

Analysis of the thermal behavior of a fixed bed reactor during the pyrolysis process

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Abstract

Pyrolysis is a thermochemical process of degradation of organic compounds where the reaction takes place in an inert atmosphere. The process scale varies between industrial, semi-industrial or laboratory. During the pyrolysis process temperature has to be controlled, but, most of pyrolysis studies do not clearly state where the temperature is measured and whether the temperature field is uniform. In this paper thermal behavior of a laboratory scale fixed-bed reactor and energy consumption during pyrolysis processes were analyzed. Three different samples were used: mixture of plastic waste (sample 1), biomass (sample 2) and mixture of plastic waste and biomass (sample 3). The analysis of the thermal behavior of the reactor indicates that with careful regulation or temperature control of the process, one can obtain diagrams that can be used for the purpose of recording thermally intensive processes, similar to more complex thermogravimetric (TG) and derivative thermogravimetric (DTG) analyses. It has been shown that it is possible to change the heating rate and the overall energy efficiency of the process by simply choosing the appropriate raw material mixture.

Keywords: Waste plastics; waste recovering; thermal reaction; heating rate; energy consumption.

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1. INTRODUCTION

Plastic waste is a common part of municipal solid waste (MSW), which is composed of different mixtures of plastic, mostly consisting of: low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), and polyethylene terephthalate (PET). The main components of municipal plastic waste are PE and PS [1]. Plastic waste is bulkier than other organic waste so that it occupies large spaces in landfills. Also, this is the main reason for the high costs of disposal and incineration of this type of waste. Waste-to-energy technologies convert plastic waste into heat, hydrocarbon fuels and chemicals [2]. Pyrolysis of plastic is a tertiary recycling method, whereby the polymer is heated in the absence of oxygen causing the polymer cracking [3]. Pyrolysis is also used for biomass conversion where the mostly used feedstock is plant matter, like forest residues, yard clippings, wood chips, and municipal solid waste [4].

Pyrolysis process represents a basis for production of the second generation of synthetic fuels, materials, and chemicals [5]. This reaction occurs in an inert atmosphere, in which organic compounds are decomposed, generating gaseous and liquid products that can be further utilized as fuels or chemicals. The inorganic material remains unchanged [6,7]. During pyrolysis of polymers, macromolecules are broken down into smaller molecules [8]. Biomass materials are mostly chemically and physically heterogeneous, whereby their components have various reactivities and yield different products [9].

Many studies have been published focusing on pyrolysis of plastic and biomass waste. A comprehensive bibliometric survey on pyrolysis of plastic waste has been done by Armenise *et al.* [10], while several studies provide detailed explanation on pyrolysis of plastic, pyrolytic reactors, effects of different parameters on the liquid oil yield and its

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characterization [11-16]. Interesting studies on the catalytic pyrolysis have been published by Budsareechai *et al.* [17], and Suhartono *et al.* [18] showing that addition of natural catalysts lead to higher yields of liquid products with better properties (no wax formation, increased calorific value, and lower viscosity) compared to the pyrolysis runs without catalysts. Catalytic pyrolysis of plastic sample based on the plastic waste composition from Portuguese municipal solid waste has been conducted by Pinto *et al.* [19]. However, this study showed that there is no big difference between thermal and catalytic pyrolysis of selected plastic waste mix (68 % PE, 16 % PP, and 16 % PS). Uthpalani *et al.* [20] have reviewed the literature on pyrolysis of HDPE and LDPE wastes. Kalargaris *et al.* have been studied diesel engines powered by pyrolytic oil gained from pyrolysis of plastic waste throughout several studies [21-24]. Some papers [25-28] confirm and prove the success of pyrolysis of the mixture in the specific configuration of the reactor with a fixed bed that was used in this work as well.

Generally, pyrolysis can be divided into two phases, primary and secondary. When a solid biomass particle is heated in the absence of oxygen heat is firstly transferred to the particle surface by radiation and/or convection and then to the interiors of the particle by conduction. The temperature within the particle increases and contributes to the removal of moisture that is contained in biomass, and the pyrolysis reaction takes place. Due to the chemical reactions heat is generated/consumed, which with phase changes cause a temperature gradient as a function of time that is nonlinear. Volatiles and gas products flow through the particle pores. The rate of pyrolysis reactions depends on the local temperature [9].

Benefit of pyrolysis is production of high energy compounds (char, tar, and gas) from low energy materials (solid waste). The conversion depends on operating conditions, *e.g.* heating rate, maximum temperature, processing time at the maximum temperature, pressure, and catalysts used [29,30]. Additionally, the quality and yield of the oil products are depending on: operating temperature, the ratio of plastic waste and catalyst, and the type of reactor [31].

1. 1. Pyrolysis reactors

There are many different types of pyrolysis reactors and their classification can be based on: the final products achieved (oil, char, heat, electricity, gases), reactor mode of operation (batch or continuous), manner in which the reactor is heated (direct or indirect heating), method used to load the reactor (manually or mechanical), the pressure at which the unit operates (atmospheric, vacuum, pressurized), material used for the construction of the reactor (soil, brick, concrete, steel), reactor portability (stationary or mobile), and the reactor position [32].

Fixed-bed reactors are commonly used on a laboratory scale for pyrolysis of municipal solid waste, while industrial applications of this reactor type are rare. The heating rate is low, and the particles are not heated uniformly. This is due to the low heat transfer coefficient within the reactor and the absence of mixing of feedstock. So, the particles located near the heating source will gain more heat, whereas those more away from the heating source would be cooler [33]. Pyrolysis of biomass in fixed-bed reactors was studied in several studies [*e.g.* 34-36]. In another study that used fixed-bed reactors for pyrolysis of plastic waste, polystyrene and multilayer plastic were used in different ratios as raw materials. This research concluded that with the longer cracking time and the higher number of plastic multilayers, the fuel volume, viscosity, and heat value were increased. The addition of multilayer plastic also decreased percentage of benzene in the final product [37].

It is important to differentiate between the temperature of the reaction and the reactor temperature. The reactor temperature must be higher because of the need for a temperature gradient to provide heat transfer [38]. The temperature profile and heat transfer that occur during pyrolysis are decisive factors that determine the reactor performance, and consequently the oil yields [39]. Since pyrolysis is a thermal degradation process, efficient heat transfer increases the process efficiency. Plastic has low heat conductivity that leads to non-uniform heat distribution [40]. Temperature profile in the reactor is used to determine the area where thermal cracking happens, since cracking is the most important step during plastic pyrolysis to produce oil (fuel) [41]. In the work of Hartulistiyoso *et al.* [41], pyrolysis of waste plastic bottles was conducted in cylindrical reactor. Five thermocouples were used to monitor temperature at the bottom, top and in the middle part of the reactor, with different arrangements, while the temperature profile within the reactor was predicted by Computational Fluid Dynamic (CFD) modeling. Predicted temperature profiles were similar

to the experimentally measured temperature values. Accurate measurement of the particle temperature is important for the development of kinetic models. In most experiments temperature is measured by thermocouples close to the sample. However, there is less information on temperature profile inside the sample [42]. Fluidized bed is one of the reactors that can provide uniform temperature and uniform heating rate during high temperature operation [40].

