

WITOLD ŻUKOWSKI*, SYLWIA ENGLOT, JERZY BARON,
STANISŁAW KANDEFER, MALGORZATA OLEK

REDUCTION OF CARBON DIOXIDE EMISSION USING ADSORPTION – DESORPTION CYCLES IN A FLUIDISED BED REACTOR

The paper discusses the possibility of applying the reversible reaction $\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2$ in cyclic capture and release of CO_2 directly inside a fluidised bed combustor. This would cause lowering CO_2 emissions to the atmosphere, thanks to obtaining energy from burning fossil fuels. Observations made on the effect of introducing an additional external stream of CO_2 on the efficiency of the chemical capture process are described. It is implied that CO_2 derived from the fuel can be temporarily retained within the bed to be released later at a higher concentration. The proposed method of burning fuel in a chemically active fluidised bed could be an available method leading to CO_2 isolation from flue gases and to its eventual sequestration.

NOTATIONS

- P_{CO_2} – partial carbon dioxide pressure, bar
- I – limestone decomposition enthalpy, kJ/mol
- R – gas constant, J/(mol·K)
- T – equilibrium temperature for calcium carbide and carbon dioxide, K
- a – inverse of excess combustion air ratio
- n_{sp} – molar stream of exhaust gases, mol/s
- $y'_{\text{CO}_2,sp}$ – molar fraction of CO_2 in exhaust gases in complete combustion
- $y'_{\text{O}_2,sp}$ – molar fraction of O_2 in exhaust gases in complete combustion
- $y'_{\text{N}_2,sp}$ – molar fraction of N_2 in exhaust gases in complete combustion
- $n_{\text{N}_2,sp}$ – molar flux of N_2 remaining in the exhaust gases, mol/s
- $n_{\text{O}_2,sp}$ – molar flux of O_2 remaining in the exhaust gases, mol/s
- $n_{\text{CO}_2,r}$ – molar flux of CO_2 resulting from CaCO_3 decomposition, mol/s

* Faculty of Chemical Engineering and Technology, Cracow University of Technology, ul. Warszawska 24, 31–155 Kraków, Poland; tel.: +48 12 628 2766; Fax: +48 12 628 2036. E-mail: pczukows@pk.edu.pl, sylwia.englot@gmail.com, baron@pk.edu.pl, kandefer@usk.pk.edu.pl, mmt.olek@gmail.com

- $n_{\text{CO}_2,p}$ – molar flux of CO₂ resulting from propane combustion, mol/s
 $n_{\text{CO}_2,\text{dod}}$ – molar flux of additional CO₂ supplied into the reactor, mol/s
 n_{pow} – molar flux of air supplied into the reactor, mol/s
 Q_{CO_2} – molar ratio of additional CO₂ to air stream
 E – enrichment factor without adding CO₂ into the bed
 E' – enrichment factor when adding CO₂ into the bed

1. INTRODUCTION

According to the Kyoto Protocol enterprises which introduce greenhouse gases into the atmosphere in volumes exceeding the established limits will experience additional costs due to emission rights trading. As most methods of combustion generate large quantities of CO₂, energy enterprises are looking for ways to reduce its emission. One of the methods of reducing CO₂ emission is sequestration. It is a complex method of separating carbon dioxide from the fume stream and further transporting it into safe storage or utilizing it in various technological processes. The most costly stage of sequestration is the first one – separating CO₂ from exhaust gases. The existing methods of CO₂ elimination from the fume stream are very costly. This thesis explores the benefits of combustion using reactors with a chemically active fluidized bed. The chemically active bed is composed of CaO/CaCO₃ and at some temperatures causes in-situ adsorption or desorption of CO₂ from the gas stream. One of the advantages of applying this method is carbon dioxide capture as the fuel is combusted – it is not considered a separate process of extracting CO₂ from the gas stream, therefore it does not require additional funding. Experiments conducted so far allowed us to increase the CO₂ volume in exhaust gases to the level of 37%. Thus, the present method can only be used for initial sequestration and has to be supplemented with other methods.

