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Optimization of product characteristics of porous carbon agglomerates using a design of experiments in fluidized bed agglomeration

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ABSTRACT

Spraying parameters during particle agglomeration processes can affect the agglomeration kinetics and particle growth. This study was conducted to better understand the influence of the spraying parameters in a fluidized bed wet agglomeration process, and the influence on the stability characteristics of carbon tablets. A formulation based on fine carbon and peroxide powder, as well as carboxymethyl cellulose as a binder, was used to produce agglomerates in a first production step. Thereafter in a second production step carbon tablets with a high porosity were molded for the customer goods industry. The optimization of the compressive strength of these carbon tablets was the goal of the trials. Carbon agglomerates were produced with a laboratory scale granulator called "ProCell" and were compressed with a five-cavity mechanical press. The screening of the agglomeration process parameters and their influence on the agglomerates quality, as well as the performance characteristics of the carbon tablets, were investigated using a multilevel factorial design. The experimental runs were done by varying atomized air pressure and feed rate of the fluid. This was determined by the design model. The findings of the statistical trials showed that low atomized air pressure and a low feed rate lead to a higher tablet compressive strength.
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1. Introduction

Significant effort has been invested in different industries to investigate the influence of process parameters on the quality of granules, as well as their interaction with the objective to find optimum process conditions (Davies & Gloor, 1971; Diez et al., 2019; Hartung, Johansson, Knoell, Valthorsson, & Langguth, 2012; Herdling & Lochmann, 2010; Merkku, Lindqvist, Leivisk, and Yliruusi, 1994; Neugebauer et al., 2017a; Rambali et al., 2001). Investigations into critical process parameters for granulation and agglomeration processes have been performed in the past (Diez, Meyer, Bück, Tsotsas, and Heinrich, 2018; Gyulai, Kovács, Sovány, Csóka, & Aigner, 2018; Han, Shin, & Choi, 2019; Himankar, Athappan, and Zhao, 2016; Neugebauer et al., 2017b; Peglow, Kumar, Hampel, Tsotsas, and Heinrich, 2007). These critical process parameters have to be understood and controlled for all granulation and agglomeration processes in order to produce a consistent-quality product. Therefore, to understand the effect of the critical process parameters is essential to make sure that the quality of the granules is consistent over a period of time. The current investigation aims to produce agglomerates in a fluidized bed with a low bulk density and high porosity. This creates a new carbon-based formulation, which lends itself to a subsequent tableting step and compelling consistency over time. Therefore, setting limits to critical process parameters to influence particle growth, as well as to improve the flowability of granules is essential. This also includes the interaction between the particles and the binder system (Lipsanen, Antikainen, Räikkönen, Airaksinen, and Yliruusi, 2007; Naelapää et al., 2009; Schaefer & Worts, 1978; Tardos, Khan, & Mort, 1997; Terrazas-Velarde, Peglow, & Tsotsas, 2011).

In this study, porous carbon agglomerates were produced using the fluidized bed agglomeration technology. Fine carbon and peroxide powders were chosen for the new formula because of their unique chemical energy properties. Carboxymethyl cellulose (CMC) was used as a binder system during the agglomeration process. After the development and validation, the carbon tablets could possibly be used as an energy source in the customer goods industry. The first objective was to detect what the main influence was on process parameters in the fluidized bed. This was done by

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using a design of experiments (DoEs). It was carried out through a predevelopment fractional factorial design on the following parameters:

- Atomized air pressure.
- Water feed rate.
- Inlet-air temperature.
- Fluidized air flow rate for the agglomeration process.

The outcome of this predevelopment fractional factorial design was that the atomized air pressure and feed rate have a statistically significant impact on the compressive strength of the carbon tablets. This was the main reason for conducting a subsequent multilevel factorial design with these two significant parameters. This is described in this manuscript.

2. Material and methods

2.1. Materials

The formulation of the powder bed consisted of:

- 47.5% fine carbon powder produced by ProFagus GmbH and grinded at Schunk Kohlenstofftechnik GmbH.
- 47.5 % peroxide powder produced by Solvay SA.
- Five percent CMC powder produced by Dupont.

The CMC powder was used as a binder in the fluidized bed agglomeration process. Tap water was sprayed onto the fluidized bed to dissolve the surface area of the CMC particles, which then formed bridges of solidified binder material to agglomerate the primary particles.

In Table 1, the raw materials used for the formulation are described. One can see that the carbon powder is the most coarse one with a d_{90} of 251.0 μm, but the material has the lowest density with 1.40 g/cm^3 and a moisture content of 1.6%. The peroxide powder has a d_{90} of 26.0 μm, which is the finest powder with the highest density of 2.91 g/cm^3 and a moisture content of 1.0%. The CMC powder that was used as a binder has the highest moisture content with 7.0%, due of its hygroscopic properties. The d_{90} of the powder is 114 μm at a density of 1.59 g/cm^3.

2.2. Equipment

All agglomeration runs were conducted using the ProCell laboratory fluidized bed granulator (Glatt, Weimar, Germany). The quantity for each agglomeration run was 10 kg. The granulator was equipped with a GF3 vessel and bottom spray technology with a two-components nozzle (Schlick, Untersiemau, Germany). The nozzle diameter was 1.8 mm. The particle size distribution (PSD) was determined with a Parsum Unit in-line during agglomeration (Parsum, Chemnitz, Germany).

The measurement principle of the Parsum Unit is based on laser techniques, in which an extended spatial filter converts light obscuration signals from individual particles into size information (Dietrich & Petrak, 2017; Schmidt-Lehr, Moritz, and Jürgens, 2007). The Parsum Unit is made out of stainless steel with a sapphire window in the front. The particle size is within the range of 50 μm and 6.000 μm, with velocity measurements between 0.01 and 50 m/s. The advantage of using the unit is that it can be directly inserted into the fluidized bed to determine the PSD in-line. Furthermore, a real-time analysis of the agglomeration process is visible over the entire process by using the Parsum-View software (Dietrich & Petrak, 2017).

2.3. Design of experiments

DoEs or experimental designs are statistical models with a systematic procedure to discover unknown effects under controlled conditions. The main objective of conducting DoEs is to obtain information about the main effect and interaction between processes and output values (Börner, Michaelis, Siegmann, Radeke, and Schmidt, 2016; Davies & Gloor, 1971; Petrak et al., 2011; Tian, Wei, Zhao, Li, & Qu, 2018).

A predevelopment fractional factorial design was used. This included using 4 factors, 17 runs, and 2 replicates to detect the process parameters that are statistically significant on the tablet compressive strength for the given formulation. The following parameters were used for the fluidized bed process to check their impact on the tablet compressive strength:

- Atomized air pressure.
- Water feed rate.
- Inlet-air temperature.
- Fluidized air flow rate.

Agglomeration trials with the given formulation were carried out prior to the fractional factorial design to detect process limits that correlate to the granules' quality. In that case, the flowability of the granules as well as the processability during molding were the main factors. Based on results, a further multilevel factorial design was conducted with the two statistically significant factors. Those being atomized air pressure and water feed rate. As explained, the compressive strength of the carbon tablets is the most important parameter and must be above 6.0 MPa to avoid any cracks or spalling during packaging.