Since the literature does not provide sufficient information on temperature distribution during plastic pyrolysis, this paper aims to investigate the uniformity of the temperature field in a pyrolytic reactor (fixed-bed reactor) that has been developed at the University of Banja Luka, at the Faculty of Technology. Energy consumption during pyrolysis of different samples was also analyzed.

2. EXPERIMENTAL

The experiments were carried out with plastic waste blends, originating from municipal solid waste, biomass sawdust and blends of plastic waste and sawdust. Plastic packaging waste originates from household waste from Banja Luka, Republic of Srpska, Bosna and Herzegovina, and the sawdust is from local sawmills from Banja Luka region. The ratio of plastic types in the blends was following: polypropylene (PP) 40 %, low-density polyethylene (LDPE), 35 %, and high-density polyethylene (HDPE) 25 %. A mixture of two typical types of waste wood biomass beech sawdust and spruce sawdust was used as the biomass sample, which were mixed in equal mass ratios (1:1).

Packaging household waste was used to prepare PP and HDPE samples, while LDPE granulates for the production of plastic bags was used as LDPE sample. The waste packaging was firstly thoroughly washed, dried, shredded and grounded in the laboratory mill. After grinding, a mixture of PP and HDPE was prepared in the selected ratios and a granulometric analysis was performed. The average diameter of the plastic mixture (PP + HDPE) was 1.40 ± 0.02 mm. The prepared plastic mixture was then mixed with cylindrical LDPE granulates (2.20 mm diameter \times 5.03 mm length). The prepared biomass sample was dried to a constant mass for 24 h at a temperature of 105 °C, in order to avoid the influence of humidity variations in the starting raw material. A granulometric analysis of the biomass mixture was carried out as well yielding the average sawdust particle diameter of 0.77 ± 0.12 mm. All samples were weighed by using a KERN KB 1200-2 laboratory scale.

Experiments were performed using a total sample mass of 200 g, and the height of the packed bed was 95 mm. Only one experiment, *i.e.* the experiment with maximum reactor loading, was performed with the sample mass of 350 g, and in that case the packed bed height was 190 mm.

Pyrolysis was performed in a laboratory scale, fixed bed reactor at the University of Technology in Banja Luka (Bosnia and Herzegovina), presented in Figure 1.

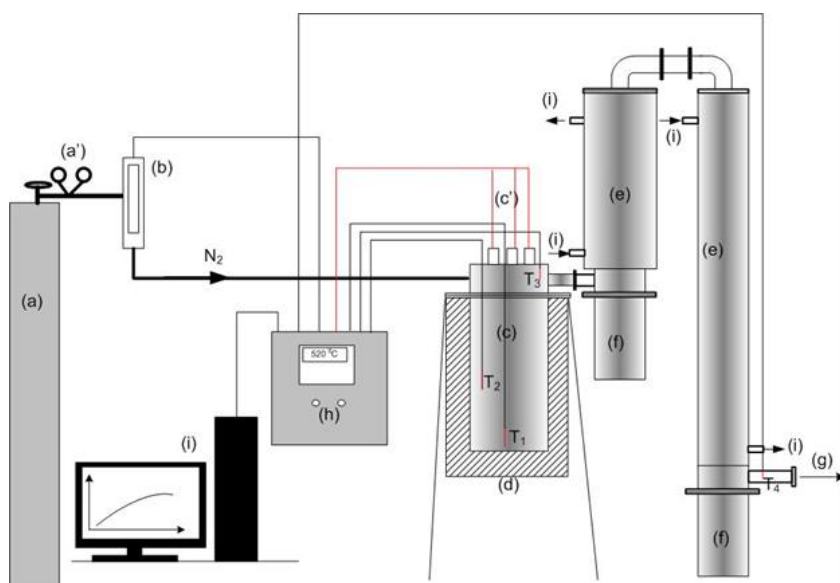


Figure 1 Block diagram of the experimental pyrolysis fixed-bed reactor: a) cylinder with nitrogen gas; b) mass gas flow meter; c) the pyrolysis reactor vessel; d) thermal insulation; e) steam condensation system; f) separation system - vessels for receiving condensate; g) discharge of non-condensable gas into the gas washing system; h) distribution cabinet with the regulation system; i) PC.

A prepared and weighed sample was placed in the reaction vessel (c) and nitrogen was used as the carrier gas, to provide inert atmosphere (a). A gas-flow meter (b) was used to adjust the gas flow ($100 \text{ ncm}^3\text{min}^{-1}$), and after 10 min, inert atmosphere was accomplished. A PC (i) using CelciuX (EJ1N-TC4A-QQ) (Omron) thermal controller and CX-Thermo (Omron) were used for automatic control and regulation of the system (h) by turning on or off the electric heaters system (c) according to the control loop [25,28]. The thermocouple T1 (Thermocouple type K, Omron, Japan) measured temperature at the bottom part of the reactor and served as a control sensor for the controlling loop of electric heaters *i.e.* as a control variable. The reactor temperature set point was $500 \text{ }^\circ\text{C}$. The time that feedstock spent on a set point temperature was considered to be a reaction time. After the chosen reaction time of 45 min, the regulation system was turned off. As the temperature of the reactor fell below $100 \text{ }^\circ\text{C}$, the reactor was taken apart and the reaction vessel was disconnected from the reactor (c). The reaction vessel was weighed before and after the pyrolysis reaction and the solid residue was determined from the mass difference. The vessels for receiving condensate (f) were disconnected from condensation system (e) and weighed as well, to determine the mass of condensable products, including a part of the condensate products mass from internal walls of condensation system (e) [28].

The reactor vessel is in the form of a vertical cylinder ($101.6 \times 2 \text{ mm}$). The vessel consists of a body (lower part) and a body cover (upper part), with bolted flange joint with gaskets. The body is 200 mm high representing a reaction vessel and it is separated from the upper part and serves as a dosing system. The design enables simple weighing of the raw material and solid residue after the process is completed, so that it is possible to set up material balances relatively easily. A second cylindrical container is attached to the reactor body from the upper side - a cover with a total length of 40 mm. This cover carries three K-type thermocouples and three stainless steel tubes (A304) in which there are cartridge-electric heaters with a total power of $3 \times 350 \text{ W}$. By connecting the cover to the reactor body, the electric heaters and thermocouples are placed in the reactor body. The heaters extend to the bottom of the reactor body, while three thermocouples are arranged in the reactor body, at different heights, as shown in Figure 1. Thermocouples T1, T2, and T3 are located: 7, 90 and 220 mm from the bottom of the reactor body, respectively. The reactor is made of stainless steel (A304) and a 3 cm thick thermal insulation layer of stone wool is applied on the outer wall of the reactor.

