Experimental study on the combustion of Lithium particles in CO_2 and CO_2-N_2 mixtures

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Abstract

Lithium particles ($d_p < 250$ µm) are burned in a drop tube reactor containing pure CO_2 atmospheres and different CO_2-N_2 mixtures. Two-colour pyrometry is used to determine the temperature and diameter of single reacting particles. Results show that Li-particle combustion with CO_2 occurs as gas-phase reaction with a stand-off flame as well as heterogeneous reaction at the particle surface. The addition of N_2 increases ignition delay times and reduces reaction rate. In addition, solid sampling was carried out to investigate the particle structure by XRD and CHN-analysis to get insight in the composition of the solid reaction product after the reaction.

Introduction

The substitution of fossil and nuclear power generation by renewable energies increases the dependency on factors such as weather, seasons and location. Therefore, energy storage capacities have to be built up to guarantee the security of power supply. Chemical based storage technologies are promising energy storage alternatives concerning storage density, load cycles and changes, storage capacity and lifetime. Due to their exothermal reactions with various gas atmospheres and their high storage density resulting of solid state, electro positive metals, especially lithium, are attractive as storage materials. Lithium reacts with all exhaust gas components (CO_2, N_2, O_2, H_2O) exothermally and therefore offers a broad band of possible applications.

The idea based on these characteristics is to design a closed-loop energy storage process. Elemental lithium is used as a fuel for a power plant process and can be easily transported as a solid. Its energy storage capacity is high, e.g. to produce 10 MJ of energy at ambient conditions, 200 cm³ carbon reacting with O_2 or 480 cm³ lithium reacting with CO_2 are required. The lithium can be burned in stand-alone lithium power plants, e.g. utilizing pure CO_2 from carbon capture processes [1] or in combination with existing power plants using the exhaust gases of power plants as "combustion air". As the reaction products of combustion are in the solid state and not gaseous as for carbon based fuels which emit CO_2, the reaction products can be captured, transported and stored easily. The idea is then to retransform the lithium salts and oxides generated by the combustion process into elemental lithium by electrolysis, whereby the power for electrolysis is supposed to be delivered by renewable energies.

Information on lithium combustion is scarce. Most literature dates back to the 70s and 90s and is focused on pool fires, rocket propulsion or block combustion, e.g. [2–4]. To achieve complete fuel conversion, the combustion concept of the system described above has to be based on either pulverized solid supply of lithium or atomization of liquid lithium with subsequent combustion [5]. Therefore, detailed knowledge on the combustion characteristics of lithium droplets/particles is necessary. In fact, knowledge of particle or droplet combustion of elemental lithium is barely existent. Only Schiemann et al. investigated lithium particle combustion using the exhaust gas of a methane-air flame as reactant atmosphere in a laminar flow reactor. The results indicated two different mechanisms: gas phase combustion in a homogeneous enveloping flame around the particle and a "second reaction zone" at the particle surface, which could not be clarified in detail [6]. Lithium gas phase combustion has been identified in literature before for the combustion of a particle bulk in N_2, CO_2 and air [7].

In order to gain detailed knowledge on the combustion characteristics of single lithium particles with typical exhaust gas components, combustion experiments in a laminar flow reactor providing pure CO_2 and different CO_2-N_2 gas mixtures have been carried out. For that purpose, imaging pyrometry is used to obtain information about particle size and combustion temperatures at the same time. Similar studies have been conducted for lithium combustion by Schiemann et al. (as already mentioned) or for coal combustion e.g. by Molina/Shaddix, Levendis and Schiemann et al. [8–10].

In the present work, the two-color pyrometer system TOSCA (Temperature measurements with electro-Optical high Speed CAmeras) is used in combination with a drop-tube reactor. Two ICCD-cameras capture two-dimensional images of the burning lithium particles, which offers the possibility to measure the particle or flame shape as well as the temperature at the same time. In addition, burnout samples are extracted and quenched from the reactor during combustion using a sampling probe to analyze the reaction products with X-Ray diffraction (XRD) and CHN-analysis.

