Research paper

Reactivity of chars gasified in a fixed bed reactor with the potential utilization of excess process heat

Magdalena Cempa a,*, Adam Smoliński b

a Central Mining Institute, Department of Environmental Monitoring, Plac Gwarków 1, 40-166 Katowice, Poland
b Central Mining Institute, Department of Energy Saving and Air Protection, Plac Gwarków 1, 40-166 Katowice, Poland

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ABSTRACT

The aim of the work presented in this paper was to determine the reactivity of chars and their selection for further research purposes concerning coal gasification processes with the utilization of process excess heat. Char reactivity can be defined as the ability of coal to react with such reactants as steam, oxygen or carbon dioxide. Reactivity determines reaction rates and therefore it is a decisive factor relating to the efficiency of combustion and gasification processes. In light of the above, reactivity may be regarded as an important parameter to be considered in the design and operation of the industrial systems of coal processing. The experimental work was conducted by means of a thermogravimetric analyzer (TGA) at temperature ranges of 700, 800 and 900 °C, with oxygen as a gasifying agent. The parameters of maximum reactivity $R_{max}$ as well as of 50% of the conversion reactivity $R_{50}$ were calculated. The times $t_{max}$ and $t_{50}$ necessary for attaining the maximum reactivity $R_{max}$ and 50% conversion reactivity $R_{50}$ were also determined. The correlation between the experimentally determined values of $R_{max}$, $R_{50}$, $t_{max}$ and $t_{50}$ and additionally the physico-chemical parameters of the coals were examined by means of PCA analysis.

1. Introduction

The process of coal gasification consists of a sequence of thermo-chemical reactions between elemental coal from fuel and a gasifying agent such as: oxygen, steam, or carbon dioxide in high temperature conditions. The product of the gasification process is a gas whose composition and energy properties predominantly depend on the gasifying agent which was used, the type of fuel, and the process conditions, i.e. the pressure and temperature (Chiesa, Consonni, Kreutz, & Williams, 2005; Cormos, 2010, 2011; Minchener, 2005; Smoliński, 2011; Starr, Tzinias, & Petevs, 2007). The fuels which are most frequently utilized in the process of gasification are hard coal, lignite, peat, wood, bio-mass, waste, coke, and semi-coke. Coal gasification constitutes a technology which was known as early as in the 19th century when the first moving bed gas generator was patented by a German chemical company, Lurgi (Chmielnik & Sciażko, 2008; Gasification World Database, 2007; Minchener, 2005). In the second half of the 20th century, some advanced pieces of work on underground coal gasification were also carried on in Poland (Gregg & Edgar, 1978; Smoliński, Stańczyk, Kapusta, & Howaniec, 2012; Smoliński, Stańczyk, Kapusta, & Howaniec, 2013; Stańczyk et al., 2011; Yang, Liang, & Yu, 2003; Yang, Liang, & Yu, 2008).

The reactivity of chars is regarded to be one of the key parameters in fuel selection for both the design and operation of coal gasification industrial systems (Alonso, Borrego, Alvarez, Parra, & Menéndez, 2001; Smoliński, 2011). The necessity of using high reactivity coals when the gasification process temperature is lower than ash melting temperature is a good illustration of the above. Char reactivity can be defined as the fuel’s ability to react with such gas reactants (gasifying agents) as steam, oxygen or carbon dioxide under given process conditions (Porada, Dzioł, Czerski, & Grzywacz, 2014; Smoliński, 2011).

As concerns the research on fuel reactivity, the analyses are mostly carried out by means of thermo-gravimetric analyzers (TGA), Field’s Drop Tube Reactors (DTR), Fluidized Bed Reactors (FBR), Hot Rod Reactors (HRR), Fixed Bed Reactors (FBR) or calorimetric bombs (Reamish, Shaw, Rodgers, & Newman, 1998; Smoliński, 2008).

There are numerous techniques applied in order to determine the reactivity of coals and chars; however, in most cases they are based on the measurement of sample mass loss in a particular
process, or the measurement of the volume gain of process products. The most commonly applied measurements of reactivity are the following: the time of 50% conversion, \( t_{50} \), the reactivity rate, \( R_x \) and the constant of gasification reaction rate, \( k \) (Porada et al., 2014; Smoliński, 2011).

