

Kinetic aspects of coal gasification with CO₂ as a gasifying agent

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Introduction

Coals were basic raw materials providing the initial development of energy and chemical technologies. Coal, gradually replaced by crude oil and natural gas, practically lost its position as a chemical feedstock. In energy production coals are regarded as an inefficient fuel and responsible for degradation of environment, primarily the greenhouse effect.

Historically, it can be noted that the development of technologies for utilization of coals as raw materials for production of energy and chemicals was usually associated with a deficiency or absence of crude oil and natural gas. These deficiencies are a consequence of changes in economic and political relations between suppliers and customers of raw materials. The dynamic development of coal technologies in Germany during the Second World War was connected with the necessity of independence on crude oil import blocked by the Allies. After the war ended, the economic isolation of South Africa was driving force in the development of technology of coal gasification and liquefaction in this country. Created in the 50s of the last century company SASOL successfully implements the synthesis of motor fuels and chemicals from syngas generated by the coal gasification.

The energy crisis in the 70s of the last century associated with a significant increase in crude oil prices and the vision of the inevitable depletion of its reserves, initiated the process of finding alternative sources of raw materials for chemicals and energy production. The possibilities were not too wide, so coal returned again to favor. World economic leaders, possessing large resources of these raw materials, have started intensive research and development of coal liquefaction technology. Such work was carried out in the 80s of the last century in Poland under the PRL government program. Pilot plant with a capacity of 300 kg/day in Tychy/Wyry, who worked for the end of 1990, was the result of these advanced research [1].

The increased interest in coal technologies precisely corresponds to fluctuations in the situation on crude oil and natural gas market. Utilization of coal, however, entails a number of problems associated with environmental degradation and the greenhouse effect. Therefore, it was raised another requirement for technologies, which allow for the substitution of crude oil and natural gas: “clean” – Clean Coal Technologies (CCT).

Are there any opportunities for innovations?

Discussed above in brief stages progressively formed the basis for the implementation of NCBiR strategic program entitled: “Development of coal gasification technology for high-efficiency production of fuel and energy” [2]. In this project, the Scientific and Industrial Consortium “Coal gasification” built two pilot plants. One of them is the pilot plant with a pressurized reactor with circulating fluidized bed (CFB) for gasification of coal using carbon dioxide as gasifying agent [2, 3]. The installation was built at the Clean Coal Technology Centre at the Institute for Chemical Processing of Coal in Zabrze.

The technological concept generated in the project assumes the incorporation of CFB coal gasification reactor as an element of the

installation providing energy production in IGCC system or optionally methanol production (Fig. 1). The considered concept also provides oxygen combustion of unreacted char from the gasifier, allowing to increase the energy efficiency of the plant [4].

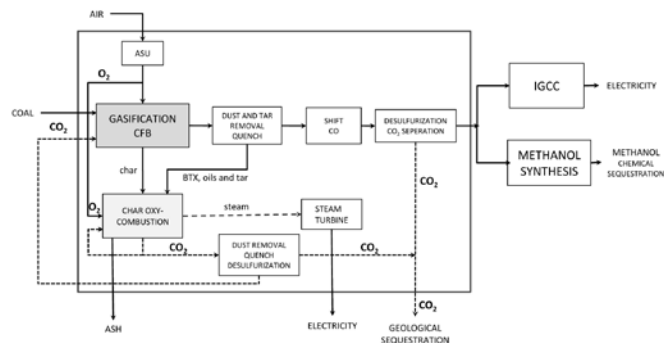
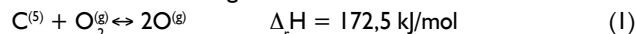


Fig. 1. The concept of coal gasification with CO₂ in a fluidized bed reactor to electricity and methanol production acc. [4]

In the proposed construction of CFB reactor, coal gasification with carbon dioxide plays special role. The complicated nature of pyrolysis and gasification processes causes the gasification kinetics is complicated due to interdependence of chemical reactions and physical phenomena. Therefore, under a part of the project implemented at the Silesian University of Technology, multidirectional studies on the kinetics of gasification process have been taken. These studies have focused on the selection of kinetic models describing the process of gasification and searching for relationships between the kinetic parameters designated on the basis of the experimental data obtained in different experimental conditions. The practical aim of the studies was to determine the kinetic constants for different raw materials, which were used as parameters for algorithms in software for simulation of reactors and processes.

