

CENOSPHERIC AND SAND FLUIDIZED BED AS AN ENVIRONMENT FOR WASTE RUBBER COMBUSTION-COMPARISONS OF DECOMPOSITION DYNAMICS AND FLUE GAS EMISSION

by

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The results of thermal recycling of rubber in the fluidized bed are presented. Two different types of the bed material were used: sand and low density spheres (cenospheres). For two bed types, rubber decomposition time, as the mass and the bed temperature functions, were determined. Time of the samples residence time was calculated with the assumption, that reactor and the analytical block may be described with the well-stirred model. Time of samples decomposition, decrease with increasing temperature, as expected. It was also established, there are significant deviations between shirking core model, and obtained results of the residence time as a mass function. Cenospheric bed application allows to reduce of the process pressure drop, and caused shift of the gas decomposition products zone to the deeper region of the bed. Acoustic and optical effects confirmed significant differences between combustion of sand and cenospheric bed. Higher frequency of bubbles explosions and reduction of diffusive flames number were observed during incineration in cenospheric bed. The relationship between exhaust emission (VOC, CO, NO_x) and type of the bed was not confirmed, the identical situation is observed for the samples combustion time. In the presented manuscript, the above physical quantity depends almost completely on sample type and bed temperature.

Key words: fluidization, rubber waste, combustion, cenospheres

Introduction

Fluidized bed incinerators are characterised by high flexibility, i. e. the possibility of burning fuels in all physical states [1-7], homogeneous thermal conditions and proper mixing of the fuel-oxidant system. They are used to burn fuels such as coal [8-10], biomass [11, 12] and to dispose of solid waste. Electronic waste [13, 14] polymers [15, 16], low calorific and water-containing waste such as wet sewage sludge [17], and rubber waste [18, 19], can be mentioned from the full range of waste types. The fluidized bed combustion of rubber waste is increasingly used commercially, and the world leader is Japan, in which between 2005 and 2010 nine installations were launched [19]. Solid fuel dispensing into a fluidized bed reactor

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requires its appropriate fragmentation. Large-scale implementation of the combustion process of this type of materials requires knowledge of the behaviour of fuel particles in the reaction environment. The first stage after introducing the solid material into the hot fluidized bed is water evaporation. As the particle temperature increases, there are two parallel processes: the pyrolysis and gaseous products oxidation. The last stage of solid fuel combustion is char afterburning. When investigating the kinetics of a solid particle burning, the diffusion of the oxidant inside the particle, the diffusion of pyrolysis products on the outside of the particle, the surface of mass and heat exchange, active catalyst centres on its surface, and the temperature gradient inside the particle, should be taken into account. The mechanism controlling solid particle combustion changes with the process temperature [10]. From the modelling point of view, the residence time of the incinerated sample is one of the most important factors. This time has to be obtained from the chemical analysis of gas products. The analytical results are influenced by factors like the inertia of the analytical system (that use various analytical method), and the gas path. In order to remove these inertias the deconvolution operation was done [16].

The conducted research aimed to compare: the time of the rubber sample's incineration, the composition of flue gases, optical and acoustic effects caused by the exploding bubbles. This research was done in two types of fluidized bed with a significant difference in density. These tests allow evaluating the possibilities of conducting the combustion processes in the fluidized bed by using low-density cenospheric bed [20].

Experimental equipment

The tests were carried out in a fluidized bed reactor made of a quartz tube with an internal diameter of 98 mm and a height of 500 mm, positioned on the distributor made of chromium-nickel steel, with holes with a diameter of 0.6 mm which were arranged on a grid plan with a side of 4 mm. The reactor was heated using an electric heating mantle. Above the reactor there was a microphone through which the acoustic signals accompanying the combustion were recorded. The acoustic signals with the frequency below 100 Hz (disturbances, *e. g.* noise of the bed) were filtered out, from the soundtrack of the recording. Above the microphone, a video camcorder was placed. The scheme of the reactor and other devices is shown in fig. 1. The exhaust gas analysis was carried out by the FTIR Gasmet™ DX-4000 analyser, performing one measurement every 8 seconds. The temperature measurement was carried out with the use of two Ni-NiCr thermocouples placed 20 and 50 mm above the perforated bottom. Thermogravimetric analyses were performed in an air atmosphere at a constant rate of temperature changes of 20 K/min with the Exstar TG / DTA 7300.

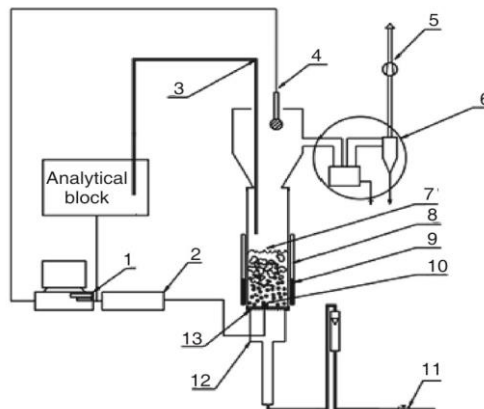
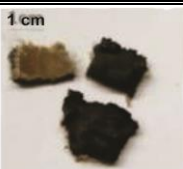
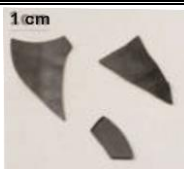


Figure 1. Experimental arrangement;
1 – computer storing chemical analyses quantities, sound and temperature signals, 2 – A/D converter for thermocouple signals, 3 – heated probe for sampling the flue gases, 4 – microphone (alternatively camera), 5 – exhaust fan, 6 – cyclone, and ash trap for coarser particles, 7 – freeboard space, 8 – movable radiation shield, 9 – heating mantle, 10 – thermocouples, 11 – air supply valve, 12 – plenum chambers, 13 – distributor

Materials

The sand bed with particles sizes between 355-400 μm (B in Geldarts class) [21] and cenospheres with the same granulation (A and B in Geldarts class) were used during the experiments. The volumetric air flow was $\sim 830 \text{ cm}^3/\text{s}$. The resting beds volume was 338 cm^3 , and the beds' masses were 111 and 500 g (for the cenospheres and the sand, respectively). Two types of rubber were used during the experiments: soft rubber (from bicycle inner tube), and strong rubber (rubber including synthetic fibers), of masses in the range of 100-500 mg. Table 1 shows the types of rubber and gives their C, H, and N contents, determined using a Perkin Elmer 2400 instrument, by the combustion method, using an IR detector.

