

KINETICS OF Fe-CATALYZED GASIFICATION OF CHARs FROM LIGNITE ADMIXTURES

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ABSTRACT

Measurements of the gasification rate of char from lignite with admixtures by steam or CO₂ showed that the admixtures of polymers, celluloses and wood reduce reactivity of resulting char. The decrease of reactivity significantly manifests itself at both 800 °C and 900 °C. This is caused mainly by lower inner surface area which resists the gasification reactions. This negative phenomenon can be compensated by addition of magnetite, which acts as Fe-catalyst of the reactions of char with steam as well as CO₂ and accelerates the gasification. Through the isoconversional analysis, it was proven that the presence of magnetite significantly lowers the effective activation energy of these reactions, thus accelerating their course. The measurements of the reaction rate showed that it leads to a two- or three-fold acceleration of gasification.

KEYWORDS: gasification, polymers, magnetite, kinetics

INTRODUCTION

The utilization of waste polymers is still a topical issue. For example, in the case of waste rubber a number of studies is devoted to its treatment, especially thermal (Murillo et al., 2006; Ucar et al., 2005), to the process conditions (Straka and Bučko, 2009), the products (Kříž et al., 2008; Troca-Torrado et al., 2011) as well as a description of the behavior of this material in pyrolysis (Rodriguez et al., 2001; Unapumnuk et al., 2006) and gasification (Leung and Wang, 2003), and reactions of char (Murillo et al., 2004). According to other works (Evans et al., 2001; Koukouzas et al., 2008) it seems that a realistic solution of thermal treatment of waste plastics could be the co-gasification with lignite in the Integrated Gasification Combined Cycle. In the case of waste rubber the recent experiments in the laboratory but predominantly commercial scale (Straka and Bučko, 2009) have demonstrated that it can without any technological difficulties thus be gasified at a content of 10-20 % in a gasified mixture. Higher content however causes an increase in the unburned carbon, whose content in generator ash grows significantly with the rising share of rubber in the mixture. The reason is apparently the significant difference between the reactivities of the lignite and lignite/rubber char in the gasification zone of the generator, where the reactivity of the lignite/rubber char is low in comparison with the reactivity of the lignite char. The removal of the negative phenomenon of the unburned carbon would contribute to the more effective treatment of waste rubber, avert the losses of energy

inserted into the process, improve the quality of the ash for its further use and facilitate the maintenance of the generator ash disposal site. From the environmental perspective, the possibility to treat greater volumes of waste rubber (e.g. waste-tire) than before is significant, whereas from the economic perspective it is important to avert energy losses.

As our preliminary experiments showed that the admixtures of polymers, celluloses and wood to lignite reduce reactivity of resulting char, it seems that the key question is a difference between the reactivities of the char from lignite and those from the lignite/polymers or lignite/celluloses mixtures in the gasification zone of the generator, where the reactivity of latter char can be low or significantly lower in comparison with the reactivity of the lignite char. A possible approach is to find the effective catalyst of the gasification reactions. Alkali metal salts, especially potassium salts, including those present in a high content potassium biomass, are considered as effective catalysts for gasification by steam and CO₂ (Zhu et al., 2008). The most recently tested catalyst requires coal modified by a solvent extraction (HyperCoal), because this catalyst reacts with the mineral components of the coal (Sharma and Takanoashi, 2010). It is, however, an unfeasible variant for the given case. According to our experience with the Lurgi gasification process, it is possible to consider iron-based catalysts, which are effective, available and industrially used. Thus, investigation of treatment of waste polymers by co-gasification can be conducted through determination

Table 1 Analyses of the Jiri lignite. O_d-by difference, a.r.-as received.

Jiri lignite	Proximate analysis			Ultimate analysis (d.a.f.)				
	Moisture (a.r.)	Ash (db)	VM (daf)	C	H	N	S _o	O _d
wt. %	5.55	7.64	50.72	75.03	4.81	1.22	0.43	18.50

Table 2 Proximate analyses of chars (without magnetite). SBR-styrene butadiene rubber, ABS-acrylonitrile butadiene styrene, PP-polypropylene, PE-polyethylene.

Char no.	Initial admixture (wt. %)	Proximate analysis (wt. %)		
		Moisture (a.r.)	Ash (db)	VM (daf)
1	Jiri lignite (no admixture)	4.30	15.18	4.19
2	SBR (50 %)	3.06	11.11	3.79
3	ABS (30 %)	2.91	17.42	3.89
4	PP (30 %)	2.26	14.95	4.91
5	Nylon 6 (30 %)	3.09	13.95	7.30
6	Methylcellulose (30 %)	4.73	14.75	6.66
7	Wood (50 %)	1.69	15.70	3.27
8	Cellulose (30 %)	2.17	15.58	2.82
9	PE (30 %)	2.81	14.52	3.81

of reactivities of the char from lignite and chars from the lignite/polymers or lignite/celluloses mixtures and testing of suitable Fe-catalyst.

