Time-Resolved Laser-Induced Incandescence for In-Situ Nanoparticle Characterisation in Different Reactors

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Primary particle size is a decisive attribute of nanosized carbon blacks. In this work time-resolved laser-induced incandescence (TIRE-LII) is presented as an online measurement technique for this quantity. The investigated particles are exposed to pulsed high energy laser radiation which heats the particles up to their vaporisation temperature. The subsequent cooling process can be observed by the detection of the thermal radiation of the particles. The LII signal decay time provides information about primary particle sizes. This has been successfully proven with carbon blacks both under laboratory conditions and in situ, i.e. in production reactors.
First tests are performed with different types of commercially available carbon black powders, which are dispersed in a measurement chamber by means of a dry ultrasonic dispersion. After the sedimentation of big clusters out of the measurement volume reproducible LII-measurements can be performed. A good correlation between LII-results and specified product properties, based on TEM-analysis, is found (cf. Fig. 1).
Furthermore a special experimental setup using a "backscattering" geometry was developed to realise online measurements at production reactors. Primary particle sizes have been measured in situ under variation of reactor parameters. The results of LII-measurements are compared with different values for the surface area provided by laboratory analysis of sampled material. It is found that particle diameter determined by LII correlate very well with the CTAB (hexadecyltrimethylammoniumbromide)-adsorption number, which is a measure for specific surface area without consideration of pores. Furthermore, it turns out that the LII-method is not affected by variations of the agglomerate structure.
Additionally, LII signal decay curves are detected both for nanoscaled silver and copper particles with a clear influence of experimental parameters, e.g. pressure and type of inert gas.
Therefore, the presented work encourages the further development of the technique for online control of nanoparticle production regarding primary particle size.

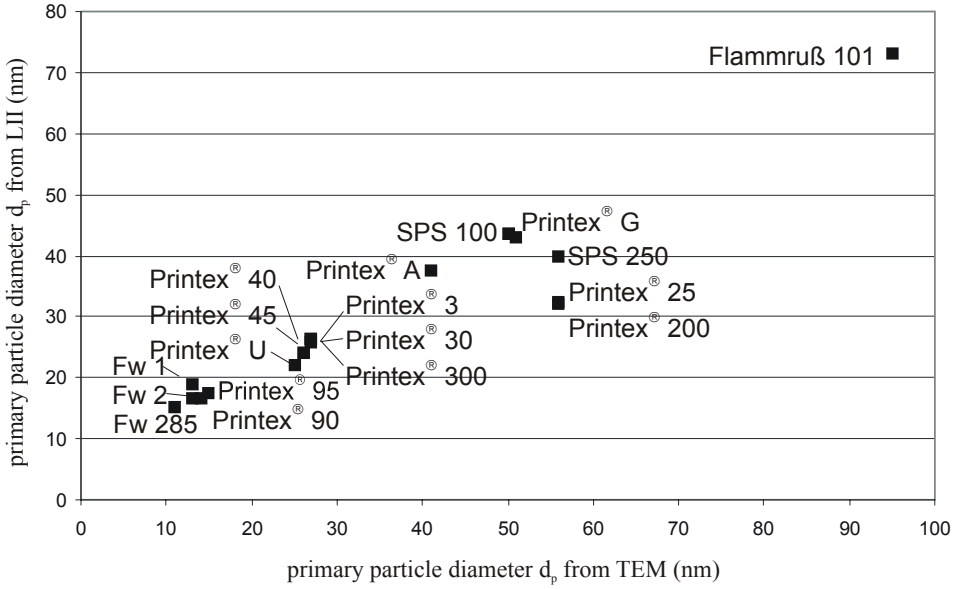

Figure 1: Primary particle sizes d_p of different types of carbon black determined by TEM and LII