2. THEORETICAL BASIS

A fluidized bed reactor (FBR) with a bubbly fluidized bed can be used to combust stable, liquid and gaseous fuels [1]–[13]. The reactor bed can be chemically inert (e.g., quartz sand), act as a catalyst or be chemically active. Previous experiments proved that combustion in a reactor with a chemically inert bed leads to low emission of CO, NO_x and organic compounds. The most common material used in such FBRs is quartz sand but calcium carbonate (of mineral origin) can also be used. Such a bed can both adsorb and desorb CO₂ and is classified as chemically active. During combustion calcium carbonate is subject to calcination when the temperature exceeds the thermal decomposition levels. Calcining enriches the reactor's bed as calcium oxide granules are being deposited. Lowering the temperature of the bed causes decalcination and the

bed saturates with CO_2 again, forming calcium carbonate as calcination is a reversible reaction, which means that calcium carbonate can decompose into CaO and CO_2 or be formed via CO_2 adsorption into a bed made of CaCO_3 . Proper temperature control is required for the occurrence of calcination and decalcination. The calcination equilibrium of calcium carbonate equation can be presented by the following reaction:



Partial pressure of carbon dioxide (P_{CO_2}) depends on the temperature and can be designated as a dependence:

$$P_{\text{CO}_2} = 2.15 \cdot 10^7 \cdot \exp(-I/(RT)), \quad (2)$$

where I states the enthalpy of calcium carbonate decomposition [14].

The dependence can also be shown as a chart of CO_2 equilibrium concentration inside the fluidized bed, which is a function of temperature at given pressure (figure 1). Establishing the ceiling temperature, in which CO_2 sorption takes place, can be done by analyzing the relationship between CO_2 concentration and calcium carbonate equilibrium. If the CO_2 concentration inside the reactor is 5–15%, then according to the dependence (figure 1) the ceiling point will be 716–774 °C. This means that combustion has to take place at a relatively low temperature of the fluidized bed. However, past experiments with combusting gaseous fuels show that such condition is acceptable [11]–[14].

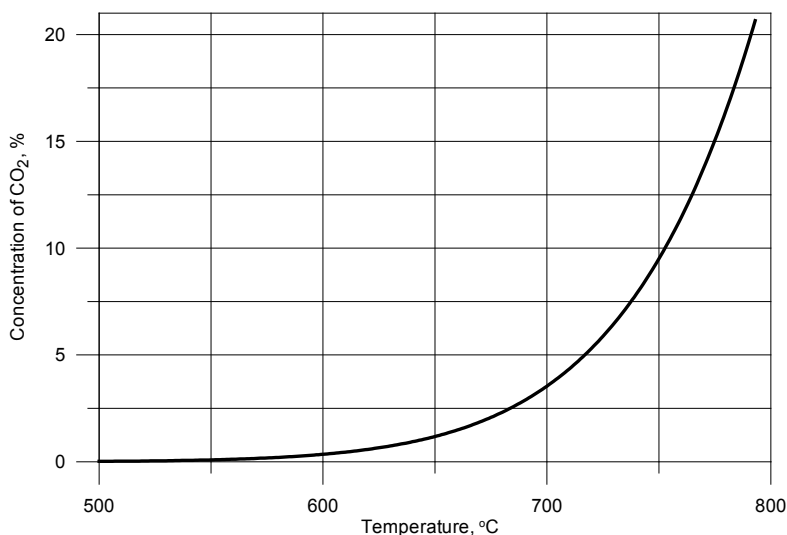
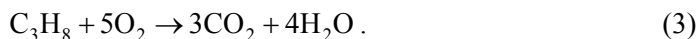


Fig. 1. Relation between CO_2 concentration in flue gases being in equilibrium with calcium and temperature at total pressure of 101325 Pa [14]

In order to raise the ceiling temperature of calcium carbonate decomposition equilibrium, the CO₂ concentration inside the reactor has to be increased. Such a case is possible when we combust fuels containing carbon dioxide (biogas, gas produced through gasification of bituminous coal). It is also possible to increase CO₂ concentration by introducing fume circulation. An additional CO₂ stream will also increase the time of contact between reacting substances and it will raise the CO₂ concentration inside the fluidized bed, which will increase the overall efficiency of the chemical reaction.

