

Effect of Operating Parameters on Agricultural Biomass Mixture Pyrolysis Process in a Batch Reactor

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Received: 31 March 2022, Accepted: 24 June 2022, Published online: 09 January 2023

Abstract

Many phenomena affect devolatilization of biomass particles, including mass and heat transfer, chemical reactions and physical transformation. Mathematical models that are capable to describe pyrolysis phenomena can greatly assist the large-scale development and optimization of pyrolysis processes, but to be implemented into large-scale simulation the models need to be simplified at a certain degree.

In the present study, an existing mathematical model is used to describe the pyrolysis of a single particle of biomass. It couples the heat transfer equations with the chemical kinetics equations. The common Euler explicit method is used for solving the heat transfer equation and the two-step pyrolysis kinetics equations. The model equation is solved for a sphere particle with a radius of 0.001 m and temperature ranging from 300 to 923 K. An original numerical model for the pyrolysis of agricultural biomass mixture is proposed and relevant equations solved using original program realized in MATLAB.

Simplified particle model was validated with the experimental data in a non-isothermal pyrolysis reactor. The sample was heated in the temperature range of 300–923 K at average heating rates of 21, 30 and 54 K/min. The model results showed reasonable agreement with experiments. The difference (between the experimental and model results) is slightly more prominent with decreasing heating rate (21 and 30 K/min), but model results are in much better agreement with the experimental data for higher heating rate (54 K/min). It is demonstrated that a constitutive equation can be used to express devolatilization rate for higher heating rates.

Keywords

agricultural biomass, mathematical modeling, pyrolysis

1 Introduction

The world's dependence on fossil fuels is increasing day by day due to rapid industrialization, economic development and population growth. Fossil fuel reserves will be depleted and the development of renewable energy sources aims to maintain energy in a sustainable form. Extensive research is being conducted around the world to reduce dependence on fossil fuels and replace them with alternative fuels.

One of the major renewable energy sources is biomass. Biomass resources (wood, agricultural residuals or municipal solid waste) consist of organic raw materials that can be converted into energy. Biomass is a renewable source of energy and has many advantages from an ecological point of view. Of all the renewable energy sources, biomass energy is the only renewable energy source of carbon and is able to convert into convenient solid, liquid and gaseous fuels. Nevertheless, most biomass wastes have

negligible sulfur content that produces lower SO₂ emissions compared to conventional fossil fuels. This will protect the environment and the health of citizens.

Fossil fuels are still the main source of energy in Serbia. Unfortunately, the production of energy from renewable sources is not widespread in most parts of the world. However, it is believed that biomass will play an important role in the world's future, and with the increase of fossil fuels prices, growing interests for such source of energy can be expected. Biomass is not currently used for electricity generation, and its utilization is limited to some new facilities installed in food and processing industry. In spite of that, the production of energy from renewable sources shows a significant potential for Serbia at this moment. Agricultural residues are the main biomass renewable sources in the northern part of the Serbia.

Agricultural biomass consists of crops residues such as: straw, corn, cob, stalks etc. High agricultural production could provide a significant amount of energy from waste if used properly.

Biomass can be used directly or indirectly by converting it into a gaseous, liquid or solid fuel. The main biomass thermo-chemical conversion processes are: combustion, gasification and pyrolysis. Some thermo-chemical biomass conversion processes could produce fuels efficiently and economically, as opposed to directly burning biomass to produce heat or energy. Biomass pyrolysis is the most preferable alternative in Serbia.

Pyrolysis of biomass is the heating of solid biomass in an inert atmosphere to produce gaseous products (such as: CO_2 , H_2 , CO , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , ...), liquid products – tar (high molecular hydrocarbons) and solid products – char. Certain factors determine the amount and variety of these outputs so that pyrolysis conditions can be optimized for char, gas or liquid production. For several decades, there have been extensive researches on biomass thermal conversion.

Extensive reviews based on a number of papers done by Di Blasi [1] show that the pyrolysis of biomass involves a complex series of reactions. Consequently, changes in the experimental heating conditions or sample composition and preparation may affect not only the rate of reactions but also the actual course of the reactions. Most of these observations which are made from reported publications have been mainly focused on woody material and, in a few cases, on agricultural residues. On the other hand, cereal straws and corn stalk are the predominant biomass in the northern part of Serbia.

There is not enough literature data regarding pyrolysis process of agricultural biomass mixture (corn stalk, wheat straw, soy straw and oat straw), so this is still not adequately researched. On the other hand, experimental investigation of individual kinds of agricultural biomass, such as corn stalk, wheat straw and oat straw has been conducted by many researchers.

Đurić et al. [2] describe an experimental investigation of pyrolysis process of agricultural biomass mixture. The mixture consists of corn stalk, wheat straw, soy straw and oat straw with equal mass fractions. During the experiment, 10 g of biomass sample inside the reactor was heated in the temperature range of 300–923 K at average heating rates of 21, 30 and 54 K/min. He pointed out that the heating rate of biomass mixture sample significantly affects the yield of pyrolytic gas and char. It was found that higher heating rates in the reactor lead to a higher yields of pyrolytic gas, while the char mass decreases.

Mlonka-Mędrala et al. [3] investigated the pyrolysis of agricultural biomass to determine the most promising process parameters for pyrolytic gas production. The pyrolysis investigations were carried out under nitrogen atmosphere at 573, 673, 773, and 873 K, using simultaneous thermal analysis and a laboratory-scale semi-batch vertical reactor.

Pešanjanski et al. [4] used a one-step global reaction to describe the thermal degradation of wheat straw samples. The influence of different factors was investigated, such as particle size, humidity levels and the heating rate in the kinetics of devolatilization.

In the field of biomass pyrolysis, there have been quite a number of works on modeling particle pyrolysis. Babu and Chaurasia [5] developed a model of pyrolysis based on the coupling of the transfer of heat with the chemical kinetics of pyrolysis. Grioui et al. [6] proposed a kinetic model comprising four stoichiometric stages. This model is used to study the pyrolysis of a cylindrical piece of wood and the operational influence of the parameters on the remaining mass and temperature profile within the particle. This model seems to be a rather simple and reliable numerical tool for testing the validity of the different hypothesis concerning kinetic parameters, thermophysical properties and heat and mass transfer during wood carbonization in comparison with experiments.

