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Using Mathematica software for coal gasification simulations – Selected kinetic model application

Sebastian Iwaszenko[*]

Department of Post-Industrial Sites and Waste Management, Central Mining Institute, Katowice, Poland

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ABSTRACT

Coal gasification is recognized as a one of promising Clean Coal Technologies. As the process itself is complicated and technologically demanding, it is subject of many research. In the paper a problem of using volumetric, non-reactive core and Johnson model for coal gasification and underground coal gasification is considered. The usage of Mathematica software for models' equations solving and analysis is presented. Coal parameters were estimated for five Polish mines: Piast, Ziemowit, Janina, Szczygłowice and Bobrek. For each coal the models' parameters were determined. The determination of parameters was based on reactivity assessment for 50% char conversion. The calculations show relatively small differences between conversion predicted by volumetric and non reactive core model. More significant differences were observed for Johnson model, but they do not exceeded 10% for final char conversion. The conceptual model for underground coal gasification was presented.

1. Introduction

Meeting the needs for the energy demands is one of most important challenge of modern world. Despite of constant development of novel technologies and increase of usage of renewable energy sources, the conventional fossil fuels plays crucial role as an energy sources (Ram & Masto, 2010; Seifi, Chen, & Abedi, 2011). Unfortunately, the fossil fuels are commonly known of theirs negative environmental impact. Therefore there is constant need for development of new technologies for their utilization. Coal gasification, and especially underground coal gasification (UCG), is recognized as one of promising technologies aimed at ecologically friendly utilization of raw material deposits (Bhutto, Bazmi, & Zahedi, 2013; Białecka, 2008; Shafirovich & Varma, 2009). The process itself, though known since late eighties, is extremely difficult in implementation underground. There are many research projects conducted worldwide, aiming in development of efficient, cost effective technology allowing underground coal gasification (Couch, 2009; Khadse, Qayyumi, Mahajani, & Aghalayam, 2006; Wiatowski et al., 2012). Among different methods used for investigations of UCG process, modeling and computer simulations plays very important role. As the gasification itself involves many processes, there are many possible approaches to using computer simulations. Some of authors (Biezen, Bruining, & Molenaar, 1995; Seifi et al., 2011; Wachowicz, Janoszek, & Iwaszenko, 2010) develop models describing whole process with significant simplification. Other try to develop models concentrating on selected aspect of UCG process. Urych (2014) developed the model for pyrolysis process and determined its parameters for two of polish coals. Some other authors focus on cavity growth modeling and visualization (Nurzyńska, Janoszek, & Iwaszenko, 2014;

* Tel.: +48 32 259 21 73; fax: +48 32 259 65 33.
E-mail address: siwaszenko@gig.eu.
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Sarraf Shirazi, Mmbaga, & Gupta, 2011), as an important aspect of process ongoing in georeactor. The comprehensive survey of models used for coal gasification was presented by Żogała (2014a, 2014b). In spite of models considered the suitable computer code has to be used for model equations solving. There are usually three main groups of code used:

- Self developed, dedicated code developed for given purpose
- Code dedicated for solving selected class of models, e.g. CFD codes
- General purpose mathematical software (MATLAB, Mathematica)

Self developed models, though used by some authors (Nurzyńska, Iwaszenko, & Choroba, 2014) are most difficult and error prone. Not only does the development of the software require appropriate skills, but also thorough testing. On the other hand it gives freedom in choosing technology, numerical method, data structures, and so on. It also gives opportunity to adjust the code to hardware possibilities. In contrast, using already developed code for calculating selected class of models are well tested and can be treated as reference in many research. This approach is also widely used in UCG process simulations (Wachowicz, Łączny, Iwaszenko, Janoszek, & Cempa-Balewicz, 2013). Unfortunately, they limit possibility of model modifications and force describing the model in terms required by the tool. Therefore it seems reasonable to investigate the possibilities offered by the tools classified in the third group. On the one hand, they give the flexibility of self developed codes while being well tested and verified. On the other hand, the models still need to be implemented in the mathematical software and the developer does not have full control on calculation process. Nevertheless, the advantages of this method overcome the potential limitations.

The utilization of general purpose mathematical software in UCG process simulations is relatively small. This is especially true in case of Mathematica. The package was used for gasification simulations with equilibrium models by Żogała (2014a). Despite of that, Mathematica is reported as a useful tool for many different applications in simulation based research in other fields (Chramcov, 2011; Mykhalchuk & Fedasyuk, 2001; Sarafian, 2011). Taking into consideration the possibilities offered by the mentioned package, its usefulness for simulations of different aspect of UCG process should not cause any doubts.