As Fe-catalyst a finely ground magnetite was selected for the laboratory tests. The experiments were conceived so that the chars from lignite and admixtures without magnetite and with magnetite were prepared first in a rotary kiln. They served for the more general determination of the impact of magnetite on the rate of the gasification reactions. The prepared chars were then gasified by steam and CO₂ and the rates of gasification measured at isothermal conditions. With char from lignite and styrene butadiene rubber (1:1) mixture, the effective activation energy and pre-exponential factor of the gasifying reaction with CO₂ were further evaluated using non-isothermal isoconversional kinetics, and these parameters were compared for the samples with and without magnetite. With this char the catalytic effect of magnetite was quite typical and demonstrative.

The objective of the work is to describe the effect of magnetite on the rate of the gasification of the chars from the mixtures of lignite and polymers or celluloses and explain the impact of magnetite on the basis of non-isothermal isoconversional kinetics.

MATERIALS AND METHODS

Materials. Chars from the mixtures of lignite with polymers, celluloses and wood were used for the experiments. The lignite came from the Jiri Mine (Table 1), the Sokolov Basin, Czech Rep., styrene

butadiene rubber (SBR) was supplied by Pneucentrum Tasy S.R.O., Czech Rep. Further, the acrylonitrile butadiene styrene (ABS) polymer, polypropylene (PP) and polyethylene (PE), Nylon 6, methyl cellulose and cellulose (Sigma Aldrich) were used. Used industrial wood was magnetically cleaned (Žezulka, 2010). As catalyst, the finely ground magnetite (under 5 microns, 98 %, Sigma Aldrich) was tested.

The preparation of the chars was conducted in a tilted rotary kiln with a retort of stainless steel with a length of 690 mm, with an inner diameter of 60 mm. The heating of the kiln was provided by three independently regulated heating sections, each with a wattage of 1 kW. The retort rotation speed was 5 rpm with a retort inclination of 3°, fed by a screw feeder at about 100-150 g.h⁻¹. At a temperature of 900 °C, 200 g of the sample was always pyrolyzed under slight overpressure of own atmosphere to avoid the oxidation by the external air. The chars from lignite alone and from mixtures of lignite with polymers, celluloses and wood, and the similar mixtures with 5 % magnetite were prepared in this way. Admixtures and their contents in the initial mixtures were as follows: SBR-50 %, ABS polymer-30 %, PP-30 %, Nylon 6-30% and PE-30 %; cellulose - 30 %, methylcellulose - 30 %, and wood-50 %. These were the maximum amounts possible while maintaining the smooth running of the rotary kiln during chars preparation. The yield of char was always around 50 %. The proximate analyses of prepared chars (without magnetite) are in Table 2.

Table 3 The gasification rate (w) of chars (without magnetite) by steam and CO₂ at temperatures of 800 and 900 °C. See Table 2 for symbols.

Char no.	Initial admixture	w (wt.%.min ⁻¹)		w (wt.%.min ⁻¹)	
		at 800 °C		at 900 °C	
		H ₂ O(g)	CO ₂	H ₂ O(g)	CO ₂
2	SBR (50 %)	2.94	0.33	4.98	2.65
3	ABS (30 %)	4.49	0.34	16.10	6.02
4	PP (30 %)	4.85	1.05	19.01	5.11
5	Nylon 6 (30 %)	5.54	1.17	18.07	5.46
6	Methylcellulose (30 %)	5.64	1.22	14.95	4.71
7	Wood (50 %)	5.98	1.30	19.86	-
8	Cellulose (30 %)	7.68	1.34	19.28	6.60
1	Jiri lignite (100 %)	8.01	1.44	18.00	5.67
9	PE (30 %)	9.40	1.49	18.37	5.42

Methods. With chars, the gasification rate (w) by steam and CO₂ was measured in the isothermal mode at temperatures of 800 and 900 °C. The rate of gasification was characterized by the percentage mass loss per minute. The measurements were conducted on the MOM thermal analyzer (MOM Comp., Budapest, Hungary) with electronics and software from TERI S.R.O., Prague, Czech Republic, adapted for a sample mass of 50-100 mg. The samples with a grain size of around 0.2 mm were heated in the inert atmosphere of nitrogen to temperature of 800 or 900 °C and after reaching it were dosed with 250 ml.min⁻¹ of CO₂ or steam. From the moment of this dosage, the relative decrease of the mass of the sample was measured for the period of the linear decrease of the thermogravimetric curve. The mass of the sample at the moment of the beginning of the dosage of the gasification medium was taken as 100 %. For measurements, it was taken into account that the gasification rate as the measure of reactivity must be measured and evaluated at the initial phase of the gasification reaction, because the reactivity of the char decreases with the continuing course of the reaction. Therefore, to compare the reactivities of various chars, it was necessary to compare them at the initial stages of the reaction.