The quality and yield of pyrolysis products mainly depend on the type of pyrolysis, operating parameters and type of biomass. Operating parameters of pyrolysis include: heating rate, temperature, type of biomass, moisture content in biomass, retention time, catalyst, mineral matter etc. The influence of heating rate on the pyrolysis performance has been studied by many. Park et al. [7] suggested that there is a competition between gas, char and oil yield during biomass pyrolysis depending on the heating rate. They revealed that high pressure is generated inside the biomass particle during pyrolysis and sample splitting was observed during the experiments. It is turned out that at low heating rate, structural weakness is the primary factor, whereas at high heating rates, internal pressure is the determining factor. Williams et al. [8] investigated a general trend that an increase in the heating rate slightly reduces the char yield and increases both the oil and gas yield.

A different mechanism for the pyrolysis of single particle of different kind of biomass and the corresponding kinetic parameters has been reported in literature [1, 5, 9].

In previous article Miljković et al. [10] used a two-step kinetic model, proposed by Babu and Chaurasia [5],

to simulate the pyrolysis progress of a bulk particles of wood chips in a batch reactor. In that work, the model has been developed and solved for a slab particle of equivalent dimension 0.001 m and temperature ranging from 300 to 923 K. To check the validity of the numerical results, experimental results of pyrolysis of woody biomass in laboratory facility was used. The experimental results showed that the simulation results are in a reasonable agreement and can be successfully used to understand the degradation mechanism of solid reaction.

In the present work, a two-step kinetic model, proposed by Babu and Chaurasia [5], is applied to a sphere particle with a diameter of 0.001 m. The mathematical model uses the results of thermal analysis from an experimental study and physical properties or correlations from the literature [5]. The mathematical model is solved using original program realized in MATLAB and program algorithm is given in Fig. A1 in the Appendix. The model was then used to analyze specific pyrolysis work strategies.

When a solid particle of biomass is heated in an inert atmosphere the following phenomena occur. Heat is first transferred to the particle surface by radiation and/or convection and then to the inside of the particle. The temperature inside the particle increases, causing the removal of moisture that is present in the biomass particle, and after that main pyrolysis reaction takes place.

The proposed model is simulated and the results are compared with the experimental results. Non-isothermal pyrolysis data are analyzed. This procedure is applied for different values of pyrolysis heating rate. By using the model proposed in this study, it is possible to predict the pyrolysis rate over a wide range of heating rates. In this work, a wide range of temperatures (300–923 K) and relevant particle dimension (1 mm) are considered.

Different factors affect the pyrolysis rate and the composition of the product classes. Temperature, pressure and heating rate are chief operating parameters [4]. Biomass properties (chemical composition, ash content and composition particle size and shape, density, moisture content, etc.) also play an important role.

The aim of this work is to investigate the pyrolysis behavior of agricultural mixture of biomass, to check the influence of experimental conditions on kinetic parameters and to provide kinetic information for evaluation of the processing of these materials. The work includes modeling studies as well as analysis of experimental results on mixture of four biomass materials – corn stalk, wheat, soy and oat straw. Using modeling and experimental approaches,

this study aims to discuss and provide insight into the pyrolysis characteristics, processing time, pyrolysis products etc.

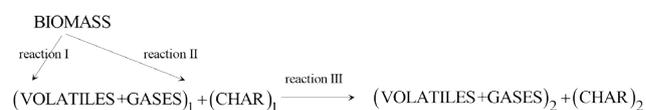
Analysis of the pyrolysis process and the impacts of process parameters on the pyrolysis products and representing them with a mathematical model can help in the design, operation and optimization of the pyrolysis process. Mathematical models that are capable to describe pyrolysis phenomena can greatly assist the large scale development and optimization of pyrolysis processes.

2 Modeling study

Biomass is a complex material which contains many compounds, but the dominant chemical species can be categorized as: cellulose, hemicellulose and lignin [4]. The three major constituents decompose in different temperature ranges resulting in a large number of parallel and consecutive reactions during particle conversion and many reaction products. The inability to develop a detailed reaction scheme has forced many authors to an approach in which the different reaction products were classified according to their aggregation state at standard conditions: gas, tar and char. This simplified reaction scheme can be represented as in [5]. This two-step kinematic model has three forms: sphere, cylinder and plate. In my work I used the sphere model (Scheme 1).

Applied model was widely available in the literature. According to Babu and Chaurasia [5], the thermal degradation processes are divided into a primary stage and a secondary stage. The products of the first reaction (volatiles and gases) further reacts with char produced by second reaction to produce volatiles, gases and char of different composition. Therefore, the primary pyrolysis products participate in secondary interactions causing a modified final product. One might imagine that these phenomena can lead to particle shrinkage. However, according to Curtis and Miller [11], during conversion of cellulose no shrinkage was observed. Instead it, proceeded by an increasing porosity of the material. In the current model, two species (biomass and char) were considered in solid phase.

In modeling biomass particle pyrolysis, it is common to employ a kinetic model to form the base of the model for describing pyrolysis reactions. Afterwards, the consideration of the physical processes that involve physical changes, heat transfer and mass transfer comes in place.



Scheme 1 Simplified reaction scheme

The developed model is a mathematical model consisting of a series of equations.

Set of equations is for sphere biomass particle pyrolysis modeling:

1. Kinetic model:

$$\frac{dC_B}{dt} = -k_1 (C_B)^{n_1} - k_2 (C_B)^{n_2} \quad (1)$$

$$\frac{dC_{G1}}{dt} = k_1 (C_B)^{n_1} - k_3 (C_{G1})^{n_3} (C_{C1})^{n_3} \quad (2)$$

$$\frac{dC_{C1}}{dt} = k_2 (C_B)^{n_2} - k_3 (C_{G1})^{n_3} (C_{C1})^{n_3} \quad (3)$$

$$\frac{dC_{G2}}{dt} = k_3 (C_{G1})^{n_3} (C_{C1})^{n_3} \quad (4)$$

$$\frac{dC_{C2}}{dt} = k_3 (C_{G1})^{n_3} (C_{C1})^{n_3} \quad (5)$$

$$\frac{d\rho}{dt} = \frac{dC_B}{dt} + \frac{dC_{C1}}{dt} + \frac{dC_{C2}}{dt} = -k_1 C_B^{n_1} \quad (6)$$

