



International Flame Research Foundation  
*The Finnish and Swedish National Committees*  
*Finnish – Swedish Flame Days 2013*

## **OPTICAL DETECTION OF KCl VAPOR AND ATOMIC K RELEASES FROM BIOMASS FUELS COMBUSTED IN SINGLE PARTICLE REACTOR**

Tapio Sorvajärvi\*, Juha Toivonen

Tampere University of Technology  
Department of Physics, Optics Laboratory

\* Corresponding author, [tapio.sorvajarvi@tut.fi](mailto:tapio.sorvajarvi@tut.fi)

---

### **ABSTRACT**

Laser spectroscopy is applied to measure the formation of KCl and atomic K during the combustion of small amount of biomass fuels in single particle reactor. The used spectroscopic technique is called collinear photofragmentation and atomic absorption spectroscopy (CPFAAS) that enables the detection of sub-ppm level KCl concentrations in laboratory and full-scale power plant environments. In this study, KCl release was measured from bagasse samples (10 – 45 mg) combusted at 800 °C, 950 °C and 1100 °C, and from reed and straw samples (20 mg) combusted at 950 °C. The release of atomic K was studied at the temperature of 950 °C from reed samples having masses of 20, 40 and 60 mg.

*Keywords: Laser spectroscopy; KCl formation; Fuel analysis*

---



## **1 Introduction**

Environmental aspects and the increasing price of the fossil fuels have increased the interest of the renewable fuels in power production. One good alternative, as a largely CO<sub>2</sub> neutral fuel, is biomass that can be harvested, for example, as agricultural residues. However, the combustion of the renewable solid fuels and the mixed fuels causes serious corrosion and slagging problems in combustion boilers. One cause of the problems is the alkali chloride vapours that are formed during combustion due to the high content of alkali and chlorine in the biomass [1]. In order to study the formation of the alkali chlorides in combustion process a well characterized combustion conditions and an accurate detection technique are needed.

Recently, an optical technique based on the collinear photofragmentation and atomic absorption spectroscopy (CPFAAS), was introduced for the real time detection of KCl vapour [2,3]. The technique is based on the photofragmentation of KCl molecules with an ultraviolet laser pulse and the detection of the temporarily increased concentration of the potassium atoms using an infrared laser. The strength of the infrared absorption depends on the intensity of UV laser pulse, which enables the customization of the technique to measure parts per million (ppm) level concentrations from samples having dimensions from millimetres to several meters.

In this study, CPFAAS technique was applied to monitor the concentration of KCl vapour and atomic potassium in combustion gas during the combustion of solid fuel in a single particle reactor. The measured KCl data was compared to temporal CO<sub>2</sub> release in order to resolve the rate of the KCl formation in different phases of the combustion. KCl release was studied from bagasse samples having different masses and combusted at three different temperatures and from bagasse, reed and straw samples having same masses and combusted at the same temperature. Atomic potassium release was studied from three reed samples having different masses.