Reactor temperature changes were monitored at three characteristic points, while the temperature of non-condensable gases was recorded at the exit from the separation unit. All temperatures were measured by K-type thermocouples and recorded using CX-Thermo software package (Omron, Japan). Regulation of the operation of the heater, *i.e.*, temperature control was performed using the temperature controller CelciuX (EJ1N-TC4A-QQ) (OMRON, Japan). Adjustment of the PID constants was carried out before the reaction started. Also, the specified constants and other characteristic values in the regulation system were set by using the software. Given the sensitivity of temperature regulation, before each experiment that included a new type of raw material (*i.e.* plastic mixture, biomass, and plastic/biomass mixture) measurements were carried out with the self-running option of PID constants (autotuning).

Inert gas flow was measured and regulated by a mass flow meter/regulator (MASS VIEW model MV-304 Mass Flow Regulator, Bronkhorst High-Tech BV, Nederland) with the measurement range 0.04 to $20 \text{ dm}^3 \text{ min}^{-1}$ and the additional possibility of fine flow regulation. Nitrogen of 99.99 % purity was used as a carrier gas. The total heat consumption was determined based on the electricity consumption, which was measured by the Wolcraft Energy Check 3000 device (Wolcraft GmbH, Germany), which covers the measurement range from 0.001 to 9999 kWh.

3. RESULTS AND DISCUSSION

The developed pilot plant provides the possibility of recording a diagram of the thermal behavior of the reactor (*i.e.* temperatures measured by thermocouples arranged within the reactor and at the exit of the condensation unit).

In Figure 2 a thermal diagram, *i.e.*, the reactor temperature profile is presented, during the empty reactor operation, *i.e.* heating the reactor without any raw material to a temperature of $500 \text{ }^\circ\text{C}$ for 45 min., at the inert gas flow of $0.1 \text{ cm}^3 \text{ min}^{-1}$, total heating power of 1050 W and the heating rate of $19.7 \text{ }^\circ\text{C min}^{-1}$ (PID characteristics of the system were $P = 24$; $I = 306$; $D = 52.1$).

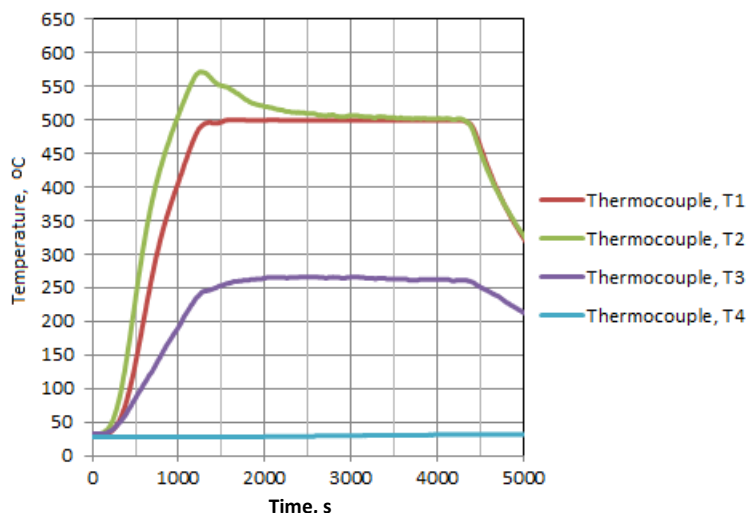


Figure 2. Thermal diagram of the empty reactor (heating rate $19.7\text{ }^{\circ}\text{C min}^{-1}$, 1050 W , PID constants: $P = 24$, $I = 306$, $D = 52$)

Figure 3 shows the thermal diagram in the pyrolysis experiment with the plastic waste mixture at the same process parameters ($500\text{ }^{\circ}\text{C}$, 45 min , $0.1\text{ cm}^3\text{ min}^{-1}$) and at the same heating conditions, where the heating rate was $12.1\text{ }^{\circ}\text{C min}^{-1}$.

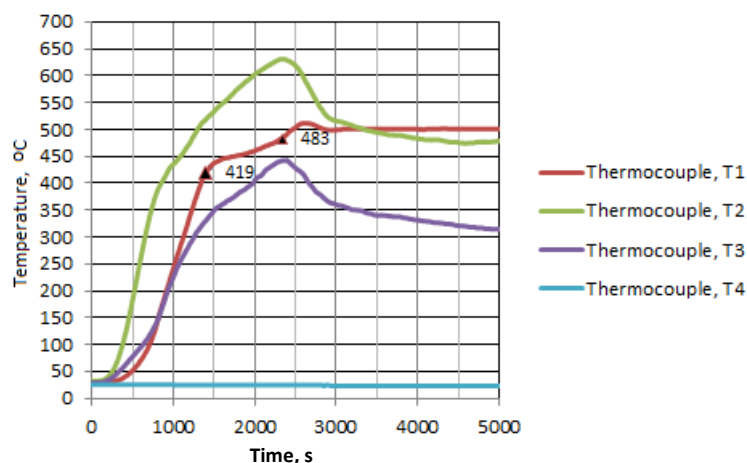


Figure 3. Thermal diagram in the reactor during pyrolysis of the mixture of plastic waste (heating rate $12.1\text{ }^{\circ}\text{C min}^{-1}$, 1050 W , PID constants: $P = 24$, $I = 306$, $D = 52$)

Both figures show non-uniform temperature distribution. The temperature in the lower part of the reactor (thermocouple T1) is lower than the temperature in the middle part of the reactor (thermocouple T2), which is very evident during pyrolysis (Fig. 3). Still, this is expected behavior, because during the heating phase, plastic is located in the upper and middle part of the reactor (measured by thermocouple T2). During heating, plastic melts, and it comes down towards the reactor bottom. This clears the upper and middle parts of the reactor, which enables intensive heating compared to the bottom part of the reactor. In the lower reactor part energy intensive processes (endothermic processes) are carried out.

The temperature in the upper part of the reactor (measured by thermocouple T3) is the lowest, which is expected. Namely, this part of the reactor, *i.e.* the lid of the reactor body, is practically non-insulated and is partly occupied by inert/non-heating parts of the cartridge-electric heaters. This behavior is additionally influenced by the fact that the carrier gas is introduced in that part of the reactor, which is not subject to pre-heating, *i.e.* the carrier gas enters the system at ambient temperature.

