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THE CONVERSION OF POLYOLEFINS USING
THERMOCATALYTIC AND BIOCHEMICAL METHODS

Summary of Doctoral Dissertation
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INTRODUCTION

Every year more than 6300 million t of plastic waste are produced, with 80% of it collected in landfills or discarded in the natural environment. Unfortunately, water undergoes the most detriment, especially when substances of plastic production get into the nutrition network where 80-95% of ocean pollutants are plastics (Le Guern Lytle, 2018). The recycling process for plastic may only be applied up to 2-3 times, and therefore later only chemical recycling may be used. One of the best technologies for obtaining energy from waste and for reducing waste volume is thermolysis. This method allows the production of a high calorific (~45 MJ/kg) liquid product, which can be used as a fuel or its component. The use of catalyst in the thermolysis process allows the production of more liquid product, also to control its composition, to increase its quality and makes it easier to control the whole process. The best conditions for obtaining the target product must be determined experimentally.

Nowadays, much attention is paid to the possibility to degrade polyolefins with microorganisms and their enzymes. The polyolefin biodegradability is increased with the insertion of heteroatoms into the macromolecules during polymerization or the final products/waste may be oxidized thermally, with UV light or using oxidative acids; as well as keeping them in the natural environment for a longer time. After biochemical treatment, the physical and chemical properties of polymers are changed and further thermal degradation allows to obtain different yields of the products.

Summing up, the thermolysis process is still lacking in comprehensive investigation results, because the chemical degradation reactions are not controlled enough to obtain the desired composition of the final liquid products from different plastic wastes.

The aim of this work is to investigate the thermolysis process and to determine the influence of anthropogenic treatment to the yields of thermolysis products.

The tasks of the work are:

1.To investigate the influence of catalyst concentration to the yields of products, thermolysis process parameters, and composition of liquid products of different raw materials.

2.To determine the influence of the catalyst concentration to the kinetic and thermodynamic parameters of thermolysis reaction using the data of thermogravimetric analysis.

3.To investigate the physical and chemical properties of solid and liquid thermolysis products.

4.To determine the optimal composition of plastics and catalyst for producing diesel and gasoline components with better yields.

5.To propose the principal technological scheme for catalytic and noncatalytic thermolysis process;

6.To investigate the influence of anthropogenic treatment of polymer films to the yields of thermolysis products.

Scientific novelty

The comprehensive investigation of the influence of the catalyst and its concentration to the thermolysis process of kinetic and thermodynamic parameters, products yields and properties of various polymeric raw materials. The determination of the influence of anthropogenic treatment of polymers films to the yields of thermolysis products were performed.

Significance of research results

The optimal composition of mixtures of aromatic and nonaromatic plastics and catalyst were determined for obtaining the highest yields of liquid products. It was determined that the catalytic process is more favorable for gasoline production, and noncatalytic one – for diesel production. The continuous plastic thermolysis technological process, when the liquid products could be separated into diesel and gasoline fractions and thermolysis gas could be reprocessed or burned in the catalyst regenerator furnace, was proposed.

Main statements of defence:

1. The plastic thermolysis process is complex, its kinetic and thermodynamic parameters and the reaction mechanism depends on the nature of the material and the catalyst concentration in the reaction mixture.

2. The better yield of gasoline fraction is obtained during the catalytic process, and more diesel fraction is obtained during the noncatalytic process.

3. The physical and chemical properties of liquid thermolysis product depends on the nature of the raw material and the starting boiling temperature of the mixture.

4. The yields of thermolysis products of antropogenically treated materials depends on the anthropogenic treatment conditions and the chemical composition of the raw materials.

Scientific approbation of dissertation

The results of the doctoral dissertation work were presented at 2 international scientific conferences, and 2 articles were published in reviewed scientific journals listed in the Journal Citation Report (ISI).

Author contribution into this work

The author performed thermolysis experiments and part of the thermogravimetric experiments, estimated kinetic and thermodynamic parameters, performed the determination of properties of thermolysis products (except the element concentration determination), chromatographic analysis, prepared the samples and the media (except the media sterilization) for biochemical degradation experiment, performed biochemical degradation experiments, visual evaluation of the samples biodegradation, mass loss determination, FT-IR spectra analysis, mechanical properties determination and the analysis of the obtained results.

Soil microbial activity, fungi suspension preparation, media sterilization, fungi identification after experiments and the images of the microscopic view of samples were performed by the Nature Research Centre Laboratory by biodeterioration research staff. FT-IR spectra were registered by KTU Polymer Chemistry and Technology Department staff. Part of thermogravimetric analysis and the elements concentration determination were performed by the Lithuanian Energy Institute staff.

1. EXPERIMENTAL SETUP AND METHODS

1.1. Research object

Thermolysis within the reactor. Various types of plastic waste were used: polypropylene (PP), polyethylene (PE), polystyrene (PS), ethylene-propylene copolymer (E/P), thermoplastic elastomer based on the ethylene–propylene–diene terpolymer and polypropylene (PP/EPDM). PP, PE and PS were collected as industrial waste. E/P and PP/EPDM were collected from the local dump of car parts. All raw materials were crushed into pieces (particle size ≤ 20 mm). Zeolite regenerated NaceR™ FCC (“Grace”, USA) catalyst (CAT) was received from PC “ORLEN Lietuva” refinery. Amounts of the catalyst in the mixtures with plastics were 0, 10 and 25%. For detailed kinetic and thermodynamic analysis the catalyst amounts were 0, 1, 3, 5, 10, 25, 50%.

Biochemical experiment. Commercial polyethylene (PE), polypropylene (PP) and polystyrene (PS) waste films were used in the experiments. Only PP waste was coloured. The thickness of each film was 0.03 mm for PE and PP and 0.07 mm for PS. The control samples were untreated. The films were thermally aged at 75°C for 200 h in a hot air oven. The irradiation of films was carried out on each side of the films for 120 h with a UV source (40 W, wavelength 254 nm, the distance from the UV source was 50 cm). Control, thermally and UV aged samples contain the abbreviations, respectively, C, T or UV. After biodegradation, the test specimens were cleaned and kept in a desiccator for 3 days before being analyzed.

1.2. Methodics

1.2.1. Experiments within a reactor

Thermolysis experiments were performed in the fixed-bed reactor (Fig.1.1). The 3 dm³ reactor was loaded with plastic (the load mass did not exceed 1kg) and catalyst (its concentration was 0%, 10% and 25%), purged with nitrogen, hermetically closed with a lid and heated by an electrical muffle furnace. The reactor temperature was raised from an ambient temperature to 500°C at atmospheric pressure. The produced thermolysis gaseous and liquid products were separated in a separator. The fractions of thermolysis oil were accumulated in the separator and its valve was opened when the separator was loaded with 250±5 ml. Non-condensable thermolysis products flowed through the gas meter into the torch. The solid product was collected from the reactor when the system had cooled down. During the experiment, the pressure and temperature were recorded. The process was terminated when the gas flow from the reactor stopped and the temperature inside it reached 500°C.

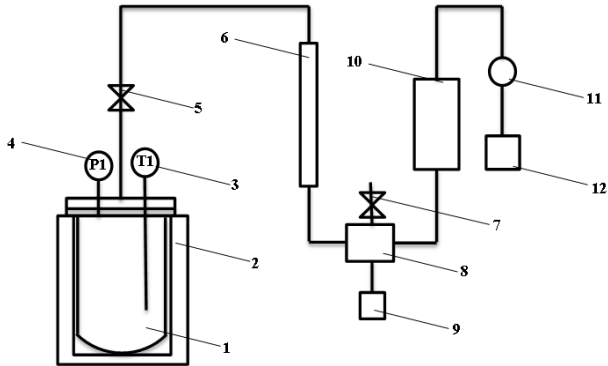


Figure 1.1. Schematic diagram of thermolysis unit: 1- reactor; 2- heating furnace; 3- thermocouple; 4- pressure transducer; 5- valve; 6- air condenser; 7- safety valve; 8- separator; 9- liquid product tank; 10- water reflux condenser; 11- gas meter; 12- torch

1.2.2. Thermogravimetry

Thermogravimetry experiments¹ were carried out with the thermogravimeter TGA 4000 (Perkin Elmer, USA) in an inert atmosphere at a temperature in the range of 20-500°C. The nitrogen gas flow rate was set to 20 ml/min. The plastics were ground into pieces and mechanically mixed with the appropriate amount of a catalyst before the experiment. Samples were loaded into an open ceramic crucible without compacting. The thermogravimetric experiments were repeated while the R² values of the plots used for activation energy estimation at each conversion for all mixtures were ≥ 0.97.

