

Received November 11, 2016; reviewed; accepted February 17, 2016

Thermogravimetric analysis/pyrolysis of used tyres and waste rubber

Katarzyna Januszewicz^{*}, Marek Klein^{}, Ewa Klugmann-Radziemska^{*},
Dariusz Kardas^{**}**

^{*}Gdansk University of Technology, Narutowicza 11/12, 80-233 Gdansk, Poland. Corresponding author: katjanus@pg.gda.pl (Katarzyna Januszewicz)

^{**}Institute of Fluid-Flow Machinery Polish Academy of Sciences, Fiszerza 14, 80-231 Gdansk, Poland

Abstract: The process of pyrolysis is investigated in this paper. The pyrolysis results of two samples: waste tyres and rubber at different heating rates (10, 20, 50 K/min), were compared. In other experiments the degradation of two pyrolysis products, char and oil was examined. The kinetic study using the thermogravimetry equipment (TG) was done, which allowed determination of the kinetic mechanism of the process. The elemental analysis of the samples was performed.

Keywords: *pyrolysis of polymers, kinetic reaction, scrap tyres, waste rubber*

Introduction

Polymer waste is one of the biggest groups, and is also a non-biodegradable part of waste. The number of cars in the world is still growing and this produces an increasing number of used tyres. It is estimated that the world production of tyres in 2007 reached 1.3 billion (Quek and Balasubramanian, 2012).

Tyres are produced using a polymerisation process. The monomers used in this reaction are butadiene, styrene and isoprene. Tyres are also composed of carbon as an extender, sulphur, natural rubber and other ingredients. Biodegradation of rubber is a difficult process and takes a long time. Therefore, rubber is recycled in another way. The most popular method is combustion of rubber in a furnace. Another method is pyrolysis. Pyrolysis is thermal degradation of organic substances under anaerobic conditions. The main products from pyrolysis are char, oil and gas. All these products could be a source of energy. Oil could be used as either a fuel or a resource for compounds such as benzene, toluene or limonene. Char could be activated (Olazar et al., 2008). During combustion, toxic gases are emitted into the atmosphere. The

process of thermal degradation takes place in a hermetic reactor, which makes the process environmentally friendly.

In the pyrolysis process, technology, such as the type of reactor, and process conditions such as the gas flow, temperature, heating rate and pressure, have a significant effect on products. Many authors have used different installations and pyrolysis parameters, causing differences in products and kinetics. Cunliffe and Williams (1998) used a static-bed batch reactor, which was electrically heated. The final temperatures obtained in the reactor were 723–873 K. Another type of reactor, a circulating fluidised bed, was used by Dai et al., (2001). The reactor contained an assembly with two cyclone separators. In this process the temperature was between 633–1083 K, the yield of gas fraction increased from 10 to 40%, while the yield of char decreased to 27%. Other equipment, used by López et al. (2010), was a conical spouted bed reactor. The process was carried out at 698–873 K and 1.8–6.8 wt % of gases, 44.5–55.0 wt % of liquid fraction, 9.2–11.5 wt % of tar and 33.9–35.8 wt % of char were obtained. Similarly a high amount of oil fraction was obtained in a continuous rotary kiln reactor at the temperature of 723–923 K (Li et al., 2004). The highest oil yield was 45.1 wt% at 773 K, the char fraction was 41.3 wt% and the gas yield was 13.6 wt%. Another type of reactor, used by Kaminsky et al. (2009), was the fluidised bed reactor, which was filled with quartz sand as the fluidised bed medium. During the process, the authors used tyres in different types of fragmentation: powdered form, as pieces, and also whole tyres. All samples were degraded at 873, 923 and 973 K. The percentage of fractions was similar: 20% of gas, 36% of oil, 30% of carbon black. In other publications, Kaminsky and Mennerich (2001), using similar installation but under different process conditions, obtained yields of 51–65 wt % of oil fraction and 3.5–9.1 wt% of gases. A horizontal oven was used by Diez et al. (2004). Tyre samples were ground and the results obtained at 823 K were: 29% yields of gas, 38% of oil and 33% of char, but at 623 K they had: 20% of gas, 30% of oil and 50% of char. The pyrolysis process was also carried out in a conical spouted bed reactor (CSBR) (Arabiourrutia et al., 2007). This type of reactor had good hydrodynamic qualities and was efficient in heat transfer between phases. The yield of liquid decreased from 30.48 to 23.70% with temperature from 698 to 883 K and the gas fraction increased from 0.7 to 3.18% at the same time. The tar fraction was obtained between 23–30% at 698–883 K and the char yield was about 34% in each experiment.