Boudouard-Bell reaction

Interest in the equilibrium reaction of CO₂ reduction to carbon monoxide in the presence of carbon, called the Boudouard-Bell reaction (abbreviated B-B), was associated with its crucial role in the steel industry. The first studies were carried out in the half of the nineteenth century, by Deville and Bell [5]. In 1900, O. Boudouard published studies describing the endothermic reversible reaction:



Therefore, this reaction is often called the Boudouard-Bell reaction (abbreviated B-B).

The ability of coals to reaction with carbon dioxide (1) is known as a reactivity in chemical technology of coal. High reactivity is unfavorable property of cokes in the blast furnace process and for graphite products, because it increases their consumption in technological processes, weakens the internal structure, and – because of the endothermic reaction – lowers the temperature of the process. This adverse effect can also be observed in industrial processes of combustion of solid fuels, particularly coals. The ability of solid fuels to reaction with CO₂ decide on possible directions of their processing. The conversion of solid fuels to gaseous fuels by gasification of carbon carriers with carbon dioxide can be solution to the problems of growing demand for gaseous fuels

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and chemical raw materials, and provide an important answer for the protection of the environment by reducing CO₂ emissions [7, 8]. It seems obvious that low reactivity is desirable for the metallurgical cokes and graphite products but high reactivity for raw materials for gasification process.

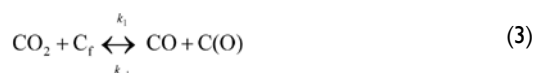
Carbon monoxide, as a product of reaction (1) can be used in many chemical syntheses, primarily for [9 – 14]:

- hydrogen production in CO shift (acronym WGS):
CO + H₂O = CO₂ + H₂ Δ_rH = -41,1 kJ/mol (2)
- Fischer-Tropsch synthesis for production of liquid motor fuels – the gasoline, diesel oil and other compounds and chemicals,
- methanol synthesis (1 mol CO + 2,2 mol H₂ + CO₂ addition),
- dimethyl ether synthesis DME,
- acetic acid synthesis,
- isocyanate production for the production of polyurethane foams,
- production of sodium formate by reaction with sodium hydroxide,
- PHB production (poly(3-hydroxybutyrate)), biopolymer for biodegradable packaging.

Carbon monoxide can also be used in catalytic processes with high environmental significance, ie. for reduction of nitrogen oxide in accordance with the reaction NO + CO = 1/2N₂ + CO₂ [15].

Kinetics of gasification reaction/process

In practice, it is very advantageous if reactivity of the fuels is closely related to the rate constant. It is generally accepted simplified, but technologically reasoned, mechanism to describe the kinetics of the reaction/process (1), which takes into account three rate constants [16]:



From a thermodynamic point of view, taking into account Le Chatelier-Braun rule (Δ_v = 2 - 1 = +1), increased pressure is a factor advancing the equilibrium of reaction (1) toward the substrates. Considering the mechanism (3) and (4) and characteristics of the various carbon carriers, the pressure may sometimes be a factor advantageously influencing the course of the reaction in direction of the products. As shown in [17], although thermodynamic limitations, conversion degree of carbon contained in the raw materials for gasification can be improved by increasing of pressure.

The course of heterogeneous reaction (1) is limited by many factors:

- thermodynamic factors (T, P, V),
- properties of the carbon carriers, due to the possibility of using coals, low and high metasedimentary chars, cokes, biomass (including wastes) and the presence of a mineral substance,
- method of solid sample preparation (grinding, porosity, initial thermal treatment) and implementation of the process (stationary, flow, fluidized bed).

