

## Effect of CO<sub>2</sub> addition on lignite gasification in a CFB reactor: A pilot-scale study

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**Abstract**—The addition of carbon dioxide to the gasification media during lignite gasification is introduced. The paper presents thermodynamic grounds of CO<sub>2</sub> enhanced gasification using a simplified equilibrium model. Experimental tests conducted using a pilot-scale circulating fluidized bed gasifier are discussed. Detailed analysis of the CO<sub>2</sub>/C ratio on process conditions, namely on the process gas composition, lower heating value and H<sub>2</sub>/CO ratio, is provided. Process gas composition implies that the gas is suitable for heat and power generation. Alternatively, CO<sub>2</sub> enhanced gasification could be considered as a carbon capture and utilization technology when external, renewable heat supply to the process is used. The results thus obtained are the initial step toward development of the CO<sub>2</sub> enhanced gasification process.

Keywords: CO<sub>2</sub>, Lignite, Gasification, Circulating Fluidized Bed Reactor

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### INTRODUCTION

Gasification is generally a process aimed to produce a fuel-rich gaseous product from fossil fuels, biomass and waste. Potential applications may be found in power generation: for electrical power and industrial steam [1], and production of chemicals: substitute natural gas used as synthesis gas for subsequent production of alcohols, gasoline, plastics [2]. The number of projects connected with gasification is constantly growing. This growth is mainly associated with a dynamic increase in the number of successful Asian gasification units. Another reason is an increasing number of biomass and waste plants in Europe and USA related to continuously growing interest in renewable energy sources in these countries [3].

Gasification units can be classified according to design, feedstock type or gasification agent. In terms of design, one can distinguish between three gasifier types: entrained flow, fluidized bed and moving (fixed) bed gasifiers. Feedstocks include biomass, municipal waste, heavy petroleum residues, natural gas (for reforming applications) and finally the most common one, coal [4]. The gasification media comprise air, oxygen, CO<sub>2</sub>, steam and its mixtures. Air is mainly used for small-scale distributed power generation gasifiers on account of the low heating value of the gas, caused by nitrogen dilution [5]. The use of oxygen eliminates this disadvantage enabling production of high quality gas with high concentration of carbon monoxide and hydrogen. The H<sub>2</sub>/CO ratio in the gas strongly depends on the feedstock used; however, it can be also altered by modifying the gasification agent. Adding steam to the gasification agent leads to the process gas enrichment with hydrogen owing to the water gas shift reaction [6]. Another gasification agent taken into consideration is carbon dioxide. The gasification process in the CO<sub>2</sub> or oxy-fuel atmosphere leads to higher CO concentrations in the

process gas through the Boudouard reaction [7,8]. This option is particularly interesting because it is a potential means of mitigating the contribution of carbon dioxide emission to global warming and ocean acidification.

Thermodynamic analysis of CO<sub>2</sub> application for gasification of carbonaceous feedstocks proves that this technology is tempting in terms of the carbon dioxide utilization [9]. A major drawback of this process is the endothermic character of the Boudouard reaction which controls CO<sub>2</sub> gasification. Significant energy must be delivered to the system, either from an external source, e.g., a solar energy source [10], or from partial oxidation of the feedstock (autothermal gasification) [11]. The latter appears to be more feasible because it is derived from well-established gasification technologies, and the major change is the gasification agent modification. CO<sub>2</sub> gasification is also limited by kinetics of the Boudouard reaction, as it proceeds at a relatively lower rate compared to the steam and O<sub>2</sub> reaction [7]. This disadvantage can be diminished by using the circulating fluidized bed gasifier, where partially converted char is recirculated, which increases times of contact between feedstock and the gasifying agent [11]. Other way to decrease the CO<sub>2</sub> gasification reaction time could be increasing gasification temperature [12].

An extensive literature review for coal gasification with CO<sub>2</sub> is presented by Irfan et al. [7]. The authors point out that carbon dioxide is the preferred agent used at the laboratory level and the C-CO<sub>2</sub> reaction is of great importance, but it is not used industrially as much as steam in the gasification or activation processes. Furthermore, the review shows that small-scale laboratory TGA analysis has mainly been used for coal CO<sub>2</sub> gasification studies and the research was focused on oxy-combustion in CO<sub>2</sub>/O<sub>2</sub> atmosphere. The authors conclude that coal gasification with the mixture of CO<sub>2</sub> and steam will be a fruitful technology in the future. Some studies have shown the gasification reactivity of char with CO<sub>2</sub> and char with steam [13] or biomass CO<sub>2</sub> gasification [5]. Kim et al. investigated CO<sub>2</sub> coke gasification reactivity depending on the type

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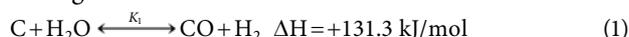
of coke and its specific surface area [14]. Marcourt et al. discussed results obtained from pilot-scale experiments on coal gasification using mixtures of carbon dioxide and oxygen under pressure [15]. Thermodynamic simulations of dry CO<sub>2</sub> gasification of lignite were presented by Kale [16]. CO<sub>2</sub> enhanced sub-bituminous coal and lignite gasification analysis and preliminary pilot tests were presented by Chmielniak et al. [11]. To the best of the authors' knowledge, no detailed study has been performed in a pilot-scale gasifier to investigate CO<sub>2</sub> gasification of lignite in the autothermal mode. In contrast, steam and oxygen gasification of lignite has received much attention [17-19].