Since the reduction of the effective activation energy of the gasification reaction through the activity of the catalyst is important for the assessment of the catalyst's efficiency, samples of lignite/SBR without magnetite and with magnetite were further examined. Experimental data were obtained by thermogravimetric method. The samples of 10-12 mg with the grain size around 0.2 mm were tested; CO₂ with a flow rate of 12 ml.min⁻¹ was used as the gasification medium. The thermogravimetric curves of the samples with the heating rates of 7, 10 and 12 K.min⁻¹ in the temperature range of 500-1100 °C were obtained and the courses of the effective activation energy and of the pre-exponential factor for the conversion of 10-90 % were evaluated. For the calculation of the

effective activation energy and the pre-exponential factor, the method of non-isothermal isoconversional analysis was selected. The thermogravimetric runs were procured on the SETARAM Setsys Evolution 18 analyzer; the AKTS Thermokinetics software, version 2.56, was used for the evaluation of the mentioned kinetic parameters.

The Raman spectra of the chars were measured by Jobin Yvon LabRam HR Raman dispersion spectrometer equipped with an Olympus confocal microscope. A laser with a wavelength of 532.2 nm and an input wattage of 50 mW served as the excitation source. The samples were measured because of the possible thermal destruction of the sample at a wattage of 5 mW, with the measurement time being 10 sec and with 30 spectra accumulations. A grating with 600 lines/mm, a split of 100, and a hole of 1000 was used. A multichannel air-cooled CCD camera served as the detector. A sample was applied without preliminary modifications on a shiny steel plate and measured with a microscope at a magnification of 50x. The measuring trace had a diameter of ca 2 micrometers. The separation of the bands in the spectrum was conducted with the Omnic 7.3 program. The spectra obtained in the region of 800-1800 cm⁻¹ were separated into four bands: at 1050-1270 cm⁻¹ (sp³-band), 1350 cm⁻¹ (disorder-, D-band), 1515-1560 cm⁻¹ (amorphous C-band) and 1590 cm⁻¹ (graphite-, G-band). As the G and D bands were of Lorentzian type they were fitted using a Lorentzian function while for the two other bands a Gaussian function was used due to their Gaussian peak type (Schwan et al., 1996).

The inner surface of chars was determined by BET method as the S_{BET} values on Sorptomatic 1990 instrument (Thermo Electron Corp.). Simultaneously, indication of iodine number by the standard test method was carried out. (The amount of iodine absorbed (in mg) by 1 g of activated carbon, e.g. char, using test conditions is called the iodine number. In our case, it was a relative indicator of porosity in

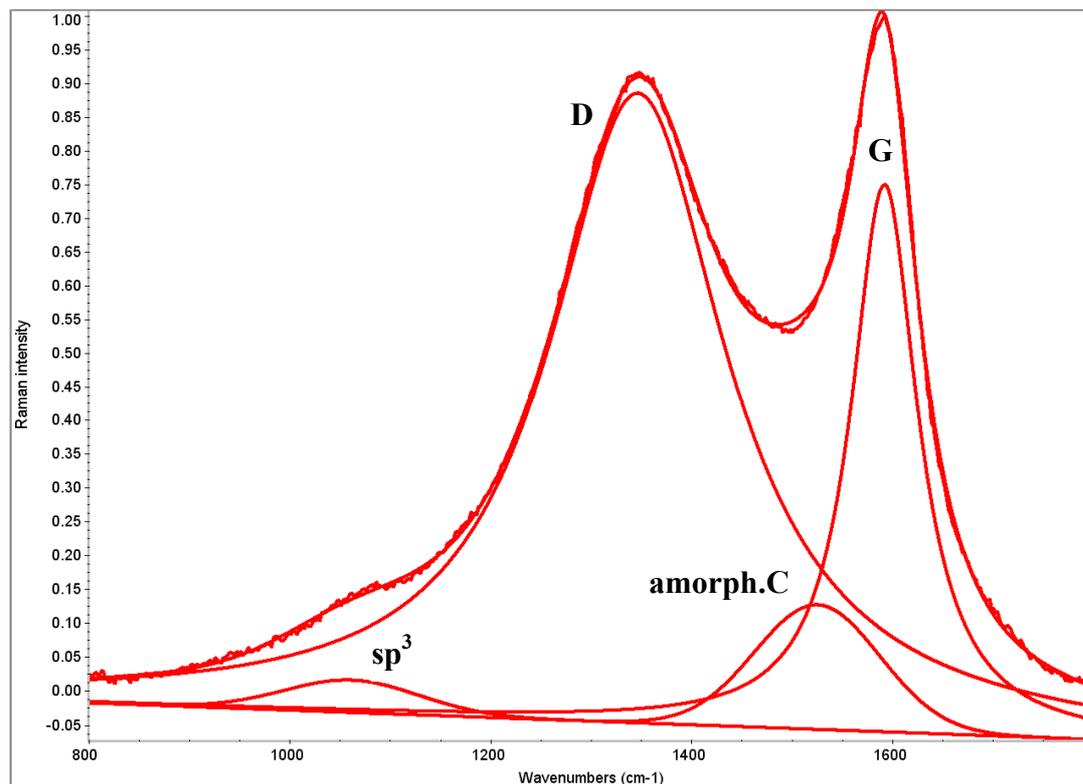


Fig. 1 The Raman spectrum of char from the lignite/polypropylene mixture (70:30) as typical spectrum of chars from lignite admixtures, and its deconvolution.

chars, generally, the iodine number represents an approximation of surface area for some types of activated carbons.)

