



Plastic Pyrolysis Using Montmorillonite-Based Catalysts

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Abstract

Waste plastic disposal and excessive use of fossil fuels have caused environment concerns in the world. Both plastics- and petroleum-derived fuels are hydrocarbons that contain the elements of carbon and hydrogen. The difference between them is that plastic molecules have longer carbon chains than those in LPG, petrol, and diesel fuels. Therefore, it is possible to convert waste plastic into fuels.

The main objectives of this study were to check in the processes of plastic pyrolysis the effectiveness of montmorillonite-based family of catalysts differently modified. The investigated catalysts were divided into three groups depending on their preparation path. The first part contains results for all catalysts tested. The catalytic degradation of polyethylene, which is the most common plastic found in waste and presents the simplest structure of all plastic materials, was analyzed using thermogravimetry (TG) and differential scanning calorimetry (DSC) methods under a nitrogen atmosphere. In the second part of this work three catalysts showing best results were tested with four different types of waste plastics.

The best results for PE degradation were obtained for montmorillonites used as supports for cations. They were also effective for the residual plastic waste pyrolysis, but to a lower extent.

KEYWORDS: Polyethylene, montmorillonite, catalytic degradation, differential scanning calorimetry (DSC), thermogravimetry (TG), plastics, pyrolysis.

NOMENCLATURE

PP – Polypropylene

PE – Polyethylene

PVC – Polyvinylchloride

PS – Polystyrene

PA – Polyamide

PMMA – Polymethyl methacrylate

ABS – Acrylonitrile Butadiene Styrene copolymer

SAN – Styrene Acrylonitrile copolymer

PET - Polyethylene Terephthalate

MSW - Municipal Solid Waste

LPG – Liquid Petroleum Gas

DSC - Differential Scanning Calorimetry

MMT – montmorillonite

CEC – cation exchange capacity

TA - Thermal Analysis

TG – Thermogravimetry

TGA - Thermogravimetric Analysis

DTG - Derivative thermogravimetry

TPD – temperature programmed desorption

S_{ext} - External surface area

E_j – energy activation in the ammonia desorption process

K_{Ei} – pre-exponential factor in acidity measurement

α, β – parameters depending on the structure of the catalyst

ΔrH – enthalpy of reaction

E_a – activation energy barrier

Υ_p – correction factor

K_0 – pre-exponential factor

q_{0i} – amount of acid sites

m_0 - Initial mass

X - ratio between the solid weight loss at a given time and the initial solid weigh

X_{max} - Maximum conversion that can be achieved

$T_{degrad.}$ - Degradation temperature

R - Universal gas constant = 0.008314 kJ (mol⁻¹K⁻¹).

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1.Introduction

Waste plastic disposal and excessive use of fossil fuels have caused environment and economical concerns in the world. USA, Europe and Japan generate about 50 million tons of post-consumer plastic waste material per year [1]. Due to the convenience to manufacturing and use, the world plastic production has been increasing since it was first commercially manufactured. One of the major concerns for the extensive use of the plastics is the disposal of the waste plastic. In addition, the plastics mostly produced from non-sustainable oil or coal, and thus they are non-sustainable products. Secondary utilization option for plastic wastes – recycling, which is reprocessing plastics into new, lower quality products, shows signs of steady growth in the recycling industry. Unfortunately, this method is not enough on its own to solve the global problem of high wastes production.

Europe consumes about 25% of the global plastic production, which is equivalent to 60 million tons per year and, to account for the growing production and consumption, tertiary recycling needs to be developed. Tertiary recycling includes all these methods of processing which attempt to convert the plastic wastes to basic chemicals by the use of chemical reactions. This returns plastics to their constituent monomers, which can be reused, or to high-value hydrocarbon feed stock and fuel oil that can be used in the petrochemical industry of as fuels.

Pyrolysis and catalytic conversion of plastic is a superior method of reusing the waste. Additionally, the distillate product is a fuel which makes the process economically feasible and environmentally friendly due to the overall lower consumption of fossil fuels. Furthermore, significantly lower net costs of waste disposal can be obtained with simultaneous increase of reused wastes [2].

In this study there are two major objectives. The first objective is to study the catalytic pyrolysis process of polyethylene, as a potential representative material of waste plastics, and as its major component. The second objective is to assess the influence of different types of montmorillonite-based catalysts on the waste plastic degradation.

The first part of the research is devoted to checking the physicochemical properties of substances that are able to speed up the reaction.

In the second part of this work, possible types of catalysts suitable to improve degradation of plastics were studied, with an emphasis on their effect on the pyrolysis temperature.

Catalytic degradation of waste polymers led to hydrocarbons production that can be used as blending components in fuels.

1.1 Polymers

Polymers are long-chain molecules composed of a large number of identical units called repeating units. The number of repeating units must be large enough that no variations in the polymer macroscopic properties occur by small changes in the number of repeating units [6].

Plastics are manufactured from monomers, i.e. a repeatable molecular unit and building block, by means of various chemical processes, such as:

- a catalytic or peroxide-initiated polymerization of monomer(s), e.g. ethylene, propylene, or butadiene + styrene (copolymers);
- a polycondensation of dissimilar monomers (e.g. bifunctional organic acids and alcohols or amines);
- polyaddition of reactive monomer molecules.

Especially the plastics from the the first group forms an attractive feedstock for pyrolysis processes. Important monomers are polymerization grade ethylene, propylene, butadiene, the three products obtained by thermal cracking or pyrolysis of e.g. naphtha, light gas-oil, or liquefied petroleum gases (LPG = propane or butane) and which are usually purified by low-temperature, high-pressure distillation, up to polymerization grade chemicals.

Before its conversion into plastic products, the resulting resin is almost always compounded with various additives of different nature and constitution, meant to improve processing, stability, or mechanical specifications as a function of a given application:

- antioxidants (1%),
- heat and light stabilizers (5%),
- plasticizers (40%),
- impact resistance enhancers (10%),
- pigments, colorants and dyestuffs (5%),

- flame retardants (15%),
- mould-release agents,
- foaming agents (2%),
- fillers (40%).

Their presence, as well as that of the chemicals used in initiating or terminating polymerization, is a complicating factor in feedstock recycling, also termed chemical recycling, since their nature, amount, and behavior during pyrolysis (thermal volatilization or breakdown) and eventual influence upon reaction products and mechanism are somewhat unpredictable, especially for waste plastics of unknown origin and formulation [23].

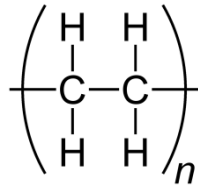
Polymeric materials can be classified in a variety of ways. First, polymers are often classified, based on their origin, as natural and synthetic. However, classification based on physical properties is more useful, in particular the elastic modulus and the degree of elongation. Following this criterion, polymers can be classified into elastomers, plastics and fibers. Elastomers (or rubbers) are characterized by a long range extensibility that is almost completely reversible at room temperature. Plastics have only partially reversible deformability, while fibers have very high tensile strength but low extensibility.

Plastics can be further subdivided into thermoplastics (whose deformation at elevated temperatures is reversible) and thermosets (which undergo irreversible changes when heated).

From a commercial point of view, the most important thermoplastics are high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC), polyethylene terephthalate (PET), polyamide (PA), polymethyl methacrylate (PMMA), acrylonitrile-butadiene-styrene copolymer (ABS), and styrene-acrylonitrile copolymer (SAN).

Polymers can also be classified in terms of their chemical composition. This gives a very important indication as to their reactivity, including their preferential mechanism of thermal decomposition and their fire performance. The main carbonaceous polymers with no heteroatoms are polyolefins, polydienes and aromatic hydrocarbon polymers (typically styrene-based). The main polyolefins are thermoplastics: polyethylene and polypropylene, which are the two of the three most widely used synthetic polymers [3].

a)



b)

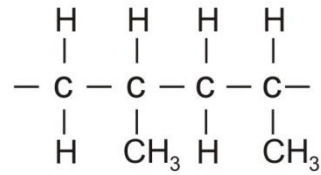


Fig. 1 Structure of a) polyethylene and b) polypropylene

At world level, polyethylene (PE) has the highest share of total production of any other polymer type as presented in the Figure 2. It is followed by polyethylene terephthalate (PET), which accounts for 20% of thermoplastic resin capacity. Polypropylene (PP) accounts for 18%, followed by polyvinyl chloride (PVC) and polystyrene/expanded polystyrene (PS/EPS).

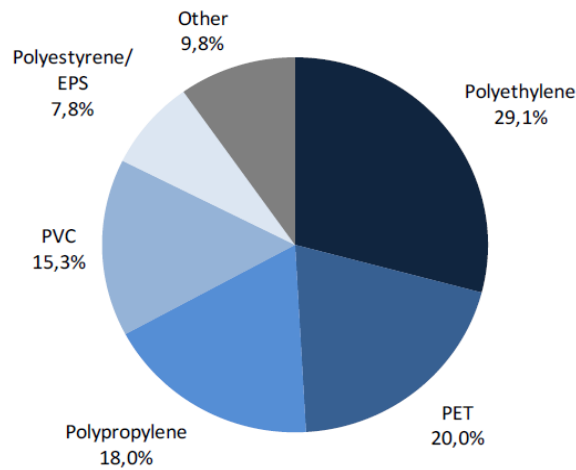


Fig.2 World thermoplastic resin capacity in 2008 by PlasticEurope report [7].

1.1.1 Plastics consumption

Today, plastics are very important materials having widespread use in the manufacture of a variety of products including packaging, textiles, floor coverings, pipes, foams, cars and furniture components. Engineering plastics, particularly thermosets, are also used in composite materials [6]. Plastics make a real contribution to meeting resource efficiency targets in many areas, both in their consumer lifetime, including those for zero-energy buildings, water saving, sustainable land use, extended shelf-life for products, and in the post-consumer phase, such as diversified raw materials, waste as a resource, greener mobility and renewable energies [7].

It is clear that, today, plastic materials are used in almost all areas of daily life. Due to their light-weight, durability, energy efficiency, coupled with a faster rate of production and design flexibility, these plastics are employed in entire gamut of industrial and domestic areas.

The average annual rate of growth in plastic consumption of 8.1% that brought all solid polymers from 7 million tons in the world in 1960 to 196 million tons in 2005, is expected to continue, reaching over 365 million tons in 2015 and leading to, using a more conservative annual increase rate of 6.5 %, 540 million tons of plastic consumption in 2020 [7].

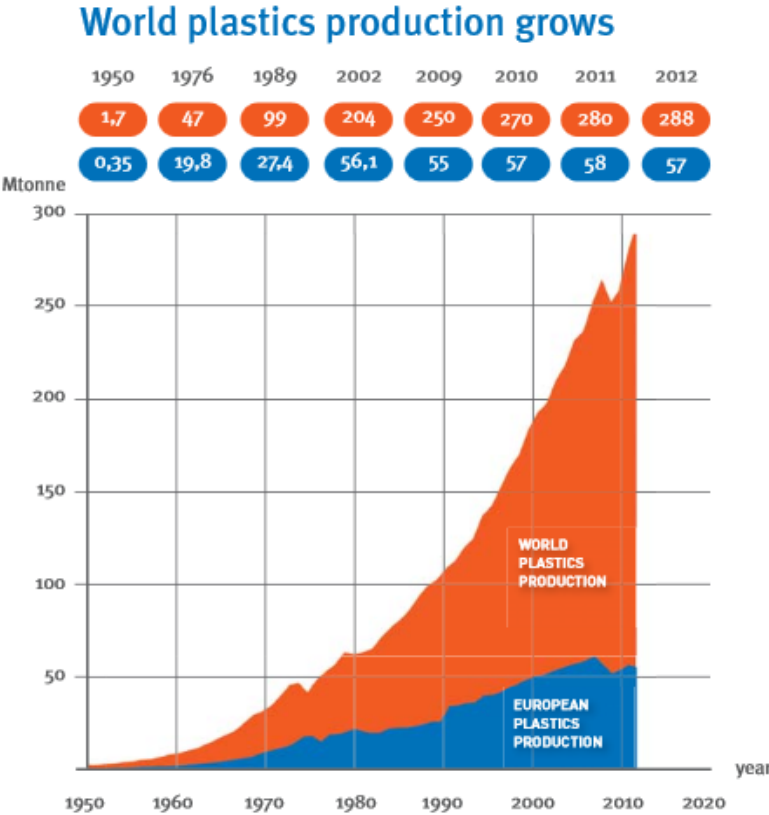


Fig.3 World plastics production over the years 1950-2012 [7].

This phenomenon indicates that an almost double increase is needed in the recycling market of plastics. Europe produced one fifth of the total world production of plastics in the last few years, which can be potentially the biggest market the reprocessing of plastic wastes, as suggested by Figure 4.

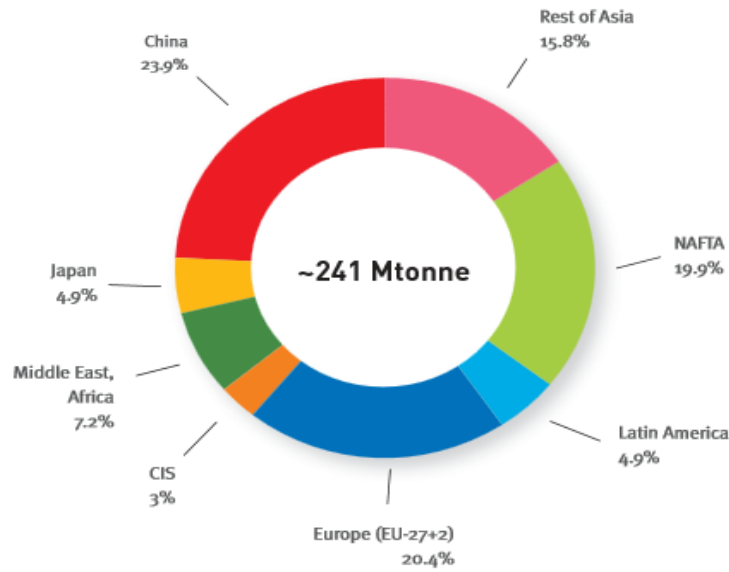


Fig.4 World plastics materials production 2012 by region [32].

Noteworthy is the fact that an average person in Western Europe consumes 136 kg of plastics per year, which shows the second highest consumption in the world right after North American countries, as shown in the Figure 5.

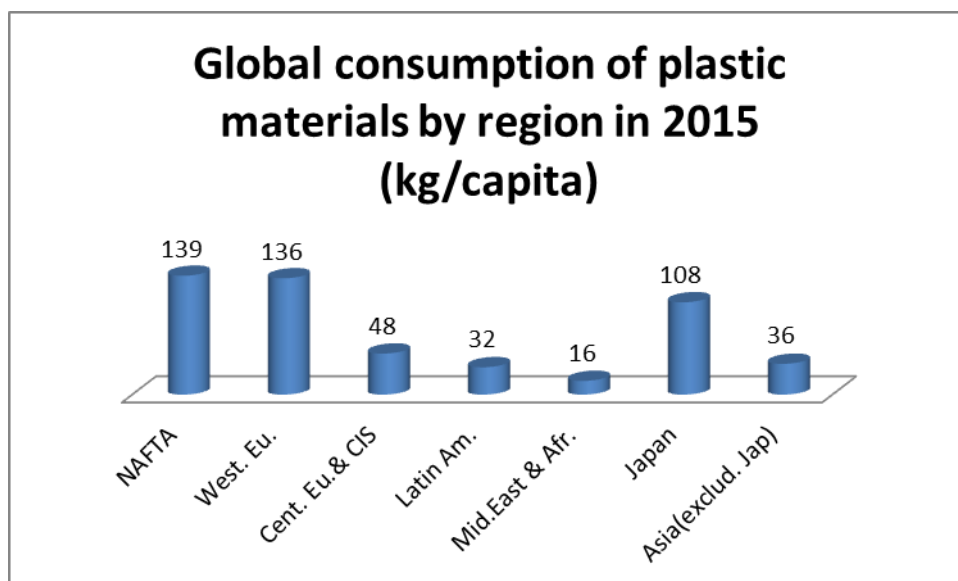


Fig. 5 Global consumption of plastic materials by region in 2015 (kg/capita).