This paper reports on lignite gasification using a pilot-scale fluidized bed gasifier on various CO<sub>2</sub> flow rates with the presence of oxygen and air. The effect of the CO<sub>2</sub>/C ratio on the process gas composition and the cold gas efficiency has been discussed. A simple equilibrium model establishing grounds for CO<sub>2</sub> enhanced gasification has additionally been shown.

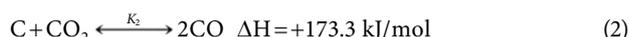
## EQUILIBRIUM MODEL

Gasification is partial thermal oxidation which results in a high proportion of gaseous products (CO<sub>2</sub>, water, carbon monoxide, hydrogen and gaseous hydrocarbons), lower quantities of char, ash, and condensable compounds (tars and oils) [20]. The process of gasification is complex and consists of different stages, all leading to the generation of gaseous fuel. The gasification steps include: feedstock drying, devolatilization, oxidation and reduction. In general, during gasification of carbonaceous fuels, the only compounds present in the product at higher concentrations are CO, CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and solid carbon (char). Limiting the analysis of the chemistry of gasification to these compounds is a correct approximation. In such a case, the gasification is governed by the following three chemical reactions [20,21]:

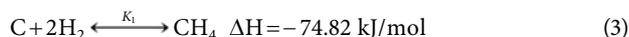
Water gas reaction:



Boudouard reaction:



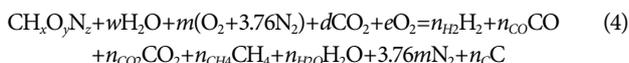
Methane reaction:



The energy demand of endothermic reactions (1) and (2) is satisfied either by the heat produced during oxidation of part of the fuel, as in the case of the autothermal (adiabatic, in other words) process, or by using an external heat source.

The beneficial effect of carbon dioxide on lignite gasification can easily be explained using a simplified lignite equilibrium gasification model introduced below. To simplify the analysis, the isothermal (i.e., with external heat source) option is described.

Lignite is a complex mixture of chemical compounds, but in an extreme simplification it can be described as a chemical having the general formula based on a single atom of carbon: CH<sub>x</sub>O<sub>y</sub>N<sub>z</sub>. The global gasification reaction can be noted as follows:



where  $w$  is used to describe the moisture content in the fuel, and  $m$ ,  $d$  and  $e$  are used to characterize the gasification agent. Coefficients on the right-hand side of the equation represent components of the product. All coefficients are the amounts of constituents per kmol of lignite. Eq. (4) has six unknowns,  $n_{H_2}$ ,  $n_{CO}$ ,  $n_{CO_2}$ ,  $n_{CH_4}$ ,  $n_{H_2O}$ ,  $n_C$  representing the unknown amounts of the constituents in the product, and therefore six equations are required to find a solution. The first three equations are formulated using balances of elements:

Carbon balance:

$$1 + d = n_{CO} + n_{CO_2} + n_{CH_4} + n_C \quad (5)$$

Oxygen balance:

$$y + w + 2m + 2d + 2e = n_{CO} + 2n_{CO_2} + n_{H_2O} \quad (6)$$

Hydrogen balance:

$$x + 2w = 4n_{CH_4} + 2n_{H_2} + 2n_{H_2O} \quad (7)$$

Remaining three equations provide definitions of the equilibrium constants of reactions (1)-(3):

$$K_1 = \frac{P_{CO}P_{H_2}}{P_{H_2O}} \quad (8)$$

$$K_2 = \frac{P_{CO}^2}{P_{CO_2}} \quad (9)$$

$$K_3 = \frac{P_{CH_4}}{P_{H_2}^2} \quad (10)$$

Values of equilibrium constants have been taken from Hou and Hughes [22]. To convert constituents' mole numbers from Eqs. (5)-(7) into corresponding partial pressures required in Eqs. (8)-(10), total pressure is needed. Solving Eqs. (5)-(10) allows for determination of the gasification products under isothermal conditions, as the temperature of the reacting mixture is included in the values of the equilibrium constant. Such an isothermal approach is sufficient to demonstrate fundamentals of the beneficial effect exerted by carbon dioxide on lignite gasification. On the other hand, based on such results, one cannot conclude if the process is autothermal. Of course, the model can easily be extended by an energy balance, thus enabling simulations under adiabatic conditions. Details of the possible model extension can be found in the literature [23,24].

