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Analysis of the energy recovery possibilities of energy from scrap tire

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The analysis of waste polymers as a source of energy is the main goal of this study. A novelty in the research is the development of a methodology for evaluating the productivity and energy efficiency of both new and existing pyrolysis systems in order to be optimize them. Two of the processes of thermochemical conversion are considered: direct combustion and pyrolysis, are compared to choose the most efficient, both economically and environmentally. This requires an assessment of their properties, which define them as fuel. The analyzes were performed with the help of literature data: for ultimate analysis of waste polymers; for analytical models of yields of pyrolysis products of waste polymers; the composition of the produced biogas; analytical dependences for determination of Heating Value (HV) of waste polymers and products of their pyrolysis; models for determining the heat of pyrolysis. The process of treatment of waste polymers by pyrolysis was investigated experimentally and a gas analysis of the obtained pyrolysis gas was performed to compare with the predicted results of the analytical calculations. An ultimate and quantitative analysis of both the raw material used and the obtained products was made. the total amount of heat used in the process was measured. The results show that the energy obtained can ensure the application of the pyrolysis process, and the residual energy can be used for other purposes.

Keywords: pyrolysis, waste tires, biomass, gas and liquid products, biogas

INTRODUCTION

The world is currently facing to significant problems, such as fossil fuel shortages and environmental pollution. The problems are constantly exacerbated due to the growing population and, accordingly, the increasing energy consumption per capita. These data can be seen in the annual report of the British Petroleum (BP Statistical Review of World Energy), showing the trends in global energy consumption.

In order to overcome the problems, more and more attention is paid to renewable energy sources, which bring economic and social benefits.

Large quantities of polymers are produced and obtained naturally worldwide, with the production and consumption are constantly increasing every year. Despite their valuable qualities, many out-of-date polymers are ones of the main polluters of the environment.

Most of them are not biodegradable, they are resistant to moisture, chemicals, sunlight and microorganisms. Dumped in landfills, their "life" continues and if stored improperly, fires and infectious diseases can occur. The impact of this waste on the environment can be minimized by recycling or using it as energy.

The pyrolysis process finds application in the treatment of solid organic waste, such as waste automotive tires, plastics, biomass, animal waste and solid waste from wastewater treatment plants. By heating in an oxygen-free environment, they decompose to give solid, liquid and gaseous products which have applications as fuels or raw materials for the chemical industry.

In recent decades, both the processing and the use of waste polymers as fuel in various industries, in households and in transport have increased. The reason for this is Directive 2009/28/EU on renewable energy, which establishes a comprehensive policy for the production and promotion of energy from renewable sources and requires the EU to meet at least 20% of it‘s total energy needs with energy from renewable sources by 2020.

The main purpose of this article is to analyze waste polymers as an energy source. This requires an assessment of their properties, which define them as a fuel.

In order to determine the energy potential of waste polymers, it is necessary to establish their energy value. Heating value is often used as an indicator of the energy contained in waste.

There are two main aspects related to the use of waste polymers as fuel: (1) expanding and improving the basic knowledge about their composition and properties and (2) the application of this knowledge to the most modern and environmentally safe use. Numerous studies have been conducted worldwide and extensive data have been obtained on the waste polymers themselves and their transformation products, which have intensified over the last two decades. These results provide a solid basis as an initial database that can be used to characterize and subsequently classify and sustainably operate this waste [1, 16, 25].

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Waste polymers can be defined as a material that consists mainly of carbon, hydrogen, oxygen, nitrogen and smaller parts of inorganic substances.

In the literature and practice [1, 2, 4, 13, 22] the following methods are known for the treatment of waste polymers for their further utilization, by converting them into liquid, gaseous and solid fuels, which is carried out in two main ways: biochemical (fermentation) and thermochemical (pyrolysis, gasification, esterification and direct incineration).

Three types of secondary fuels are produced from waste polymers:

- Liquid (ethanol, biodiesel, methanol, vegetable oil and pyrolysis oil);
- Gaseous (biogas (CH_4, CO_2), industrial gas (CO, H_2, CH_4, CO_2, H_2), synthetic gas (CO, H_2), natural gas substitute (CH_4));
- Solid (coal, purified biomass).

