

Influence of Natural Zeolites on the Thermal Decomposition of Multi-layered Plastic Waste

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Abstract: The pyrolysis process drew scientific attention lately, as it represents the basis for the production of second generation of synthetic fuels and other chemicals. The process takes place in inert atmosphere, and liquids, gases, and small number of solid particles represent main reaction products. Pyrolysis can be thermal or catalytic. Thermal pyrolysis requires very high temperatures, and products do not have high quality, while addition of catalysts reduces the reaction time, there is a better conversion rate, and lower operation temperature. In this paper, multi-layered plastic waste is used as raw material for thermogravimetric analysis (TGA). The composition of used plastic waste was previously determined based on the analysis of a large number of samples from fraction of mechanically non-recyclable plastic waste collected from waste treatment facilities in Croatia. Two natural zeolites with the most promising catalysts properties were selected for the reaction. Thermogravimetric analysis was used to understand the pyrolysis process of multi-layered plastic waste and to determine the thermochemical behavior and kinetics. Kinetic analysis was performed using the isoconversional Kissinger-Akahira-Sunose method. The aim of this paper was to investigate how selected natural zeolite catalysts influence the kinetics of the pyrolysis process of multi-layered plastic waste.

Keywords: multi-layered plastic waste; pyrolysis; TGA; zeolites

1 INTRODUCTION

Since 1970s, the ratio of plastic production has been growing. According to the historic growth of plastic production, primary plastic is expected to reach 1 100 million tonnes by 2050. According to the UNEP statistic, about 36% of all produced plastic are applied in packaging sector (UNEP). In Europe, 40% of 55 Mt of plastics is produced only for packaging [1]. Multi-layered plastic is mostly used for food packaging, personal hygiene products (e.g., shampoo, conditioner) [2]. Multi-layered plastic food packaging makes up 17% of total plastic packaging film production. The thickness of multi-layered plastic food packaging differs from 30 μm to 1 mm. Also, the number of the layers varies between 3 and 20 [1]. Multi-layer plastic improves properties of packaging, like barrier performance, which leads to longer shelf-life. Multi-layers are made of materials with different physical and chemical properties. Polymers like polyethylene, polypropylene, polyethyleneterephthalate, and polylactic acid [3]. Multi-layered packaging also contains a thin layer of aluminum foil and different layers of lamination in paper and plastics that act like a barrier to light, moisture, oxygen, and CO_2 . Also, multiple-layer plastics comprise other components, like chemical additives (fillers, plasticizers, flame-retardants, colorants, stabilizers, lubricants, foaming agents, and antistatic agents). Due to the complex structure, multi-layered plastic waste is very difficult to be processed at the large scale [4].

Every country has different waste management strategy, which influences the sorting and recyclability of plastic waste. Also, the food packaging contains high amounts of impurities, such as food residues. Typical sorting steps are not adjusted for high-quality sorting of flexible films, but near-infrared technology can detect different material layers. Therefore, new procedures for sorting are needed, in order to improve recyclability of multi-layered plastic food packaging [5]. Recovery of those materials is possible only if materials can be separated or in case that they can be processed together. However, both methods are considered impossible, since today's recycling plants aim to recycle only

mono-materials, and different polymers or materials are unmixable. Therefore, multi-layered plastic is non-recyclable, and only thermal recovery or disposal are possible options [6].

1.1 Pyrolysis of Plastics

Pyrolysis is a thermo-chemical process that occurs in the inert atmosphere (with no oxygen present), whereby organic compounds are decomposing, generating gaseous and liquid products that are used as fuels and chemicals [7, 8]. It can be distinguished between thermal and catalytic pyrolysis [9]. Thermal pyrolysis requires high temperatures, between 350 and 900 $^{\circ}\text{C}$, with liquids as the main reaction products [7]. Catalytic pyrolysis needs lower temperatures and the reaction time is shorter [10]. Catalysts enhance the hydrocarbon distribution [11]. Catalysts can be either homogeneous or heterogeneous. The most utilized catalyst from the first category is aluminum chloride [12]. Heterogeneous catalysts are more widely used for plastic pyrolysis. Some from this category are: ZnO , MgO , CaCO_3 , CaC_2 , SiO_2 , Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, ZSM-5 zeolite, red mud, and FCC [11, 13]. Generally, catalysts lower the activation energy, and accelerate the reaction rate [14].