In the article practical application of Mathematica environment in simulation research of coal gasification is presented. Three selected models, known from literature were implemented in Mathematia. Models parameters were determined basing on experimental determination of coal reactivity. It is presented how calculations and model analysis can be performed using mentioned universal mathematical software.

2. Conceptual model

Underground coal gasification process is composed of many physical and chemical processes taking place in the same time, in different parts of gasification reactor. The complexity can be controlled by introducing simplifying assumptions and dividing the complex process into several, interconnected but simpler partial processes. In proposed solutions both ways are addressed. First of all, it is assumed that gasification channel is divided into sequence of sections. Each section exchanges mass and energy with surrounding sections by interfaces. The exchange process can be modeled as a set of boundary condition. Inside the section a set of physical and chemical processes are considered. The gasification channel and the coal seam surrounding it forms the place, where most of interesting phenomenon occur. It was assumed, that the space will be divided into two domains: the gasification channel itself, where most of the ongoing reactions are connected with mas and energy transport in gaseous phase, and the gasification channel wall, where heterogeneous reactions take place (Fig. 1).

The domains are tightly coupled by mass and energy transport processes as well as model calculating changes in gasification channel geometry. In the gasification channel domain the following processes were identified:

Flow model, responsible for simulation the gaseous phase flow through the georeactor. The model should allow determination of gaseous phase flow velocity and pressure in time and space for each considered compound.

Gaseous phase reactions model, used for calculations of reactions ongoing in bulk of gasification channel. For most of the cases, as temperature values are high enough, the reactions and gas compositions can be calculated using equilibrium models.

Energy transport model, which is crucial for appropriate predictions of thermal conditions in the gasification channel. The model should take into consideration not only transport phenomena but also thermal effects of reactions ongoing in gaseous phase.

The processes taking place in gasification channel wall are more complex than the ones observed in gasification channel. Therefore, for gasification channel wall following models were proposed:

Macropores flow model, predicting the mass transport behavior in cracks and relatively big voids in coal seam.

Transport phenomena in micropores model, describing mass transport ongoing in micropore structure of coal and char being gasified. The transport phenomena differs significantly from the ones considered for bulk gaseous phase. The models used for porous catalyst pellet in chemical engineering can be adopted for that purpose.

External diffusion model, responsible for describing the mass flow from micropores or solid surface into bulk gaseous phase in macropores.

Surface reactions model, which is crucial for simulations of gasification process. The set of heterogeneous reactions used for simulations *de facto* determine the scope of the model and its usefulness for selected conditions. With first approach kinetic models concentrating on char conversions can be considered up to models including pyrolysis and catalytic influence of mineral matter.

Gaseous phase reactions model, representing the reactions taking place in gaseous phase in macropores. As the time for the reactions is limited, the kinetic models seem more appropriate than equilibrium ones suggested for gasification channel.