## **2 Methodology**

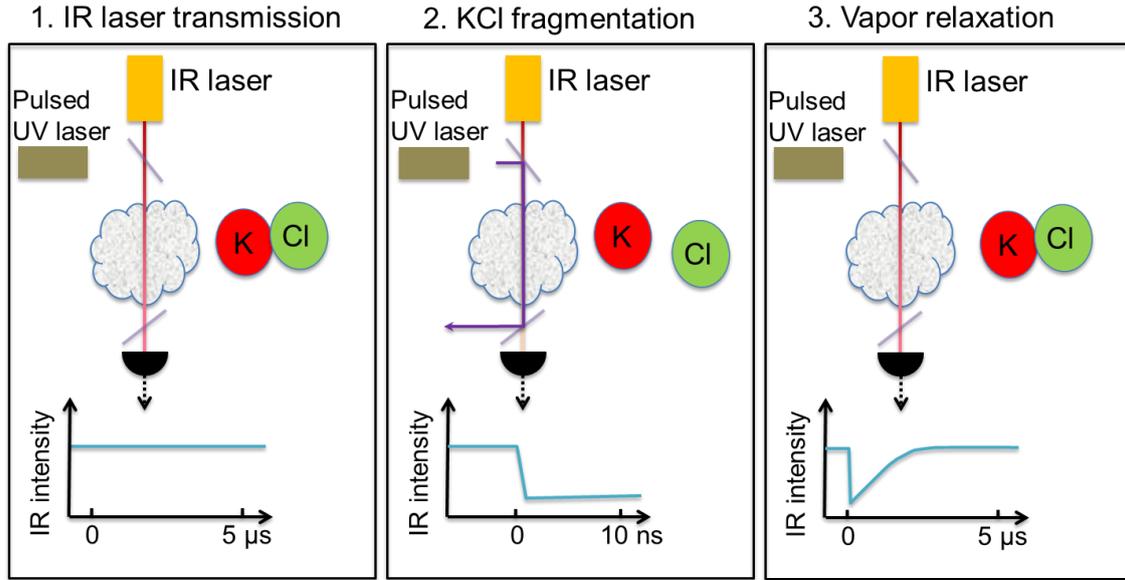
In this section the principles of CPFAAS and the measurement conditions are presented.

### **2.1 CPFAAS**

CPFAAS technique is based on the photofragmentation of the sample molecules with a light pulse and the detection of the fragments with collinearly aligned probe beam. In case of KCl the dissociation can be induced with 266 nm laser pulse [4] and the released potassium atoms can be detected with monochromatic near infrared (NIR) laser beam having wavelength of 766.5 nm.[2,3]. A typical measurement event is presented in Figure 1. First, the NIR laser is aligned to go through the sample and its transmission is measured with a photodetector. In the absence of the UV light the intensity of the transmitted NIR laser remains at a constant level. Next, a UV pulse is triggered to pass the sample collinearly respect to the NIR laser beam, when a part of KCl molecules in



sample volume is dissociated. The temporal increase of the K atoms, due to the dissociation, is seen as decreased NIR laser transmission. The laser induced additional K atoms has only a short life time and they react fast with ambient gas components. Thereby, the intensity of the NIR laser at the photodetector recovers to its original level within a limited time. In the experiments the recovery time has been found to be around 1  $\mu$ s.



**Figure 1. Principle of the CPFAAS detection**

Since the depth of the observed dip in the transmission curve depends on the amount of the released K atoms that further depends on the amount of the KCl and intensity of the laser pulse, the intensities before UV excitation  $I_{k0}$  and right after excitation  $I_k$  can be used to calculate the concentration of the KCl vapour in the sample. The calculations are based on the Beer-Lambert's law and can be derived in form

$$x_{KCl} = -\ln \left( 1 + \ln \left( 1 - \frac{I_{k0} - I_k}{I_{k0}} \right) \frac{hc/\lambda_p A_p}{E_{p0} \sigma_K} \right) \frac{k_B T}{p} \frac{1}{\sigma_{KCl} L}. \quad (1)$$

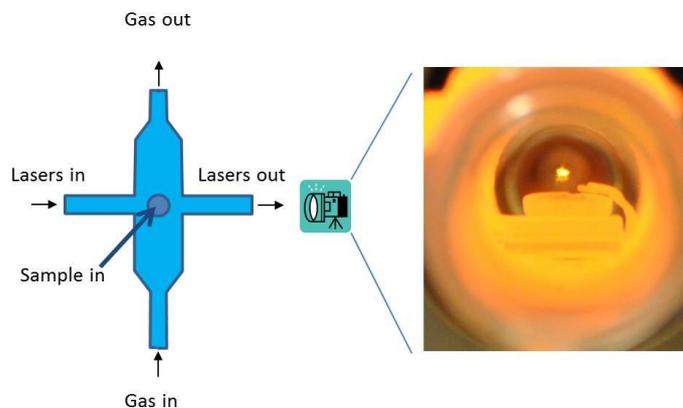
( $I_{k0}$  intensity of the probe laser before photofragmentation,  $I_k$  minimum intensity of the probe laser after the photofragmentation,  $h$  Planck's constant,  $c$  speed of the light,  $\lambda_p$  wavelength of the pump laser,  $E_{p0}$  pulse energy of pump laser before sample,  $A_p$  cross-sectional area of the pump laser beam,  $\sigma_K$  absorption cross section of the potassium atoms,  $k_B$  Boltzmann constant,  $T$  temperature of the sample,  $p$  gas pressure,  $\sigma_{KCl}$  absorption cross section of the potassium chloride,  $L$  sample length) [3]