Pyrolysis process of plastic waste is influenced by several factors: temperature, retention time, composition of feedstock, moisture, particle size, catalyst presence, type of the reactor, pressure, carrier gas, etc. All of these factors can affect quality, quantity and distribution of the pyrolysis products [15, 16]. Many studies on thermal and catalytic pyrolysis of plastics have been conducted lately. Polyolefin-based plastics are decomposed through a random chain scission mechanism in order to produce heterogeneous products (linear paraffin, olefin) [15]. Thermal pyrolysis generally leads to higher production of waxes in comparison to catalytic pyrolysis [11, 17-21]. Catalytic pyrolysis has more advantages compared to the thermal pyrolysis, because the energy consumption decreases, and a narrow range of hydrocarbons is produced [15, 22]. Only limited number of papers were published on the catalytic pyrolysis of multi-layered plastic waste [4, 23-27]. Those studies have mostly

concentrated on catalytic pyrolysis products and their characterization. Also, low number of studies has focused on reaction kinetics during catalytic pyrolysis of multi-layered plastic waste [1, 20, 28, 29].

1.2 Thermogravimetry as a Tool for Pyrolysis Studies

One of the most common approaches to pyrolysis process research, including catalytic pyrolysis as well, is thermogravimetric analysis [30]. Thermogravimetry or thermogravimetric analysis (TGA) is used for monitoring of a substance mass as a function of temperature or time. Sample is subjected to a controlled temperature and controlled atmosphere [31]. TGA is used for investigation of thermal stability, oxidative stability, composition. The weight gain/loss of the samples can be assigned to different factors. The gain of the weight means adsorption or oxidation, while weight loss describes the decomposition, desorption, dehydration, desolvation or volatilization [32]. In another technique, derivative thermogravimetry (DTG), the derivative of mass-change with respect to time is recorded in a function of time or temperature. Also, the derivative of the mass-change in regard to time can be recorded as a function of time or temperature. In both cases, as the result, the first derivative of the TGA diagram is obtained, which is in form of peaks, instead of a stepwise curve [33].

Many studies have been conducted on pyrolysis of plastic materials through TGA analysis [21, 34-40]. These studies are based mostly on the pyrolysis of a single type of plastic or co-pyrolysis of two or more different types of plastics, like LDPE, PP, PS, PET, and PP. Several studies focused on TGA with different carrier gasses like N₂, CO₂ or He [41, 42]. Only limited number of studies has investigated the TGA analysis of multi-layered plastic food packaging plastics [1, 20, 43]. In the work of Kremer et al. [1] the ZSM-5 catalyst modified with iron (III) oxide showed good results during the catalytic pyrolysis of multi-layered plastic waste, in a way of lowering activation energy of reaction, increasing of the acidity of the zeolites, and improving the reactivity of the catalyst's surface.

So, the aim of this study is to investigate the effect of natural zeolite in the pyrolysis of multi-layered plastic packaging waste. This was achieved by conducted thermogravimetric analysis and reaction mechanism (kinetic study) was done by using isoconversional Kissinger-Akahira-Sunose (KAS) method. Natural zeolites were chosen because they are available and affordable compared to the synthetic catalysts, and they have shown a great result in pyrolysis of plastic waste. Following papers gave a great insight in pyrolysis of plastics in the presence of natural zeolites [44-48].

2 MATERIALS AND METHODS

2.1 Materials

As previously explained, the multi-layered plastic food packaging is formed through layering of several thin plastic layers, accompanied with other materials like paper or/and aluminum. The composition of multi-layered plastic waste was previously determined based on the analysis of a large number of samples from the fraction of mechanically non-

recyclable plastic waste collected from waste treatment facilities in Croatia. The realistic multi-layered plastic food packaging had following composition: PE 71.17 %, EVOH 0.42 %, PP 9.70 %, PET 11.62%, PA 3.36 %, Cellulose 0.45%, and Aluminum 3.30 %.