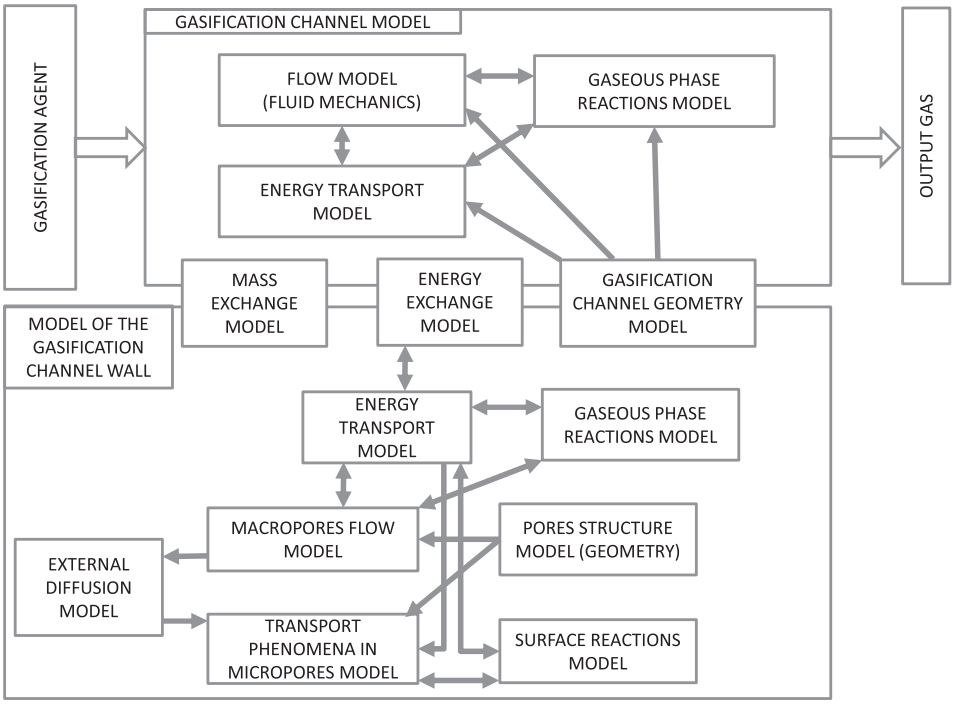

Fig. 1 – Concept model of gasification process in georeactor.

Pores structure model, describing changes to the micro and macro pore structure of coal and char due to ongoing gasification reactions. The changes in pore structure influence transport phenomena and heterogeneous reactions, therefore being important part of whole gasification model.

Energy transport model, describing the thermal conditions in the gasification channel wall. The model have to consider the thermal effect of ongoing chemical and physical processes.

For the presented paper, the surface reactions model were chosen for further investigations. It was assumed, that the models are selected from kinetic models for char gasification reported in literature. The model parameters are calculated basing of coal reactivity tests (Smoliński, 2011). The predictions given for the models are compared and the possibilities of using Mathemetica software for gasification models are presented.

3. Model equations and parameters identifications

For further investigations three models were selected: volumetric, non reactive core and Johnson. The models represent different approach to modeling gasification reactions. All of them assume, that the only measure of the reaction is char conversion x defined as follows (Molina & Mondragón, 1998):

$$x = \frac{W_0 - W}{W_0}$$

where W_0 stands for coal/char content at the beginning of the process and W represents the coal/char content after time t. The volumetric model assumes that the gasification reaction is homogenous and goes in all volume of the char particle. The limitation for process is availability of char. The mathematical representation of the model is described by equation (Molina & Mondragón, 1998):

$$\frac{dx(t)}{dt} = k(1 - x(t))$$

The k coefficient is called reaction rate constant. The quantity is in fact dependent on temperature according to Arrhenius law.

The non reactive core model assumes, that reaction occurs only on coal/char surface. The solid under the surface does not participate in the reactions, forming non reactive core. As the reactions advance, the non reacting solid shrinks. In higher temperatures the reaction kinetics is a limiting factor for the proces, and the model equation can be written as follows (Molina & Mondragón, 1998):

$$\frac{dx(t)}{dt} = k(1 - x(t))^{\frac{2}{3}}$$

Johnson model is the most complicated from all taken for further analysis. The model takes into account the resistances which occur in porous medium for substrate and products transportation to and from the surface. The resistance is a result of both: the porous structure of coal/char itself and a porous structure of ashes layer, which develops on reacting gasified particle. It also assumes that during the reaction, there is a significant change of the surface available for chemical processes. The model is given by following equation (Molina & Mondragón, 1998):

$$\frac{dx(t)}{dt} = f_1 k_t (1 - x(t))^{\frac{2}{3}} \exp\left(-\alpha x(t)^2\right)$$

The k_t is reaction constant, and f_1 is called relative reactivity factor. It is dependent on char type and its thermal processing. Its value can be determined upon experimental data. The αx^2 factor represents the influence of changing surface and transport resistance on reaction rate. During the calculations, the product $f_1 k_t$ can be substituted with single constant k.

4. Results

4.1. Models characterization

A rough characterization of each of selected models were carried out. The characterization based on determination of models' predictions for different values of parameters. The models were implemented in Mathematica environment and for each of models the solutions were found for each of defined constant parameter values. The definition of Johnson model equation, time scale and initial conditions in Mathematica language can be written in the following way:

```
jhnEqn = D[x[t], t] == f1 k (1 - x[t])^(2/3) Exp[-\[Alpha] x[t]^2]
jhnInit = x[0] == 0;
jhnVars = {x[t], x'[t]};
jhnTime = {t, 0, 2000};
```

The simulations were done using NDSolve function, which finds solution(s) for ODE or PDE equations. Where used with default parameters, the function uses Runge-Kutta 4th order method. The Mathematica script used for finding solutions of models' equations for chosen set of parameters' values are presented below.

```
jhnSolTab =
  Table[NDSolve[{jhnEqn /. {k -> 0.001 ki, f1 -> 1, \[Alpha] -> 10},
    jhnInit},
   jhnVars, {jhnTime[[1]], jhnTime[[2]], jhnTime[[3]]}], {ki, {0.1,
    0.2, 0.5, 1, 2, 5, 10, 20, 50, 100}}];
```

The solutions are memorized in list, for further usage.