The study of the mechanism of the pyrolytic reaction could be useful for to design the installation. Basic kinetics parameters of polymers could be analysed by thermal degradation. These values could be useful for gaining a better understanding of the mechanism of reaction. On the other hand, this analysis could be useful in designing industrial solutions in pyrolysis, gasification, hydrocracking of polymers and also to gain knowledge in this subject (Gonzalez et al., 2001). In this article a comparison of the thermal degradation of waste rubber and used tyres is made (Januszewicz, 2013).



Using the thermogravimetric analysis it is possible to obtain the characteristics of the temperature dependence of the sample mass (or weight loss) $m = f(T)$, at a constant heating rate. The first order reaction model can be used to describe different thermal reactions. This model assumes formation of several products from a single substrate (decomposition reaction). Therefore, it can be assumed that the number of products is proportional to the change of mass decomposition.

Pyrolysis or thermal degradation of solid substrates to gaseous products can be described by:



where: S – solid, V – volatile, I – one of component.

Aboulkas et al. (2008) proposed the following reaction scheme for the pyrolysis process, which is the first order reaction:



The first order reaction rate is described by the equation:

$$\frac{dV_i}{d\tau} = k_i(V_i^* - V_i) \quad (2)$$

where: τ – time, k – reaction rate constant, $*$ – final value.

The general expression for decomposition of solid sample is (Heydari et al., 2015):

$$\frac{dx}{d\tau} = k(T)f(x) \quad (3)$$

where: x – degree of conversion/normalized form of mass loss data, $k(T)$ – rate constant at temperature T , $f(x)$ – function of x depending on the reaction mechanism/conversion function.

$$x = \frac{m_o - m}{m_o - m_\infty} \quad (4)$$

where: m_o – initial mass of component, m – mass of component at a given time, m_∞ – mass of component at the end.

The Arrhenius equation:

$$k(T) = Ae^{-\frac{E_a}{RT}} \quad (5)$$

where: A – pre-exponential factor in the Arrhenius equation, E_a – activation energy, R – molar gas constant, T – temperature at time τ .

Substituting of (5) into (3) gives:

$$\frac{dx}{d\tau} = f(x)Ae^{-\frac{E_a}{RT}}. \quad (6)$$



The conversion function can be represented by the following equation (Matala 2013; Maaten et al., 2016):

$$f(x) = (1 - x)^n \quad (7)$$

where n is the order of reaction.

Under isothermal conditions x is dependent on time. Substitution of (7) into (6) gives:

$$\frac{dx}{d\tau} = Ae^{-\frac{E_a}{RT}} (1 - x)^n . \quad (8)$$

Under non-isothermal condition, where heating rate is constant, the following equation is (Olazar et al., 2008):

$$T = \beta\tau + T_o \quad (9)$$

where: β – heating rate ($\frac{dT}{d\tau}$), T_o – initial temperature. Also another equation can be considered (Heydari et al., 2015):

$$\frac{dx}{dT} = \frac{dx}{d\tau} \cdot \frac{d\tau}{dT} \quad (10)$$

where: $\frac{dx}{d\tau}$ – isothermal reaction rate.