The utilization of waste polymers, in the aspect of this study, is for the purpose of obtaining heat to be put back into the process and obtaining fuels for use in other processes. In this sense, the present study considers only thermochemical treatments, comparing them in order to choose the most efficient of them, both economically and environmentally. The aim of the study is to create a methodology for evaluating the productivity and energy efficiency of both new and existing pyrolysis systems in order to be optimize them. We have no evidence that other researchers conducted similar studies.

The authors of [17, 18] determine that the amount of gases obtained in the pyrolysis process is sufficient to realize the process without additional energy sources. As a rule, this kind of gas has a heating value of about 13-15 MJ/m^3.

The study shows that many researchers study the processes of obtaining volatile substances from various solid materials, such as solid fuels, polymers, industrial waste, agricultural waste and wastewater treatment plants. The interest in the processes of gasification and pyrolysis in recent years is very high and this is justified from an environmental, economic and social point of view.

This study analyzes the properties of the waste polymers and the products of it‘s processing into secondary fuels, which characterize them as fuels. For this purpose were used literature data such as: proximate and ultimate analysis of waste polymers; for the analytical models of the yields of the products of their pyrolysis; for the composition of the obtained pyrolysis gas; for analytical dependences for determination of High HV (HHV) or Low HV (LHV) of the waste polymers and the products of their pyrolysis.

The process of processing the waste polymers by pyrolysis was experimentally studied, and a gas analysis of the obtained pyrolyzed gas was performed in order to compare the predicted results of the analytical calculations. Samples for elemental qualitative and quantitative composition are given in the Microanalytical Laboratory for "Elemental Analysis" at the Institute of Organic Chemistry With Center of Phytochemistry – Bulgarian Academy of Sciences.

MATERIALS, METHODS AND DATA USED

Analytical investigation of thermochemical conversion of waste polymers and it‘s products

1. **Models for determining the yields of individual products**

The creation of a model and its comparison with similar ones by other authors is aimed at using the process parameters as independent variables. The following models are known in the literature.

The authors of [14] have established the proportions of char and gases, products of pyrolysis, as well as the ratios of some of them as a function of temperature. Particle size, heating rate, and reactor size have limited influence on these empirical relationships.

$$Y_{ch,F} = 0.106 + 2.43 \cdot \exp(-0.66 \cdot 10^{-2} \cdot T) \quad (1)$$

$$\mathrm{Y}_{\mathrm{H_2,F}} \approx \mathrm{Y}_{\mathrm{H,F}}; \; Y_{CO,F} \approx Y_{O,F} \frac{28}{16}; \quad (2)$$

$$Y_{CH_4,F} = -2.18 \cdot 10^{-4} + 0.146 \cdot Y_{CO,F}; \quad (3)$$

$$\frac{Y_{H_2,F}}{Y_{CO_2,F}} = 3 \cdot 10^{-4} + \frac{0.0429}{1 + \left(\frac{T}{632}\right)^{-7.23}}. \quad (4)$$

After using the statistical method Box-Behnken design (BBD) to process the results of a test study of pyrolysis of organic materials in argon field empirical relationships were obtained between the amount of pyrolysis oil and the process parameters, as well as between the obtained solid residue and the process parameters [20].

$$\begin{aligned} Y_1 = {} & 107.70125 + 0.59689 \cdot X_T + 0.043345 \cdot X_P - \\ & -6.06250 \cdot X_N - 1.607 \cdot 10^{-4} \cdot X_T \cdot X_P + \\ & +1.125 \cdot 10^{-5} \cdot X_T \cdot X_N + 1.4333 \cdot 10^{-4} \cdot X_P \cdot X_N - \\ & -6.96412 \cdot 10^{-5} \cdot X_T^2 - 3.415 \cdot 10^{-5} \cdot X_P^2 - \\ & -1.28472 \cdot X_N^2 \end{aligned} \quad (5)$$

$$\begin{aligned}&Y_2 = 144.2165 - 0.3277 \cdot X_T - 0.04226 \cdot X_P + \\ &+0.035275 \cdot X_N + 1.15 \cdot 10^{-4} \cdot X_T \cdot X_P + \\ &+5.8333 \cdot 10^{-6} \cdot X_T \cdot X_N - 8.33333 \cdot 10^{-5} \cdot X_P \cdot \\ &\cdot X_N + 3.79575 \cdot 10^{-4} \cdot X_T^2 + 1.473 \cdot 10^{-4} \cdot X_P^2 - \\ &-1.43611 \cdot 10^{-4} \cdot X_N^2\end{aligned} \qquad (6)$$