Introduction

Nanotechnology is thought to be the key technology of the 21st century, because possible applications promise enhanced performance or completely new features, e.g. in the field of computer processing. Therefore, in future research and development nanotechnology will gain even more attention, however it is already a technique of today. The use of nanostructured materials is indispensable in many fields, e.g. carbon black, which is the most popular and widely used material, is important as a filler in tyres or in toner or titanium dioxide (TiO_2) for lacquers or creams.
The primary particle size is a main property of nanoscaled materials, since it significantly influences product properties (Fulcheri et al. (1997)). Thus, it is a major issue in nanoparticle production to control and maintain a desired primary particle size. There are many production parameters, which have an effect on the final particle size and so this quantity has to be measured continuously and preferably online. The latter requirement, however, cannot be met by conventional techniques. In carbon black production the specific surface area is determined by adsorption measurements of sampled material in the laboratory. This approach is very elaborate and time-consuming and far from an online method.
Therefore, the development and evaluation of alternative measurement methods is motivated with the aim to make an online technique available. TIme REsolved laser-induced incandescence (TIRE-LII) is an non invasive optical technique which Will et al. (1995) have successfully applied to determine primary particle diameters d_p in the nanometer range. LII has been successfully used both for comprehensive characterisation of soot in laboratory flames (e.g. Will et al. (1996), Puri et al. (1993) and Shaddix et al. (1994)) and soot analysis in the exhaust of Diesel engines with a compact sensor (Schraml et al. (SAE paper 2000)). It is obvious to examine and to extend the applicability of the technique for an in situ and online determination of d_p of nanoparticles during the production process.
To prove the practicability of TIRE-LII with commercially produced particles in principal avoiding problems that might occur in a rough industrial environment first tests with dispersed carbon black particles have been performed in a small measurement chamber. A dry ultrasonic dispersion was used in contrast to the work of Snelling et. al (2000), who sprayed carbon black particles suspended in a solution through a nebulizer. The LII-results are compared with product specifications, which are measured by transmission electron microscopy (TEM).
Beside these preliminary tests (provided that they are successful) it is reasonable to adapt the measurement technique for in-situ investigations at production and research reactors. This has been done at the Deutsche Gasrußwerke (DGW) and Degussa AG in the frame of several measurement campaigns. Thereby also the reliability of the method in a rough, industrial environment is examined. For a reasonable estimation of the usability of TIRE-LII measured d_p are compared with results from different conventional diagnostics.

Theory

Laser-induced incandescence relies on the fast heating of particles by a short laser pulse and the subsequent detection of particles thermal radiation.
Soot particles reach, depending on the incident laser energy, temperatures slightly above their vaporisation temperature. After the end of the laser pulse the particles lose their energy via three paths: vaporisation, heat conduction and radiation. These mechanisms are discussed in more detail by Hofeldt (1993), Melton (1984) and Dasch (1984). For soot particles it has been predicted from theoretical considerations and proven by many investigators that both soot volume concentration, primary particle sizes and aggregate sizes (in combination with elastic scattering) are accessible with this technique. The maximum LII-signal at the moment of the laser pulse is proportional to soot volume concentration and the temporal decay of the LII signal provides the specific surface area and with it for spherical particles the primary particle size.
The latter applies due to the fact that about 100 ns after the laser pulse heat conduction to the surrounding medium is the significant heat loss mechanism, since vaporisation is negligible because of decreased particle temperatures and the contribution of thermal radiation to the energy loss is small for all times. Nevertheless, the radiation is important since it represents the detected LII-signal.
The energy loss by heat conduction is proportional to the surface area and in consideration that the internal energy scales with the volume of the particle the particle cooling rate for late detection times is a measure for the specific surface area. In fact small particles cool down and the corresponding LII-signal decreases faster. A more detailed description of the TIRE-LII-technique is given by Will et al. (1998).
In the presented measurements complete temporally LII-signal decays were detected with a fast photomultiplier, what improves the signal to noise ratio as compared to two-dimensional measurements evaluating the signal ratios at certain times. This procedure only allows the acquisition of pointwise information, but this is no drawback in systems with spatially distributed particles which have all the same attributes. From the experimental LII-signal curves a signal decay time τ is determined by an exponential fit in a time interval where

heat conduction dominates the particle cooling process. Under consideration of the surrounding temperature T_0, τ is unambiguously associated to a mean d_p.