RESULTS AND DISCUSSION

Firstly, with chars the rate of gasification (w) by steam and CO_2 was measured in the isothermal mode at temperatures of 800 and 900 °C. These measurements served to assess an influence of polymers or celluloses admixtures of lignite in the gasification rate of resulting chars. The results of the measurement are summarized in Table 3. From this table, the differences in the gasification rates of the char from lignite alone (no. 1) and from mixtures in question (nos. 2-9) are evident. It further arises from the data in Table 3 that the admixtures reduce the reactivity of the chars at 800 °C in comparison with the char from lignite alone. An exception was the 30 %-admixture of PE, which on the other hand increased the reactivity of the resulting char (no. 9), although only slightly in the case of gasification with CO_2 . Contrary, at 900 °C, the rates of gasification both by steam and CO_2 were quite similar, with the exception of the char from lignite/SBR mixture (no. 2).

The reason of these phenomena can be both different chemical structure of chars and the diversity of porous texture of them. Therefore, an explanation of these phenomena might be provided by the Raman

spectra and the inner surface area measurements of chars in question. The chars contained mainly relatively high percentages of disordered carbon structures, which was reflected in the Raman spectra as a wide band at a wavenumber of 1350 cm^{-1} (disorder band, D-band), whereas the band at 1590 cm^{-1} (graphitic band, G-band) is narrower. Typical spectrum of examined chars is in Figure 1. By analyzing the Raman spectra taken it was found that a) after deconvolution (Fig. 1), in all the cases, spectra provided four bands belonging to different forms of carbon, b) within the investigated chars the Raman spectra were not very different.

According to (Sekine et al., 2006) the contents of the various types of carbon structures affect the reactivity of chars, but the question is what is decisive for their reactivity whether the chemical structure or porous texture. A rough explanation can be provided by the quantitative evaluation of Raman spectra of chars after deconvolution (Table 4). The chars mostly contain relatively high shares of disordered carbon structures (D-values, Table 4), whereas shares of the ordered structures (G-values, Table 4) are lower. It can be expected with the carbonaceous structures that the disordered, more hydrogenated structures will be more reactive than the ordered, more aromatized structures. In the tested chars the ratio of the areas of these bands (D/G) was 2.8-3.4. It means that the ratios of the disordered, more reactive structures to the more

Table 4 The areas of the bands from the Raman spectra of the chars. D-band (disorder-band), G-band (graphite band), sp^3 and amorphous carbon bands.

Char no. (initial admixture)	D (1350 cm^{-1})	G (1590 cm^{-1})	D/G	Band sp^3 (1050-1270 cm^{-1})	Amorphous C (1515-1560 cm^{-1})
1 (Jiri lignite, -)	313.30	92.73	3.38	7.36	31.04
2 (SBR, 50 %)	319.05	96.69	3.30	16.64	27.92
4 (PP, 30 %)	311.60	102.10	3.05	8.10	28.88
5 (Nylon 6, 30 %)	311.16	103.71	3.00	5.13	21.05
7 (Wood, 50 %)	247.27	88.08	2.81	18.96	22.53
8 (Cellulose, 30 %)	312.46	93.45	3.34	10.19	31.86

ordered, less reactive structures are quite comparable. Moreover, no significant differences in the acquired Raman spectra in the area of the band at 1050-1270 cm^{-1} (Table 4) were observed. This band belongs to sp^3 bonds, which were observed in relatively small amounts with the investigated chars. On the other hand, the sp^3 band is also important for our considerations as increasing amounts of sp^3 bonds may cause changes in the char reactivity. For example, in the case of char from rubber alone it was found that an increased amount of these bonds caused a significant reduction of char reactivity. Another band was observed at 1515-1560 cm^{-1} and was attributed to amorphous carbon and hydrogenated amorphous carbon. This form of carbon is created in the pyrolysis of brown coal and carbon-containing materials (Li X. et al., 2006) and in the given case its content in the observed chars was quite similar as is evidenced by the areas of the bands shown in Table 4. The amorphous carbon has thus influenced the reactivity of the observed chars roughly in the same way. From these data it is clear that the reactivities found must be caused by yet another factor. Therefore, the inner surface of chosen chars was investigated through the S_{BET} values and iodine numbers.