The authors of [23] propose empirical dependences for calculating the share of bio-char and the H/C ratio as a function of the process parameters: T_{py}, HR and RT. The dependencies are different for different materials. For straw there are types:

$$\begin{aligned}&Yb(\%) = 89.29 - 0.131 \cdot T_{py} - 0.622 \cdot HR - \\ &-0.587 \cdot RT - 0.001 \cdot T_{py} \cdot HR - \\ &-0.001 \cdot T_{py} \cdot RT \qquad R2 = 0.929\end{aligned} \qquad (7)$$

2. Modeling of the heating value

The raw material (waste polymers)

There is a standard defining the approach for experimental determination of the upper heat capacity of solid biofuels - BDS EN ISO 18125: 2017. The cited standard can be successfully applied to waste polymers. An alternative to experimental measurements is the approximate estimation of the upper heating value of waste polymers by means of analytical dependences. Similar models are available in the literature, some of which indicate a relationship between the upper heating value of dry fuel, Q_{HHV}, and its chemical composition, others - between Q_{HHV} and fixed carbon, volatiles and ash content [22]. The influence of the ash content and humidity of the biomass is negative.

$$\begin{aligned}&Q_{HHV,Dry} = 0.341 \cdot C + 1.323 \cdot H - 0.12 \cdot O - \\ &-0.12 \cdot N + 0.68 \cdot S - 0.015 \cdot ASH, \ \text{[MJ/kg]}\end{aligned} \qquad (8)$$

Note: The elemental composition in Eq.(8) is related to the working mass of the fuel.

$$\begin{aligned}&Q_{HHV,Dry} = 0.1559 \cdot VM + 0.3536 \cdot FC - \\ &-0.0078 \cdot ASH, \ \text{[MJ/kg]}\end{aligned} \qquad (9)$$

The third group of dependencies gives the connection between Q_{HHV} and the content of lignin, L, in the fuel, and the fourth group of dependences - between the upper heating value and the structural composition of the biomass (the content of lignin, cellulose and hemicellulose) [19].

$$Q_{HHV,Dry} = 0.0979 \cdot L + 16.292, \ [MJ/kg] \qquad (10)$$

$$\begin{aligned}&Q_{HHV,Dry} = 0.1739 \cdot Ce + 0.2663 \cdot L + \\ &+0.3219 \cdot E, \ [MJ/kg]\end{aligned} \qquad (11)$$

In the case of wet raw material the heat obtained from the combustion of 1 kg of fuel is due only to the share of dry biomass, ie. (1- W_{wb}). Then [22]:

$$Q_{HHV} = (1 - W_{wb}) \cdot Q_{HHV,Dry}, \ [MJ/kg] \qquad (12)$$

On the other hand, the expression for the lower heating value of waste polymers, taking into account its operating humidity, yields the form [22]:

$$\begin{aligned}&Q_{LHV} = (1 - W_{wb}) \cdot Q_{HHV,Dry} - \\ &-2.447 \cdot \left[W_{wb} + 9 \cdot (1 - W_{wb}) \cdot H\right], \ [MJ/kg]\end{aligned} \qquad (13)$$

In the present study, the dependencies with data from ultimate analysis for waste tires are used, due to the lack of data from proximate analysis of the same.

On the products

The heating value, according to [24] of solid and liquid fuels is determined by:

$$\begin{aligned}&Q_{LHV} = 339.39 \cdot C + 1257 \cdot H - 108.94 \cdot \\ &\cdot (S - O) - 25.14 \cdot (9 \cdot H - W_{wb}), \ \text{[kJ/kg]}\end{aligned} \qquad (14)$$

The heating value of gaseous fuels is determined, according to [24], by:

$$\begin{aligned}&Q_{LHV} = 0.127 \cdot CO + 0.108 \cdot H_2 + \\ &+0.358 \cdot CH_4, \ [\text{MJ/Nm}^3]\end{aligned} \qquad (15)$$

3. Energy balance models

The analysis of the energy balance of the pyrolysis processes was made using the scheme of Fig.1 [1].