2.2 Catalyst Characterization

Surface properties (surface area, prosity, acidity, cation exchange capacity) have strong influence on catalytic activity. The catalyst that has the highest cation exchange capacity also tends to show maximal convection rate. Seven different natural catalysts from the wider region of the municipality of Celinac (Republic of Srpska, Bosnia and Herzegovina) were tested on specific surface area, capacity of cation exchange, Si-percentage, Al-percentage, pore volume, pore diameter. Among tested natural zeolites, third and seventh sample had the highest capacity of cationic exchange, and therefore these zeolites were chosen for the further process of pyrolysis of multiple-layered plastic waste packaging.

Natural zeolites were used in the experiments. Physico-chemical properties of natural zeolites were determined with following techniques: low-temperature nitrogen adsorption (LTNA), thermogravimetric analysis (TGA), differential thermogravimetric analysis (DTG), infrared spectroscopy with Fourier transformation (FTIR), scanning electron microscopy and energy dispersive X-ray analysis (SEM-EDS), and X-ray diffraction analyses (XRD). The cation exchange capacity was also determined. Textural properties of samples (specific surface area, mean pore diameter, pore volume, external specific area, micropore volume and micropore area) were determined from adsorption/desorption isotherms obtained by adsorption of gaseous nitrogen at temperature of liquid nitrogen (-196 °C), when He was used as a carrier gas. For the measurements, instrument Micrometrics ASAP-2000 was used. Specific surface was calculated with BET-equation, while pore volume and mean pore diameter were determined based on the adsorption branch of the isotherm according to the Barrett, Joyaner, Halenda (BJH) method. Examination of the morphological characteristics of the samples was done using scanning electron microscopy and energy dispersive X-ray analysis on JEOL-JSM-5300 device. Cation exchange capacity was determined by standard ammonium-acetat method, where the concentration of exchangeable cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) is determined by applying atomic absorption spectroscopy (AAS) Varian Spectra AA 55B. Following table (Tab. 1) contains the most important characteristics of the chosed natural zeolite for the pyrolytic run.

Table 1 Characteristics of chosed natural zeolite with most promising properties for the pyrolysis

Sample	Zeolite 3	Zeolite 7
Specific surface area (m ² /g)	26.6	113.27
Mean pore diameter (mm)	15.97	10.99
Pore volume (cm ³ /g)	0.081	0.20
Si	30.65	32.92
Al	6.09	7.32
Cation exchange capacity (mmol/100 g)	186.12	254.6

Natural zeolites with most promising catalyst properties were selected for the process, which means that two zeolites (zeolite 3 and zeolite 7) were chosen among the tested zeolites, because of the high cation exchange capacities. Surface area is an important factor for the application of natural zeolites as catalysts [49]. Therefore, zeolites 3 and 7 seem as the most perspective catalysts for the TGA run and further kinetic analysis.

As it can be seen from the Fig. 1, microscopic tests have shown that natural zeolite consists of a large number of plates, clearly defined shapes, many of them have a plate shape, which is characteristic for the crystal structure of clinoptilolite [50]. Following studies have used clinoptilolite natural zeolites for pyrolysis of plastic waste [51, 52].