It was found that in the case of char from lignite/cellulose mixture (no. 8) the specific surface area S_{BET} was 228.64 $m^2.g^{-1}$, contrary, in the case of char from lignite/PP mixture (no.4) S_{BET} was significantly lower, 31.86 $m^2.g^{-1}$. Iodine numbers were of 203.5 $mg.g^{-1}$ for char no. 8 and only 150.3 $mg.g^{-1}$ for char no.4. Correspondingly, with char no. 8 the gasification rate at 800 °C by $H_2O(g)$ was 7.68 $wt.\% \cdot min^{-1}$, but with char no.4 it decreased to 4.85 $wt.\% \cdot min^{-1}$ (Table 3). Further, char no. 3 was measured. S_{BET} was very low, 5 $m^2.g^{-1}$, and iodine number too, 75.0 $mg.g^{-1}$. Simultaneously, the gasification rate at 800 °C by CO_2 was low, 0.34 $wt.\% \cdot min^{-1}$, in contrast to that for char no. 8 (w 1.34 $wt.\% \cdot min^{-1}$, Table 3) with significantly higher surface parameters mentioned above. These data indicate that the decisive factor for reactivity of chars is the specific surface area. Structural parameters derived from Raman spectra play a minor role.

Further, the question of activation energy was investigated. For the assessment of the efficiency of the catalyst, the reduction of the activation energy of the gasification reaction through the catalyst's activity is significant. In principle, chars undergo thermo-oxidative degradation. Thus, the effective activation energy can be calculated from the data of thermogravimetric runs by isoconversional kinetic analysis which enables evaluating a dependence of the effective activation energy (E_α) on reaction progress (extent of conversion, α) particularly for the thermally stimulated processes, whose kinetics are multi-step and/or non-Arrhenius (Vyazovkin and Lesnikovich, 1990; Vyazovkin and Sbirrazzuoli, 2006). Xi et al. (2005) used isoconversional analysis to express a catalytic effect of metal sulfates (e.g. $Fe_2(SO_4)$) on thermo-oxidative degradation of poly(methyl methacrylate) on the basis of dependence of E_α on α . For virgin polymer the E_α values changed around 250 $kJ.mol^{-1}$, but in the presence of metal sulfates the E_α values decreased with α to 140-150 $kJ.mol^{-1}$. In our case, analogous procedure was used. The results achieved at char from lignite/SBR (1:1) mixture by CO_2 are pictured in Figures 2-5, clearly are shown in Figures 6 and 7. It arises from Figure 6 that without magnetite the values of the effective activation energy varied in the range of approximately 370-470 $kJ.mol^{-1}$ for α 10-90 %, but with magnetite they dropped to values of approximately 260-270 $kJ.mol^{-1}$ in the same range of α . The values of the pre-exponential factor ($\ln A$) were 30-40 sec^{-1} for α 10-90 % in the case without magnetite, and 20-22 sec^{-1} when it was used (Fig. 7).

The mentioned dependencies show that a) E_α and pre-exponential factor varied with α , therefore, gasification of chars is a complex (multi-step) process as independence of E_α and pre-exponential factor on α is a sign of a single-step process, b) the decrease of E_α from 370-470 $kJ.mol^{-1}$ up to 260-270 $kJ.mol^{-1}$ indicates a significant catalytic effect of magnetite.

Finally, the mixture of lignite with SBR in a high content of 60 % and a 5 %-addition of magnetite catalyst was tested and the influence of the catalyst on the increase of the gasification rate was monitored.

