Lasers in Manufacturing Conference 2015

Analysis of potentially hazardous substances emitted during laser processing of carbon fiber reinforced plastics

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Abstract

Lasers are promising tools to cut, ablate or even weld carbon fiber reinforced plastics (CFRP). Nowadays, it is possible to achieve very good product qualities (especially relevant for lightweight constructions) using specific laser processing strategies such as multipass cutting or short-pulsed ablation. The intention of these processing strategies is to minimize laser energy deposition within the material, because excessive heat causes defects such as pores, blowholes or delamination.

Nevertheless, CFRP laser processing is connected with the emission of potentially hazardous substances, i.e. particles and fiber segments as well as inorganic and organic gases.

This work describes a generalized approach to investigate hazardous emissions released during laser processing of CFRP. Measurement methods to quantify the emitted particles and gases in the exhaust air as well as in the air at the workplace are presented. These methods are applied to determine emission rates of specific material process combinations. The obtained values are implemented into a specific database to enable a fast access to the comparison with existing limit threshold values, maximum permissible exposures and adequate protective measures. The thorough analysis of various processes will help to assess the risks related to laser processing of CFRP in general and thus to create the framework, including standardization, for a safe handling of the emitted hazardous substances.

Keywords: laser; carbon fiber reinforced plastics; process emissions; measurement; hazards; risk assessment; occupational safety; environmental protection

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1. Introduction

Carbon fiber reinforced plastics (CFRP) represent a remarkable group of organic composite materials with outstanding mechanical properties in relation to the comparably low specific weight. These properties result from the inner structure of the composite material containing matrix and carbon fiber reinforcement (unidirectional layer, bi- or multi-axial non-woven fabrics, or woven fabrics). The matrix material is either a thermosetting resin, such as epoxy, or a thermoplastic polymer, such as polypropylene (PP), polyamide 6.6 (PA 6.6) or polyphenylene sulfide (PPS). Due to the carbon fibers, CFRP parts have a high specific strength parallel to the composite layers, whereas the strength perpendicular to these layers is mainly determined by the matrix properties. The described properties lead to a very high potential regarding the production of lightweight structures. This was first recognized by the aircraft industry, helping to reduce fossil fuel and energy consumption. Increasing interest in such CFRP materials is noticed by the automotive industry. Nowadays, relevant applications can also be found in the wind-energy industry, the sports segment and, as an exotic example, the fabrication of music instruments (see the carbon violin in Fig. 1).

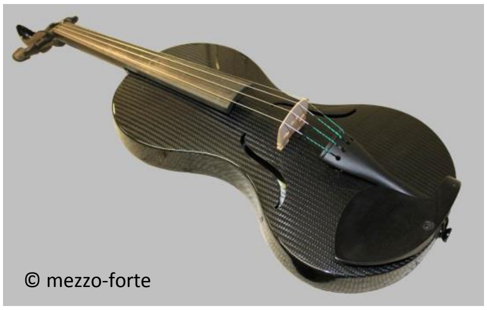
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Fig. 1. Carbon-violin

The major challenge with respect to CFRP products is the realization of an economically efficient processing. Due to the specific strength and hardness of the fibers and the viscoelastic behavior of the matrix material, conventional processing techniques such as milling or water jet cutting are slow, affected by substantial tool wear, and consequently expensive (Sheikh-Ahmad, 2009). In contrast, lasers can deposit the energy precisely without direct contact to the processed parts. Moreover, relatively high cutting and ablation speeds can be achieved (see e.g. Bluemel et al., 2012). Nevertheless, processing results of good or even excellent quality can be obtained, if specific processing strategies, e.g. multipass or contour processing using short-pulsed laser systems with high brilliance, are applied (see e.g. Jaeschke et al., 2014).

The laser energy input causes considerable emission of fumes and inorganic and organic gases, influenced by various material and process parameters. The composition of these emissions is complex, and they may contain significant amounts of toxic components or substances which are carcinogenic, mutagenic or toxic for reproduction (CMR substances). Moreover, a lot of ultrafine particles, showing the potential to be incorporated into the pulmonary alveoli, may be generated (see e.g. Haferkamp et al., 1998). So far, there is little quantitative information concerning particulate and gaseous emissions during CFRP laser processing as well as the requirements for adequate measures to ensure occupational safety and environmental pollution control (see e.g. Walter et. al., 2014). For instance, it is not known whether the fumes contain fibrous particles which may behave similar to asbestos fibers in human lung tissue due to their geometry.