1.2.3. Estimation of kinetic and thermodynamic parameters

Iterative method. Iterative equation of Kissinger–Akahira–Sunose equation (*it*-KAS) (Liqing & Donghua, 2004) is presented below:

$$\ln \frac{\beta}{h(x)T^2} = \ln \frac{AR}{g(\alpha)E} - \frac{E}{RT} \quad (1)$$

where: T – temperature, R – universal gas constant, E – activation energy, A – pre-exponential factor, $g(\alpha)$ – mechanism function, β – heating rate,

$$h(x) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (\text{Senum and Young function}) \quad (2)$$

$$x = \frac{E}{RT}; \quad (3)$$

¹ The experiments were performed at the Lithuanian Energy Institute (LEI).

The iterative procedures were performed by the following steps (Genieva, Vlaev, & Atanassov, 2010): (1) assuming that $h(x) = 1$ for the initial value of activation energy E_i ; (2) using E_i value, the new E_2 is estimated from the plot of $(\ln[q/h(x)T^2]) - 1/T$; (3) the 2nd step is repeated while $E_i - E_{i-1} < 0.0001$ kJ/mol kJ/mol. The last value was considered to be the exact value of the activation energy.

The estimated E_a value does not depend on the reaction E/RT value (Gao, Nakada, & Amasaki, 2001).

Activation energy estimation according to Flynn-Wall method (Xu & Chen, 2013) the E_a value is calculated from the slope of $\log\beta$ vs $1/T$ for the given mechanism function $g(\alpha)$. The advantage of this method is that the activation energy is directly calculated without using the mechanism functions, which would result in errors (Nam & Seferis, 1991)

$$\log\beta = \log \frac{AE_a}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E_a}{RT} \quad (4)$$

The most probable mechanism function determination. The logarithmic equation is applied for $g(\alpha)$ determination (Liqing & Donghua, 2004) (Genieva, Vlaev, & Atanassov, 2010), (Vlaev, Georgieva, & Genieva, 2007):

$$\ln[g(\alpha)] = \left[\ln \frac{AE}{R} + \ln \frac{e^{-x}}{x^2} + \ln(h(x)) \right] - \ln\beta \quad (5)$$

For determination of the most probable mechanism function, the values of the conversion corresponding to multiple rates taken at the same temperature were put into the left side of Eq. 5 and all types of mechanism functions presented in (Vlaev, Georgieva, & Genieva, 2007) were tested. The slope and correlation coefficient were obtained from the plot of $\ln[g(\alpha)]$ versus $\ln\beta$. The most probable mechanism function was assumed to be the one for which the value of the slope of the straight line was closest to -1.0000 and the correlation coefficient R^2 was the highest.

The pre-exponential factor A can be estimated from the intercept of the plots of Eq. 1, inserting the most probable $g(\alpha)$ function determined (for *it*-KAS methods).

At T_p temperatures, A value is estimated by the following equation (Xu & Chen, 2013):

$$A = \beta \cdot E_a \cdot \exp\left(\frac{E_a}{R \cdot T_p}\right) / (R \cdot T_p^2) \quad (6)$$

Thermodynamic parameters estimation.

Graphic method. The correlation between kinetic and thermodynamic parameters of the investigated process results from the combination of Arrhenius and Eyring laws related to the temperature dependence of the rate constant ($k(T)$) (Vlaev, Georgieva, & Genieva, 2007), (Ptacek, Soukal, Opravil, Havlica, & Brandstetr, 2013). The rearranged logarithmic equation of this dependence is presented below:

$$\ln \frac{kh}{\chi k_B T} = \frac{\Delta S^\ddagger}{R} - \frac{\Delta H^\ddagger}{RT} \quad (7)$$

where χ is the transmission coefficient, which is unity for monomolecular reactions; k_B is the Boltzmann constant, h is the Plank constant, ΔS^\ddagger and ΔH^\ddagger are the changes of entropy and enthalpy, respectively, for the formation of the activated complex from the reagent. By plotting $\ln(kh/\chi k_B T)$ versus $1/T$ and using a linear regressive of the least square method, the values of the changes of entropy ΔS^\ddagger and enthalpy ΔH^\ddagger may be calculated from the intercept and the slope of the draw straight line respectively. The change of the Gibbs free energy ΔG^\ddagger can be calculated using the following equation:

$$\Delta G^\ddagger = \Delta H^\ddagger - T_a \Delta S^\ddagger \quad (8)$$

Mathematical method. Thermodynamic parameters may be estimated by the following equations (Xu & Chen, 2013) at temperature T_p :

$$\Delta H^\ddagger = E_a - RT \quad (9)$$

$$\Delta G^\ddagger = E_a + R \cdot T_p \cdot \ln \left(\frac{K_B \cdot T_p}{h \cdot A} \right) \quad (10)$$

$$\Delta S^\ddagger = \frac{\Delta H^\ddagger - \Delta G^\ddagger}{T_p} \quad (11)$$

where K_B is the Boltzmann constant, and h is the Plank constant, T_p is the peak temperature.

1.2.4. Biochemical experiment

Preparation of spore suspension.² The test-fungi for the experiment was obtained from the collection of the Nature Research Centre (Lithuania): *Aspergillus terreus* Thom 1084-10, *Aureobasidium pullulans* (de Bary & Löwenthal) G. Arnaud 794-12, *Penicillium ochrochloron* Biourge 985-14, *Microascus brevicaulis* S.P. Abbott (= *Scopulariopsis brevicaulis* Bainier) 200-06. Spore suspension of every strain was prepared from well sporulating culture by washing the slant of culture tube with 5 ml of salt solution (0.9% NaCl) and was adjusted to about 1×10^6 spores/ml using a counting chamber. Equal volume of each fungal strain was mixed to obtain a mixed suspension for inoculation. For the experiments in the liquid media, the mixed suspension of 1×10^9 spores/ml was prepared.

Medium preparation. The stock mineral-salt solution was prepared by the following composition: 1000 ml distilled water, $\text{NaNO}_3 - 2$ g, $\text{KH}_2\text{PO}_4 - 0.7$ g, $\text{K}_2\text{HPO}_4 - 0.3$ g, $\text{KCl} - 0.5$ g, $\text{MgSO}_4 \times 7\text{H}_2\text{O} - 0.5$ g, $\text{FeSO}_4 \times 7\text{H}_2\text{O} - 0.01$ g. The medium was sterilized in an autoclave at 120°C for 20 min.

² Spore suspension was prepared by workers from the Nature Research Centre.

1.2.5. Biodegradation and thermolysis experiments.

Experiments in the liquid media. The prepared mineral-salt medium was poured into Erlenmeyer flasks and sterilized. When the media cooled down, 30 sterile plastic samples (150x30 mm size) per flask were placed in the liquid media. 1 ml of mixed fungal suspension was pipetted into each flask. The uninoculated flasks with unsterilized samples of every type with background contamination served as a control. The flask with mineral-salt/glucose medium and the spore suspension served as a fungi growth control.

Soil buried test. Plastic films (150x30 mm size) were incubated in glass desiccators filled with soil. Unsterile plastic films (30 replicate samples) were placed in the soil. Loss of water during incubation was supplemented with distilled water.

For both experiments, the polymeric films remained in the soils or media at $24\pm 1^{\circ}\text{C}$ for 12 months.

Plastic thermolysis. Plastic thermolysis experiments were carried out in 20 ml test-tubes covered with a cap containing a glass tube for gas release. This tube was also used as an air condenser for collecting the liquid thermolysis product into 3 ml eppendorf. The test-tubes and eppendorfs were weighed before and after the experiments with accuracy of 0.00001 g.