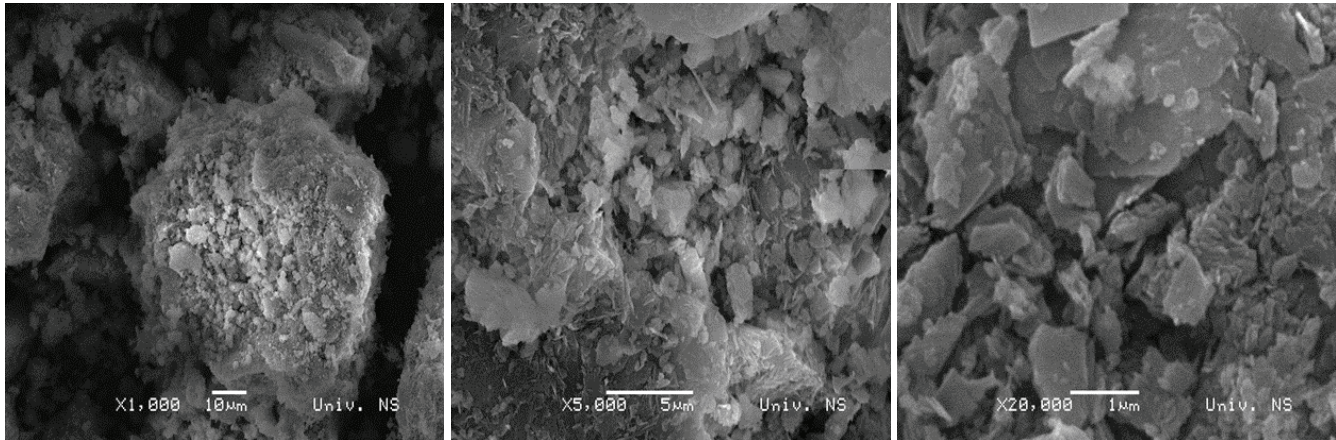


Figure 1 SEM pictures of zeolite sample number 3

2.3 Analytical Equipment

Thermogravimetric analyzer Q500 (TA Instruments, DE, USA) performed the pyrolysis experiment. The experiments were done in inert atmosphere (nitrogen flow), at different heating rates (5, 10, 15, and 20 °C/min) ranging from 40 to 600 °C. The weight of the sample and catalyst loading was 10 mg.

2.4 Kinetic Study – Overview

In order to describe the principles and mechanisms of pyrolysis reaction, kinetic study needs to be done. The rates of conversion are proportional to the concentration of reacted material. Therefore, the conversion rate can be expressed on following way (Eq. (1)) [53]:

$$\frac{dy}{dx} = \beta \frac{dx}{dT} = K(T)f \quad (1)$$

where x is the reaction extent, i.e., degree of advance defined as (Eq. (2)) [53, 54]:

$$x = \frac{w_0 - w}{w_0 - w_f} \quad (2)$$

w is the weight of the sample at the given time t , while w_0 and w_f refer to values at the start and at the end of the weight loss process. $f(x)$ and $K(T)$ are functions of conversion and temperature [53]. β is the linear heating rate (°C/min) [54]. $K(T)$ is the temperature dependence of the weight loss rate can be modeled by Arrhenius equation (Eq. (3)) [53]:

$$K(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

E stands for the activation energy, A is the pre-exponential factor and R is the gas constant [53].

When the Eq. (1) and Eq. (3) are combined, the reaction rate can be accessed in the following form (Eq. (4)) [53]:

$$\beta \frac{dx}{dT} = A \exp\left(-\frac{E}{RT}\right) f(x) \quad (4)$$

2.4.1 Kissinger-Akahira-Sunose Method – KAS Method

There are different methods for non-isothermal degradation kinetic study of thermodiagrams. Following five methods are mostly used for obtaining degradation mechanisms and kinetics of polymers: Coats-Redfern method, Coats-Redfern (modified) method, Flynn-Wall-Ozawa method, Kissinger-Akahira-Sunose method, and Friedman method [55]. The model-free approaches are built on the Arrhenius parameters, with no dependence on the reaction order. The model-free methods are also known as isoconversional, because the reaction rate is a function of the temperature, at constant extent of conversion. By isoconversional method, isothermal and non-isothermal pyrolysis can be analyzed [56]. Vyazovkin et al. [57] suggested the Kissinger-Akahira-Sunose method, because of its accuracy in estimation of energy activation values.