In a further study, a multilevel factorial design has been created:

- Two factors.
- One center point for each factor.
- Three replicates.
- Fifteen runs.

The following were the two factors used in the multilevel factorial design:

- Atomized air pressure.
- Water feed rate.

Table 1
Characteristics of the raw materials.

ID	Quality	Mean particle size distribution			Raw material densities (g/cm^3)	Moisture content (%)
		d_{10} (μm)	d_{50} (μm)	d_{90} (μm)		
Carbon powder	Q018	5.1	56.1	251.0	1.40	1.6
Peroxide powder	Ixper 75C	1.2	6.8	26.0	2.91	1.0
Carboxymethyl cellulose powder	Walocel CRT 2.00 PPA	17.0	47.0	114.0	1.59	7.0

Before conducting the multilevel factorial design, a predevelopment fractional factorial design was created and analyzed. The outcome of the predevelopment fractional factorial design stated atomized air pressure and water feed rate as statistically significant parameters for this investigated formulation. Furthermore, predevelopment trials have shown that a good central point for the atomized air pressure is 1.4 bar and 3.6 g/s for the feed rate. This leads to good, flowable agglomerates. These predevelopment trials included the examination of spraying process limits for the current formulation. This would determine the flowability of the agglomerates and further processability during molding. Atomized air pressure as well as water feed rate have been decreased and increased by 0.3 points in each direction around the central point. It is shown in Table 2. This was done in order to check the impact of the spraying parameters on the agglomerate characteristics.

2.4. Analytical methods

The PSD during agglomeration was determined using the Parsum Unit. The bulk density of the agglomerates was determined using the ERWEKA SMG 697 bulk density tester (ERWEKA GmbH located in Langen, Germany). The bulk density determination was carried out by measuring the mass of agglomerates in a receiver of known dimension and volume (500 mL) after filling from a funnel according to DIN ISO 697. The moisture analysis of the agglomerates took place with a KERN moisture analyzer DBS (KERN & SOHN GmbH, Balingen, Germany). Loss of drying was determined at a temperature of 120 °C; Abort criterion: Constant mass for 30 s within $\leq$5% mass variation. The flowability of agglomerates has been determined with the BEP2 with funnel and timer attachments (Copley Scientific Limited, Nottingham, United Kingdom). The flowability of agglomerates is defined as the relative movement of a particle bulk between a wall surface and neighboring particles. The flow time analysis was carried out in accordance with DIN 53211 (DIN 53211, 1987). The bulk density analysis was carried out in accordance with DIN 52102 (DIN 52102, 2013). The tablet compressive strength was analyzed using an automatic compressive strength–testing machine (Instron, Norwood, USA, testing system 5944L6553). The testing speed of the compression punch was 2 mm/min. The tablet density was measured with the HST software, which is an automatic density tester (Borgwaldt, Hamburg, Germany). The tablet density was measured with a laser-based system, in which the outer diameter, the length, and weight were analyzed. The density of the tablet was then calculated by the HST software through the equation density is equal to the mass divided by the volume. The porosity of the final tablets was determined by high-pressure mercury intrusion according to DIN 66133 (DIN 66133, 1993). Statistical analysis was carried out using the statistical software Minitab (DIN 66133, 1993). A fractional factorial design was conducted to find the statistically significant process parameters for the given formulation on the tabled compressive strength. This DoE included 4 factors, 17 runs, and 2 replicates. A further multilevel factorial design was created including central points as well as lower and upper limits for the spraying parameters. Three replication runs were conducted in order to study the statistical scattering.

2.5. Process parameters and performance

A constant inlet-air temperature of 45 °C was set for each run. The granulator ran fully automated without any influence of the operators, for all runs produced. These, for example, include fluidization air flow rate, inlet-air temperature, and filter-cleaning intervals. The spraying parameters were set according to the DoE test plan. The central points for the DoE spraying parameters were chosen through predevelopment DoE. The description of the variation of the DoE is listed in Table 3. The inlet-air temperature was preheated to 45 °C before agglomeration. After reaching an inlet air temperature of 45 °C, the raw materials were then loaded into the vessel of the granulator. The agglomeration temperature was kept constant at 45 °C based on the results of the predevelopment DoE during agglomeration. The raw materials were blended in the granulator for 10 s. After blending, the spraying began. The total drying time after spraying was around 30 min to reach a target moisture content of the agglomerates of approx. 30.0%. The inlet fluidization air flow rate during agglomeration and drying was kept constant. Increased fluidization air flow rate causes higher particle friction through impact forces. This phenomenon was avoided through a constant fluidization air flow rate for agglomeration and drying. As in-process control parameters, the bulk density, moisture content, PSD, and flow time were considered. These parameters were checked after drying when the agglomeration and drying process was finished. The agglomerates were then filled in a Polyethylene bag (PE bag) and were blended by hand. A sample of approximately one kg was taken out to determine the moisture content, bulk density, and flow time according to the DIN methods described in section 2.4. The PSD was determined in-line. The PSD values for the DoE analysis were manually recorded by on operator just before stopping the process. It was necessary to spray 5000 g of water onto the fluidized particles to reach a moisture content of approximately 30.0%. During the predevelopment trials, 5.0 g samples were taken out of the granulator vessel every 5 min through a sampler to determine the moisture content. Through these tests, the drying time could be precisely

Table 2
Experimental design for fluidized bed agglomeration process.

Std order	Run order	Center Pt	Blocks	Atomized air pressure (bar)	Water feed rate (g/s)
1	1	1	1	1.1	3.3
12	2	1	1	1.7	3.9
11	3	1	1	1.1	3.9
2	4	1	1	1.7	3.3
14	5	0	1	1.4	3.6
5	6	1	1	1.1	3.3
4	7	1	1	1.7	3.9
3	8	1	1	1.1	3.9
9	9	1	1	1.1	3.3
10	10	1	1	1.7	3.3
7	11	1	1	1.1	3.9
6	12	1	1	1.7	3.3
13	13	0	1	1.4	3.6
8	14	1	1	1.7	3.9
15	15	0	1	1.4	3.6

Table 3
Agglomeration process parameters.

Parameter	Unit	Lower level	Upper level
Atomized air pressure	bar	1.1	1.7
Water feed rate	g/s	3.3	3.9
Agglomeration temperature	°C	Constant at 45	
Inlet fluidization air flow rate during spraying	m^3/h	Constant at 125	
Inlet fluidization air flow rate during drying	m^3/h	Constant at 225	

defined to obtain a moisture content between 29.0% and 31.0%. For each run, 23000 tablets were molded and immediately dried in a belt dryer (type TT-3A from Ring Maschinenbau GmbH) at 105 °C/25 min. Every 10 min; 10 carbon tablets were taken as samples from the belt throughout the whole molding process. In terms of the compressive strength determination, 69 tablets were randomly taken and analyzed for each run according to DIN ISO 2859-1 (DIN ISO 2859, 2004).

2.6. Target parameters

In Table 4, the target parameters and variables are shown. From a technical point of view, the process can run well within the lower and upper levels of the DoE.