2. THE MAIN RESULTS AND DISCUSSION

2.1. Catalyst influence on the thermolysis of various plastics and their products

2.1.1. The influence of catalyst on the liquid thermolysis product and its chemical composition

The chromatographic data of thermolysis (Fig.2.1) shows that the catalyst leads to the formation of C7-C9 hydrocarbons as the main products. The predominant compounds are branched, aromatic, and unsaturated hydrocarbons due to the spatial factors (form selectivity, catalyst pore size and volume, pore concentration). The amount of aromatic increases with increasing the catalyst concentration, and for this reason the octane number of the product is also increased (Scheirs & Kaminsky, 2006). For PS thermolysis (Fig.2.2), the styrene concentration decreases and other aromatic compounds concentration increase with increasing the catalyst concentration. Due to over-cracking, the amount of C7-C9 may decrease and the amount of C5-C6 may increase during the catalytic process. For all raw materials all the main products of the catalytic thermolysis are liquids at room.

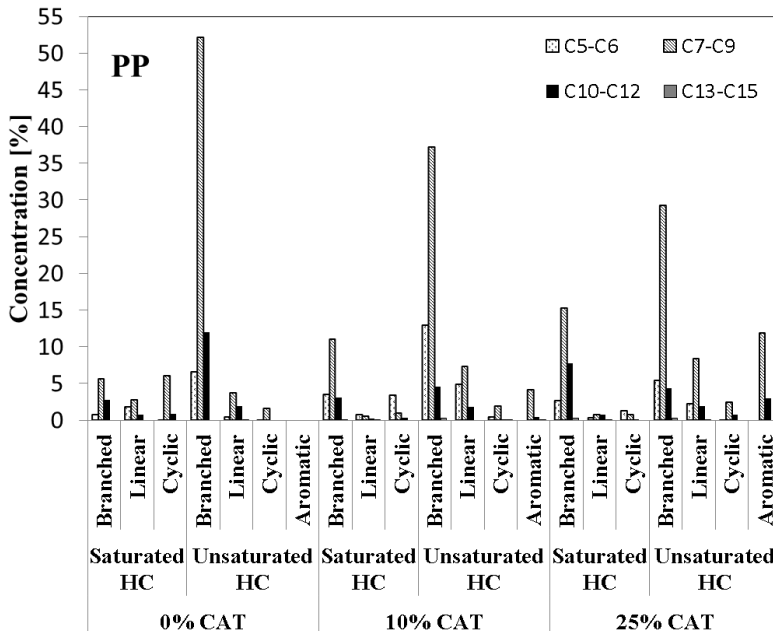


Figure 2.1. Average thermolysis products yields for PP

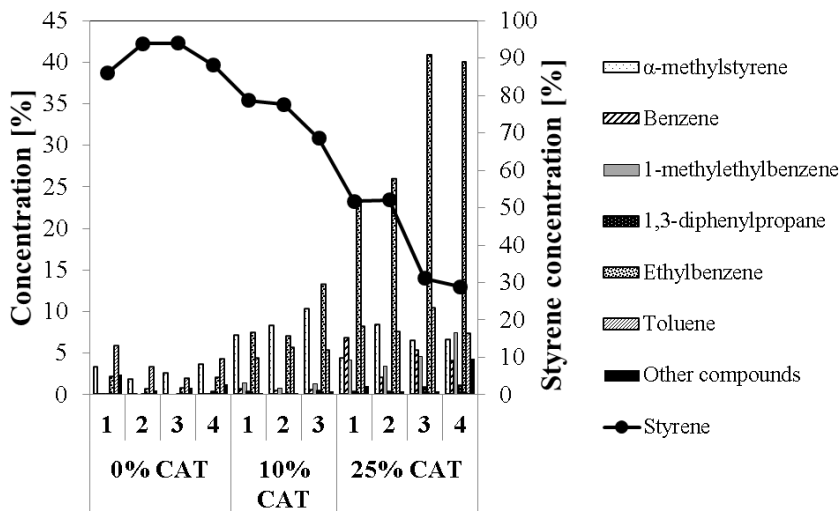


Figure 2.2. Thermolysis products yields for PS

2.1.2. The influence of FCC catalyst on the reaction time and products yields

The catalyst concentration influences the reaction temperature, time and liquid product release temperature, as well as the products yields (Table 2.1). The reaction time for the process and produced gas volumes increase with increasing the catalyst concentration, due to the different thermal conductivity of the mixtures and slower diffusion of the products. Consequently, the primary products stay longer in the reaction zone, resulting in the increasing thermolysis gas production; which impairs a thermal conductivity of the reaction mixture. During the thermolysis process, the reaction temperature may increase-decrease-increase in the reaction zone (Fig. 2.3). For all the reactions, the temperature sometimes decreases; mostly in the temperature range of 350-450°C, due to the energy absorption of the secondary endothermic reactions (alkane cyclization, aromatization reactions).

Table 2.1. The dependence of reaction parameters and product yields of different plastics thermolysis on the catalyst concentration

Feedstock	Catalyst amount, %	Products yields, %			Gas volume, l	Reaction time, min
		Solid	Liquid	Gas		
PS	0	0.56	97.4	2.04	3	135
	10	4.10	92.67	3.231	7	152
	25	10.49	89.44	0.07	26	162
PE	0	0.44	84.07	15.49	24	146
	10	0.40	85.9	13.7	26.5	152
	25	1.52	86.58	11.9	51.5	172
E/P	0	7.36	84.5	8.13	35.5	154
	10	8.15	81.91	9.94	39	177
	25	8.4	70.12	21.48	112.7	210
PP/EPDM	0	7.57	67.45	24.98	35.5	155
	10	8.68	79.95	11.37	37	170
	25	11.28	71.85	16.87	81.5	192
PP	0	4.35	81.76	13.89	18.5	146
	10	3.98	85.08	10.94	37.5	172
	25	5.07	75.95	18.98	74	185

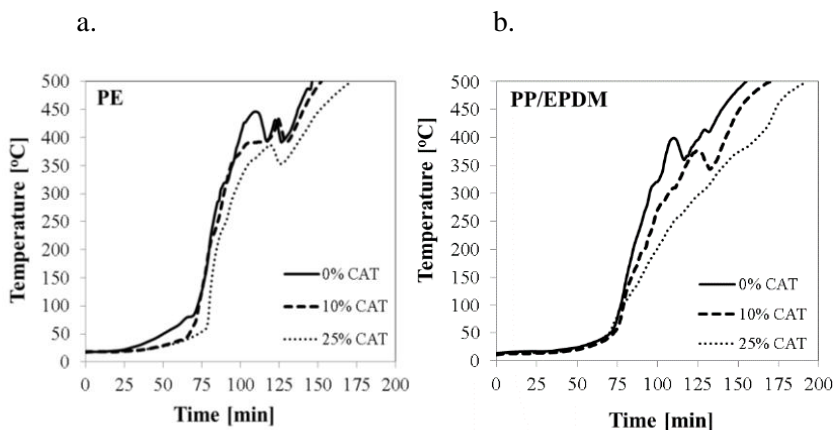


Figure 2.3. Reaction temperature dependence on reaction time for PE (a), PP/EPDM (b)

The yields of solid products increase with increasing catalyst concentration (Table 2.1), due to the coke formation. The exceptions are PP+10% CAT and PE+10% CAT, because the solid product yields are slightly lower than those of the pure feedstocks due to insufficient condensation and the hydrogen transfer reactions needed for coke formation. The liquid thermolysis

products yields increase with increasing catalyst concentration for PE, PP, PP/EPDM, because the branched products have lower boiling points allowing them to escape from the reaction zone faster. Due to over-cracking PP+25% CAT and PP/EPDM+25%CAT do not fulfil the aforementioned tendency. The opposite tendency is determined for E/P and PS liquid product yields, because of over-cracking and coke formation reactions.