Compare combustion reactions, most gasification reactions are endothermic.

For this reason, heat must be supplied to the gasifier in order to carry out these reactions at the planned temperature. The amount of external heat supplied to the gasifier depends on the heat demand of the endothermic reactions, as well as on the gasification temperature.

The total heat balance, according to Fig.1 [1] is:

- incoming energy:

$$\begin{aligned}&A \cdot Cp_a \cdot T_0 + F \cdot Cp_f \cdot T_0 + W \cdot H_0 + \\ &+F \cdot Q_{HHV} + Q_{ext}\end{aligned} \qquad (16)$$

- energy of the outgoing streams:

$$(C_{CO}\cdot V_{CO}+C_{CO_2}\cdot V_{CO_2}+C_{CH_4}\cdot V_{CH_4}+ \\ +C_{H_2}\cdot V_{H_2}+C_{O_2}\cdot V_{O_2}+C_{N_2}\cdot V_{N_2})\cdot T_g+ \\ +\left(1-X_g\right)\cdot W\cdot H_g+P_c\cdot q_c+Q_{gasif}+ \\ +Q_{loss}+Q_{product} \qquad (17)$$

According to authors of [24]:

$$Q_{LHV}^{raw}+Q_{pyr}=g_{gas}\cdot Q_{LHV}^{gas}+Q_{phh}^{gas}+ \\ +g_{char}\cdot Q_{LHV}^{char}+Q_{phh}^{char} \qquad (18)$$

$$Q_{phh}^{gas}=c_{gas}\cdot g_{gas}\cdot\left(t_{pyr}-t_0\right)+ \\ +c_{steam}\cdot g_{steam}\cdot\left(t_{pyr}-t_0\right)+r\cdot g_{steam} \qquad (19)$$

$$Q_{phh}^{char}=c_{char}\cdot g_{char}\cdot\left(t_{pyr}-t_0\right) \qquad (20)$$

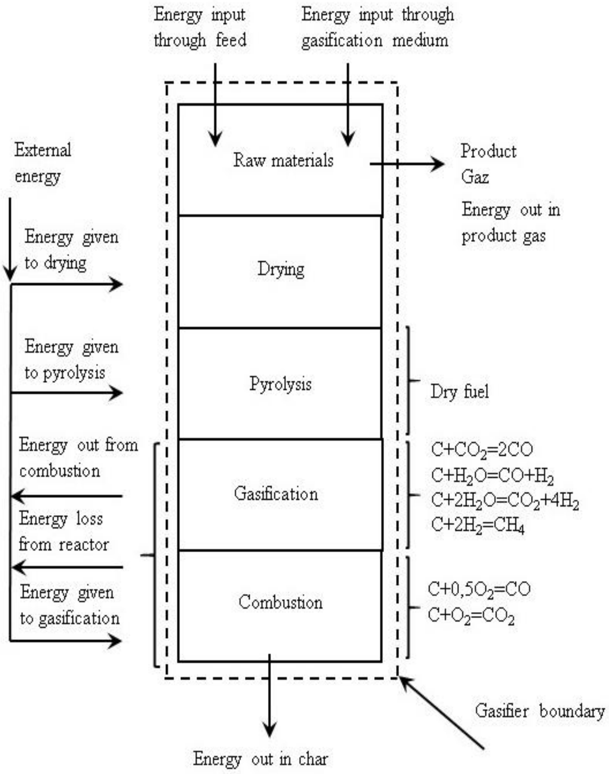

Fig.1. Energy balance of a pyrolysis reactor [1]

According to authors of [21], the heat required for pyrolysis is calculated by:

$$Q_{pyr}=\Delta H_S+\Delta H_r \qquad (21)$$

$$\Delta H_S=\dot{m}_{tire}\cdot\left(\int_{T_0}^{T_{reac}}c_{p,tire}dT\right) \qquad (22)$$

$$\Delta H_r=\dot{m}_{tire}\cdot(553-3142\cdot\mu_{char}) \qquad (23)$$

In the present study, a methodology for determining the energy balance based on experimental studies has been used. The obtained results are compared with those calculated by the analytical models, proposed by other authors.