A second objective was to vary the spraying parameters during the agglomeration process around defined central points. This was done in order to identify the influence of the spraying parameters on the flowability and bulk density of the final agglomerates. The flowability of the carbon agglomerates was important because it affects the final molding process. For the statistical analysis, it was chosen to analyze the d_{50} values, which were determined with a Parsum Unit during agglomeration. The carbon tablets were compressed using 60 strokes per minute in a 5-cavity-matrix single-punch machine. The molding speed and therefore a constant cavity filing was targeted. The carbon tablets were molded into a cylindrical shape with an outer diameter of 7.75 mm and a height of 9.00 mm. In this case, the cavity diameter defined the outer diameter of the carbon tablets. These dimensions lead to a mean tablet density of approximately 0.940 g/cm^3, with a standard deviation of 0.005 g/cm^3. The pressing force of the upper punches was not measurable because of the low density of the tablets. Therefore, the tablets were compressed to a height of 9.00 mm according to the filling height of the cavity.

Furthermore, the compressive strength of the carbon tablets is the most critical final testing parameter as explained before. The tests aim for a compressive strength above 6.0 MPa to make sure that the tablets do not break or crack during further processing as well as in packaging machines.

Table 4
Target parameters of limits for agglomerates and carbon tablets.

Parameter	Unit	Target value	Lower limit	Upper limit
Bulk density	g/cm^3	0.575	0.540	0.610
Moisture content	%	30.0	29.0	31.0
Tablet density	g/cm^3	0.940	0.920	0.960
Tablet compressive strength	MPa	8.0	7.0	9.0

3. Results and discussion

3.1. Predevelopment desigm of experiment

A Pareto chart was created for the predevelopment fractional factorial design to detect the statistically significant parameters. The Pareto chart shows that the spraying parameters, such as atomized air pressure and feed rate, can be considered as those parameters with the biggest influence on the fluidized bed agglomeration process for this formulation. This is shown in Fig. 1

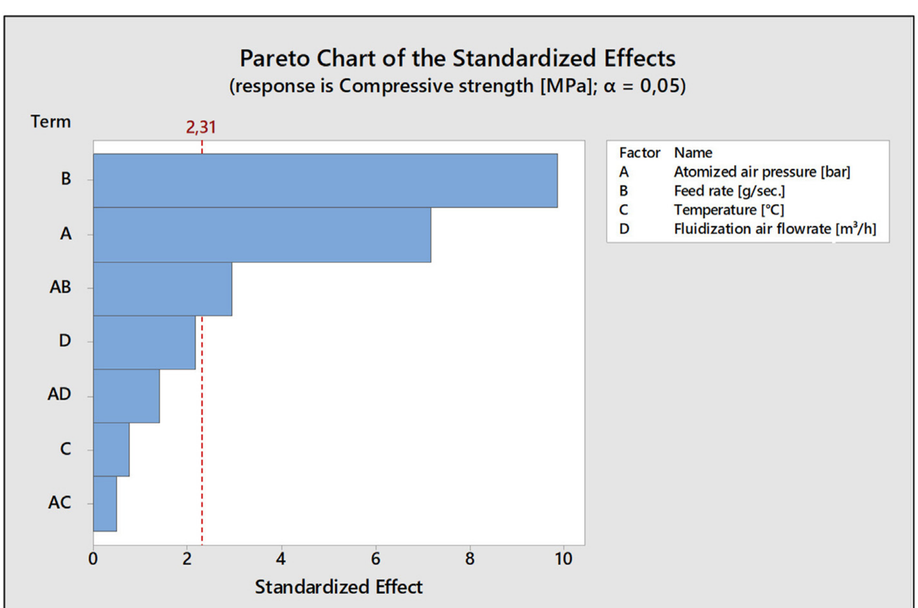

Fig. 1. Pareto chart with compressive strength as the response variable.

in the Pareto chart for the DoE. The inlet air temperature and fluidized air flow rate are not statistically significant parameters for the formulation (Davies & Gloor, 1971; Himankar et al., 2016; Neugebauer et al., 2017a). Pareto charts are used to compare the relative magnitude and the statistical significance of main and interaction effects. The Length's method is used to draw the reference line for statistical significance. The impacts are plotted in a decreasing order of the absolute value of the findings. The red vertical reference line on the chart indicates which effects are statistically significant (Minitab 17 Statistical Software & StatGuide, 2014).

By analyzing the results, it is shown in Fig. 1 that atomized air pressure and feed rate as well as the combination of both are statistically significant at an α-level of 0.05. The α-level of 0.05 was set as a statistical standard that is also a standard in the pharmaceutical industry. This points out which effects are important for the process and which are statistically significant (Minitab 17 Statistical Software & StatGuide, 2014).

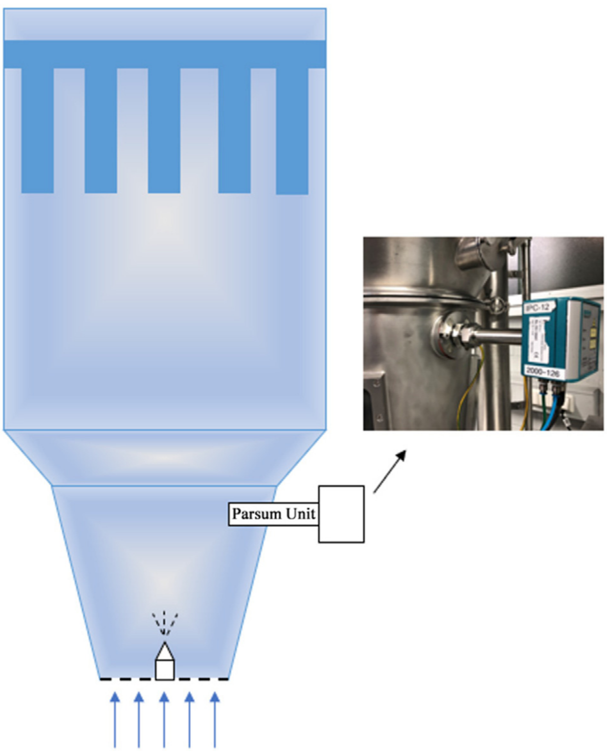

Fig. 2. Position of Parsum Unit in laboratory ProCell granulator for this study including picture.

3.2. Parsum unit

Fig. 2 shows the position of the Parsum Unit in the fluidized bed granulator. The Parsum Unit was fixed in a flange on the upper-right part of the granulator vessel. The distance between the measuring unit and the vessel wall was 50 mm. As shown in Fig. 3, the Parsum Unit determined the PSD, e.g., $d_{10}/d_{50}/d_{90}$ during the agglomeration process including drying.

In Fig. 3, the Parsum PSD of production run number five is shown as an example during the agglomeration process.

3.3. Statistical analysis

The output results of each run are listed in Table 5. The bulk density, moisture content, flow time, and PSD were measured on the agglomerates after agglomeration off-line by an operator. The tablet density and compressive strength were measured on the final product. The PSD values shown in Table 5 represent the PSD of the agglomerates just before stopping the production process.