## EXPERIMENTAL

### 1. Materials

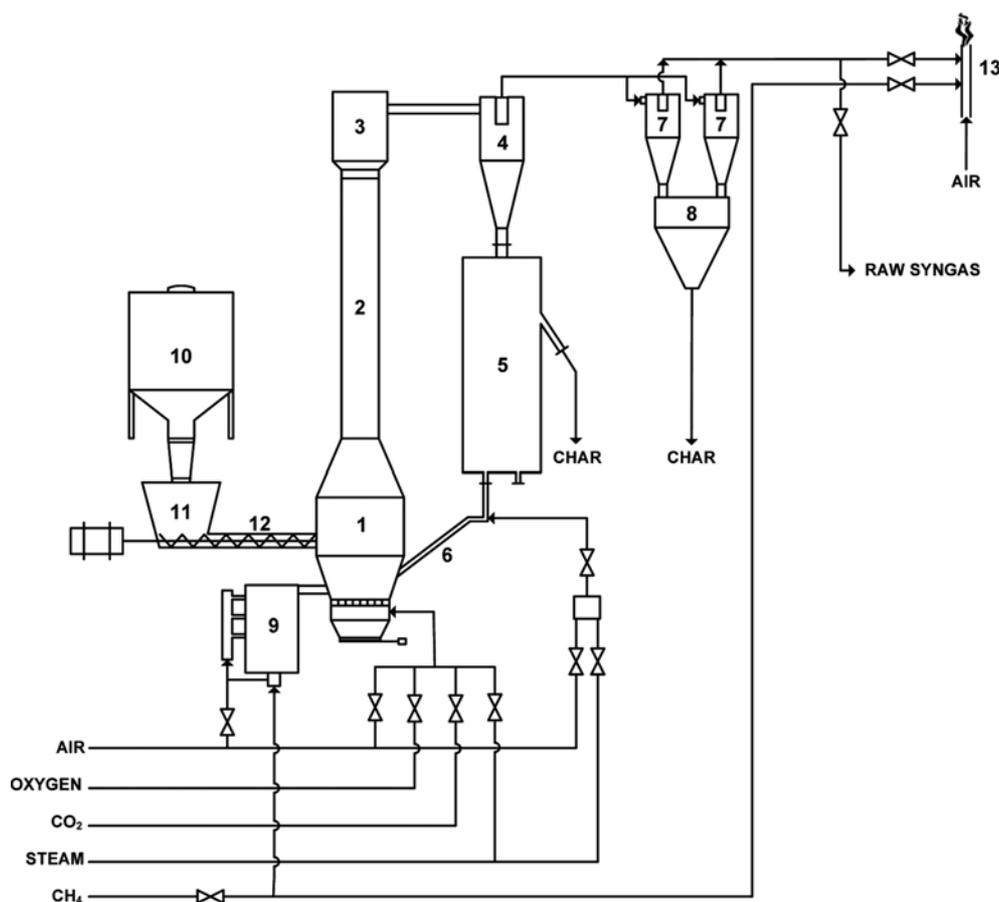
Lignite delivered from the Polish open pit mine of "Bełchatów" was used as the test material. The lignite was dried, ground and sieved to prepare the raw material with grain size required to develop the reactor bed in the pilot plant. Properties of the lignite prepared for that purpose are presented in Table 1. The preparations applied dramatically reduced the moisture content in lignite (the pre-drying moisture content in raw lignite exceeded 50 mass%) and consequently increased its calorific value. The content of carbon and hydrogen as well as of volatile matter also increased. The fuel grain size mostly ranged between 1 and 2 mm.

### 2. Pilot Plant

A pilot plant for solid fuel gasification in a circulating fluidized

**Table 1. Physiochemical properties of the fuel prepared**

Symbol	Description	Unit	"Bełchatów" lignite
Proximate analysis			
$W_t^r$	Total moisture concentration in raw material (as received, wet basis)	mass %	5.8
$A^r$	Ash content in raw material (as received, wet basis)	mass %	10.0
$V^a$	Volatile matter content (analytical condition)	mass %	47.6
Ultimate analysis			
$C_t^a$	Total carbon content	mass %	57.2
$H_t^a$	Total hydrogen content	mass %	4.53
$N_t^a$	Total nitrogen content	mass %	0.6
$S_t^a$	Total sulphur content	mass %	0.69
$O_t^a$	Total oxygen content (calculated)	mass %	22.68
$Q_i^r$	Calorific value (as received, wet basis)		21 030
$Q_i^a$	Calorific value (analytical condition)	kJ/kg	21 304

**Fig. 1. Flow sheet of the pilot plant for solid fuel gasification in a CFB reactor.**

- |             |                    |                                |                       |           |
|-------------|--------------------|--------------------------------|-----------------------|-----------|
| 1. REACTOR  | 4. PRIMARY CYCLONE | 7. SECONDARY CYCLONES          | 10. FUEL TANK         | 13. FLARE |
| 2. RISER    | 5. CHAR VESSEL     | 8. CHAR VESSEL                 | 11. SCREW FEEDER TANK |           |
| 3. EXPANDER | 6. RECYCLE FEEDER  | 9. START-UP COMBUSTION CHAMBER | 12. SCREW FEEDER      |           |

bed allows for thermal conversion of solid fuels at temperatures of up to 1,200 °C. A flow sheet of the plant has been provided in Fig. 1 and the reactor dimensions have been summarized in Table 2.