Propane was the fuel combusted during the experiment. Propane decomposition is as follows:



Chemical reactions inside the furnace are described by dependencies (1) and (3). Therefore, the amount of carbon dioxide in the fumes is the sum of CO₂ resulting from the combustion and CO₂ from the additional fuel stream. That amount is also increased by the CO₂ amount, which comes from CaCO₃ calcining, or reduced by the CO₂ adsorbed during decalcining.

The main goal of the experiment is to establish the contribution of CO₂ sorption (or calcium carbonate calcination) to the overall amount of CO₂ in the fumes. In order to achieve that, we introduced a non-dimensional enrichment factor (E), which is a quantitative measure of increase (or decrease) of CO₂ during calcination or decalcination measured against CO₂ amount created via combustion and externally added into the combustion chamber.

3. CALCULATION METHOD

The first step to obtain proper calculations is establishing the fume composition. For clarification: the initial calculations were done without considering an additional CO₂ stream into the reactor, which was considered in the calculations in the later stage. Input data of CO₂, O₂ and CO concentration in the fumes were collected using an exhaust gas analyzer. Incomplete combustion in excessive air was performed. In actual conditions, it is possible to conduct after-combustion. Thus, in order to simplify the calculations, CO concentration in exhaust gases was converted into CO₂ concentration, which would normally take place in complete combustion. The resulting mole fractions are:

$$y'_{\text{CO}_2,sp} = \frac{y_{\text{CO}_2,sp} + y_{\text{CO},sp}}{1 - 0.5y_{\text{CO},sp}} , \quad (4)$$

$$y'_{\text{O}_2,sp} = \frac{y_{\text{O}_2,sp} + y_{\text{CO},sp}}{1 - 0.5y_{\text{CO},sp}} , \quad (5)$$

$$y'_{N_2,sp} = \frac{1 - (y_{CO_2,sp} + y_{CO,sp} + y_{O_2,sp})}{1 - 0.5y_{CO,sp}}. \quad (6)$$

Subsequently molar streams of exhaust gases were calculated:

$$n_{N_2,sp} = 79.1\% \cdot n_{pow}, \quad (7)$$

$$n_{O_2,sp} = 20.9\% \cdot (1 - a) \cdot n_{pow}, \quad (8)$$

$$n_{CO_2,r} = \left(\frac{79.1}{y'_{N_2,sp}} + 8.36 \cdot a - 100 \right) \cdot n_{pow} / 100, \quad (9)$$

$$n_{CO_2,sp} = n_{CO_2,r} + n_{CO_2,p} = n_{CO_2,r} + 0.6 \cdot 20.9\% \cdot a \cdot n_{pow}. \quad (10)$$

The above-mentioned equations were used to establish the dependencies describing the molar flux of exhaust gases (n_{sp}), the inverse of the excess combustion air ratio (a) and the enrichment ratio (E) [11]–[13]:

$$n_{sp} = n_{CO_2,r} + 0.126 \cdot a \cdot n_{pow} + 0.209 \cdot (1 - a) \cdot n_{pow} + 0.791 \cdot n_{pow}, \quad (11)$$

$$a = 1 - \frac{3.7847 \cdot y'_{O_2,sp}}{1 - y'_{O_2,sp} - y'_{CO_2,sp}}, \quad (12)$$

$$E = \frac{n_{CO_2,r}}{n_{CO_2,p}} = \frac{\frac{79.1}{1 - y'_{O_2,sp} - y'_{CO_2,sp}} + 8.36 \cdot a - 100}{12.54 \cdot a}. \quad (13)$$

Values 8.36 and 12.54 (eq. (13)) depend on the stoichiometric factors of the combustion equation depending on the type of fuel – in this case: propane (3).