The obtained results of calculations are presented in Figs. 2–4. For each model the dependence of char conversion on time as well as phase chart are presented. For Johnson model

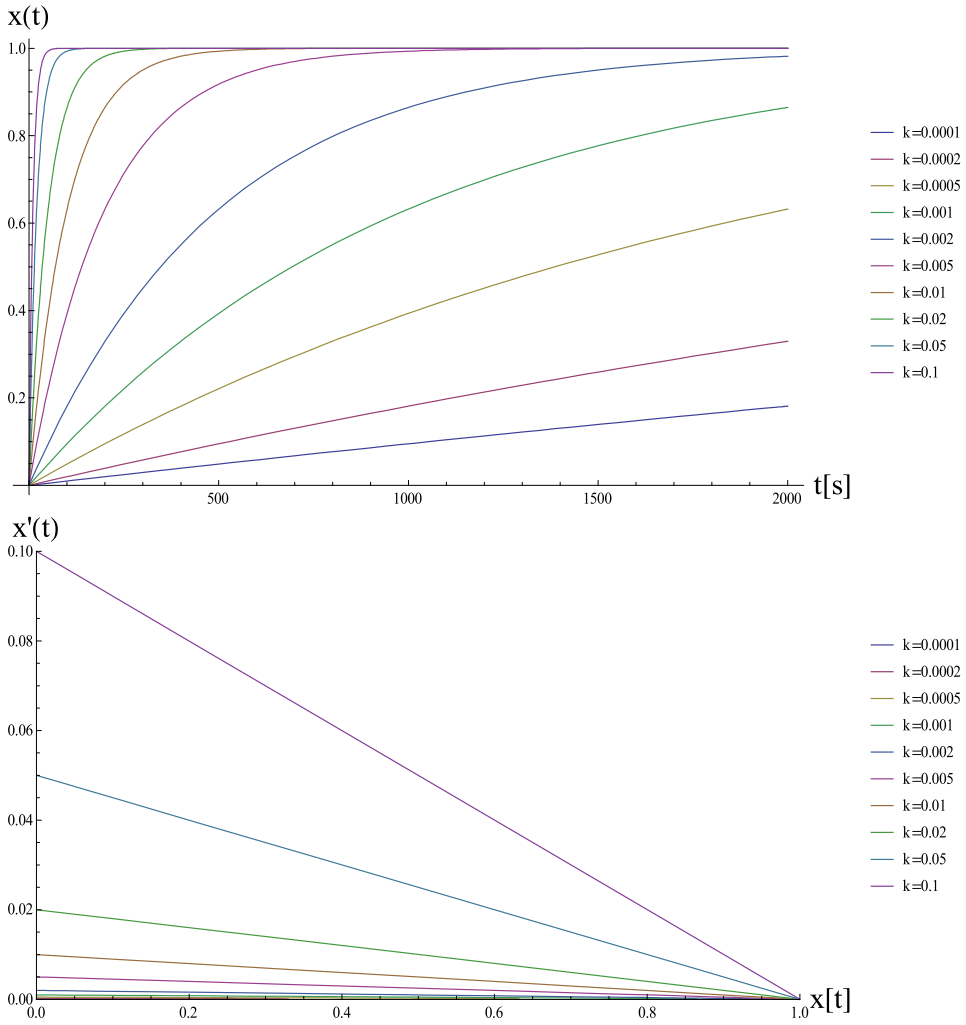

Fig. 2 – Char conversion in time predictions and phase chart of volumetric model.