The main component of the pilot plant equipment is a reactor. Solid fuel and gasification agents are delivered to the bottom part

of the reactor (1). The gas-solid suspension starts to react in the gasification zone (1) and is further transported vertically upwards through the riser (2). In the expander (3), the axial velocity of the gas-solid suspension abruptly drops so that larger particles of the unreacted char can fall along the riser walls. The fall of the unre-

**Table 2. Dimensions of the circulating fluidized bed gasification reactor**

	Item	Dimensions, mm	
		Height	Diameter
Reactor	Conical bottom	220	200÷380
	Central cylinder	300	380
	Conical top	480	140÷380
Riser		3700	140
Expander		880	220

acted char is possible because of the non-uniform velocity distribution in the riser. The velocity in the core is higher than that in the annulus, and the drag force is accordingly lower there. The lower drag force in the annulus is overcome by gravity and larger particles can freely fall along the riser. This effect causes internal circulation of the solids in the reactor, thus extending times of contact between gas and solids. As the gasification agent, one can use a mixture of gases, namely of air, oxygen, CO<sub>2</sub> and steam. The flow of the gases is measured by means of separate flow meters. Prior to operation, the reactor interior is preheated using the flue gases generated in the start-up combustion chamber (9). The interior of the reactor gasification zone (1) is lined with ceramic material resistant to high temperature and abrasion. If conditions in the reactor are sufficient, i.e., a suitable temperature of approximately 400 °C is reached, the supply of fuel and gasification agent is initiated. The fuel, stored in the mobile fuel tank (10), is delivered to the gasification zone (1) by means of a screw feeder (12). The gas-solid suspension leaves the reactor through the expander (3) and enters the primary cyclone (4), where solid particles (char) are pre-separated. The char is stored in the char vessel (5) located below the cyclone (4). It is possible to recycle the char from the char vessel (5) back to the reactor by means of the recycle feeder (6); however, during the present tests this feature was not used. The initially dedusted gas from the cyclone (4) is transported to secondary cyclones (7) for fine dedusting. Fine particles of ash and char are stored in the char vessel (8). The cleaned gas leaving the secondary cyclones (7) is sampled and analyzed in an on-line FTIR analyzer. Finally, the gas is combusted in the flare (13).

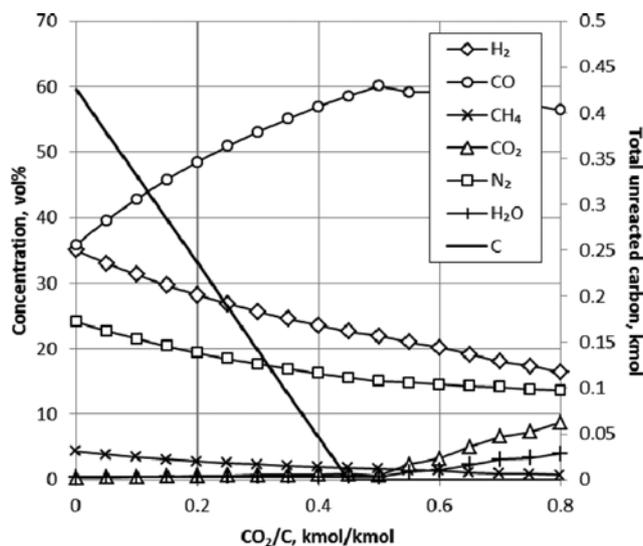
### 3. Experimental Procedures

The following methodology was applied during the experiments. After initial preheating, the process was started using air as a gasification agent. Later, when steady state was achieved, part of the air was replaced by carbon dioxide and oxygen. Composition of the gasifying agent and the fuel flow rate were adjusted to satisfy two conditions: constant volumetric flow rate of the gasifying agent at ~120 m<sup>3</sup>/h and the temperature in the gasification at ~900 °C. These assumptions assure uniform velocity profiles and gasification conditions during the tests.

## RESULTS AND DISCUSSION

### 1. Model Simulations

Bearing in mind that the model is shown to establish grounds for CO<sub>2</sub> enhanced gasification for illustrative purposes, the conclu-

**Fig. 2. Equilibrium composition of the lignite gasification product.**

sions drawn are based on the isothermal approach. Using data from Table 1, the formula of lignite was calculated, and the result was CH<sub>0.997</sub>O<sub>0.312</sub>N<sub>0.009</sub>. The simulations were conducted for temperature set to 900 °C, total pressure was set to atmospheric, 101.325 kPa. The moisture content per kmol of the fuel was  $w=0.07$ . Such fuel was reacted with a gasification agent containing air ( $m=0.1$ ) and CO<sub>2</sub>. Carbon dioxide ranged at 0÷0.8 kmols per kmol of lignite ( $d=0÷0.8$ ). The equilibrium composition of the gaseous product of lignite gasification and the amount of the unreacted char are shown in Fig. 2. Note that the concentration of carbon monoxide increases along with the increasing concentration of CO<sub>2</sub> in the gasification agent (depicted as the CO<sub>2</sub>/C ratio, namely the molar ratio representing the proportion between carbon dioxide in the gasification agent and carbon in the fuel). The CO concentration increase stops when the fuel is consumed, i.e., when the amount of the total unreacted carbon drops to zero. Further increase of the CO<sub>2</sub> concentration in the gasification agent does not bring beneficial effects in terms of the CO concentration in the process gas, while an increase of the CO<sub>2</sub> concentration in the process gas is visible. This phenomenon can be explained by the Boudouard reaction (2). Past the point where carbon has been consumed, the Boudouard reaction can no longer occur, and the CO<sub>2</sub> delivered with the gasification agent is left unreacted and is transferred to the process gas. The exothermic methane reaction (3) is favored by low temperatures; therefore, the CH<sub>4</sub> concentration in the process gas is low, as the gasification temperature in the example shown is 900 °C.