Table 1. Pictures of the samples and the CHN analysis results

	Strong rubber, % _{mass}			Soft rubber, % _{mass}	
	C	64.5		C	85.40
	H	6.30		H	9.28
	N	0.31		N	0.08

Results and discussion

Rubber polymers differ in their degree of cross-linking, depending on the application. The crosslinking degree affects the material thermal properties and the decomposition course at elevated temperature.

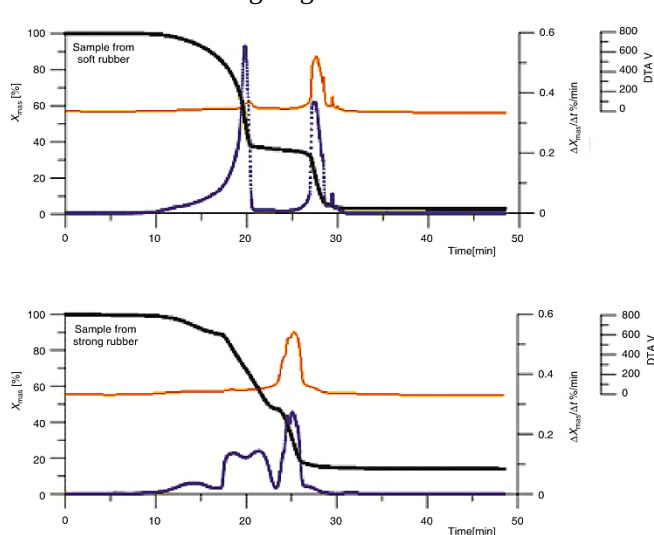


Figure 2. Thermogravimetric analysis

Figure 2 presents the results of thermogravimetric analysis of hard and soft rubber samples made in an air atmosphere. In each case, a two-stage course of the sample decomposition was observed. The first stage of decomposition began at approximately 200 °C. The highest decomposition rate in the first stage was observed for soft rubber samples at 380-390 °C. In the dynamics of both examined samples decomposition, a definite process slowdown was observed, that preceding the second stage of the decomposition. The second stage is characterised by a high decomposition rate, particularly visible for the soft rubber sample, for which slowdown took place in the range of 400-540 °C (20-27 minutes), after losing about 65% of its original weight.

During the slower decomposition course, the weight loss reaches only 5% of the total sample weight. For a hard rubber sample, a significant slowdown in the sample decomposition, in a narrow temperature range 460-480 °C (23-24 minutes) was observed, after losing 50-55% of the sample weight. Further heating causes a rapid increase in the rate of decomposition, reaching the highest values at 590 °C (soft rubber) and 540 °C (hard rubber). This