The reactivity of chars depends on numerous factors such as the initial composition of the fuel, the way in which the fuel has been prepared, the size of the grains, and finally, the conditions in which the processes of pyrolysis and gasification take place (Ash & Walker, 1977). The differences in char reactivity rates in the process of gasification can amount to up to 30% in the case of chars which come from the same sample, but have been obtained in different conditions of the pyrolysis process (Smoliński, 2008). The lengthening of the time in which a given sample is kept at a temperature of 1000–1400 °C during pyrolysis results in a significant decrease of reactivity. In the case of lower temperature ranges, the time in which the sample is treated at maximum temperature has a lower impact (Lee, 1987).

Due to the fact that coal gasification is a strongly endothermic process, the development of contemporary gasification technologies is directed towards its efficiency improvements. It has been postulated that the heat necessary for the gasification reaction should be supplied from outside sources, i.e. allothermic processes rather than autothermic ones wherein the heat required for the gasification reaction comes from the partial combustion of coal fed into the reactor. Such an option is possible, inter alia, in the case of the application of excess heat coming from other processes utilized to initially heat up the gasifying agent before feeding it in to the bed. An interesting solution seems to be the utilization of the excess heat generated by high temperature reactors (HTRs). These reactors are characterized by a relatively low thermal power output which does not exceed a few hundred MWth; in addition, they are also characterized by the capacity to generate high temperature steam under high-pressure and a relatively high temperature of the coolant (helium) at the outlet amounting to 750–950 °C. Therefore, they are perfectly suited for the potential utilization of the heat accumulated in the coolant for the purpose of energy consuming processes, mainly in coal processing technologies, including the process of coal gasification (Howaniec, Smoliński, & Cempa-Balewicz, 2015). Contemporary water cooled reactors generate heat which does not go beyond the temperature of 350 °C whereas their thermal power exceeds the requirements of a typical industrial installation. Modern high temperature reactors (HTRs) are such an advanced technology that their implementation into industrial applications seems possible within the next several years (Arndt et al., 1979; Barnett, 1985; Belghit, Gordillo, & El Issami, 2009; Filipov, Bogoyavlenskii, Ponomarev-Stepnoi, & Gola-postsev, 2004; Gordillo & Belghit, 2011; Hart, Jansing, & Teubner, 1990; Hori et al., 2005; Hori, 2011; Inaba, Fumizawa, Tonogouchi, & Takenaka, 2000; NFE, 1985; Kubiak, Van Heek, & Staniczuk, 2011; Piera, Martinez-Val, & Montes, 2006). The aim of the research presented in this paper was to determine the reactivity of chars in the process of air coal gasification at temperature ranges of 700, 800 and 900 °C and to enable the selection of the most suitable fuel for the purpose of investigating the process of gasification which utilizes excess heat.

2. Materials and methods

Seven types of hard coal were selected in order to determine their reactivity rates. The samples were chosen from different, Polish coal-seams in Piast Mine and Knurów-Szczygłowice Mine. The selected coals were examined in terms of their physico-chemical properties and parameters which are potentially relevant to the gasification process (see Table 1, Table 2). The research was conducted in an accredited laboratory of the Central Mining Institute and according to the following binding standards: PN-G-04560:1998 (the content of moisture, ash), PN-G-04516:1998 (the content of volatiles), PN-G-04513:1981 (the heat of combustion), PN-G-04571:1998 (the content of carbon, hydrogen and nitrogen), PN-G-04584: 2001 (the content of total sulphur).