Consequently, a number of kinetic equations describing reaction/process (1) were established. These equations may include changes only within a solid or gaseous phase or within both phases together. An intermediate complex of the carbon and oxygen remaining on the surface of the solid phase included in equations (3) and (4) as a C(O) is a factor impeding the clear and complementary approach the kinetics of reaction (1).

Laboratory studies on the gasification kinetics

The development of a simple methodology which allows to determine the parameters of kinetic models useful for simulation

purposes based on various micro- and small-scale measurement of gasification carried out under dynamic and isothermal (*quasi-isothermal*) was assumption of the studies. As a result, the numerous kinetic models based on thermal transformation of model substances (mainly CaCO₃) have been verified. The kinetic parameters of the gasification reaction for coals and chars were determined based on classical methods, as well as on the basis of own concept, so-called Finite Elements Method (finite time). It has been proved that the classic methods for determining kinetic parameters suite for reactions of simple substances, while in case of complex substances the results are too divergent. The proposed finite element method produces satisfactory results, allowing comparison of kinetic constants designated in dynamic and isothermal conditions. However, achieving complete or high (at least 50%) conversion degree of substrates in experimental conditions is a condition for compatibility results. The results were described detailed in published own works [18 – 22] and sent to the editor [23].

Three coals were selected for kinetic studies in the project: coal from Wieczorek and Janina mine, Bełchatów lignite mine and chars from these coals. Chars were prepared by pyrolysis of coals at 600 and 900°C in Karbotest equipment. The properties of coals and chars are shown in Table 1.

Table 1

Proximate analysis of coals and chars selected to kinetic studies

Sample	W ^a , %	A ^a , %	V ^a , %	V ^d , %	A ^d , %	V ^{daf} , %	C _{fix} ^a , %
Coal Janina	12.00	9.84	31.24	35.50	11.18	39.97	46.92
Char J-600	3.35	14.34	6.83	7.07	14.84	8.30	75.48
Char J-900	4.22	15.12	2.72	2.84	15.79	3.37	77.94
Coal Wieczorek	2.38	17.08	30.51	31.25	17.50	37.88	50.03
Char W-600	2.24	25.52	5.16	5.28	26.10	7.14	67.08
Char W-900	1.40	25.54	0.75	0.76	25.90	1.03	72.31
Coal Bełchatów	12.02	21.70	41.12	46.74	24.66	62.04	25.16
Char B-600	2.06	37.29	9.06	9.25	38.07	14.94	51.59
Char B-900	1.90	41.28	1.88	1.92	42.08	3.31	54.94

The values of the kinetic parameters, i.e. activation energy (E) and preexponential factor (A) in the Arrhenius equation were determined based on the results of gasification of selected coals and chars with CO₂ carried out by various laboratory tests for samples with different weights.

The kinetic parameters determined on the basis of studies carried out in apparatus for determining the reactivity by the Geneva method are presented in Table 2. The sample mass was approx. 10 g, particle size of 0.315-0.5 mm, and the CO₂ flow of 180 cm³/min. Gasification processes was carried out at temperatures of 850, 900 and 950°C. The kinetic parameters E and A were determined for the three models: VM (volumetric model):

$$\frac{dx}{d\tau} = k_{VM} \cdot (1 - x) \quad (5)$$

GM (grain model):

$$\frac{dx}{d\tau} = k_{GM} \cdot (1 - x)^2 \quad (6)$$

RPM (random pore model):

$$\frac{dx}{d\tau} = k_{RPM} (1 - x) \sqrt{1 - \Psi \ln(1 - x)} \quad (7)$$

where Ψ is an experimentally determined structural parameter.