Experimental investigation of thermochemical conversion of waste polymers and it's products

The laboratory system is shown in Fig.2. Thermometers have been installed to measure the temperature at various points in the system, as well as taking samples to determine the composition and concentration.

Experiments were performed in which different waste tires were subjected to pyrolysis.

A discrete amount of feedstock is placed in the pyrolysis reactor and heated. The vapors obtained from the decomposition of the raw material are cooled in a heat exchanger and some of them condense. The liquid product is collected in a tank, and the non-condensed gases leave the system by passing through a hydraulic seal, which does not allow atmospheric air to enter the system.

The waste rubber that undergoes pyrolysis has a known qualitative and quantitative composition. The experiment was performed at a predetermined temperature in the reactor. The amount of pyrolysis oil obtained and solid residue after completion of the experiment are taken into account. The products are analyzed to determine their elemental, qualitative and quantitative composition.

The pyrolysis gas obtained is also analyzed. Its composition is determined by a gas analyzer, and the quantity is determined by weight, based on the material balance. The consumption of cooling water by a rotameter and the inlet and outlet temperature of the heat exchanger are also taken into account. The energy imported into the system is also taken into account for the needs of the energy balance. It is accepted that the process proceeds until the moment when gas is no longer released from the reactor. The pyrolysis oil obtained from the experiments was further subjected to distillation.

RESULTS AND DISCUSSIONS

An experiment was performed in which two types of waste raw materials were subjected to pyrolysis. Waste car tire (Model-1) and waste tire from the conveyor belt (Model-2).

In the pyrolysis reactor is maintained at a temperature of about 300/400/500 ^{0}C under stationary conditions. Under these conditions, gaseous, liquid and solid products are obtained. In the course of the experiment, the amount of liquid obtained, the energy consumed to maintain the operating conditions in the pyrolysis reactor, the flow rate of the cooling water are monitored and the time for which the process takes place is taken into account.

The resulting pyrolysis oil was further subjected to atmospheric distillation and divided into fractions with different boiling points.

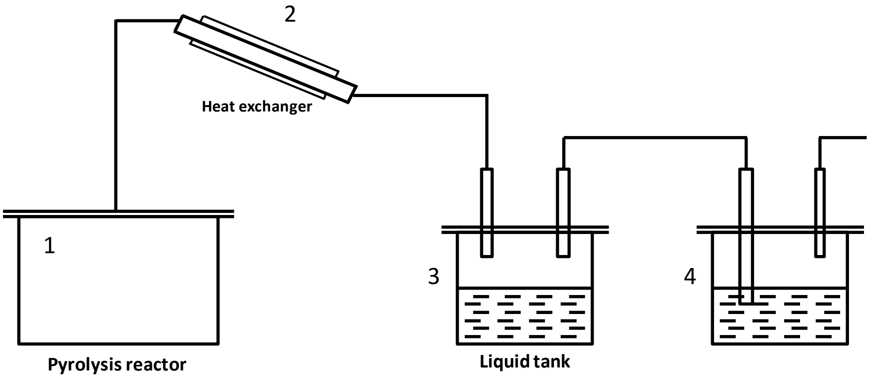

Fig.2. Principal scheme of the experimental system: 1 – Pyrolisys reactor; 2 – Heat exchanger; 3 – Liquid tank, 4 reservoir - hydraulic shutter

The results are presented in Tab.1.

Table 1. Yields of the obtained products at different temperatures

Raw	Temp.	Char	Oil	Gas
	^{0} C	wt%	wt%	wt%
Scrap tire	300	45	45	10
Model-1	400	30	62	8
	500	30	62	8
Scrap tire	300	41	48	11
Model-2	500	32	56	12

The reason for the observed differences in the amount of products obtained is that at low temperatures, the process proceeds to an equilibrium state, which stops the decomposition of the polymer compounds and the production of hydrocarbons with a shorter chain. This coincides with the published results of Thermogravimetric Analysis (TGA) of many researchers [5] and does not contradict the accepted models describing the process [3, 5, 9, 7].