1.1.2 The economic and environmental impact of plastic wastes

From an economic point of view, used plastic can be considered as both an important source of valuable chemicals, mainly hydrocarbons, and an energy source. The calorific value of most plastics is

similar to that of fuel oils and higher than that of coals. Plastic wastes can therefore be viewed as potential fuels, when other alternatives of valorization are not possible.

Plastic wastes represent a significant environmental impact when sent to landfills due to the following facts:

- resistance to degradation, plastic materials exist for a long time when disposed of in landfills
- the influence of a variety of additives such as fillers, stabilizers, plasticizers, reinforcing agents, colorants
- as a consequence of their low density, plastics cause a greater visual impact on disposal than many other materials
- complex and costly separation steps are required to produce used plastic streams of relatively high purity.

The first step in dealing with plastic waste is recycling, which already occurs on global scale. Extensive recycling and reprocessing of plastics are performed on homogeneous and relatively contaminant free plastic wastes. Most recycling schemes require a feedstock that is reasonably pure and contains only items made from a single polymer type. Mentioned requirement may not always be fulfilled which is why it has given an opportunity to develop alternative techniques called chemical or feedstock recycling. This term has been used to describe a variety of thermal processing approaches, including pyrolysis and gasification. Pyrolysis of waste plastic seems to be one of the most promising emerging technologies that may prove to be an economical method to solve non-recyclable waste plastic problem and to produce quality liquid fuel which can have similar properties to the commonly used petroleum fuels.

It is noteworthy, however, that the management of plastic wastes cannot be treated as an individual problem; it must be considered as an integral part of the global waste management system, as presented in the Figure 6.

The scheme below illustrates that various different types of feedstock recycling that exist. It shows the material chain for these and other recycling routes, in relation to some relevant input criteria for each route.

Aguado and Serrano survey [6] confirms that the solution to the problem of plastic wastes should be based on an integrated approach through the application of mechanical recycling, feedstock recycling and energy recovery processes.

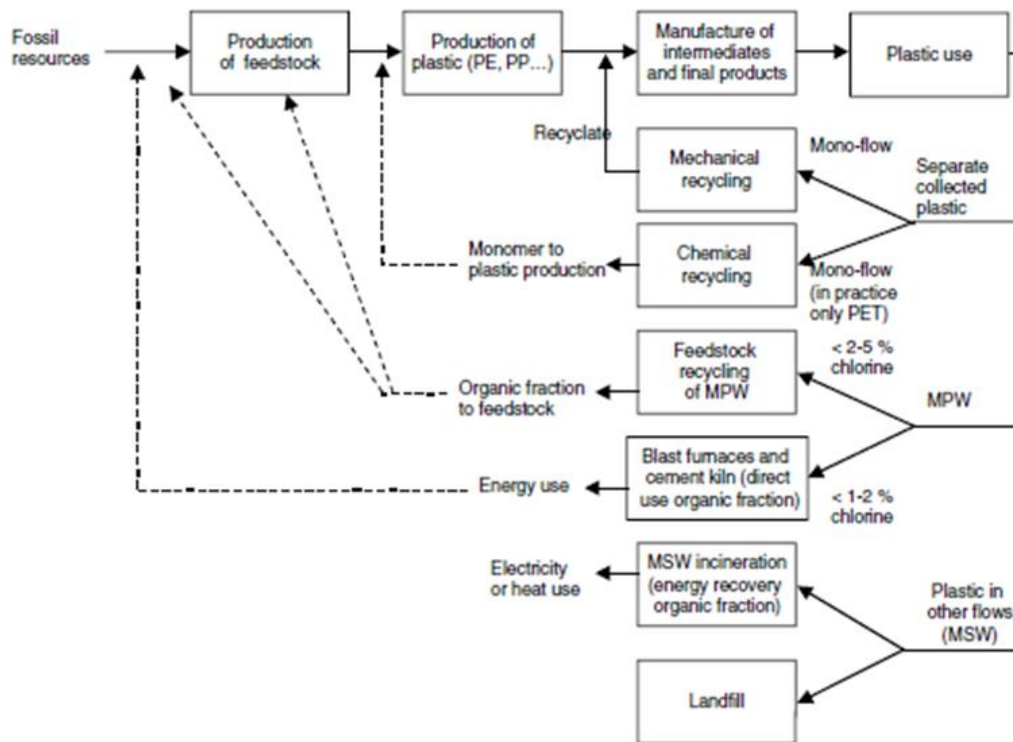


Fig. 6 Schematic of material chains related to plastics from production to waste disposal routes [6].

1.2 Pyrolysis of plastic materials

Traditional treatments for post-consumer plastics were landfills or incineration. However, landfilling of the post-consumer plastics has potential problems because of the limited land resource and high durability of plastics. Incomplete incineration may generate poisonous substances and causes serious health problems. Other methods, such as gasification and bioconversion are mainly used for organic materials [9]. That is why the thermal cracking process seems to be the most suitable and reasonable from all forms of utilization.

Pyrolysis, also termed thermolysis (Greek: pyro = fire; lysis = separating), is a process of chemical and thermal decomposition, generally leading to smaller molecules. Semantically, the term thermolysis is more appropriate than pyrolysis, since fire implies the presence of oxygen and hence of reactive and oxygen-bearing intermediates. In most pyrolysis processes, however, air is excluded, for reasons of safety, product quality and yield [23].

Pyrolysis can be conducted at various temperature levels, reaction times, pressures, and in the presence or absence of reactive gases or liquids, and of catalysts. Plastics pyrolysis proceeds at low (<400°C), medium (400–600°C) or high temperature (>600°C). The pressure is generally atmospheric. Subatmospheric operation, whether using vacuum or diluents, e.g. steam, may be selected if the

most desirable products are thermally unstable, e.g. easily repolymerizing, as in the pyrolysis of rubber or styrenics. The thermal decomposition of polymers yields gases, distillates and char, albeit in widely variable relative amounts. These can be applied as fuels, petrochemicals, and monomers. Depending on the polymers or polymer mixtures fed and the operating conditions used, yields can vary widely [23].

In pyrolytic processes, a portion of the species generated directly from the initial degradation reaction are transformed into secondary products due to the occurrence of inter and intramolecular reactions [10].

HDPE, LDPE, PP and PS are all hydrocarbons consisting entirely of carbon and hydrogen, which are similar to hydrocarbon fuels such as liquefied petroleum gas (LPG), gasoline and diesel. Plastics are derived from petroleum and have calorific values in a similar range as those of LPG, petrol and diesel as given in Figure 7.

Material	Calorific value (MJ/kg)
Polyethylene	46.3
Polypropylene	46.4
Polystyrene	41.4
Polyvinyl chloride	18.0
Coal	24.3
Liquefied petroleum gas	46.1
Petrol	44.0
Kerosene	43.4
Diesel	43.0
Light fuel oil	41.9
Heavy fuel oil	41.1

Fig. 7 The comparison of energy density of plastics and different types of fuels.

As mentioned previously, the two types of the plastics that, collectively, represent the largest share in municipal solid waste are polyethylene and polypropylene. Pyrolysis of PE, PP and other carbonaceous fuels have been studied extensively in the past. Kaminsky, Scheirs and coworkers [11]

investigated the effects of reaction conditions on the pyrolysis product. Williams studied the products from pyrolysis of different individual and mixed plastics [12]. Aguado investigated the effect of catalysts on the pyrolysis reactions [13]. Carniti and Gervasini focused on catalysts representing different surface acidity, while Cardona and Corma worked on better understanding of acidity considering number of acid sites and their strength separately [36]. Lin and Young studied PE degradation over various catalysts in fluidized bed reactor, and Kim investigated the process in semi batch reactor [36]. Murata created a comparison of products from polyolefin degradation with and without catalysts.

In this work the behavior of different types of montmorillonite catalysts in the lab-scale pyrolysis of polyethylene are investigated.

1.2.1 Reaction mechanism

Plastic pyrolysis is a complex process of breaking the long polymer chains into short ones. In many books and researches, this thermal degradation process is usually considered as depolymerisation of polymers [14].

As a rule, the pyrolysis of plastics follows complex routes that cannot be described by one or more chemical reactions, but only, and still rather imperfectly, by either empirical formulas featuring fractional stoichiometric coefficients or comprehensive systems of elementary reactions, i.e. reactions that really proceed as written. Moreover, the composition and structure of these reaction systems may vary with the details of the molecular structure of the actual polymer, such as chain irregularities, incorporation of initiators or catalysts, etc. As a consequence, precise mechanisms are mostly of scientific interest, whilst an industrial process approach is usually limited to overall considerations [23].

Thermal cracking

With temperature increasing, the plastics undergo three major thermal transitions: glass transition, melting, and decomposition. Figure 8 represents the changes in mechanical properties related to the physical and chemical ones.

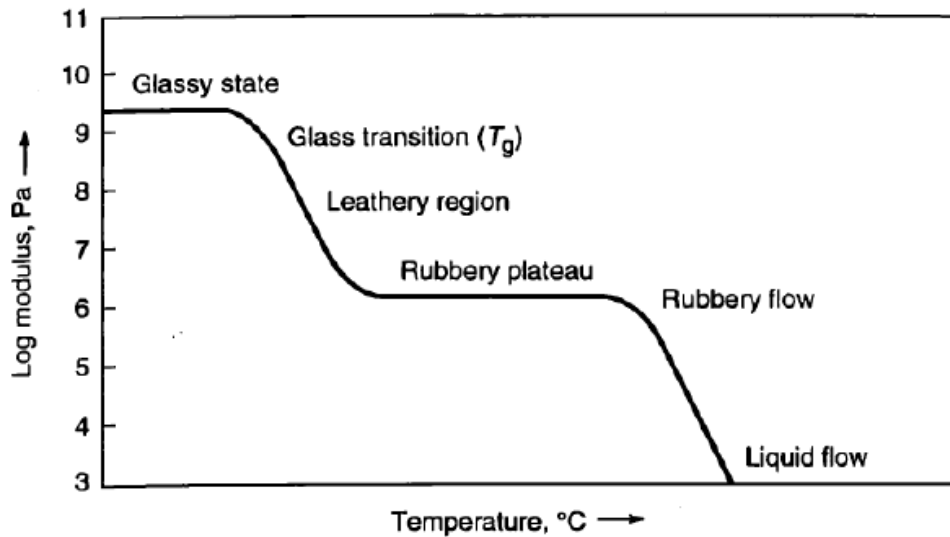
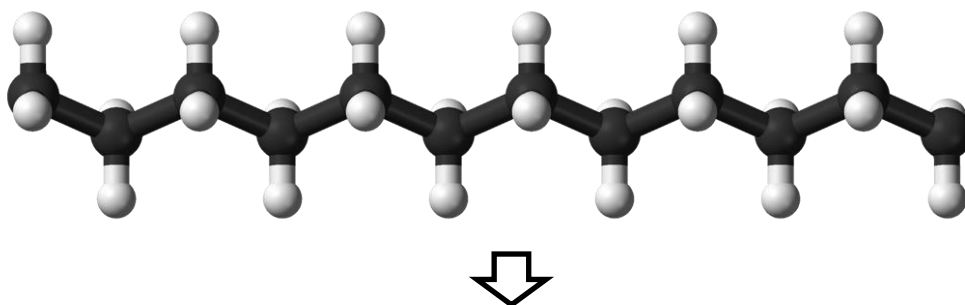


Fig. 8 The effect of temperature on elastic modulus of polymers.

With the temperature increasing, small molecules will escape the reaction medium by evaporation. However, before molecules can escape by evaporation, the energy supplied will have to overcome the bond enthalpy between atoms in the molecule structure so that the long molecules will rather crack.

The process is usually conducted at temperatures between 500- 800°C and results in the formation of a carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil and a non-condensable high calorific value gas [8].

The polyethylene structure consists of a large number of smaller molecules, monomers, which are joined together by bonds with a specific energy, giving rise to a long hydrocarbon chain. Most carbons in linear PE are on the long straight carbon chains so that one can assume that the cracking on these carbons has the same chance to occur, which is called random cracking. The products are in the form of different alkanes and alkenes of smaller size or, in the limit, the chain can be broken down into the smallest possible moieties as shown in the Figure 9.



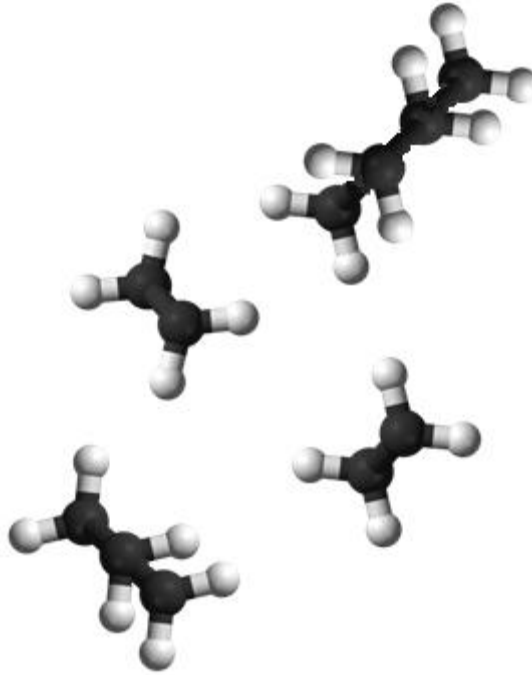


Fig. 9 Random depolymerization.

For thermal cracking the accepted mechanism implies the formation of free radicals in the polyethylene chain, originated by the hemolytic scission of a C-C bond, and causes the polymer to undergo scission leading to the formation of saturated and unsaturated smaller molecules.

Recent progress in converting plastic wastes into petrochemicals by means of pyrolysis in the absence of a catalyst has been reviewed by Kaminsky [16]. Four types of reactions have been proposed for the thermal processing of polymers:

- (a) End-chain scission or depolymerization: The polymer is broken up at the end groups successively yielding the corresponding monomers.
- (b) Random-chain scission: The polymer chain is broken up randomly into fragments of uneven length.
- (c) Chain-stripping: Reactive substitutes or side groups are eliminated on the polymer chain, leading to the evolution of a cracking product on one hand, and a charring polymer chain on the other.
- (d) Cross-linking: When thermosetting polymers are heated a chain network is formed.

These different reactions generate a corresponding product distribution that is related to bond dissociation energies, the presence of chain defects in the polymers, as well as to the presence of halogen, other hetero-atoms in the polymer chains or even catalysts.

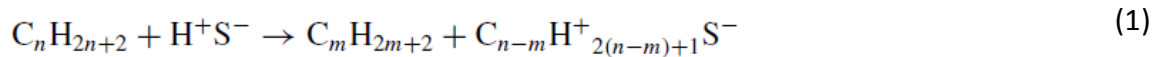
Catalytic cracking:

Catalytic cracking is potentially an important route to produce high-value products from plastic feedstock. Catalytic cracking catalysts are used to convert naphtha to higher-value petrol (gasoline).

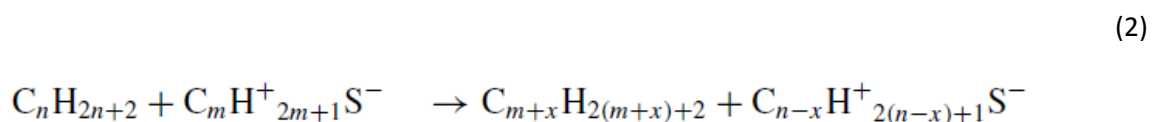
Pyrolysis in the presence of a catalyst usually requires less energy than it is needed in the non-catalytic process. Consequently, the catalysts allow the reduction of the process temperature that leads to a decrease in energy consumption; at the same time it improves the output quality and the corresponding yield (both gas and liquid hydrocarbons used as fuels) [15].