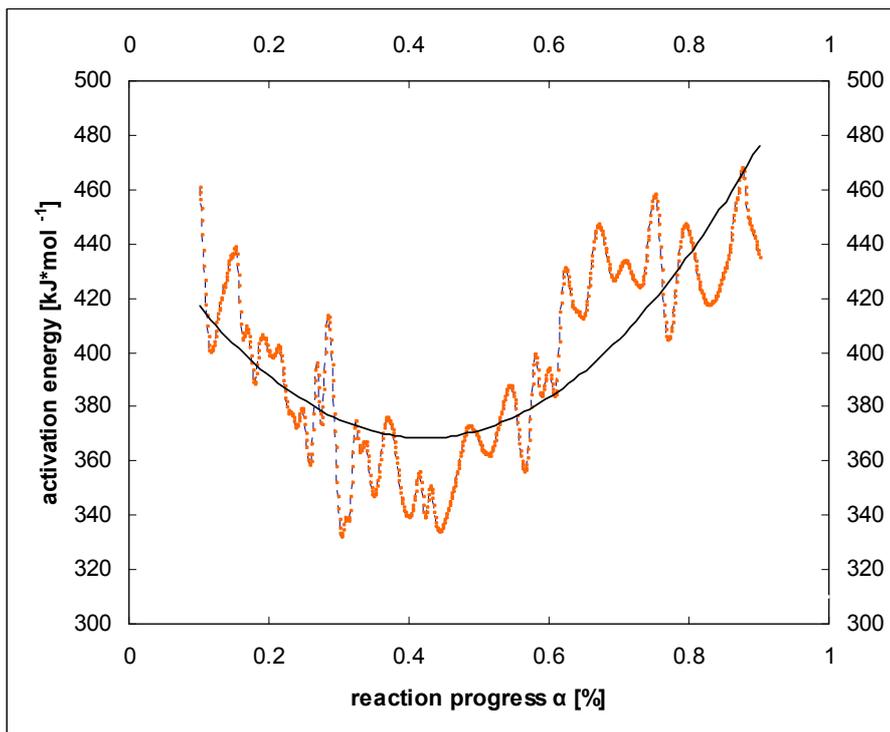


Fig. 2 The course of the effective activation energy of the gasification of char from the lignite/SBR (1:1) mixture by CO_2 for conversion of 10-90 %. (Dashed line-real course; full line-simplified course obtained by polynomial regression).

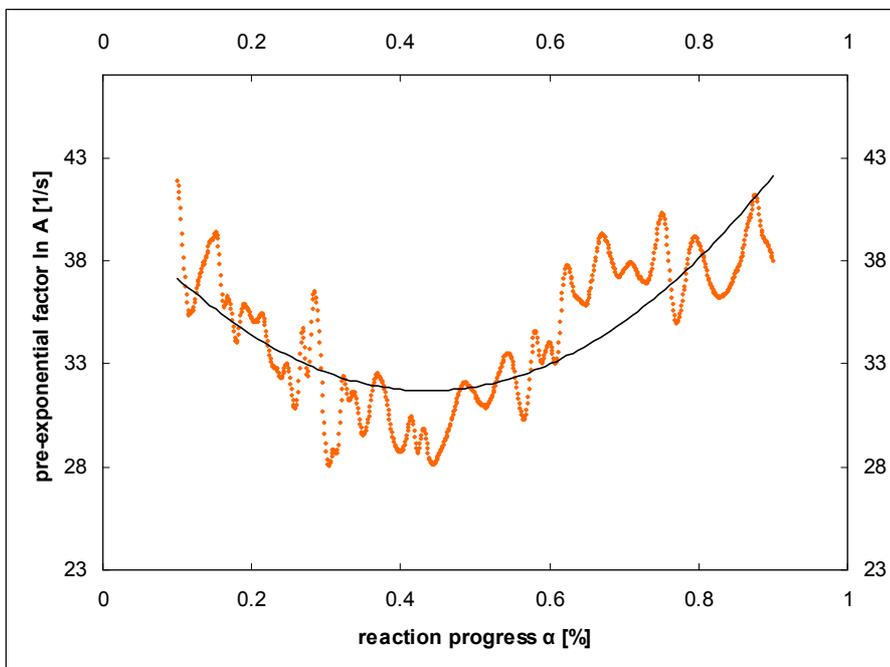


Fig. 3 The course of the pre-exponential factor of the gasification of char from the lignite/SBR (1:1) mixture by CO_2 for conversion of 10-90 %. (Dashed line – real course; full line – simplified course obtained by polynomial regression).

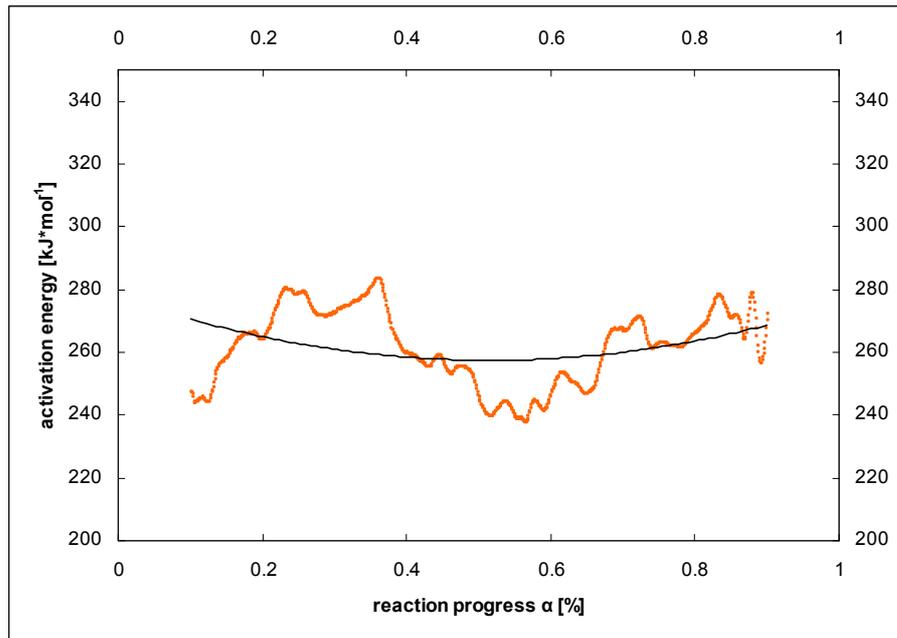


Fig. 4 The course of the effective activation energy of the gasification of char from the lignite/SBR (1:1) mixture with 5 % magnetite by CO_2 for conversion of 10-90 %. (Dashed line – real course; full line – simplified course obtained by polynomial regression).