Experimental setup

The experiments were carried out in a drop tube reactor (DTR) presented in Figure 1. To evaluate the influence of various CO_2 partial pressures on the combustion, four different CO_2-N_2-mixtures were investigated, containing 100%, 50%, 25% and 10% CO_2. The gas flow (purity of both gases: 99.995%) is adjusted with mass flow controllers. As CO_2 and N_2 differ in their heat capacity, density and thermal conductivity clearly, the total gas flow is modified for each atmosphere, to provide similar gas temperatures in the reactor. The resulting gas flows are presented in Table 1 for each atmosphere.

The gas flow is heated up to approx. 830 K with a gas preheater (HTM Reetz) using a KANTHAL heating wire consisting of FeCrAl. To establish a laminar flow in the drop tube, the hot gas is guided through a ceramic honeycomb with approx. 900 capillary tubes. The reactor is enveloped by a quartz glass tube (d = 65 mm) to conserve the laminar flow and to provide optical access to the burning particles. Reynolds numbers are low (< 80), which is typical for drop tube reactor experiments.

The feeding of the solid lithium particles to the drop tube reactor is arranged by a small-scale star feeder with mass flows of a few grams per hour. The particles are transported with a small Argon carrier flow (approx. 0.4% of the total gas flow) from the feeder to the reactor. The Argon carrier flow and additional water cooling of the injector prevent the particles from melting or reacting before entering the reactor tube. Due to the low particle mass flow, the particles are well separated and do not affect each other during combustion.

Figure 1 also shows gas phase temperature profiles along the reactor tube axis for each gas mixture investigated. The temperature profiles were measured without Li particles using thermocouples (radiation correction has been carried out, described e.g. in [11]). The lowest gas temperature occurs at the particle inlet due to the small Argon carrier flow at room temperature. The mixing of the cold Argon flow and the hot gas is completed between 150 and 200 mm path length for all atmospheres. Afterwards the gas temperature starts to decrease along the tube axis due to heat losses at the quartz glass walls.

The lithium particles were produced the same way as described in [6]: Bulk lithium rods (Sigma Aldrich – CAS number 7439-93-2) were used as starting material for the preparation of the lithium particles. First, the lithium rods (purity 99,9%; <1.500 ppm metal traces) were washed with cyclohexane prior to the dispersion process. To prevent any reaction of the lithium, the rods were heated up to 200 °C in degassed Vaseline (Sigma Aldrich – CAS number 8009-03-8). The dispersion was carried out with an Ultra-Turrax for 3 min up to 20 000 rpm and the particles obtained were again washed with cyclohexane and packed in 6 ml batches. The particle production, the packing and the fill of the star feeder were arranged under inert conditions (Argon) to avoid coatings and contamination of the particles.
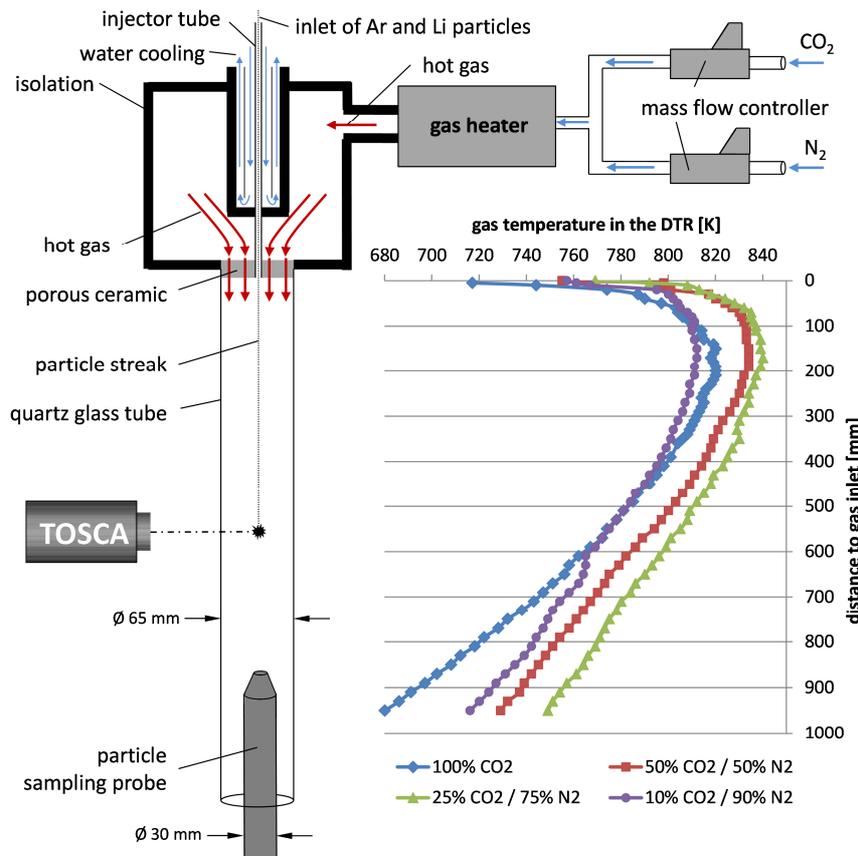