Volatile products derived from cracking PE with solid acid catalysts can be rationalized by carbenium ion mechanisms, described by White [23]:

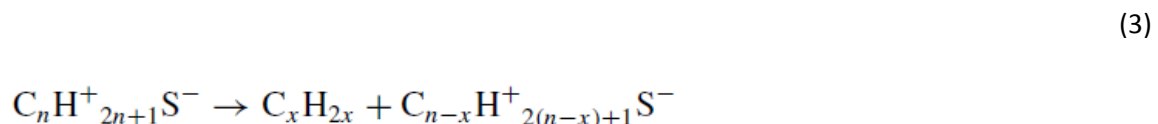
Under steady-state conditions, hydrocarbon cracking processes that yield volatile products can be represented by initiation, disproportionation, β -scission, and termination reactions. Initiation involves the protolysis of PE with Brönsted acid sites ($H^+ S^-$) to yield paraffins and surface carbenium ions:



Propagation reactions involve disproportionation between feed molecules and surface carbenium ions to yield paraffins:



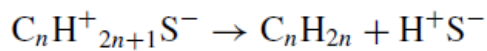
When a surface carbenium ion undergoes β -scission to form olefin products, smaller carbenium ions are left on the catalyst surface:



When sufficiently small, olefins may desorb from the catalyst surface. Surface olefins may also be protonated to form new carbenium ions. Termination reactions involve the destruction of surface

carbenium ions. For example, surface carbenium ions may desorb to produce olefins and regenerate Brönsted acid sites:

(4)



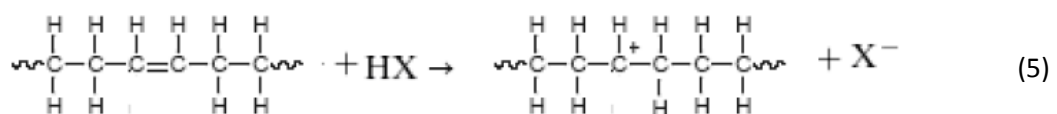
These chain reactions describe how paraffin and olefin cracking products are formed, but do not explain residue or aromatic product formation. Like the other reactions, aromatic and coke-forming reactions involve surface carbenium ions. Carbenium ion thermal cracking can result in olefin ions, which may undergo dehydrogenation and cyclization reactions that are assumed to be the source of aromatic products from straight-chain paraffin feeds. When unsaturated ions are protonated, di-ions are produced. Doubly charged ions can also be formed by disproportionation reactions between adjacent surface carbenium ions. Multiply charged ions are strongly bound to surface conjugate base sites and are less likely to participate in reactions with feed than singly charged carbenium ions.

Consequently, catalyst sites occupied by any multiply charged ion are unavailable for further reaction. Catalyst acidity and pore size dictate the relative rates of protolysis, disproportionation, β -scission, and termination reactions, which determine the abundance of volatile paraffin, olefin, aromatic, and nonvolatile hydrocarbon products [23, 17].

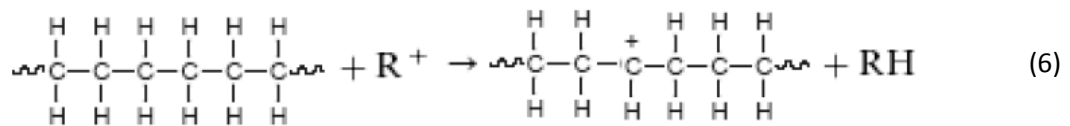
The mechanism of catalytic pyrolysis of polyethylene was also proposed by Buekens [37] and it mainly evolves:

Initiation, involving a carbenium ion formation by proton addition to unsaturated bond or hydride abstraction from a saturated one.

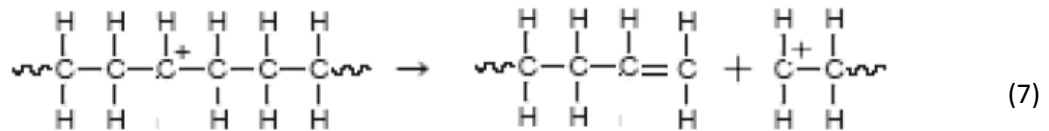
At defect sites of the polymer chain, molecule can be converted into an on-chain carbenium by adding a proton. This step might also take place through random hydride ion abstraction by low-molecular-weight carbenium ions. Then, the polymer chain is broken through β -scission.



or



than

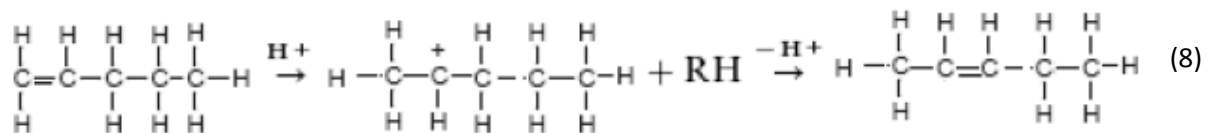


Propagation, where chain cleavage yields an oligomer fraction by β -scission.

Successive attacks by acidic sites or another carbenium ions and chain cleavage can lower the molecular weight of the main polymer chain, yielding oligomer fraction. Then, gas and liquid fraction is formed through later cleavage of the oligomer fraction by direct β -scission of chain-end carbenium ions.

Isomerization.

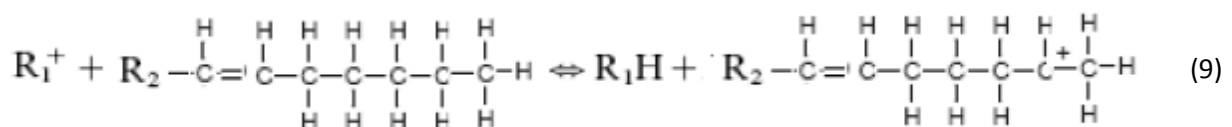
A double-bond olefin isomerization occurs by hydrogen or carbon atom shifts causing rearrangement of an intermediate carbenium ions.



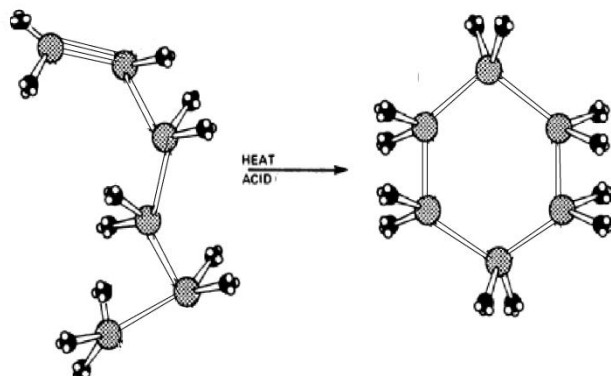
The isomerization process includes also shifts of methyl groups and saturated carbons isomerization.

Aromatization.

It is also possible that intermediate carbenium ions undergo cyclization process. Due to the fact hydride ion abstraction first takes place on olefin, several carbons are taken from the double bond, and olefinic carbenium ion is being formed.



An ion double bond can be influenced by intermolecular effect which provides a route to the formation and, in consequence, cyclization of the molecule. Strong acidic sites can also cause protolytic scission of the C-C bond.



(10)

Both mechanisms are very similar and include four main stages, with a carbocation ion properly defined as penta- or tricoordinated carbocation such as R_5C^+ or R_3C^+ . The first carbocation mechanism is described as monomolecular cracking. Here a penta-coordinated carbonium ion is formed from an alkane or alkane with functional group and this subsequently undergoes cracking and evolution of an alkane containing a hydrogen. This reaction is considered relatively slow at lower pyrolysis temperatures and the second type of carbocation mediated reaction is probably more important: this is known as the bimolecular or β -cracking mechanism. This process is initiated by a carbenium ion (a trivalent carbocation of type R_3C^+) which subsequently undergoes hydrogen or hydride transfer followed by β -bond scission. Since scission occurs with the formation of an additional adsorbed carbenium ion, the mechanism is generally considered to be much faster than the monomolecular route.

Separating the mechanism into two quite separate routes, free-radical and carbocation-mediated, is probably not possible and both reaction mechanisms may contribute to the product formation although the relative importance of each is likely to vary with temperature.

Whatever the nature of reaction mechanism, it is clear that the catalyzed pyrolysis must involve a number of different reactions [17].

1.3 Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) analysis

Thermogravimetric analysis is by far the most commonly used thermal decomposition test, used for assessing thermal stability and decomposition temperatures.

In TGA experiments, the sample can be quickly brought up to the desired temperature (isothermal procedure) or it can be heated up at a constant rate, and the weight of the sample is monitored during the course of thermal decomposition. It is mainly used to study the thermal stability of the plastic wastes at the certain heating rate used for each test. [$^{\circ}\text{C}/\text{min}$] while the sample is purged with certain flow of an inert gas [mL/min]. Thanks to this method it is possible to follow the reaction from the start, since each bond of polymer that is broken consumes some amount of energy, even though products might become small enough to evaporate into the gas phase, leading to the decrease of observed polymer mass [3].

Another method, which yields quantitative results is a differential scanning calorimetry - DSC, for measurements of specific heat and enthalpies of phase transition.

In this test procedure, both the sample and the reference material are kept at the same temperature during the linear temperature program. The heat of reaction is measured as the difference in heat input required by the sample and the reference material. DSC experiments are normally carried out by placing the sample inside sealed sample holders.

In this measurement it is possible to trace the rate of breaking bonds even if this leads to species that are still too heavy to evaporate and do not produce any significant mass losses and, thus, cannot be seen in the TG signal.

Examples of studies using above-mentioned methods in pyrolysis process examination are provided by Beyler and Hirshler [3] and by Feng Gao [9], who were focused on kinetic models creation.

1.4 Catalysts

Catalysts are a class of compounds specially selected, designed and optimized for influencing the reaction mechanism. The main purpose of the use of catalysts in the process of polymer degradation is to convert vapor-phase and liquid phase compounds into a higher-octane petrol (gasoline) under

lower temperature conditions than thermal cracking. Another purpose may be in accelerating decomposition, using acids and bases influencing selectivity in the decomposition of polyamides and polyesters. Thus, catalyst activity, selectivity, and stability are major considerations.

Natural phyllosilicates are a very interesting raw materials for the synthesis of catalysts and adsorbents. This is due, on the one hand, to their relatively easy accessibility in the form of a number of fields. On the other hand, a great variety of minerals, both in terms of chemical composition and structure. Many methods of modification have been developed, and they allow to design such catalysts and adsorbents with specific properties [27].

Montmorillonite is a soft phyllosilicate group of minerals that typically take the form of microscopic crystals, forming a clay. It is named after Montmorillon in France where it was first discovered.

Montmorillonite belongs to the smectite group and it has tetrahedral sheets sandwiching a central octahedral sheet (as shown in Fig. 10) with oxygen atoms binding the sheets. The particles are plate-shaped with an average diameter of approximately one micrometer. Chemically its composition hydrated sodium calcium aluminum magnesium silicate hydroxide $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2(\text{Si}_4\text{O}_{10})(\text{OH})_2 \cdot n\text{H}_2\text{O}$.

The main frame of silicates are SiO_4 tetrahedra in which the oxygen atoms occupy the corners, and the silicon atom is in the middle. Al^{3+} cations can be substituted for silicon atoms in the skeletal structure, and create a tetrahedron $(\text{AlO}_4)^-$ having a negative charge. Phyllosilicates (MMT) are also termed as a 2: 1 polysilicate. They form two outer layers of tetrahedral and octahedral one inside - forming a kind of a package.

The layers are continuous in a and b axis directions and are stacked one above other in c direction. The degree of order is dependent on the smectite clay mineral kind. There can also be partially isomorphic substitutions varying on the kind of mineral, but the general structure is as shown in Fig. 11.

Isomorphic substitution of Si_4^+ and Al^{3+} cations by Mg^{2+} or Fe^{2+} creates a negative charge-layer packet. This charge must be balanced, usually by alkaline cations Na^+ , K^+ , Li^+ , H^+ or an alkaline earth metal cations, e.g. Ca^{2+} . Then an interlayer of these "loose" cations formed balancing electric charge in the total structure. The thickness of the layer packet is approx. 1 nm, and the transverse dimensions range from approx. 0,03 μm to several micrometers - depending on the composition and structure of

the silicate. Thus the type of charge-balancing cations should be given and thus we may have e.g. "sodium montmorillonite" etc. Such cations may be exchanged for other cations.

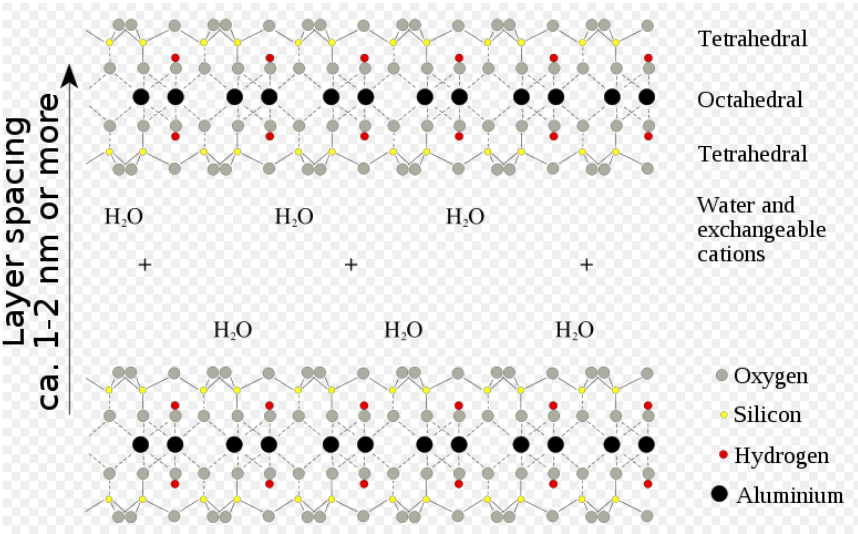


Fig. 10 The structure of montmorillonite

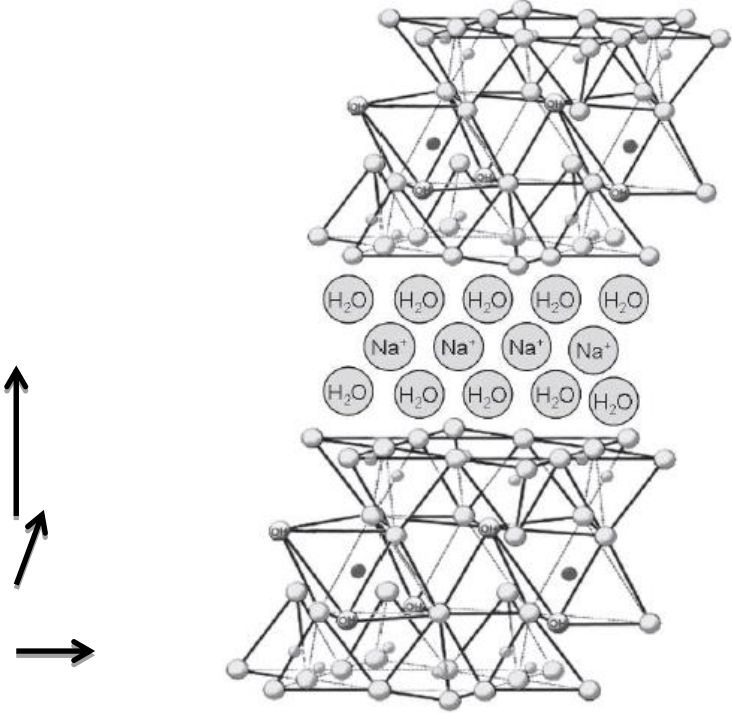


Fig. 11 Montmorillonite three-dimensional structure

The above-mentioned silicate lamellae form primary particles Mt (Fig. 12) - consisting of a few (8-10) fins [28]. These particles may in turn, form aggregates with dimensions up to approx. 10 microns. Electric forces occurring between the layers are not too large and the interlayer cations may be replaced with other cations and small polar molecules, and thus they may be intercalated between the silicate layers. This phenomena may increase the spacing between the packet layers called swelling.