In Germany, environmental protection is regulated by law (BImSchG, 2013) and the corresponding regulation TA Luft, 2002. Here, threshold limit values for hazardous substances in the exhaust air are defined, and emissions have to be reduced accordingly. Apart from the German law ArbSchG, 2013, the European regulation REACH, 2012, is the basis for the employees' protection against hazardous substances. The German law ChemG, 2013, and the regulation GefStoffV, 2013, refer to this European regulation. The exposure limit values for hazardous substances in the air at the workplace are listed in the technical rule TRGS 900, 2014. The limit values have to be met by adequate measures, starting from technical measures to reduce hazardous substances, to organizational measures such as preventing access to the working area. Finally, personal protective equipment is stipulated for employees who have to stay in the working area in spite of hazardous substances, which cannot be reduced sufficiently due to technical reasons.

In this paper, a generalized approach and corresponding initial investigations concerning the systematic qualitative and quantitative analysis of particulate and gaseous process emissions during laser processing of exemplary CFRP materials are presented, taking into account the process conditions. The aim is to evaluate the total emission rates of potentially dangerous organic components, the amounts of emitted particles, and the occurrence of toxicologically critical fibrous particle morphologies. The concentrations of the organic gases and particles as well as the particle morphologies in the exhaust air are measured using well-established analytical methods and commercially available instrumentation, such as flame ionization detection, infrared sensor technology, electrical low-pressure cascade impaction, and scanning electron microscopy. The results shall be used to assess the potential hazards, to define the necessity of protective measures, and to develop strategies for adequate process management and handling of the emissions. The investigations will help to create the framework for a safe handling of the hazardous substances emitted during laser processing of CFRP, including standardization issues.

2. Emission prognosis

In order to prepare the emission characterization of the laser machining processes of interest, emission prognoses of the CFRP materials selected are performed first. For this purpose, small material samples are pyrolyzed by CO_2 laser radiation. The resulting mixtures of organic substances are injected into a gas-chromatography mass-spectrometry system (GC-MS), using a defined helium flow, and thus analyzed with respect to the contained organic substances. Exemplary results of the analysis are shown in Fig. 2 and Fig. 3.

Analyzing the main components of the material used, bisphenol A (see the mass spectrum in Fig. 3) and some other key substances with smaller percentages were identified. The composition of the gas mixture emitted from the laser pyrolysis indicates a CFRP material with thermosetting matrix based on bisphenol A.

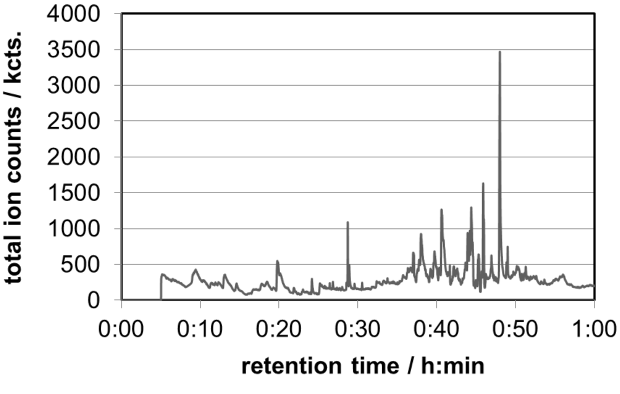

Fig. 2. Gas chromatogram of an unspecified CFRP material measured after laser pyrolysis, using the GC-MS. Here, the evaluation (see e.g. the mass spectrum in Fig. 3) indicates a material with epoxy matrix based on bisphenol A.

In particular, the mentioned substances and related decomposition products can also be expected in the exhaust air of laser processes in which material decomposition is relevant. Bisphenol A is toxicologically relevant: the limit value (TLV) for this substance in the air at the working-place is 5 mg/m^3 according to TRGS 900 (as the respirable fraction), the mass flow rate in the process exhaust air must be smaller than 0.10 kg/h according to TA Luft, and a mass concentration of 20 mg/m^3 must not be exceeded.