Figure 1. Schematic drawing of the drop tube reactor including gas temperature profiles along the reactor tube axis for the investigated atmospheres.

Table 1. Gas flows of the investigated atmospheres

atmosphere	$\dot{V}_{CO_2}$ [sl/min]	$\dot{V}_{N_2}$ [sl/min]
100% CO₂	60.0	-
50% CO₂, 50% N₂	37.3	37.3
25% CO₂, 75% N₂	21.3	63.8
10% CO₂, 90% N₂	7.8	70.3

As Figure 1 indicates, the combustion is characterized with the two-color pyrometer system TOSCA and a particle sampling probe simultaneously.

The camera system used here determines the intensities emitted by a radiation source in two different wavelength ranges. In general, the intensity ratio I_1/I_2 with corresponding emissivities is given by:

$$\frac{I_1}{I_2} = \frac{k_1}{k_2}\frac{\varepsilon_1}{\varepsilon_2}\frac{\Delta\lambda_1}{\Delta\lambda_2}\frac{\lambda_1^5}{\lambda_2^5} exp\left[\frac{-C_2}{T}\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)\right] \qquad (1)$$

where ε_i means the emissivity in the chosen wavelength range, $\Delta\lambda_i$ is the bandwidth of the used filter, λ_i is the center wavelength of the filters, and k_i is the detector sensitivity. C_2 is Planck's second constant of radiation. If the emissivity is assumed to be equal in both wave length ranges, it can be neglected and equation (1) can be used to determine the temperature of the radiation source (two-color pyrometry [10]). Rosenberg et al. showed, that for lithium the assumption of constant emissivity is acceptable for wavelengths less than 1 µm [12].

The TOSCA system uses two image-intensified high-speed CCD cameras as radiation detectors. The exposure time is set to 40 µs. Both cameras investigate the same small window (5x4 mm^2) of the particle streak. The image is focused with a telemicroscope. A beam splitter and two filters provide wavelength separation. The wave length ranges of the installed filters (green: 550 nm/40 nm FWHM, red: edge filter >735 nm) avoid an influence of the emission lines of atomic lithium at $\lambda = 610$ nm and $\lambda = 670$ nm on the temperature determination [13]. The temperature calibration of the pyrometry system was carried out using a tungsten ribbon lamp and a calibrated one-dimensional pyrometer for a temperature range from 1350 to 2600 K. The particle temperatures can be calculated from the calibration curves (emissivity correction for tungsten has been conducted using [14]) by interpolating the intensity ratio of each imaged particle.