The equations above represent combustion processes when there is no additional stream of CO_2 into the combustion chamber. If we want to consider an additional stream we have to introduce another factor:

$$Q_{CO_2} = \frac{n_{CO_2,dod}}{n_{pow}}. \quad (14)$$

Considering an additional CO_2 stream and the enrichment factor, depending on the molar flux of the exhaust gases, leads to equations:

$$n_{sp} = n_{CO_2,r} + 0.126 \cdot a \cdot n_{pow} + 0.209 \cdot (1 - a) \cdot n_{pow} + 0.791 \cdot n_{pow} + Q_{CO_2} \cdot n_{pow}, \quad (15)$$

$$E' = \frac{n_{CO_2,r}}{n_{CO_2,p}} = \frac{\frac{79.1}{1 - y'_{O_2,sp} - y'_{CO_2,sp}} + 8.36 \cdot a - 100 \cdot (1 + Q_{CO_2})}{12.54 \cdot a}. \quad (16)$$

The enrichment factor E is within the range $(-1; \infty)$ if the combustion takes place without an additional CO_2 stream. If E is positive then calcination takes place inside the reactor's bed. If E equals 0 that means that CaCO_3 inside the reactor's bed is in a state of equilibrium or that the calcinations is not taking place. A negative E means that CO_2 adsorption is taking place inside the bed.

4. EXPERIMENTAL

The present results were obtained during two independent experiments. The first one utilized a fluidized bed composed of limestone with grain diameter of 0.385–0.43 mm and the second one was carried out with a fluidized bed composed of carbide residue, 1.02–1.2 mm granulation. The main improvement, which was made after the previous experiments [13]–[14], was the increase of the CO_2 stream added into the combustion chamber. The main goal was to obtain higher periodical CO_2 concentration in exhaust gases. The experiments were conducted using a reactor on the side of which there was a quartz pipe, 96 mm in diameter, 3 mm thick and approx. 500 mm tall. Air, propane and carbon dioxide were introduced into the mixing chamber linked to a distributor sealing off the reactor from the bottom side. Concentrations of gases introduced into the mixing chamber were measured using MRU Vario Plus exhaust-gas analyzer. Oxygen, carbon oxides, nitrous oxides and sulphur dioxide concentrations were measured using Horiba and Ecom analyzers. The gases were collected approx. 200 mm above the bed. Combustion temperature was recorded using Ni-NiCr thermocouples placed at various heights above the distributor. The research station diagram is shown in figure 2.

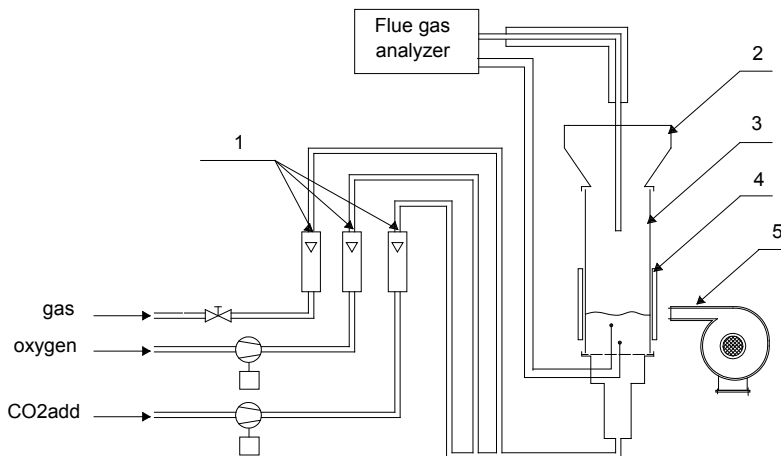


Fig. 2. The bubbling fluidised bed and associated equipment (schematic):
1 – rotameters; 2 – metal cover; 3 – freeboard, 4 – movable radiation shield, 5 – fan