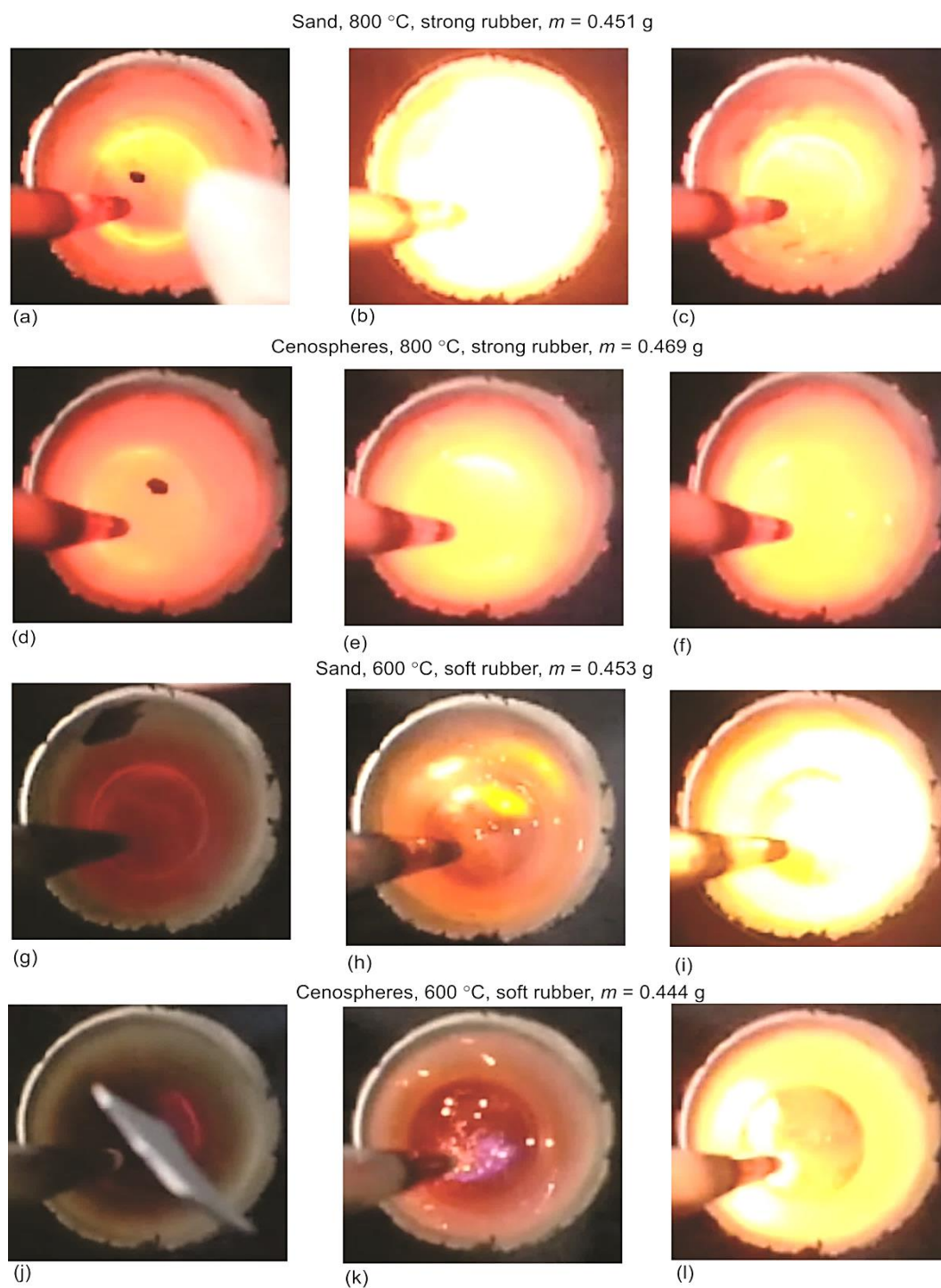


Figure 3. Selected frames depict combustion process, as the rubber sample and temperature function; (a) 1:24.025 – start, (b) 3:42.020, (c) 3:54.016, (d) 00:19.976 – start, (e) 01:48.066, (f) 04:02.864, (g) 00:24.858 – start, (h) 00:37.516, (i) 00:46.978, (j) 00:36.494 – start, (k) 01:55.989, and (l) 02:15.844 (for colour image see journal web site)

process was accompanied by exothermal effects, coming from the combustion of remaining char and heavy decomposition products. For hard rubber sample, more substantial thermal effects were observed. For each sample after reaching 600 °C, the complete combustion process occurred. The thermogravimetric analysis indicate that the composition of gases obtained during combustion of rubber samples in the fluidized bed may depend on the place where the process takes place. Significant emission of gases in the first phase of the heating rubber samples occurs. So before the sample reaches a temperature close to the temperature of the fluidized bed, it may cause the bursting of unburned gases above the surface of the bed. This effect can be partially neutralised by the fact that in a low-density cenosphere bed, incinerated samples can be located closer to the distributor, despite the intensive transfer of the deposit particles.

Figure 3 present frames recorded above the reactor, illustrating the process of burning hard and soft rubber in the sand and cenospheric beds, at 800 °C and 600 °C. During combustion of a hard rubber in a sand bed at 800 °C, light yellow diffusion flames (b frame) often appear in the freeboard. This effect is not observed during combustion in the cenospheric bed. In addition, explosions of gas inside the bubbles are observed in the bed upper part. It may indicate that in the cenospheric bed, a sample of the rubber material, due to a significant difference in the density of the rubber and fluidized bed, stays much longer in the lower part of the bed, where is subjected to thermal degradation. The gases generated during this degradation, after mixing with the air may form exploding mixture - even in the lower part of the bed. During the flow of the gas bubble towards the upper surface of the cenospheric bed, the auto ignition may occur. In the case of a sand bed, the sample of burned rubber has a density lower that of the fluidized bed and may degrade closer to the upper surface of the bed. It allows the discharge of a non-flammable gas mixture (due to lack of oxygen) to the freeboard. Gases are then burnt in the space above the bed. After burning a hard rubber sample, the appearance of a luminous char, ejected into the upper space of the bed was observed. This effect was more frequent when combustion was carried out in a sand bed (c frame). The frames from the process of soft rubber burning at 600 °C in sand and cenospheric beds, are also shown in fig. 3. In both cases, diffusion flames (h, l frames) appeared above the bed, while in the case of the cenospheric bed they lasted for a short time, and the first flame appeared after approximately 100 seconds from the moment when the sample was introduced into the bed - for comparison for the sand bed it was after approximately 20 seconds. In both cases, combustion began with the appearance of exploding bubbles in the upper layers of the bed. For cenospheric bed, a blue flame was observed, which indicates a better mixing of oxidant and combustible gaseous in the bed. Immediately after rubber sample introduction the process of decomposition and gasses (CO_2 , NO_x , VOC, and CO) release occurs.

Figure 4 shows the relationship between released gasses concentration, for two rubber types, during the combustion in the bed of the sand at the 800 °C. The emission of flue gases depends on the type of combusted material and the temperature of the bed. An increase in the bed temperature increases the rate of oxidation of VOC and CO.

Emissions of CO and VOC gasses, figs. 5(A) and 5(B) during hard rubber sample burning at 600 °C, in the cenospheric bed are larger than in the sand bed. The CO emission is in the range of 40-160 mg in the cenospheric bed and it varies from several to 120 mg in the sand bed. In the VOC case, it is 30-100 mg and 20-30 mg, respectively. These concentrations are reduced to trace values at 800 °C. During the soft rubber burning, at 800 °C, regardless of the bed type, CO emission increased as the sample mass increased. Emissions of CO during the combustion of soft rubber samples at 600 and 700 °C bed temperature do not differ signif-

icantly in both the sand and cenospheric beds, reaching maximum values 80-100 mg for samples with approximate mass 0.45g.