As TOSCA provides a two-dimensional image, the particle diameter can be determined in addition to the particle temperature. The size calibration was carried out using different aperture blades with diameters in the range of particle size to counterbalance diffuse edge effects. The parallel information of temperature and diameter for each particle offers the possibility to characterize the combustion and to calculate reaction rates, as reaction kinetics depends on both particle temperature and size [15].

The particle burnout is analyzed using a particle sampling probe (PSP), which allows extraction and quenching of combusting particles at various residence times. As indicated in Figure 1, the PSP is inserted from the bottom up into the reactor. The burning lithium particles and a part of the hot reactant gas (approx. 2 sl/min) are sucked isokinetically into the inner tube of the PSP using a hot gas pump, where they get in contact with a cooled Argon flow (approx. 8 slpm). This causes cooling and quenching of the reacting particles along the inner tube axis (600 mm). Separation of the particles from the gas is conducted by a Polytetrafluoroethylene (PTFE) filter. As the remaining hot gas flow passes the PSP, it is water-cooled to ensure a fast and complete quenching of the particles.

Results

After feeding the solid lithium particles to the drop tube reactor, the particle ignite forming a burning particle streak along the reactor tube axis. The ignition delay and the burnout time depend heavily on the atmosphere constitution: Generally, ignition delay and particle burnout time rise with decreasing CO_2 partial pressure. Thus, CO_2 plays an important role for the ignition and reaction kinetics.

This conclusion is supported by analyzing the particle temperatures measured with the TOSCA system. For each investigated atmosphere the particle statistics (temperature, event diameter) were measured at the approximate optical middle of the particle streak. The event diameter is the diameter calculated from the TOSCA images, in which a defined threshold was used to estimate a particle/gaseous flame boundary. Due to the different ignition delays and particle velocities, the center of the streak varies for each atmosphere. For each atmosphere at least 250 particles were measured to gain statistically meaningful data. The particle statistics are presented in Figure 2 for all four atmospheres. Each diagram shows two main groups of events which are clearly separated from each other in terms of temperature as well as event diameter for the atmospheres with a CO_2 partial pressure above 50%. For the atmospheres with lower CO_2 partial pressure, the groups move closer together: Generally, the first group covers diameters from 40 to 220 µm and temperatures between 1350 and 1800 K, while the second group is located at diameters above 250 µm and temperatures above 2000 K.

Note, that the presented temperatures of the gas-phase combustion events (>2000 K) have to be interpreted very carefully, as the surrounding flame is not a gray body. Therefore, the error of the presented gas-phase temperatures might be large. Particularly temperatures of 3000 K or higher might be not reasonable due to dissociation effects of the product species.

The two different phenomena have been reported before by Yuasa/Isoda for the combustion of a small lithium block and Schiemann et al. for the combustion of single lithium particles in a mixed hot gas atmosphere [6,16]. Yuasa and Isoda found that lithium burned in the vapor-phase first. After that it burned/glowed red at the particle surface. Schiemann et al. identified the two event types as two different combustion mechanisms, analyzing the event diameters and the gradients of the intensity profiles for each type, which were also measured with the TOSCA system. The high temperature events represent gas phase combustion of vaporized lithium at an enveloping flame