Equation 1 contains physical constant ( $h$ ,  $c$ ,  $k_B$ ) application specific factors ( $\lambda_p$ ,  $E_{p0}$ ,  $A_p$ ,  $T$ ,  $p$ ,  $L$ ), and molecular and atomic specific constant that can be found from literature or can be measured in laboratory ( $\sigma_{KCl}$ ,  $\sigma_K$ ).



## 2.2 Single particle reactor

A schematic of single particle reactor and the location of the laser beams above the sample are shown in Figure 2. The single particle reactor is an advanced tool to study the combustion properties of different fuels in well controlled conditions [5]. In our experiment a sample was inserted into the preheated reactor in a quartz bowl having diameter of 15 mm. The laser beams were aligned to measure KCl concentration in the flue gas 3 mm above the sample bowl. The diameters of the laser beams were 2 mm and the average UV pulse energy was 12  $\mu$ J.

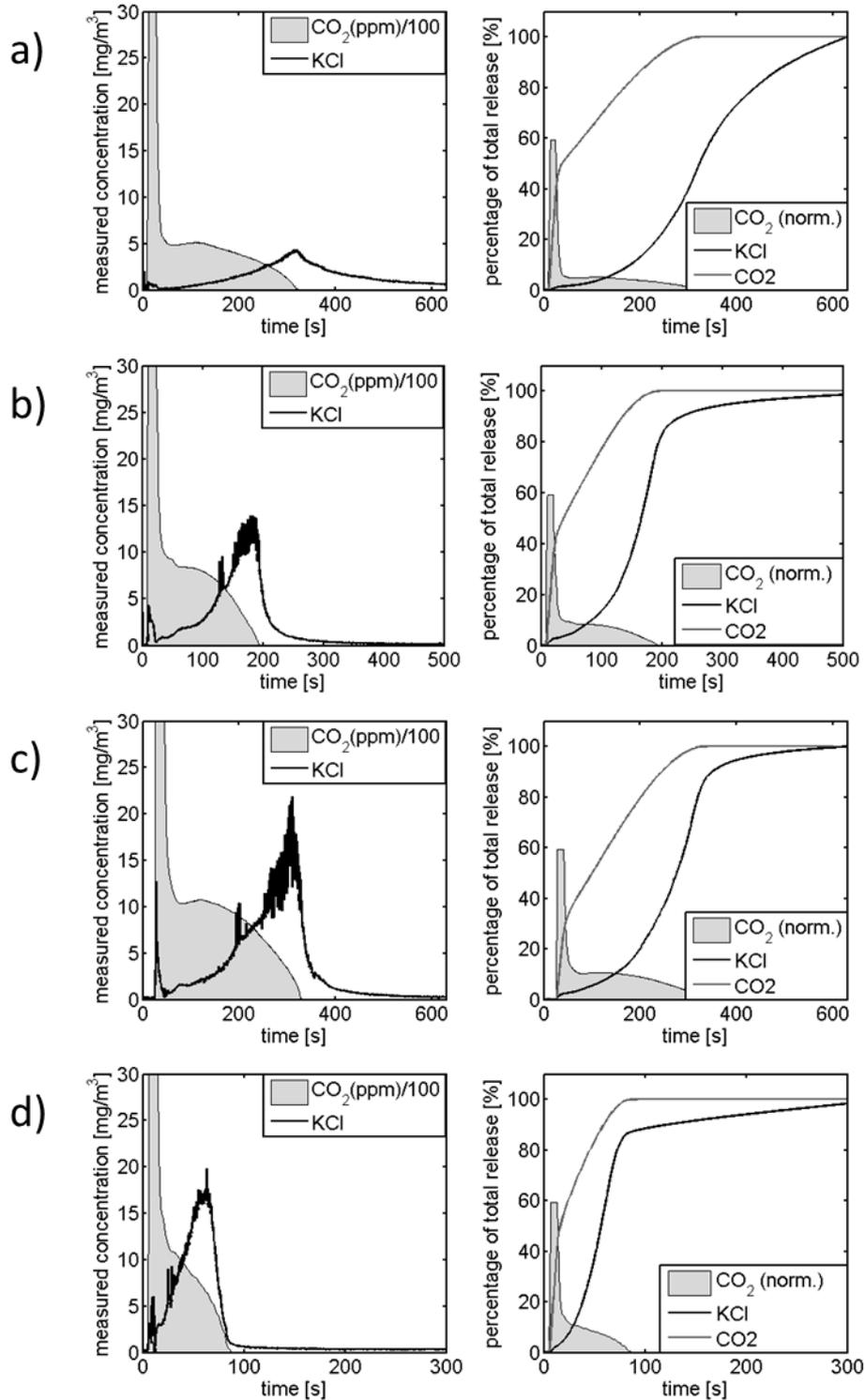


**Figure 2. Schematic of single particle reactor. The laser beam location compared to the sample cup is shown as a bright spot in the picture, about 3 mm above the sample cup.**

## 3 Results

Temporal and cumulative KCl and CO<sub>2</sub> releases from four bagasse powder samples are presented in Figure 3. The masses of the sample and the combustion temperatures were a) 20 mg and 800 °C, b) 20 mg and 950 °C, c) 45 mg and 950 °C, and d) 10 mg and 1100 °C. The combustion experiments were done with 3 % of oxygen. The CO<sub>2</sub> releases were measured by sampling the combustion gas to a Fourier Transform Infrared (FTIR) spectrometer. The upper limit for CO<sub>2</sub> concentration was 6000 ppm that was seen as temporarily saturated readings during the volatilization phase. A typical warm-up time of the sample to the temperature of the reactor was approximately 20 s.