The beneficial effect of CO<sub>2</sub> is even clearer in Fig. 3, showing molar totals of the process gas components. The CO amount increases constantly while elemental C from the fuel is consumed, and at the same time, the amounts of the remaining components are almost constant. Therefore the H<sub>2</sub> concentration decrease, shown in Fig. 2, is not caused by reduction of the hydrogen amount but by the increasing number of CO kmols, thus increasing the number of kmols of the process gas. The CO<sub>2</sub> enhanced gasification is therefore beneficial in terms of cold gas efficiency, since the process gas contains more and more combustible components, while

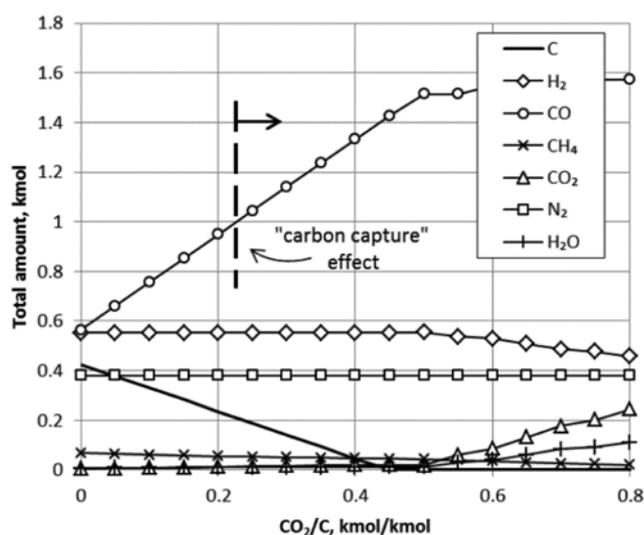


Fig. 3. Molar totals of the process gas components.

the feedstock amount is constant and equal to 1 kmol.

Additionally, as shown in Fig. 3, the number of kmols of CO in the product exceeds 1. Knowing that only 1 kmol of the fuel (containing 1 kmol of C) reacts, it can be concluded that the fuel is not the only source of carbon in the process gas. It is obvious that the remaining carbon comes from the CO<sub>2</sub> delivered with the gasification agent. This phenomenon may be referred to as the “carbon capture” effect, as the CO<sub>2</sub> from the gasification agent is converted into a valuable product: carbon monoxide.

This simplified thermodynamic analysis implies that CO<sub>2</sub> enhanced gasification can increase the carbon monoxide content in the process gas, that it increases the cold gas efficiency and leads to conversion of the CO<sub>2</sub> from the gasification agent to valuable CO in the process gas. The optimal gas composition is obtained at the point where solid carbon in the reacting mixture has been completely consumed, namely, at the carbon boundary point [9]. The conclusions thus drawn highlight several possible advantages of CO<sub>2</sub> enhanced gasification. The analysis is, however, not exhaustive, because it does not include an energy balance or kinetics of

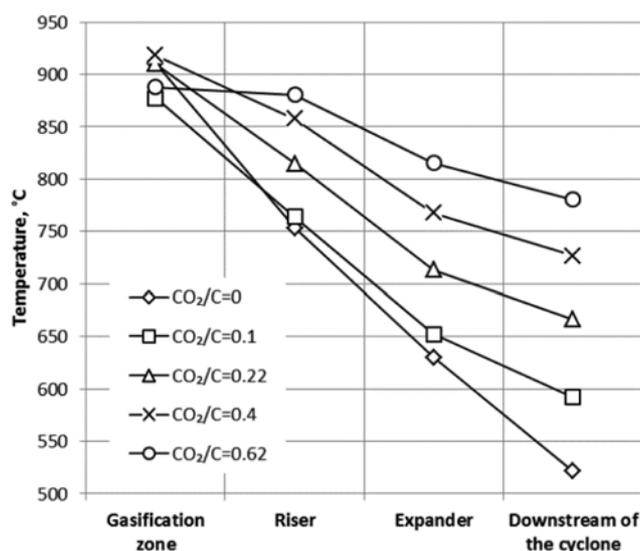


Fig. 4. Effect of the CO<sub>2</sub>/C ratio on the gasifier temperature profile.

gasification. Despite its flaws, this analysis provides sound grounds for CO<sub>2</sub> enhanced gasification and underpins the necessity of experimental verification, which will be described below.

## 2. Pilot Tests

Table 3 summarizes the process conditions and gasification results of 13 gasification tests. During the tests, the composition of the gasification agent was altered by increasing the CO<sub>2</sub> amount. The CO<sub>2</sub>/C molar ratio ranged between 0÷0.6. The amounts of fuel and oxidation agents were altered to match the gasification temperature (the temperature in the gasification zone) of approximately 900 °C. The detailed analysis of the effect of the CO<sub>2</sub>/C ratio on various process aspects is described below.