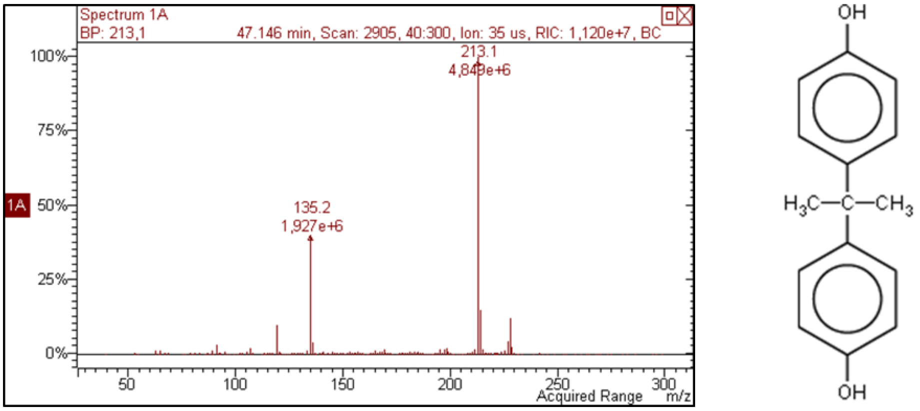

Fig. 3. Measured mass spectrum (a) of the major peak in the chromatogram of Fig. 2 (identification of bisphenol A (b)). In addition to bisphenol A, further key components were identified by mass spectrometry of individual chromatogram peaks.

Potentially hazardous components which exhibit a threshold (limit) value either in accordance with TRGS 900 and TRGS 910 or according to TA Luft, have not been identified for the CFRP material considered here. The analysis of further CFRP and additionally GFRP materials is in progress.

3. Experimental setup of a laser cabin specifically equipped for emission sampling and analysis

To carry out the emission characterization according to applicable rules, a specific exhaust system has been designed and built up on top of a high-power laser-cabin in the LZH facilities. An overview of the piping installation as well as of several instruments used for the emission sampling and analysis are shown in Fig. 4.

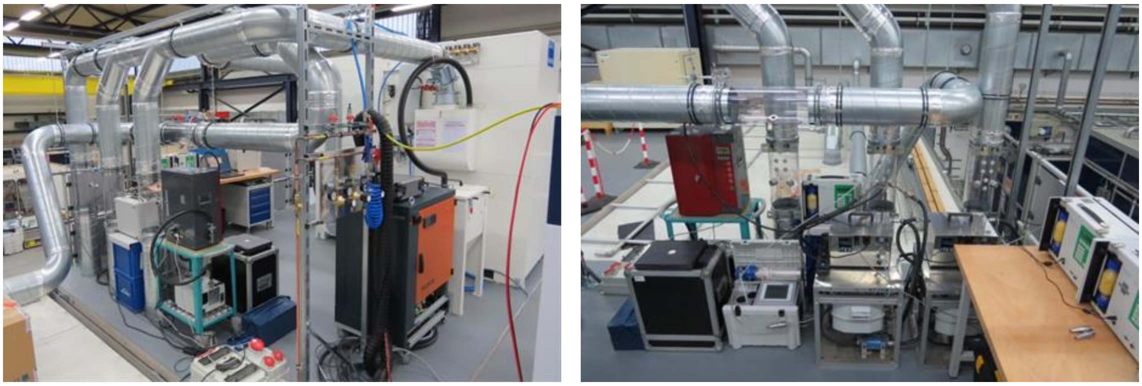

Fig. 4. Piping installation for exhaust air capturing and analysis on top of a high-power laser cabin and various measuring instruments.

Three exhaust channels, including sampling cells (called metering boxes) have been realized. The exhaust air metering boxes are integrated into the perpendicular parts of the pipe. The three exhaust channels allow for separate analysis of three different local or global sampling positions in the cabin. To enable the quantitative analysis of the cleaned process gas as well, an additional metering box has been implemented into the clean gas pipe behind the filter system. By comparing the corresponding measurement results with the emission rates determined in the exhaust air, an evaluation of the filter system efficiency is possible. Apart from the possibility of local capturing and suction cleaning of emissions, global cabin extractions by suction have been installed in the high-power cabin considered here.