Table 2

Kinetic parameters of the B-B reaction determined on the basis of studies in the apparatus for the reactivity determination by Geneva method

Parameter	Sample					
	B-600	B-900	J-600	J-900	J-600	J-900
VM Model						
E, kJ/mol	57.02	251.69	176.16	217.36	140.73	199.39
A, l/min	1.799E+00	1.195E+09	2.636E+05	1.420E+07	5.187E+03	1.865E+06
r ²	0.5820	0.8926	0.9227	0.9986	0.9999	0.9906
GM Model						
E, kJ/mol	57.76	179.06	150.89	171.16	144.86	171.82
A, l/min	1.399E+00	3.785E+05	1.241E+04	7.179E+04	4.962E+03	7.040E+04
r ²	0.5646	0.8930	0.9939	1.0000	0.9996	0.9894
RPM Model						
E, kJ/mol	57.35	206.26	154.00	186.30	143.48	178.01
A, l/min	1.135E+00	5.731E+06	1.514E+04	3.079E+05	3.800E+03	1.171E+05
r ²	0.5634	0.8840	0.9794	0.9993	1.0000	0.9900

Table 3 summarizes the kinetic parameters E and A for tested materials designated by finite element method based on the formula:

$$-\ln \tau = \ln A - \frac{E}{RT_f} \quad (8)$$

Gasification tests were carried out in MOM Q-1500D under isothermal conditions at temperatures 850, 900 and 950°C. The sample mass was 100 mg and CO₂ flow of 180 cm³/min. The relationship between time of gasification process τ as a function of the inverse of the isothermal temperature for tested samples of coals and chars is presented in Figure 2.

Table 3

Kinetic parameters of the gasification process with CO₂ for examined materials calculated by finite element method

Sample	E, kJ/mol	A, l/min	r ²
Coal Bełchatów	80.11	6.637E+01	0.9275
Char B-600	47.71	3.693E+00	0.9846
Char B-900	59.08	8.369E+00	0.9132
Coal Janina	142.75	2.084E+04	0.9981
Char J-600	162.05	8.128E+04	0.9826
Char J-900	118.64	7.643E+02	0.9936
Coal Wieczorek	116.37	6.195E+02	0.9527
Char W-600	68.71	3.730E+00	0.9465
Char W-900	79.75	1.258E+01	0.9981