Chamber measurements

Experimental setup

In the first part of this work the technique was tested with commercially available carbon black powders which were dispersed by a simple dry ultrasonic dispersion. The particles were placed on an ultrasonic transmitter on the bottom of an optically accessible chamber (cf. Fig. 1).

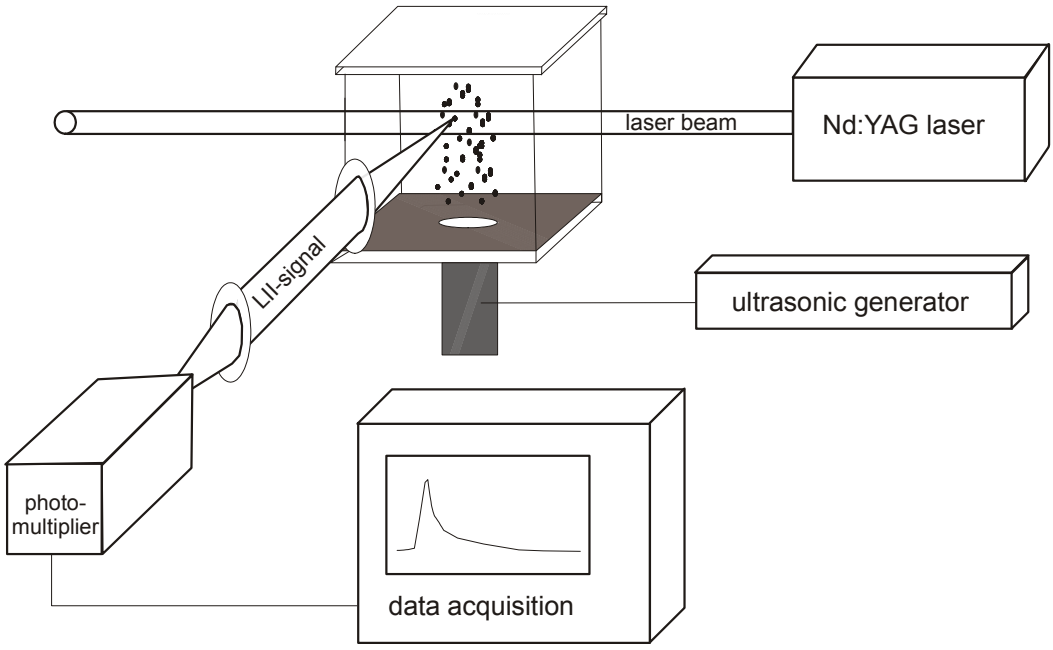

Figure 1: Schematic of experimental setup for laboratory measurements

The pulse from a frequency-doubled Nd:YAG laser emitting light with a wavelength of 532nm with a beam diameter of 8mm was directed without further optics into the measurement chamber, in which the particles were dispersed.
The LII-signal was detected by a photomultiplier being placed orthogonally to the laser beam. A filter combination was applied to suppress elastic scattered light and to filter out an appropriate spectral region of the signal, which was. The measurement volume (about $0.3cm^3$) is defined by the spatial overlap of laser beam and detected solid angle. One measurement curve is the average of LII-signals generated from 10 laser pulses resulting in a measurement frequency of 1 Hz.

Results

During the initial laboratory measurements the dispersion had to be modified. First, the dispersion was realised with ultrasonic pulses transmitted permanently, what provided a homogeneous particle distribution, but the particle sizes, which were determined with LII were much bigger than the corresponding values from TEM analysis and varied in a wide range, which was caused by statistical fluctuations of different structures in the measurement volume. It has to be pointed out that the fluctuations are not caused by the measurement technique, as the reproducibility of the results in stationary objects, such as laminar diffusion flames, is very good with a standard deviation less than 3%.
The reason for these effects can be found in an incomplete dispersion of the powder. There are still dense structures inside the measurement chamber, what results in a delayed energy transfer of the single carbon black particles. The existence of these structures, which are bigger than the agglomerates and aggregates, that are generated during the carbon black production, can be attributed to the storage of the powder before the dispersion.