The previous equation (Eq. (4)) can be written on following way (Eq. (5)) [53, 58]:

$$\frac{dx}{f(x)} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) dT \quad (5)$$

This equation integrated with the conditions $x = 0$ at $T = T_0$ gives following expression (Eq. (6)) [53, 58]:

$$g(x) = \int_0^x \frac{dx}{f(x)} = \frac{A}{\beta} \int_0^T \exp\left(-\frac{E}{RT}\right) dT \equiv \frac{AE}{\beta R} p\left(\frac{E}{RT}\right) \quad (6)$$

This method assumes that A , $f(x)$, and E are independent of T , and A and E are independent of x , then the Eq. (6) can be integrated to give the following logarithmic equation (Eq. (7)) [53, 58]:

$$\ln g(x) = \ln\left(\frac{AE}{R}\right) - \ln\beta + \ln p\left(\frac{E}{RT}\right) \quad (7)$$

The KAS method also uses the Coats-Redfern approximation, according to which it applies (Eq. (8)) [53, 58]:

$$p\left(\frac{E}{RT}\right) \equiv \frac{\exp\left(-\frac{E}{RT}\right)}{\left(\frac{E}{RT}\right)^2} \quad (8)$$

When the Eq. (6) and Eq. (8) are combined, following expression is obtained (Eq. (9)) [53, 58]:

$$\ln \frac{\beta}{T^2} = \ln \frac{AR}{Eg(x)} - \frac{E}{RT} \quad (9)$$

3 RESULTS OF THERMOGRAVIMETRIC ANALYSIS AND KINETIC STUDY

3.1 Thermogravimetric Analysis

The thermogravimetric (TG) diagram is recorded at four different heating rates (5, 10, 15, and 20 °C/min) and the first-derivative TG curves (DTG) are shown in Fig. 2a and 2b.

Degradation of individual polymers occurs in following order $PS < PET < PP < PE$ [59]. Only degradation of PS happens in the temperature range from 350 to 450 °C. Temperature degradation of pure PET is between 390 and 470 °C, while PP, LDPE, and HDPE degrade between 450 and 510 °C [19]. PP pyrolysis temperatures are lower than that of HDPE and LDPE because of the third carbon atom, which reduced the polymer stability [60]. From the Fig. 2a it can be seen that the thermal degradation occurs in two steps, in temperature range between 300 and 450 °C.

On the following Fig. 3a and 3b, the TGA and DTG diagrams of degradation of each component from the obtained plastic mix are shown.

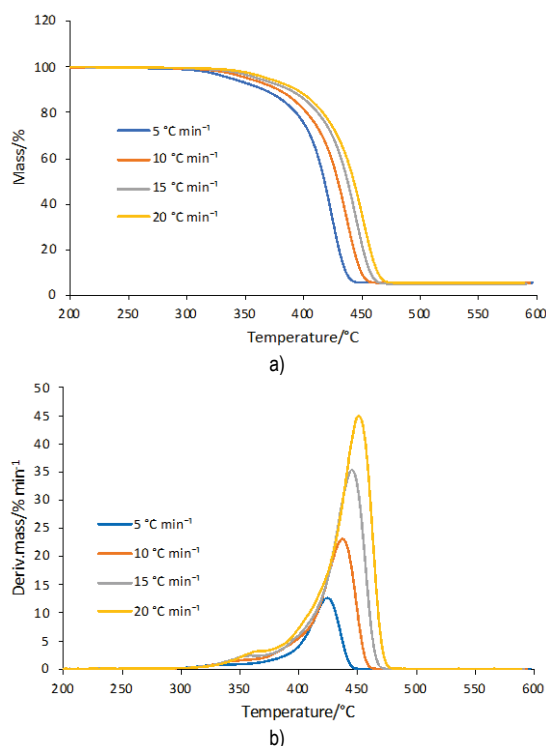


Figure 2 a) TGA diagrams of mixed plastic and different heating rates (5, 10, 15, and 20 °C/min); b) DTG curves of mixed plastic and different heating rates (5, 10, 15, and 20 °C/min)