Fig. 4 shows the temperature profile of the gasification plant as a function of the CO<sub>2</sub>/C ratio of the gasification agent. The temperature in the gasifier ranged at 850÷950 °C and was maintained approx. constant by changing the oxidation agent amount (air, oxygen), as described in the Experimental section. Temperature in subsequent locations of the pilot plant (in the riser, expander etc.)

Table 3. Summary of process conditions and gasification results

Test no.	Fuel flow, kg/h	Gasifying agent flow, m <sup>3</sup> <sub>n</sub> /h			Gasif. temp., °C	CO <sub>2</sub> /C ratio, kmol/kmol	Process gas flow, m <sup>3</sup> <sub>n</sub> /h	Process gas composition, vol%				Char, kg/h
		Air	CO <sub>2</sub>	O <sub>2</sub>				H <sub>2</sub>	CH <sub>4</sub>	CO	CO <sub>2</sub>	
1	83	119.6	0.0	0.0	911	0.00	174	13.0	3.0	15.0	13.4	30
2	83	109.5	8.9	0.0	877	0.10	171	11.7	2.2	13.3	21.9	30
3	83	107.7	13.2	2.4	885	0.15	171	11.1	2.3	13.2	23.4	31
4	88	96.3	17.5	4.5	943	0.19	181	12.5	2.3	16.4	26.4	27
5	91	90.8	21.0	4.4	910	0.22	174	11.4	2.4	15.8	28.9	32
7	93	75.6	30.9	8.4	922	0.31	170	9.6	2.2	17.6	35.2	33
8	93	61.3	40.0	11.2	918	0.40	169	9.0	2.1	18.4	41.4	32
9	93	50.7	49.9	13.9	952	0.50	164	8.0	2.0	17.9	47.5	35
10	99	49.6	57.0	14.0	889	0.54	179	9.0	1.9	17.1	49.8	36
11	99	40.0	64.7	18.7	901	0.61	193	10.0	1.9	17.2	54.4	27
12	97	42.4	64.5	15.7	888	0.62	186	9.0	1.9	19.0	52.0	30
13	112	44.7	64.2	15.2	860	0.54	211	11.0	2.2	19.8	50.2	30

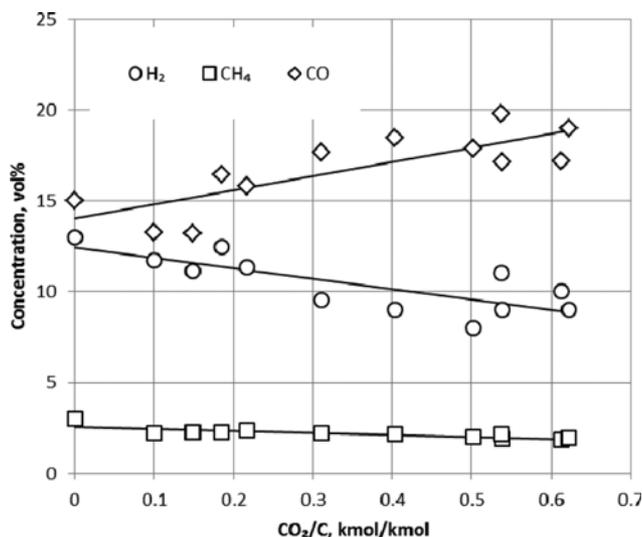


Fig. 5. Effect of  $\text{CO}_2$  flow rate in the gasifying agent on process gas composition. CO evolution enhancement with  $\text{CO}_2$  clearly shown.

increased as the  $\text{CO}_2/\text{C}$  ratio increased. This can be explained by the combustion of a larger amount of fuel during the  $\text{CO}_2$  gasification than during air gasification. Combustion of a larger amount of fuel is necessary to provide the energy for heating of the  $\text{CO}_2$  in the gasification agent ( $\text{CO}_2$  has a higher molar heat capacity of  $C_p = 37.84 \text{ J/mol K}$  than nitrogen  $C_p = 28.86 \text{ J/mol K}$ ) as well as for the endothermic Boudouard reaction. Assuming that the heat reception in the plant is approximately constant, when the heat capacity of the gas increased, its temperature had to increase as well. To some extent, the higher temperatures observed during the  $\text{CO}_2$  gasification can also be explained by the limited diffusion of  $\text{O}_2$  in  $\text{CO}_2$ -rich atmospheres [25]. Lower aggressiveness of  $\text{O}_2$  in  $\text{CO}_2$  rich gas decreases the combustion rate. Consequently, the combustion reactions, causing the temperature increase, cannot only occur in the gasification zone, but also in further units, for example in the raiser.

Extending the high temperature zone in the plant may be beneficial for enhancing the endothermic reactions proceeding at low reaction rates (i.e., the Boudouard reaction).

Fig. 5 shows the effect of the  $\text{CO}_2/\text{C}$  ratio on the gas composition. Along with the increasing  $\text{CO}_2/\text{C}$  ratio, the CO content in the gas increased, the hydrogen content decreased and the methane content remained approximately constant. The conversion of  $\text{CO}_2$  to CO with the simultaneous reduction of  $\text{H}_2$  suggests that composition changes are caused by the Boudouard reaction described in Eq. (2) and the reversed water gas shift reaction. The latter reaction is a combination of Eq. (1) and Eq. (2):



According to Eq. (11), hydrogen is consumed with  $\text{CO}_2$  and converted to carbon monoxide. Certainly, to some extent, dry reforming of  $\text{CH}_4$  and higher hydrocarbons [26] might occur during conversion reactions. However, low and approximately constant concentration of the methane present in the process gas suggests that the reaction proceeds in a limited scope.

