates the need for thorough research on alkali salts which can be impregnated easily and contribute to the fuel conversion, tar/soot reduction and catalyst recovery. In this work, several alkali salts were tested by impregnation and gasification of biomass char to select an alkali salt for further evaluation. Then experiments were conducted in an entrained flow reactor to have a comparison of tar/soot yield of impregnated and untreated biomass. Morphological investigation was also carried out for novel information about the differences in structure of unconverted residues.

2 MATERIALS AND METHODS

2.1 Samples

Sawdust samples were prepared by soaking in the solutions of alkali salts overnight. The alkali salts used were K_2CO_3, Na_2CO_3, NaOH to give an ionic concentration of 1M and 0.1M. The sawdust samples for isothermal-TGA (i-TGA) had an initial particle size of 355 to 400 micron whereas 90-200 micron particle size was used for entrained flow reactor. Sawdust of larger particle size was used to produce char particles for the i-TGA experiments due to the sample basket mesh size (220 μm). For the experiments under entrained flow condition, one selected alkali salt (0.5M K_2CO_3) was used for impregnation. Optimization of the impregnation process is described in section 3.1.

2.2 Experimental

Pyrolysis was conducted at 600 ^{o}C to produce char in the i-TGA. The TGA uses a constant temperature where the sample is lowered to give rapid heating. Further details about the instrument can be found elsewhere [8]. To keep the alkali salts stable during pyrolysis, CO_2 was used instead of N_2. The formed chars were then gasified at different temperatures between 750 and 900 ^{o}C.

Complementary experiments under entrained flow condition were also conducted at the temperatures between 900 ^{o}C and 1200 ^{o}C with impregnated and untreated sawdust samples of 90-200 μm particle size. For these experiments, an entrained flow reactor (EFR) was used with 5.1% CO_2 in N_2 with a combined flow of 5.06 NL/min. An alumina tube was used to minimize the interaction of alkali with reactor wall. Detail description of the equipment is available in [9].

2.3 Analytical

The morphology of chars and residues was studied with FEI Magellan 400 XHR-SEM (FEI Company, USA). Total organic carbon and alkali content were analyzed by ALS Scandinavia, Sweden. Higher heating values of the samples were determined by a bomb calorimeter (IKA C200). For analyzing the gas produced from gasification, Agilent 490 micro-GC was used.

2.4 Kinetic models

The kinetics modeling for gasification was performed with i-TGA data and three available kinetic models. These models were used to find the suitable model to describe the gasification kinetics and conversion time as accurately as possible. The structural models used in this paper are volumetric [10], shrinking core [11] and random pore model [12] respectively. A general expression for the structural models could be, $dx/dt=k(C_g,T)f(x)$, where, k is the apparent reaction rate, x is the conversion, t is the time, C_g is the gas concentration, T is the temperature and f(x) is a function of conversion which varies based on the modeling assumption. The conversion can be defined as

$$x=(m_t-m_i)/(m_f-m_i) \qquad (1)$$

where m_t is the mass of sample at time t, m_i is the intial mass and m_f is the final mass when conversion was complete.

Under constant pressure of gasifying agent, the kinetic expression can be, $dx/dt=k_o \exp(-E/RT) f(x)$. Here, ko is the frequency factor and E is the activation energy. As for the function, f(x), it can be expressed by volumetric $[(1-x)]$, shrinking core $[(1-x)^{2/3}]$ and random pore model $[(1-x) \{(1-\psi ln(1-x)\}^{1/2}]$. For random pore model, ψ is an additional parameter which is dependent on the surface area, pore length and porosity of the initial sample. To calculate the characteristic value of k , a best fit up to 50 % conversion was considered. Further details about the procedure can be found elsewhere [13].

2.5 Residence time and conversion calculation

Considering the gasification kinetics and particle motion in an entrained flow reactor, particle scale simulation was carried out to determine the conversion times for different temperature. As the particle size was small (90-200 μm) for entrained flow case, only heat transfer calculation was considered (i.e. mass transfer was not accounted for). For heat transfer calculation, the following equation was used

$$\rho C_p \frac{\partial T_p}{\partial t} = \lambda \left[\frac{\partial^2 T_p}{\partial r^2} + \frac{b-1}{r} \frac{\partial T_p}{\partial r} \right] + q_{reac} \left(-\frac{d\rho}{dt} \right) \qquad (2)$$

Where, ρ and C_p represent the particle density and heat capacity respectively. T_p expresses the particle temperature, b is the shape factor, r represents the radial position in the particle, t is time, λ is the thermal conductivity and q_{reac} is the heat of reaction. The physical parameters for biomass chars were taken from [14] and the average heat capacity of ash was calculated based on their composition.