The gas yield decreases with increasing catalyst concentration for PE, PP/EPDM, PP and the reverse dependence is determined for PS and E/P. The gas yield decreases is a result of the condensation and coke formation reactions, and the gas amount increase happens due to over-cracking reactions occurring during the process. The gas volume increases with increasing the catalyst concentration, because the low molecular mass compounds are produced when short side chains of the aromatic compounds are dealkylated using acidic catalyst due to the strong acidic properties of the catalyst (López, de Marco, Caballero, Laresgoiti, Adrados, & Aranzabal, 2011). The time of producing the main amount of gases is shortest for the noncatalytic process, which increases with increasing the catalyst concentration. Consequently, the control of catalytic thermolysis process is more flexible and easier compared to the noncatalytic one.

2.1.3. The influence of catalyst to the kinetics and thermodynamics

For all raw materials, the apparent activation energy and the pre-exponential factor decrease with increasing catalyst concentration (Table 2.2). All thermodynamic parameters show similar variations with the catalyst concentration as the kinetic ones. The values of ΔH^\ddagger and of ΔG^\ddagger for all reactions are positive and, therefore all thermolysis reactions are endothermic and non-spontaneous. The absorbed energy from the surroundings decreases with increasing the catalyst concentration. The decreased values of ΔS^\ddagger indicate that a more ordered structure of the system is obtained using the higher catalyst concentrations.

Table 2.2. The dependence of different plastic thermolysis kinetic and thermodynamic reaction parameters on the catalyst concentration

Feedstock	CAT concentration n,%	E_a , kJ/mol	$\ln A$, [A/min ⁻¹]	ΔS^\ddagger , J/(mol K)	ΔH^\ddagger , kJ/mol	ΔG^\ddagger , kJ/mol
E/P	0	187.9	30.4	-7.6	182.1	187.4
	10	167.5	27.4	-32.1	161.9	183.7
	25	106.0	17.2	-116.7	100.7	175.9
PP/EPDM	0	201.0	31.3	-0.4	194.9	195.2
	10	166.6	26.5	-40.1	160.8	188.7
	25	102.8	15.8	-129.0	97.2	183.9
PE	0	204.7	31.9	4.7	198.7	195.3
	10	190.5	30.1	-9.9	184.6	191.6
	25	170.4	27.8	-29.4	164.7	184.9
PS	0	248.9	43.1	98.3	243.4	177.8
	10	214.4	36.2	40.7	208.8	181.3
	25	213.7	36.0	39.2	208.1	181.5
PP	0	251.0	40.6	77.2	245.1	190.3
	10	173.6	29.1	-18.0	168.0	180.0
	25	136.6	23.4	-65.4	131.3	173.1

2.2. Detailed kinetic and thermodynamic analysis of PP thermolysis

2.2.1. Effective activation energy

The values of estimated activation energy for PP and PP+CAT at each conversion are presented in Table 2.3. E_a values decrease with increasing the catalyst concentration at the beginning (when $\alpha=0.1$) and the end of the reaction (when $\alpha=0.9$). E_a significantly increases when conversion is in the range of 0.1-0.3, and later it slightly increases or shows no significant change until the reaction end. The increase in the E_a of thermolysis reactions is caused by a shift of the rate limiting step from initiation to the degradation initiated by a random scission and due to the side reactions, as well as thermal conductivity, the size of volatile compounds, coke formation, limited diffusion and catalyst deactivation.

Table 2.3. The dependence of values of activation energy (kJ/mol) on the conversion and catalyst concentration

α	Actyvation energy (kJ/mol), when CAT concentration, %						
	0	1	3	5	10	25	50
0.1	125.1	120.5	113.1	93.6	91.5	74.7	57.9
0.2	153.7	171.9	133.9	137.8	123.6	98.4	81.0
0.3	158.7	181.0	193.6	151.5	133.5	136.3	131.1
0.4	194.9	179.7	201.3	164.5	132.5	142.4	151.1
0.5	186.5	179.5	206.8	151.5	135.0	147.9	163.9
0.6	187.7	179.1	200.1	163.4	142.6	152.7	171.5
0.7	211.8	204.9	199.0	176.2	151.9	156.4	177.1
0.8	210.8	197.0	199.4	176.5	163.9	161.7	179.4
0.9	207.3	202.7	201.3	178.1	173.7	172.3	170.3

2.2.2. Reaction model

The $g(\alpha)$ function necessary for a complete kinetic description of any solid-state reaction (Khawam & Flanagan, 2006) and its values are presented in Fig. 2.4. The order-based models describe thermolysis reactions most accurately. Reaction orders vary with the conversion because the thermolysis reactions are complex and during the reaction of the catalytic process the random scission mechanism changes from formation of carbenium in to the radical chain scission (when the catalyst is deactivated).

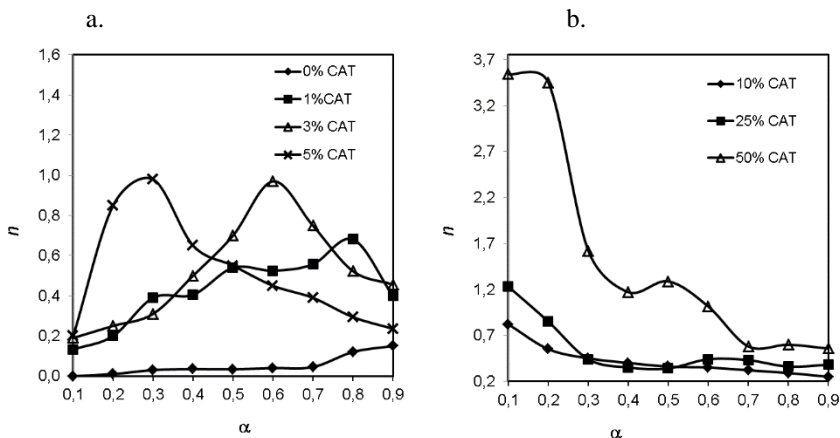


Figure 2.4. Reaction order n dependence on α , when catalyst concentration is 0-5 % (a) and 10-50 % (b)

2.2.3. Pre-exponential factor

The pre-exponential factor shows the frequency of the collisions and the fraction that have the necessary orientation for reaction to occur. The values of $\ln A$ (Table 2.4) decrease with increasing the catalyst concentration when $\alpha = 0.1$. Due to mineral content in the raw material and coke formation reactions the values of $\ln A$ and E_a do not show the same tendencies at the later stages of the decomposition reaction. For PP+CAT mixtures containing 10-50 % catalyst, the values of $\ln A$ increases with decreasing catalyst concentration (when $\alpha \leq 0.2$) and the reverse dependence is valid when $\alpha > 0.2$, because of limited diffusion of products and side reactions.

Table 2.4. The dependence of $\ln A$ (A [s^{-1}]) values on the conversion and catalyst concentration

α	$\ln A$ (A [s^{-1}]) values, when CAT concentration, %						
	0	1	3	5	10	25	50
0.1	14.190	13.530	12.518	9.231	9.161	6.606	4.063
0.2	19.337	22.987	16.474	17.501	15.482	11.442	8.987
0.3	20.226	24.635	27.493	20.119	17.391	19.188	18.813
0.4	26.650	24.445	28.931	22.932	17.212	20.342	22.677
0.5	25.165	24.507	29.999	20.532	17.715	21.383	25.239
0.6	25.352	24.464	28.955	22.685	19.173	22.322	26.670
0.7	29.487	29.155	28.701	25.038	20.919	23.022	27.574
0.8	29.289	27.937	28.642	25.046	23.121	23.982	28.002
0.9	28.619	28.677	28.936	25.293	24.954	25.952	26.197

2.2.4. Thermodynamic parameters

Thermodynamic parameters are related with kinetic ones: the values of ΔS^\ddagger correlate with the values of the pre-exponential factor A , in the same manner as the values of E_a correlate with ΔH^\ddagger , and these changes occur due to the same reasons (Tables 2.5 and 2.6).