in a certain stand-off distance to the particle, while the low temperature events show a surface reaction. This reaction was not fully clarified and assumed to result from condensation or solidification of the gaseous reaction products and/or a second reaction zone at the particle surface.
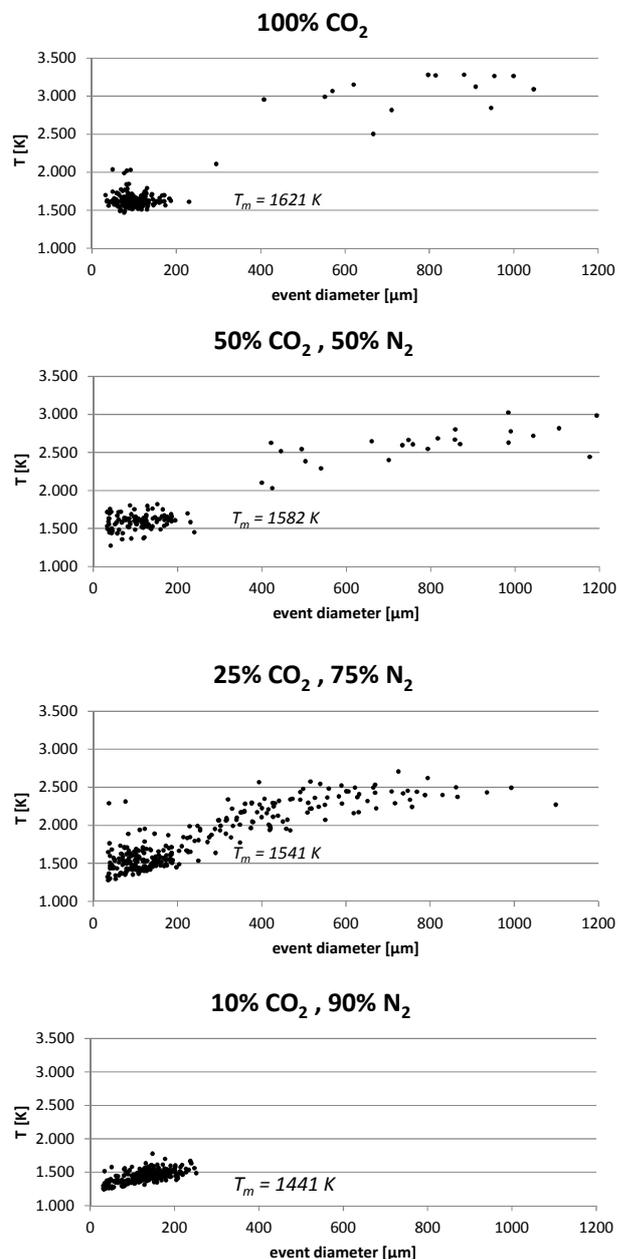
Comparing the measured temperatures of the four plots,

100% CO$_2$

50% CO$_2$, 50% N$_2$

25% CO$_2$, 75% N$_2$

10% CO$_2$, 90% N$_2$

Figure 2. Particle statistics (temperature, event diameter) for various CO$_2$ partial pressures at the center of each particle streak and median temperature of the surface combustion events

the temperature of both combustion phenomena decrease for lower CO$_2$ partial pressures. To point out the dependency of the combustion temperatures on the CO$_2$ partial pressure especially for the near surface reaction, the median temperatures of the surface reactions are also depicted in Figure 2. The decreasing temperatures indicate lower reaction kinetics, which fits

to the described increase of the particle burning time for lower CO$_2$ partial pressures.

In addition, a dependency of the gas phase combustion on the CO$_2$ partial pressure in terms of temperature, burning time and flame diameter becomes visible: While the two groups of events are clearly separated in the first two plots, the temperature and flame diameter decrease with decreasing CO$_2$ partial pressure: In the 25% CO$_2$ atmosphere the two groups of events merge, while the gas phase combustion is no longer visible in the 10% CO$_2$ atmosphere. Besides, the quantity of detected gas phase combustion events differs for all atmospheres, though the total number of images is similar: In the first two plots, the number of gas phase combustion events is very low, due to the very fast gas-phase reaction mechanism (burning time approx. 2 – 4 ms). Thus, the probability of catching a particle burning in the gas phase is low. In the 25% CO$_2$ atmosphere much more gas phase combustion events are detected, which leads to the conclusion, that the gas phase combustion is much slower here. This assumption was confirmed using single lens reflex camera photos of the different particle streaks.