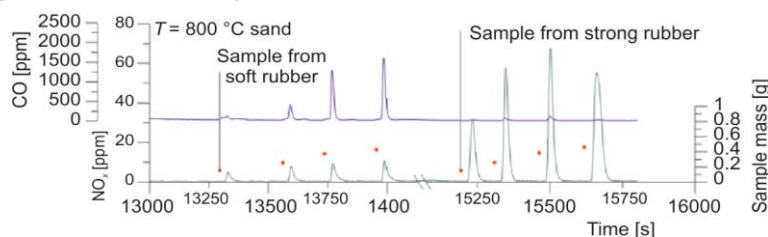


Figure 4. Emission of selected gases during combustion in the sand's bed

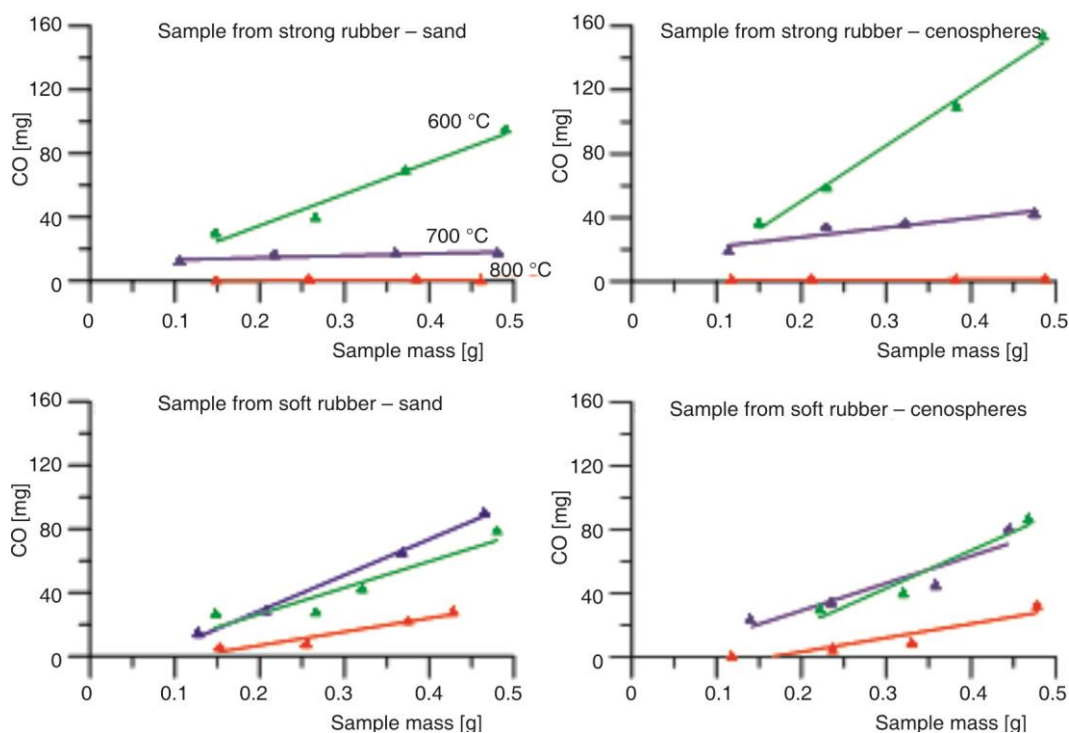


Figure 5A. The CO emission during rubber samples combustion

At 800 °C soft rubber is a source of CO emission, reaching 20-30 mg for the heaviest samples regardless of the type of bed. It was found that the increase in the bed temperature in which the sample's combustion process is carried out causes a higher emission of VOC. This is in accordance with the TGA results of rubber samples, according to which the thermal destruction process of the tested rubber samples is two-stage, and its first stage at 200-450 °C is the source of significant quantities of gaseous components.

The emission of NO_x , fig. 6, at a higher bed temperature is lower, regardless of the type of bed material. For hard rubber, at 600 °C, NO_x emissions are higher (20-50 mg) when cenospheres are used as the bed material, but for sand bed it does not exceed 40 mg. When soft and strong rubber samples are burned at 800 °C, the NO_x emission is less than 20 mg the material used as the bed.