Fig. 5 shows detailed images of two metering boxes with the corresponding sampling inlets. In particular, bent tubes with specific nozzles at the end can be seen in the left image, enabling the isokinetic (same-speed) sampling for the gravimetric measurement of the total particulate matter and the determination of the particle size distribution, which is based on an Electrical Low-Pressure Cascade Impactor (ELPI).

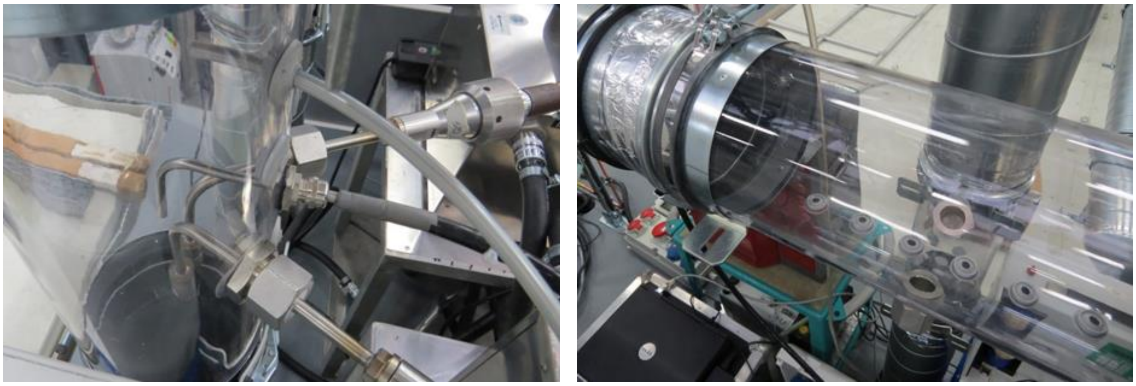

Fig. 5. (a) Particulate matter sampling devices in the exhaust gas (the nozzles on the bent tubes are selected depending on the flow rate in the exhaust air channel for isokinetic sampling). (b) Metering box with openings for various sampling tubes (including organic gases).

The sampling nozzles are adjusted to the actual flow velocity measured in the exhaust pipe (depending on the capturing flow conditions inside the laser cabin between 6 and 20 m/s). In addition, Fig. 5 shows the sampling inlets used for sampling of gaseous organic hazardous compounds. Four different sampling tubes can be used simultaneously to assign specific organic substances.

In order to achieve an optimal capturing and extraction of the emissions released from the laser process and to minimize the concentrations of hazardous substances in the cabin, a defined air supply rate must be guaranteed. The released particles and gases should be forced to enter directly into the local capturing vents to prevent spreading into the cabin. Therefore, the air supply flow is carefully adjusted to the exhaust air flow. In general, the exhaust air flow must be higher than the supply airflow. This generates a pressure difference which reduces significantly the amount of emissions leaving the laser-cabin. This has to be taken into account for the final design of any industrial CFRP machining process.

4. Quantitative emission characterization

The emission characterization is performed for different laser processes and process strategies with various laser systems. For experiments concerning contour and multipass cutting, a ROFIN-SINAR FL015C single-mode continuous-wave fiber laser system (1070 nm, 1.5 kW) was applied. In further experiments also concerning multipass cutting, a pulsed Trumpf TruDisk laser (1030 nm, 1.5 kW average power, nanosecond pulses) was used. To ablate CFRP layers, a pulsed cleanLASER CL 50 solid-state laser (1064 nm, 50 W average power, nanosecond pulses) was chosen.

Fig. 6 shows the percentage emission composition of the total process emissions in the exhaust air during ablation of CFRP. Obviously, the aerosols (79%) represent the biggest piece of the pie chart, followed by CO (16%) and VOCs (5%) which are of less relevance in this specific case.

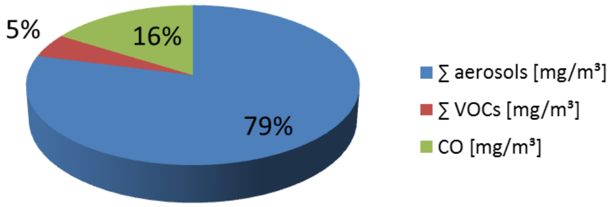

Fig. 6. Exemplary composition of process emissions during ablation of CFRP epoxy.