Substituting (8) into (10) equation gives:

$$\frac{dX}{dT} = \frac{1}{\beta} Ae^{-\frac{E_a}{RT}} (1 - X)^n , \quad (11)$$

and after transformation is:

$$\ln\left(\frac{dX}{dT}\right) = \ln\frac{A}{\beta} - \frac{E_a}{RT} + n\ln(1 - X). \quad (12)$$

Materials and methods

The most common rubbers used in tyres are natural (NR), butadiene (BR) and styrene-butadiene (SBR) rubbers. Also, tyres contain relatively small amount of oil, plasticiser, carbon and metals, such as zinc. Different brands use various types of constituents in different proportions. Waste rubber samples used in investigations were different kinds of objects, such as gaskets. The fact that other authors have used different polymer samples, different tyre brands and different rubber wastes has caused the experimental data in the literature to differ.

In the experiment two kinds of sample were used: rubber waste and used tyres (Januszewicz, 2013). The vulcanised rubber and tyre samples were granulated, and then were shredded using a mortar. It was proved by other researchers (Leung and



Wang, 1998) that a sample size of less than 0.4 mm had no significant effect on the pyrolysis process. Gonzalez et al. (2001) described the comparison of reaction kinetics with different sample sizes, of 0.2–0.5, 0.5–1 and 1–1.6 mm, and the results confirmed that sample sizes used in the investigation had no significant influence on the pyrolysis process.

In the second experiment a comparison of the degradation of the pyrolysis products, char and oil, was performed. In addition, oil sample degradations were compared under different conditions, that is with and without oxygen (combustion and pyrolysis).

Pyrolysis was conducted using a thermogravimeter (Q600, TA Instruments) combined with FTIR (IS10, Thermo Scientific). The study of the elemental composition was performed using an elemental analyser IHD-O Flash 2000 (Thermo Scientific). The thermogravimetric analysis (TGA) was carried out under nitrogen flow at a heating rate of 15 K/min. Gases generated in the process were directed to the spectrometer, which allowed the analysis of online storage. The study used a combined gas flow cuvette with a thermoweight, thermostatted transfer line. The pyrolysis process was conducted in the flow of inert gas with the volume flow 100 cm³/min. In the investigation different heating rates of samples were used. The rubber as a polymer with additional compounds has a different thermal degradation curve and these could have an influence on the results (Gonzalez et al., 2001). It was reported that, for example, NR had the maximum mass loss at about 640 K, BR at 640 K and 733 K, and SBR at 643 K and about 703–733 K (Islam et al., 2009). A comparison was made of thermal decomposition of oil samples in an inert gas and in the presence of air. During the research the oil samples were examined to determine distillation fractions and to analyse the temperature of distillation.

Results and discussion

Samples of granulated waste rubber, tyres and char were analysed. Char is one of the pyrolysis products. Table 1 presents the results of the elemental analysis from the rubber waste, char and waste tyres. It was determined that the elemental composition of waste tyres and rubber waste was quite similar in this case. Comparison of samples showed higher nitrogen content and lower carbon and sulphur contents in the waste rubber samples. In the second experiment degradation of the pyrolysis products (used tyre samples) (oil and char) was determined and the obtained elemental composition of char is given in Table 1.

Table 1. The results of the elemental composition of waste rubber, waste tyres and char

Element (wt %)	N	C	H	S
Rubber waste, granulate	1.2	79.9	7.4	1.1
Char, granulate	0.9	76.4	3.7	2.2
Waste tyres, granulate	0.7	82.0	7.1	1.9



The mass loss at the function of temperature for both samples are presented in Figs. 1 and 2. The results are compared on the plot for tyre and waste rubber samples at different heating rates (10, 20, 50 K/min). The results of the waste tyres and rubber are not significantly different from each other. It can be seen that the slower process of pyrolysis is associated with greater mass loss. This is related to the lower rate of temperature which causes a more complete degradation of the polymer. It can be seen that the highest heating rate makes the pyrolysis process more rapid and also uniform. The maximum of conversions are at 734 K for SBR, 348 K for NR and 740.5 K for BR (Kim et al. 2000). Figures 1 and 2 show that the mass loss depends on the sample composition. Also, the heating rate of a single sample affects the pyrolysis, with the increase in the heating rate of reaction the temperature of decomposition increases. It is shown that tyre samples degradation starts from 600 to 750 K and for rubber samples about from 650 to 750 K. The final mass after degradation for both samples is about 30–40% of initial mass.