$$k_1 = A_1 \exp\left[\left(D_1/T\right) + \left(L_1/T^2\right)\right]$$

$$k_2 = A_2 \exp\left[\left(D_2/T\right) + \left(L_2/T^2\right)\right]$$

$$k_3 = A_3 \exp\left[-E_3/(R_c T)\right]$$

2. Heat transfer model:

$$k \left[\frac{2}{r} \frac{dT}{dr} + \frac{d^2 T}{dr^2} \right] + (-\Delta H) \times \frac{d(-\rho)}{dt} = \frac{d(c_p \rho T)}{dt}$$

$$k \left[\frac{2}{r} \frac{dT}{dr} + \frac{d^2 T}{dr^2} \right] + (-\Delta H + c_p T) \times \frac{d(-\rho)}{dt} = \rho c_p \frac{d(T)}{dt} \quad (7)$$

$$c_p = 1112 + 4.85(T - 273)$$

$$k = 0.13 + 0.0003(T - 273)$$

$$\text{I.C. 1: } T(r, 0) = T_0 \quad (8)$$

$$\text{B.C. 1: } \left. \left(\frac{dT}{dr} \right) \right|_{r=R_0} = 0 \quad (9)$$

$$\text{B.C. 2: } -k \left(\frac{dT}{dr} \right)_{r=R} = h(T_f - T) + \sigma \varepsilon (T_f^4 - T^4) \quad (10)$$

The model describes the pyrolysis progress of multiple particles that are subjected to pyrolysis condition within a pyrolyzer reactor. The pyrolyzer operates more like a batch reactor in which the temperature of the heating gas rises with different heating rates. By inputting the heating rates and the heating time as model variables, the model can simulate the pyrolysis progress and output the relative remaining mass (shorter form: remaining mass) profiles and the temperature profiles of individual particles during pyrolysis and the processing time. According to some studies, the particle model agrees well enough with the experimental data, taking into account only the conductivity and the devolatilization reaction [5].

A proper model could show which chemical and/or physical phenomena are relevant in this respect and how to control the process. In this work special attention was given to the effects of heating rate. My study focused on small particles with a diameter of 0.001 m.

It is clear that the modeling of the physical and chemical processes involved in the pyrolysis of a single particle is so complex that many simplifying assumptions must be made:

1. Single solid particle is spherical in shape.
2. It is assumed that heat is transferred inside the solid particle by conducting.
3. Temperature gradients are along radial position only.
4. External heat transfer is considered to occur by a combination of convective and radiation mechanisms.

Based on that, the mathematical form of developed model is presented by a set of nonlinear partial differential equations which can be solved numerically. The common Euler explicit method [12] is suitable in this case. This method, however, requires simultaneous solution for the unknowns at each new time step.

3 Numerical solution

In this study the particle is treated as a continuous porous medium and numerical calculations are carried out by dividing the particle into many cells, as shown in Fig. 1. Inside each cell the parameters of concern (e.g. temperature, percentage of gases, carbon) are assumed to be uniform. The model assumes that the devolatilization of biomass particle proceeds as the propagation of infinitely thin reaction front from the surface to the centre of particles.

It is assumed that the particle can be considered as porous medium and during the pyrolysis process, the cell size remains constant and only its porosity changes.

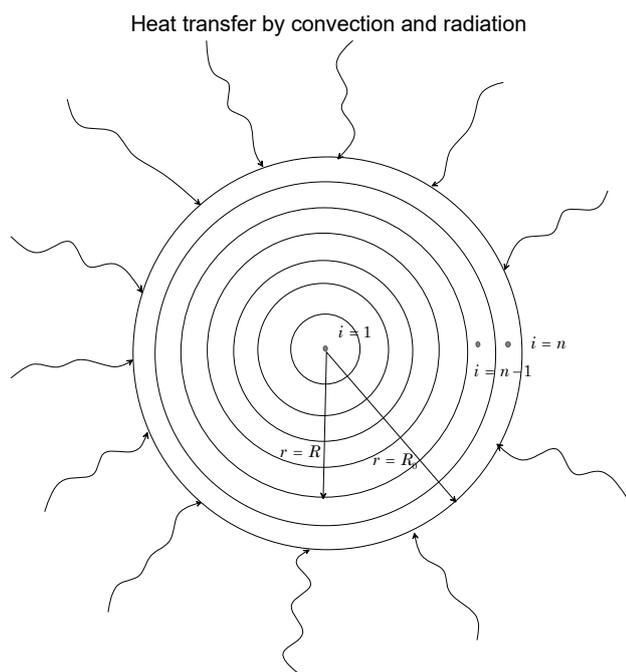


Fig. 1 Cross section grid diagram of the sphere particle

In order to numerically solve mathematical model, initial conditions for differential Eqs. (1)–(6) and initial and boundary conditions for differential Eq. (7) are listed.

4 Results

To validate the results obtained by the model during the pyrolysis of a sphere biomass particle, the experimental results [2] were used. The change of particle mass over time represents the fuel conversion of biomass particles during the devolatilization.

4.1 Model validation

Đurić et al. [2] carried out experiments on pyrolysis of agricultural biomass mixture, without the addition of inert gas. Agricultural biomass samples were collected for research from an agricultural area near Novi Sad (Serbia). The sample is a mixture of four different kinds

of agricultural biomass: corn stalk, wheat straw, soy straw and oat straw with equal mass fractions. Proximate and ultimate analysis of used biomass is given in Table 1 [2]. During the experiment, 10 g of the sample in the batch reactor was heated in the temperature range of 300–923 K at average heating rates of 21, 30 and 54 K/min. Figs. 2–4 show a comparison of the model to experimental data.

Five experiments were done in conditions with a heating rate of 21 K/min, and two experiments each with a heating rate of 30 K/min and 54 K/min. Figs. 2–4 show the variations in mass between the experimental results [2] and the calculated values of remaining mass (defined as m/m_0 , where m is the actual and m_0 the initial mass of the sample) obtained during heat treatment of the biomass sample, for three cases of heating rate. The first observation is that the remaining mass of the biomass particles has three phases.

First phase: Actual mass readings of biomass samples in function temperatures do not change in the range of 300 to 500 K (inflection point); this is the result of the drying process during which pyrolysis has not yet begun.

Second phase: In Figs. 2–4 the temperature interval that is significant for pyrolysis is in the range of 500 to 923 K (inflection point). This middle part of the curves is characterized by the intensive process of volatile extraction, which results in a steeper curve of mass change in that temperature interval.

Third phase: There is no mass change temperature gradient greater than 923 K, indicating the fact that up to this temperature they have all solids already finished with pyrolytic reactions.