Table 2.5. The dependence of ΔH^\ddagger (kJ/mol) values (kJ/mol) on the conversion and catalyst concentration

α	ΔH^\ddagger (kJ/mol) values, when CAT concentration, %						
	0	1	3	5	10	25	50
0.1	119.4	114.9	107.6	88.2	86.2	69.6	53.1
0.2	147.9	166.1	128.2	132.1	118.2	93.1	76.0
0.3	152.8	175.2	187.8	145.8	128.0	131.0	125.8
0.4	189.0	173.8	195.6	158.9	126.9	137.1	145.9
0.5	180.5	173.6	201.0	145.8	129.3	142.5	158.6
0.6	181.7	173.1	194.3	157.6	136.9	147.2	166.2
0.7	205.8	198.9	193.1	170.4	146.2	150.9	171.7
0.8	204.7	191.0	193.4	170.7	158.2	156.2	173.9
0.9	201.2	196.7	195.3	170.7	168.0	166.7	164.8

Table 2.6. The dependence of ΔS^\ddagger values (J/mol·K) on the conversion and catalyst concentration

α	ΔS^\ddagger (kJ/mol) values, when CAT concentration, %						
	0	1	3	5	10	25	50
0.1	-142.1	-147.5	-155.8	-182.9	-183.4	-204.3	-224.9
0.2	-99.5	-69.1	-123.1	-114.5	-131.0	-164.3	-184.4
0.3	-92.2	-55.5	-31.6	-92.8	-115.3	-100.0	-103.0
0.4	-38.9	-57.1	-19.7	-69.4	-116.9	-90.5	-70.9
0.5	-51.3	-56.7	-10.8	-89.4	-112.8	-81.9	-49.7
0.6	-49.8	-57.1	-19.6	-71.6	-100.7	-74.1	-37.9
0.7	-15.4	-18.1	-21.7	-52.0	-86.2	-68.4	-30.4
0.8	-17.1	-28.2	-22.3	-52.0	-67.9	-60.4	-26.9
0.9	-22.8	-22.1	-19.9	-50.0	-52.7	-44.1	-42.0

The change of the Gibbs free energy ΔG^\ddagger shows the total energy increase of the system at the approach of the reagents and the formation of the activated complex. The ΔG^\ddagger values (Fig. 2.5) decrease with increasing concentration of catalyst at each conversion. For every mixture, at the beginning of the reaction (when $\alpha \leq 0.3$) the values of ΔG^\ddagger have an obvious increase due to the change in the rate limiting step of the degradation kinetics. Later ΔG^\ddagger remains practically stable until the end of the reaction.

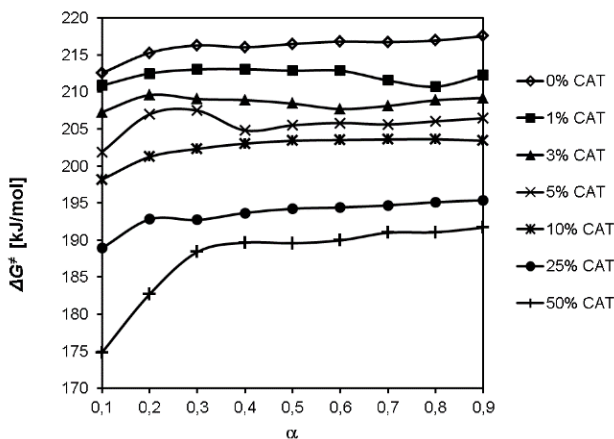


Figure 2.5. The variations of ΔG^\ddagger values versus conversion

2.3.1. Liquid product properties

The calorific value of liquid thermolysis products was determined for each fraction of all raw materials. The average calorific values are 46.2 MJ/kg for PP and PP/EPDM, 45.6 MJ/kg for PE, 45.8 MJ/kg for E/P, and 41.3 MJ/kg for PS. The calorific values do not depend on the fraction and the amount of the

catalyst in the primary mixture, but depends only on the chemical structure of the raw material: aromatic materials have lower calorific value than aliphatic ones.

The kinematic viscosities, the densities and the flash points, pour points increase with increasing the boiling starting temperature (BPST) (Fig. 2.6, Table 2.7). These parameters depend on the raw material, molecular structure and the intermolecular interaction of the liquid product.

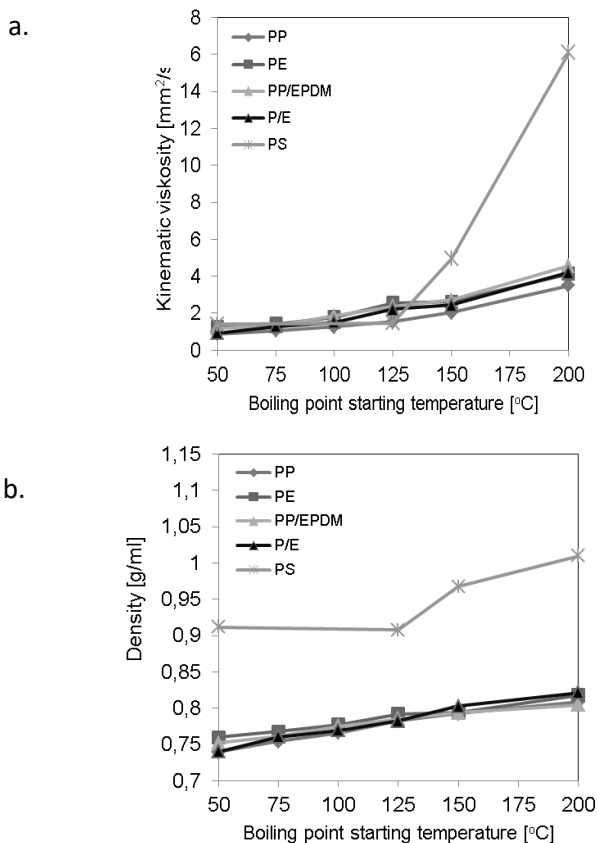


Figure 2.6. Kinematic viscosity and density dependences on BPST

Table 2.7. Flash points and pour points dependence on BPST of the distillate for E/P

CAT concentration, %	BPST, °C	Pour point, °C	Flash point, °C
0	50	-4	23.1
	100	-3	27.2
	150	11	52
	200	17	74
10	50	< -122	<1
	100	-112	18.3
	150	-102	44.3
	200	-82	75.2
25	50	< -122	2.5
	100	-111	28.8
	150	-105	46.1
	200	-92	76

Element concentration. The liquid products were contaminated with P, Ti, Fe, Cu and other elements (Table 2.8). After the liquid product rectification process, the metals concentrations would be reduced.

Table 2.8. Element concentrations in liquid products of noncatalytic thermolysis of PP, PP/EPDM and E/P

Raw material		PP/EPDM			E/P	PP		
BPST, °C		50	100	150	200	50	100	150
Concentration, mg/kg	Ca	14.45	4.41	16.29	201	899	780.4	674
	P	86.83	33.89	38.33	26.35	-	14.92	27.25
	Ti	2.099	0.17	0.021	11.18	612.30	509.0	464.50
	Other*	20.901	16.88	18.232	370.83	133.14	114.48	103.59
	Total:	124.28	55.35	72.87	609.36	1644.4	1418.7	1269.3

* As, Cd, Cr, Cu, Fe, Mg, Mn, Ni, V, Zn

Gasoline and diesel yields are presented in Table 2.9. The yields of gasoline may reach up to 60-70% for nonaromatic feedstocks (for catalytic process with 25% CAT), and for PS; better results are obtained using 10% of catalyst. Due to the large aromatic content, PS may be used only as an octane number booster for gasoline. The highest yields of diesel may be produced during noncatalytic thermolysis of nonaromatic feedstocks. The obtained liquid products of thermolysis have to be chemically stabilized before using them for the final preparation of commercial gasoline and diesel.

Table 2.9. The dependence of gasoline and diesel yields on the catalyst concentration for different raw materials

Catalyst concentration, %	Gasoline yield, %					Diesel yield, %				
	PP/EPDM	PE	PP	E/P	PS	PP/EPDM	PE	PP	E/P	PS
0	45.3	11.3	29.7	42.0	65.4	37.4	49.9	44.5	39.2	28.8
10	51.9	46.7	60.4	58.6	66.7	38.1	28.7	32.1	35.2	23.6
25	69.4	59.0	62.5	71.8	63.4	22.5	28.7	31.3	25.2	22.5

2.3.2. The properties of solid products

Coke yields and ash content. The determined coke yields tend to increase with increasing the catalyst concentration (Table 2.10). The coke formation depends on the polymer structure. The highest values of coke yields are determined for PS and PE thermolysis due to the aromatic precursors and the secondary products polymerization, respectively. The ash content (Table 2.10) increase with increasing the catalyst concentration and depends on the formed coke content.