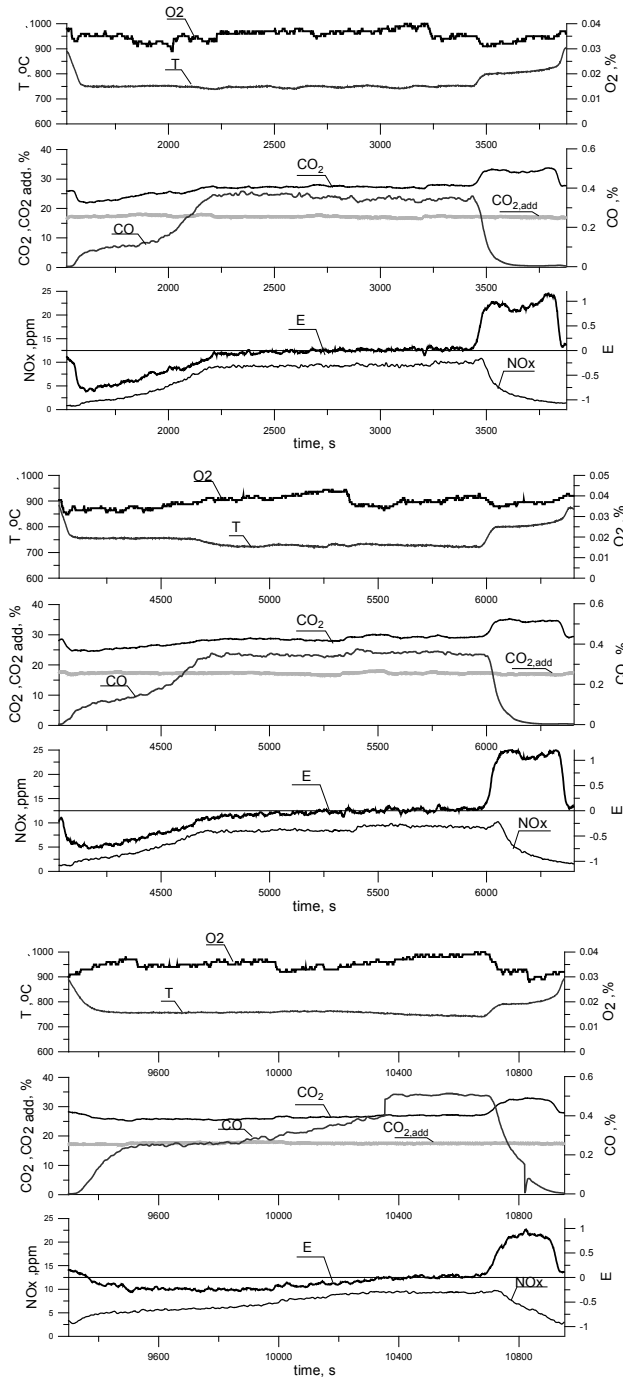


Fig. 3. Flue gas composition during the capture and release of CO_2 (limestone)