As can be seen, the mass change profiles obtained in the present study are in reasonable agreement with the experimental data. The difference (between the experimental and model results) is slightly more prominent with decreasing heating rate, but model results are in much better agreement with the experimental data for higher heating rate, Fig. 4. A similar trend was shown in an earlier paper for

Table 1 Proximate and ultimate analysis of agricultural biomass [2]

	Proximate analysis				Ultimate analysis					
	Moisture	Ash*	Fixed carbon, C_{fix}	Volatiles	Carbon C	Hydrogen H	Nitrogen N	Total sulfur S	Oxygen O^{**}	Lower heating value H_d (kJ/kg)
Corn stalk	13.17	11.52	16.60	60.23	48.23	8.18	0.81	0.18	31.08	16291
Wheat straw	14.77	7.80	16.35	62.23	48.23	8.30	1.09	0.19	34.38	16590
Soy straw	12.08	3.02	18.74	66.52	53.05	7.78	0.89	0.16	35.10	17465
Oat straw	12.22	15.06	15.38	59.18	44.82	7.88	1.20	0.14	30.89	16676

* Dry basis

** Oxygen content was calculated from the formula $C^{dry} + H^{dry} + O^{dry} + N^{dry} + S^{dry} + Ash^{dry} = 100\%$. C^{dry} , H^{dry} , N^{dry} , S^{dry} and Ash^{dry} are the mass fractions of carbon, hydrogen, oxygen, nitrogen, sulfur and ash, respectively, in the dry agricultural biomass, expressed in %.

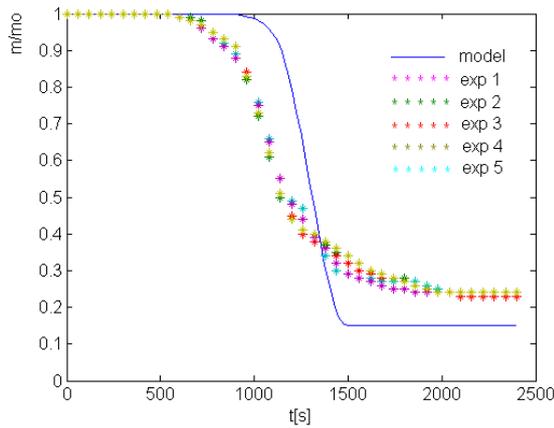


Fig. 2 Remaining mass of agricultural sample as a function of reaction time and heating rate 21 K/min for model and experiment

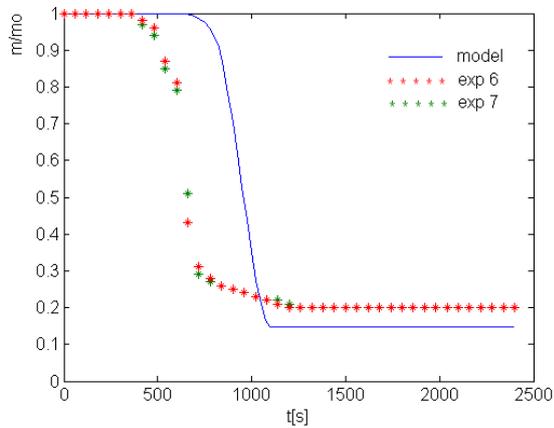


Fig. 3 Remaining mass of agricultural sample as a function of reaction time and heating rate 30 K/min for model and experiment

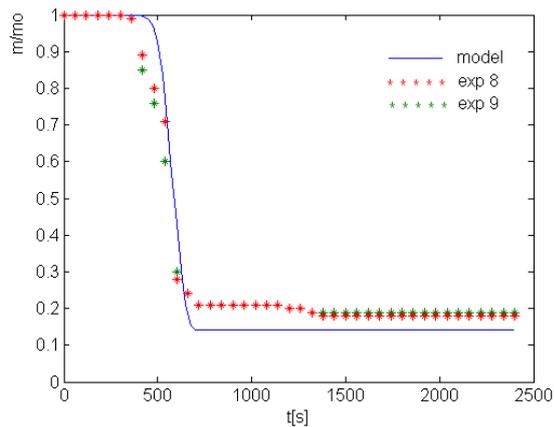


Fig. 4 Remaining mass of agricultural sample as a function of reaction time and heating rate 54 K/min for model and experiment

wood biomass sample [10]. According to the experimental data, in the case of low heating rates, results are shown in the form of saddle curve, Figs. 2 and 3. As shown, kinetics of thermal destruction of biomass particles depict a saddle curve with two emphasized characteristic segments in the

second phase (phase of intensive pyrolysis process): temperature intervals 500–650 K and 650–923 K. First segment in the second phase is characterized by the intensive process of volatile extraction, which results in a steeper curve of mass change in the temperature interval from 500 to 650 K. In the region of higher temperatures it comes to a gradual slowing down of reactions, which is reflected with an approximately constant slope of mass functions.

Furthermore, it can be noticed that a reduction in the temperature of the furnace generates a reduction the speed of loss of density which is in conformity with the experimental results [2].

4.2. Effect of heating rate

Experimental investigation of the effect that the heating rate of the sample in the reactor has on pyrolysis process is shown in Figs. 2–4. Three different heating rates in the reactor were investigated: 21, 30 and 54 K/min. For this reason, the set of equations, Eqs. (1)–(7), is solved numerically for the biomass sample when exposed to the heat flux of the same heating rate as in the experiment. The main result of the mathematical investigation is the remaining mass curve for the biomass sample as a function of reaction time and heating rate. The effect of heating rate is shown in Figs. 5 and 6. Heating rate affects the position of the remaining mass curve as well as the maximum decomposition rate. Fig. 5 shows the remaining mass of sample as a function of reaction time at different heating rates. It can be noticed that, as the heating rates increase, the pyrolysis process is faster, but when the process starts, it ends very fast and the slope of the curve is similar in each case. As the heating rate increases, the remaining mass curve shifts to a lower temperature. According to the model, the duration of the pyrolysis process was 1450, 1100 and 670 s with heating rates of 21, 30 and 54 K/min, respectively.