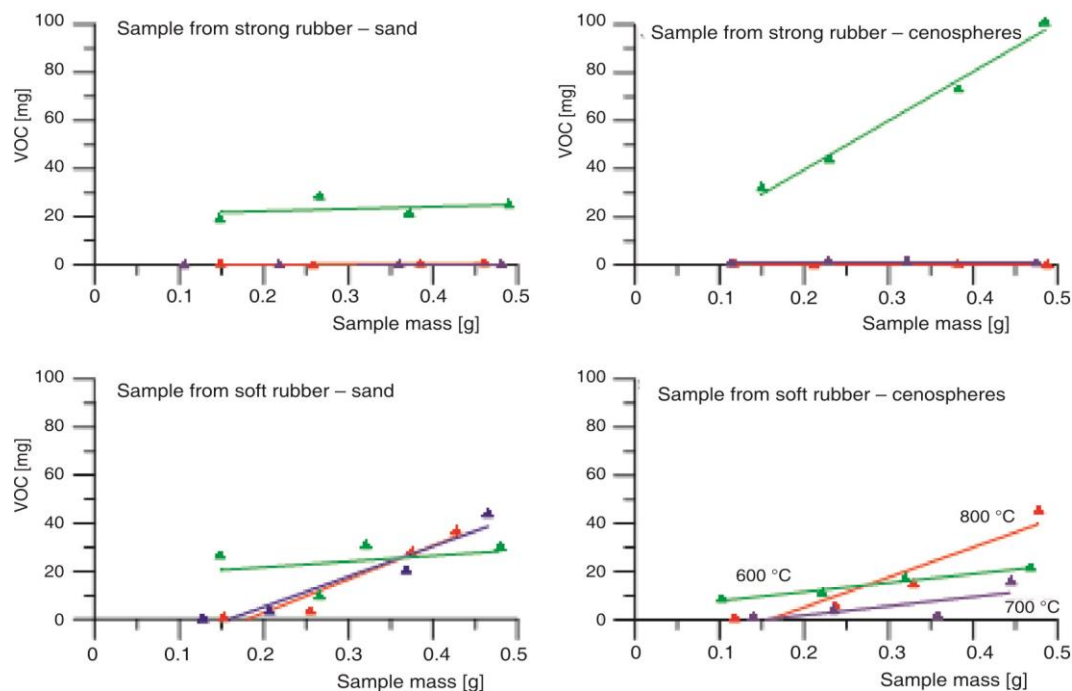


Figure 5B. The VOC emission during rubber samples combustion

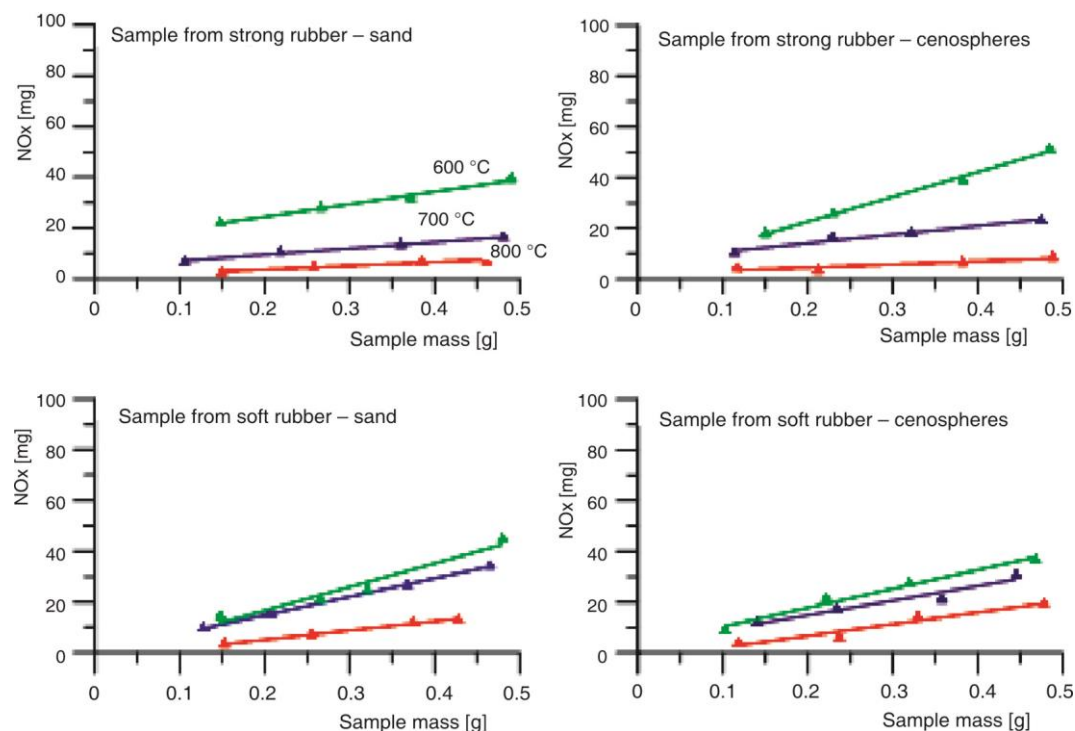


Figure 6. The NO_x emission against the sample mass in different bed kinds

Time of the sample combustion is a crucial factor that characterised rubber decomposition. Cause this determination is not possible by way of direct observation, to establish this time, the results of CO, CO₂ concentration were subjected to a deconvolution process. When the rubber sample is introduced to a hot fluidized bed, the process of its decomposition is connected with gas products release. Due to the analytical block inertia, gas products concentration is deformed and whole analytical block can be treated as the well-stirred reactor. To determine the signal distortion, a stream of CO₂ for ~2 minute was fed into the reactor. Ideally, the system's response should have a rectangular shape. In fact, the registered response looks like a trapezoid. Assuming that the whole apparatus is modelled with a complete mixing system, the rate of measured CO₂ concentration change is:

$$\frac{dC_M}{dt} = \frac{C_{IN} - C_M}{\tau} \quad (1)$$

After integration in the 0, C_M and t_i , t_t limits the following equation is obtained:

$$\ln\left(1 - \frac{C_M}{C_{IN}}\right) = -\frac{t_i - t_t}{\tau} = -\frac{t}{\tau} \quad (12)$$

which allows $1/\tau$ calculation [10]. In the experimental practice, $1/15$ seems to be the best-fitted value. Based on the $1/\tau$ constant CO₂ and CO concentration were transformed, fig. 7.

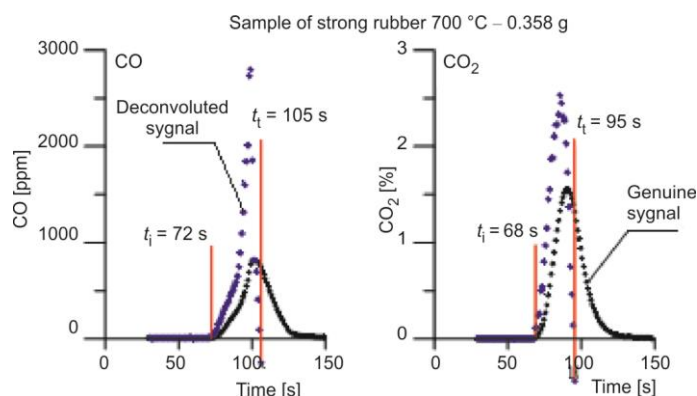


Figure 7. Plots of CO and CO₂ signals obtained by analyzers before and after deconvolution

Time, t_i , is the value of first nonzero CO, CO₂ data. In turn, t_t is the time when the graph of deconvoluted signal intersect x-axis. The results of t_i for a CO and CO₂ are 72, 68 seconds, respectively, and for the t_t 105, 95 seconds. The obtained time ($\Delta t = t_t - t_i$) are 33 and 27 seconds (the higher value is considered as decomposition time). The time decomposition as the sample mass function were approximated in two ways: by the linear function, and by the shrinking core model [22] where the mass is raised to 2/3 power.

The comparison between the samples decomposition time, in two types of the bed was presented in fig. 8. When the temperature rises, the decomposition time decreases as expected. For strong rubber, at 600 °C and for the sand bed the longest time was registered (60-120 seconds). For the strong rubber sample incineration time is shorter in the cenospheres bed (at 600 and 800 °C), but for soft rubber this dependency is not confirmed. Burgess *et al.* [16] proved that the heat radiation is the key factor that controls the rate of HDPE polymer

combustion at 600 °C, so besides the sample location in the bed, the different emissivity of cenospheric bed may also have the impact on the incineration time.