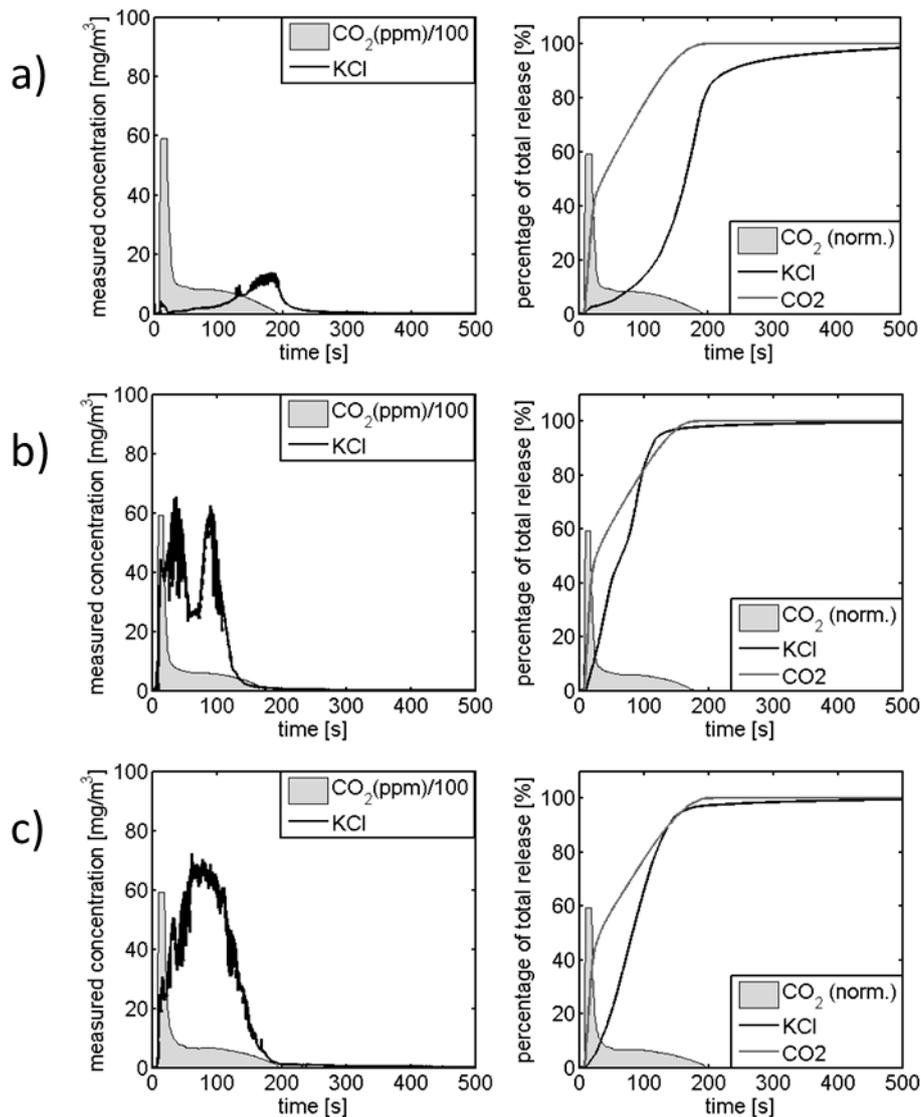
The temporal KCl release profiles show that the KCl release becomes faster as the combustion temperature is increased. At the temperature of 800 °C only 50 % of total KCl was released during volatilization and char burning phases while at the temperature of 1100 °C 85 % of KCl was released during the burning. The integrals of the measured KCl curves normalized with the sample masses were found to be approximately same in all experiments. The combustion of 20 mg and 45 mg samples at 950 °C resulted very similar KCl release profiles. At the end of the char burning the KCl release became instable in both 950 °C experiments.



**Figure 3** Temporal and cumulative release of KCl and  $\text{CO}_2$  from bagasse powder having mass and combustion temperature of a) 20 mg and 800 °C, b) 20 mg and 950 °C, c) 45 mg and 950 °C, and d) 10 mg and 1100 °C. The combustion was carried out with  $\text{O}_2$  concentration of 3 %



Temporal and cumulative KCl and CO<sub>2</sub> releases from a) 20 mg of bagasse, b) 22 mg of reed and c) 22 mg of straw powders combusted at 950 °C with 3 % of oxygen are presented in Figure 4. The different fuels are known to contain different amounts of chlorine and potassium, which is seen as different rates and total formations of KCl. Bagasse shows to produce the smallest amount of KCl. The formation of KCl is quite equal in cases of reed and straw. The combustion of reed produced a KCl release profile having two maxima, while the KCl release from bagasse and straw had only one maximum.



**Figure 4** Temporal and cumulative release of KCl and CO<sub>2</sub> from a) 20 mg of bagasse C, b) 22 of reed c) 22 mg of straw combusted at temperature of 950 °C with 3 % of oxygen.