By the comparison of the two figures (Figs 2 and 3), the difference can be clearly observed. During the operation of an empty reactor, the heating of the system was faster *i.e.* a faster rise in temperatures measured by thermocouples T1, T2, and T3 (Fig. 2) occurred. However, during pyrolysis of the raw material (Fig. 3) this temperature increase was

slower. The decrease in the heating rate in the temperature interval from 419 to 483 °C of the lower reactor part (measured by T1) *i.e.* the reactor part where the feedstock material is placed, is particularly characteristic for pyrolysis of plastic. This finding is in accordance with thermogravimetric (TG) and derivative thermogravimetric (DTG) diagrams reported in literature [32,50]. Individual polymers degrade in the following order PS < PET < PP < PE [3]. Only PS decomposition occurs in the range between 350 and 450 °C, while pure PET degrades at temperatures between 390 and 470 °C, and PP, LDPE, and HDPE degrade between 450 and 510 °C [25].

Figure 4 shows the thermal diagram of empty reactor operation and Figure 5. shows the thermal diagram of the reactor filled with the biomass sample, during pyrolysis at 500 °C, time of 45 min, and nitrogen flow rate of 0.1 cm³ min⁻¹ and heating rate 28.6 °C min⁻¹. Both experiments were carried out under identical heating conditions (total heating power: 1050 W, PID characteristics of the system: $P = 121$, $I = 718$, $D = 122.3$), whereby the heating rate of the empty reactor was 15.8 °C min⁻¹.

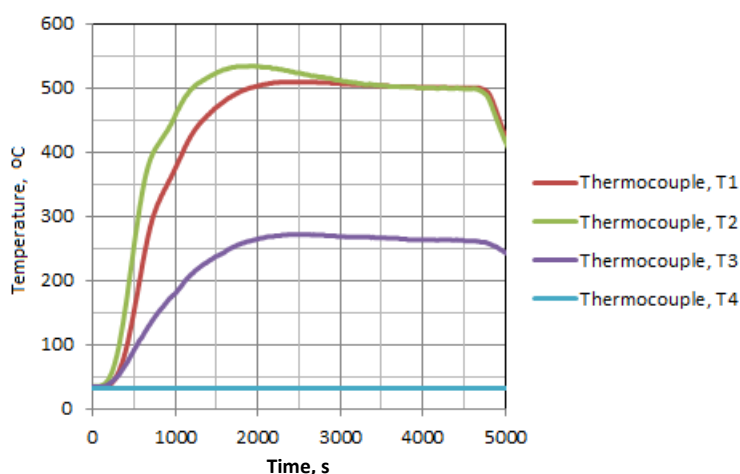


Figure 4. Thermal diagram of the empty reactor (heating rate 15.8 °C min⁻¹, 1050 W, PID constants: $P = 121$, $I = 718$, $D = 122.3$)

Unlike the diagram in Figure 3, the diagram in Figure 5 shows a much faster increase in temperatures measured by thermocouples T3, T2, and T1, at temperatures above 200 °C, and at the same time a faster temperature increases than during the operation of the empty reactor under identical conditions (Fig. 4). This directly implies the existence of exothermic effects in the biomass pyrolysis process, and that the biomass pyrolysis process itself is less energy demanding than plastic pyrolysis. Pyrolysis kinetics of biomass was investigated in literature [43] showing two stages: drying stage and devolatilization stage.

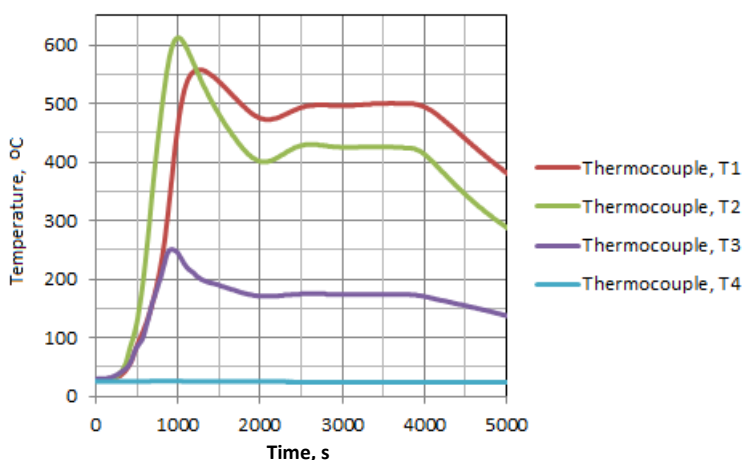


Figure 5. Thermal diagram of the reactor during biomass pyrolysis (heating rate 28.6 °C min⁻¹, 1050 W, PID constants: $P = 121$, $I = 718$, $D = 122.3$)

In the first stage, at temperatures between 50 and 70 °C, the moisture content drops resulting in mass loss. In the temperature range between 130 and 150 °C, TGA/DTG studies provide a flat line as a sign of water removal. And this point (150 °C) is the drying end temperature. During the second, devolatilization stage, biomass undergoes depolymerization and restructuring (mass loss is recorded at temperatures from 150 to 200 °C). After that, thermal chemical reactions occur, and TGA curves show a drop in the interval between 200 and 400 °C. The volatile matter yield depends on temperature and gas atmosphere [43]. It is possible to additionally analyze the obtained thermograms by mathematical methods and based on different slopes of the curves during the operation of the empty and reactor filled with raw materials, at the same operation conditions, to obtain the exact values of the thermal effects in the investigated process.

Considering the above statements, it can be concluded that in the developed pilot plant it is possible, with careful regulation or temperature control of the process to record diagrams that can be used for the purpose of identifying thermally intensive processes, similar to more complex TG and DTG analyses.

Figure 6 shows the thermal diagram of the pyrolysis experiment of a mixture of plastic/biomass in a ratio of 3:1, at 500 °C and a time of 45 min, at the inert gas flow of 0.1 cm³ min⁻¹ and under the conditions of heating waste plastic (total heating power: 1050 W; PID constants: P = 24, I = 306, D = 52.1), while the heating rate was 15.2 °C min⁻¹.