Table 2.10. The dependence of coke yields and ash content on the catalyst concentration for different raw materials

CAT conc., %	Coke yields, %					Ash content, %				
	PP	PP/EPDM	E/P	PS	PE	PP	PP/EPDM	E/P	PS	PE
0	4.61	95.39	5.64	28.35	21.05	95.39	86.74	94.36	71.65	78.95
10	17.42	82.58	9.80	31.37	53.11	82.58	85.32	90.2	68.63	46.89
25	31.56	68.44	26.85	81.81	99.35	68.44	70.12	73.15	18.19	0.65

Calorific value. The heat values were estimated for these noncatalytic process products: PE – 6.35 MJ/kg, PS – 13.39 MJ/kg, PP/EPDM – 3.54 MJ/kg. Other solid products were incombustible due to high ash content or the poor oxygen diffusion into the catalyst pores.

2.4. Thermolysis technological flowsheet

The recommended plastic thermolysis flowsheet is presented in Fig. 2.7. The whole process is continuous and is applied to 100kg of plastic for 12h at atmospheric pressure. The process should be noncatalytic for diesel production and catalytic for gasoline production. 100kg of shredded plastics and the

appropriate amount of catalyst from tanks (T-2 and T-3) are mixed in mixer (M-1) and processed in a horizontal reactor (R-1). The operating temperature of the reactor is from 25-550 °C using inert N₂ atmosphere. The process gaseous products are separated from solid particles in the cyclone and are cleaned from the solid particles in the cascade of cyclones (CS-1). Following this, they move to the condenser (TK-1), where the diesel fraction (>200 °C) is separated; and the gasoline fraction is separated in the condenser (TK-2). Condensed gasoline and diesel fractions are transported to the hydrogenation device (Fig. 8). The remaining lightest thermolysis gas from the condenser (TK-2) transfer into catalyst regeneration furnace or may be processed. The obtained solid products are removed as the trash (for noncatalytic process) or go into the catalyst regenerator (for catalytic process). The catalyst regeneration may be performed up to 3 times, depending on the raw material contamination. In the regenerator, the catalyst is burned off at atmospheric pressure and after that is mixed with fresh catalyst and can be recycled in the process. The cleaned combustion gas produced during catalyst regeneration is used for the heating of the cyclone (CS-1).

The process may be suspended when the raw material is not supplied, the reactor is cooled by coller A-1, the condensed products are pumped out of the condensers (TK-1/2), the thermolysis gas flows into the gas processing system, and catalyst regenerator is not heated, air supply is stopped and the hot catalyst is cooled down in tank T-2.

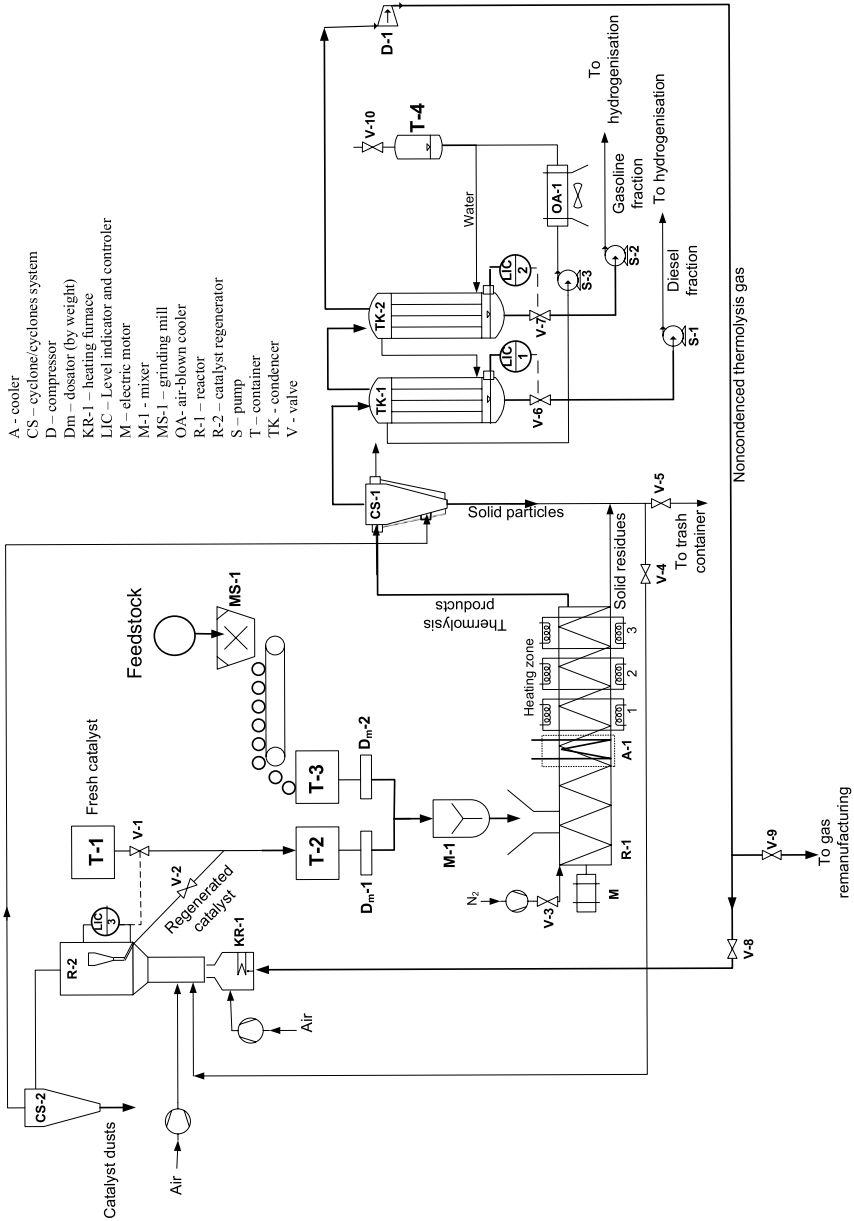


Figure 2.7. Technological flowsheet of thermolysis process

2.5. The influence of anthropogenic treatment to the yields to the thermolysis products

Identified fungi in the soil and liquid media after biodegradation. The fungi isolated from the soil were identified as *Aspergillus fumigatus*, *A. niger*, *Fusarium sp.*, *Leptographium sp.*, *Mortierella sp.*, *Penicillium spp.*, *Trichoderma sp.*, *Verticillium cyclosporium*, *V. tenerum*. In the liquid medium, from all the test-fungi only, *Penicillium ochrochloron* was viable. The liquid medium was also contaminated with fungi of *Penicillium* and *Trichoderma* genus from the surroundings. In the liquid medium, with background contamination the predominant genus of fungi, was *Penicillium sp.*, such as *P. ochrochloron*. These results show that only *P. ochrochloron* from all test-fungi is able to take part in degradation of polyolefins directly during the experimental conditions.

The yields of thermolysis products. Before the experiment, the liquid products yields of PS and PE are highest for the control samples (Table 2.11) and the lowest yields for UV samples, however, for the solid and gaseous products yields the backwards dependence was determined. For PP, the highest liquid and solid products yields were obtained for PP-C, and the lowest yields for PP-T, but the highest and lowest yields of gaseous product were determined for PP-UV and PP-T, respectively. After biodegradation the products yields change due to changes in the crystallinity, branching and density of the plastic samples and due to the random scission mechanism of plastic degradation. In addition, the yields also depend on the molecular structure of the feedstock and the biodegradation conditions. The highest liquid product yields were determined for all UV treated samples and for PP-C and PE-T after the soil buried test. However, for PS-T the best results were obtained after the experiment in the liquid medium with test-fungi. For PP-T, PE-C and PS-C, the liquid product yields were reduced after biodegradation. The solid product yields were mostly increased after biodegradation in the liquid medium with background contamination for all thermal treated samples and PS-C, and with test-fungi for PE-C. The biodegradation in soil increased solid product yields for PE-UV and PS-UV. Solid products yields decreased due to biodegradation for PP-C and PP-UV. The gas yields were increased for all samples after biodegradation and the best conditions were: in liquid medium with background contamination for PP-C, PE-T and PS-UV; in liquid medium with test-fungi for PP-T, PP-UV and PE-UV; in soil for PE-C, PS-C and PS-T.