To extend the analysis of the process gas composition, the effect

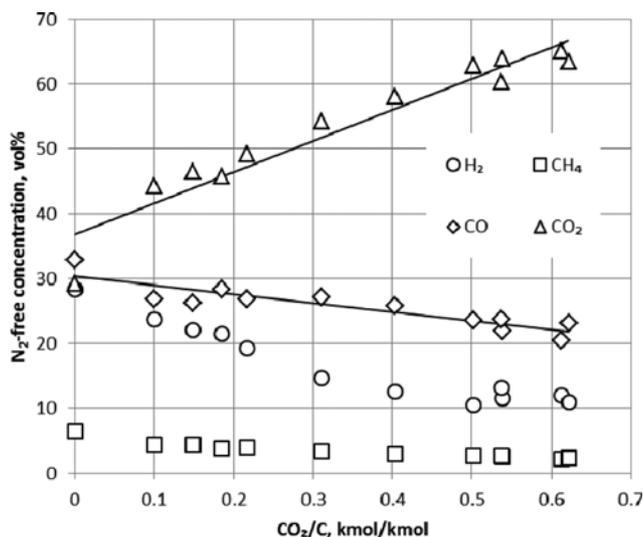


Fig. 6. Effect of the  $\text{CO}_2/\text{C}$  ratio on  $\text{N}_2$ -free gas composition, simulating a gasification process using the mixture of  $\text{CO}_2$  and  $\text{O}_2$  as the gasification agent.

of the  $\text{CO}_2/\text{C}$  ratio on the  $\text{N}_2$ -free gas composition is shown in Fig. 6. The figure roughly simulates a gasification process using the mixture of  $\text{CO}_2$  and  $\text{O}_2$  as the gasification agent. It implies that the process gas was diluted with the unreacted  $\text{CO}_2$  when the  $\text{CO}_2/\text{C}$  ratio increased. At the same time, the CO concentration decreased, but the decrease was less significant compared to the  $\text{CO}_2$  concentration increase. This observation indicates that the CO amount had to increase as  $\text{CO}_2$  was injected and confirms the conversion.

Note that estimation of the exact amount of  $\text{CO}_2$  contributing in the Boudouard reaction, i.e., reacting directly with elemental carbon, is not possible in the present tests. Presence of other oxidation agents (air,  $\text{O}_2$ ) and the autothermal mode of operation of the gasifier requiring combustion of the fuel precludes indication of  $\text{CO}_2$  source in the process gas. Thus, the process gas contains both unreacted  $\text{CO}_2$  from the gasification agent and  $\text{CO}_2$  produced during the combustion and gasification with  $\text{O}_2$ . Estimation of the exchange between  $\text{CO}_2$  and C would be possible by replacing the flow of ordinary  $\text{CO}_2$  in the gasification agent with radioactive  $\text{C}^{14}\text{O}_2$  followed by separation of components of the process gas [27]. This method is hardly attainable in the pilot scale and was beyond the scope of this study.

Additionally, such poor  $\text{CO}_2$  conversion performance can be attributed to the low  $\text{CO}_2$  gasification reaction rate. Kajitani et al. [28] investigated the gasification rate of coal char using a pressurized drop tube furnace. It has been shown that the intrinsic kinetics of the char- $\text{O}_2$  reaction is about three to four orders of magnitude larger than that of the char- $\text{H}_2\text{O}$  and char- $\text{CO}_2$  reactions, whereas the char- $\text{H}_2\text{O}$  reaction is several times faster than the char- $\text{CO}_2$  reaction. Not surprisingly then, the  $\text{CO}_2$  gasification performance was rather disappointing. This was a result of using the same reactor, designed for air or oxygen gasification, for processes characterized by significantly different kinetics. Despite this shortcoming, it was possible to demonstrate that the autothermal  $\text{CO}_2$  gasification was possible. It must be also stressed that the gasification experiments were conducted at the same initial temperature (approx.  $900^\circ\text{C}$ ); thus, the

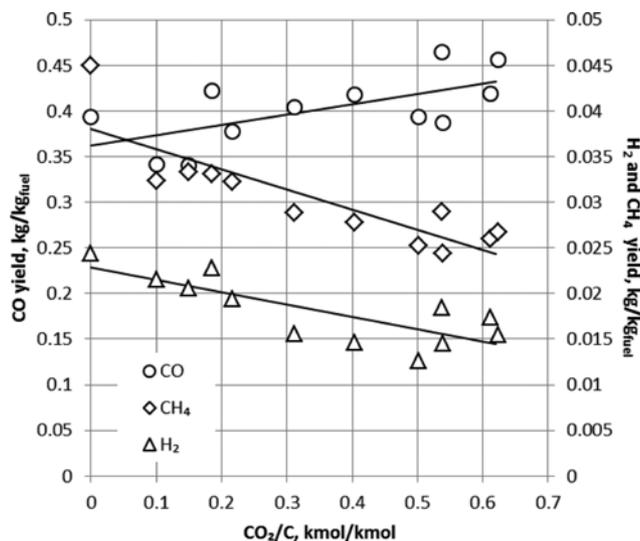


Fig. 7. Effect of the CO<sub>2</sub>/C ratio on yield of combustible gas components.

reaction rates were not increased by increasing temperatures.