Nevertheless, meaningful measurements can be performed if the sedimentation of these clusters out of the measurement volume is awaited. First the particles were dispersed by one or two ultra sonic pulses and subsequently LII-measurements were performed while sedimentation took place.
The temporal development of signal decay time after dispersing of the particles is shown in Fig. 2. In the beginning large decay times τ are measured indicating big clusters in the measurement volume, but then τ decreases to a stationary value when due to sedimentation only smaller agglomerates and aggregates remain in the measurement volume. After a certain time period which is different for each type of carbon black signal decay times remain constant.

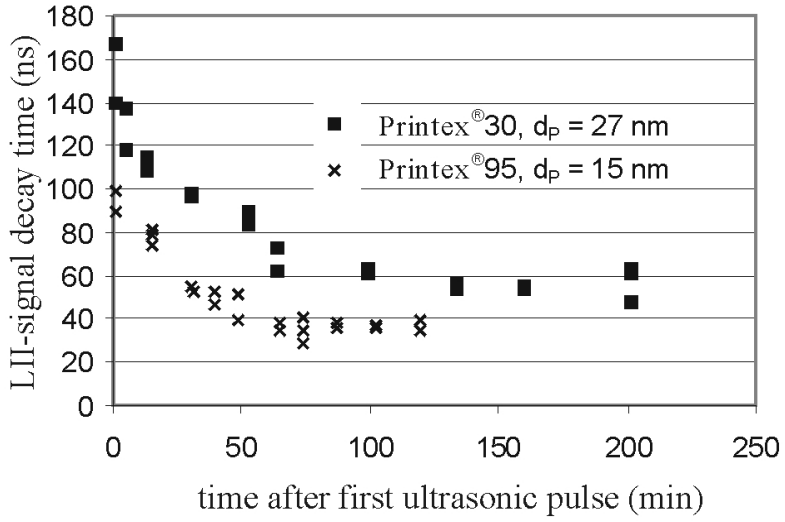

Figure 2: Temporal decrease of signal decay time τ

An estimation of the sedimentation velocity, calculated from the balance of friction forces and gravity, yields 2mm/h for a diameter of 100nm. Hence, small structures with sizes in this range are even dispersed inside the measurement chamber after hours when bigger clusters have already fallen out. This is in agreement with the detection of a weaker but sufficient LII-signal.

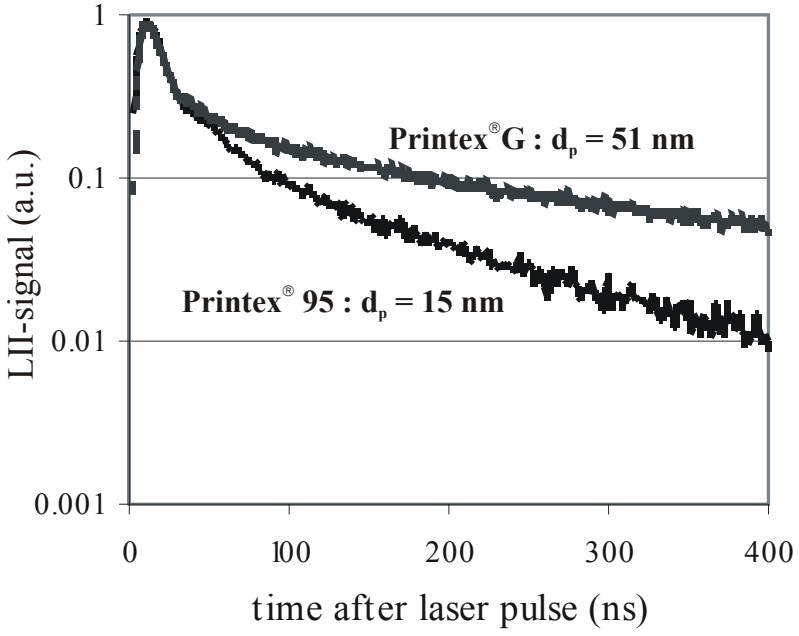

Figure 3: Experimental LII-signal curves

Primary particle sizes were evaluated from the constant value of τ under consideration of the surrounding temperature of T=298K. The results show a good reproducibility with a standard deviation <5%.