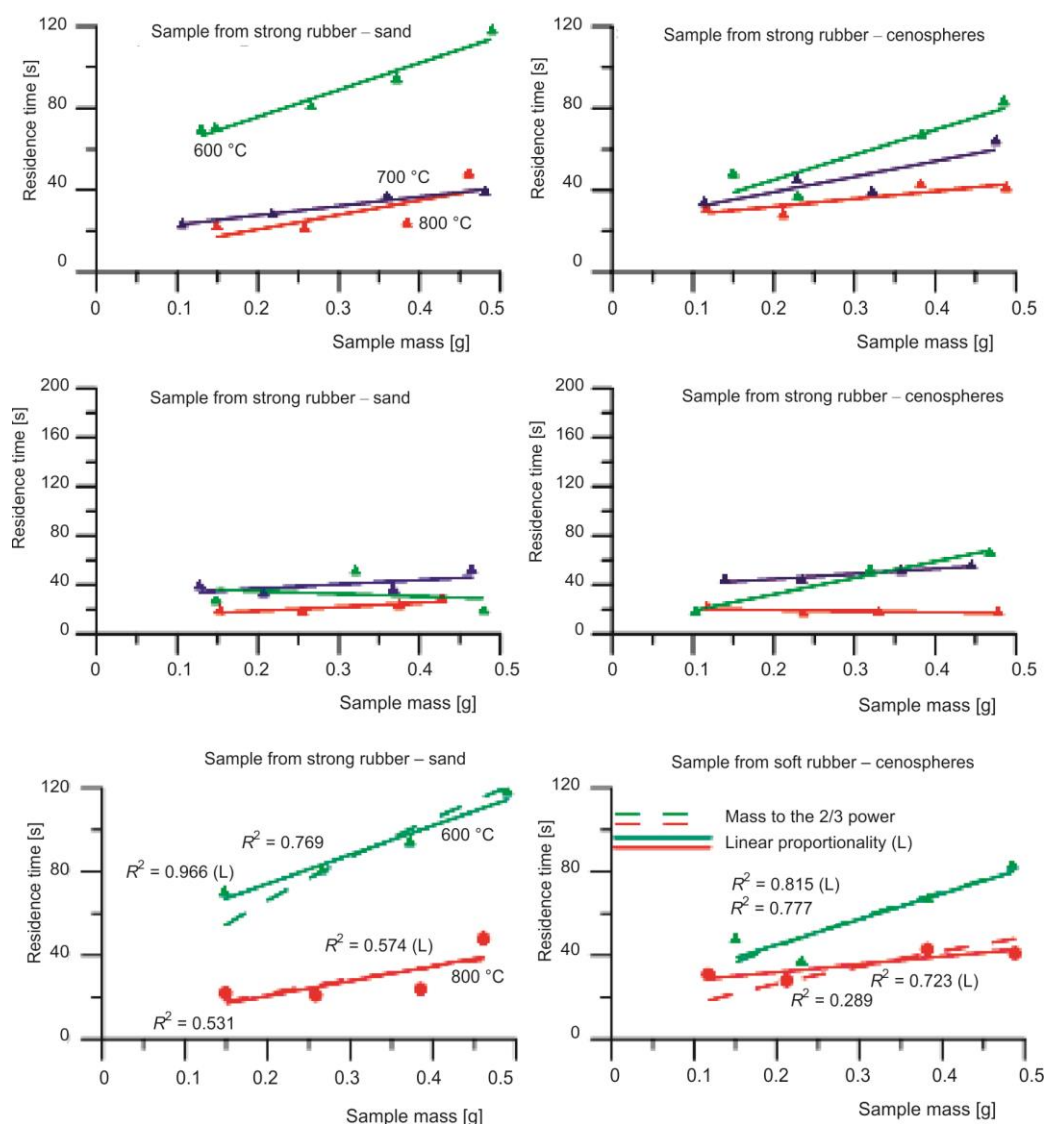


Figure 8. Time of sample combustion and comparison of linear and shrinking core models

The NO_x , CO, and VOC emission strongly depend on the incineration time: for example at $T = 600$ °C decomposition time of strong rubber in cenospheric bed are clearly shorter than during combustion in sand bed, and simultaneously higher emission of said gases is observed. It is clearly because, the rate of the rubber combustion rises, but rate of the gaseous products combustion is constant. Lack of significant differences in decomposition time during soft rubber combustion correlates with lack of the emission differences in both types of the bed. The relationship between sample residence time and its mass is shown in the fig. 8.

Two kinds of approximation (linear and shrinking core model $t(m) = \text{const. } m^{2/3}$) were used. In the range of the tested sample masses, the linear function is better fitted than the shrinking core model. Differences between results and shrinking core model are more pronounced in hotter bed and may be explained by the stochastic defragmentation (to the particles with varies sizes) of the rubber sample during combustion and circulation in the hot bed.

Figure 9 presents a comparison of acoustic effects recorded during the combustion of a hard rubber sample in a sand and cenospheric bed at 700 °C. The rapid amplitude changes of sound signals are the result of explosive combustion of gasses inside the bubbles. The calculated degradation time for hard rubber samples with masses of approx. 0.47 g is 37 seconds in the sand and 64 seconds in the cenospheric bed. The period of explosive combustion of gases in the bubble is shorter than the time of sample decomposition. It can be seen from the figure that the period of explosive combustion is slightly shorter in the cenospheric bed than in the sand one. The illustration also shows that combustion in the cenospheric bed is characterised by a higher frequency of bubble explosions, and more sound signals with relatively low amplitude (low amplitude was also observed for other samples burnt in the cenosphere bed).

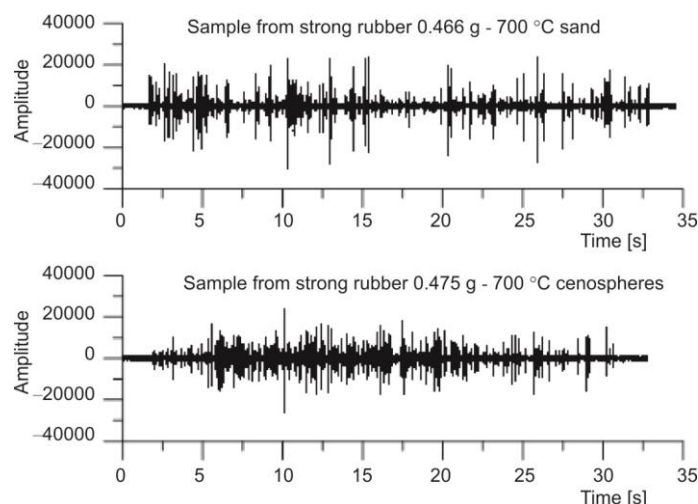


Figure 9. Acoustic effects during a hard rubber

The low amplitude of sound signals is the result of two important reasons. The first is the significant attenuation of sound signals through the bed layer. A low signal amplitude means that the explosions take place near the perforated distributor, and the sound signal travels a longer distance in the highly vibration-damping fluidized bed environment. The second reason is the small volume of the explosive gas mixture contained in the bubbles, or (in the case of low bed temperatures) composition of the exploding gas far from the stoichiometric conditions. Further analysis of the acoustic signals is shown in figs. 10 and 11. The frequency and the number of explosions during the combustion of hard rubber increases with increasing bed temperature. This effect is more pronounced in the cenospheric bed. During the soft rubber samples combustion, a similar effect is observed, however, in the sand bed, the determined frequency of explosions at 800 °C is lower than at 600 °C and 700 °C, and in the cenospheric bed does not show an upward trend with increasing mass of the burned samples. The reason for this effect is the fast release of combustible components from the samples decom-