Finally, to demonstrate the influence of the CO<sub>2</sub> present in a gasification agent on the process gas, the effect of the CO<sub>2</sub>/C ratio on values of yield of combustible process gas components is shown in Fig. 7. The yield of carbon monoxide increased by approximately 25% as the CO<sub>2</sub>/C ratio increased from 0 to 0.6. Simultaneously, the yield of H<sub>2</sub> and CH<sub>4</sub> decreased. This observation provides grounds for another application of CO<sub>2</sub> gasification, namely, for adjusting the H<sub>2</sub>/CO ratio of the process gas, as shown in Fig. 8. The addition of CO<sub>2</sub> to the gasification agent lowers the H<sub>2</sub>/CO ratio. This effect may prove useful when reducing the hydrogen content in the gas used for power generation.

High hydrogen content is recognized as being one of the most important factors causing engine knocking [29,30]. The phenomenon of knock in spark ignition engines results from the uncontrolled rapid energy release well ahead of the turbulent propagating flame front, due to autoignition of part of the unburned fuel-air mixture. Knocking leads to excessive engine wear and, in severe cases, to rupture of the combustion chamber. Hydrogen in the process gas has a tendency to generate combustion knock, whereas other combustible gases as methane and carbon monoxide are knock resistant fuels [30]. Therefore, it is advantageous to reduce hydrogen content of the gas used in reciprocating gas engines to avoid knocking [31].

Lowering H<sub>2</sub>/CO ratio of the process gas may also prove useful to production of chemicals. The most important hydrogen lean and carbon monoxide rich syngas processes include the oxo process for the production of aldehydes, acetic acid and acetic anhydride or Koch acids production [32].

Note that the H<sub>2</sub>/CO ratio was changed without reducing the lower heating value of the gas (LHV). This effect is presented in Fig. 8. The figure shows that the process gas LHV remained approximately constant, while the H<sub>2</sub>/CO ratio was altered. For process gas, the lower heating value was calculated according to the following expression:

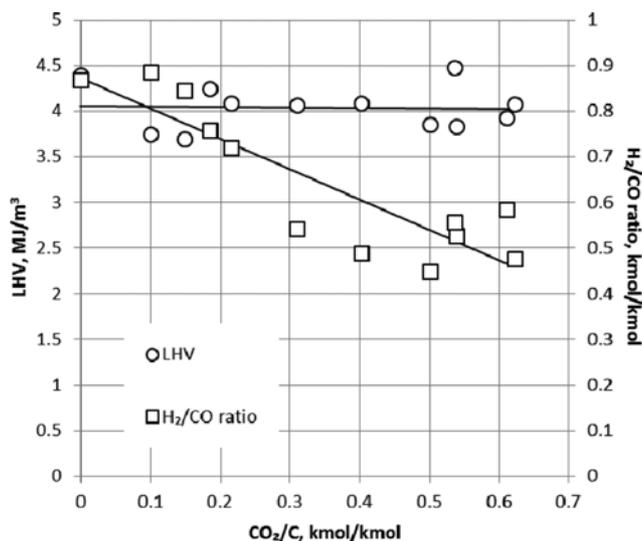


Fig. 8. Effect of the CO<sub>2</sub>/C ratio on the gas LHV and the H<sub>2</sub>/CO ratio.

$$\text{LHV} = \sum_i y_i \cdot \text{LHV}_i \quad (12)$$

where  $y_i$  - volume fraction of combustible gas component (unitless) and  $\text{LHV}_i$  - lower heating value of combustible gas component (MJ/m<sup>3</sup>).

## CONCLUSIONS

This paper has demonstrated the effect of adding carbon dioxide to the gasification agent for lignite gasification in a pilot-scale circulating fluidized bed gasifier. The increase in the CO yield was observed as the CO<sub>2</sub>/C ratio increased. The results show that the LHV of the process gas remains approximately constant, while the H<sub>2</sub>/CO ratio is adjusted as the CO<sub>2</sub>/C ratio increases. Considering all aspects, these results suggest that autothermal CO<sub>2</sub> gasification of lignite is possible and that it increases the CO yield. There are clearly some limitations to the study conducted. The pilot plant used during experiments was designed for air or oxygen gasification, while CO<sub>2</sub> gasification differs significantly. The CO<sub>2</sub> gasification reaction rates are much lower than those of the air or oxygen, and this aspect has significant influence on the process. Despite the fact that the pilot plant was by no means adapted to the new gasification agent, we managed to obtain promising results. Further potential application of the CO<sub>2</sub> gasification was demonstrated using the simplified thermodynamic model. In isothermal mode (with an external heat source), CO<sub>2</sub> gasification can be perceived as a potential carbon capture and utilization process. This scenario is particularly tempting if the heat is supplied from renewable sources.

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