Several different carbon blacks from Degussa AG were analysed : on the one hand Colour Blacks with primary particle sizes between 11 and 13nm (FW 1, FW 2, and FW 285) and Lamp Black 101 (d_p=95nm), which are produced in a channel black process, and on the other hand Special Black 100 and 250 and a number of Printex® types representative for furnace blacks. Exemplarily measured LII-curves for two different carbon blacks (Printex® 95 und Printex® G) are shown in Fig. 3. The faster signal decay for Printex® 95 (d_p=15nm, from TEM-analysis) in contrast to Printex® G (d_p=51nm) due to the larger specific surface area is clearly observable.
In Fig. 4 the results from LII-measurements for the d_p for all investigated carbon blacks are compared to values from TEM-analysis of Degussa AG (technical data sheet).
Primary particle diameters derived from the a-priori LII-model correlate very well with the corresponding product specifications. There is only a slight systematic deviation resulting in higher values from LII than from TEM-analysis for small particles and smaller values for larger particles, which may be attributed to an overestimation of the energy loss due to vaporisation in the beginning of the LII-process (Schraml et al. (Comb. Flame 2000)). Particularly interesting is that for Printex® 3, 30, and 300, which differ completely regarding their agglomerate structure, LII provides an identical d_p in agreement with TEM-analysis.
Deviations from the correlation are only observable for Special Black 250, Printex® 25 and 200, which have different material properties than the other carbon blacks, which was not explicitly considered in the LII-evaluation, as not all properties, needed for a full numerical evaluation, such as vaporisation parameters, are available for all individual samples. Thus, all calculations were based on material properties of soot.
Furthermore, tests regarding the influence of laser irradiance and carbon black concentration were realised. The results were not affected by a variation of laser irradiance from 2-4·10^7 W/cm^2. Relative particle concentration in the measurement volume was determined from the maximum prompt-LII-signal; there was no dependence of d_p observable for a variation in concentration by a factor of 50.