It can be seen that the amount of liquid obtained at 400 ° C and 500 ° C is the same, but the liquids differ in their fractional composition.

In this experiment, the raw material (waste rubber model-1) and the pyrolysis products - pyrolysis gas, pyrolysis oil and solid carbon residue, were subjected to additional analyzes.

Samples for elemental qualitative and quantitative composition are given in the Microanalytical Laboratory for "Elemental Analysis" at the Institute of Organic Chemistry With Center of Phytochemistry – Bulgarian Academy of Sciences.

The pyrolysis gas obtained is also analyzed by a gas analyzer to give a qualitative and quantitative composition of the main gases contained therein.

The results are presented in Tab.2, Tab.3, Tab.4 and Tab.5.

Table 2. Elemental qualitative and quantitative composition

Component	Scrap Tire	Char	Oil	Gas
	mass%	mass%	mass%	mass%
C	85.08	90.48	87.00	72.40
H	9.76	3.68	10.00	13.00
N	2.93	2.71	2.00	11.00
S	0.97	2.84	0.00	0.00
O	1.26	0.29	1.00	3.67

Table 3. Qualitative and quantitative composition of pyrolysis gas

Component	H_2	CO	CO_2	NO	NO_2	CH_4	C_6H_6
mass%	2.08	34.20	27.48	6.63	15.89	12.66	1.06

Table 4. Heat of combustion of raw materials and pyrolysis products

Parameter	Units	Scrap Tire	Char	Oil	Gas
Specific heat, Cp	kJ/kg.K	9.348	5.843	10.848	1.382
LHV	kJ/kg	37 656	13 882	40 752	34 811

Table 5. Comparative data from the conducted tests

Temp.	Method of heating	Time	Fuel	Energy	Primary energy
°C		min	g	kWh/kg raw	kWh/kg raw
300	Propane-butane	43	64,50	8.90	9.73
300	electricity (induction heating)	26	-	6.20	18.60
400	Propane-butane	35	52.53	7.30	8.03
500	Propane-butane	35	58.33	8.10	8.91

A comparison of the obtained experimental data with those published by other researchers is made. The comparison is presented in Tab.6 and Tab.7.

Table 6. Quantitative comparison of experimentally obtained products by pyrolysis

Autor	Temp.	Char	Oil	Gas
	°C	wt%	wt%	wt%
Williams, [6]	300-720	35	55	10
Chang, [12]	200-600	14-28	28-42	30-53
Berrueco, [11]	400-700	47-63	30-43	4-11
Barbooti, [7]	400-460	32.5	51	16.6
González, [10]	350-700	37-40	55	4-11
This paper Model-1	300	45	45	10
This paper Model-1	400	30	62	8
This paper Model-1	500	30	62	8
This paper Model-2	300	41	48	11
This paper Model-2	400	36	50	14
This paper Model-2	500	32	56	12

Table 7. Ultimate analysis of waste tires

Autor	C	H	O	N	S	Inorganic residue
	%	%	%	%	%	%
Williams, [8]	85.8	8.0	0.4	1.0	2.3	2.4
Barbooti, [7]	83.8	7.6	0.4	1.4	3.1	3.7
Wang, [15]	81.2	7.2	0.5	1.6	2.1	7.4
Berrueco, [11]	88.5	6.6	0.4	1.6	3.0	-
González, [10]	86.7	8.1	0.4	1.4	1.3	2.9
This paper	85.1	9.8	2.9	1.0	1.3	-

A comparison of the results shows that the researchers worked in a very wide temperature range in the reactor. An exception is the study of [7], where the temperature in the pyrolysis reactor is maintained at 400-460 °C. It can be seen that the quantity of the obtained pyrolysis products is the same, but there are no published data on the elemental qualitative and quantitative composition of the raw material. If the same raw material is subjected to a pyrolysis process under the same conditions, the same amounts of pyrolysis products will be obtained. This is proven by the experiments that are the subject of this study.

In order to make any correct comparison of the pyrolysis process, it is necessary that the experiments be carried out in narrow temperature ranges and, if possible, under stationary conditions. The abrupt and prolonged change in the conditions disturbs the stationarity and leads to a change in the quantity of the products obtained, and the generation of losses, which in an experimental system cannot always be registered.