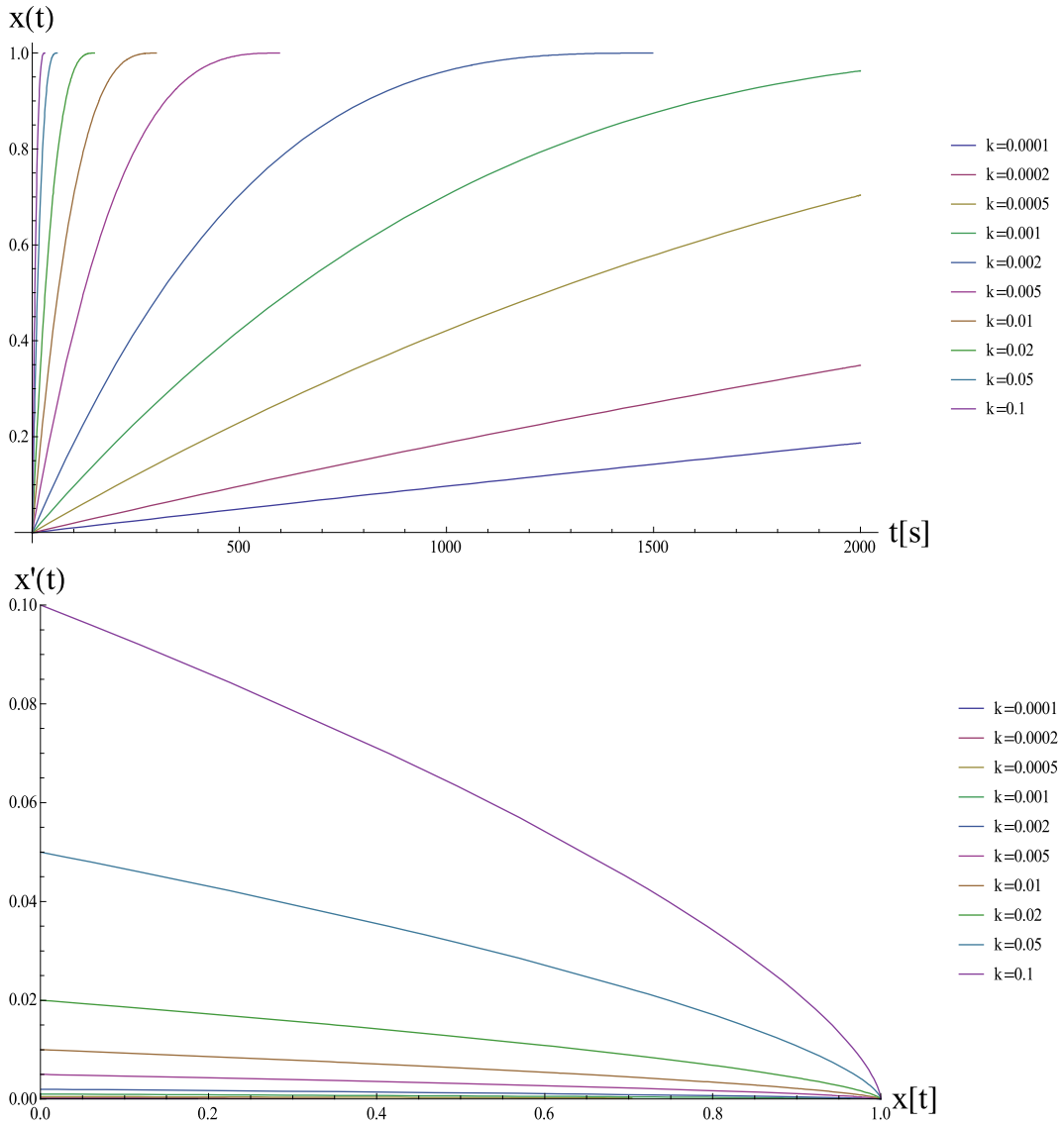

Fig. 3 – Char conversion in time predictions and phase chart of non reactive core model.

additional chart is presented for different values of α parameter.

Each of examined models show similar dynamic behavior, which can be observed in the charts presenting phase plane. As only positive and less or equal 1 values of char conversion have physical meaning, it is sufficient to focus on selected part of phase plane. Each of models have stable stationary point for $x = 1$ and it is also an attractor. However, the systems approach the attractor in significantly different way. In case of volumetric model, the rate of conversion changes is constant, and it uniformly decreases to zero when the modeled system approaches $x = 1$. For non reactive core model, the rate decreases non linearly, having higher values than observed in volumetric model. Therefore, the non reactive core model predicts the shortest times for char conversion for given rate constant parameter. The most complicated behavior can be observed in Johnson model predictions. This is the only model capable of predicting residual of unconverted char. Though the system finally reaches $x = 1$ point, for high α values the rate is practically equal zero, and can be interpreted as marker of process stopping. It can be useful when modeling gasification in places where gasification products or char porous structure make some part of reagent unavailable for the process. Choice of model which should be used for modeling should be done after at least qualitative analysis of experimental data.