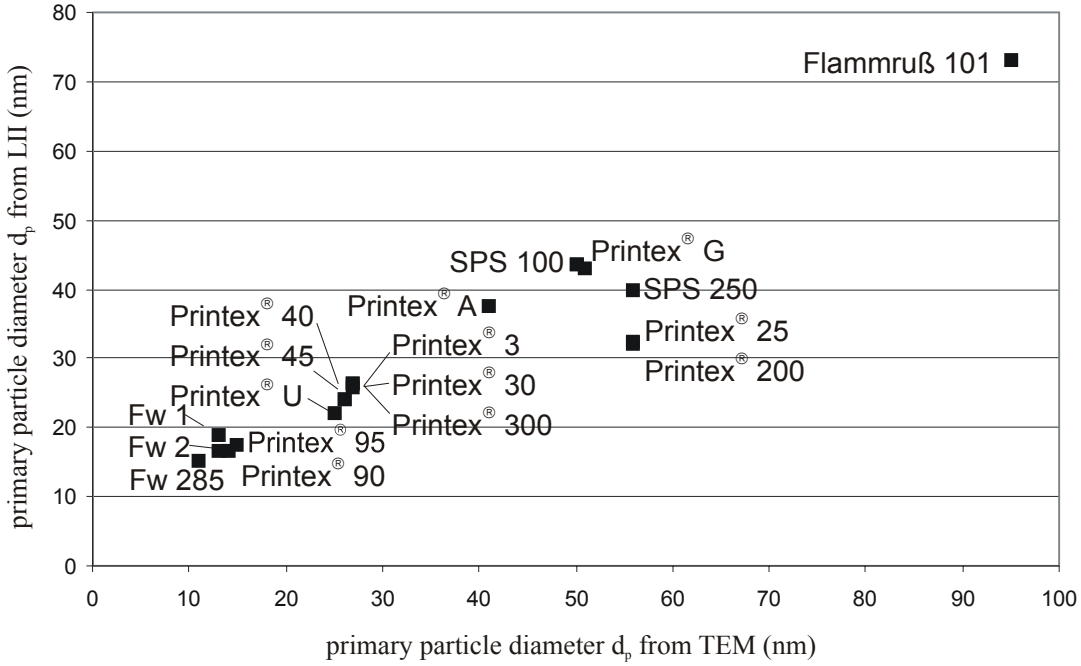

Figure 4: Comparison of primary particle size d_p determined by TEM and LII

In-situ reactor measurements

Experimental setup

One possible way for the production of carbon black is the furnace process. Thereby preheated oil is sprayed into a flame where the oil molecules are cracked and the resulting carbon molecules form under lack of oxygen carbon black particles. The particle growth is terminated downstream by a water quench (Kühner (1993)).
For the online measurements at a furnace reactor a new experimental setup had to be realised, since it is not possible to detect the LII-signal orthogonally to the irradiating laser beam due to the strong absorption resulting from the high particle volume concentration (up to $f_V = 10^{-4}$) inside a production reactor. Therefore, a backscattering geometry was developed, i.e., the LII-signal is detected via the same path that is used for the

exciting laser beam (Fig. 5). The laser beam is guided into the reactor by a beam splitter, which transmits the blackbody radiation emerging from the particles. Only one optical access is necessary for this layout. Again a frequency–doubled Nd:YAG laser was used.
The window and the tube which allows the optical access were purged with nitrogen. As the purge gas was much colder than the process gas, a mixing temperature establishes in the measurement volume in the reactor, depending both on the temperature difference of the two gas streams and on the ratio of mass flows. Thus, the purge gas flow was kept constant resulting in an almost constant mixing temperature. Free optical access could be guaranteed for all measurements.

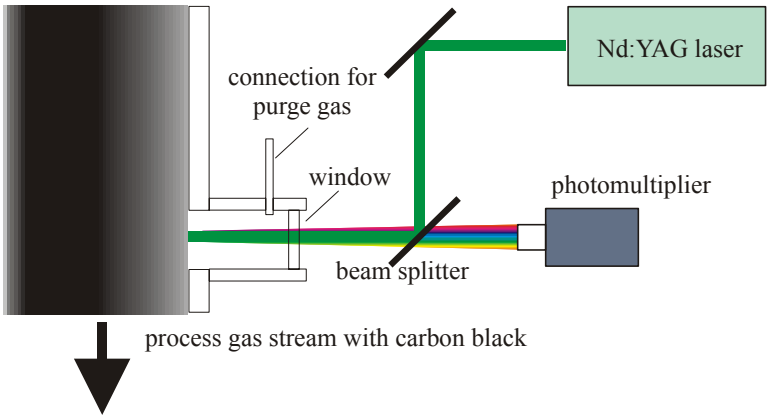

Figure 5: Experimental setup with backscattering geometry for online-measurements at a industrial carbon black furnace reactor

The gas temperature in the reactor was measured by two thermocouples upstream and downstream of the measurement volume, respectively. For every reactor setting the upstream temperature is about 30-40K higher than the downstream temperature because of the mixing with the cold purge gas. For evaluation of d_p the higher temperature is used, what results in an uncertainty of less than 1nm. Signal decay times are measured with a frequency of ca. 1Hz during a longer time period. This provides information about the reproducibility of the results and about the steadiness of the measurand.