For the sake of simplicity, the criteria for laminar flow were used to calculate the slip velocity [15] using following expression by Schiller and Nauman for drag coefficient C_D.

$$C_D = \frac{24}{Re_p}(1+0.15 Re_p^{0.687}) \qquad (3)$$

Here, Reynolds number is denoted by Re_p. Further details about the modeling procedure can be found in [14].

3   RESULTS AND DISCUSSION

3.1 Optimizing alkali impregnation

In initial tests wood samples were treated with different alkali salt solutions overnight at room temperature. A ratio of 16 ml of solution per g of sample was maintained for all cases. After that, the solution was filtered out and the solid samples were dried overnight. The wood particles changed color after impregnation and turned slightly darker (darkest with 1M NaOH). Also, treated samples were found to be more brittle than raw wood and formed swelled particles. Stronger alkali solutions resulted in a lot of smaller particles after drying due to particle fragmentation. It is interesting to note that the particles were not sticky after the treatment.

A general trend of impregnating higher amount of alkali in wood was observed for relatively stronger alkaline solutions. The highest amount of alkali loading on mass basis was observed for 1M NaOH solution whereas 0.5M K_2CO_3 was the second highest. The performance of all the solutions is listed in Table 1. Another important outcome from the impregnation studies was the carbon loss in presence of the alkaline solution. Carbon leaching was measured by analyzing the filtrate from the impregnations tests for total organic carbon (TOC) and sugars (Table 1). It was observed that 1M NaOH leached almost ~10% of the initial carbon in the wood whereas 0.5M K_2CO_3 caused about ~5% carbon loss. As no sugar was detected in any of the solutions, it can be said that the loss did not result from the decomposition of cellulose. Considering lower amount of carbon loss, 0.5M K_2CO_3 is preferable over 1M NaOH.

Table 1: Impregnation efficiency of different alkali salts along with carbon loss from wood

Salt solution	Na/K (kg/100 kg of dry wood)	C leached (kg/100 kg of C)
1M NaOH	5.43	9.50
0.5M K_2CO_3	4.15	5.32
0.5M Na_2CO_3	1.64	5.51
0.1M NaOH	0.88	7.63
0.05M K_2CO_3	0.85	5.10
0.05M Na_2CO_3	0.58	6.26

As the impregnation time was significantly long for the method described above, further tests were performed with 0.5M K_2CO_3 solution to optimize. It was found that 30 minutes of impregnation time was sufficient to maintain the same level of impregnation (~4%) if the temperature of the solution was increased to 80 °C. It is to be noted that the carbon loss amount was slightly higher (~6.9 kg/100 kg of C) for high temperature impregnation. However, determination of higher heating values showed that it was only ~0.7 MJ/kg biomass lower (dry ash free basis) for K^+ loaded sawdust due to this carbon loss. Therefore, the optimized method is considered suitable for large scale implementation.

Also selected tests were carried out to check the dependence of alkali impregnation on particle size of initial samples. Two particle sizes (<200 micron and 355-400 micron) were considered in this case with various alkali salts. For the particle size under consideration, insignificant variation in impregnation amount was observed. Based on that, it can be said that impregnation process would not be influenced by the particle size range below 1 mm.

3.2 Char gasification in TGA

The char yields (on ash free basis) from different

samples in the TGA showed differences, perhaps due to the charring reactions promoted by alkali. The impregnated chars showed overall higher reactivity that untreated sawdust char. This was strongly linked to the char morphology and the catalytic effects of alkali in the chars.

Based on the alkali amount, the reactivity of the char varied significantly. For highly alkali loaded samples, the reactivity was significantly high at around 900 °C. On the other hand, samples with low alkali content showed consistent increase in reaction rate with temperature. A reaction rate increase in the second half of the fuel conversion was observed clearly (Figure 1) for the samples with low alkali loading.

Figure 1 shows that the models were not describing the conversion curves accurately. They were overestimating the conversion time in most cases. So an advanced modeling approach would be preferable over these models. The kinetic parameters from these models are still useful for relative comparison of reactivity among the samples. They are used in a particle model to calculate and compare the untreated and one of the selected impregnated samples (0.5M K_2CO_3) for entrained flow condition.

The Arrhenius plot (Figure 2) shows that the reactivity of the impregnated samples was not yet as high as black liquor. However, the increase in reaction rate was clearly visible from the untreated sawdust. As the effect of alkali was prominent during fuel conversion, it is important to evaluate the role alkali in gas phase and tar/soot reduction.