During multipass laser cutting, a typical particle size distribution of a CFRP material with epoxy matrix measured with the ELPI is shown in Fig. 7. The qualitative difference between the distributions for the number of particles and for their mass frequency is significant. While the largest number of particles can be found in the range of an aerodynamic diameter near 100 nm, the majority of the particle mass is represented by relatively few large particles with an aerodynamic diameter of more than 6.6 µm.

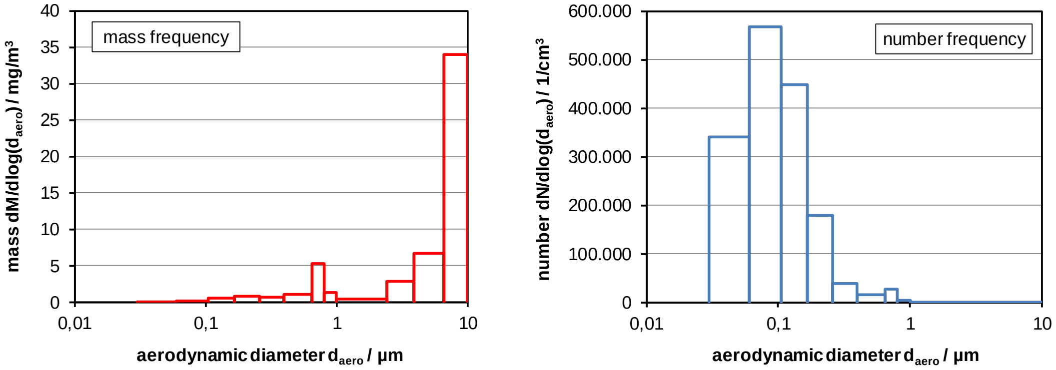

Fig. 7. Particle size distribution of a carbon fiber composite material with epoxy matrix, measured by the ELPI during multipass cutting with a 1.5 kW fiber laser (cw); (a) number frequency, (b) mass frequency.

In future investigations, the particle size distributions will be measured systematically as part of the emission characterization work. Furthermore, the machining parameter sets have to be optimized individually for all materials processed in order to identify characteristic dependencies.

To assess the release of fiber segments during laser processing of CFRP, sampling by means of gold-coated track etched filters made from polycarbonate is performed. Exemplary SEM pictures of such filter foils covered with fiber segments and particles are shown in Fig. 8. Multipass laser cutting with additional breaks of CFRP epoxy obviously generated relatively long fibers (> 600 µm). In comparison, the contour process generated few and short fiber segments. However, the result has to be interpreted with caution, as the overall laser energy input was kept constant for these experiments, whereas the capturing time differed strongly between the cutting strategies. According to the World Health Organization (WHO), fibers with a diameter < 3 µm, a length > 5 µm and a length-to-diameter ratio > 3 : 1 can penetrate the lower respiratory tract (so-called WHO fibers). Almost all fiber segments found on the filter foils have a diameter significantly larger than 3 µm and are therefore not classified as WHO fibers. According to the producer of the CFRP material considered, the original fiber diameter is in the range of 7 µm (carbon fibers type T-300).

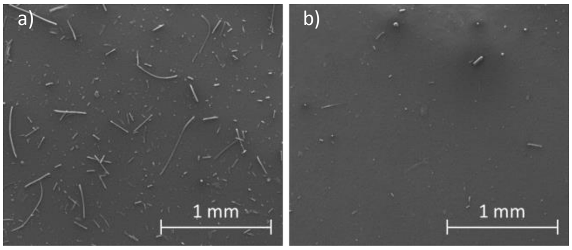

Fig. 8. SEM pictures of gold-coated track etched filters made from polycarbonate, used to collect fibers and fiber segments during CFRP laser cutting. (a) CFRP epoxy, multipass cutting with breaks, (b) CFRP epoxy, contour cutting.

5. Workplace measurements

Occupational exposure assessment is used to evaluate hazardous risks for the workers in the occupational environment during laser operation. This includes issues related to selection, use, and disposal of substances, as well as to the production processes and the materials themselves. To obtain reliable data, 2 strategies for measuring are available, e.g. personal and stationary sampling (see Fig. 9).

Fig. 9. (a) Occupational exposure assessment sampling strategies and sampling heads, (b) personal, (c) stationary measurement.