Results

For the evaluation of the method at a production reactor phased variations of reactor operation parameters were performed.
Particles were sampled to determine the iodine number, the CTAB(hexadecyltrimethylammoniumbromide)-value (characterises primary particle size without consideration of small porosities) and the di-butyl phthalate (DBP)-value (measure for agglomerate structure) by laboratory adsorption measurements.
The results from this analysis are compared with values for d_p from LII-measurements, which are the diameters averaged during the sampling period of typically 20 minutes. The averaging is done for better comparison because the different adsorption numbers only provide averaged information about a longer time period determined by the sampling. LII, however, also allows the instantaneous detection of changes in particle size. For the comparison of LII-results with corresponding values from laboratory analysis it is indispensable to accurately determine the period the particles need to cover the distance from the LII measurement volume directly in the reactor to the end of the system where the sampling assembly is located. A medium period of 20 minutes had been determined earlier and so the LII-signal decay times were averaged during 20-15 minutes before the samples were taken for 5 minutes.
It turned out that the LII values correlate very well with CTAB-adsorption number, whereas a correlation with iodine number is not clearly observable. It is reasonable to assume that small porosities do not affect the energy loss after the laser pulse because of an obstruction of heat conduction in these holes and thus, the LII-technique determines an enveloped particle diameter. The iodine number, however, increases with increasing porosity (Kühner (1993)). Thus, LII-results correlate with iodine numbers only if different specific surface areas are caused by variations in d_p and not in porosity. This assumption was tested at a research reactor, where smoother variations of reactor parameters can be realised. It was the aim to produce carbon blacks with same primary particle sizes but different surface structures. Thereby one setting was kept for hours to guarantee a stationary state of the reactor, which is important to detect small variations.

Table 1 gives an overview of the results of the variation of porosity. The first parameter change decreases iodine number by about 10%, the small reduction of the CTAB-value indicates that d_p increases slightly with a simultaneous variation of porosity. During the next phase bigger particles are produced (CTAB-value is decreased) with a more porous surface, since the iodine number remains constant. The last variation led to a higher iodine number while the CTAB-value does not change. The LII-results correlate clearly with the CTAB-value.

phase	iodine number	CTAB-value	primary particle size by LII (nm)
1	206	157	27,0
2	179	155	27,9
3	179	148	29,9
4	190	149	29,5

Table 1: Results of variation of porosity

Another set of measurements was used to check the influence of agglomerate structure on LII-results. Particles with similar d_p but different state of agglomeration were investigated. The primary particle size determined with LII shows no systematical dependence on the DBP-value, what is in agreement with the results obtained with dispersed powders in the measurement chamber.

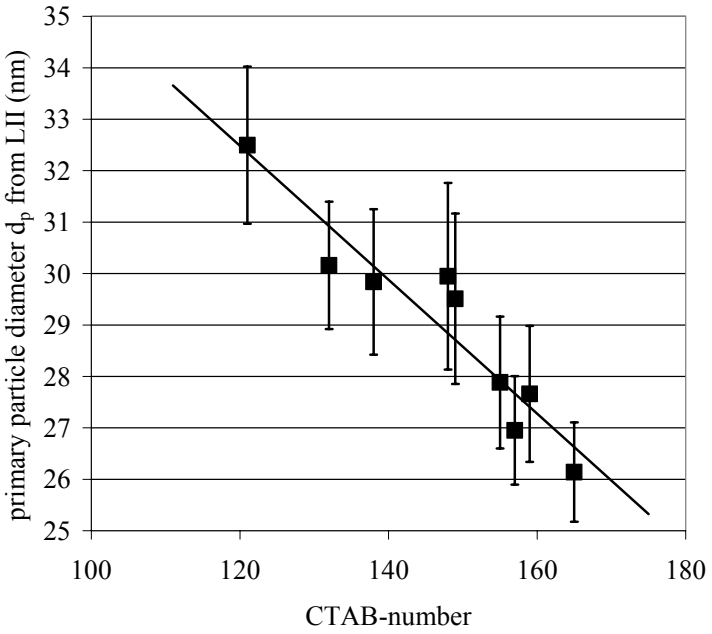

Figure 6 : Correlation between primary particle size d_p from LII and CTAB-number

In contrast a correlation of particle diameter from LII-measurements and the CTAB-value, i.e. the specific surface area without consideration of small micro pores, is in Fig. 6 for a wide range of operation parameters clearly observable. The error bars correspond to the standard deviation of the decay times averaged during 5 minutes. It should be noted that the magnitude of the standard deviation is mostly determined by fluctuations in d_p itself and is not to be attributed to the measurement technique, as it has been proven in earlier laboratory investigations of stationary flames.