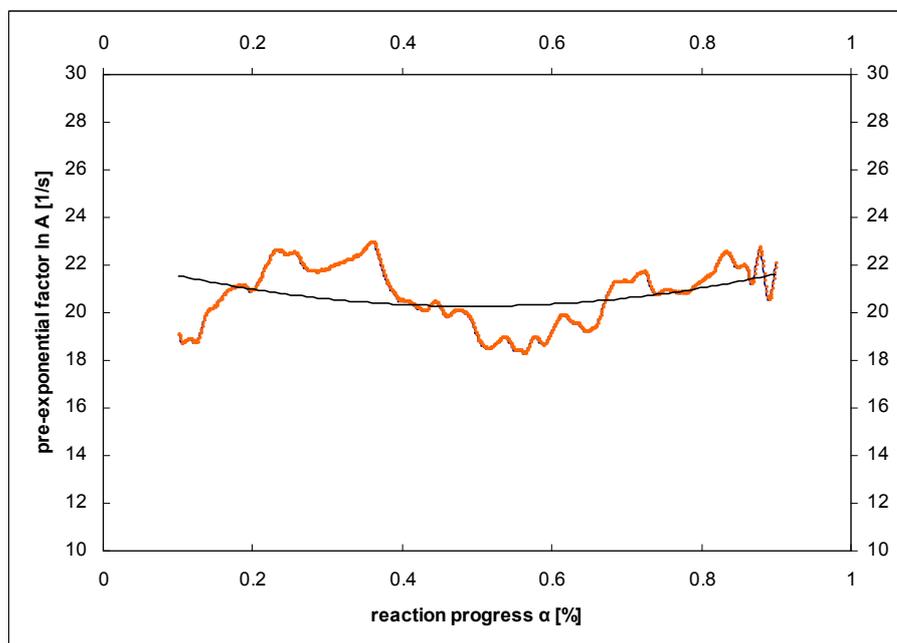


Fig. 5 The course of the pre-exponential factor of the gasification of char from the lignite/SBR (1:1) mixture with 5 % magnetite by CO_2 for conversion of 10-90 %. (Dashed line – real course; full line – simplified course obtained by polynomial regression).

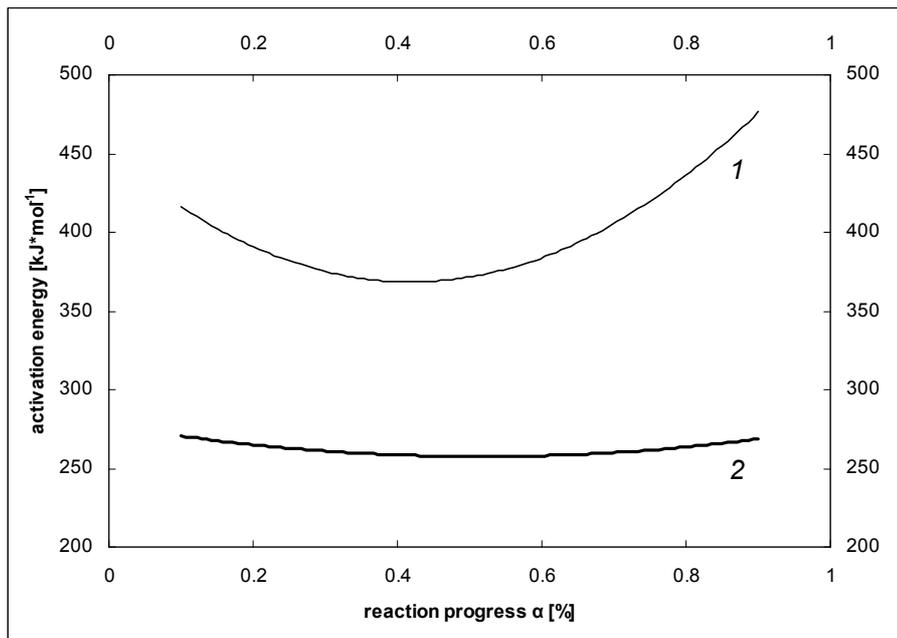


Fig. 6 The course of the effective activation energy of the gasification of char from the lignite/SBR (1:1) mixture by CO_2 for conversion of 10-90 %. Line 1- without magnetite, line 2- with magnetite.