In a first step, key components depending on the material to be processed by laser radiation have to be found. Secondly, the location of the workplace has to be analyzed. This enables the definition of the exposure area dimensions in which the influence of the process emissions released into the air at the workplace is relevant. Inside this exposure area, several sampling locations have to be defined and, if applicable, to be supplemented by a sampling worn by an employee. Thirdly, the sampling time which depends on the process has to be determined. In the case of processing CFRP, VOCs are measured beyond aerosols (total and alveolar dust). If key components are known or identified, specific substances such as bisphenol A, 1,3 butadiene, benzene etc. will be sampled and analyzed as well. In Fig. 10, two measurements of total VOC concentrations are compared, the curves being generated by two stationary flame ionizing detectors. Here, the red curve represents the VOCs captured locally from the process zone (exhaust air), whereas the green curve denotes the background signal corresponding to the ambient air at the workplace.

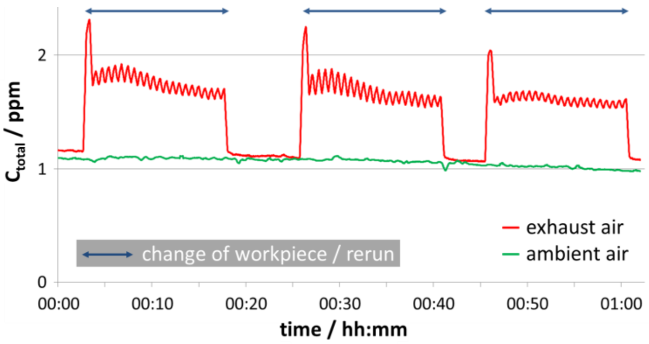

Fig. 10. Comparison of the concentrations of total hydrocarbons at the workplace (green curve) with the exhaust air (red curve) during laser ablation of CFRP epoxy using a pulsed solid-state laser.

Fig. 10 is showing a typical curve progression for the VOC concentration during ablation of CFRP using a short-pulsed laser. The concentration of total hydrocarbons measured in the air of the workplace is significantly lower than the concentration in the exhaust air and not influenced by the laser process at all. This means that the capturing is sufficient respectively excellent.

6. Database development to structure the results of the various emission analyses

Based on standards defined for the measurement datasets, the collected information shall be stored in a database to enable easy comparison of different processes. As a first step, typical database management systems (DBMSs) have been evaluated. Among other things, the main tasks of a DBMS are to store data consistently, efficiently and durable as well as to provide the data for users in the desired way. The expected main usage scenario of the database is to perform queries for statistical analyses or other kinds of reports.

The tabular structure of the specifically standardized datasets is reflected excellently by the structure of relational databases. Moreover, relational databases provide a profound scientific standardization as well as the performance required for the envisaged application, and they are widely distributed even on desktop computers. Typically, the structured query language SQL is used to communicate with relational databases. This language can be used to define and change the structure of a relational database, which includes the definition of tables and relationships between them. Using SQL, data can be transferred to the database. Furthermore, data can be updated, deleted or requested by formulating appropriate selection criteria.

With respect to the planned task, the DBMS software programs Libre Office 4.1/Base, MS Access 2010, PostgreSQL and Sqlite were tested. Because of its properties and the implemented features, the server based PostgreSQL has shown to be advantageous for the database development process.

Starting point of the database development is an analysis of the application domain and the selection of the data to be stored. Especially to preserve the consistency of the database, it is mandatory to define which of the test results have to be stored as raw data. During the analysis carried out, the data structure was normalized. So far, the analysis was restricted to a subset of the application domain. However, a flexible database scheme has been aspired, which can easily by extended by additional data structures.

The basic concept of the database scheme is a separation into data describing test results and data describing test parameters. Whereas the test results are associated to an individual test entity, test parameters are associated to a test series entity, because they can be identical for a number of tests. Both, test and series entities are identified by individual unique identification numbers (IDs). Since the IDs are defined as primary key attributes in the table definitions, the DBMS will automatically preserve their uniqueness. By using a foreign key attribute, a test is associated to a test series. Specific experimental test results such as particle emission data are stored in tables designed correspondingly.