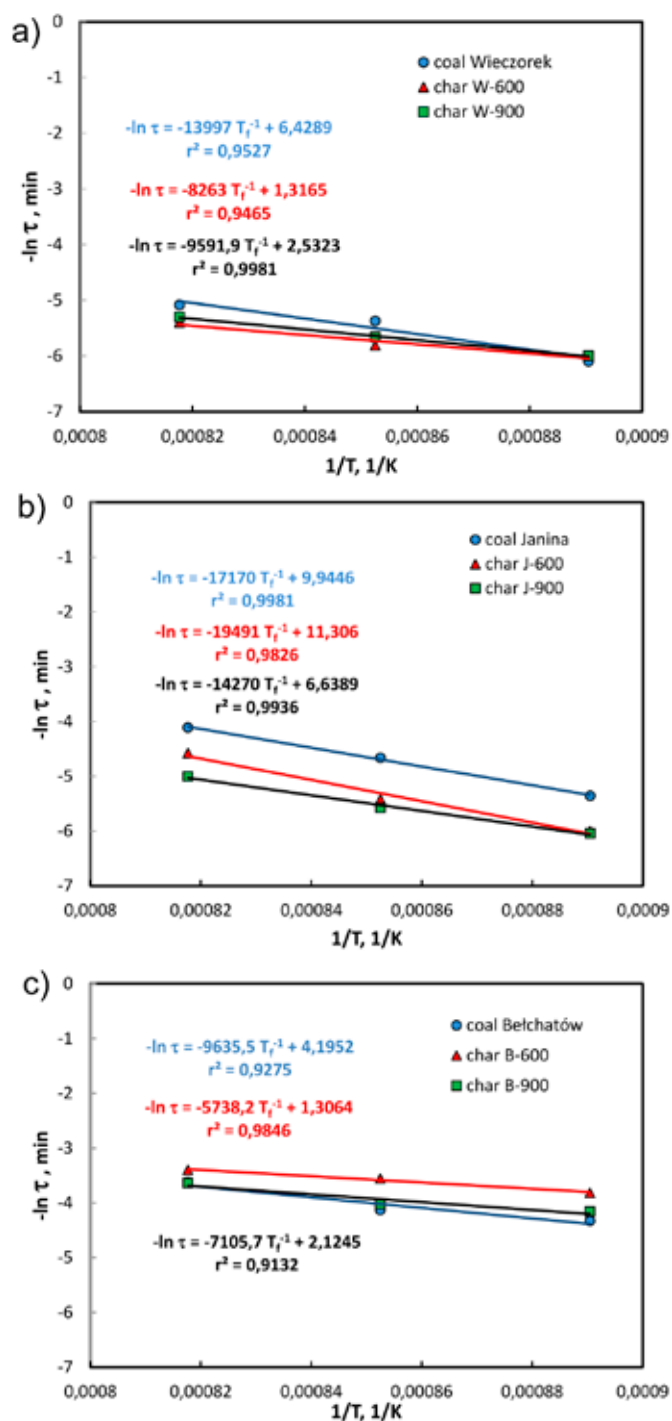


Fig. 2. Time of the gasification process τ as a function of inverse of the isothermal temperature for tested samples of coals and chars

The kinetic parameters determined on the basis of tests performed in a prototype reactor for the determination of fuel reactivity, built in Institute for Chemical Processing of Coal in Zabrze, are summarized in Table 4. Studies on the chars were carried out under isothermal conditions at three temperatures (850, 900 and 950°) and three different pressures: 0.1; 0.6 and 1.1 MPa. The sample mass was approx. 500 mg, and the CO₂ flow: 600 cm³/min. During the measurements it was not possible to record on-line weight changes gasified samples. The precise profile of gas flow volume and analysis of the gas composition at the outlet of the reactor allowed for precise balance of carbon (based on the method presented in [24]), which allowed to determine conversion degree x and calculate the kinetic parameters E and A acc. to model (5)-(7).

Even a cursory analysis of the data presented in Tables 2-4 allows to observe a significant difference of the kinetic parameters. It was applied own procedure to verify the kinetic parameters designated by various laboratory methods. Figure 3 presents own experimental data (points) and literature data (lines) in the coordinate system (8).

Adopted coordinate system can be regarded as a kind of analogy to the relationship, known as the Arrhenius plot: $\ln A$ vs. $1/T$, therefore slopes of the lines allow to determine the activation energy. It can be noted that the experimental points and corresponding values of the activation energy, are arranged practically between isolines and refer to the gasification process in the kinetic area $E > 0$. In the vicinity of the coordinate "P" transition to the diffusion area occurs $E \rightarrow 0$, characteristic for the high temperatures.

Table 4

Kinetic parameters determined for gasification of chars with CO_2 in elevated pressures

Sample	Pressure, MPa	Model	E w kJ/mol			A, min ⁻¹			r ²		
			0.1	0.6	1.1	0.1	0.6	1.1	0.1	0.6	1.1
char Belchatów 900	Kinetic model	VM	119.43	157.00	113.52	1.40E+04	6.71E+05	7.29E+03	0.9097	0.9993	0.9991
		GM	110.77	142.52	104.70	3.79E+03	9.92E+04	1.96E+03	0.9598	0.9992	0.9869
		RPM	115.67	142.03	106.73	4.89E+03	7.77E+04	1.92E+03	0.9715	1.0000	0.9990
char Janina 900	Kinetic model	VM	237.28	179.77	120.25	6.24E+08	1.74E+06	4.57E+03	0.9994	0.9982	0.9861
		GM	214.84	159.99	107.88	5.36E+07	1.96E+05	1.11E+03	0.9952	0.9998	0.9652
		RPM	181.51	140.21	91.71	1.42E+06	2.14E+04	1.72E+02	0.9704	0.9961	0.8810
char Wieszorek 900	Kinetic model	VM	197.65	184.23	188.80	5.89E+06	1.87E+06	3.32E+06	0.9795	0.9893	0.9679
		GM	195.41	160.12	164.19	3.29E+06	1.20E+05	2.08E+05	0.9997	0.9941	0.9752
		RPM	194.66	74.03	88.00	2.38E+06	1.13E+01	5.74E+01	0.8444	0.5318	0.3874