3.3 Influence of alkali on tar and soot in an EFR

To identify the relevant temperatures to study the gas phase reactions, particle scale simulation was used as a tool. Based on the calculation, the conversion time (14 s) was found to be suitable around 1150 °C for alkali catalysis. On the other hand, non-catalytic gasification took around 70 s at the same temperature. If the temperature was increased to 1500 °C, the conversion time became suitable for entrained flow reactors. This can be viewed in Figure 3.
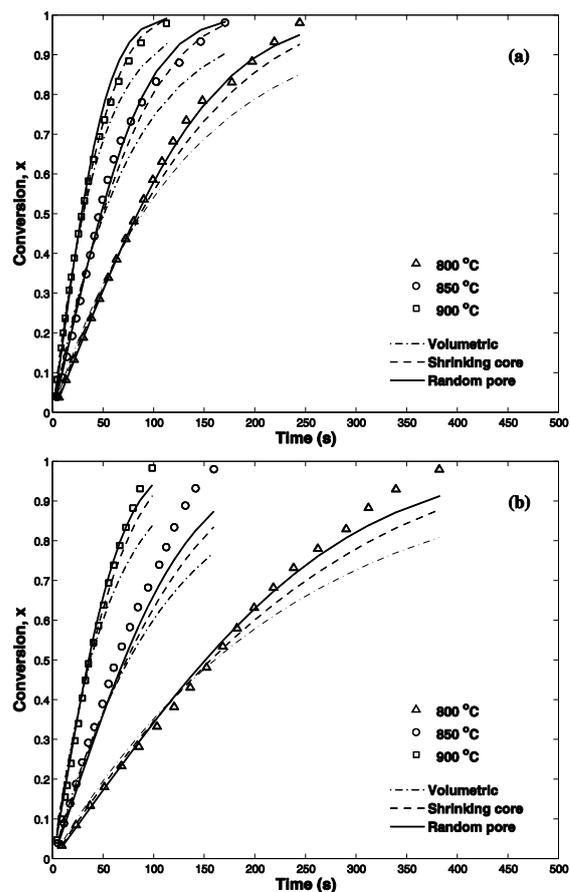

Figure 1: Performance of the structural (kinetic) models for describing fuel conversion characteristics for − (a) 0.5M K_2CO_3 and (b) 0.1M NaOH impregnated samples
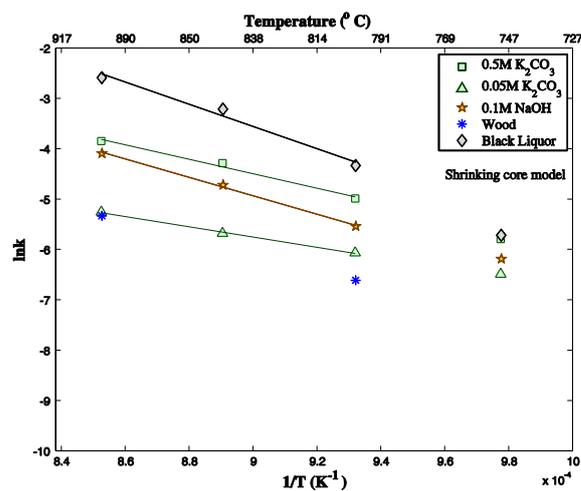

Figure 2: Comparative reactivity of selected samples in Arrhenius plot (Black liquor data is adopted from [16])
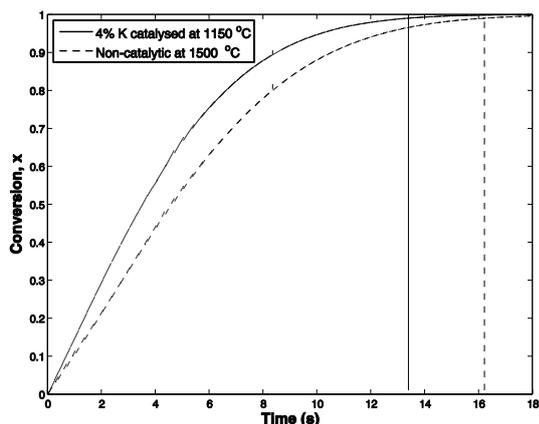
Figure 3: Desired conversion times for catalytic and non-catalytic gasification at relevant temperatures – vertical lines are denoting 99% conversion time for respective samples