A very important condition for making a correct comparison is the requirement to know the composition of the raw material that is subjected to pyrolysis.

Regression analysis was performed with the experimental data. The target function shows the amount of product obtained from the pyrolysis process under different conditions (independent variables). The independent variables involved in the model are the temperature at which the process takes place in the pyrolysis reactor (x_1) and the heating rate (x_2).

Equation (24) describes how much pyrolysis gas is produced depending on the temperature in the reactor and the heating rate.

$$\begin{aligned} y_1 &= 74.75 - 0.34 \cdot x_1 + 0.0004 \cdot x_1^2 + \\ &+ 0.16 \cdot x_2 \quad \mathrm{R}^2 = 0.99 \end{aligned} \tag{24}$$

The influence of the heating rate and the maintained temperature in the pyrolysis reactor on the amount of pyrolysis oil obtained is given by equation (25).

$$\begin{aligned} y_2 &= -58.50 + 0.51 \cdot x_1 - 0.00056 \cdot x_1^2 + \\ &+ 0.0018 \cdot x_2^2 \quad \mathrm{R}^2 = 0.99 \end{aligned} \tag{25}$$

How the heating rate and the maintained temperature in the pyrolysis reactor affect the obtained carbon residue is given by equation (26).

$$\begin{aligned} y_3 &= 80.65 - 0.13 \cdot x_1 - 0.34 \cdot x_2 + \\ &+ 0.00014 \cdot x_2^2 \quad \mathrm{R}^2 = 0.99 \end{aligned} \tag{26}$$

Tab.8 presents the results for product yields from the experiment and compares with the predicted values calculated from the described models in the literature.

Table 8. Yields of pyrolysis products

Temp.	Heating rate	Pyrolysis products char predic.	char exp.	oil predic.	oil exp.	gas predic.	gas exp.
℃	℃/min	wt%	wt%	wt%	wt%	wt%	wt%
300	27.5	45.00	44.15	45.00	33.15	10.00	22.70
400	62.5	30.00	27.94	62.00	41.20	8.00	30.86
500	59.3	30.00	19.56	62.00	50.80	8.00	29.64

In the Tab.9 and Tab.10 are present the results of the calculations of the calorific value of the raw material and the products of pyrolysis and are compared with the results of the experiment.

Table 9. Low Heating Value for solid and liquid materials

Material	C	H	O	N	S	LHV Predict.	LHV Exper.
	%	%	%	%	%	kJ/kg	kJ/kg
Scrap tire	85.08	9.76	1.26	0.93	0.97	38 904	37 656
Char	90.48	3.68	0.29	2.71	2.84	34 779	34 811
Oil	87.00	10.00	1.00	2.00	0.00	39 725	40 752

Table 10. Low Heating Value for pyrolysis gas

CO	CH_4	H_2	C_6H_6	LHV Predict.	LHV Exper.
mass%	mass%	mass%	mass%	kJ/kg	kJ/kg
34.20	12.66	2.08	1.06	9 712	13 882

The main problem in compiling the energy balance of the pyrolysis process is the determination of the heat required for the realization of the gasification process. Different authors offer different approaches. In the Tab.11 are present the results of the experiment and are compared with the analytical calculations of the models presented with equations (16) – (23).

Table 11. External addition heat

Temp.	External addition heat Predicted (from eq. 16-20)	Experimental
°C	kWh/kg raw	kWh/kg raw
300	1.569	8.900
400	2.067	7.300
500	2.565	8.100

According to the author of [1], the calculation of the heat required to carry out the endothermic reactions of Fig.1 is 1,683 kWh / kg raw, which is comparable to the values obtained from the calculation according to equations (16) – (23). The larger values of the experiment are due to environmental losses and unused in the process heat from incomplete combustion.

The analysis of the results in Tabs.9 to 11 shows that the heat obtained from the combustion of 1 kg of waste tires is 37 656 kJ. The heat obtained from the combustion of the pyrolysis products per 1 kg of waste tires is 36 820 kJ. Including the costs of endothermic gasification reactions, it is clear that it is more cost-effective to burn waste tires directly. From the point of view of ecology and environmental pollution, however, pyrolysis is a more gentle technology for obtaining energy from waste polymers, which has become increasingly important in recent years.