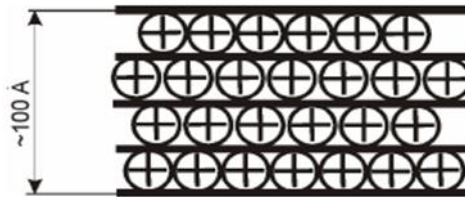


Fig. 12 Charge distribution in a montmorillonite structure. Where: (+) counterbalanced cations

The size of the negative surface electric charge depends on the type (composition) of the phyllosilicate. It defines the cation exchange capacity CEC - cations sorption capacity, expressed in equivalents per 100 grams: milliequivalents/100 g. Montmorillonite CEC value ranges from 80 to 150 meq / 100 g. One replaceable position falls for approximately 8 nm surface of the silicate layers[28].

The silicates are hydrophilic in nature and are incompatible with most polymers, especially non-polar polymers, such as polyolefin (PE and PP). Therefore, to use them as nanofillers it is necessary to modify them, to achieve the organophilic properties and swelling capacities. For this purpose, the intercalation of quarternized ammonium or phosphonium cations, preferably with long alkyl chains is needed [27].

The acidity modification which is a much cheaper way to modify the phyllosilicates, also tends to increase their surface area and porosity, but in this case, the materials may gain a high heterogeneity in terms of pore sizes.

The diversified chemical composition of the mineral, depending on the deposit, from which it was derived, may pose a serious problem with repeatability of catalysts parameters obtained from layered silicates. Therefore, research on the design of catalysts based on natural minerals must include studies on the characterization of materials and their impact on the effectiveness of their work.

Montmorillonite clays have been broadly used in industrial processes and extensively utilized in catalytic processes. Catalytic cracking catalysts have used montmorillonite clays for over 60 years,

because of their properties, such as large specific surface area and high thermal stability and, what is the most important, their acidic nature.

Activated montmorillonites are used to catalyse various chemical reactions. The activation process is similar to that used for the bleaching of clays. An early example of their use was the catalytic cracking of petroleum. This process, which is used for increasing the yield and quality of gasoline from petroleum, involves splitting the heavier molecular weight hydrocarbons into lighter ones with lower boiling points. The catalyst used must promote rupture of the carbon to carbon bond near the middle of the hydrocarbon chain. The first cracking catalysts were montmorillonite-derived ones but now they were mainly replaced by synthetic catalysts. The Present applications of activated clays are as alkylation catalysts, particularly for the alkylation of phenols. These alkylated phenols have many uses and are intermediaries in the formation of detergents. Clays are also used to promote polymerization, dehydration and various other chemical reactions. In addition, the activated clays are used as delicate pH adjusters where the last traces of alkalinity have to be removed from organic liquids. The natural clay is similarly used for the removal of traces of acidity[21].

In this work montmorillonites, extracted from bentonite, were used. The starting material was montmorillonite which has undergone two main modifications: acid treatment and cation exchange process.

The parameters of montmorillonite (surface area and high thermal stability) are related to the changes produced in the crystal structure by isomorphic substitutions. These substitutions take place both in a tetrahedral and octahedral layers, producing a negative charge density in the crystal structure.

This is why, it is expected to obtain different catalysts after changing parameters of treatments that modified the structure of the crystals, either cation exchange, thermal, and/or mechanical treatments. As shown in literature [21] acid treatment changes some properties of montmorillonites surface and alters the pore size distribution by removing aluminum and other ions from the octahedral layer. Activation with hydrochloric acid modifies the clays surface by replacing the exchangeable ions with hydrogen and aluminum.

A natural clay and its aluminum pillared analogues have been tested for the catalytic cracking of polyethylene by i.a. De Stefanis and Cafarelli [38] Montmorillonite possess a layered structure which can be converted into a two-dimensional network of interconnected micro pores by intercalation of molecular moieties. In the case of aluminum pillared clays, these materials show a mild acidity and an accessible pore size structure.

The consideration of pillared clays as possible catalysts for plastic cracking is mainly supported by the fact that their acidity is weaker than that of zeolites. Accordingly, they show a lower cracking activity, but also the catalyst deactivation by coke formation takes place to a lower extent when compared with zeolitic catalysts. Moreover, the liquid products obtained over the clay catalysts are heavier, as the strong acidity of zeolites is responsible for over-cracking reactions, resulting in the production of lighter hydrocarbons. Likewise, the mild clay acidity leads to a lower occurrence of hydrogen-transfer reactions when compared, for instance, with US-Y zeolite, which in turn causes the formation of alkenes as the main products of the polyethylene cracking over clay catalysts [26].

2. Experimental Procedures and Apparatus

This chapter includes a description of materials used to study the degradation of polyethylene and also an outline of methods and techniques used in the survey. First part presents the specification of the polymer material and the catalyst. Second part is focused on the method used in the Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) analysis.

2.1 Polymer material

The material used in this work was pure, high density polyethylene kindly supplied by Borealis company. According to data received from the material supplier polyethylene in a powder form presents density 0.941 g/cm^3 and shows melt flow index 0.35.

2.2 Catalyst material

The base mineral was montmorillonite extracted from bentonite from Milowice (Mt) and commercial montmorillonite (K30) from Sigma Aldrich. The following materials (after base materials modification) were used as a catalysts:

Mt, K30H15, K30H60, K30H90, K30H120, MtH60Al, MtH90AlCu, K30Al, K30H15Al, K30H60Al, K30H90Al, K30H120Al. The preparation and partial characterization of the catalysts investigated in this work was conducted by PhD student Dominik Wierzbicki and some details are presented below. D. Wierzbicki carried out XRD measurements for K30 group catalysts and found that acidic treatment led to delamination of the structure for all samples. Pillaring process was unsuccessful due to former delamination, and thus it should be assumed that Al was introduced onto the surface in the form of

alumina aggregates. The discussed group of catalysts is divided into three main subgroups (Figure 13) depending on their modification routes.

The first group consists of montmorillonite treated with hydrochloric acid (HCl) for 15, 60, 90 and 120 minutes, respectively.

The second group are montmorillonite samples activated with acid (HCl) for 15, 60, 90, 120 minutes, respectively and subsequently modified with hydroxo-aluminum cations.

In the last group there are four other catalysts: raw montmorillonite, K30 commercial acid-activated montmorillonite pillared additionally with hydroxo-aluminum cations, montmorillonite acid activated for 60 minutes and pillared with alumina hydroxycations, and the montmorillonite activated with acid for 90 minutes and modified with alumina hydroxycations (Al^{3+}), followed by impregnation with copper ions (Cu^{2+}).

Modification	acid treated	pillared
I group		
K30 H15	■	
K30 H60	■	
K30 H90	■	
K30 H120	■	
II group		
K30 H15Al	■	■
K30 H60Al	■	■
K30 H90Al	■	■
K30 H120Al	■	■
III group		
Mt		
K30Al		■
Mt H60Al	■	■
Mt H90AlCu	■	■

Fig. 13 Catalysts preparation table.

The details of modification procedures are:

Acid exchange process:

Per 1g of montmorillonite material 20ml of 20% hydrochloric acid were used. Acid activation reaction was performed in a round bottom flask with reflux condenser. The mixture was heated up to the boiling point. Time of the treatment was counted from the beginning of boiling (15 min., 60 min., 90

min. or 120 min., respectively). After activation, the solution was filtered and washed with distilled water until a loss of response to chlorine ions, and then dried at 80 ° C.

Ion intercalation process:

For the ion intercalation process two different solutions were used. After acid activation samples K30H60, K30H90 and K30H120 were supported by chlorhydrol solution. While samples K30H15 and K30 were treated by separately prepared supporting solution described below.

The first group of three activated montmorillonites mentioned at the beginning were modified as follows: to each sample distilled water was added in such an amount that the starting material was 0.65 wt% of the resulting mixture. Then, chlorhydrol was added to obtain a proportion of the mixture: 1.3 g of chlorhydrol per 1 g of montmorillonite. After addition of chlorhydrol, the solution was stirred vigorously for 30 minutes and then pH was lowered down to 2 by HCl. Then the solution was relatively fast heated up to the temperature of 70°C and maintained for 30 minutes. After staying in a thermostat bath the solution was filtered, washed with distilled water and dried at 80 ° C.

For the two of activated montmorillonites (K30H15 and K30), the treatment solution was obtained by slowly adding of 0.4 M NaOH into 0.4 M solution of AlCl₃ while stirring. The volumes of the two solutions were chosen so that in the final solution the molar ratio of OH / Al was 2.4. The temperature during the preparation of the solution was maintained at 80°C.

In case of the catalyst modified with two cations: Al³⁺ and Cu²⁺, acid activated montmorillonite MtH90 was pillared with aqua hydroxyalumina cations, and subsequently 5% copper was introduced by incipient wetness impregnation.

2.3 Thermogravimetric (TG) and Differential Scanning Calorimetric (DSC) analysis

2.3.1 Samples investigation

Ammonia desorption process was carried out in a TA Instruments SDT 2960.

Most of the TG/DSC experiments (calcination, pyrolysis, activation testing) were carried-out in a PerkinElmer Simultaneous Thermal Analyzer STA6000. Before the runs, nitrogen flow was maintained through the system for 5 min with the flow rate of 19.8 ml/min to purge all air. The same flow rate was maintained during the experiments.

The investigated polyethylene samples and samples with previously calcined in 500°C catalysts were placed on an alumina TG pan and the thermal degradation was analyzed. The PE/catalyst mixture was prepared at room temperature in order to obtain a mixture of 10 - 11 mg. The quantity of catalyst used was approximately 1 mg, depending on the experiment.

2.3.2 Profile of the temperature

The runs were performed under nitrogen with continuous flow and with continuous heating rate of 10°C/min. For each experiment there were four stages carried out, as schematically shown in Fig. 14. The first one was isothermal stabilization at 30°C for 10 minutes. At the second stage, temperature was increased from 30 to 700°C with a heating rate of 10°C per minute and at the third stage the final temperature (700°C) was maintained for 10 minutes, followed by the last stage - the sample cooling to 30°C with the rate of 100°C per minute.

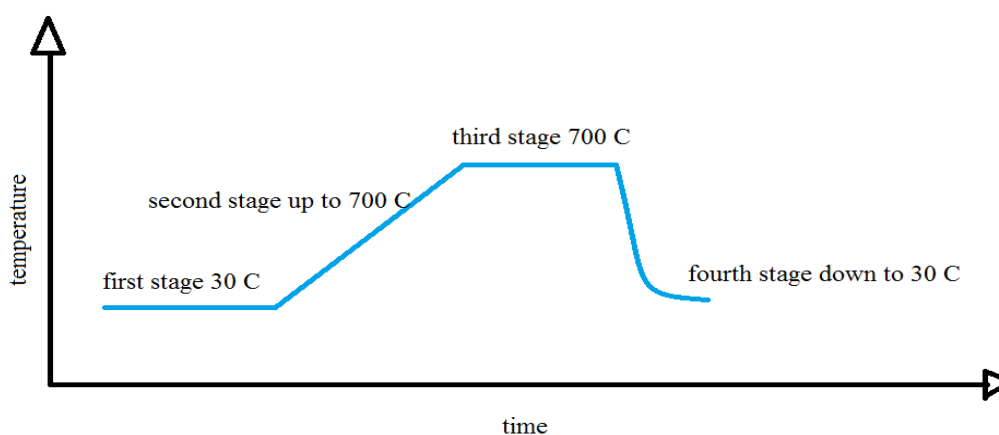


Fig. 14 Temperature profile for the polyethylene degradation

Because of the fact that the layout of the pan inside the furnace influences the DSC signal and may influence the real results, the cycle was repeated. In the second cycle the data necessary for the correction of the heat flow profile baseline was obtained.

2.3.3 Equipment

The thermal analysis simultaneous DSC-TGA apparatus consists of three parts:

- The furnace with the built-in sensitive recording balance connected to the atmosphere controller
- The computer equipped with a special software tracking of measurements.
- Cooling system

The instruments presented in the Figure 15 are:

1. Computer
2. The gas line (N₂)
3. Discharge line of gaseous products
4. Furnace
5. Cooler

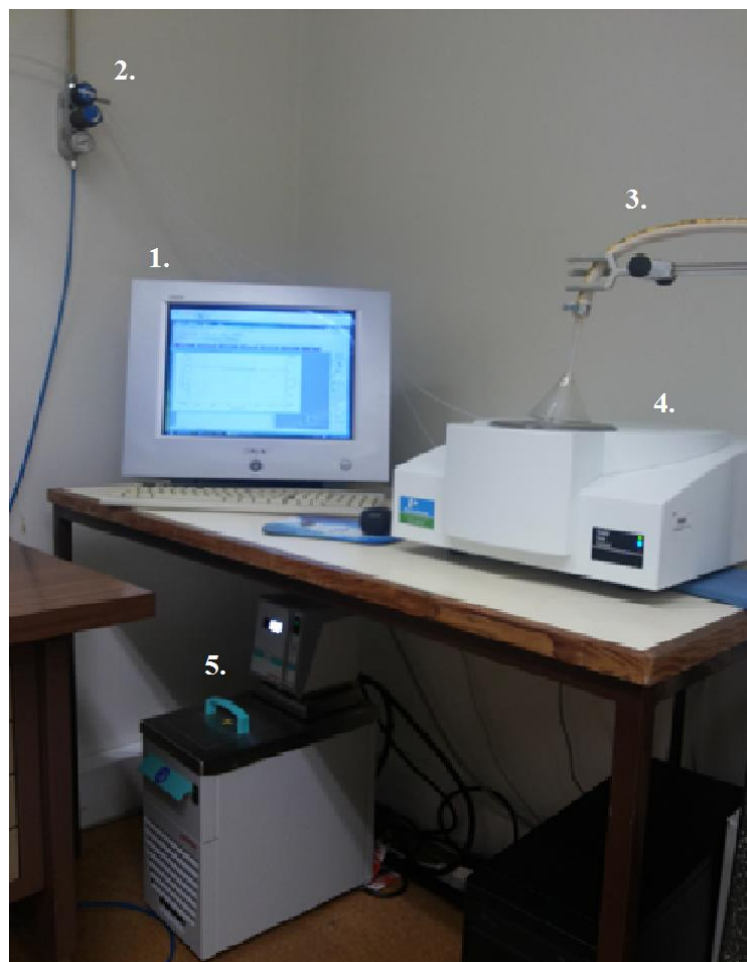


Fig. 15 DSC-TGA equipment

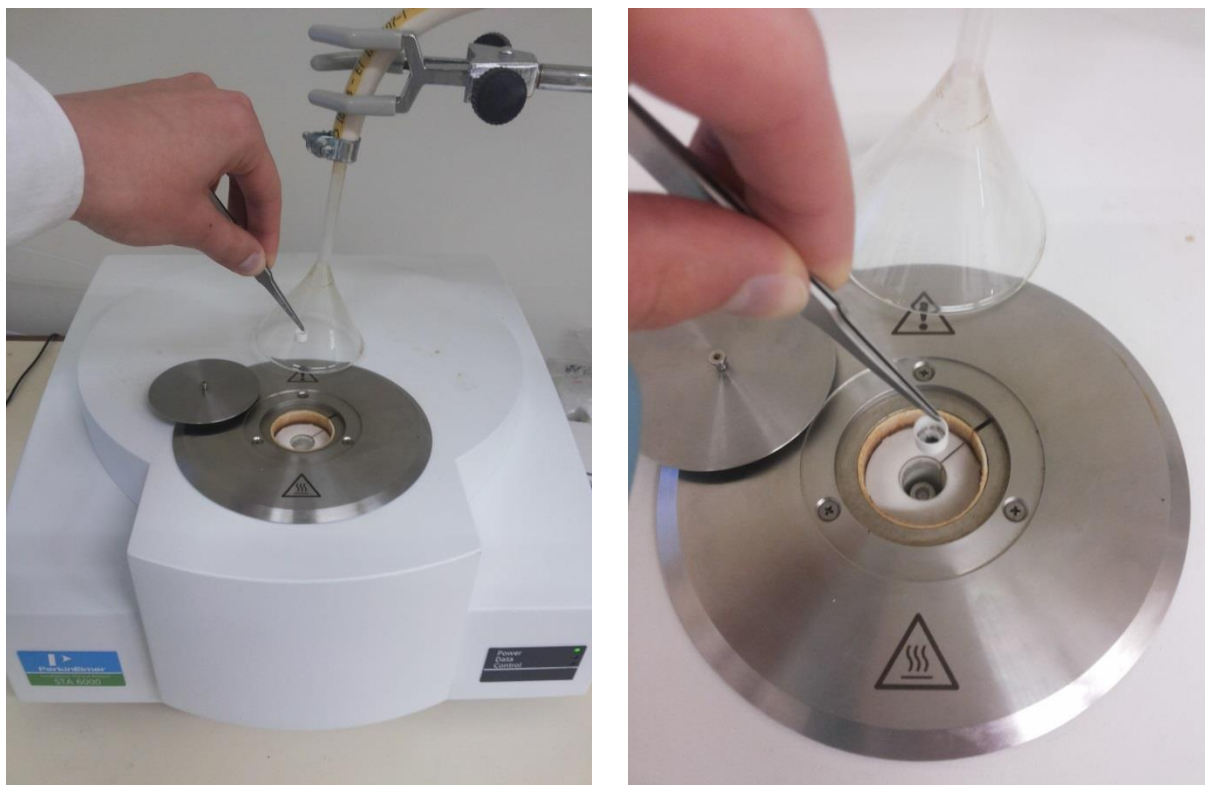


Fig. 16 The loading sample pan inside the furnace.