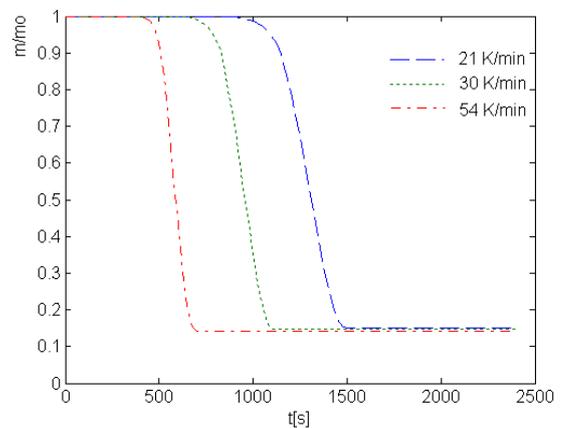


Fig. 5 Remaining mass of agricultural sample as a function of reaction time and heating rate

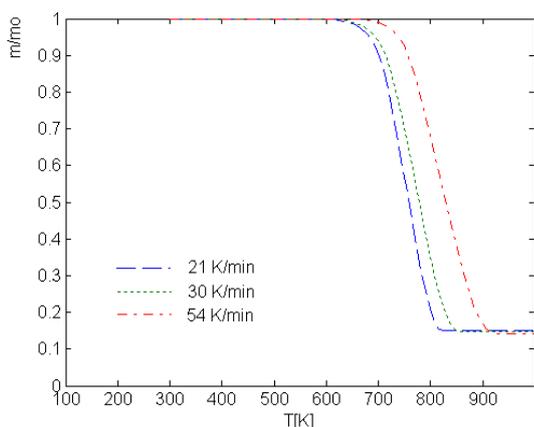


Fig. 6 Remaining mass of agricultural sample as a function of temperature and heating rate

Fig. 6 shows the remaining mass of sample with temperature at different heating rates (21 K/min, 30 K/min and 54 K/min). It can be noticed that the pyrolysis process starts at the same temperature (about 650 K), and proceeds rapidly with increasing temperature. During pyrolysis process, it is common that there is a shift of the remaining mass curve to higher temperature when the heating rate increases [2, 8, 10], as shown in Fig. 6. The position of peak remaining mass shifts to a higher temperature when the heating rate increases. Obtained results indicate that increasing the heating rate of the sample inside the reactor during the pyrolysis process leads to decrease of char yield and increase of pyrolysis gas, Figs. 5 and 6. Many authors observed, in their works, that high heating rate was in favor of volatile formation than char formation [7, 8, 13]. An increase in heating rate decreased both the char yield and the conversion time. The char yield increase is due to the secondary reactions between tar vapor and solid in the particle and the lower temperature heat up. For the analyzed biomass mixture and the heating rate range studied, the effect of heating rate on the final remaining mass is insignificant. The same trend showed the experimental results.

Figs. 7–9 show the temperature profile as a function of particle radius at different times progression of pyrolysis (250, 500, 750, 1000, 1250, 1500, 1800 and 2400 s). It can be noticed that as the pyrolysis time increases, the temperature increases in all positions. The difference in temperatures at different positions is negligible. The reason for this is the fact that the biomass particle is very small, sphere with a radius of 0.001 mm.

According to the model results, as shown in Figs. 7–9, duration of the heating process to the maximum temperature was 1800, 1250 and 750 s with heating rates values of 21, 30 and 54 K/min, respectively. These results show that

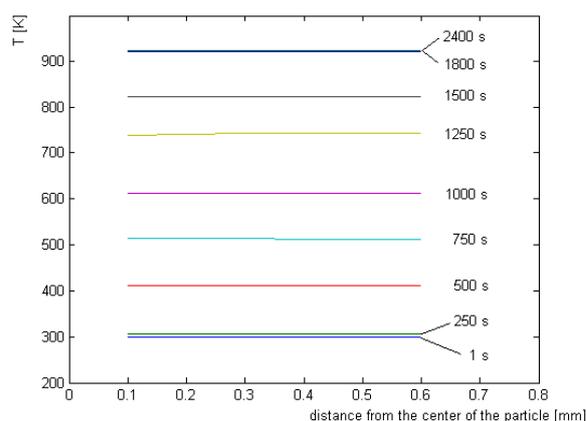


Fig. 7 Temperature profile as a function of position – Case I: heating rate 21 K/min

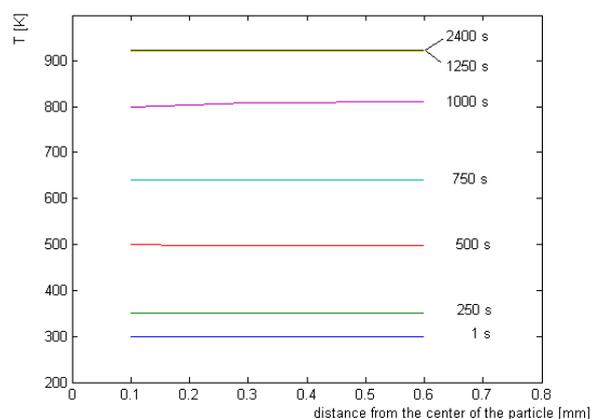


Fig. 8 Temperature profile as a function of position – Case II: heating rate 30 K/min

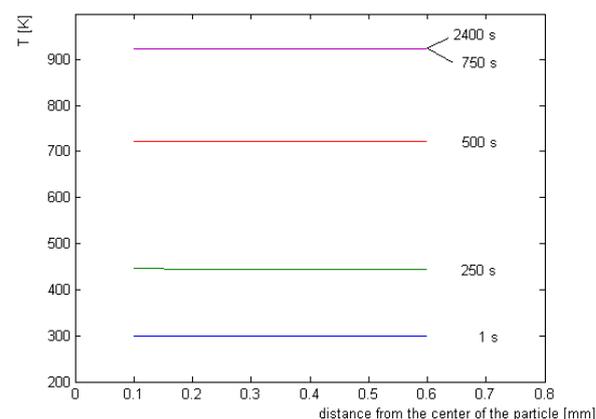


Fig. 9 Temperature profile as a function of position – Case III: heating rate 54 K/min

when the temperature of the furnace is increased, the time of pyrolysis becomes shorter. In the initial stages of pyrolysis, the heating process is very fast, and as time progresses, the heating process decreases. This can be explained by the fact that heat transfer by convection and radiation from

the gas phase to the wall surface in the initial stages of pyrolysis is very high. On the other hand, when the temperature of the particles is close to the temperature of the reactor gas, the heat transfer to the wall surface is much lower. As expected, the results show that as the heating rate increases, the time required for temperature rise decreases.

Fig. 10 shows the evolution of the temperature in the center of the biomass particle at different positions according to time. As can be seen, the temperature linearly increases with time and when it reaches about 750 K it starts to increase faster. That is the temperature when rapid degradation begins, Fig. 6. But, when the heating rate increases, the time to reach the critical temperature decreases. Higher heating rate has a short heating time. Remaining mass of biomass sample as a function of reaction time and position at different heating rates are given in Figs. A2–A7 in the Appendix.