In the present DoE in Fig. 4, for PSD d_{50} and flow time, there are two significant effects ($\alpha = 0.05$). These include the two main effects, atomized air pressure and feed rate. Furthermore, it is shown that in both cases, the atomized air pressure (A) has the largest effect. This indicates that the atomized air pressure as well as the feed rate directly influences the liquid droplet size and the behavior of the particles during agglomeration. The atomized air pressure in the fluidized bed also affects the tablet density and its pore and volume structure. For the tablet density, it is shown that atomized

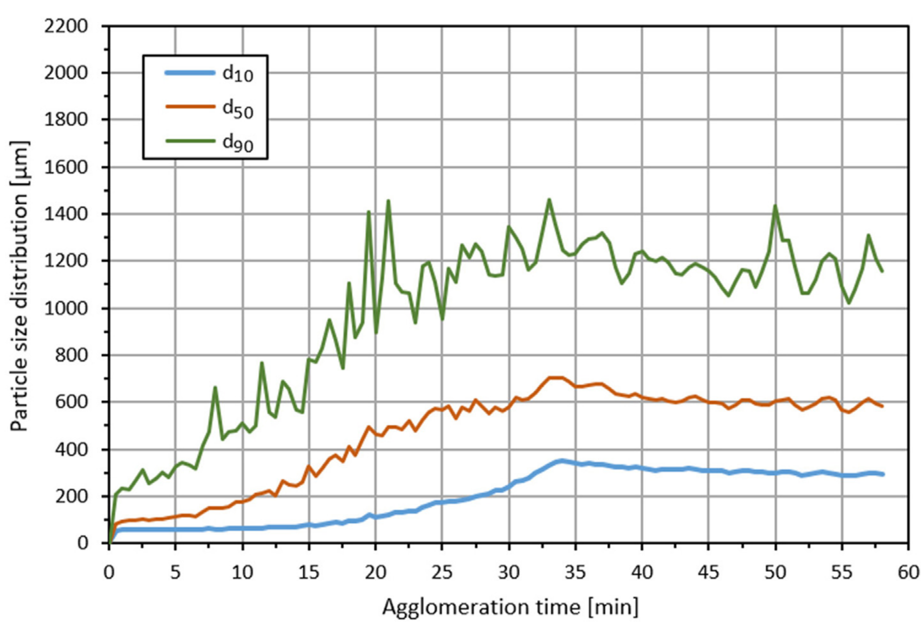

Fig. 3. Example of Parsum PSD during agglomeration process of production run number 5. Abbreviation: PDS = particle size density.

Table 5
Mean output results of the multilevel factorial design.

No.	Atomized air pressure (bar)	Feed rate (g/s)	Tablet density (g/cm^3)	Tablet compressive strength (MPa)	Bulk density (g/cm^3)	Moisture content (%)	Flow time (s)	PSD d_{10} (μm)	PSD d_{50} (μm)	PSD d_{90} (μm)
1	1.1	3.3	0.942	8.5	0.574	30.0	8.45	288	814	1726
2	1.7	3.9	0.944	7.4	0.562	30.9	11.02	375	707	1357
3	1.1	3.9	0.939	8.4	0.585	30.6	8.01	316	890	1519
4	1.7	3.3	0.932	8.4	0.585	30.1	11.57	338	821	2078
5	1.4	3.6	0.941	8.3	0.549	29.9	7.53	292	578	1121
6	1.1	3.3	0.945	8.6	0.591	30.4	8.67	333	868	1502
7	1.7	3.9	0.941	8.2	0.565	30.7	10.91	386	733	1424
8	1.1	3.9	0.947	8.7	0.603	30.3	7.87	311	742	1542
9	1.1	3.3	0.943	8.7	0.594	30.9	8.51	316	890	1519
10	1.7	3.3	0.939	8.8	0.557	29.7	11.23	326	766	1736
11	1.1	3.9	0.943	8.3	0.562	30.4	8.24	272	811	1761
12	1.7	3.3	0.927	8.2	0.563	30.3	11.46	355	783	1749
13	1.4	3.6	0.942	8.5	0.54	30.4	7.32	301	566	1065
14	1.7	3.9	0.938	8.3	0.606	30.2	10.78	384	734	1373
15	1.4	3.6	0.941	8.3	0.559	30.0	7.28	298	582	1092

Abbreviation: PDS = particle size density.

air pressure is the significant effect. Due to the fact that the atomized air pressure defines the pore and volume structure during agglomeration, a moisture content of the agglomerates between 29.0% and 31.0% was reached for each production run. After molding and drying of the tablets, the evaporation of water through the heat treatment process gave the tablets their defined pore and volume structure.

A further indication of how well the model fits the data is the calculation of S, R^2, and adjusted R^2 (R^2 adj). S represents the standard distance that data values fall from the regression line and is measured in the units of the response variable. The values represent a coefficient of variation. Another important parameter is the R^2 value, which describes the amount of variation in the observed response values that is explained by the predictors. When comparing models of the same size, R^2 is a useful parameter. The adjusted R^2 is a modified R^2 that has been adjusted for the number of terms in the model. It is used to compare models with different numbers of predictors (Minitab 17 Statistical Software & StatGuide, 2014). These values help to select the model with the best fit. In Table 6, the R^2 values are listed. It shows that the model explains the value of 99.4% for the flow time and the value of 95.0% for the PSD d_{50} of the variation in the data for the R^2 values. Furthermore,