The char samples obtained from selected hard coals were examined in this study so as to determine their reactivity rates during the process of air gasification by means of a SDT Q600 thermo-gravimetric analyzer (TA Instruments). A sample of coal of 20 ±0.4 mm and granulation below 0.2 mm was heated in an atmosphere containing an inert gas (nitrogen) at 16.6 °C/min to the predetermined temperature of 700, 800 or 900 °C. The heating rate as well as the temperature range were selected in order to reflect the heating rate which is characteristic for a laboratory installation used to examine the potential of utilizing excess process heat for the purpose of coal gasification. When the predetermined temperature was attained and stabilized (after approximately 10 min), the process of the air gasification of the char obtained in the initial stage was started at the rate of 50 mL/min. A period of 25 min was allowed for the gasification process. The weight changes of the sample were recorded as a function of time. The sample mass which was obtained after the temperature was attained and stabilized for the predetermined temperature in a nitrogen atmosphere was assumed to be the starting weight of the char. Then, the parameters of maximum reactivity \( R_{max} \) as well as of 50% conversion reactivity \( R_{50} \) were calculated by means of the following equations:

\[
R_x = \frac{1}{m_0 - m_0} \frac{dm}{dt} \quad (1)
\]

\[
X = \left( \frac{m_0 - m}{m_0 - m_0} \right) \cdot 100 \quad (2)
\]

where: \( R_x \) – char reactivity at conversion rate \( X, \, \text{s}^{-1} \); \( X \) – char conversion rate, %; \( m_0 \) – char starting weight, g; \( m \) – char weight after the experiment, g; \( m_0 \) – char weight during the time \( t \) of the gasification process, g; \( \frac{dm}{dt} \) – weight loss at char conversion rate \( X, \, \text{g} \, \text{s}^{-1} \).

Then, the times \( t_{max} \) and \( t_{50} \) necessary for attaining the maximum reactivity \( R_{max} \) and 50% conversion reactivity \( R_{50} \) were determined.

3. Results and discussion

Table 3 below demonstrates the values of maximum reactivity \( R_{max} \) and 50% conversion reactivity \( R_{50} \) for the chars examined in this study as well as the times necessary to attain maximum reactivity \( t_{max} \) and 50% conversion reactivity – \( t_{50} \). In all temperatures, coal sample W1 revealed the highest maximum reactivity \( R_{max} \) and the highest 50% conversion reactivity \( R_{50} \), whereas samples W6 and W7 had the lowest values of maximum reactivity \( R_{max} \) and 50% conversion reactivity \( R_{50} \). The increase in reactivity \( R_{max} \) with the increase of pyrolysis temperature from 700 °C to 900 °C equalled 2.1% for sample W1 and 7.5% for sample W4.

The correlation between the experimentally determined values of \( R_{max} \), \( R_{50} \), \( t_{max} \) and \( t_{50} \) as well as physico-chemical parameters characteristic of the selected coals was examined by means of PCA (Principal Component Analysis) analysis (Howaniec & Smoliński, 2014; Joliffe, 1986; Smoliński, Howaniec, & Staniczuk, 2011; Smoliński, Walczak, & Einax, 2002; Wold, Esbensen & Geladi, 1987). PCA is a data compression technique. On the condition that the data compression is effective, PCA allows for the interpretation and
visualization of experimental results. The application of Principal Component Analysis yields two data matrices, i.e. the matrix of the objects S and the matrix of weights D. Matrix S represents the information concerning the examined samples whereas matrix D represents the information concerning the measured parameters. The said matrices are orthogonal. Matrix S columns and matrix D rows are called Principal Components (PC) and they are constructed to make their contributions uniform to data variances. The application of PCA for the analysis of standardized parameters occurs in different units, they were standardized in order to examine the similarities among the samples and trace the correlations among the parameters. In order to examine the similarities among the samples and trace the correlations among the parameters, it is necessary to project the objects and the parameters down onto the planes determined by pairs of significant principal components while Euclidean distance constitutes a similarity measure. The objects which are located close to one another in the principal component space are also close to one another in the original variables space. Each parameter may be treated as a vector in the object space whereas the angles between particular vectors representing the examined parameters indicate their mutual correlation. Due to the fact that the measured parameters occur in different units, they were standardized in order to make their contributions uniform to data variances. The model of four principal components described 97.27% of the total data variances. Fig. 1 shows the projections of objects (the coal samples examined) and the parameters (see Table 4) onto the planes determined by particular pairs of principal components.

The first two principal components described 84.54% of the total data variance. The projection of objects onto the plane defined by PC1-PC2 shows a clear distinction of particular samples along the first axis. PC1 described 73.90% of the total data variance resulting from the largest differences observed between sample W1 and samples W6 and W7. In addition, the projection of parameters down onto the plane determined by PC1-PC2 allows the observation to be made that of all the examined samples, sample W7 was specified as having the highest heat of combustion and calorific value, the lowest content of C, H, and N as well as the shortest times of maximum reactivity and 50% conversion reactivity were attained.