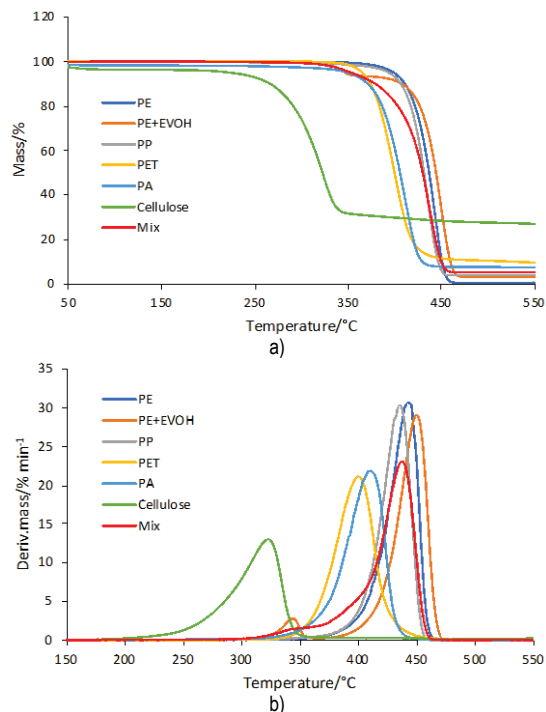


Figure 3 a) TGA diagram of degradation of each component of obtained plastic mix; b) DTG curves of degradation of each component of obtained plastic mix

TGA curves refer to degradation of PE, PP, PET, PA, and cellulose in one stage, degradation of PE+EVOH, plastic mix, and plastic mix with natural zeolites in two stages.

TGA plots and DTG plots for plastic mix with chosen zeolites are shown in the Fig. 4a, and 4b, at heating rate of 10 °C/min.

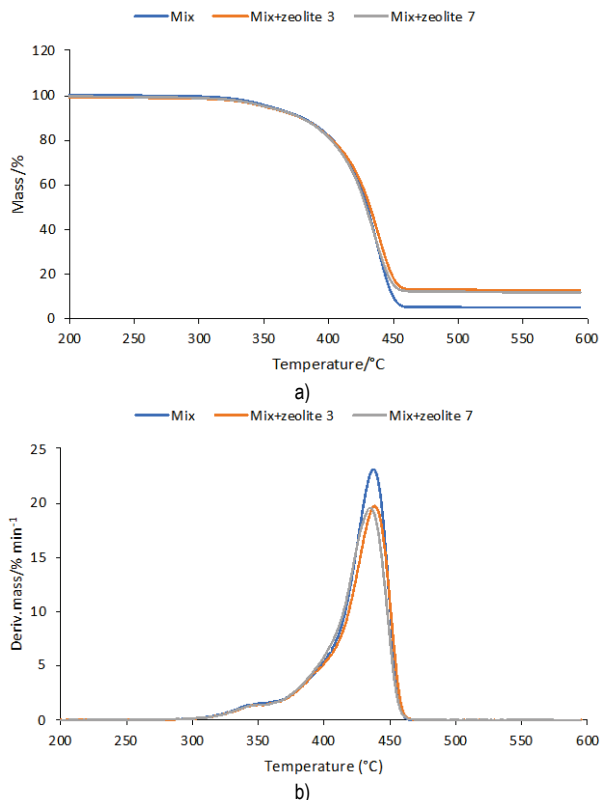


Figure 4 a) TGA plots for plastic mix with zeolite 3, and zeolite 7, at heating rate 10 °C/min; b) DTG plots for plastic mix with zeolite 3, and 7, at heating rate 10 °C/min

Table 2 Thermogravimetric parameters for plastic mix, by heating rate of 10 °C/min