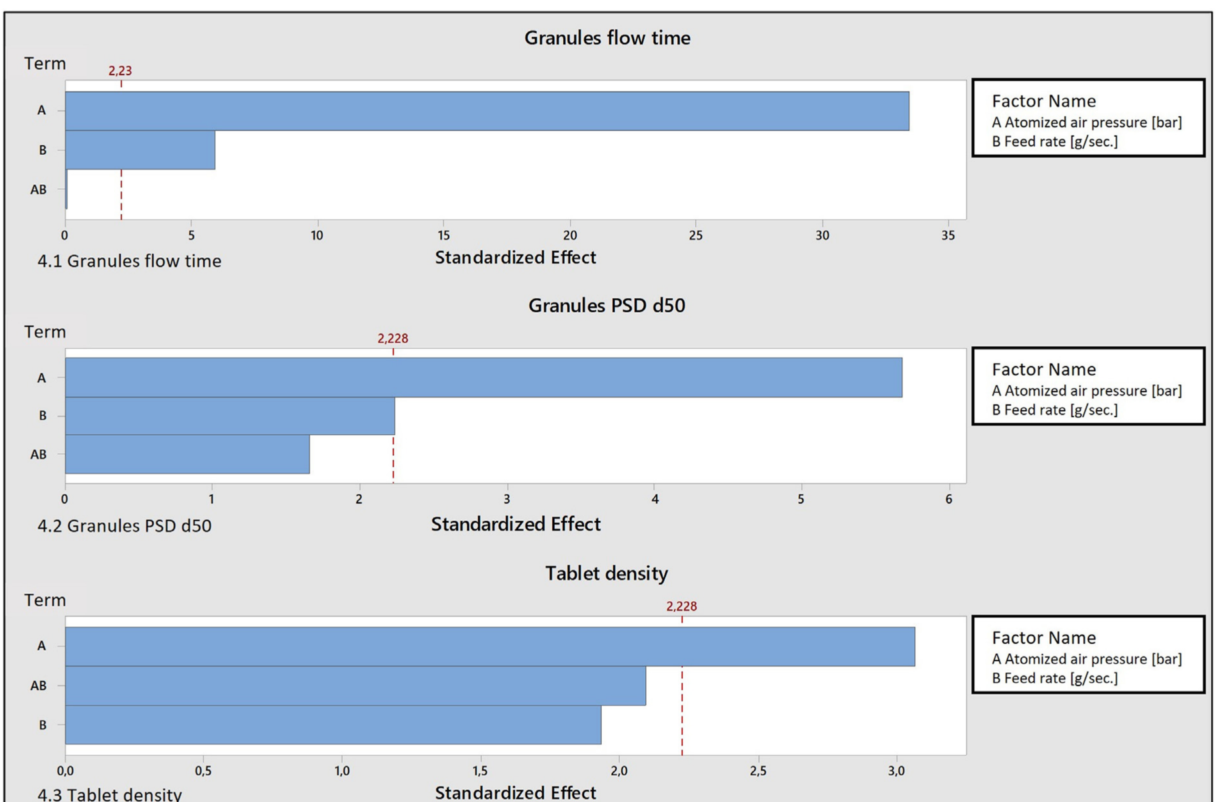

Fig. 4. Pareto charts of standardized effects of atomized air pressure and feed rate on response variables of granules and compressed cylinders (i.e., 4.1: granules' flow time, 4.2: granules' PSD d50, and 4.3: tablet density). Abbreviation: PDS = particle size density.

Table 6
DoE model summary.

Parameter	S	R^2	R^2 (adj)
Granules bulk density (g/cm^3)	0.0170	47.9%	27.0%
Granules moisture content (%)	0.3225	40.4%	16.5%
Granules flow time (s)	0.1486	99.4%	99.2%
Granules PSD d_{50} (μm)	29.0184	95.0%	93.0%
Tablet density (g/cm^3)	0.0036	64.1%	49.8%
Tablet compressive strength (MPa)	0.2840	46.6%	25.2%

Abbreviations: DoE = design of experiment; PDS = particle size density.

the model explains the value of 47.9% for the granules' bulk density and the value of 40.4% for the moisture content. The R^2 value for the tablet density is 64.1% and 46.6% for the compressive strength. To verify the results of the compressive strength, the decision was made to conduct three more runs with the promising spaying parameters, which refers to an atomized air pressure of 1.1 bar and a water feed rate of 3.3 g/s.

In the main effects plot, the fitted means for each value of a variable in the model is plotted. The lines provide information as to whether a main effect is present for a variable. The greater the angle of the vertical position, the greater is the main effect (Minitab 17 Statistical Software & StatGuide, 2014). In Fig. 5, it is shown that the flow time of the granules is mainly affected by the atomized air pressure. Furthermore, atomized air pressures in the range of 1.1–1.4 bar lead to lower flow times between 7.4 and 8.5 s. At this point, it seems that the agglomerates show a greater flowability behavior when the PSD d_{50} is just below 600 μm. It is shown in Table 5 for the different runs. This leads to the lowest flow time of a mean flowability of approximately 7.4 s. In this case, it seems that the growth rate of the granules during agglomeration declines because of an insufficient re-wetting of the agglomerates. This also indicates the previous analysis of the Pareto chart of the granules' flow time. This parameter shows the significance of the 0.05 a-level. A further interesting observation is that an atomized air pressure of 1.1 bar and a water feed rate of 3.3 g/s have a positive influence on the compressive strength of the carbon tablets. This result is shown in the main effect plot for the tablet compressive strength. In Fig. 5, it is also clear the higher the tablet density is, with values above 0.942 g/cm^3 lead to a higher tablet compressive strength with values above 8.5 MPa. This can be reached with an atomized air pressure of 1.1 bar and a water feed rate of 3.3 g/s. At this point it seems that higher tablet density values lead to a lower porosity of the tablets which results in a higher tablet compressive strength.

The interaction plots are used to assess two-way interactions. The greater the angle of the lines, the greater the strength of the interaction. Parallel lines indicate that there is no interaction (Minitab 17 Statistical Software & StatGuide, 2014). In Fig. 6, the interaction plots are shown. In the case of the granules' bulk