The data collected during the experiments were stored in the computer connected with the equipment. The evaluation of the data received from the analyzer was conducted by the specialized software Pyris Series STA6000. This tool was used for converting the obtained data points into plots used for the further interpretation of the results.

2.4 Characterization methods

The acid strength distribution was determined by temperature-programed desorption (TPD) of ammonia.

The catalyst samples were saturated with ammonia by placing them in a closed test-tube with an ammonium solution; this solution saturated the atmosphere within the vessel with gaseous ammonia and was kept at 40 °C for 4 hours in the thermostat, as presented in Figure 20.

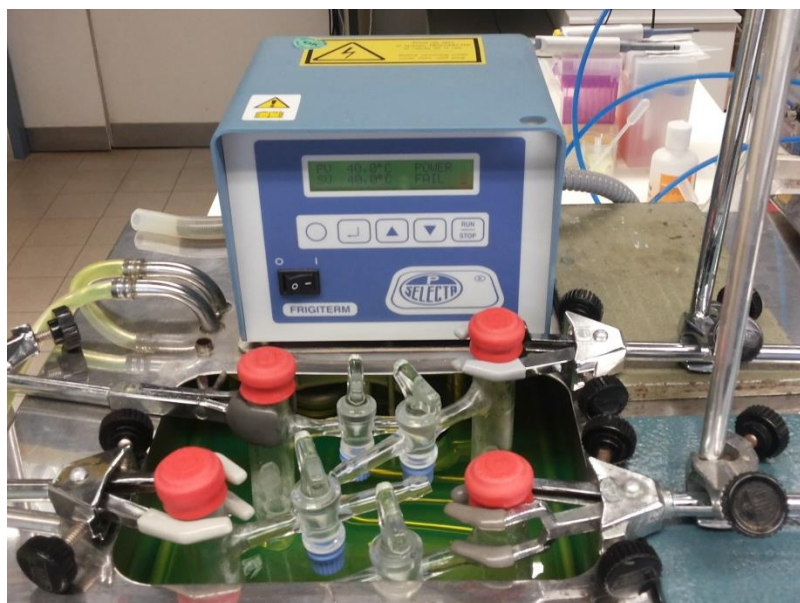


Fig. 17 Ammonia sorption stand.

After saturation, desorption experiments were carried out in a DSC/TG apparatus, using a quartz pan. The samples were heated up to 500 °C with a heating rate equal to 10°C/min.

The acid strength distribution was obtained for all three groups of catalysts from the NH₃-TPD by a numerical deconvolution method [29].

The method assumes an irreversible ammonia desorption process with first order kinetics and with no interactions between two different acid sites. The strength of an acid site can be approximated by the activation energy for desorption of ammonia whose absolute value can be assumed to be equal to the ammonia adsorption enthalpy, and its adsorption has no or negligible adsorption activation energy [30].

The desorption rate from a set of sites with uniform adsorption energy is given by an Arrhenius law (11), to which experimental data were fitted.

2.5 Waste plastic investigation

In waste plastic pyrolysis tests all of the TG/DSC experiments were carried-out in a TA Instruments SDT 2960 simultaneous DSC-TGA apparatus. Before the runs, nitrogen flow was maintained through the system for 10 min to purge all air. The same flow rate 19.8 ml/min was maintained during the

experiments. The plastic/catalyst mixture was prepared at room temperature in order to obtain a mixture of 11 mg (10 mg of material with 1 mg of catalyst). Then the prepared sample was placed on a quartz TG pan and the thermal degradation was analyzed. At the beginning of the process the temperature was increased from room temperature up to 700 °C, and then maintained for an additional 10 min that it could be cooled later on. The heating rate was maintained at the level of 10 °C/min.

Additionally, the pure plastic waste thermal degradation was performed in order to obtain curves that will serve as reference curves during the discussion of research results. Thermal degradation was carried out under the same conditions as the catalytic degradation, with no catalyst involved.

3. Results and Discussion

Catalytic pyrolysis of Polyethylene (PE)

This chapter is dedicated to description of the results obtained from the Thermogravimetric (TG) and Differential Scanning Calorimetry (DSC) analysis.

The influence of the temperature was analyzed. All experiments were carried-out with a heating rate 10°C per minute. During the heating, measurement of changes in weight and heat flow were performed in order to investigate the behavior of the sample as a function of temperature.

The experiments of catalytic degradation of polyethylene in nitrogen atmosphere were carried out for one family of catalyst but divided in three groups. Catalysts division was created in order to facilitate the summary of results and their further interpretation.

The first group consists of four catalysts that were prepared from the same type of montmorillonite but subjected to the influence of the hydrochloric acid for different time periods. The second group of catalysts starting material is the same as in the previous group and all catalysts were treated with acid for various lengths of time, but they were also treated by aluminum hydroxycations. The last group consists of catalysts described in Experimental chapter.

3.1 Calcination process

The pretreatment of catalysts is established to be among the effective means of enhancing the catalytic performance. The objective of calcination in an inert gas environment is to activate a catalyst by removing any undesired species from the surface.

The procedure started with a 10 minutes long isotherm kept at 30°C and then the heating process occurred. The reactor was heated up to 500°C with a heating rate of 10°/min with simultaneous N₂ feeding at a rate of 19 ml/min. When the highest temperature was obtained, the sample was been kept under this condition for 10 minutes and after cooled down to 30°C.

The calcination of deposited substances brings transformations and some reactions of decomposition, but primary the water is removed.

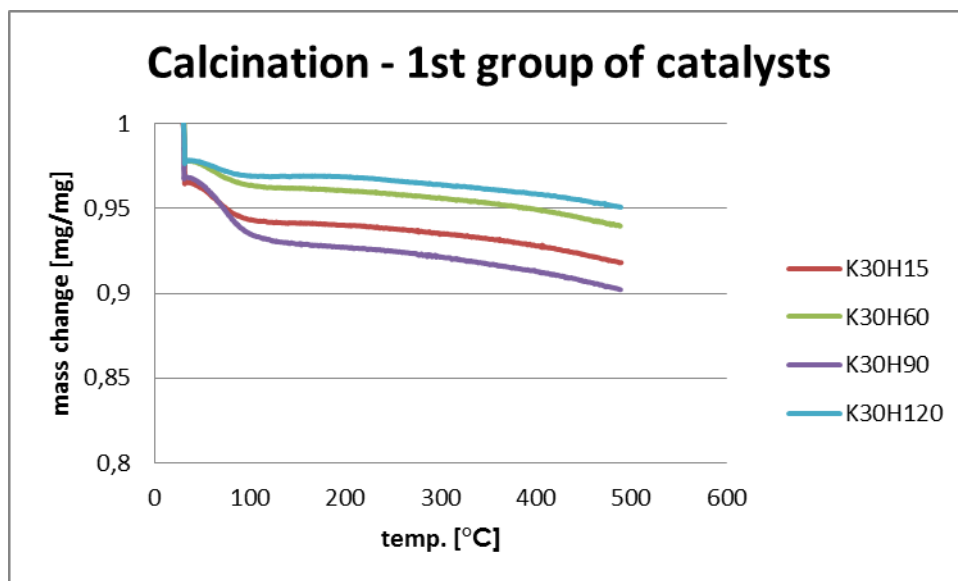


Fig. 18 The mass change as a function of temperature for the first group of catalysts in the calcination process.

At the beginning of the calcination process, up to 130°C, water is evaporated, further mass change is caused by removing substances covering the surface of the catalyst.

In the first plot (Figure 18) all curves are above the reference pure montmorillonite curve (Mt), which indicates that the acid treatment slightly affects the structure of the catalysts. It can be seen that, the longer the time of acid treatment of the base material smaller overall mass change is observed. This effect might be caused by the fact that with a longer interaction with a strong acid on the structure of the clay a greater delamination occurs, and thus the porosity decreases. In some cases losing water at the beginning of the process is faster (higher slope at the beginning of the function) but all of the catalysts show mostly the same behavior due to the same shape of the calcination function for all catalysts.

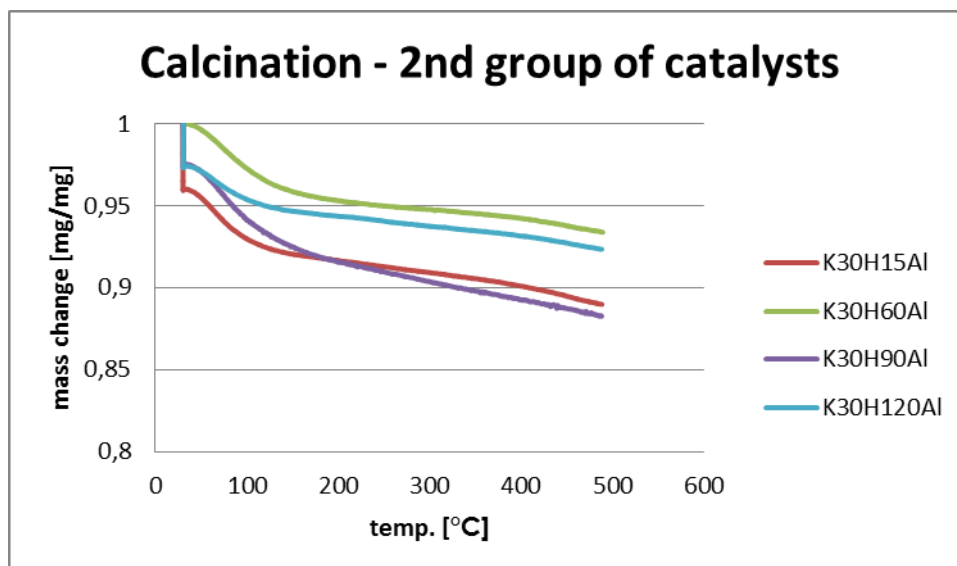


Fig. 19 Weight change over temperature of the second group of catalysts in the calcination process.

The second group of studied catalysts presents different relations to the reference pure montmorillonite curve (Figure 19). All curves of catalysts follow the tendency observed in the first group. After losing some amount of water, they show small changes of mass over temperature. The only exception might be catalyst K30H90Al demonstrating a bit different curve form others, but there is no information to indicate how the surface is developed.

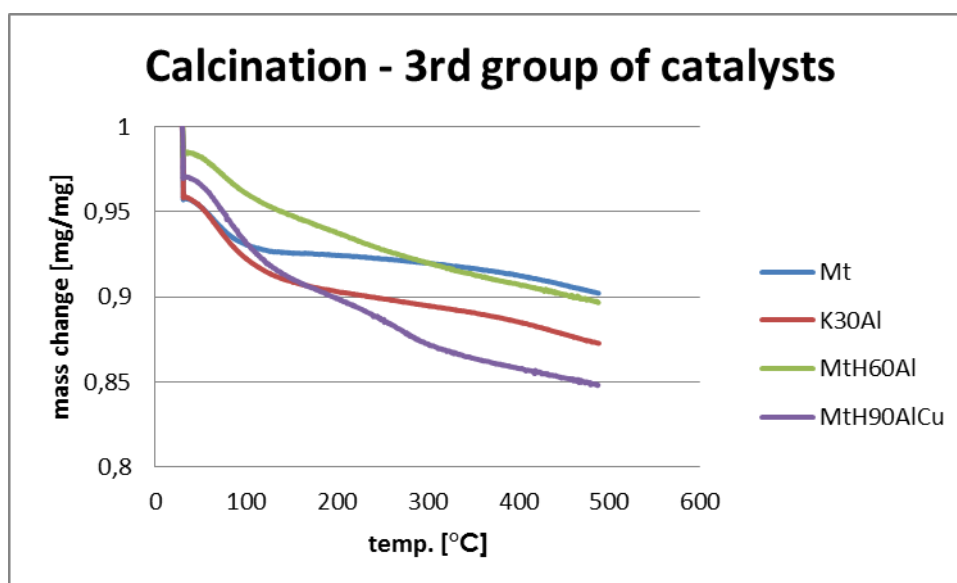


Fig. 20 Weight change over temperature of the third group of catalysts in the calcination process.

In the third group of catalysts treated with high temperature in inert gas conditions, only montmorillonite treated with acid and intercalated with aluminum hydroxycations and copper (MtH90AlCu) responded with the two-step process. It might signify that mass decrease may arise

from the decomposition of copper salt because the bulk $\text{Cu}(\text{NO}_3)_2$ decomposition temperature is 250 °C.

3.2 Acid strength distribution

Acid sites in montmorillonites have different strengths, depending on their position in the framework and their environment. The experimental ammonia TPD spectrum is the sum of several desorption curves corresponding to the different types of acid sites. As acid sites having different acid strength they have different activation energies for ammonia desorption.

$$-\frac{dq}{dt} = \sum_i K E_i \cdot e^{-\left(\frac{E_i}{RT}\right)} \cdot q_{E_i} \quad (11)$$

In order to obtain, through multi-linear last-square regression, the values of q_i , that represent the initial amount of acid sites with E_i desorption energy, the pre-exponential factor must be known. To simplify the problem, Hashimoto assumption [32] represented by Equation (12) has been used.

$$K_{E_i} = \alpha \cdot e^{\beta \cdot E_i} \quad (12)$$

Where:

dq/dt – overall rate of desorption of ammonia at instant t and temperature T

E_i - energy activation of the desorption of ammonia

K_{E_i} -pre-exponential factor

α, β - parameters depending on the structure of catalyst

Fig. 21 to 23 compare acid sites strength distribution for the studied groups of catalysts.