The unified modeling language (UML) provides a standardized graphical notation which allows for clear visualization of the relationships between the tables stored in a database. Specific stereotypes, which were defined during the modeling phase of the database, indicate key relationships. Tables are modelled as classes while the relationships between the tables are represented by unidirectional aggregations (arrows) and the foreign keys name. To create the models, a graphical editor was used. The editor enables saving of the created model in a file format which can be read by a converter script. The converter script transforms the model data into SQL source code for the tested DBMSs Access, Base and PostgreSQL. By executing the generated SQL code, the DBMSs automatically create the tables and their relationships.

7. Summary and outlook

This work provides an overview of investigations and analyses to be performed in order to generate comprehensive data concerning the release of particulate and gaseous hazardous substances during laser processing of CFRP materials. In this context, several consecutive steps have been discussed.

The 1st step is the emission prognosis to determine key components which are expected as important parts of the exhaust gas mixture released during laser processing. The prognosis is based on the laser pyrolysis of small material pieces and the subsequent GC-MS analysis of the generated organic gas mixture.

The 2nd step is the quantitative emission characterization of the process exhaust air which has to be performed during the considered laser processes using optimized parameters, as amount and composition of the emitted material are strongly dependent on the specific process conditions. Important parts of this procedure are the gravimetric measurement of released aerosols deposited on specific filter elements and the determination of particle size distributions using a cascade impactor, taking into account isokinetic sampling conditions. Furthermore, volatile organic components are measured using a flame ionization detector. Spectrometric methods allow for the detection of carbon monoxide and nitric oxides, and specific gold-coated filter foils are used to collect fibrous particles to be analyzed by means of scanning electron microscopy. Different organic substances are enriched by means of specific sampling tubes, which are analyzed offline. To perform emission characterization investigations, a stationary measurement setup has been installed in the LZH facilities, enabling the analysis of contaminated air captured at three different local or global sampling positions in the laser cabin and additionally of the cleaned exhaust air behind the filter system, enabling the assessment of the filter efficiency. An adequate mobile measurement setup is also available, enabling emission characterization for laser processes performed on-site in industry.

The 3rd step is the analysis of the air at the workplace, which may contain hazardous substances causing risks for the employees. This analysis, performed to assess the occupational exposure, is dependent on the specific conditions in the industrial laser processing facilities. The concentration of hazardous substances can be minimized by an optimal arrangement of the components to capture the emitted substances, combined with the proper dimensioning of the exhaust systems. The measurements of the air at the workplace are performed as stationary measurements near the laser processing machine as well as personal measurements, where the machine operator wears specific sampling instruments during a complete shift.

The exemplary results discussed in the previous chapters show that the emissions generated during laser material processing of CFRP is relevant with respect to occupational safety and environmental pollution control. As far as German rules are relevant, limit threshold values according to TRGS 900 and TRGS 910 (considering occupational safety) as well as TA Luft (considering environmental pollution control) have to be met. However, the available information concerning emissions released during CFRP laser processing is limited. Thus, it is planned to collect data of many different CFRP and additionally GRFP laser processes, which are developed in the course of the BMBF funding initiative “Photonic Processes and Tools for Resource-Efficient Lightweight Construction”. To collect and structure the gained information, a specific database is developed. Based on the evaluation of the comprehensive data, a catalogue of measures to realize CFRP laser processes which provide optimal occupational safety and environmental protection shall be derived, taking into account the capturing and exhaust systems, specifically adapted to the processing conditions, as well as the air flow conditions at the workplace influenced by the fresh air supply. Furthermore, recommendations concerning personal respiratory protective equipment shall be given if necessary. An important goal of the investigations is the discussion of the results and the derived catalogue of measure with official institutions such as the German Federal Institute for Occupational Safety and Health (BAuA) and the German Social Accident Insurance (DGUV). This way, it is intended to initiate the implementation of the investigation results into standardization processes or further research e.g. concerning the toxicological effects of CFRP and GFRP laser process emissions.

Acknowledgements

Important parts of the work described here have been performed in the course of the cooperative research project “HoLQueSt 3D” (3D high-power laser processing for quality and throughput increase for the reliable, automated manufacturing of CFRP light-weight structures – subproject: development of processes for CFRP processing using a fiber-guided ns high-power laser). This project (ref. no. 13N12763) is funded by the German Federal Ministry of Science and Education (BMBF) in the course of the initiative “Photonic Processes and Tools for Resource-Efficient Lightweight Construction”, which is gratefully acknowledged.

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