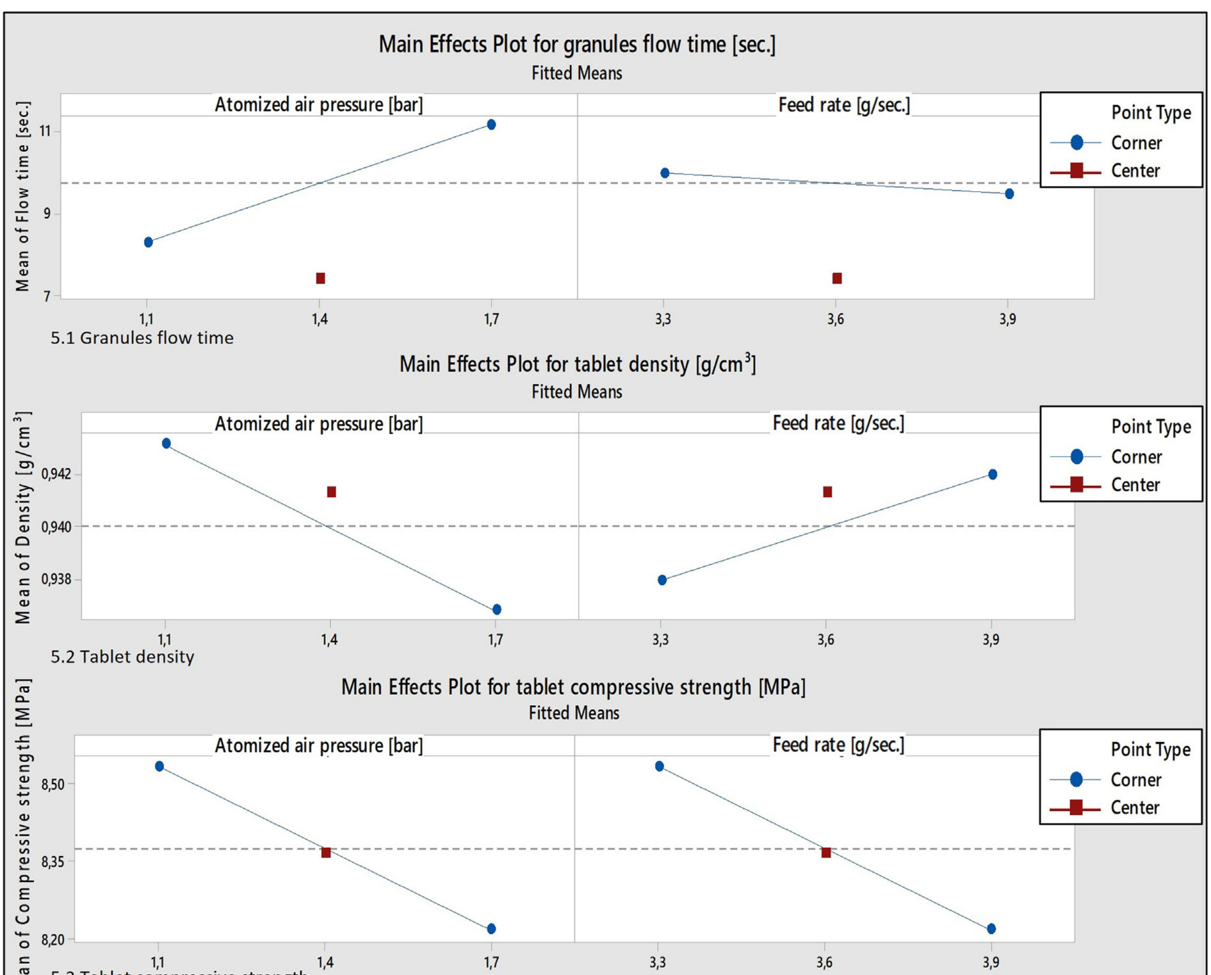

Fig. 5. Main effects plots (i.e., 5.1: granules' flow time, 5.2: tablet density, and 5.3: tablet compressive strength).

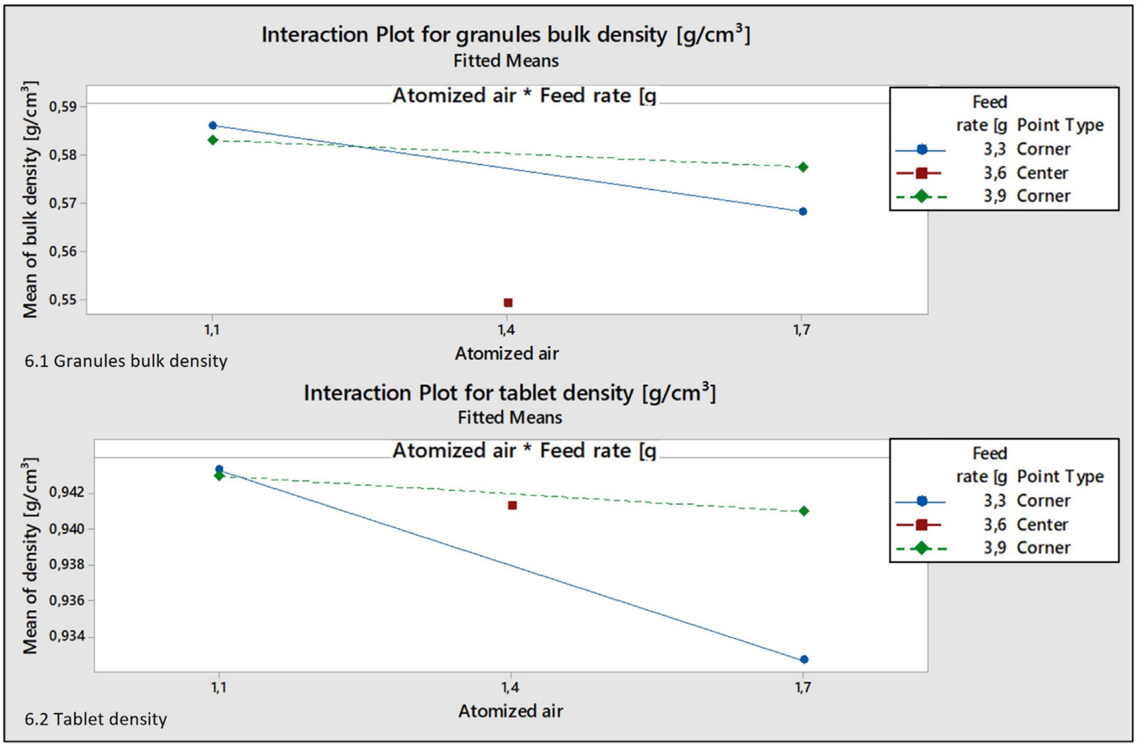

Fig. 6. Interaction plots (i.e., 6.1: granules' bulk density and 6.2: tablet density).

density, it can be observed that there is an interaction between the atomized air pressure and the water feed rate. An atomized air pressure of 1.1 bar, in combination with a water feed rate of 3.3 g/s, leads to higher bulk densities. Another interesting outcome reflects that tablet density is affected by the interaction between lower atomized air pressure and feed rates. This indicates that larger droplet sizes lead to a more compact structure of the agglomerates. This again leads to higher tablet densities and therefore slightly higher tablet compressive strength values because of a lower porosity.

Contour plots are used to explore the relationship between three variables on a single plot (Minitab 17 Statistical Software & StatGuide, 2014). In Fig. 7, it is shown that higher bulk densities are reached at lower atomized air pressures and water feed rates. In terms of the d_{50} values of the PSD, it is visible that the lowest values were produced with an atomized air pressure and feed rate around the center points. By analyzing the contour plot of the flow time, it is clearly visible that the lowest flow times below 8.0 s are shown around the center points of the atomized air pressure and feed rate. This is a clear indication that the flowability of the agglomerates performs best at around 1.4 bar and 3.6 g/s. Another interesting observation is that d_{50} values of the PSD are below 600 μm around the center points. Good flowability of the agglomerates and processability as well as high tablet compressive strength values were desired. The contour plot of the tablet compressive strength shows the relationship between the atomized air pressure and the feed rate. It is shown that lower atomized air pressures below 1.3 bar and water feed rates below 3.5 g/s lead to higher strength values. Lower atomized air pressures and water feed rates lead to a larger droplet size during spraying. The larger droplet sizes affect the agglomeration behavior in more compact agglomerates and therefore higher compressive strength values. Lower water feed rates and atomized air pressures lead to higher bulk densities and higher PSDs. That is a clear indication that lower water feed rate and atomized air pressure lead to more compact agglomerates and therefore higher bulk densities and larger agglomerates.

In Fig. 8, the single values of each run of the DoE of the tablet compressive strength and the tablet porosity are displayed. It is visible that the tablets with higher compressive strength values have a lower porosity. Furthermore, the spearman rank correlation coefficient between the tablet compressive strength and the tablet porosity were calculated to check correlation between the two variables. A spearman rho of −0.946 was analyzed, which indicates a very strong correlation between the variables. A higher porosity leads to a larger pore and volume structure, which is equatable to a more fragile tablet structure because of more predetermined breaking points.

3.4. Response optimizer

Response optimization can be a useful tool in product development. The aim of the response optimizer is to determine the operating conditions that will result in a product with desirable properties. It can help to identify the variable settings that optimize a single response or a set of responses (Minitab 17 Statistical Software & StatGuide, 2014).

In Fig. 9, an optimization plot is shown. The two columns of the graph show the variables. In the first row, the global desirability is displayed and in the remaining rows, the response variable(s). The numbers in red at the top of the column show the current variable settings. Furthermore, in each cell, it is shown how the response variables change as a function of one of the factors, while the other factors still remain fixed. In blue, the predicted response variables are displayed at the fixed variable settings as well as the desirability score. The three points in each cell represent the categorical variables. It is shown that decreasing the atomized air pressure and water feed rate increases the compressive strength of the carbon tablets. This behavior was also shown in previous graphs, e.g., main effects plots.