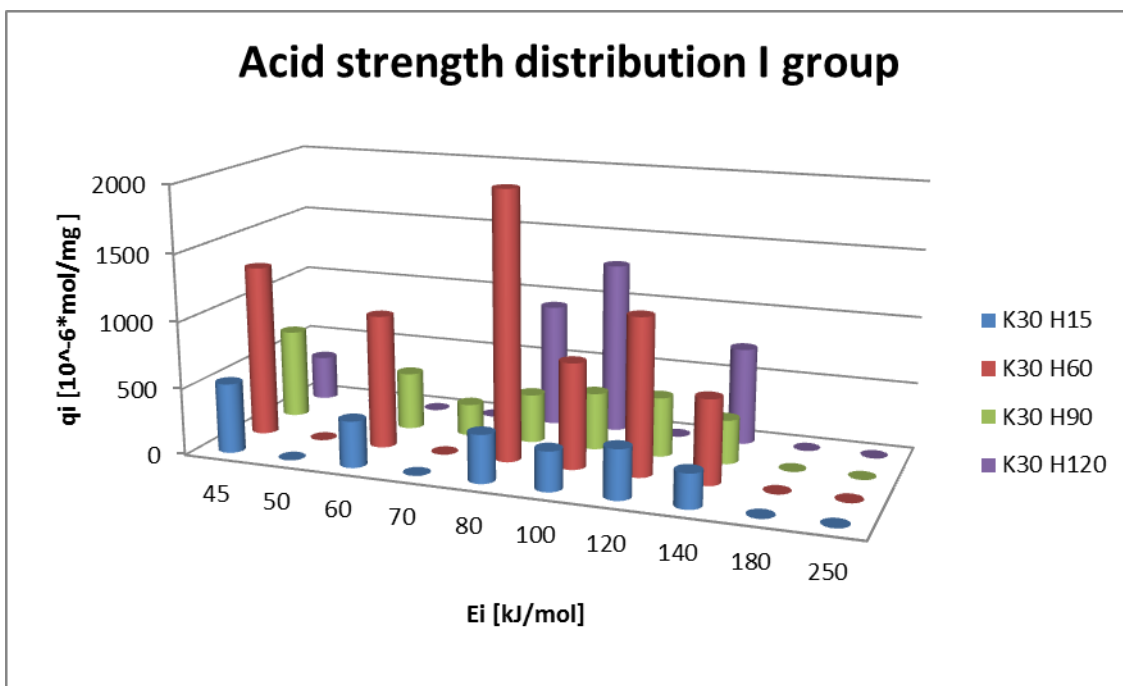


Fig.21 Acid sites strength distribution in the first group of catalysts

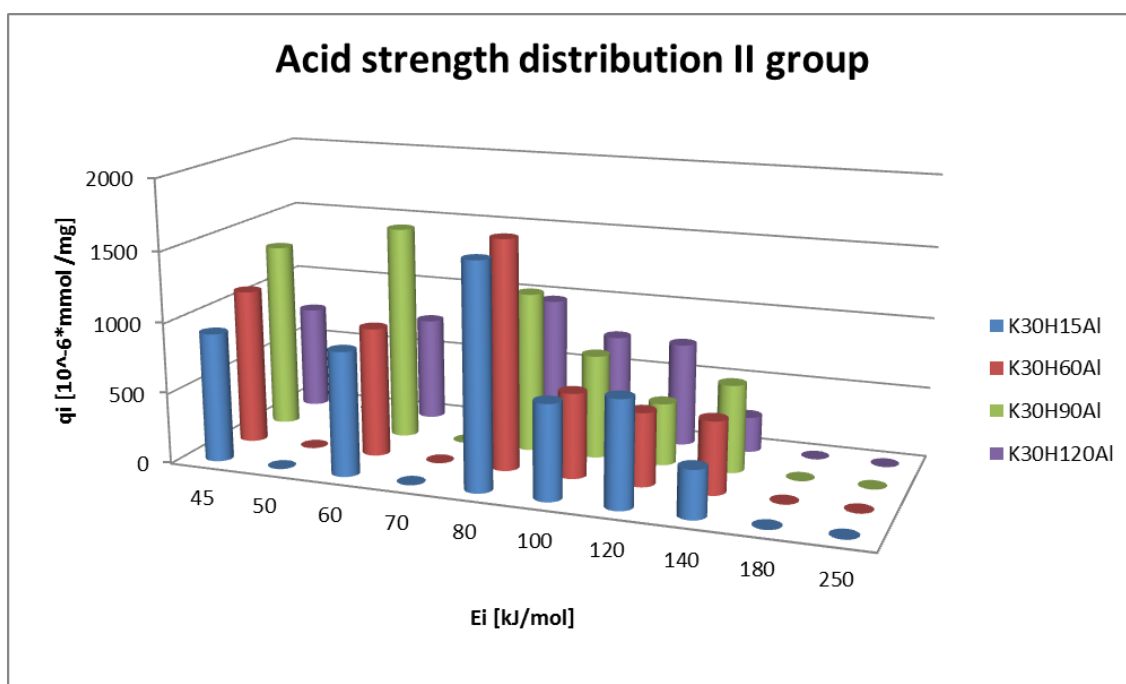


Fig.22 Acid sites strength distribution in the second group of catalysts

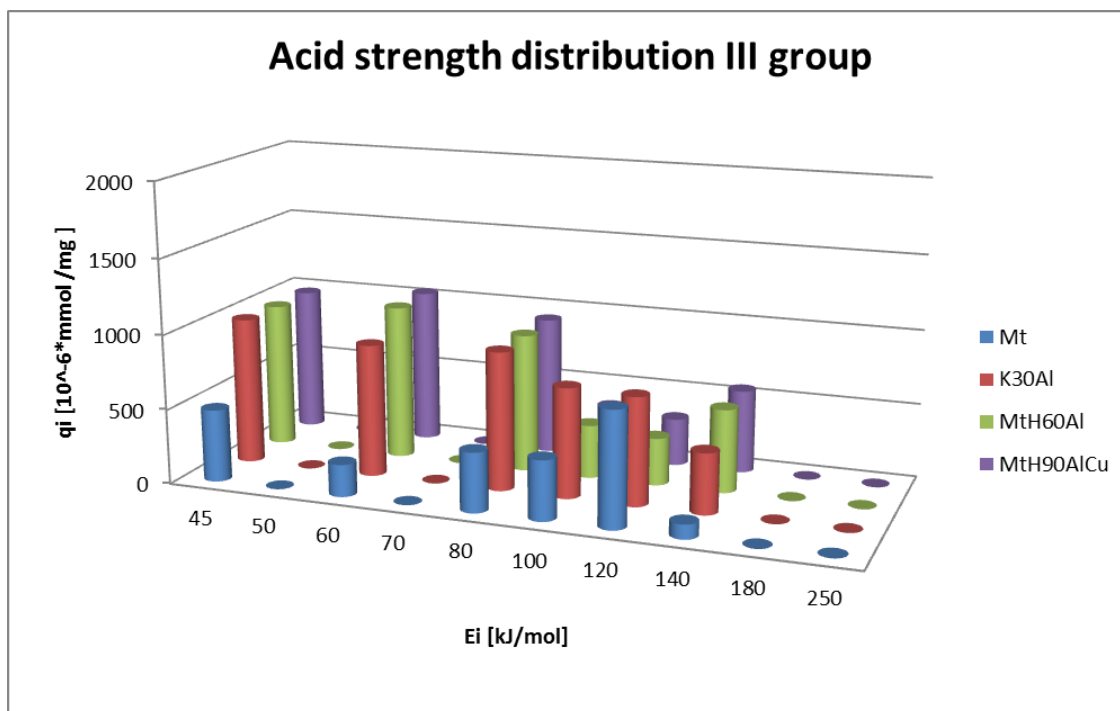


Fig.23 Acid sites strength distribution in the third group of catalysts

All acid site distribution plots can be analyzed by considering three different regions of acidity. Sites corresponding to the lowest energy level equal to 45 kJ per mol correspond to physical adsorption of ammonia, which are not important for the process. The second group of sites at level of 60 kJ/mol correspond to loosely bound ammonia to weak acid sites, with low relation to the process. Finally the last group of sites present at energy levels from 80 to 140 kJ/mol are those with the highest relevance to the active site involved in the catalytic process.

Based on the previous conclusions the number of acid sites influencing the right overall acidity of catalysts was calculated as a sum of acid sites from energy ranges 80 - 140 kJ/mol. The results are presented below in the Table 1.

catalyst	number of acid sites [10 ⁻⁶ *mol/mg]
K30H15	1281
K30H60	4823
K30H90	1561
K30H120	2931
K30H15Al	3339
K30H60Al	3254
K30H90Al	2927
K30H120Al	2703
Mt	1665
K30Al	2795
MtH60Al	1438
MtH90AlCu	2159

Table 1 Numbers of acid sites for all catalysts investigated

The first group results obtained for the NH₃ desorption from each type of acid site q_i are depicted in Figure 21.

I group results

The lowest amount of sites is presented for K30H15, which represents the shortest time of acid influence on the structure. On the other hand, the highest number of acid site belongs to K30H60, which represents the second shortest time of acid treatment. The K30H120 catalysts shows the second highest number of acid site presence, while, the K30H90 presents an almost uniform distribution of acidity over a relatively wide range of acid strengths, with desorption energy levels from 45 to 140 kJ mol⁻¹, but with the very small overall amount of sites. All catalysts present significant heterogeneity of acid strength.

II group results

Second group results are illustrated in Figure 22 and they represent significantly higher amount of acid sites presented, but with the selective distribution of sites with high desorption energy levels: 80, 100, 120 and 140 kJ/mol. All catalysts show the highest amount of acid sites at energy level of 80 kJ/mol.

An interesting fact is that the overall number of acid sites obtained after cation intercalation is around 3000 [10⁻⁶mol/mg] for all catalysts. Uniformity results from the growth of the number of acid

sites in the two catalysts presenting the lowest amount of acid sites before cations were pillared (K30H15, K30H90). At the same time there was a drop of the number of acid sites in catalysts which showed the highest amount of sites before alumina intercalation (K30H60, K30H120).

III group results

The third group of investigated catalysts results are presented in Figure 23, which does not indicate any tendencies in the amount of the strongest acid sites. Noteworthy is that K30Al catalyst has the highest amount of high energy sites among all the other catalysts in the group and the second highest number of sites is presented by Mth90AlCu.

Surprisingly, the amount of acid sites of pure unmodified montmorillonite is higher than some of the modified catalysts investigated, in particular Mth60Al.

3.3 DSC/TG analysis for the catalytic degradation of polyethylene using the first group of catalysts

The results obtained from the DSC/TG analysis of the polyethylene (PE) degradation using the first four catalysts investigated are shown in Figure 24 and Figure 25.

The first graphic shows the curve corresponding to the DSC signal with two endothermic peaks. The first peak with no accompanying weight loss corresponds to the melting of the PE sample. It can be observed that the melting point remains constant for all experiments, which for the tested polyethylene, is obtained at 127 °C. Additionally the shapes of peaks are very similar. It can be concluded that the melting temperature is not influenced by the catalysts, as expected.

The second endothermic peak at the higher temperature is related to the degradation process. This peak is accompanied with a considerable weight loss. The formation of gas phase products involves two steps. The first one corresponds to the breakage of the bonds and the formation of smaller molecules and the second one corresponds to the evaporation of these smaller products. Each of the steps is associated with different energy consumption. The beginning of the second DSC signal is due to the energy which is given to the sample when the bonds in the polymer begin to break. This breakage of the bonds in the polyethylene produces lighter products that eventually become sufficiently small to be volatile at the temperature of reaction and evaporate from the pan, leading to

the easily observed mass losses. Additional consumption of energy can also occur due to the evaporation process and the potential further degradation of released, newly created compounds.

The second graphic presents mass change dependence as a function of temperature, which is the result of TG analysis.

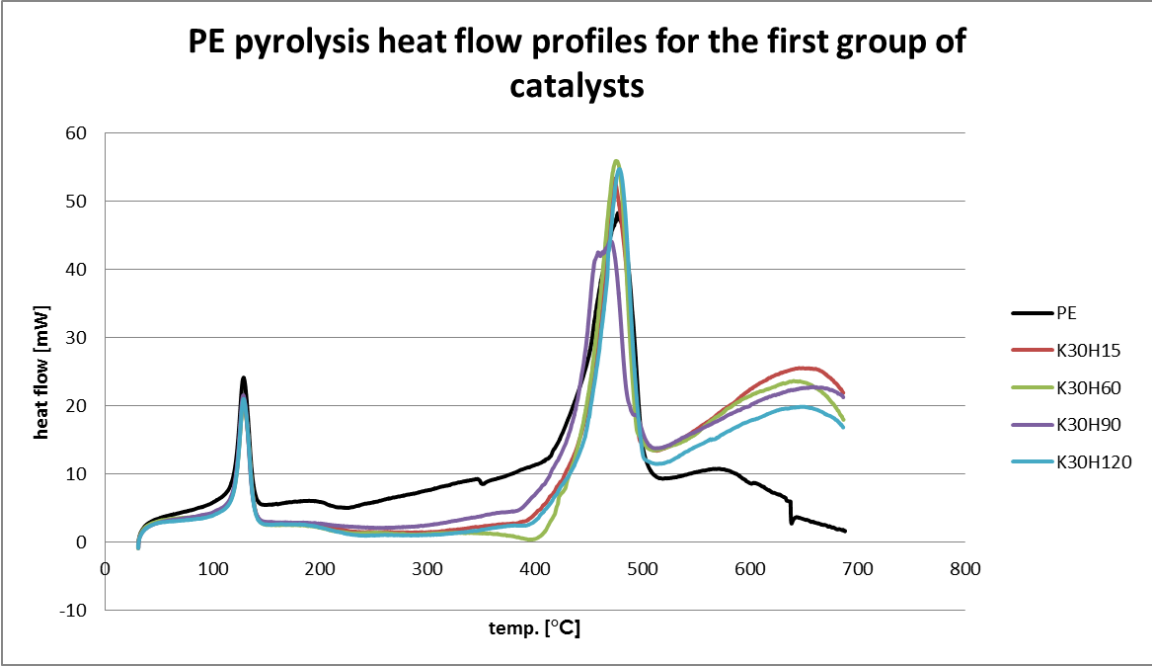


Fig. 24 Heat flow curves obtained from the catalytic degradation of polyethylene with the first group catalysts.

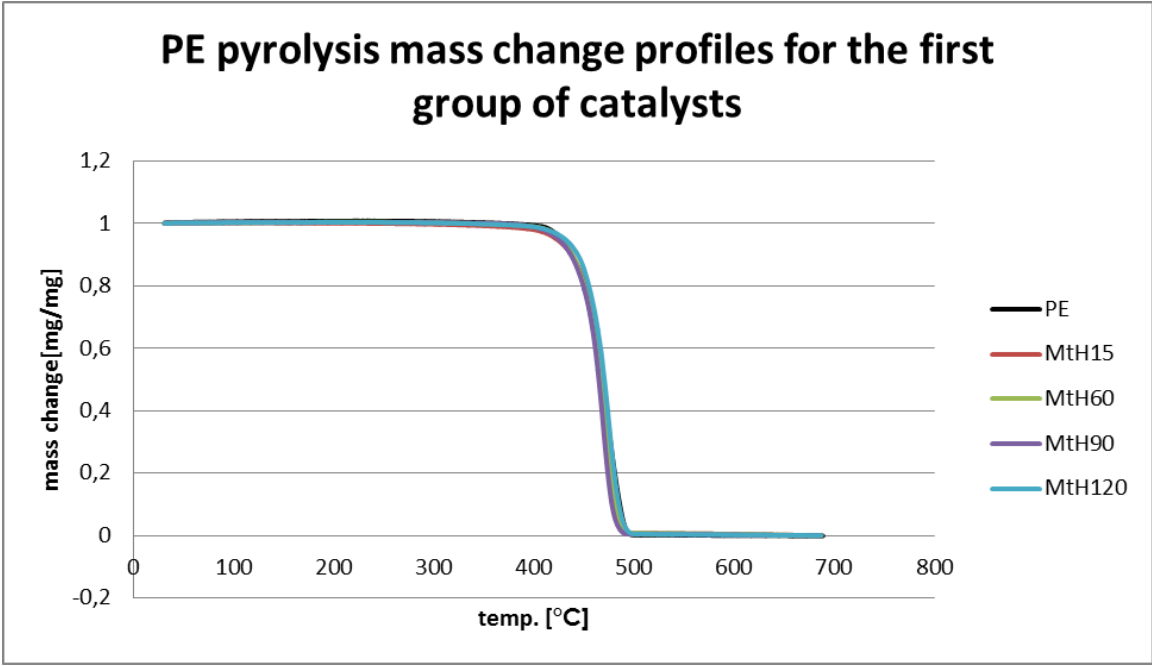


Fig. 25 TG curves obtained from the catalytic degradation of polyethylene with the first group catalysts.