Plasma reactor

Additionally, primary particle sizes of carbon black were determined during the production process in a plasma reactor. The precursor is sprayed into the plasma that is electrically generated. The experimental LII-setup was similar to that used at the furnace reactors, i.e. a backscattering geometry was realised. In the plasma reactor, however, particle concentrations are so small that the resulting weak absorption of the irradiating laser beam, does not allow to specify the penetration depth of the laser beam in the reactor. There is a steep temperature gradient along the laser beam path. Therefore, only an approximate value for the surrounding gas temperature of the particles, that emit the LII-signal, is provided. This temperature, however, is an input parameter for the evaluation of the LII-measurement. Consequentially, only a range for the primary particle size can be calculated, but which is in good agreement with corresponding results of BET surface area determination as shown in table 2 for different reactor settings.

Setting no.	LII primary particle size range (nm)	Calculated particle size from BET value (nm)
1	29-35	31
2	29-32	31
3	30-34	33

Table 2 : Comparison of LII primary particle size d_p range from LII and results from BET analysis

Besides the carbon black measurements, first test measurements have been conducted with copper and silver nanoparticles. During these investigations LII-signal decay curves could be detected for both metals (Fig. 7). A clear influence of reactor parameters, e.g., pressure and type of inert gas, on LII signal decay times was observed. The quantified evaluation in terms of primary particle size requires the adaptation of the LII model with the material data, what is currently in progress.

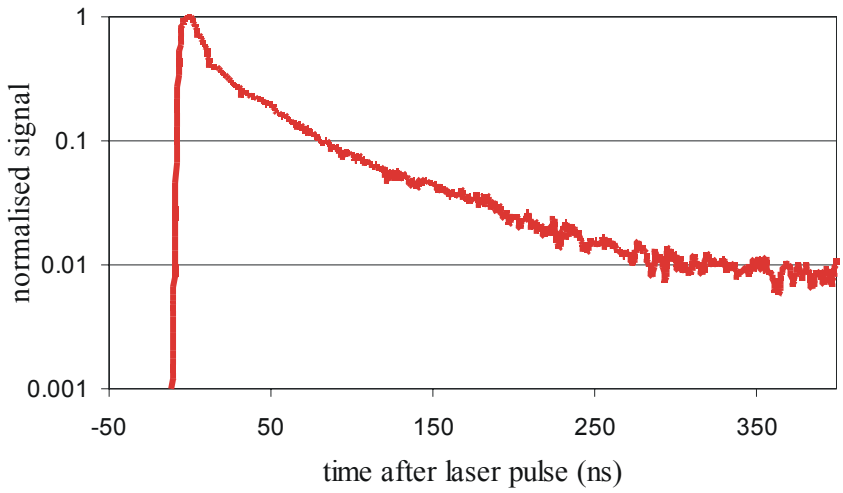

Figure 7: LII-signal decay curve obtained with silver nanoparticles

Conclusions

The presented results demonstrate that Time-Resolved Laser-Induced Incandescence (TIRE-LII) is a powerful tool for the in-situ determination of primary particle size in the nanometer range during combustion synthesis in different production and research reactors. LII-results obtained with dispersed powders correlate very well with product specifications. Reactor measurements were successful regarding both the applicability in an industrial environment and the determination of primary particle sizes in situ.
Furthermore, first in-situ measurements with copper and silver particles indicated the principal applicability of the measurement technique for the characterisation of these metal nanoparticles. The results obtained for the metal particles encourage further research work, in particular regarding the adaptation of the theoretical models to evaluate the TIRE-LII-measurements quantitatively in terms of particle size.
From the online measurements of carbon blacks at research and production reactors a clear correlation between primary particle size d_P by LII and CTAB-number from laboratory analysis of sampled particles is found. The

relationship between iodine number and LII-results, however, is not distinctive, i.e., variations in micro-porosity, which influence the iodine number, do not affect the LII-result for a constant d_p. Both the measurements in the chamber and online at the reactors show no influence of agglomerate structure on particle sizing with LII.
Especially measurements with small variations in reactor parameters reveal the potential of the technique to detect small changes in d_p instantaneously. The little experimental effort makes the application of a LII-sensor for production control interesting. Apart from an online determination of particle size the process stability can also be monitored by a continuous measurement.

Acknowledgements

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