5 Conclusions

This paper aims to use both experimental and modeling approaches to perform analysis on agricultural biomass mixture - corn stalk, wheat straw, soy straw and oat straw, and to provide insight into operation of the pyrolysis process.

For the modeling part, a kinetic-heat transfer model was used to simulate the pyrolysis progress of selected biomass particles for reactor scenarios. For the experimental part, the study used published experimental results [2]. The study investigated the effect of heating rate on pyrolysis using common thermal analysis techniques.

In the main part of this work, a mathematical model was used to simulate the pyrolysis progress of biomass particles in a reactor. It forms the basis for the discussion on the considerations of and interrelation between heating rate, processing time and product quality for the design and operation of pyrolysis processes.

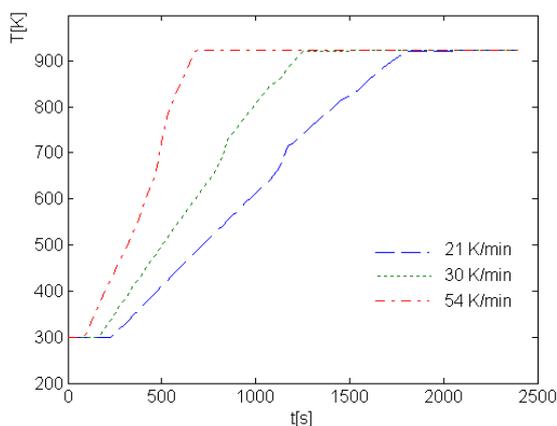


Fig. 10 Temperature profile as a function of reaction time at the center of the particle – Case I: heating rate 21 K/min, Case II: heating rate 30 K/min, Case III: heating rate 54 K/min

The model has been found to predict the pyrolysis characteristics of biomass particles. In particular, the solutions compared the effects of heating rate. Fig. 5 shows that with the lower heating rate the same size of biomass sample takes more time to pyrolyze than in the case with the higher values of heating rate. It clearly shows that lower heating rate pyrolysis produces more char and higher heating rate of pyrolysis produces more amounts of volatiles and gases and smaller amount of char. The effect of heating rate on the yield distribution is insignificant for the range of heating rate 21–54 K/min being studied.

Experimental results showed a similar trend. The simplified model is found to explain the pyrolysis behavior well. The mass change profiles obtained in the present study are in reasonable agreement with the experimental data. The difference (between the experimental and model results) is slightly more prominent with decreasing heating rate, but model results are in much better agreement with the experimental data for higher heating rate. Therefore, further model development is recommended for lower heating rate.

The main conclusion resulting from this study concerns the possibility of modeling the pyrolysis of a single biomass particle by coupling the heat transfer equation with the pyrolysis chemical kinetics equations. The models are optimization tools to achieve the desired product composition. However, they are very often not correlated with the real working conditions.

Mathematical models are one of the tools for development different process systems, but they require a lot of kinetic and design data from the literature.

Acknowledgements

This research is supported by the Ministry of Education and Science of the Republic of Serbia within the project "Development of methods, sensors and systems for monitoring of water, air and soil quality" (Project No. III 43008).

Nomenclature

C_B	concentration of B , kg/m^3
C_{C1}	concentration of C_1 , kg/m^3
C_{C2}	concentration of C_2 , kg/m^3
C_{G1}	concentration of G_1 , kg/m^3
C_{G2}	concentration of G_2 , kg/m^3
c_p	specific heat, J/kg K
h	convective heat transfer coefficient, $\text{W/m}^2 \text{K}$
k	thermal conductivity, W/m K
m	actual mass of the sample, kg
m_0	initial mass of the sample, kg

m/m_0	remaining mass of the sample, -
T	temperature, K
T_0	initial temperature, K
T_f	final temperature, K
T_g	temperature of gas, K
ΔH	heat of reaction, kJ/kg
r	radial distance, m
R	radius for sphere, m
t	time, s
ρ_0	density, kg/m ³
σ	Stefan-Boltzmann constant
ε	emissivity coefficient

Indexes

B	virgin biomass
G_1	gases and volatiles 1
C_1	char 1
G_2	gases and volatiles 2
C_2	char 2

Constants

k_1, k_2, k_3	rate constants, s ⁻¹
A_1, A_2, A_3	constants, s ⁻¹

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L_1, L_2	constants, K ²
D_1, D_2	constants, K
n_1, n_2, n_3	orders of reactions

Characteristic values for wheat straw

$h = 8.4$ W/m ²
$A_1 = 9.973 \times 10^{-5}$ s ⁻¹
$D_1 = 17254.4$ K
$L_1 = -9061227$ K ²
$A_2 = 1.068 \times 10^{-3}$ s ⁻¹
$D_2 = 10224.4$ K
$L_2 = -6123081$ K ²
$A_3 = 5.7 \times 10^5$ s ⁻¹
$E_3 = 81000$ J/mol
$\Delta H = -255000$ J/kg
$\rho_0 = 650$ kg/m ³
$n_1 = 1$
$n_2 = 1.5$
$n_3 = 1.5$
$T_0 = 300$ K
$T_f = 873$ K
$\varepsilon = 0.95$
$\sigma = 5.67 \times 10^{-8}$ W/m ² K ⁴