Table 2.11. The dependence of different plastic foils thermolysis products yields on the anthropogenic treatment conditions

Sample	Experimental conditions	Products Yields, %		
		Liquid	Gas	Solid
PP-C	-*	26.94	48.12	24.94
	Control	23.70	56.96	19.34
	Suspension	38.97	41.46	19.57
	Soil	42.41	47.13	10.46
PP-T	-	43.46	43.10	13.43
	Control	29.07	56.73	14.20
	Suspension	21.11	66.33	12.55
	Soil	24.83	60.87	14.30
PP-UV	-	27.58	54.01	18.41
	Control	25.44	59.36	15.21
	Suspension	27.98	66.53	5.49
	Soil	36.27	56.08	7.65
PE-C	-	79.93	11.30	8.77
	Control	79.68	11.01	9.31
	Suspension	69.31	12.94	17.75
	Soil	60.32	24.65	15.03
PE-T	-	74.11	17.40	8.49
	Control	59.71	24.13	16.16
	Suspension	73.42	20.26	6.33
	Soil	84.18	0.97	14.85
PE-UV	-	68.02	22.34	9.64
	Control	70.97	19.02	10.00
	Suspension	61.07	22.73	16.19
	Soil	71.57	12.18	16.25
PS-C	-	84.51	7.52	7.97
	Control	68.01	15.84	16.15
	Suspension	73.92	16.05	10.03
	Soil	69.01	16.66	14.33
PS-T	-	58.76	20.74	20.50
	Control	59.20	18.66	22.13
	Suspension	68.47	17.25	14.28
	Soil	46.04	44.42	9.54
PS-UV	-	15.22	50.15	34.63
	Control	15.31	58.63	26.06
	Suspension	16.85	48.05	35.10
	Soil	28.94	28.71	42.35

* Before experiment.

In conclusion, the highest yields of liquid thermolysis products are obtained, when PE is thermally aged and treated with fungi in soil, PP is only aged thermally, and for PS it was determined that antropogenic treatment reduces the main product yield.

CONCLUSIONS

1. In the fixed-bed reactor, the use of catalyst prolongs the time of the process but reduces the liquid product release. The yields of solid products increase with increasing the catalyst NaceRTM concentration, and the yields of liquid and gaseous products yields also depends on the chemical composition of the raw materials. The main (liquid) products yields increase with increasing the catalyst concentration for PE, PP/EPDM and PP thermolysis, and the dominant compounds obtained are branched C7-C9 hydrocarbons. The obtained liquid products are with impurities of other element compounds (Mg, Zn, Fe, Mn, and other).
2. Thermolysis reactions are complex ones. During catalytic thermolysis the degradation reactions occur via radical and ionic mechanisms. At the constant conversion, during the initial stage of the reaction the kinetic and thermodynamic parameters decrease with increasing the catalyst concentration, and their values vary with conversion.
3. The physical and chemical properties of thermolysis liquid products depends on the chemical nature of the raw material. The liquid products properties (viscosity, density, flash point and pour point) can be changed by removing the lower boiling point compounds. The determined liquid products calorific values are similar to petroleum products. The calorific values of solid thermolysis products are rather low (up to 13.39 kJ/mol) and depend on the produced coke amount.
4. For nonaromatic plastics, the highest gasoline cut yield (up to 72 %) is obtained during catalytic thermolysis with 25% of catalyst, and the highest diesel cut yields (up to 50 %) are obtained during the noncatalytic thermolysis process.
5. The principal plastic thermolysis flowsheet was proposed. In this flowsheet, the separation of liquid thermolysis products into gasoline and diesel cuts, and the catalyst regeneration using thermolysis gas were predicted.
6. The products yields of thermolysis of antropogenically treated materials depend on the chemical nature of raw material and the condition of anthropogenic treatment. Abiotic treatment (thermally or with ultraviolet radiation) decreased the yields of thermolysis liquid product. Only for PE, biochemical degradation using fungi in soil increased the yields of liquid (wax) thermolysis products.

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LIST OF PUBLICATIONS

Articles in journals from Thomson Reuters “Web of Knowledge” list:

1. VALANČIENĖ, E., MIKNIUS, L., PEDIŠIUS, N. The influence of zeolite catalyst on kinetics and thermodynamics of polypropylene waste thermal degradation (doi:10.1007/s10973-015-5150-7) // Journal of Thermal Analysis and Calorimetry. ISSN 1388-6150. 2016. Vol. 124. Iss. 1. p. 341-354.
2. VALANČIENĖ E., MIKNIUS L., MARTYNAITIS V., STRIŪGAS N. Influence of equilibrium fluid catalytic cracking catalyst amount on the thermolysis process of various polyolefin plastic wastes in a fixed-bed reactor for gasoline and diesel production (<http://pubs.acs.org/doi/10.1021/acs.energyfuels.7b01472>) // Energy Fuels. ISSN 0887-0624. Vol. 31 (10). 2017. p. 11194-11210.

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1. VALANČIENĖ, E., MIKNIUS, L., PEDIŠIUS, N. (2015). The influence of zeolite catalyst on polypropylene waste thermal decomposition kinetics and thermodynamics.//Chemistry and Chemical Technology 2015 : Programme and Proceedings of the International Conference, Vilnius, Lithuania, January 23, 2015, 347-349. ISBN: 9786094594618.
2. VALANČIENĖ, E., MIKNIUS, L., PEDIŠIUS, N., MARTYNAITIS, V. (2016). The influence of zeolite catalyst on kinetics and thermodynamics of various plastic waste thermolysis.//Chemistry and Chemical Technology : International Conference of Lithuanian Society of Chemistry, Lithuanian Academy of Science, Vilnius, Lithuania, April 28-29, 2016 : Book of Abstracts, 139. ISBN: 9786099551135.

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REZIUOMĖ

Temos aktualumas

Dėl kasmet augančios įvairių prekių / produktų paklausos didėja įvairiausių gaminamų prekių kiekis bei trumpėja vartojamų produktų eksploatacijos trukmė, susidaro vis daugiau atliekų, kurias būtina sutvarkyti taip, kad jos nebūtų kaupiamos sąvartynuose. Poliolefinai atmosferinėmis sąlygomis yra beveik neskylandčios medžiagos, kurios gali būti panaudotos kaip alternatyva neatsinaujinantiems energijos šaltiniams.

Kasmet pasaulyje susikaupia daugiau nei 6300 mln. tonų plastiko atliekų, iš kurių apie 80 % patenka į sąvartynus arba aplinką. Pasaulyje jūros ir vandenynai daugiausiai patiria žalos dėl šių atliekų, nes plastikų gamybai naudojamos medžiagos patenka į mitybos grandinę – pirmiausia žuvis praryja plastikų gabaliukus, arba juos mitusius vandens gyvūnus, o vėliau, pagautos žmonių, naudojamos kaip žmonių maistas. Galima sakyti, kad per mitybos grandinę į žmonių organizmą taip pat patenka tam tikras kiekis šių teršalų. Be to, nemaža dalis plastiko atliekų iš vandenynų (jūrų) yra išskalaujama į pakrantes, kurios padengia storu šiukšlių sluoksniu paplūdimius. Paminėtina tai, kad jos taip pat gali mechaniškai sugadinti laivus. Vandenyneose palaidotos atliekos iki 80–95 % yra plastikai. Nors pastaruoju metu siekiama perdirbti iki 85 % tokio plastiko atliekų, tačiau reikia nepamiršti, kad tos pačios medžiagos perdirbimas gali būti atliktas tik 2–3 kartus, todėl toliau tokios atliekos gali būti perdirbamos

tik cheminiu būdu. Vienas iš pažangiausių būdų, kurio metu netinkamos perdirbti poliolefinų atliekos gali būti konvertuotos į skystąjį kurą arba į žaliavas, ir skirtas siekiant sumažinti kietųjų atliekų tūrį – yra termolizė. Priklausomai nuo gauto termolizės skystojo produkto sudėties, jis gali būti naudojamas kaip įvairios paskirties degalai arba kaip priedas degalų gamyboje. Termolizės proceso metu gautas kuras pasižymi dideliu šilumingumu (~45 MJ/kg). Termolizė taip pat svarbi anglies nanovamzdelių gamyboje. Katalizatoriaus naudojimas termolizėje leidžia reakcijas vykdyti žemesnėje temperatūroje, gauti didesnę tikslinio produkto išeigą siekiant geriau kontroliuoti jo kiekybinę bei kokybinę sudėtį, gauto produkto mažesnę užterštumą. Gautų produktų sudėtis taip pat priklauso ir nuo pradinės žaliavos cheminės prigimties, naudojamos aparatūros bei procesų sąlygų. Norint gauti geriausias tikslinio produkto išeigas, reikia eksperimentiškai nustatyti tinkamiausias sąlygas kiekvieno tipo reaktoriui ir turimoms medžiagoms.