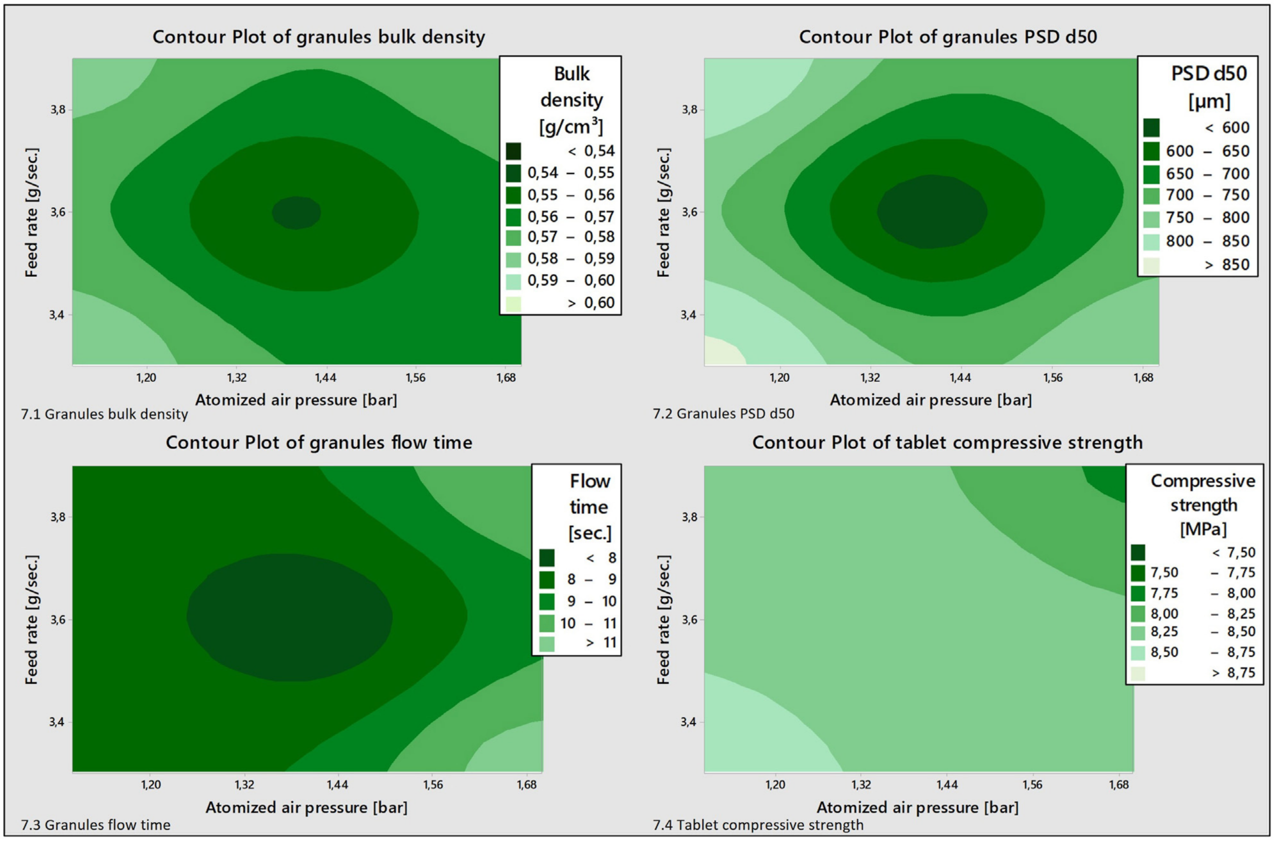

Fig. 7. Contour plots (i.e., 7.1: granules' bulk density, 7.2: granules' PSD d50, 7.3: granules flow time, and 7.4: tablet compressive strength). Abbreviation: PDS = particle size density.

As an important quality parameter of the carbon tablets, the single optimization plot for the compressive strength has been created. The goal was to maximize the compressive strength of the carbon tablets with the two variables atomized air pressure and water feed rate. The mathematic model calculated a compressive strength with a mean of around 8.6 MPa by choosing an atomized

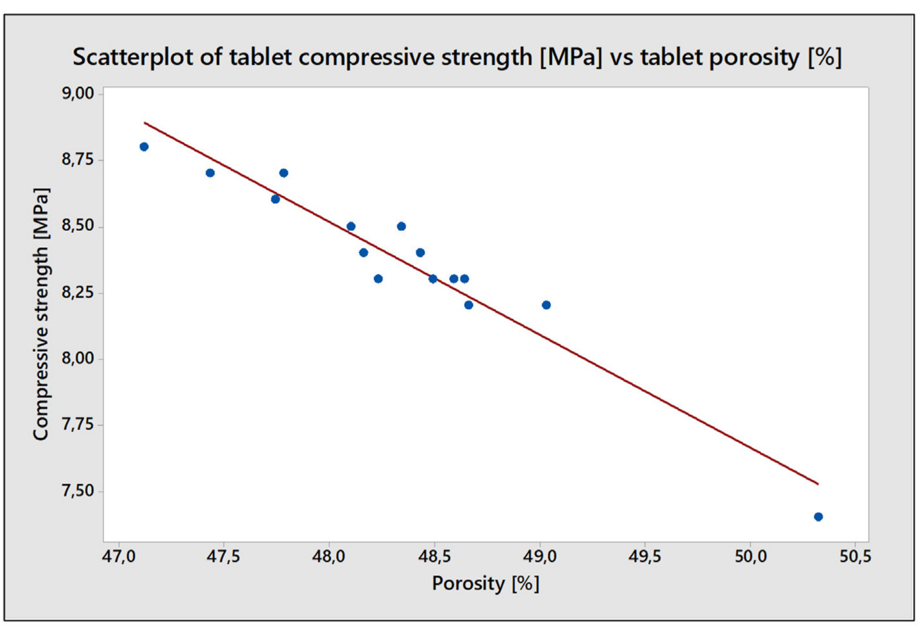

Fig. 8. Correlation between tablet compressive strength and porosity.

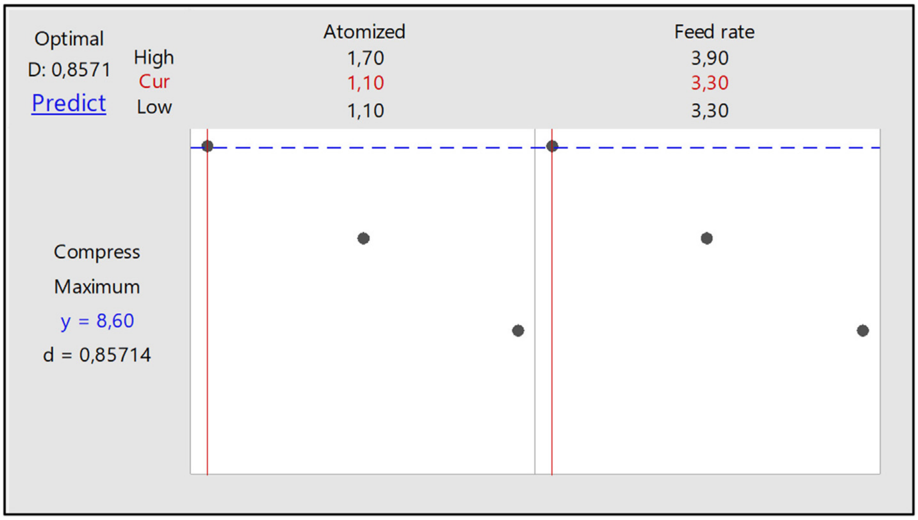

Fig. 9. Optimization plot for compressive strength.

air pressure of 1.1 bar and a water feed rate of 3.3 g/s. Three more testing runs were produced with spraying parameters to verify a compressive strength of around 8.6 MPa.