4.2. *Determination of model parameters*

For determination of model parameters data from former experiments, reported in literature were used. Smoliński (2011) determined the coal reactivity for 17 samples taken from coal of selected Polish mines: Piast, Ziemowit, Janina, Szczygłowice and Bogdanka. From some of the mines as many as 8 samples were taken, while the others were represented by only one sample. The reactivity was determined for 50% char conversion and for maximum rate. For determination of model parameters the reactivity for 50% was used. The model

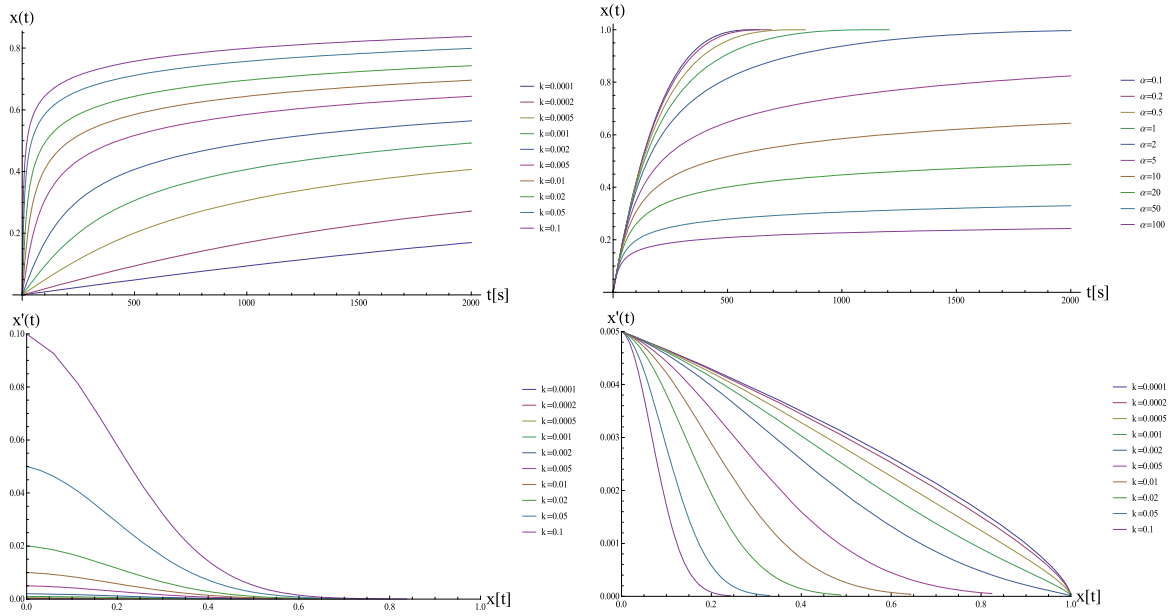

Fig. 4 – Char conversion in time predictions and phase chart of Johnson model.

parameters were calculated using following formula bounding reactivity and char conversion (Molina & Mondragón, 1998):

$$R = \frac{1}{W}\frac{dW}{dt} = \frac{1}{1-x}\frac{dx(t)}{dt}$$

The reactivity was tested in laboratory fixed bed reactor by Smoliński (2011). The reactor was placed inside an electric furnace. Coal samples of 3 g each were placed in the reactor between the quartz wool. The reactor was heated in an inert atmosphere, to 973 K. After that a steam was introduced into inert gas, flowing through the reactor bed. The output gases composition was measured every 192 s. Upon gathered data, the reactivity of the coal samples were calculated.

The reactivity for coal from each mine were determined as an average of all samples for the mine. The results are presented in Table 1.

The presented values were used or determination of models' reaction constant determination. The values were obtained using Mathematica Solve function. The model equation were rewritten putting $x = 0.5$ and known value of char reactivity for that conversion. In first step, the differential equation for the model was defined, then the equations were used as an input parameter for solve method. The Mathematica script for volumetric model and reactivity obtained for Piast originating char can be written as follows:

$$\text{volEqn} = D[x[t], t] == k(1 - x[t]);$$

$$\text{Solve}\left[\text{volEqn}/.\{x'[t] \to 0.5 \cdot 1.962 \cdot 10^{-4}, x[t] \to 0.5\}, k\right]$$

The values obtained for considered models are presented in Table 2.