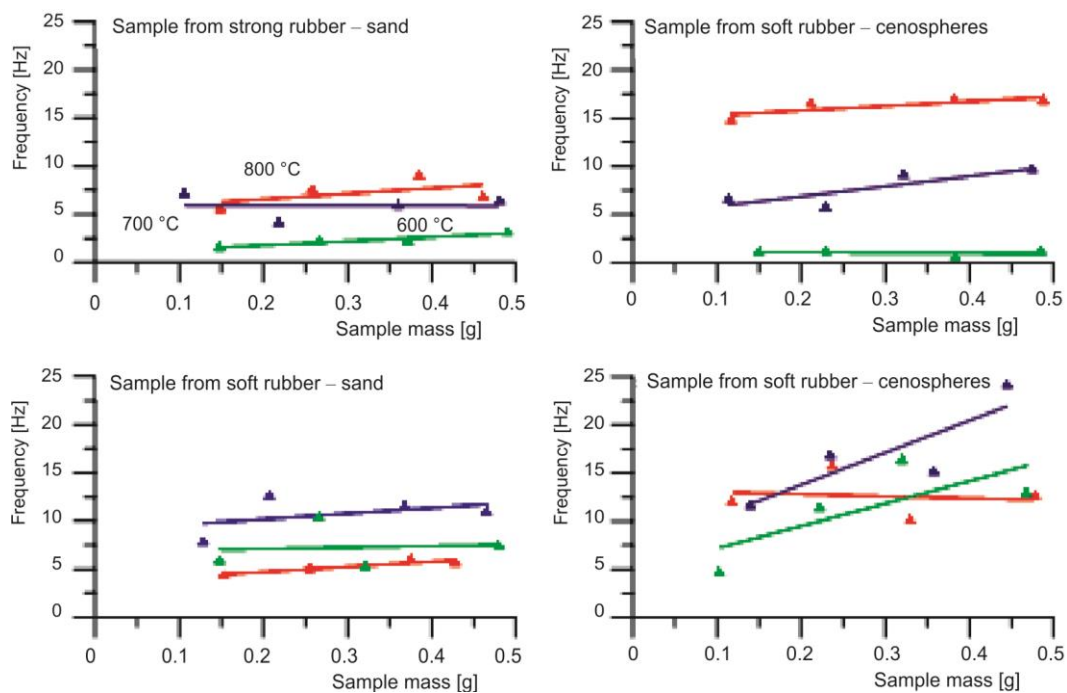


Figure 10. Frequency of bubbles explosions

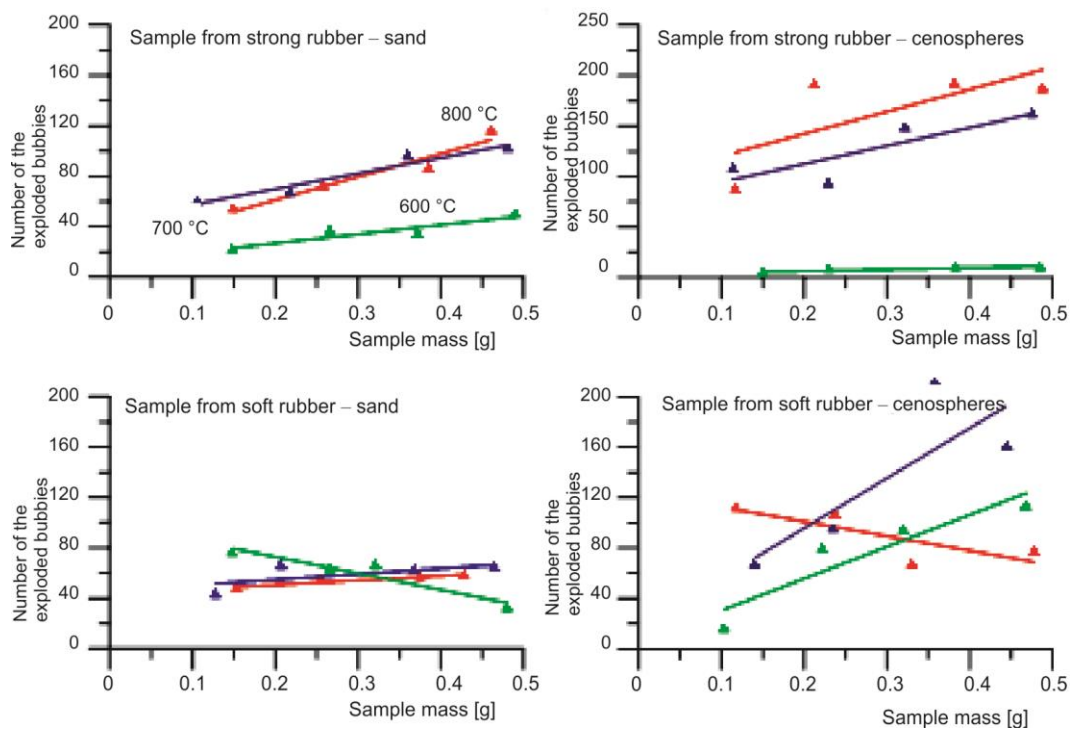


Figure 11. The total number of bubbles explosions

position, causing the considerable amount of these gases to escape from the bed before they reach the flammability limit in the bubbles. This situation was even reached for soft rubber samples with the lowest mass. These observations are also confirmed by the total number of explosions, fig. 11. At 800 °C, the combustion in the cenospheric bed is accompanied by a larger number of exploding bubbles. The formation of a combustible mixture in a larger number of bubbles depends on the position of the gases release zone from the circulating particle in the space of the bed. It affects the mixing time of bubbles filled with combustible gaseous decomposition products with air-filled bubbles.

The increased frequency of bubble explosions, during combustion in the cenospheric bed, indicates the transfer of the particle circulation zone to the deeper bed layers, which is possible due to the lower density of the bed. The experiments indicate the possibility of using a cenosphere as an alternative to the sand in the fluidized bed.