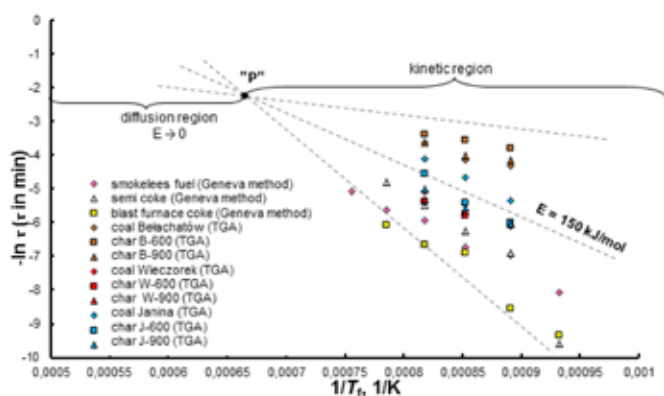


Fig. 3. Own experimental data (points) and literature data (isolines) in the coordinate system - $\ln A$ vs. $1/T_f$

Placement of calculated kinetic parameters in the coordinate system $\ln A$ vs. E (Fig. 4) defines isokinetic effect, known by the acronym KCE (Kinetic Compensation Effect). Presented example indicates that, although the various laboratory techniques, sample mass and kinetic models, the kinetic compensation effect (KCE) may provide the test to verify correctness of obtained results.

The coordinate according to the literature [25] calculated for the 1st-order kinetics in the fluidized bed reactor (FBR) is indicated in Figure 4. Compatibility of prediction of kinetic parameters is surprisingly good, although it concerns the experiment carried out in completely different conditions.

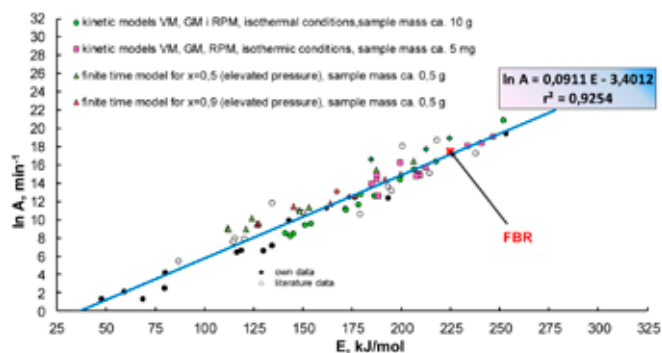


Fig. 4. KCE determined on the basis of own data and literature data with additional point representing the gasification in fluidized bed [25]

Evaluation of different measuring techniques for the determination of kinetic parameters

The performed theoretical considerations, as well as a number of experiments made by various measurement techniques and for different sample mass, allowed to collect many experiences. The observations can be helpful in the future in planning and implementing research on gasification of carbon carriers, in particular with carbon dioxide.

Thermogravimetric analysis

Thermogravimetric analysis under isothermal conditions is the easiest and fastest method, which allows to evaluate the gasification process. Based on changing the sample weight as a function of time the rate constant k can be determined by using the verified kinetic models for this process: VM, MVM, GM, and RPM. For studies carried out for at least three different temperatures it is possible to determine the activation energy E and preexponential factor A from Arrhenius relation.

The possibility of studies on fuels with different carbon content is an important advantage of the thermogravimetric method – in particular coal and biomass – the raw materials with a high content of volatile matter. However, in this case simultaneously coupled analysis of gaseous products is not recommended because heavy volatile products (tar products) may cause clogging of transfer lines and damage gas analyzers. Moreover, when interpreting the results it should be remembered that the initial stage of gasification is usually disturbed by the pyrolysis process. Amount of such disorders will be proportional to the amount of volatile matter.

In the case of analysis of char samples with low volatile content, a quantitative analysis gaseous products can be used and the procedure of determining the rate constants of formation and disappearance of activated complex (3) and desorption of CO_2 according to (4) can be applied.