The results also show that the energy of the pyrolysis products is 10.23 kWh/kg raw, the energy required for the pyrolysis process, minimizing losses, is about 3 kWh/kg raw. It can be seen that the profit from 1 kg of raw material is about 6 kWh.

CONCLUSIONS

The conducted experiments show that the speed of the pyrolysis process strongly depends on the maintained temperature in the reactor. The quantities of the obtained pyrolysis products also depend on it.

The raw materials that undergo pyrolysis are diverse and have characteristic properties and their elemental qualitative and quantitative composition affects the quantity of pyrolysis products. This has been proven by experiments conducted under the same conditions with different types of raw material.

Subjected to atmospheric distillation, pyrolysis oil is divided into four main fractions, which are very close to the fractions obtained by atmospheric distillation of oil. This allows the treatment of waste polymers by pyrolysis to find its place in large oil refineries, where the efficiency of the process can be improved by utilizing waste heat from other industries.

The comparison of experimental results and obtaining significant conclusions from them for the pyrolysis process is correct, in cases when the experiments are carried out in stationary conditions and narrow limits of the observed process parameters.

The results of the conducted experiments and the performed analytical calculations are coordinated with those of other authors, published in literature sources.

Energy analysis has led to the conclusion that the energy contained in waste polymers can be utilized preferably by pyrolysis, which is a environmentally friendly technology.

NOMENCLATURE

Y - mass ratio, kg / kg fuel;

T, T_{reac}, t_{pyr}, X_T, T_{py}, x_1 – temperature in the reactor, °C;

X_P – pressure in the reactor, Pa;

X_N, RT - residence time of products in the reactor, min;

Y_1, y_2 – mass ratio of pyrolysis oil, kg/kg fuel;

Y_2, μ_{char}, y_3 - mass ratio of char, kg/kg fuel;

y_1, - mass ratio of pyrolysis gas, kg/kg fuel;

HR, x_2 - heating rate (°C/min);

VM - volatile substances, kg/kg daf fuel;

FC - fixed carbon, kg /kg daf fuel;

Q_{HHV} - high heating value, MJ/kg;

Q_{LHV} - low heating value, MJ/kg;

Ce - mass ratio of cellulose and hemicellulose, mass %db;

L - lignin, mass %db;

E - proportion of extracts, mass %db;

W_{wb} - working humidity, kg/kg wet mass;

C, O, H, N, S and ASH - mass fraction of carbon, oxygen, hydrogen, nitrogen, sulfur and ash in the fuel on a dry basis (db), kg/kg fuel;

A, W, F - the amount of air, of steam needed to gasify, fuel to produce 1 Nm^3 of product gas, kg;

C_i - the volumetric specific heat of the gas species, i, at temperature Tg, kJ/(m^3.K);

V_i, the volume of the gas species, i, m^3;

Tg - gasifier exit temperature,°C;

T_0 - reference temperature, °C;

P_c - the quantity of char produced, kg/kg fuel;

Q_{gasif} , Q_{pyr} - the net heat of the reaction, kJ;

Q_{loss} - total heat loss, kJ;

q_c - heating value of the char, kJ/kg;

$(1-X_g)W$ - the net amount of steam remaining in the product gas of the gasification, kg;

H_0, H_g – enthalpies of steam at the reference and the gasifier exit temperatures, kJ/kg;

$Q_{product}$ -the energy in the product gas, kJ;

Q_{ext} - external heat addition, of product gas to the system, kJ;

c– mass specific heat of gas, steam and char, kJ/(kg.K);

g - and the mass ratio of gas, steam and char, kg;

Q_{phh} – physical heat of gas and char, kJ/kg;

r - the water vaporization heat, kJ/kg;

t_0 – initial fuel temperature, °C;

ΔH_S – the sensible heat for the temperature rise of biomass to the reaction temperature, kJ/kg;

ΔH_r - the heat of reaction, kJ/kg;

$\dot{m}_{tire}$ - tire flow rate, kg/s.

Subscripts

F – dry ash free (daf) fuel.

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