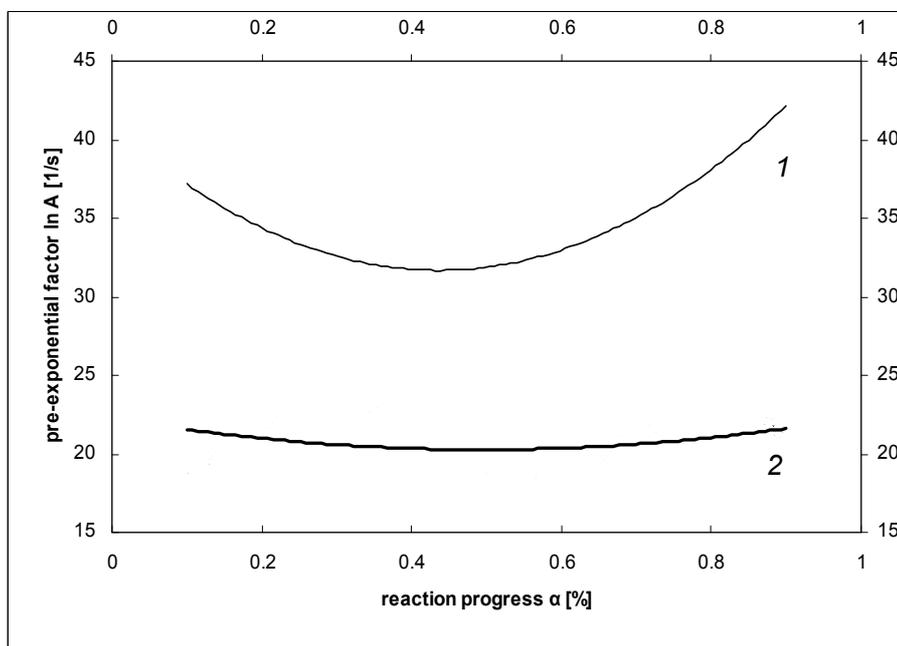


Fig. 7 The course of the pre-exponential factor of the gasification of char from the lignite/SBR (1:1) mixture by CO_2 for conversion of 10-90 %. Line 1- without magnetite, line 2- with magnetite.

Table 5 The rate of the gasification of the chars from the lignite/rubber mixture (35:60) with and without magnetite (5 %-addition) by steam and CO₂.

Char from:	w (wt.%.min ⁻¹) at 800 °C		w (wt.%.min ⁻¹) at 900 °C	
	H ₂ O(g)	CO ₂	H ₂ O(g)	CO ₂
Lignite/SBR	2.94	0.33	4.98	2.65
Lignite/SBR with magnetite	5.31	1.05	11.71	5.89

Table 6 The rate of the gasification of the chosen chars without and with magnetite by CO₂ at 900 °C (5 %-addition of magnetite).

Char (admixture)	w (wt.%.min ⁻¹) at 900 °C	
	Without	With
ABS (30 %)	6.02	11.73
PP (30 %)	5.11	9.70
Methylcellulose (30 %)	4.71	8.97
Cellulose (30 %)	6.60	11.88
PE (30 %)	5.42	12.46

This high content of SBR was chosen to test the effectiveness of the catalyst when processing larger quantities of waste SBR.

The measurement of the gasification rate of the chars from the mentioned lignite/SBR mixture has shown that in the presence of magnetite the gasification reactions significantly accelerate both in the case of gasification by steam and when using CO₂. It is clearly demonstrated in Table 5, from which it arises that the rate of the gasification of the chars with magnetite is two to three times greater in comparison with the rate achieved in the gasification of chars without it. Similarly in gasification of the other chars by CO₂ at 900 °C, the rate when using a 5 %-addition of a magnetite increased by almost two times. Particularly char from the mixture of lignite with PE was tested, where the rate of gasification in the presence of magnetite increased by more than two times (Table 6).

All of the findings listed so far show a favorable influence of the discussed catalyst on the rate of the gasification reactions and thus also a reduction of unburned carbon. Using this catalyst the gasification rates of chars in question are fully comparable with those obtained with char from lignite alone (Table 3, Tables 5 and 6).

CONCLUSION

Through the measurement of the gasification rate of the chars from lignite with admixtures by steam or CO₂, it was discovered that the admixtures of polymers, celluloses and wood reduce their reactivity. In practice, this reduced reactivity is manifested in an increased amount of unburned carbon during co-gasification of waste rubber with lignite. This negative phenomenon can be compensated by an addition of

magnetite, which acts as catalyst of the reactions of chars with steam as well as CO₂ and accelerates the reactions. Through the isoconversional analysis, it was proven that the presence of magnetite significantly lowers the effective activation energy of these reactions, thus accelerating their course. The measurements of the reaction rate showed that it leads to a two- or three-fold acceleration of gasification. The catalyst activity of magnetite showed itself during the gasification of chars from the lignite/polymers and lignite/celluloses mixtures, particularly from the lignite/PE mixture, when the gasification rate increased by more than two times.

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