Because it is not possible to determine the value of the parameter α in Johnson model, it was assumed that calculations will be performed for arbitrary chosen values.

Table 1 – Average values of char reactivities from selected Polish mines.

Mine	R_{50} [1/s]
Piast	1.962×10^{-4}
Ziemowit	1.975×10^{-4}
Janina	1.800×10^{-4}
Szczygłowice	1.850×10^{-4}
Bogdanka	2.000×10^{-4}

Table 2 – Reaction constants' values determined on char reactivity basis.

Mine	Volumetric	Non reactive core	Johnson
Piast	1.962×10^{-4}	1.558×10^{-4}	$1.558 \times e^{-0.25\alpha} \times 10^{-4}$
Ziemowit	1.975×10^{-4}	1.567×10^{-4}	$1.567 \times e^{-0.25\alpha} \times 10^{-4}$
Janina	1.800×10^{-4}	1.429×10^{-4}	$1.429 \times e^{-0.25\alpha} \times 10^{-4}$
Szczygłowice	1.850×10^{-4}	1.468×10^{-4}	$1.468 \times e^{-0.25\alpha} \times 10^{-4}$
Bogdanka	2.000×10^{-4}	1.587×10^{-4}	$1.587 \times e^{-0.25\alpha} \times 10^{-4}$

4.3. *Calculations and results*

The calculations for each of the model were done using Mathematica NDSolve function. The function solves numerically given differential equations set. For considered problem typical ordinary differential equation (ODE) is solved. It was assumed that for each model, that the char conversion for $t = 0$ is zero. The Mathematica script for solving non reactive core model with estimated parameters is given as follows:

```
nrcEqn = D[x[t], t] == k (1 - x[t])^(2/3);
nrcInit = x[0] == 0;
nrcVars = {x[t], x'[t]};
nrcTime = {t, 0, 8000};
nrcSol = NDSolve[{nrcEqn /. k -> 0.0003115274564487592, nrcInit},
  nrcVars, nrcTime]
```

The first four lines define the ODE used for simulation, the initial condition, variables and time range. The end time, 8000 s was chosen arbitrary as twice the time of the experiments. Figs. 5–7 shows char conversion in time for considered mines, using volumetric, non reactive core and Johnson model respectively.

The calculations shows that only slight difference can be observed between conversion predicted by volumetric model and non reactive core model. Both models estimate the char conversion at ~0.77 at the end of simulation time (8000 s). For the volumetric model, the reaction rate is slightly bigger in the first part of the process. The predictions given by Johnson model show, that after relatively fast reaction in the first 1500 s, the process slows down, and after the assumed calculation times, predicted the char conversion is lower than for volumetric and non reactive core model. The calculated reactions' constants for selected polish coals do not differed much. Depending on model used, the differences at the end of the process do not exceed 10%. Therefore, as long as the volumetric model predictions satisfy the real process behavior, this model should be preferred for calculations. When experimental data shows that process significantly slows down and not all char is converted, there is a potential for using Johnson model.

5. Conclusions

In the article the comparison between volumetric, non reactive core and Johnson model was presented. The model parameters were calculated using char reactivity estimate for selected coals from Polish mines. All calculations were

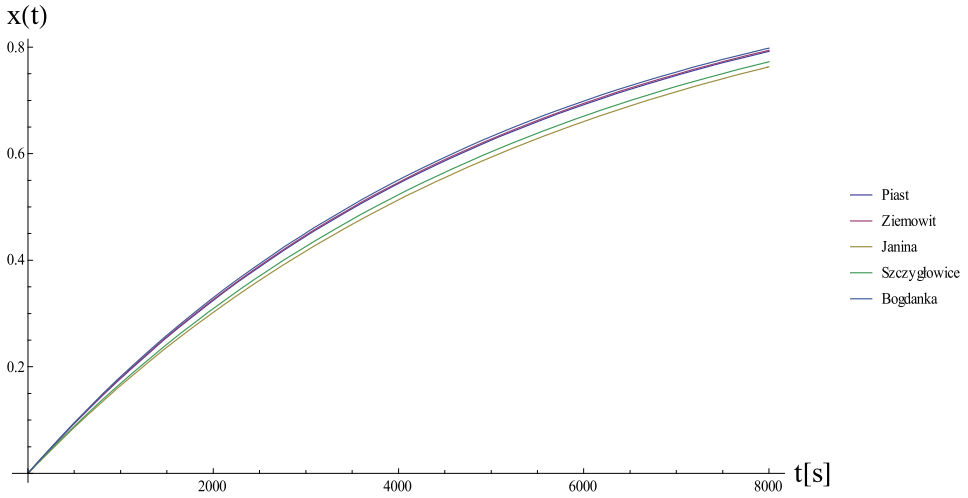

Fig. 5 – Char conversion in time predictions using volumetric model.