Particle sampling has been carried only for the pure CO$_2$ atmosphere and the atmospheres with low CO$_2$ partial pressure (25% and 10%), so far. X-ray diffraction was conducted for the extracted mix of solid particle residue covered with aerosol to determine the constituents of the extracted reaction products. The qualitative analysis identified only Li$_2$CO$_3$, Li$_2$O, Li, and LiOH. No Carbides or elemental carbon (neither graphite nor amorphous carbon) were observed. In addition, no products containing nitrogen such as Li$_3$N were detected. Thus, the reaction of lithium with CO$_2$ to Li$_2$CO$_3$ and Li$_2$O is preferred and nitrogen acts just as an inert gas, here. The formation of LiOH does not occur during the combustion process due to the absence of H$_2$O in the reactor. The particle extraction from the filter and the XRD analysis could not be carried out under inert conditions. Because elemental lithium and Li$_2$O are both hygroscopic, they absorb water from the ambient air forming enough LiOH to be detected at X-Ray diffraction analysis.

The quantitative analysis using XRD is difficult since quantitative data maps are not available for Li and LiOH. Only the amount of Li$_2$O and Li$_2$CO$_3$ can be derived from X-Ray diffraction analysis. To compute the quantity of Li and LiOH, each probe was also examined with a CHN-analyzer (Leco TruSpec Micro) to gain information on the fraction of carbon and hydrogen. Calculating the elemental mass balance as well as the species mass balance and accounting the quantitative results of the XRD and the CHN-analysis yields to a set of eight variables and eight linear equations. The solution of the equation system provides the quantitative information of the amount of Li and LiOH.

For each atmosphere, sampling was conducted at six or more sampling points at the beginning, in the middle

and at the end of each particle streak. Thus, the quantity and the positions of the measurement points depend on the investigated atmosphere. To ensure comparable results, the measurement points are converted to particle residence times, which were determined by integrating the particle velocity measured with the TOSCA system using multiple exposure, as conducted in [17]. The results are depicted in Figure 3 for the pure CO_2 atmosphere and the atmospheres with CO_2 partial pressure of 25% and 10%.
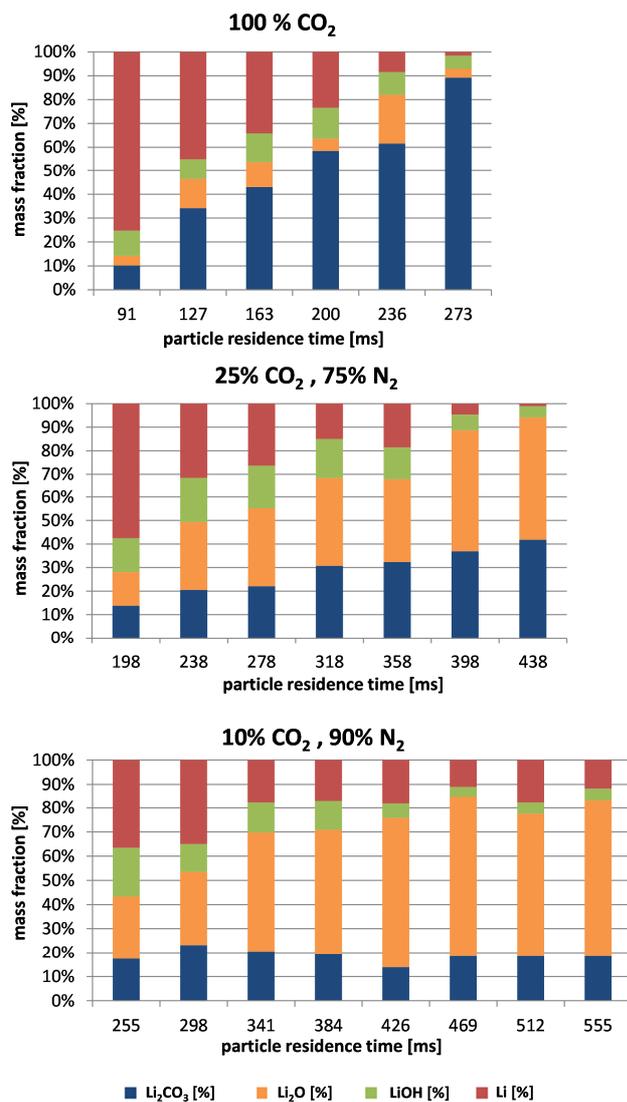

Figure 3. Burnout constituents at various particle residence times and CO_2-N_2 mixtures

The analysis shows a decreasing fraction of elemental lithium along the reactor tube axis for all three atmospheres, while the amount of Li_2O and/or Li_2CO_3 increases. The fraction of LiOH is below 20%, and was detected only due to the absorption of water during the removal of the sample from the probe.