Therefore, the experiments were of interest between the temperatures 900 ^{o}C and 1200 ^{o}C . The results in that range would reflect the most relevant conditions for alkali catalysis. The residence time in the entrained flow reactor was around ~12s. Figure 4 shows that the effect of alkali on tars was already visible at a lower temperature (900 ^{o}C). But it became prominent around 1000 ^{o}C - 1100 ^{o}C. It was observed from i-TGA experiments that the presence of alkali favored charring reactions. By the same token, it can be considered that some of the organic fractions responsible for tar formation convert to char during pyrolysis. Then this char is gasified at a faster rate than untreated sawdust char. Consequently, soot yield would become lower due to less tar formation. However, there might be other parallel mechanisms for tar reduction. At a higher temperature (1200 ^{o}C), the yield of tar became similar for both untreated and impregnated samples delineating that catalytic gasification would not be beneficial at a higher temperature for tar reduction.

The soot yields were also measured for selected temperatures. At 1000 ^{o}C, the soot yield for impregnated samples was less than one tenth (~0.3 kg/100 kg impregnated biomass fed) of the soot produced by the untreated sample (3.5 kg/100 kg untreated biomass fed). The soot production peaked for untreated biomass around 1100 ^{o}C (also reported by Zhang et al. [17]), then became lower at 1200 ^{o}C. In contrast, the soot yield from impregnated samples was still one order of magnitude lower for those temperatures. This also indicates that the soot precursors were actually minimized due to the presence of alkali.
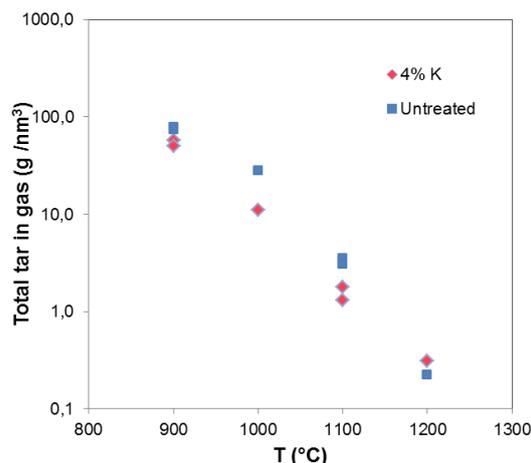

Figure 4: Tar reduction due to the presence of K-salt

3.4 Morphology of the unconverted residues

The unconverted residues from entrained flow reactor showed significant difference between alkali impregnated and untreated samples. Figure 5 shows that the surface of the alkali impregnated sample (4% K$^+$ loaded) had a deformed plastic surface while releasing the volatiles. It had numerous pockets on the surface from where the volatiles were released and subsequently, gasification took place. The surface tension on the surface could be still visible. This might be due to the alkali salts producing a eutectic mixture of low boiling point.

On the other hand, after going through the surface melting, untreated samples resulted in a smooth surface. Most of the cases, it released the volatiles by making a large hole through the surface resulting in a cenosphere.
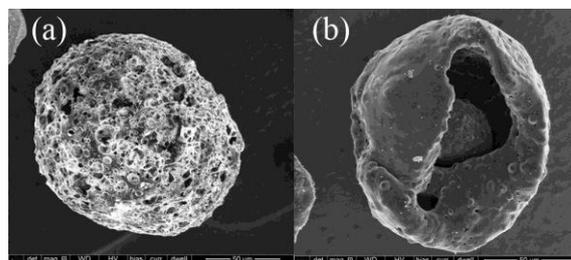

Figure 5: SEM images of unconverted residue from EFR at 1000 ^{o}C – (a) 4% K loaded and (b) untreated

The differences in the surface morphology indicate the process of volatile release and gasification followed a different mechanism. Several mechanisms for catalytic gasification has been proposed by different researchers [18], [19]. These studies discuss about formation of intermediates which accelerates the gasification process. It is believed that if the surface was molten and boiling, it might be easier for the salts to ionize and form intermediate compounds.

4   CONCLUSIONS

Alkali as catalyst showed a maximum of about fivefold increase in char gasification reactivity at 900 ^{o}C. This fuel conversion efficiency was complemented by a strong tar and soot reduction under entrained flow condition up to 1100 ^{o}C. At 1200 ^{o}C, the catalytic

efficiency was diminished for tar reduction, presumably, due to alkali evaporation. The unconverted residues found from the entrained flow experiments at 1000 and 1100 ^{o}C for alkali catalyzed and untreated samples showed significant difference in morphology. The cause of this dissimilarity is currently being investigated.

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6 ACKNOWLEDGEMENTS