Appendix

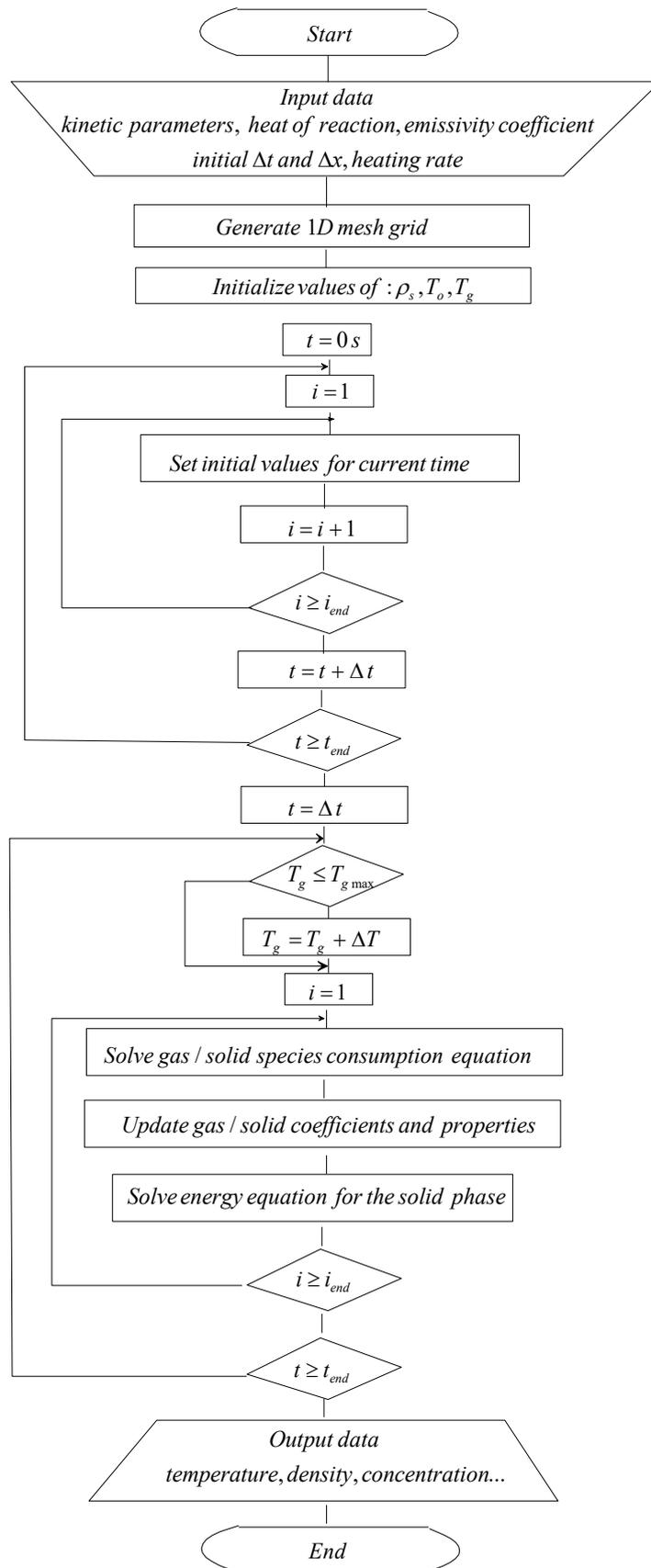
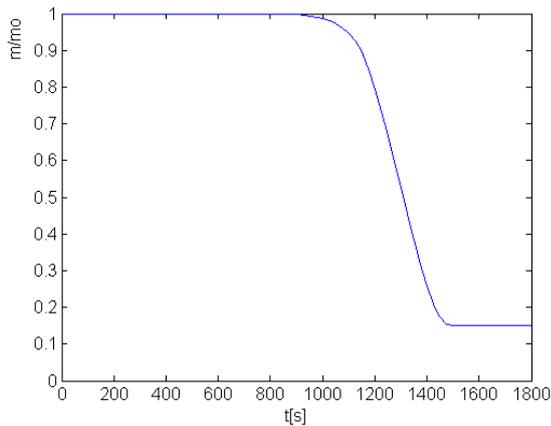
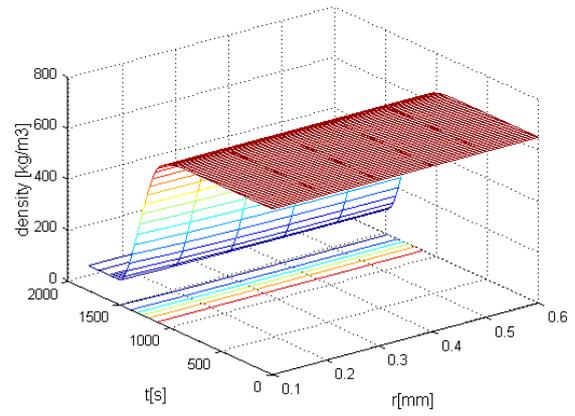


Fig. A1 Program algorithm

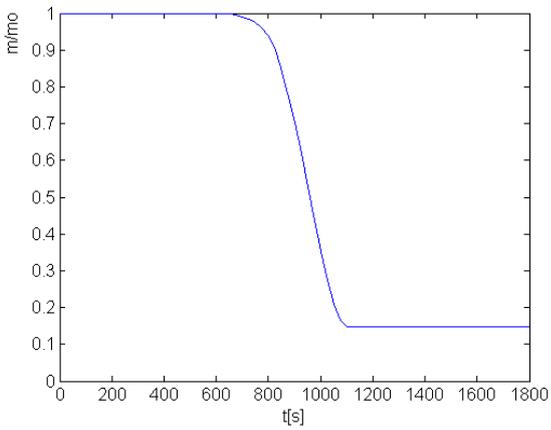


(a)

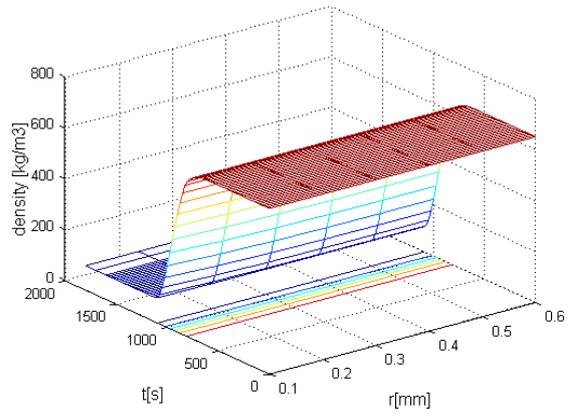


(b)

Fig. A2 Remaining mass of agricultural sample: (a) as a function of reaction time, (b) as a function of reaction time and position – Case I: heating rate 21 K/min

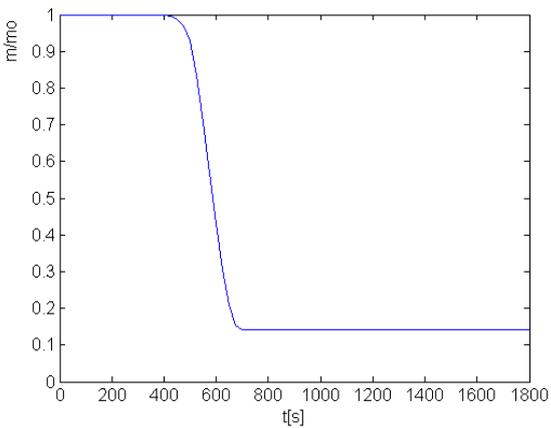


(a)