The derivative thermogravimetric curves (DTG) in Figs. 3 and 4 show derivative of the time and mass loss dependences at the function of temperature. Both samples degrade in two steps, but for rubber samples two peaks are more noticeable. The large and small peaks are in good agreement with the literature (Yao et al., 2008; Syed et al., 2011). Gonzales et. al (2001) obtained similar results. This may be due to the different sample contents of SBR, NR, BR, also oil, carbon and other additives like plasticisers. These compounds have different temperatures ranges of degradation. The first stage in the curve corresponds to the release of volatile hydrocarbons which starts at 650–700 K, and then continues. The second stage could be the release of the rest of the hydrocarbons with higher boiling point (Syed et al., 2011). The maximum temperature of degradation rate can be determined from DTG curves and it is about 650 K for tyre samples and 750 K for rubber samples. Figure 5 in the form of the mass loss versus process temperature shows the results of thermal degradation of the pyrolysis products oil and char. The samples of oil were degraded with and without oxygen (pyrolysis and combustion), and the curves obtained in this experiment are similar. Total degradation of the oil samples was achieved at about 700 K, and the hydrocarbon compounds of oil were destroyed. This information could be useful when it is desired to reuse the pyrolytic oil and transform it into the gas. On the other hand char was reduced by a mass loss of only 30% at 700 K and the highest temperature did not affect the sample. The samples during the pyrolysis process were analysed by FTIR (Figs. 6 and 7). Figures 6 and 7 show a peak in the region of 2800–3200 cm^{-1} . It is the absorbance peak of the C–H bond in polymer compounds. Also, the results from the chromatography analysis presented in the literature confirm the presence of hydrocarbons such as alkanes. That could demonstrate the presence of hydrocarbons such as methane, ethane and butane. The FTIR results confirm the reaction mechanism of the pyrolysis process that the increasing temperature improves cracking of the polymers and leads to generation of simple compounds like alkanes.



The results obtained in this experiment are comparable with a previous study (Gonzales et al., 2001; Olanzar et al., 2008; Islam et al., 2009; Quek and Balasubramanian, 2012). This and future studies of the mechanism of polymer thermal degradation could be useful when carrying out the pyrolysis process in both laboratory and industrial scales. In addition, a comparison of the results of pyrolysis parameters for samples of waste tyres and rubber shows similar results. The mechanism of the process is the same and the only differences may result from other polymers and their composition in each sample.

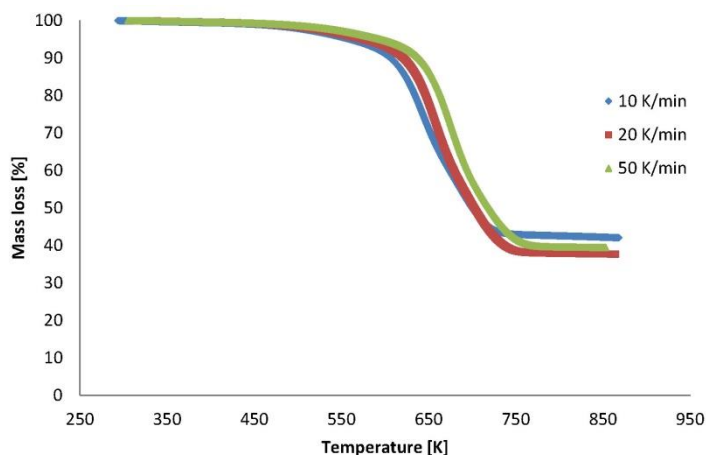


Fig. 1. Dependence of mass loss with temperature during pyrolysis of tyre samples, heating rates 10, 20 and 50 K/min