In Fig. 10, the boxplots of the summarized reference runs as well as the three reproduced testing runs are shown. Table 6 shows the descriptive statistics of the reference runs and the reproduced testing runs.

To sum up, it could be demonstrated and verified through the production of three more separate testing runs that a compressive strength of the carbon tablets around 8.6 MPa can be reached by setting the atomized air pressure at 1.1 bar and the feed rate at 3.3 g/s. For the tablet compressive strength analysis, 90 tablets in total of the three further runs have been analyzed. As discussed in this study, a tablet compressive strength of above 6.0 MPa was targeted. A further production and verification of three more test runs with the spraying parameters recommended out of the optimization plot could demonstrate that a tablet compressive strength of approximately 8.5 MPa can be reached. At this point, there is no need for further improvement of the tablet compressive strength. In Fig. 9, the boxplots of the tablet compressive strength values of the reference runs of the DoE and three further test runs are shown. The boxplot shows the spread and skewness of the data as well as their quartiles. It is visible that 50% of the values spread around 8.3 MPa and 8.8 MPa. However, there are even low compressive strength values of 7.3–7.5 MPa that could have a slightly lower tablet density and porosity. Table 7 shows the mean values as well as the standard deviation. This gives an indication that >68% of the values were analyzed between 8.1 and 9.1 MPa, which shows again the validity of the analysis. In Table 8, the *P*-value of 0.426 at a significance level of 0.05 ($F(1,178) = 0.64$, $p > 0.05$) is shown. In that case, the one-way analysis of variance is the desired statistical method to investigate statistical differences (Naelapää et al., 2009).

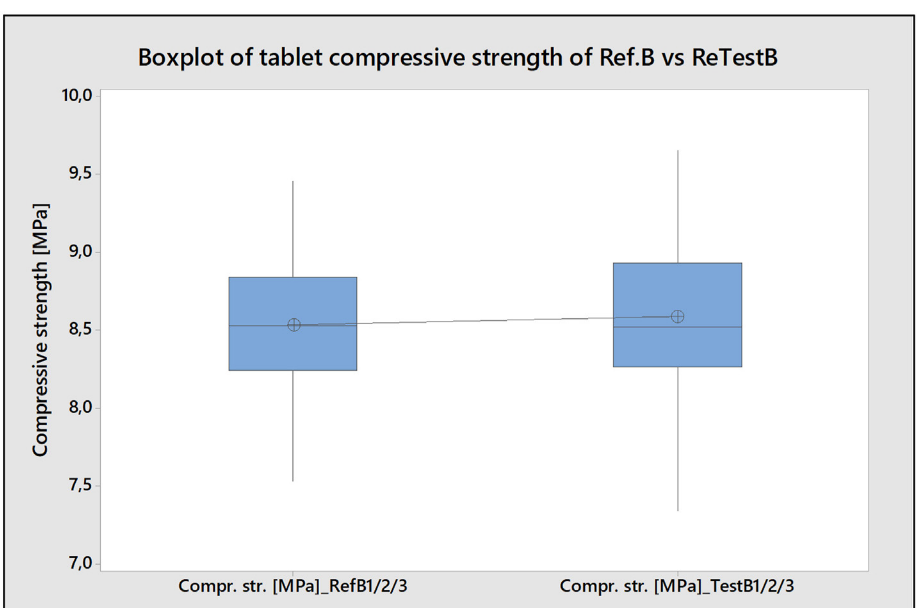

Fig. 10. Boxplot for compressive strength.

Table 7
Descriptive statistics: Compressive strength of Ref.B1/2/3 and TestB1/2/3.

Variable	Mean compressive strength (MPa)	Sta Dev compressive strength (MPa)	Minimum compressive strength (MPa)	Maximum compressive strength (MPa)
Compressive strength (MPa) Ref.B1/2/3	8.5	0.432	7.5	9.5
Compressive strength (MPa) TestB1/2/3	8.6	0.458	7.3	9.7

Table 8
One-way ANOVA of tablet compressive strength data.

Method Analysis of Variance Significance level: $\alpha = 0.05$	F-Value	P-Value
Ref.B1/2/3 vs. TestB1/2/3	0.640	0.426

Abbreviation: ANOVA = analysis of variance.

4. Conclusions

The aim of this study was to investigate the influence of process parameters on the carbon agglomerates as intermediates and the compressive strength of carbon tablets. This is in order to achieve a consistent process and a high-quality end product. The critical process parameters have been identified through the spraying parameters during agglomeration by conducting a pre-development fractional factorial design. The critical process parameters for the formulation used in this study were identified as atomized air pressure and water feed rate. A further scope of this study was to obtain information about the particle size growth during the fluidized bed agglomeration process. The Parsum Unit was used to measure the particle size in real-time during the entire process. It could be seen that with the spraying parameters, the flowability of the agglomerates can be affected. A very good flowability has been reached around the center points of the conducted multilevel factorial design. On the one hand, it is important to optimize the flowability of the agglomerates and on the other hand, to make sure a consistent cavity-filling during molding is achieved. After identifying and mechanically understanding the interaction of the critical process parameters, the main purpose was then to find optimal process parameters to locate a process window that ensures an optimal flowability of the carbon agglomerates. It was also important to make sure that the integrity of the final carbon tablets fulfill the given interim requirements. The atomized air pressure and feed rate clearly affect agglomerate particle attributes. Another outcome of the main effects plot was that the lower atomized air pressures and the lower feed rates lead to a higher granules' bulk density and tablet density. Therefore, it could be shown that larger droplet sizes lead to a more compact structure of the agglomerates. This in turn leads to higher tablet densities and thus to higher compressive strength values of the tablets. Furthermore, it could be demonstrated that lower porosities lead to higher tablet compressive strength values. Tablet compressive strength values around 8.5 MPa were achieved as a main result of the trials. For several process parameters, it could be shown that interactions take place, but the defined end product qualities were ultimately achieved. An increased water feed rate leads to higher moisture contents because of an increase of the agglomeration liquid supply. Through the spraying parameters and the agglomeration liquid supply, moisture contents around 30.0% were reached with tablet porosity values between 47.0% and 50.5%. It is therefore demonstrated that porous carbon agglomerates were produced with the used formulation. The outcome of the study was to understand the interactions of the critical process parameters. The interaction between the atomized air pressure and water feed rate helps to understand the process and to produce high-quality carbon tablets.

Declaration of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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