Sample	$T_{on}/^{\circ}C$	$T_1/^{\circ}C$	$R_1/^{\circ}min^{-1}$	$T_2/^{\circ}C$	$R_2/^{\circ}min^{-1}$	$T_f/^{\circ}C$	$M_f/mass\%$
PE	411.29			442.99	30.64	453.07	0.62
PE+EVOH	325.92	339.97	3.09	443.29	32.19	453.44	3.27
PP	400.88			427.86	33.78	438.92	3.90
PET	369.51			400.12	21.15	417.66	9.01
PA	375.83			410.71	21.91	424.90	7.51
Paper	270.05			322.95	13.01	336.39	23.44
Mix	330.57	342.00	1.41	437.44	23.13	449.63	5.20
Mix+z3	324.83	341.11	1.29	438.45	19.75	451.32	12.84
Mix+z7	328.39	343.63	1.36	435.42	19.56	448.29	11.83

The TGA plots of plastic mix with and without catalysts is relatively similar. The form and shape of DTG diagram of the sample in presence of catalysts are similar to the original sample, implying that there is a slight change in the reaction mechanism. This further indicated that the kinetic study of plastic mix with catalysts was not necessary. Tab. 2. shows thermogravimetric parameters for obtained plastic mix, by heating rate of 10 °C/min.

As it can be seen from the Tab. 2, mass loss for the plastic mix with zeolite 3 begins at temperature of 324.83 °C, and for the plastic mix with zeolite 7 at temperature of 328.39 °C. Maximum mass loss rate of the first peak for the plastic mix

with zeolite 3 was 1.29 % min⁻¹, and for the plastic mix with zeolite 7, 1.36 % min⁻¹. Beside temperature of the second peak, and mass loss at the second peak, Tab. 2. contains values of final temperature of degradation of plastic mix. By subtraction of T_{on} from T_f , the decomposition temperature interval can be calculated.

Pore size and acidity are important factors for the catalytic cracking of polymers [7]. The obtained catalysts have low silicium to alumina ratio (SiO₂/Al₂O₃). Low SiO₂/Al₂O₃ ratio is related to the high acidity [52, 53] and lower mass loss rates. Only a negligible difference was obtained between mass loss rates of the original samples and the samples in the presence of catalysts. Coke formation could be another explanation for the lower mass loss rate. The utilization of a macroporous catalysts may reduce the coke formation. But, macroporous catalysts are not acidic, and do not have polymer active sites. Also, microporous catalysts could improve the catalytic reaction by producing more gases and lowering the liquid yield, but more qualitative than in the case with macroporous [22]. Additionally, natural zeolites have impurities in forms of Na, Mg, S, K, Ca, Ti, or Fe, which could influence the further reactions. However, industrial application of catalytic pyrolysis for recovering of plastic materials needs to be done with well-controlled catalysts in order to ensure coherent and repeatable products. So, natural catalysts might have undesirable impurities, quality, and composition for industrial utilization [54]. However, results of this study have shown that addition of catalyst slowed down the degradation process of our plastic mixture, so that the rate of polymer degradation is lower in comparison to the process with no catalysts. Study of Kremer et al. [20] showed good results by using Fe-ZSM catalyst for pyrolysis of multi-layered plastic waste.

3.2 Kinetic Study

Data and information on used kinetic study are provided in the subsection 2.4 and 2.4.1.

The Fig. 5 shows variation of activation energy in dependance of x parameter.

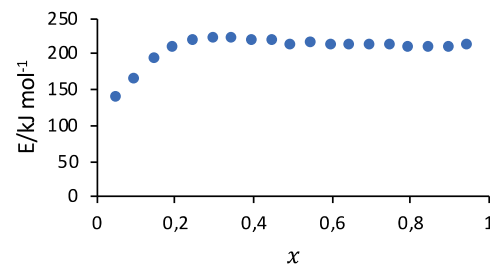


Figure 5 Dependence of activation energy on x parameter

The average activation energy amounted 204.37 kJ/mol, and minimal activation energy amounted 136.85 kJ/mol, while maximal activation energy was 219.10 kJ/mol. The dependance of activation energy from the x parameter provides information about complexity of the process – if it is linear, it occurs in one step, or if it is complex (when activation energy changes more than 30% related to the

average value of activation energy), the reaction occurs in at least two stages. Obtained results refer to two stage process, one from the beginning of the reaction until conversion rate is 0.25, and the second stage from the conversion rate of 0.25 until the end of reaction. Fig. 6. shows conversion curves for different heating rates.