The polyethylene thermal degradation curves are treated as reference curves in relation to which changes influenced by introduction of the catalyst can be observed.

From the first plot, where the heat flow is presented heat consumption of the process was obtained, by calculation of the area under the graph's second peak, which represents degradation process, the heat absorbed in the process can be estimated. Table 2 presents the ratio of the heat used in the catalytic degradation of polyethylene and heat consumed in the thermal polyethylene pyrolysis.

sample	Q _{cat.} /Q _{non-cat.}
PE+K30H15	0,727
PE+K30H60	0,773
PE+K30H90	0,735
PE+K30H120	0,794

Table 2 Share of heat consumed in the catalytic process over non-catalytic PE pyrolysis.

As expected, the introduction of the catalysts caused a drop of the heat consumption in comparison to the thermal PE degradation. It indicates that acid treated montmorillonites decreases the heat demand by more than 20% in the process (Table 2).

On the second plot (Figure 25), the mass change profiles are almost totally overlapping, which shows small, or in most of cases, no effect of used catalysts on the process, in terms of degradation temperature change.

The list of all temperatures at which polyethylene undergoes thermal and catalytic degradation using the first group of catalysts is presented in Table 3.

sample	T _{degradation} [°C]
PE	477
PE+K30H15	474
PE+K30H60	476
PE+K30H90	471
PE+K30H120	479

Table 3 Summary of thermal PE degradation temperature and catalytic degradation with the first group of catalysts tested.

It is clear that all montmorillonites treated only with acid for different lengths of time show little activity, leading to the negligible decrease in the degradation temperature. The lowest obtained temperature is noted for MtH90 catalyst and is equal to 471 °C , which gives a difference of 6 °C. Acidic activation should cause an increase in acidity of montmorillonites as well as the increase in surface area. For this reason, it was expected that the longer the effect of acid treatment of the montmorillonite the stronger the influence on the degradation reaction. But considering the results from the acidity measurements referred above, only two catalysts of the first series (K30H60 and K30H120) reflected, in fact, an increase in the number and in strength of the acid sites upon acid treatment. Although, as it can be seen in Table 2 there is no success in lowering the temperature of degradation. Moreover the catalyst modified with the longest time of acid treatment, K30H120, caused an opposite effect than intended by increasing the degradation temperature. In conclusion, there is no success or no relevant change from the economical point of view in lowering the temperature of the degradation by only acid modification of montmorillonite.

The treatment with hydrochloric acid may lead to higher surface and/or porosity, but acid treatment might also lead to the delamination of the clay structure. Since, in this series of catalysts, present better results after shorter time under the acid influence it might be expected that they have a more stable structure. What is interesting, there is no specific dependency of the degradation temperature change with the time of an acid treatment.

3.4 DSC/TG analysis for the catalytic degradation of polyethylene using the second group of catalysts

Results presented for the second group of catalysts from the Differential Scanning Calorimetry analysis and the Thermogravimetric analysis are presented in Figure 26 and 27 respectively.

The second group of catalysts consists of montmorillonite treated with acid, like the previous group tested, but also intercalated with alumina hydroxycations. Introduction of the mentioned cations into the structure of clays was performed to increase acidity, which is why better results were obtained.

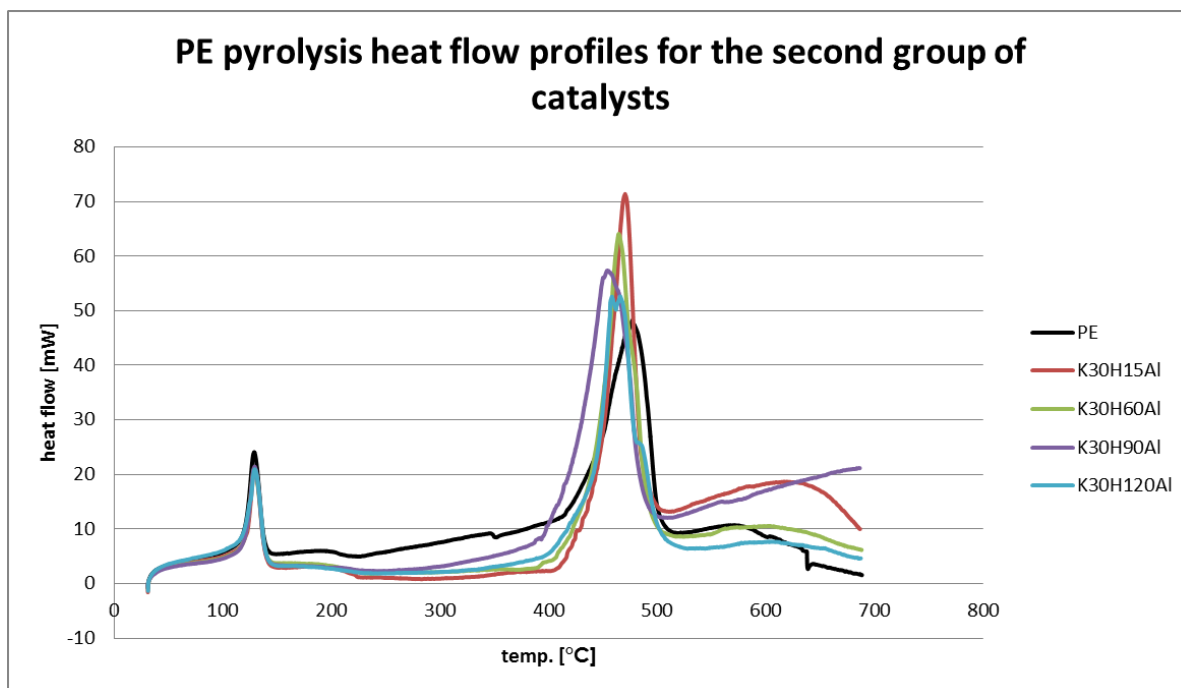


Fig. 26 Heat flow curves obtained from the catalytic degradation of polyethylene with the second group catalysts.

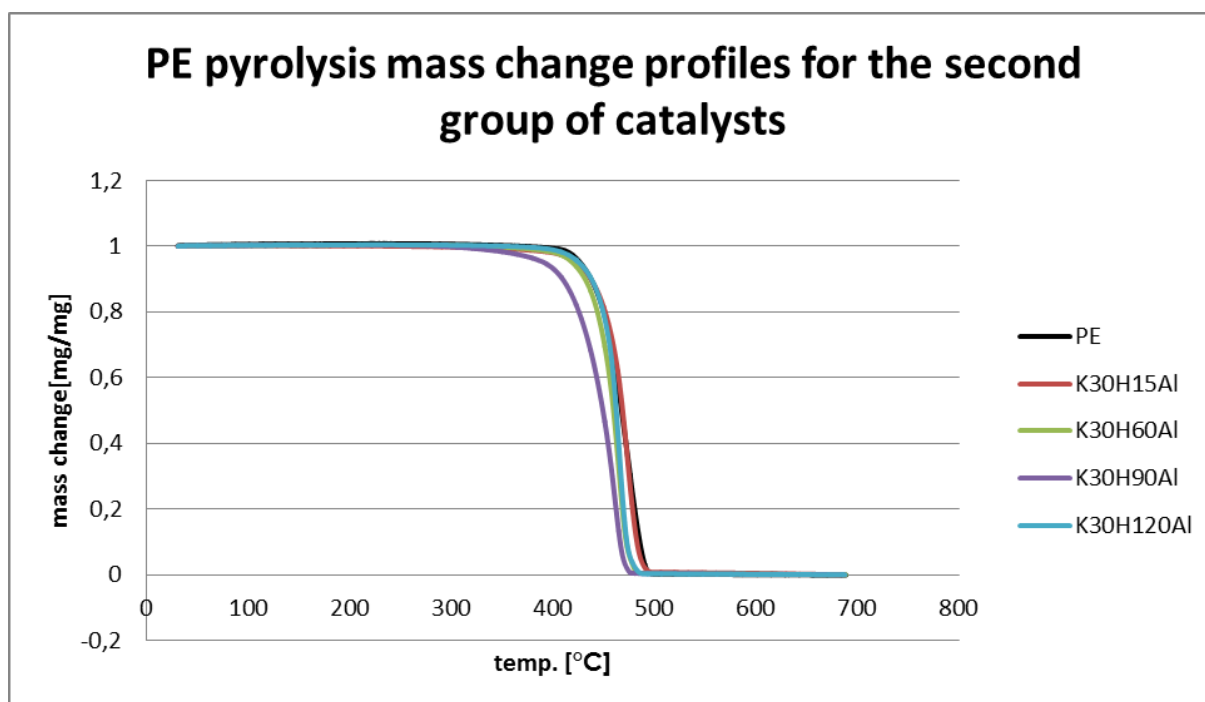


Fig. 27 TG curves obtained from the catalytic degradation of polyethylene with the second group catalysts.

The DSC signals presented in the Figure 26 for the second group of catalysts show much more varied results than the previous group. As expected, the first endothermic peak, corresponding to the

melting process is not influenced by any of the catalysts tested as all curves are fully coincident. In contrast to the melting peak the second endothermic peak recorded for each catalyst shows different trends of the degradation path. The only common feature of the degradation peaks is that they are shifted to the left of the PE degradation peak temperature. It indicates that all catalysts tested decreased the degradation temperature.

sample	Q _{cat.} /Q _{non-cat.}
PE+K30H15Al	0,925
PE+K30H60Al	0,977
PE+K30H90Al	1,048
PE+K30H120Al	0,973

Table 4 Share of heat consumed in the catalytic process over non-catalytic PE pyrolysis.

Contrary to expectation, further modification of the montmorillonites represented by the second group of catalysts resulted in a small heat consumption drop. The most unexpected change is recorded for the Mth90Al, which required even more heat than for the polyethylene thermal degradation. It might be explain by the existence of further bond-breaking process of already disconnected from the polyethylene heavy particles. The best case in terms of heat consumption is observed for Mth15Al. It showed the drop of the process heat demand for 7%. On the other hand, it represents the lowest drop of the degradation temperature.

The plot obtained from the TG analysis signals revealing a significant PE/Mth90Al pyrolysis curve shift, while all the others studied presented only a slight change.

The list of all temperatures at which polyethylene suffers thermal and catalytic degradation using the second group of catalysts is presented in Table 5.

sample	T _{degradation} [°C]
PE	477
PE+K30H15Al	471
PE+K30H60Al	465
PE+K30H90Al	454
PE+K30H120Al	466

Table 5 Summary of degradation temperature for the second group of catalysts tested.

The catalysts produced by the two modifications shows improvement in pyrolysis process in all studied samples. The smallest difference in degradation temperature noted for K30H15Al equal to 6°C is almost the same as the best obtained temperature drop for the first group tested.

The greatest influence to the pyrolysis process is shown by the K30H90Al catalyst, which presence lead to a temperature drop of 23°C. The other two investigated catalysts show 12-13°C of a difference in temperature required for the process. It indicates that cation pillared structures after a mild acid treatment noticeably decrease the activation energy of the degradation process.

3.5 DSC/TG analysis for the catalytic degradation of polyethylene using the third group of catalysts.

Results obtained from testing the third group of catalysts are presented on Figure 28 and Figure 29. The last group differs from the previous, because catalysts that belong to this group are not characterized by one common modification characteristic or origin.

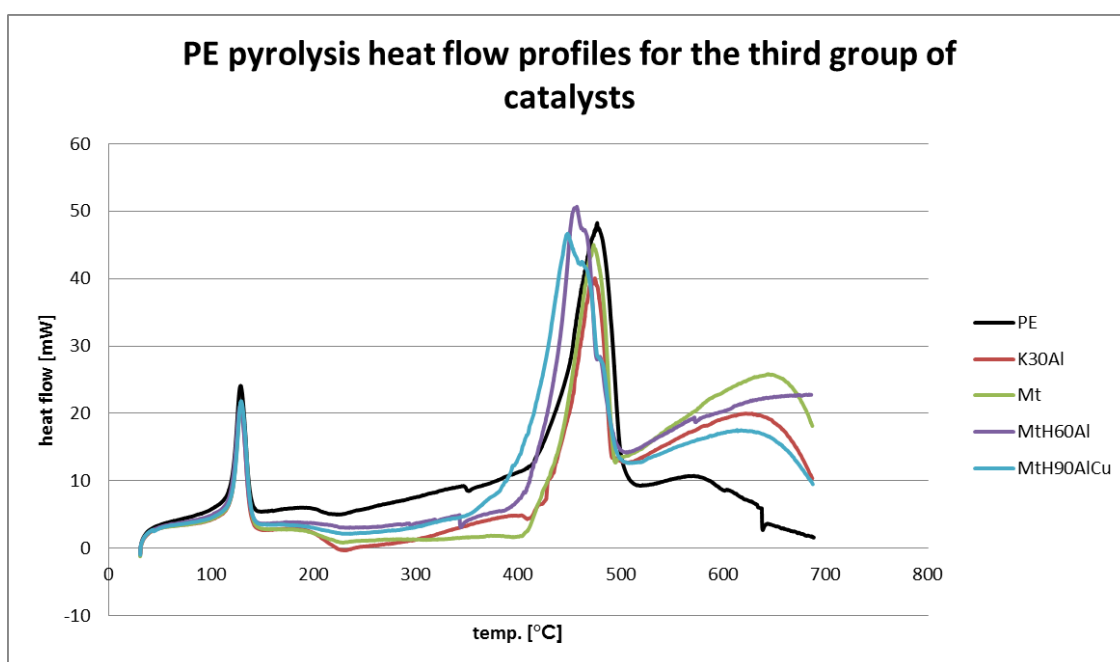


Fig. 28 Heat flow curves obtained from the catalytic degradation of polyethylene with the third group catalysts.

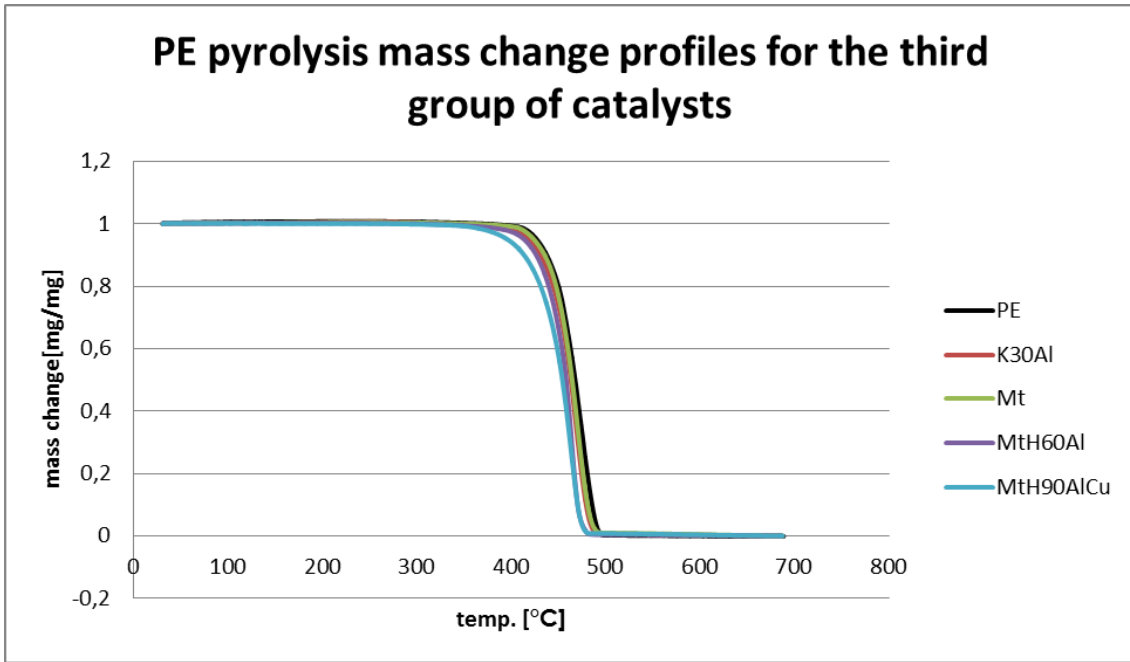


Fig. 29 TG curves obtained from the catalytic degradation of polyethylene with the third group catalysts.