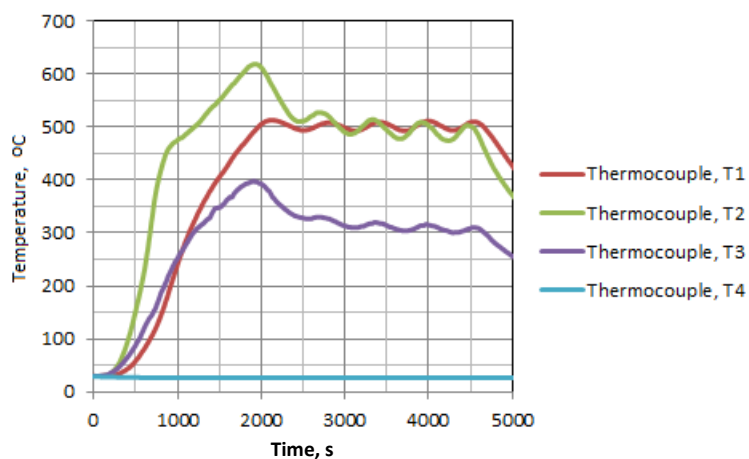


Figure 6. Thermal diagram of the reactor during pyrolysis of plastic/biomass mixture in the ratio 3:1 (heating rate 15.2 °C min⁻¹, 1050 W, PID constants: P = 34, I = 306, D = 52.1)

By comparing the obtained curves with the corresponding ones in Figure 3, a more intense increase in temperature is observed measured by thermocouples T1, T2, and T3, where the characteristic interval (419 to 483 °C), observed during the plastic pyrolysis, is almost completely absent. This means that part of the heat released during the devolatilization of biomass was directly used for the endothermic parts of the plastic pyrolysis process. Thus, it can be concluded that the co-pyrolysis of plastic and biomass, in the examined ratio of 3:1, had a favorable effect in terms of reducing the heat consumption. This behavior was additionally proven by measurement of the total consumption of electricity or heat for the analyzed processes.

From all the thermograms shown above, it can be seen that temperatures measured by thermocouple T3 were lower during the operation of the empty reactor compared to those during the pyrolysis of the investigated raw materials. This could be explained by the fact that the gaseous or steam products of pyrolysis additionally heat up the upper part of the reactor with their sensible heat compared to the conditions during the empty reactor operation.

It can be assumed that different temperatures in the vertical reactor section, above all temperatures measured by T2 and T3, affect the distribution and quality of the products. Namely, higher temperatures in the middle part of the reactor (T3) compared to the lower part of the reactor cause a larger cracking volume of steam products compared to the expected cracking volume, which would have occurred at a lower temperature (T2), *i.e.* under the conditions of a uniform temperature field within the reactor. Examination of the mentioned assumption is the subject of further research and modification of the heating system within the reactor, which will allow comparison of the yield and quality of the products at two different heating modes, *i.e.* at the existing and with the uniform temperature field.

Temperature distribution during the pyrolysis process is in accordance with monitored temperature profiles reported in literature [53], where pyrolysis of PP was carried out in a fixed-bed reactor at different temperatures (300, 400, 500, and 600 °C).

3. 1. Heat consumption and heating dynamics analysis

Table 1 provides values of the consumed electricity for the experiments, presented by the above shown thermal diagrams. The electric heaters are pure so-called “Ohm-consumers”. Therefore, one can assume that the measured values of electricity consumption correspond to the heat consumption in the analyzed processes.

Table 1. Heat consumption during pyrolysis of plastic, biomass, and plastic/biomass mixture

| Feedstock | Heat consumption, Wh | | | Specific heat consumption, Wh kg ⁻¹ |
|------------------------------------|-------------------------------|---------------|--------------|--|
| | Reactor filled with feedstock | Empty reactor | Process heat | |
| Plastic, 200 g | 835 | 482 | 353 | 1765 (1386*) |
| Biomass, 200 g | 269 | 459 | -190 | -950 |
| Plastic/biomass mixture 3:1, 200 g | 702 | 482 | 220 | 1100 |

*Value for the experiment in which the reactor was filled with 0.35 kg of plastic

Presented data in Table 1 can serve as an assessment of the energy intensity of the process. In the fourth column, the heat consumption of the process is given as a difference between the total heat used for the reactor operation during the pyrolysis of 0.2 kg of the feedstock material and the total heat used for operating the empty reactor under identical conditions. From these data, it can be seen that pyrolysis of plastics is the most energy-demanding process with a total heat consumption of 835 Wh, and the estimated heat consumption of the process of 353 Wh for 0.2 kg of the raw material, *i.e.* 1765 Wh kg⁻¹ (6354 kJ kg⁻¹). Pyrolysis of biomass is the least energy-demanding process with a total energy consumption of 269 Wh, and a difference of -190 Wh (-950 W kg⁻¹) compared to the consumption of the empty reactor. This indicated the exothermic nature of the biomass pyrolysis process, and it favors reduction in the heat consumption for the 3:1 plastic/biomass co-pyrolysis process, amounting to 220 Wh for 0.2 kg of the raw material (1100 Wh kg⁻¹).

In order to analyze the possibility of further filling the reactor and the impact on energy consumption, research on the pyrolysis of plastics was carried out with the reactor filled with 0.35 kg of the plastic mixture. The aforementioned tests showed a total heat consumption of 967 Wh, and if the heat consumption of the empty reactor of 482 Wh is taken into account (Table 1), the process heat is 485 Wh, yielding 1386 Wh kg⁻¹ (4989 kJ kg⁻¹). In the experiment, the yield in the reactor was the same as in the experiment when the reactor was filled with 0.2 kg of raw material. These results indicate higher reactor efficiency at higher loadings, which is expected considering that lower heat fraction is released through the reactor walls. In practice, the total heat required for the pyrolysis process consists of the heat required to heat the raw material to the appropriate temperature, the heat of depolymerization of the raw material, the heat of evaporation and obtaining gaseous products, the heat for heating the inert gas, and the heat required to maintain the reactor at a given temperature, which includes also heat losses through the reactor walls. Therefore, the analyses of the thermal energy in the developed laboratory scale reactor, which included all the mentioned effects, can serve as an estimate for the thermal analysis of larger pilot, semi-industrial and industrial reactors.

In the work of Xingzhong *et al.* [45] the total energy required for the pyrolysis of PE was 1316.1 kJ kg⁻¹. Also, similar result is presented in literature [46], for the same raw material, theoretical heat consumption was 1.075 1075 kJ kg⁻¹. Another study [47] investigated the temperature influence on conversion of polystyrene to liquid oil by using pyrolysis in a fixed-bed reactor. It was concluded that the temperature of 500 °C yielded the maximum oil amount. At the temperatures below 500 °C, wax was produced, and above this temperature gases were the main reaction products [56]. Energy demand of the conventional pyrolysis process ranges between 23 and 30 MJ kg⁻¹, however information on processing scale are lacking. Microwave pyrolysis seems to be more energy efficient in comparison to conventional pyrolysis, because of the fast and selective heating [48]. Energy consumption during microwave pyrolysis is between 5 and 10 MJ kg⁻¹ [49]. This agrees with the result obtained in this work (1765 Wh kg⁻¹ ~ 6.35 MJ kg⁻¹), which further indicates that the applied pyrolysis process is more energy efficient than the conventional one (regarding the mentioned

literature values for energy consumption). Furthermore, the results obtained in this work are in the range of energy consumption values for microwave pyrolysis. Considering that the used reactor provides heating directly in the raw material layer, unlike classic batch or fixed-bed reactors, where the heat comes from the outer walls, this type of pyrolysis seems more energy efficient, resulting in lower energy consumption.