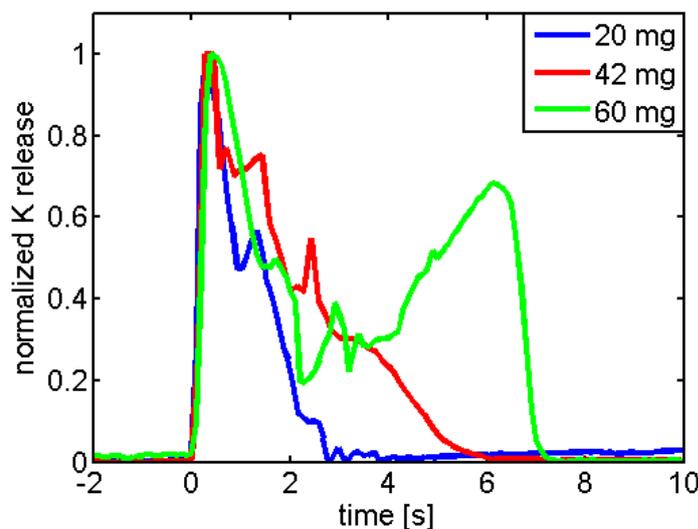
Figure 3 and 4 showed that only small part of KCl is released during the volatilization phase of the combustion while at the same time the major part of CO<sub>2</sub> is released. The small KCl formation at the beginning of the combustion is assumed to be related to the sample heating. As mentioned earlier, it takes about 20 s for sample to reach the



ambient temperature, while the volatilization phase starts immediately. The relation between sample temperature and KCl formation rate is also supported by bagasse experiment at 800 °C. Figure 3 a) showed how the KCl concentration in combustion gas increases over whole char burning period, and when the burning ends and the sample stops producing heat the concentration of KCl starts to decrease.

The release of atomic potassium during the combustion is demonstrated in Figure 5. The timescale in Figure 5 is set to zero at the point when the sample enters to the reactor. Atomic K release was measured using the base level of the NIR laser intensity. The measured K releases were normalized with their maximum values, so that their profiles and durations could be compared.

Figure 5 shows the atomic K release from three reed samples having masses of 20 mg, 42 mg and 60 mg. The K release from the smallest sample lasted 2.5 s in total and its profile showed only one maximum, while the release from 60 mg sample lasted 7 second and had two profile maxima. The release profile from 42 mg sample was between two other profiles. The maximum K concentration in combustion gas was estimated to be around 0.5 – 1 ppm in all reed experiments. The maximum K emission was found to occur during the ignition and the flame.



**Figure 5 Atomic potassium releases from three reed powder samples having different masses. The reed samples were combusted at 950 °C with 3 % of oxygen.**



#### **4 Acknowledgements**

The authors are grateful for the support by Doctoral Programme of TUT's President. The authors acknowledges the Process Chemistry Centre at Åbo Akademi University for providing facilities to the single particle reactor measurements and Aerosol Physics Laboratory at Tampere University of Technology for providing CO<sub>2</sub> data from single particle reactor experiments.

This work has been partly carried out within the consortium FUSEC (2011 – 2014) with support from National Technology Agency of Finland (Tekes), Andritz Oy, Metso Power Oy, Foster Wheeler Energia Oy, UPM-Kymmene Oyj, Clyde Bergemann GmbH, International Paper Inc. and Top Analytica Oy Ab.

#### **REFERENCES**

- [1] H. Nielsen, F. Frandsen, K. Dam-Johansen, and L. Baxter. The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. *Progress in energy and combustion science* 26(3):283 – 298, 2000.
- [2] T. Sorvajärvi, J Saarela and J. Toivonen. Optical detection of potassium chloride vapor using collinear photofragmentation and atomic absorption spectroscopy. *Optics Letters* 37:4011 – 4013,2012
- [3] T. Sorvajärvi, J. Toivonen. Principles and characterization of collinear photofragmentation and atomic absorption spectroscopy. *Applied Physics B: Lasers and optics* manuscript submitted
- [4] P. Davidovits and D. Brodhead. Ultraviolet absorption cross sections for the alkali halide vapors. *Journal of Chemical Physics* 46:2968 – 2973, 1967.
- [5] N. DeMartini, E. Monedero, P. Yrjas and M. Hupa. Co-firing Black Liquor and Biomass in a Laboratory Single Droplet Reactor – Effects on Emission and Combustion Characteristics. *International Chemical Recovery Conference*, Williamsburg, VA, March 29 – April 1, 2010.