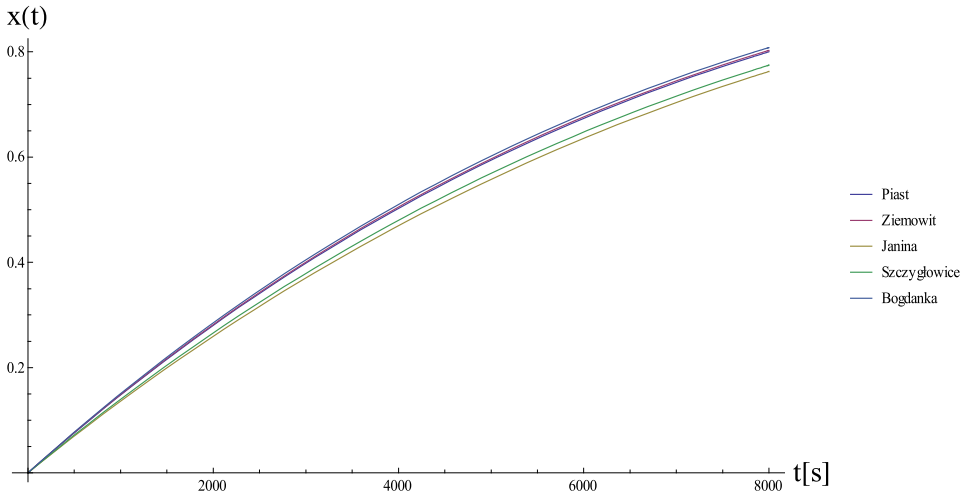

Fig. 6 – Char conversion in time predictions using non reactive core model.

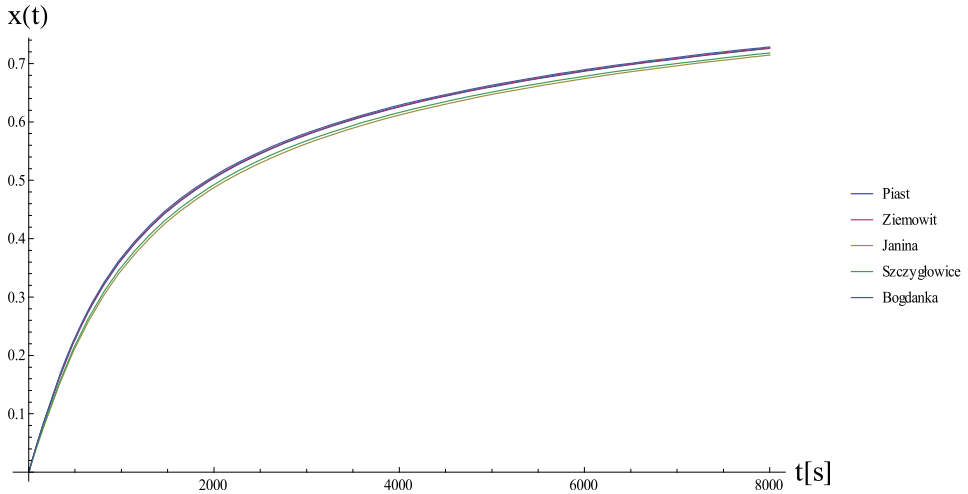

Fig. 7 – Char conversion in time predictions using Johnson model.

performed within Mathematica environment. Upon performed calculations, following conclusions were formulated:

1. The differences between predictions of volumetric model and non reactive core model were relatively small. For that reason, the volumetric model, as simpler, should be preferred over non reactive core model.
2. The Johnson model is especially useful for simulation of process, where not all char is converted or when a significant reaction slow down is observed. Appropriate adjustment of exponential factor allow fitting to wide range of modeled system behavior. It has to be stressed, the model will approach $x = 1$ after sufficiently long time, but as the reaction rate slows down to values very close to zero, the process has practically stopped, with conversion values still lower than one.
3. Mathematica proved its usefulness in application to coal gasification process modeling and data analysis.

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