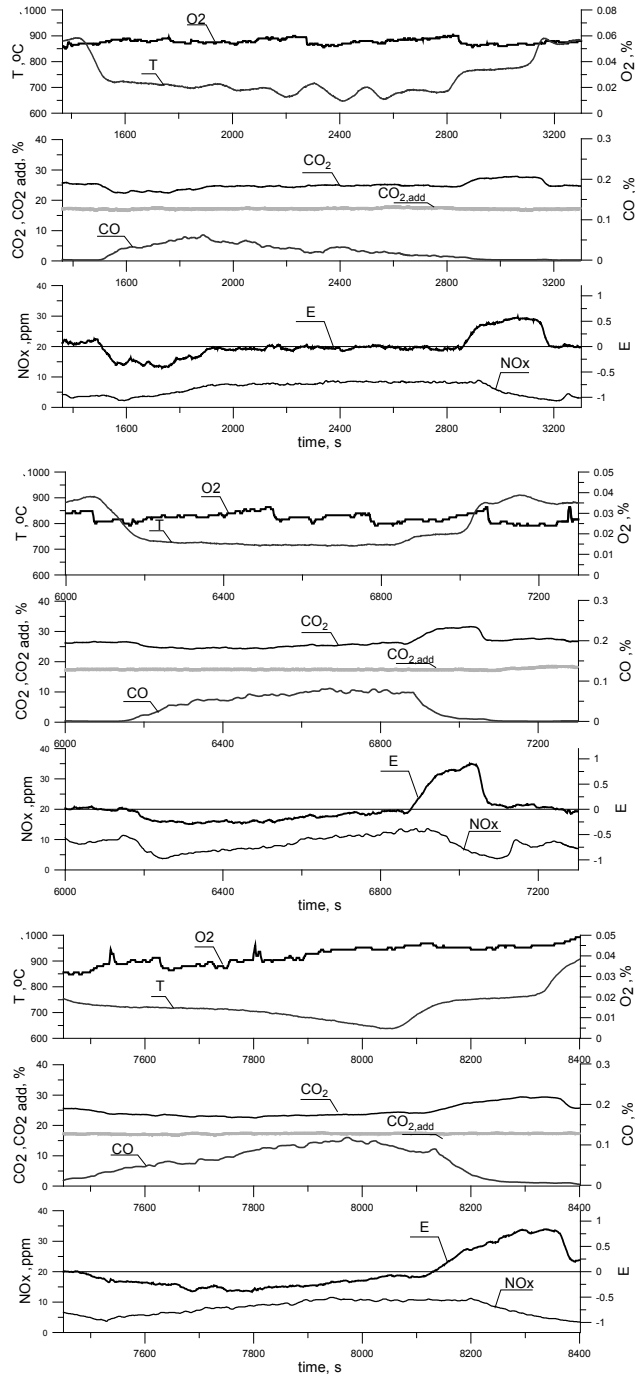


Fig. 4. Flue gas composition during the capture and release of CO₂ (carbide residue)

During combustion, the variables were: propane and air volume stream and the bed temperature. The solid layer temperature inside the furnace was changed by adjusting heat removal from the reactor.

In phase 1 of the experiment, the bed was heated above the ceiling temperature for limestone decomposition, which changed the bed composition into CaO granules. Thus, the fluidized bed was prepared for the main part of the experiment. The next part was obtaining alternate cycles of adsorption and desorption. These cycles were obtained by periodically changing the bed temperature from 730 to 900 °C for limestone and from 630 to 930 °C for carbide residue. The results are shown in figure 3 (for limestone) and 4 (for carbide residue). Each chart illustrates CO₂ adsorption and desorption.

During CaCO₃ decomposition, the temperature rise of the bed was halted. The reason is the fact that process is endothermic. After CaCO₃ decomposed the temperature increased again. Similarly, during CO₂ sorption a halt in temperature decrease is observed. During CO₂ desorption, the concentration in the exhaust gases reaches 29–37% during experiment I (limestone) or 24–32% during experiment II (carbide residue). In the previous experiments [12]–[13], the CO₂ concentration in exhaust-gases varied from 14 to 22%. In similar conditions during propane combustion (without additional CO₂) in a quartz sand bed, the CO₂ concentration in the exhaust gases coming from the fluidizing layer was in the range of 9–12% [11].

Another phenomenon, which was observed, is the significant increase of CO concentration in exhaust gases during decalcination. Combustion in large-scale furnaces with proper volume above the bed could provide complete combustion of this gas. During the first phase of combustion (preparation phase) NO_x concentration was high but during the main part of the experiment it did not exceed 10 or 14 ppm (for limestone and carbide residue).

5. CONCLUSIONS

The above-described experiments proved that combusting gaseous fuel inside an FBR with a chemically active bed is a low-emission process. NO_x concentration in the main part of the experiment did not exceed 14 ppm, which is approx. twice as much as in experiments carried out with a smaller CO₂ stream added into the mixing chamber [12]–[13].

During adsorption the CO₂ concentration in the exhaust gases was reduced from 29 to 23% for limestone and from 25 to 23% for carbide residue. The CO₂ stream added to the exhaust fumes was at 18%. In the previous experiments [12]–[13] with a smaller stream of CO₂ (approx. 10%), it was possible to reduce CO₂ emission resulting from the combustion stoichiometry to zero value, i.e. the emitted CO₂ stream was equal to the amount of CO₂ introduced into the combustion process.

Desorption allowed us to increase the CO₂ concentration in the exhaust gases to 37% for limestone. Such concentrations enable a more economically effective application of additional carbon dioxide sequestration from the exhaust gas stream in order to achieve concentration in the range of 90–95%.