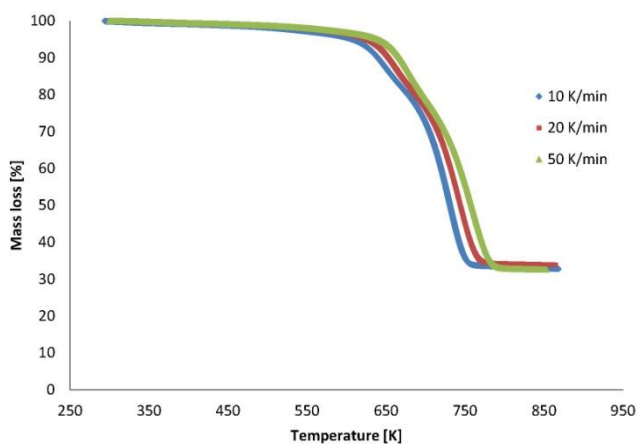


Fig. 2. Dependence of mass loss with temperature during pyrolysis of waste rubber samples, heating rates 10, 20 and 50 K/min

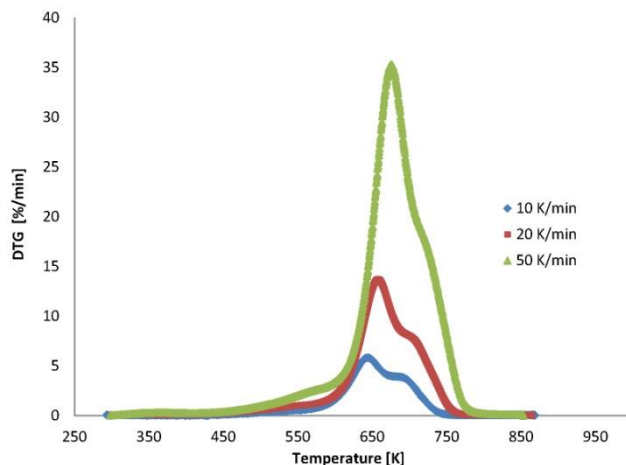


Fig. 3. Experimental DTG curves of the tyre samples for different heating rates 10, 20 and 50 K/min

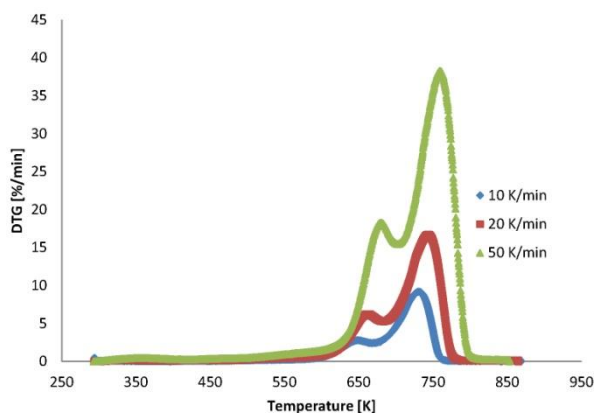


Fig. 4. Experimental DTG curves of the waste rubber samples for different heating rates

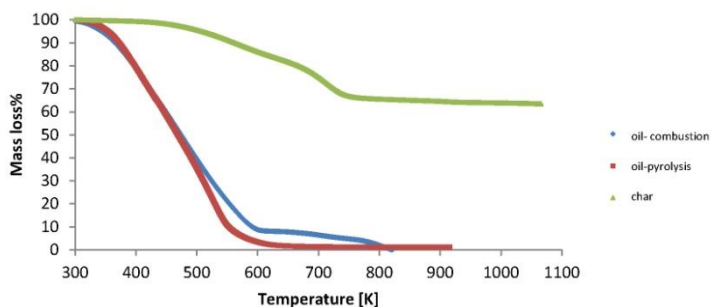


Fig. 5. Temperature dependence of relative mass loss for two processes: pyrolysis of oil and char, and combustion of oil