### Table 1
Proximate analysis of selected coal samples (in analytical condition).

<table>
<thead>
<tr>
<th>Parameters, unit</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>W2</td>
</tr>
<tr>
<td>Moisture, %w/w</td>
<td>9.15</td>
</tr>
<tr>
<td>Ash, %w/w</td>
<td>8.93</td>
</tr>
<tr>
<td>Volatiles, %w/w</td>
<td>30.49</td>
</tr>
<tr>
<td>Heat of combustion, Qc, kJ/kg</td>
<td>28.855</td>
</tr>
<tr>
<td>Calorific value, Qf, kJ/kg</td>
<td>24.655</td>
</tr>
</tbody>
</table>

### Table 2
Ultimate analysis of selected coal samples (in analytical condition).

<table>
<thead>
<tr>
<th>Parameters, unit</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>W1</td>
<td>W2</td>
</tr>
<tr>
<td>Total sulphur content, Sp, %w/w</td>
<td>0.71</td>
</tr>
<tr>
<td>Carbon, C, %w/w</td>
<td>63.72</td>
</tr>
<tr>
<td>Hydrogen, H, %w/w</td>
<td>3.82</td>
</tr>
<tr>
<td>Nitrogen, N, %w/w</td>
<td>0.67</td>
</tr>
<tr>
<td>Fixed carbon, Cfixed, %w/w</td>
<td>51.43</td>
</tr>
</tbody>
</table>

### Table 3
Values of maximum reactivity Rmax, 50% conversion reactivity R50 and times in which maximum reactivity tmax and 50% conversion reactivity were attained t50.

<table>
<thead>
<tr>
<th>Process temperature, T, °C</th>
<th>Parameter, unit</th>
<th>Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>Rmax 10^3/s</td>
<td>W1</td>
</tr>
<tr>
<td>1.426</td>
<td>1.268</td>
<td>1.313</td>
</tr>
<tr>
<td>800</td>
<td>1.447</td>
<td>1.346</td>
</tr>
<tr>
<td>700</td>
<td>R50 10^3/s</td>
<td>W1</td>
</tr>
<tr>
<td>1.330</td>
<td>1.160</td>
<td>1.230</td>
</tr>
<tr>
<td>800</td>
<td>1.309</td>
<td>1.199</td>
</tr>
<tr>
<td>900</td>
<td>1.298</td>
<td>1.236</td>
</tr>
<tr>
<td>700</td>
<td>tmax s</td>
<td>W1</td>
</tr>
<tr>
<td>857.0</td>
<td>1002.0</td>
<td>915.0</td>
</tr>
<tr>
<td>800</td>
<td>812.0</td>
<td>945.5</td>
</tr>
<tr>
<td>900</td>
<td>966.5</td>
<td>956.5</td>
</tr>
<tr>
<td>700</td>
<td>t50 s</td>
<td>W1</td>
</tr>
<tr>
<td>687.0</td>
<td>788.0</td>
<td>757.5</td>
</tr>
<tr>
<td>800</td>
<td>636.0</td>
<td>713.0</td>
</tr>
<tr>
<td>900</td>
<td>720.0</td>
<td>737.5</td>
</tr>
</tbody>
</table>

The first two principal components described 49.54% of the total data variance. The application of PCA for the analysis of standardized X (7 x 21) data allowed for their effective compression. The model of four principal components described 97.27% of the total data variances.
described 10.64% of the total data variances was constructed because of significant differences between sample W5 and samples W3 and W4. Sample W5 had the highest content of ash (parameter no. 2), whereas samples W3 and W4 showed the highest content of volatiles (parameter no. 3). PC3 which described 7.60% of the total data variance additionally demonstrated the differences between sample W2 and all the remaining samples, mainly on account of it having the highest value of total sulphur content (parameter no. 6) as well as a low value of the heat of combustion and short time $t_{\text{max}}$ at temperature 900 °C (parameters nos 4 and 18). PC4 which described 5.13% of the total data variance indicated that sample W7 was specific because of it having the longest time $t_{\text{max}}$ at temperature 900 °C (parameter no. 18) and the lowest ash content (parameter no. 2) of all the examined samples.