Analysis in apparatus for reactivity determination by the Geneva method

Laboratory apparatus for determining the reactivity of cokes by the Geneva method after modifications also provides extensive research capabilities. In order to obtain valuable data, the apparatus should allow gas sampling or on-line analysis of gas leaving reactor, as well as continuous measurement of the reactor weight. This apparatus allows the analysis of carbon carrier samples of weight up to 10g. The integration with gas analyzer allows assessment of the gasification process based on analysis of the gaseous phase and determination of the rate constants of formation and disappearance of activated complex (3) and desorption of CO_2 according to (4).

Modification of the apparatus allowing to register changes in the mass of the reactor, due to technical difficulties, give moderately accurate results. The "start-stop" method is an alternative to on-line

measurements. It involves the repetition of the gasification process for the samples of exactly the same initial weight ("start" mass) for different times of the process. After the scheduled time of the gasification, measuring retort is rapidly cooled down to ambient temperature under a stream of nitrogen and then final weight of the sample is determined ("stop" mass). This creates a discreet dependence of the sample mass and the time for established temperature. The resulting relationship allows to use the procedures for determination of the kinetic parameters of gasification process based on changes in solid phase.

Analysis of gasification process in apparatus for reactivity determination in elevated pressures

The prototype reactor for determining reactivity of fuels in elevated pressures allows to very precise analysis of the gasification process. Analyzer installed at the output of volatile products reflects very accurately changes in the content of CO and CO₂ in the exhaust gas. This allows to use the procedure for determining the rate constants of formation and disappearance of activated complex (3) and CO₂ desorption process acc. to (4). Precise measurement of gasification agents flow allows for balancing of reagents and tracking carbon conversion in the sample through the balance equations. It makes possible to estimate changes in weight of the sample and using models for the solid phase – to determine the rate constants. Performing analyzes for at least three temperature allows to determine the activation energy and preexponential factor in the Arrhenius equation.

Unfortunately limit related to the content of volatile components in the tested samples is weakness of the presented method. Generating a "heavy" volatile products resulting from the pyrolysis process, restricts use of the method only for samples with volatile matter content of no more than 2%.

The relationship between laboratory tests and gasification process in pilot plant

The possibility of verifying the results obtained in laboratory tests with gasification in pilot plant was considered in the project. In retrospect, it has to be admitted that such assumption was too optimistic.

In case of laboratory tests (micro and small-scale), the gasification process is carried out in a fixed deposit with the flowing gaseous phase. In the fluidized-bed reactors, in which gasification process will be ultimately realized, two phases are mobile. This results that conditions associated with the processes are not comparable: heat and mass exchange, streams, the residence time of the grains of the raw material in the reactor, composition of gasifying agents etc.

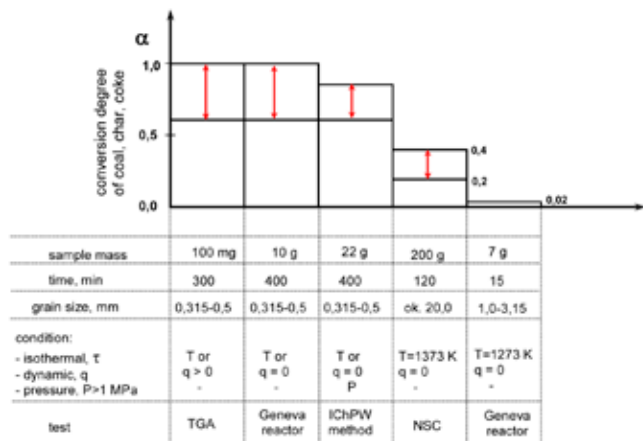


Fig. 5. The comparison of laboratory test conditions used in studies on the B-B reaction (1)

To illustrate the above problem, basic differences in the conditions of the laboratory tests used in studying the reaction of

B-B (1) are presented (Fig. 5). Studies on kinetics of the process require to achieve an appropriate conversion degree (preferably the highest). Taking into account that the gasification process acc. to (1) is strongly dependent on the temperature and the reactivity of the raw material, long tests carried out at high temperatures are preferred. On the other hand, confrontation of micro- and small-scale laboratory tests with large scale tests (Fig. 6) indicates scale of difficulties for direct comparison of results. In the case of gasification time – for the fluidized bed reactor gasification is counted in seconds, while for laboratory tests in minutes and hours.