Looking at the enrichment factor E we can record its increase to values above 1 during desorption. During adsorption its value falls to a maximum of -0.8 for limestone and -0.5 for carbide residue. During the previous experiments [12]–[13] it was possible to temporarily obtain even $E = -1$. Considering the E factor definition, this means that a chemically active fluidized bed is capable of adsorbing carbon dioxide in-situ at a rate close to (although smaller) the rate of carbon dioxide generation during combustion.

REFERENCES

- [1] AVEDESIAN M.M., DAVIDSON J.F., *Combustion of carbon particles in a fluidised bed*, Trans. I. Chem. E., 1973, 51, 121–131.
- [2] DENNIS J., HAYHURST A.N., MACKLEY I.G., *The Ignition and Combustion of Propane/Air Mixtures in a Fluidised Bed*, 17th Symposium (Int.) on Combustion, The Comb. Inst., Pittsburgh, 1982, 1205–1212.
- [3] HAYHURST A.N., *Does carbon monoxide burn inside a fluidized bed? A new model for the combustion of coal char particles in fluidized beds*, Combust. Flame, 1991, 85, 155–168.
- [4] HESKETH R.P., DAVIDSON J.F., *Combustion of methane and propane in an incipiently fluidized bed*, Combust. Flame, 1991, 85, 449–467.
- [5] STUBINGTON J.F., CLOUGH S.J., *The combustion rate of volatiles in a fluidized bed combustor*, 14th Int. Fluidized Bed Conf., Vancouver, Ed. F.D.S. Preto, ASME, New York, 1997, Vol. 2, 1111–1122.
- [6] ŻUKOWSKI W., *The pressure pulses generated by the combustion of natural gas in bubbling fluidized beds*, Combust. Flame, 2001, 130, 15–26.
- [7] ŻUKOWSKI W., BARON J., KOWARSKA B., ZABAGŁO J., *N₂O conversion in active and chemically inert fluidized bed*, Environment Protection Engineering, 2010, 36 (3), 15–32.
- [8] PILAWSKA M., BARON J., ŻUKOWSKI W., *Combustion of Aromatics and Esters in an Atmospheric Bubbling FBC, in Comparison with that of Natural Gas*, 7th Int. Conf. on Energy for a Clean Environment, Lisbon, Portugal, 2003, paper 36.3.
- [9] BULEWICZ E.M., ŻUKOWSKI W., KANDEFER S., PILAWSKA M., *Flame flashes when bubbles explode during the combustion of gaseous mixtures in a bubbling fluidized bed*, Combust. Flame, 2003, 132, 319–327.
- [10] BARON J., BULEWICZ E.M., KANDEFER S., PILAWSKA M., ŻUKOWSKI W., HAYHURST A.N., *The combustion of polymer pellets in a bubbling fluidised bed*, Fuel, 2006, 85, 2494–2508.
- [11] ŻUKOWSKI W., BARON J., BŁASZCZYK-PASTECZKA A., KANDEFER S., OLEK M., *Efekty spalania propanu w inertnym i aktywnym chemicznie złożu reaktora fluidyzacyjnego*, Przem. Chem., 2008, 87, 2, 214–218.
- [12] ŻUKOWSKI W., ENGLÓT S., BARON J., KANDEFER S., OLEK M., *Wykorzystanie procesów kalcynacji i karbonizacji złoża wapiennego w palenisku fluidalnym do oddzielenia CO₂ ze spalin*, Termodynamika w nauce i gospodarce, 2008, T. II, 668–675.
- [13] ŻUKOWSKI W., ENGLÓT S., BARON J., KANDEFER S., OLEK M., *Reduction of carbon dioxide emission through the sorption in situ using a fluidised bed reactor*, Polish Journal of Chemical Technology, 2008, Vol. 10, No. 4, 45–48.
- [14] BES A., *Dissertation, Dynamic Process Simulation of Limestone Calcination in Normal Shaft Kilns*, Fakultät für Verfahrens- und Systemtechnik, Otto-von-Guericke-Universität, Magdeburg, 2006.