Comparing the three plots with different CO_2 partial pressures leads to the following observations:

- The conversion rate of lithium to Li_2CO_3 is fastest for the atmosphere containing pure CO_2 (approx. 140 ms from 0% to 90% Li_2CO_3). At the end of the

particle streak, the major part of the lithium is converted to Li_2CO_3. The reaction rate of the other two atmospheres is much lower and a complete conversion to Li_2CO_3 was not detected in both cases.
- With decreasing CO_2 partial pressure, the amount of Li_2CO_3 decreases while the fraction of Li_2O grows strongly. Thus, the reaction from Li to Li_2O seems to be much faster for low CO_2 partial pressures than the reaction from Li_2O to Li_2CO_3.
- At the end of the streak in the 10% CO_2 atmosphere, the fraction of elemental lithium remains constant and is not converted to Li_2O or Li_2CO_3. This could be caused by the broad particle diameter distribution, as bigger particles ignite further downstream and therefore are not or only partly reacted. Besides some particles may not ignite at all as the gas atmosphere is getting too cold further downstream.

Note, that during the analysis of the 10% CO_2 atmosphere, the results of the CHN-analysis did not fit exactly to the XRD plots for the last four measurement points concerning the amount of Li_2CO_3. Nevertheless, the conclusion of a dominating reaction to Li_2O for lower CO_2 partial pressures is not affected by this error.

Conclusions

The combustion of single lithium particles ($d_p < 250\,\mu m$) in pure CO_2 and CO_2-N_2 mixtures was investigated using two different measurement techniques: Two-color pyrometry for the determination of particle/flame temperatures and diameters as well as sampling probe analysis with X-Ray diffraction and elemental analysis for the determination of the product constituents.

The experiments confirmed the findings of Yuasa/Isoda and Schiemann et. al. concerning two different combustion phenomena for the combustion of lithium in CO_2: The particles burn in the gas phase first with temperatures above 2000 K. In fact, temperature determination of the gas-phase combustion is difficult, as the surrounding flame is probably not a gray body. Afterwards, the combustion continuous with a reaction at the particle surface and temperatures around 1620 K. Adding N_2 to the atmosphere reduces the temperatures of the surface reaction at the particle surface indicating lower reaction kinetics. Besides, the flame diameters and temperatures of the gas phase combustion decrease for lower CO_2 partial pressures until no gas phase combustion was detected for the 10% CO_2 atmosphere. Simultaneously, the gas-phase burning times increase for lower CO_2 partial pressures.

As sampling probe results indicated, N_2 does not take part significantly as a reactant and acts only as an inert gas slowing down the reaction of Li + CO_2. In addition, a decreasing CO_2 partial pressure shifts the fraction of reaction products from Li_2CO_3 to Li_2O indicating a dominating reaction to Li_2O for lower CO_2 partial

pressures. A comparison of the findings with the results of Rhein, who burned a bulk of Lithium particles in simulated Venus and Mars atmosphere (CO_2, N_2 and Ar) is difficult due to the clearly different surface-volume-ratio of the fuel.

In the next step, reaction kinetics will be determined for the near surface reaction depending on the CO_2 partial pressure. For that purpose, pyrometry measurements are foreseen for all the presented atmospheres at various particle residence times, as the combined information of diameter and temperature for each particle measured with the TOSCA system enables the derivation of reaction kinetics, which has been performed before e.g. for coal [17].

Acknowledgements

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