Conclusions

The use of the cenospheric bed has two important benefits: the bed weight decreases, which reduces the operating costs of the fluidized bed reactor, and during the combustion of the rubber in the cenospheric bed, the location of the emission zone of the gaseous products from rubber degradation is transferred to the vicinity of the perforated bottom. It increases the combustible gaseous products residence time in the bed. When a sample of hard rubber is burning at 800 °C, the emission of incomplete combustion products has a trace value regardless of the type of material used as. However, during the soft rubber incineration process this emission does not disappear completely.

The decomposition of the hard rubber during combustion in the sand bed was the longest. The residence time as a function of the sample mass, do not correspond to the model of the shrinking core, which possible explanation is the defragmentation of the particle to the smaller parts with various sizes. The optical effects confirm that during combustion in the cenospheric bed the number of diffusion flames is much fewer than during combustion in the bed of sand. Also, the analysis of acoustic signals indicates a distinctly higher frequency of the bubbles explosions during combustion in the cenospheric bed. For example, at temperatures above 700 °C, during the combustion in the cenosphere bed, almost double increase in the frequency of recorded explosions was observed. Both observations confirm the thesis that the release of combustible gaseous products of rubber decomposition in the cenospheric bed occurs closer to the air distributor. This extends the time when coalescence of bubbles occurs, thus improve mixing of the gases with the air, and much more bubbles are containing fuel and air mixtures in the proportions allowing ignition, reached the upper bed zone.

Nomenclature

C_{IN}	– concentration of i^{th} gaseous ingredients in the reactor inlet, [ppm]	t_i	– an initial time of sample decomposition, [s]
C_M	– concentration of i^{th} gaseous ingredients, measured by the analyser, [ppm]	t_t	– a terminal time of sample decomposition, [s]
m	– rubber sample mass, [g]	<i>Greek symbol</i>	
t	– sample residence time (time of the combustion), [s]	$\bar{\tau}^{-1}$	– parameter of analytical block inertia, [1/s]

References

- [1] Scala, F., *Fluidized Bed Technologies for-Near Zero Emission Combustion and Gasification*, Woodhead Publishing Limited, Cambridge, UK, 2013

- [2] Zukowski, W., et al., An Optical Method of Measuring the Temperature in a Fluidized Bed Combustor, *Combust. Flame*, 156 (2009), 7, pp. 1445-1452
- [3] Okasha, F., Modeling of Liquid Fuel Combustion in Fluidized Bed, *Fuel*, 86 (2007), 15, pp. 2241-2253
- [4] Gibson, I., et al., The Continuous Combustion of Glycerol in a Fluidized Bed, *Combust. Flame*, 200 (2019), Feb., pp. 60-68
- [5] Baron, J., et al., Combustion of Hydrogen in a Bubbling Fluidized Bed, *Combust. Flame*, 156 (2009), 5, pp. 975-984
- [6] Čojbašić, Z., et al., Computationaly Intelligent Modeling and Control of Fluidized Bed Combustion Process, *Thermal Science*, 15 (2011), 2, pp. 321-338
- [7] Baron, J., et al., Premixed LPG + Air Combustion in a Bubbling FBC with Variable Content of Solid Particles in the Bubbles, *Flow Turbul. Combust.*, 110 (2018), 3, pp. 953-969
- [8] Diaz-Bautista, M. A., et al., AFBC of Coal with Tyre Rubber Influence of the Co-Combustion Variables on the Mineral Matter of Solid By-Products and on Zn Lixiviation, *Fuel*, 106 (2013), Apr., pp. 10-20
- [9] Bu, C., et al., Oxy-Fuel Combustion of a Single Fuel Particle in a Fluidized Bed: Char Combustion Characteristics, an Experimental Study, *Chem Eng J*, 287 (2016), Mar., pp. 649-656
- [10] Fennell, P. S., et al., The Measurement of the Rate of Burning of Different Coal Chars in an Electrically Heated Fluidized Bed of Sand, *Chem. Eng. Sci.*, 62 (2007), 1, pp. 608-618
- [11] Davidsson, K.O., et al., Countermeasures Against Alkali-Related Problems During Combustion of Biomass in a Circulating Fluidized Bed Boiler, *Chem. Eng. Sci.*, 63 (2008), 21, pp. 5314-5329
- [12] Khan, A., et al., Biomass Combustion in Fluidized Bed Boilers: Potential Problems and Remedies, *Fuel Process. Technol.*, 90 (2009), 1, pp. 21-50
- [13] Woynarowska, A., et al., Thermal Treatment of Electronic Waste in a Fluidized Bed and Chemical Digestion of Solid Products, *Waste Manage. Res.*, 34 (2016), 7, pp. 605-618
- [14] Woynarowska, A., et al., Combustion of Electronic Waste in the Reactor with Bubbling Fluidized Bed (in Polish), *Przem. Chem.*, 92 (2013), 6, pp. 997-1005
- [15] Baron, J., et al., The Combustion of Polymer Pellets in a Bubbling Fluidized Bed, *Fuel*, 85 (2006), 17-18, pp. 2494-2508
- [16] Burgess, F., et al., Combustion of Polymer Pellets in a Bubbling fluidised Bed, *Combust. Flame*, 158 (2011), 8, pp. 1638-1645
- [17] Urciuolo, M., et al., Fluidized Bed Combustion and Fragmentation of Wet Sewage Sludge, *Exp Therm Fluid Sci*, 43 (2012), Nov., pp. 97-104
- [18] Duan, F., Combustion Behavior and Pollutant Emissions of Batch fluidized Bed Combustion, *J Taiwan Inst Chem Eng.*, 44 (2013), 6, pp. 1034-1038
- [19] Leckner, B., Developments in Fluidized Bed Conversion During 2005– 2010, *Proceedings*, A Summary from the Member Countries of the IEA-FBC Implementing Agreement, Goteborg, Sweden, 2011
- [20] Navid, R., Carsten K., Cenospheres: A review, *Fuel*, 207 (2017), Nov., pp. 1-12
- [21] Geldart, D., *Gas Fluidization Technology*, John Wiley and Sons, New York, USA, 1986
- [22] Levenspiel, O., *Chemical Reaction Engineering*; John Wiley and Sons, New York, USA, 1972