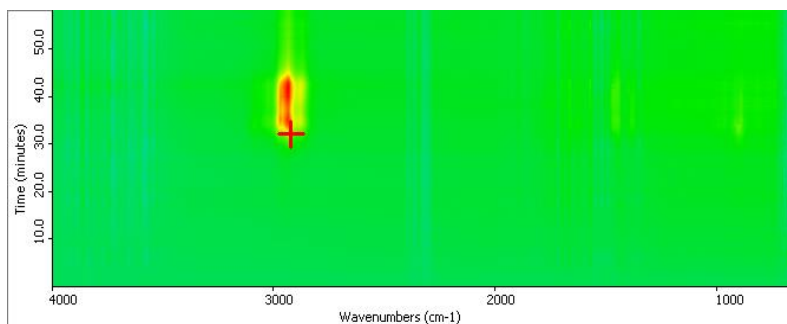


Fig. 6. FT-IR result (dependence of wavenumbers and time) for tire pyrolysis, heating rate 10 K/min

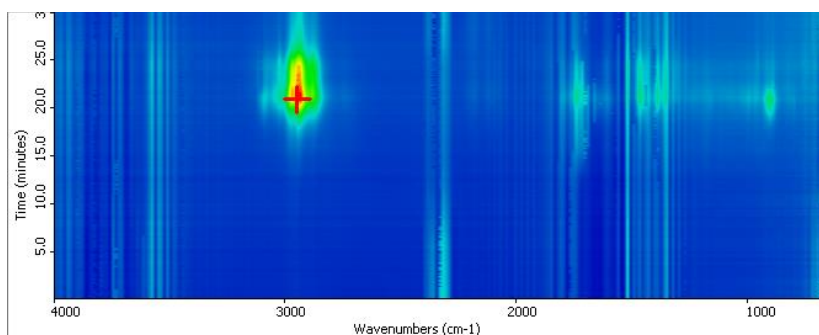


Fig. 7. FT-IR result (dependence of wavenumbers and time) for waste rubber pyrolysis, heating rate 20 K/min

Conclusions

In this paper the mass loss kinetics and DTA of waste rubber and tyres at different heating rates was studied. It was shown that the maximum of samples degradation of rubber and tyres was at 650–750 K. The results can be useful in choosing parameters for the pyrolysis process, while the equations obtained can be used for design and numerical simulations of commercial reactors. A kinetic model was used to explain the mechanism of pyrolysis. The samples of waste tyres and rubber were compared, and the elemental analysis was performed. The mechanism of degradation was similar for both samples. Small differences may be due to the quantitative composition of the polymers in the test samples, and other pyrolysis profile. These results show that this kind of waste (rubber and tyres) could be degraded together without significant influence on the process.

References

- ABOULKAS A., EL HARFI K., EL BOUADILI A., 2008, *Kinetic and mechanism of Tarfaya (Morocco) oil shale and LDPE mixture pyrolysis*, J. Mater. Process. Technol. 206, 16–24.
- ARABIOURRUTIA M., LOPEZ G., ELORDI G., OLAZAR M., AGUADO R., BILBAO J., 2007, *Product distribution obtained in the pyrolysis of tyres in a conical spouted bed reactor*, Chem. Eng. Sci. 62, 5271–5275.