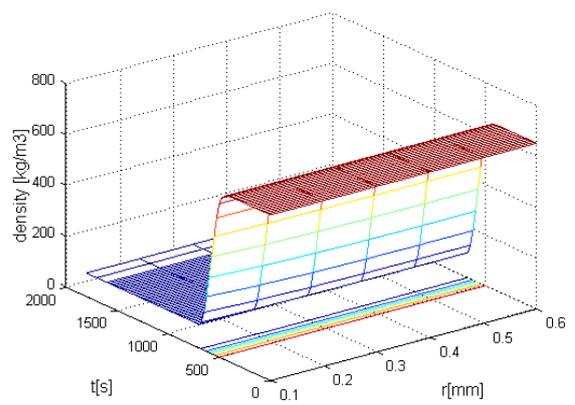


(b)

Fig. A3 Remaining mass of agricultural sample: (a) as a function of reaction time, (b) as a function of reaction time and position – Case II: heating rate 30 K/min

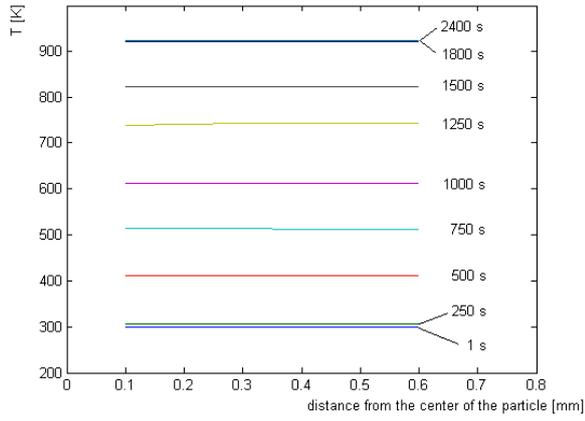


(a)

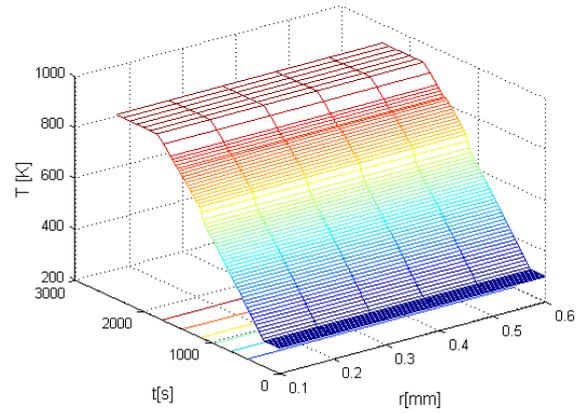


(b)

Fig. A4 Remaining mass of agricultural sample: (a) as a function of reaction time, (b) as a function of reaction time and position – Case III: heating rate 54 K/min

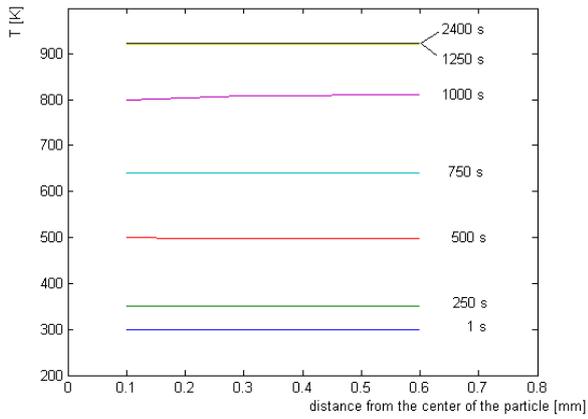


(a)

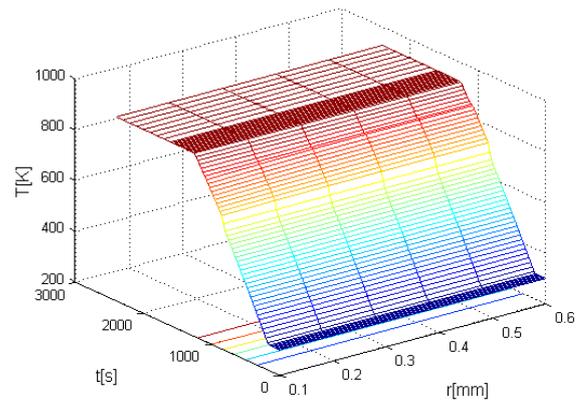


(b)

Fig. A5 Temperature profile as a function of reaction time and position – Case I: heating rate 21 K/min

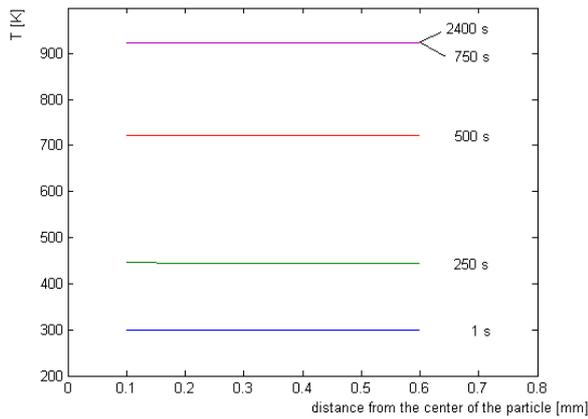


(a)

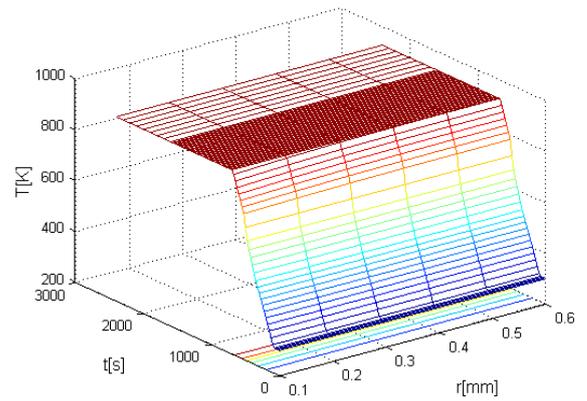


(b)

Fig. A6 Temperature profile as a function of reaction time and position – Case II: heating rate 30 K/min



(a)



(b)

Fig. A7 Temperature profile as a function of reaction time and position – Case III: heating rate 54 K/min