Šiuo metu daug dėmesio yra skiriama ir biocheminiam poliolefinų suskaidymui, kaip vienam iš švaresnių poliolefinų perdirbimo būdų. Mažesnės molekulinės masės polipropileno bei polietileno plėvelės gali skaidyti aplinkoje esantys mikroorganizmai. Kadangi bioskaidymui yra svarbu, kad polimerų makromolekulės turėtų heteroatomų, todėl yra gaminami bioskaidūs poliolefinai, kuriuose, į polimero makromolekulę kas tam tikrą grandžių skaičių yra prijungiamos karbonilgrupės, dėl kurių pagerėja plastikų bioskaidumas, beveik nepakinta mechaninės savybės, tačiau sumažėja tokių produktų naudojimo laikas. Poliolefinų atliekų bioskaidumas taip pat gali būti pagerinamas, kai jos yra oksiduojamos termiškai, UV spinduliuote, veikiant rūgštimis arba aplinkos klimato sąlygomis ilgesnį laiką. Tokio antropogeninio apdorojimo metu kinta plastiko atliekų dydžiai / storai, molekulinė masė, sudėtis, todėl termolizės proceso metu šių žaliavų produktų sudėtis ir išeigos taip pat pakinta.

Vienas pagrindinių termolizės trūkumų yra proceso metu tikslaus norimos cheminės sudėties produkto gavimas, nes vis dar trūksta išsamių tyrimų apie pagrindinių termolizės reakcijų vyksmą bei jų optimizavimą.

Šio **darbo tikslas** – ištirti poliolefinų atliekų termolizės procesą bei nustatyti antropogeninio apdorojimo įtaką termolizės produktų išeigai.

Darbo tikslui pasiekti suformuluoti šie **uždaviniai**:

1. nustatyti katalizatoriaus koncentracijos įtaką termolizės produktų išeigai, proceso parametrus, skirtingų žaliavų skystųjų produktų komponentinei sudėčiai;
2. nustatyti katalizatoriaus koncentracijos įtaką terminio skilimo reakcijų kinetiniams bei termodinaminiams parametrus, panaudojant termogravimetrinės analizės domenį;
3. nustatyti kietųjų ir skystųjų termolizės produktų fizikines ir chemines savybes;

4. nustatyti optimalią plastikų ir katalizatoriaus mišinių sudėtį didesnei benzino ir dyzelino išeigai gauti;
5. pasiūlyti principinę technologinę schemą, tinkamą katalizinei ir nekatalizinei termolizei;
6. ištirti polimerinių plėvelių antropogeninio poveikio įtaką termolizės produktų išeigoms.

Darbo mokslinis naujumas

Išsamiai ištirta katalizatoriaus ir jo kiekio įtaka įvairių polimerinių žaliavų termolizės proceso kinetiniams ir termodinaminiams parametrams, produktų išeigoms bei savybėms. Nustatyta polimerinių plėvelių antropogeninio apdoravimo įtaka termolizės produktų išeigoms.

Darbo praktinė vertė

Nustatyta optimali aromatinių ir nearomatinių plastikų ir katalizatoriaus mišinio sudėtis, leidžianti gauti didžiausią skystojo produkto išeigą. Nustatyta, kad katalizinis procesas tinkamesnis benzinui gaminti, o nekatalizinis – dyzelinui gaminti. Pasiūlytas nuolatinio veikimo plastikų termolizės technologinis procesas, kurio metu būtų galima išskirstyti skystąjį produktą į benzino bei dyzelino frakcijas, o termolizės dujas perdirbti bei deginti katalizatoriaus regeneratoriaus krosnyje.

Pagrindiniai ginamieji disertacijos teiginiai

1. Plastikų termolizės procesas yra kompleksinis, jo termodinaminiai ir kinetiniai parametrai bei reakcijos mechanizmas priklauso nuo medžiagų prigimties bei katalizatoriaus kiekio reakcijos mišinyje.
2. Katalizinės termolizės metu gaunama didesnė benzino frakcijos išeiga, o nekatalizinio proceso metu – didesnė dyzelino.
3. Skystojo termolizės produkto fizikinės ir cheminės savybės priklauso nuo pradinės žaliavos cheminės sudėties bei mišinio virimo pradžios temperatūros.
4. Antropogeniškai veiktų plastikų termolizės produktų išeigos priklauso nuo antropogeninio apdoravimo sąlygų ir pradinių žaliavų sudėties.

IŠVADOS

1. Nejudančio sluoksnio reaktoriuje katalizatorius pailgina proceso trukmę, bet sumažina skystojo produkto ištekėjimo temperatūrą. Didėjant balansinio katalizatoriaus NaceRTM koncentracijai kietųjų produktų išeiga didėja, o skystosios ir dujinės frakcijos išeiga priklauso ir nuo naudoto plastiko. Didėjant katalizatoriaus koncentracijai PE, PP/EPDM ir PP termolizės metu pagrindinio (skystojo) produkto išeiga didėja, o pagrindinę jos dalį sudaro

šakotos struktūros C7–C9 angliavandeniliai. Be to, skystajame produkte yra kitų cheminių elementų (Mg, Zn, Fe, Mn ir kt.) junginių priemaišų.

2. Termolizės reakcijos yra kompleksinės. Katalizinio proceso metu skilimo reakcijos vyksta pagal karbkatijoninę bei radikalinę mechanizmą. Esant vienodai konversijos vertei, didėjant katalizatoriaus koncentracijai, reakcijos pradžioje kinetinių bei termodinaminių parametru vertės mažėja bei kinta, keičiantis konversijos laipsniui.

3. Termolizės skystųjų produktų fizikinės ir cheminės savybės priklauso nuo žaliavos prigimties. Skystųjų produktų savybes (klampą, tankį, pliūpsnio ir stingimo temperatūrą) galima pakeisti pašalinant mažesnės virimo temperatūros junginius. Nustatytos skystųjų produktų šilumingumo vertės yra panašios į naftos produktų. Kietųjų produktų šilumingumo vertės yra palyginti mažos (iki 13,39 MJ/kg) ir priklauso nuo susidariusio kokso ir suodžių kiekio.

4. Didžiausia benzino frakcijos išeiga (iki 72 %) gaunama nearomatinių plastikų katalizinės termolizės, naudojant 25 % konc. katalizatoriaus, metu, o dyzelino frakcijos (iki 50 %) – nekatalizinės termolizės metu.

5. Pasiūlyta plastikų termolizės technologinė schema, kurioje numatytas skystųjų termolizės produktų išskirstymas į nestabilizuotas dyzelino ir benzino frakcijas, katalizatoriaus regeneravimas panaudojant termolizės dujas.

6. Antropogeniškai skaidytų žaliavų termolizės produktų išeigos priklauso nuo naudotos žaliavos cheminės prigimties bei antropogeninio apdorojimo sąlygų. Abiotinis apdorojimas (terminis arba ultravioletiniais spinduliais) sumažino skystojo produkto išeigą. Biocheminis skaidymas mikromicetais dirvožemyje padidino tik termiškai sendinto polietileno skystųjų termolizės produktų (vaško) išeigą.

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