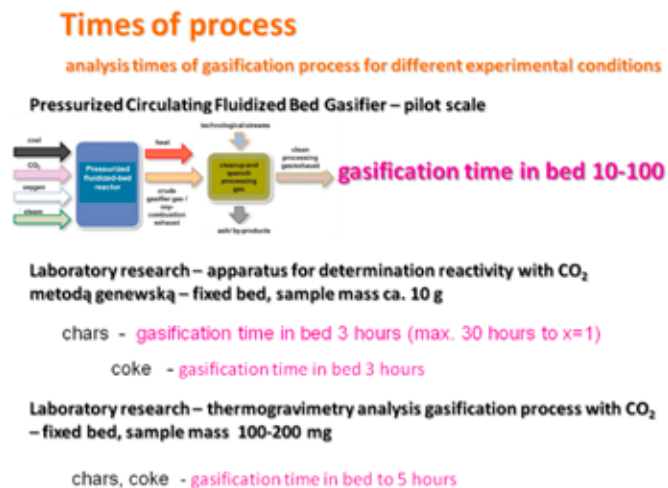


Fig. 6. The comparison of time of the process in pilot scale with laboratory studies on the kinetics of gasification

Conclusions

1. Based on the experience gained during the project it can be stated that thermogravimetric methods are most suitable for the quick assessment of raw materials and gasification processes and for determination of kinetic parameters based on models of changes in the solid phase.
2. It is not possible direct and simple verification of kinetic parameters determined on the basis of laboratory tests and gasification in pilot plant in circulating fluidized bed reactor in elevated pressures. The kinetic constants determined for the different materials in laboratory measurements can be used as parameters in the algorithms in simulation software (ChemCAD, Barracuda). Numerically determined parameters in the fluidized bed reactor for established raw materials (exhaust gas composition, efficiency of the process, temperatures, etc.) can be compared with the parameters obtained in the pilot plant. Thus, the verification of determined parameters can only be indirect. It should be noted that the kinetic constants are only one of the many parameters for computer simulation programs, and its accuracy is not necessarily reflected in compliance model with achieved operating parameters of the gasification reactor in pilot plant.

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Symbols

- A – ash content (proximate analysis), %
- A – preexponential factor in Arrhenius equation, 1/s, 1/min or dimensionless
- C_{fix} – fixed carbon (proximate analysis), %
- E – activation energy, J/mol

$\Delta_r H$ – enthalpy of reaction, J/mol
 k – reaction rate constant, 1/s or 1/min
 Δv – the sum of stoichiometric coefficients of gaseous products,
 P – pressure, MPa
 R – gas constant, $R = 8,314 \text{ J}/(\text{mol}\cdot\text{K})$
 r^2 – determination coefficient, $0 \leq r^2 \leq 1$
 T – temperature of the reaction/process, K
 V – volatile matter content in sample (proximate analysis), %
 V – volume, m^3
 W – moisture content in sample (proximate analysis), %
 Ψ – structural parameter in RPM model
 x – conversion degree of solid phase, $0 \leq x \leq 1$
 τ – time, s

Superscripts:

a – analytical state (air-dry),
 d – dry state,
 daf – dry ash-free state.

Shortcuts (acronyms):

ASU – air separation unit
 CFB – circulating fluidized bed
 FBR – fluidized bed reactor
 GM – grain model
 IGCC – integrated gasification combined cycle
 KCE – kinetic compensation effect
 MVM – modified volumetric model
 RPM – random pore model
 SCM – shrinking-core model
 VM – volumetric model
 WGS – water gas shift.

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