The obtained theoretical results differ from the results obtained in this research, primarily because pyrolysis is observed at a temperature lower than 100 °C, without taking into account heat losses and operating conditions of a real processing plant.

By analyzing the thermal diagrams from Figures 3, 4, and 5, i.e., by observing the time required to reach the pyrolysis temperature, the heating rate is obtained, which is presented in Table 2.

Table 2. Heating rates during pyrolysis of plastic, biomass, and plastic/biomass mixture

| Feedstock | Heating rate, °C min ⁻¹ | |
|-----------------------------|------------------------------------|---------------|
| | Reactor filled with feedstock | Empty reactor |
| Plastic | 12.1 | 19.7 |
| Biomass | 28.6 | 15.8 |
| Plastic/biomass mixture 3:1 | 15 | 12.1 |

From the table 2 and the corresponding thermal diagrams, it is clearly seen how the dynamics of reactor heating changes with the change of raw material., even at the same heating conditions (pyrolysis of plastic and pyrolysis of the mixture

4. CONCLUSION

The main conclusions of this work can be summarized as follows.

- The analysis of the thermal behavior of the reactor indicates that in the developed pilot plant it is possible, with careful regulation or temperature control of the process, to record diagrams that can be used for the purpose of detecting thermally intensive processes, similar to more complex TG and DTG analyses. The obtained thermal diagrams of pyrolysis of plastics indicate an extremely endothermic phase of the process in the interval from 419 to 483 °C, while thermal diagrams of biomass pyrolysis indicate an extremely exothermic phase of the process at temperatures higher than 200 °C. The thermal diagram of co-pyrolysis of plastic and biomass in ratio 3:1 indicates a favorable effect of biomass addition in terms of lowering the energy consumption of the process; this is additionally proven by measurements of the total electricity consumption for the analyzed processes.
- Plastic pyrolysis is the most energy-demanding process with the specific heat consumption of 1765 Wh kg⁻¹ at a heating rate of 12.1 °C min⁻¹, while the biomass pyrolysis is the least an energy-demanding process with a total consumption of 269 Wh for 0.2 kg of raw material, at a heating rate of 28.6 °C min⁻¹, and specific heat consumption 950 Wh kg⁻¹. The specific heat consumption for the co-pyrolysis of the plastic/biomass mixture was 1100 Wh kg⁻¹ at the heating rate of 15.2 °C min⁻¹.
- When the reactor is filled with 0.35 kg of plastic, the reactor shows higher energy efficiency with the specific heat consumption of 1386 Wh kg⁻¹.
- The analyses of heating dynamics and the total energy consumption during the co-pyrolysis of a 3:1 plastic to biomass mixture, shows that it is possible to change the heating rate of the process and the overall energy efficiency of the process by simply choosing the appropriate mixture.

REFERENCES

- [1] Miandad R, Barakat MA, Aburizaiza AS, Rehan M, Nizami AS. Catalytic pyrolysis of plastic waste: A review. *Process Saf Environ Prot.* 2016; 102: 822-38. <https://dx.doi.org/10.1016/j.psep.2016.06.022>.
- [2] Xue Y, Johnston P, Bai X. Effect of catalyst contact mode and gas atmosphere during catalytic pyrolysis of waste plastics. *Energy Convers Manag.* 2017; 142: 441-51. <https://dx.doi.org/10.1016/j.enconman.2017.03.071>.
- [3] Marcilla A, Gómez-Siurana A, Berenguer D. Study of the influence of the characteristics of different acid solids in the catalytic pyrolysis of different polymers. *Appl Catal Gen.* 2006; 301(2): 222-31. <https://doi.org/10.1016/j.apcata.2005.12.018>