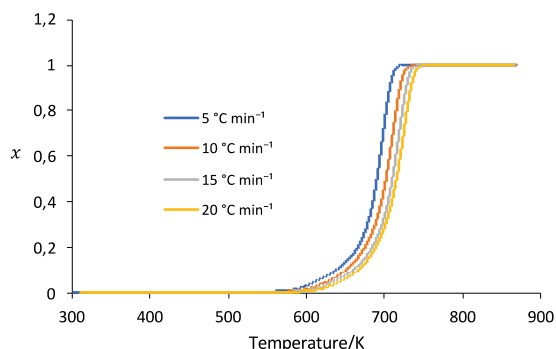


Figure 6 Dependence of activation energy on x parameter

The KAS plots of $\ln(\beta/T^2)$ versus $1/T$ (K^{-1}) for different values of conversion are shown in the Fig. 7.

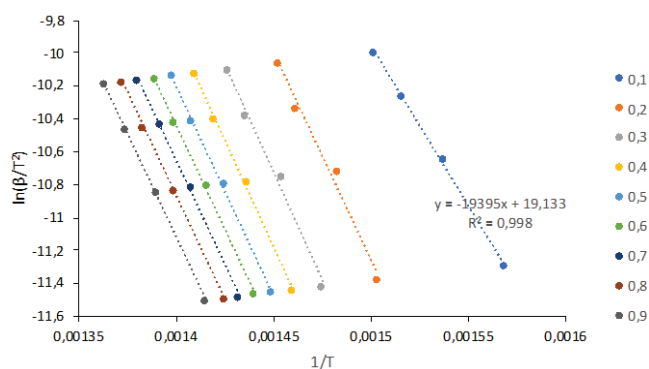


Figure 7 KAS plots for different values of conversion

According to the Eq. (9), the activation energy is calculated from the slope of the line, and the pre-exponential factor A from the segment on the y -axis, when the appropriate function $g(x)$ is used (Tab. 3).

Table 3 Values of activation energy E_a and values of R^2 corresponding to the linear fittings in the Fig. 7

x	E_a	R^2
0.1	161.27	0.9980
0.2	207.56	0.9948
0.3	218.66	0.9923
0.4	215.89	0.9967
0.5	211.64	0.9977
0.6	211.46	0.9987
0.7	209.83	0.9993
0.8	208.41	0.9998
0.9	208.37	0.9998

The calculated values of the correlations coefficients (R^2) are corresponding to the linear fittings in the Fig. 7 and are between 0.9923 and 0.9998.

4 CONCLUSION

This work focused on the analysis of catalytic degradation of multi-layered plastic waste through thermogravimetric analysis in order to provide information and understand the mechanism of catalytic degradation of plastics. Because of their affordable price and availability, natural zeolites could be potentially used as catalysts for the plastic pyrolysis. Their great properties have already shown good results in previous investigations and experiments. Beside thermogravimetry, kinetic study (KAS method) was obtained aiming to understand influence of natural zeolites on the pyrolysis process of multi-layered plastic waste. However, thermogravimetric analysis showed that kinetic study of selected plastic mix in presence of catalysts was not needed, due to the similar form and shape of DTG diagram of the sample with catalyst and without catalyst. Also, thermogravimetry analysis showed that degradation rate of plastic mix with catalyst is actually lower than the degradation rate with no catalysts.

However, kinetic study was performed only on the plastic mix, without any catalysts. It was found out that non-isothermal decomposition of selected plastic waste occurred in two stages. The values of activation energy, calculated with the KAS method were between 136.85 and 219.10 kJ/mol. Results of this study showed that utilization of natural zeolites as catalysts slowed down the process of degradation of investigated plastic mixture, so that the rate of catalytic degradation of polymer was slower in comparison to the process with no catalysts. Therefore, this study concluded that application of other catalysts may be more efficient than the utilization of the selected natural zeolites.

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