- CUNLIFFE A.M., WILLIAMS P.T., 1998, *Composition of oils derived from the batch pyrolysis of tyres*, J. Anal. Appl. Pyrolysis 44, 131–152.
- DAI X., YIN X., WU C., ZHANG W., CHEN Y., 2001, *Pyrolysis of waste tires in a circulating fluidized-bed reactor*, Energy 26, 385–399.
- DIEZ C., MARTINEZ O., CALVO L.F., CARA J., MORAN A., 2004, *Pyrolysis of tyres. Influence of the final temperature of the process on emissions and the calorific value of the products recovered*, Waste Manage. 24, 463–469.
- ENCINAR J.M., GONZALEZ J.F., CANITO J.L., RODRIGUEZ J.J., 2000, *Fixed-bed pyrolysis of Cynara cardunculus L. Product yields and compositions.*, Fuel Process. Technol. 68 (3), 209–222.
- GONZÁLEZ, J. F., ENCINAR, J. M., CANITO, J. L., RODRÍGUEZ, J. J., 2001, *Pyrolysis of automobile tyre waste. Influence of operating variables and kinetics study.* J. Anal. Appl. Pyrolysis 58–59, 667–683.
- HEYDARI M., RAHMAN M., GUPTA R., 2015, *Kinetic study and thermal decomposition behavior of lignite coal*, Int. J Chem. Eng, vol. 2015.
- ISLAM M.R., HANIU H., FARDOUSHI J., 2009, *Pyrolysis kinetics behavior of solid tire wastes available in Bangladesh*, Waste Manage. 29, 668–677.
- JANUSZEWICZ K., 2013., *Analiza własności fizykochemicznych i możliwości wykorzystania oleju i gazu, powstających w procesie pirolizy opon samochodowych. in Polish (Analysis of the physicochemical properties and the development of methods of management of oil and gas formed by tire pyrolysis)*, Thesis for the degree of Doctor of Science, Gdansk University of Technology.
- KAMINSKY W., MENNERICH C., 2001, *Pyrolysis of synthetic tire rubber in a fluidized-bed reactor to yield 1,3-butadiene, styrene and carbon black*, J. Anal. Appl. Pyrolysis 58–59, 803–811.
- KAMINSKY W., MENNERICH C., ZHANG Z., 2009, *Feedstock recycling of synthetic and natural rubber by pyrolysis in a fluidized bed*, J. Anal. Appl. Pyrolysis 85, 334–337.
- KIM W.I., KIM S.D., LEE S. B., HONG I.K, 2000, *Kinetic characterization of thermal degradation process of commercial rubbers*, J. Ind. Eng. Chem. 5 (vol. 6).
- LI S.-Q., YAO Q., CHI Y., YAN J.-H., CEN K.-F., 2004, *Pilot-Scale Pyrolysis of Scrap Tires in a Continuous Rotary Kiln Reactor*, Ind. Eng. Chem. Res. 43, 5133–5145.
- LOPEZ G., AGUADO R., OLAZAR M., ARABIURRUTIA M., BILBAO J., 2009, *Kinetics of scrap tyre pyrolysis under vacuum conditions*, Waste Manage. 29, 2649–2655.
- LOPEZ G., OLAZAR M., AGUADO R., BILBAO J., 2010, *Continuous pyrolysis of waste tyres in a conical spouted bed reactor*, Fuel 89, 1946–1952.
- MAATEN B., LOO L., KONIST B., NESUMAJER D., PIHU T., KULAOTS I., *Decomposition kinetic of American, Chinese and Estonian oil shales kerogen*, 2016, Oil shale 33, 167–183.
- MATALA, A., *Methods and applications of pyrolysis modeling for polymeric materials*, 2013, Thesis for the degree of Doctor of Science.
- OLAZAR M., LOPEZ G., ARABIURRUTIA M., ELORDI G., AGUADO R., BILBAO J., 2008, *Kinetic modelling of tyre pyrolysis in a conical spouted bed reactor*, J. Anal. Appl. Pyrolysis 81, 127–13.
- SYED S., QUDAIH R., TALAB I., JANAJREH I., 2011, *Kinetics of pyrolysis and combustion of oil shale sample from thermogravimetric data*, Fuel 90, 1631–1637.
- QUEK A., BALASUBRAMANIAN R., 2012, *Matematikal modeling of rubber tire pyrolysis*, J. Anal. Appl. Pyrolysis 95, 1–13.
- YAO F., WU Q., LEI Y., GUO W., XU Y., 2008, *Thermal decomposition kinetics of natural fibers: Activation energy with dynamic thermogravimetric analysis*, Polym. Degrad. Stabil. 93, 90–98.