- [4] Sharma A, Pareek V, Zhang D. Biomass pyrolysis—A review of modelling, process parameters and catalytic studies. *Renew Sustain Energy Rev.* 2015; 50: 1081-96. <https://dx.doi.org/10.1016/j.rser.2015.04.193>
- [5] Gvero P, Mujanić I, Papuga S, Vasković S, Anatinović R. Review of Synthetic Fuels and New Materials Production Based on Pyrolysis Technologies. In: Pellicer E, Nikolic D, Sort J, Baró M, Zivic F, Grujovic N, et al., editors. *Advances in Applications of Industrial Biomaterials* [Internet]. Cham: Springer International Publishing; 2017; . 65-85. Available from: http://link.springer.com/10.1007/978-3-319-62767-0_4
- [6] Almeida D, Marques M de F. Thermal and catalytic pyrolysis of plastic waste. *Polímeros.* 2016; 26(1): 44-51. <https://dx.doi.org/10.1590/0104-1428.2100>
- [7] Gvero P, Papuga S, Mujanic I, Vaskovic S. Pyrolysis as a key process in biomass combustion and thermochemical conversion. *Therm Sci.* 2016; 20(4): 1209-22. <https://dx.doi.org/10.2298/TSCI151129154G>
- [8] Kyaw KT, Hmwe CSS. Effect of various catalysts on fuel oil pyrolysis process of mixed plastic wastes. *Int J. Adv. Eng. Technol.* 2015; 8(5): 9. <https://www.proquest.com/openview/5244b40561785593e77c906355ca14f9/1?pq-origsite=gscholar&cbl=1486350>
- [9] Babu BV. Biomass pyrolysis: a state-of-the-art review. *Biofuels Bioprod Biorefining.* 2008; 2(5): 393-414. <https://dx.doi.org/10.1002/bbb.92>
- [10] Armenise S, SyieLuing W, Ramírez-Velásquez JM, Launay F, Wuebben D, Ngadi N, Rams J, Munoz M. Plastic waste recycling via pyrolysis: A bibliometric survey and literature review. *J Anal Appl Pyrolysis.* 2021; 158: 105265. <https://dx.doi.org/10.1016/j.jaap.2021.105265>
- [11] Kunwar B, Cheng HN, Chandrashekar SR, Sharma BK. Plastics to fuel: a review. *Renew Sustain Energy Rev.* 2016; 54: 421-8. <https://dx.doi.org/10.1016/j.rser.2015.10.015>
- [12] Vijayakumar A, Sebastian J. Pyrolysis process to produce fuel from different types of plastic - a review. In: *IOP Conf Ser Mater Sci Eng.* Kerala State, India, 2018; 396: 012062. <https://dx.doi.org/10.1088/1757-899X/396/1/012062>
- [13] Lopez G, Artetxe M, Amutio M, Bilbao J, Olazar M. Thermochemical routes for the valorization of waste polyolefinic plastics to produce fuels and chemicals. A review. *Renew Sustain Energy Rev.* 2017 Jun; 73: 346-68. <https://dx.doi.org/10.1016/j.rser.2017.01.142>
- [14] Sharuddin SDA, Abnisa F, Daud WMAW, Aroua MK. Pyrolysis of plastic waste for liquid fuel production as prospective energy resource. In: *IOP Conf Ser Mater Sci Eng.* Banda Aceh, India, 2018; 334: 012001. <https://dx.doi.org/10.1088/1757-899X/334/1/012001>
- [15] Maqsood T, Dai J, Zhang Y, Guang M, Li B. Pyrolysis of plastic species: A review of resources and products. *J Anal Appl Pyrolysis.* 2021; 159: 105295. <https://dx.doi.org/10.1016/j.jaap.2021.105295>
- [16] Aguado J, Serrano DP, Escola JM. Fuels from Waste Plastics by Thermal and Catalytic Processes: A Review. *Ind Eng Chem Res.* 2008; 47(21): 7982-92. <https://dx.doi.org/10.1021/ie800393w>
- [17] Budsareechai S, Hunt AJ, Ngernyen Y. Catalytic pyrolysis of plastic waste for the production of liquid fuels for engines. *RSC Adv.* 2019; 9(10): 5844-57. <https://dx.doi.org/10.1039/C8RA10058F>
- [18] Suhartono, Kusumo P, Romli A, Aulia MI, Yanuar EM. Fuel Oil from Municipal Plastic Waste through Pyrolysis with and without Natural Zeolite as Catalysts. Hadiyanto, Maryono, Warsito B, editors. *E3S Web Conf.* 2018; 73: 01021. <https://dx.doi.org/10.1051/e3sconf/20187301021>
- [19] Pinto F, Costa P, Gulyurtlu I, Cabrita I. Pyrolysis of plastic wastes 2. Effect of catalyst on product yield. *J Anal Appl Pyrolysis.* 1999; 51: 57-71.
- [20] Uthpalani PGI, Premachandra JK, De Silva DSM, Weerasinghe VPA. Pyrolysis as a value added method for plastic waste management: A review on converting LDPE and HDPE waste into fuel [Internet]. In Review; 2022 Jul [cited 2022 Oct 4]. Available from: <https://www.researchsquare.com/article/rs-1693804/v1>
- [21] Kalargaris I, Tian G, Gu S. Combustion, performance and emission analysis of a DI diesel engine using plastic pyrolysis oil. *Fuel Process Technol.* 2017; 157: 108-15. <https://dx.doi.org/10.1016/j.fuproc.2016.11.016>
- [22] Kalargaris I, Tian G, Gu S. The utilisation of oils produced from plastic waste at different pyrolysis temperatures in a DI diesel engine. *Energy.* 2017; 131: 179-85. <https://dx.doi.org/10.1016/j.energy.2017.05.024>
- [23] Kalargaris I, Tian G, Gu S. Investigation on the long-term effects of plastic pyrolysis oil usage in a diesel engine. *Energy Procedia.* 2017; 142: 49-54. <https://dx.doi.org/10.1016/j.egypro.2017.12.009>
- [24] Kalargaris I, Tian G, Gu S. Experimental characterisation of a diesel engine running on polypropylene oils produced at different pyrolysis temperatures. *Fuel.* 2018; 211: 797-803. <https://dx.doi.org/10.1016/j.fuel.2017.09.101>
- [25] Kremer I, Tomić T, Katančić Z, Erceg M, Papuga S, Vuković JP, Schneider DR. Catalytic pyrolysis of mechanically non-recyclable waste plastics mixture: Kinetics and pyrolysis in laboratory-scale reactor. *J Environ Manage.* 2021; 296: 113145. <https://dx.doi.org/10.1016/j.jenvman.2021.113145>
- [26] Kremer I, Tomić T, Katančić Z, Hrnjak-Murčić Z, Erceg M, Schneider DR. Catalytic decomposition and kinetic study of mixed plastic waste. *Clean Technol Environ Policy.* 2021; 23(3): 811-27. <https://dx.doi.org/10.1007/s10098-020-01930-y>
- [27] Kremer I, Tomić T, Katančić Z, Hrnjak-Murčić Z, Erceg M, Vecchio Cipriotti S, Schneider DR. Effect of Zeolite Catalyst on the Pyrolysis Kinetics of Multi-Layered Plastic Food Packaging. *Symmetry.* 2022; 14(7): 1362. <https://dx.doi.org/10.3390/sym14071362>