Due to the fact that data compression was effective, it may be concluded that a correlation between the examined parameters exists. The following parameters had the largest contribution to the first PC1 axis: correlated parameters 4, 5, 7, 16, 17, 19 and 20 (which describe heat of combustion, calorific value, the content of C and time $t_{\text{max}}$ at temperatures of 700 and 800 °C as well as $t_{50}$ at all the examined temperatures); parameters 8 and 9 (which describe the content of H and N); parameters 12 and 15 (which describe maximum reactivity $R_{\text{max}}$ and 50% conversion reactivity $R_{50}$ at 900 °C); as well as parameters 1, 10, 11, 13 and 14 (which describe

![Fig. 1. PCA results for Xc(7 × 21) data: (a) the projections of objects, (b) the projections of parameters onto the planes determined by particular pairs of principal components.](image-url)
the content of moisture and the values of the maximum reactivity $R_{\text{max}}$ and 50% conversion reactivity $R_{50}$ at temperatures of 700 and 800 °C.

In addition, it was observed that a negative correlation exists between parameters 1, 10, 11, 13 and 14 (i.e. the ones which describe the content of moisture as well as the values of the maximum reactivity $R_{\text{max}}$ and 50% conversion reactivity $R_{50}$ at temperatures of 700 and 800 °C) and parameters 4, 5, 7, 16, 17, 19 and 20 (i.e. the ones which describe the heat of combustion, the calorific value, the content of C, the times $t_{\text{max}}$ at 700 and 800 °C as well as $t_{50}$ at all the temperatures examined). Between parameters 12 and 15 (i.e. the ones which describe the maximum reactivity $R_{\text{max}}$ and 50% conversion reactivity $R_{50}$ at 900 °C) and parameter 21 (i.e. the one which describes time $t_{50}$ at 900 °C): parameters 1, 10, 11, 13 and 14 (i.e. the ones which describe the content of moisture, the value of maximum reactivity $R_{\text{max}}$ and 50% conversion reactivity $R_{50}$ at 700 and 800 °C) and parameters 8 and 9 (i.e. the ones describing the content of H and N).

4. Conclusions

Based on PCA analysis the biggest differences were observed between sample W1 and samples W6 and W7. Sample W1 was characterized by having the highest values of $R_{\text{max}}$ and $R_{50}$ at all temperature ranges (700, 800 and 900 °C). The said reactivity rates were attained at the shortest times $t_{\text{max}}$ and $t_{50}$. In addition, sample W1 revealed the highest content of moisture as well as the lowest values of combustion heat and calorific value and the lowest content of C, H, and N of all examined samples. Samples W6 and W7 were characterized by having the lowest values of $R_{\text{max}}$ and $R_{50}$ attained at the longest times $t_{\text{max}}$ and $t_{50}$ at all temperature ranges (700, 800 and 900 °C) as well as high contents of carbon, hydrogen, and nitrogen. Sample W2 had the highest content of total sulphur, whereas samples W3 and W4 had the highest content of volatiles, and sample W5 had the highest content of ash.

A correlation exists between the experimentally determined values of $R_{\text{max}}$, $R_{50}$, $t_{\text{max}}$ and $t_{50}$ and the physico-chemical parameters characteristic of coals relevant for the gasification process (Table 4). The following parameters made the largest contribution to the first PC1 axis: heat of combustion, calorific value, the content of C and time $t_{\text{max}}$ at temperatures of 700 and 800 °C. $t_{50}$ at all the examined temperatures, content of hydrogen and nitrogen, maximum reactivity $R_{\text{max}}$ and 50% conversion reactivity $R_{50}$ at 900 °C, the content of moisture, the values of maximum reactivity $R_{\text{max}}$ and 50% conversion reactivity $R_{50}$ at temperatures of 700 and 800 °C.

Based on the measurements of the reactivity of char obtained from the examined samples of hard coals as well as the results of PCA analysis, sample W1 was selected for the purpose of further research.

References