- [28] Papuga S, Gvero P, Vukic L. Temperature and time influence on the waste plastics pyrolysis in the fixed bed reactor. *Therm Sci*. 2016; 20(2): 731-41. <https://dx.doi.org/10.2298/TSCI141113154P>
- [29] Dewangga PB, Rochmadi, Purnomo CW. Pyrolysis of polystyrene plastic waste using bentonite catalyst. In: *IOP Conf Ser Earth Environ Sci*. Bogor, Indonesia, 2019; 399(1): 012110. <https://dx.doi.org/10.1088/1755-1315/399/1/012110>
- [30] Papuga S, Djurdjevic M, Ciccioli A, Vecchio Cipriotti S. Catalytic Pyrolysis of Plastic Waste and Molecular Symmetry Effects: A Review. *Symmetry*. 2022; 15(1): 38. <https://dx.doi.org/10.3390/sym15010038>
- [31] Fadillah G, Fatimah I, Sahroni I, Musawwa MM, Mahlia TMI, Muraza O. Recent Progress in Low-Cost Catalysts for Pyrolysis of Plastic Waste to Fuels. *Catalysts*. 2021; 11(7): 837. <https://dx.doi.org/10.3390/catal11070837>
- [32] Garcia-Nunez JA, Pelaez-Samaniego MR, Garcia-Perez ME, Fonts I, Abrego J, Westerhof RJM, et al. Historical Developments of Pyrolysis Reactors: A Review. *Energy Fuels*. 2017; 31(6): 5751-75. <https://dx.doi.org/10.1021/acs.energyfuels.7b00641>
- [33] Gholizadeh M, Li C, Zhang S, Wang Y, Niu S, Li Y, et al. Progress of the development of reactors for pyrolysis of municipal waste. *Sustain Energy Fuels*. 2020; 4(12): 5885-915. <https://dx.doi.org/10.1039/D0SE01122C>
- [34] Kabir G, Mohd Din AT, Hameed BH. Pyrolysis of oil palm mesocarp fiber and palm frond in a slow-heating fixed-bed reactor: A comparative study. *Bioresour Technol*. 2017; 241: 563-72. <https://dx.doi.org/10.1016/j.biortech.2017.05.180>
- [35] Wang Z, Cao J, Wang J. Pyrolytic characteristics of pine wood in a slowly heating and gas sweeping fixed-bed reactor. *J Anal Appl Pyrolysis*. 2009; 84(2): 179-84. <https://dx.doi.org/10.1016/j.jaap.2009.02.001>
- [36] Kremer I, Tomić T, Katančić Z, Erceg M, Papuga S, Parlov Vuković J, Schneider DR. Catalytic pyrolysis and kinetic study of real-world waste plastics: multi-layered and mixed resin types of plastics. *Clean Technol Environ Policy*. 2022; 24(2): 677-93. <https://dx.doi.org/10.1007/s10098-021-02196-8>
- [37] Selpiana, Aprianti T, Rayosa I, Fuspitasarie D. Expanded polystyrene and multilayer plastic waste conversion into liquid fuel by the pyrolysis process. In Surakarta, Indonesia; 2018 [cited 2022 Oct 7]. p. 020151. Available from: <http://aip.scitation.org/doi/abs/10.1063/1.5054555>
- [38] Bridgwater AV, Meier D, Radlein D. An overview of fast pyrolysis of biomass. *Org Geochem*. 1999; 30(12): 1479-93. [https://dx.doi.org/10.1016/S0146-6380\(99\)00120-5](https://dx.doi.org/10.1016/S0146-6380(99)00120-5)
- [39] Lee CG, Cho YJ, Song PS, Kang Y, Kim JS, Choi MJ. Effects of temperature distribution on the catalytic pyrolysis of polystyrene waste in a swirling fluidized-bed reactor. *Catal Today*. 2003; 79-80: 453-64. [https://dx.doi.org/10.1016/S0920-5861\(03\)00060-9](https://dx.doi.org/10.1016/S0920-5861(03)00060-9)
- [40] Pandey U, Stormyr JA, Hassani A, Jaiswal R, Haugen HH, Moldestad BME. Pyrolysis of plastic waste to environmentally friendly products. In 2020 [cited 2022 Aug 15]. p. 61-74. Available from: <http://library.witpress.com/viewpaper.asp?pcode=EPM20-007-1>
- [41] Hartulistiyoso E, Sigiro FAPAG, Yulianto M. Temperature Distribution of the Plastics Pyrolysis Process to Produce Fuel at 450oC. *Procedia Environ Sci*. 2015; 28: 234-41. <https://dx.doi.org/10.1016/j.proenv.2015.07.030>
- [42] Bockhorn H, Hornung A, Hornung U, Jakobströer P. Modelling of isothermal and dynamic pyrolysis of plastics considering non-homogeneous temperature distribution and detailed degradation mechanism. *J Anal Appl Pyrolysis*. 1999; 49(1-2): 53-74. [https://dx.doi.org/10.1016/S0165-2370\(98\)00130-2](https://dx.doi.org/10.1016/S0165-2370(98)00130-2)
- [43] Chen D, Zheng Y, Zhu X. In-depth investigation on the pyrolysis kinetics of raw biomass. Part I: Kinetic analysis for the drying and devolatilization stages. *Bioresour Technol*. 2013; 131: 40-6. <https://dx.doi.org/10.1016/j.biortech.2012.12.136>
- [44] Swamardika IBA, Winaya INS, Hartati RS. Utilization plastic waste using pyrolysis fixed bed. In: *IOP Conf. Ser. Mater Sci Eng*. Bali, Indonesia, 2019; 9. <https://dx.doi.org/10.1088/1757-899X/539/1/012021>
- [45] Xingzhong Y. Converting Waste Plastics into Liquid Fuel by Pyrolysis: Developments in China. In: Scheirs J, Kaminsky W, editors. *Feedstock Recycling and Pyrolysis of Waste Plastics* [Internet]. Chichester, UK: John Wiley & Sons, Ltd; 2006 [cited 2022 Aug 15]. p. 729-55. Available from: <https://onlinelibrary.wiley.com/doi/10.1002/0470021543.ch28>
- [46] Gao F. Pyrolysis of Waste Plastics into Fuels. Dissertation, 2010; Available from: <https://ir.canterbury.ac.nz/handle/10092/4303>. <https://dx.doi.org/10.26021/3251>
- [47] Abdullah NA, Novianti A, Hakim II, Putra N, Koestoer RA. Influence of temperature on conversion of plastics waste (polystyrene) to liquid oil using pyrolysis process. *IOP Conf Ser Earth Environ Sci*. 2018; 105: 012033. <https://dx.doi.org/10.1088/1755-1315/105/1/012033>
- [48] Job S, Mativenga P, Shuaib NA, Oliveux G, Leeke G, Pickering S. Composites Recycling - Where are we now? *Composites UK*. 2016. <https://compositesuk.co.uk/system/files/documents/Recycling%20Report%202016%20-%20Light%20Background.pdf>
- [49] van Oudheusden AA. Recycling of composite materials. :68. Student thesis. <http://resolver.tudelft.nl/uuid:0749ed5c-7aeb-4275-abee-0f904a08ea4d>

Analiza termičkog ponašanja reaktora sa nepokretnim slojem u procesu pirolize

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Izvod

Piroliza je termo-hemijski proces u kojem dolazi do razgradnje organskih jedinjenja. Proces se odvija u inertnoj sredini, a može se primeniti na industrijskom, polu-industrijskom i laboratorijskom nivou. Tokom procesa pirolize, kontroliše se temperatura, međutim, studije i radovi koji se bave pirolizom ne naglašavaju gdje se temperatura mjeri i da li je temperaturno polje ujednačeno. U ovom radu se istražuje termičko ponašanje laboratorijskog reaktora sa nepokretnim slojem, kao i potrošnja energije tokom procesa pirolize. Korišćene su tri varijante polaznih sirovina: mješavina plastičnog otpada (uzorak 1), biomasa (uzorak 2) i mješavina plastike i biomase (uzorak 3). Analiza termičkog ponašanja reaktora ukazuje da se uz pažljivu regulaciju ili kontrolu temperature procesa mogu dobiti zavisnosti koje se mogu koristiti u svrhu registracije termički intenzivnih procesa, slično složenijim analizama odnosno termogravimetrijom (TG) ili derivativnom termogravimetrijom (DTG). Pokazalo se da je moguće promijeniti brzinu zagrijavanja i ukupnu energetska efikasnost procesa jednostavnim odabirom odgovarajuće sirovinske mješavine.

Ključne reči: plastični otpad; reciklaža; termalna reakcija; brzina zagrijavanja; potrošnja energije