In the plot obtained from the DSC analysis depicted in the Figure 28, two degradation peaks are noticeably shifted to the left side, which indicates a significant decrease of the degradation temperature. They belong to Mth60Al and Mth90AlCu catalysts introduced into the PE sample. The first mentioned catalyst Mth60Al was modified only by the cation intercalation of pure montmorillonite, with no acid pretreatment. The second one Mth90AlCu was first subjected to the hydrochloric acid treatment and then pillared with alumina hydroxycations and promoted with copper cations. Besides the temperature drop effect, the energy needed for the reaction had changed (Table 6). Comparing to the pure PE sample investigated, the introduction of Mth90AlCu slightly increased the heat demand while for the Mth60Al it decreased. Catalysts Mt and K30Al present very low influence on the degradation temperature of the process, but caused significant cut in the heat used in the reaction.

sample	$Q_{cat.}/Q_{non-cat.}$
PE+Mt	0,689
PE+Mth60Al	0,87
PE+K30Al	0,538
PE+Mth90AlCu	1,042

Table 6 Share of heat consumed in the catalytic process over non-catalytic PE pyrolysis.

In the Figure 29, where the Thermogravimetric analysis result are summarized, one curve is visibly moved from the others, and it belongs to the MtH90AlCu as expected from looking at the DSC analysis signals.

sample	Tdegradation [°C]
PE	477
PE + K30Al	475
PE + Mt	474
PE + MtH60Al	465
PE + MtH90AlCu	448

Table 7 Summary of degradation temperature for the third group of catalysts tested.

The Table 7 presents the obtained degradation temperatures. As seen from the DSC plot the lowest degradation temperature was obtained for the sample of plastic where the MtH90AlCu was introduced. The temperature change is 29°C, which is the best result in terms of temperature of all catalysts studied in this work. Second best result presents temperature drop of 12°C and it belongs to the test where MtH60Al has been used. Two remaining catalysts used in the pyrolysis process (Mt, K30Al) have shown almost unnoticeable change of the temperature: 4°C and 2 °C respectively.

3.6 Activity-acidity relationship

It is well known, that the cracking performance of montmorillonites as catalysts, including activity and selectivity, depends on their number and strength of the acid sites, together with their pore size. The conversion of hydrocarbons over montmorillonites is catalyzed by their Brönsted acid sites whose acidity was evaluated by temperature-programmed desorption (TPD) of ammonia in the previous chapter.

As studied by others [30, 31] Brönsted-type relationships relate the rate constant of reactions catalyzed by acids with dissociation constant of bases. In other words, ammonia desorption energies, which depends on the strength of the acid sites, can be related with the polyethylene degradation

reaction constant rate. This statement leads to the conclusion that activity-acidity relationships derived from acid-catalyzed reactions could be obtained for the family of montmorillonite catalysts.

The Arrhenius equation has been popularly used in the pyrolysis of different materials to present the rate data as a function of temperature (13). The Arrhenius equation is expressed as:

$$k_r = A \exp(-E_a/RT) \quad (13)$$

where k_r is the rate constant, A is the pre-exponential factor and E_a is the activation energy. The logarithmisation of pre-exponential factors (A), when plotted with the activation energies (E_a) could exhibit a linear relationship for a series of related reactions. This relation is referred to as the "compensation effect". Compensation effect is of interest to pyrolysis reaction since it expounds the relation given a group of rate processes. The linear relation may be obtained from linearized Arrhenius Equation that was expressed as follow:

$$\ln A = \ln k_r + E_a/RT \quad (14)$$

where k_r is the rate constant and T is the temperature.

Pyrolysis kinetics of plastic samples showed a considerable variation in the kinetics constants derived from using the non-isothermal thermogravimetry analysis (TGA) [2]. The variation in the kinetic constants within the same thermochemical regime for plastic samples was large and random, showing different values of activation energies. A full analysis of the influence of the acid strength distribution, using, for example, a compensation effect approach, is outside the scope of this work, but the a first approach was attempted to check the influence of acidity in the observed kinetics.

In this work, the stated above dependence was calculated for the best four catalysts tested in the polyethylene degradation process, resulting in obtaining four plots for each catalyst with two curves representing experimental data of behavior of the PE mass and a fitted model curve of the same process. Expression (14) can be fitted to the experimental mass change curve taken from the correction DSC curve after baseline removal. Due to the presence of the model curve calculated with a solver, two fitting parameters could be estimated: energy of activation of the reactions [E_a] and their rate constants [k_r].

The equation 14 was solved numerically, with use of the Euler method. The model parameters were estimated by a least-squares procedure, using the sum of the squares of the residues on the mass as the objective function, to be minimized:

$$\text{Min } Z = \sum_{\text{all data points}} [\text{experimental mass} - \text{model calculated mass}]^2 \quad (15)$$

The optimization procedure was carried out using 'Solver' tool from the Excel (© Windows) spreadsheet. The model provided a good fittings of the experimental data. The simulated curves are plotted in figures 29, 30, 31, 32 and all the kinetic parameters obtained by fitting the kinetic model for the pyrolysis of PE are listed in Table 8.

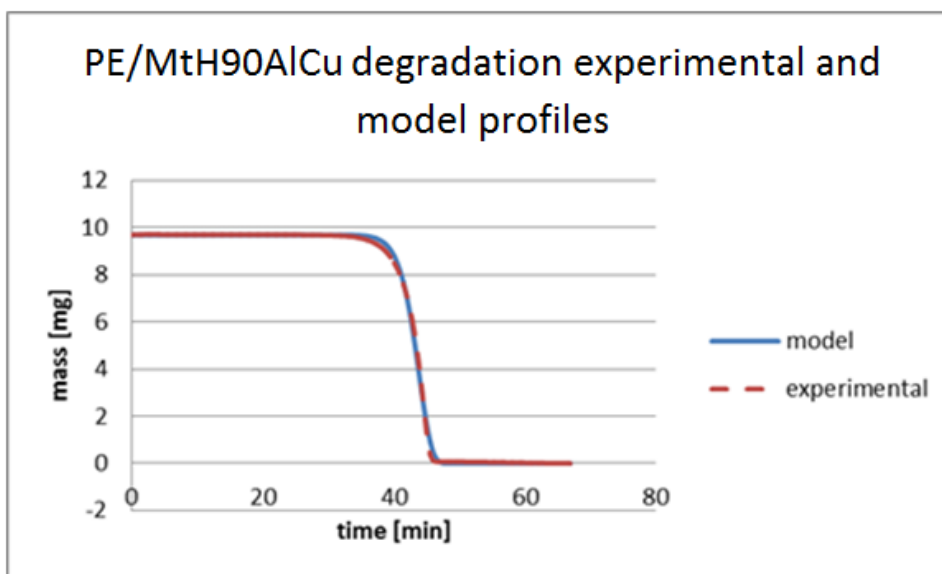


Fig. 30 Experimental and calculated mass change curves for PE pyrolysis in presence of MtH90AlCu catalyst

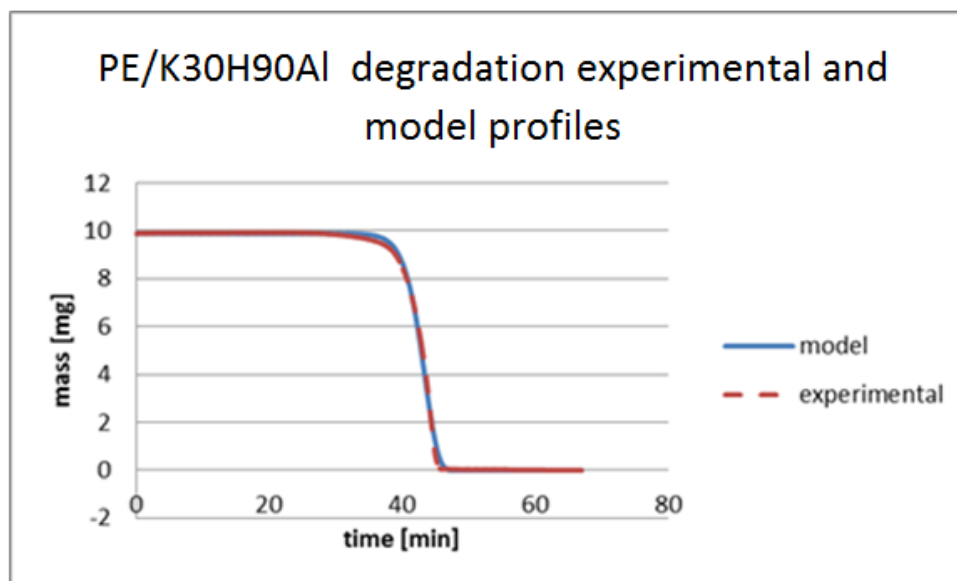


Fig. 31 Experimental and calculated mass change curves for PE pyrolysis in presence of K30H90Al catalyst

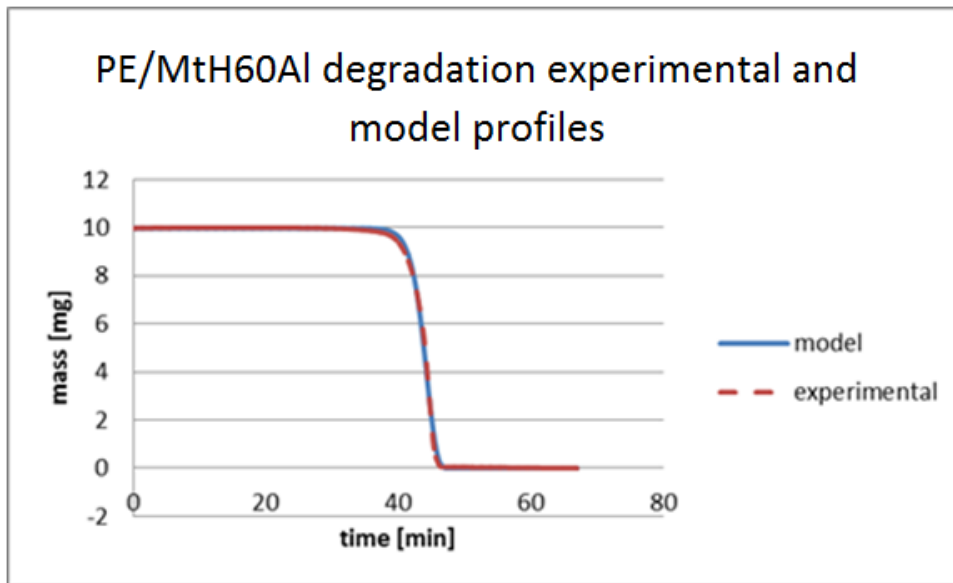


Fig. 32 Experimental and calculated mass change curves for PE pyrolysis in presence of MtH60Al catalyst

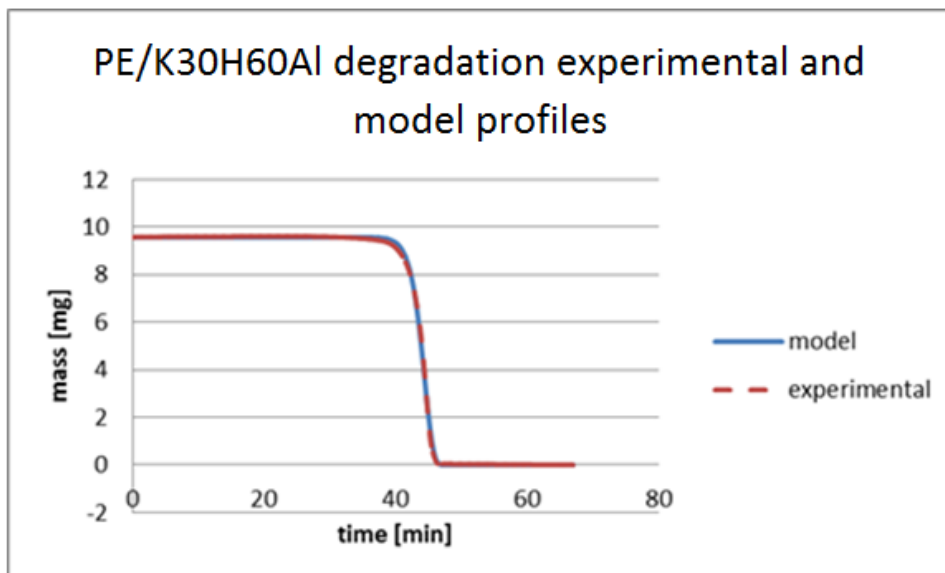


Fig. 33 Experimental and calculated mass change curves for PE pyrolysis in presence of K30H60Al catalyst

The number of active sites and the activation energy E_a for the scission of polyethylene as well as rate constant k , are presented in Table 8.

catalyst	k(T)	Ea [kJ/mol]	number of active sites
MtH90AlCu	0,0989	55850	2159,13
K30H90Al	0,1312	53222	2926,55
MtH60Al	0,0615	73081	1437,62
K30H60Al	0,0454	80963	3253,91

Table 8 Energy values, rate constants and number of acid sites obtained for polyethylene decomposition reaction and from the adsorption of ammonia over various catalysts.

Comparing MtH90AlCu and MtH60Al created from the same starting material the influence of the higher number of active sites is evident. The catalyst MtH90AlCu which affected the biggest temperature decrease in the polyethylene degradation presents a higher number of acid sites for over 700 than the MtH60Al. It seems that introduction of copper cations is highly responsible for increasing acidity. In the case of the activation energy MtH90AlCu presents lower value than the other catalyst, which confirms higher efficiency of the MtH90AlCu catalyst. For the considered above pair of catalysts it seems to be obvious that the modification procedures are an advantage.

Catalysts K30H90Al and K30H60Al, which are also made from the same base material K30, show different numbers of acid sites, but the difference is not significant. What is interesting, the amount of active sites for the catalyst K30H60Al with the smallest influence on the degradation temperature, is the highest. At the same time the activation energy value for the catalyst with the highest number of acid sites K30H60Al is the highest as well.

Obviously, obtained results show no linear relation between calculated number of acid sites and energy received from a model.

However we can see that, if we exclude for the moment K30H60Al, the catalysts with the larger amount of acid sites do present the higher frequency (pre-exponential) factors and the lower activation energies, when compared with MtH60Al. The case of K30H60Al is peculiar since it has a large number of acid sites but has the lowest frequency factor and the highest activation energy; this may be related to the fact that this catalyst has many acid sites but mostly in the low acidity range.

Most probably there are several parameters influencing degradation apart from acidity. The accessibility of porous system is one of them. Ammonia can enter even very small pores while the polymer most probably cannot. Another important parameter might be a certain strength of acid sites necessary to start the reaction. Figure 21-23 show that the distribution does not follow the same trend for all catalysts. Furthermore, montmorillonites MtH90AlCu and MtH60Al have different origin from other montmorillonites and, as montmorillonites contain different natural additives, this may also play the role.

Analyzing the model fitted into the experimental data, a more detailed look into the mass degradation processes, occurring in the sample during the pyrolysis, is required. The simultaneous use of TG and DSC signals allows us to have a clearer picture of the process. However, a detailed kinetic model is rather more complicated since it involves the simultaneous modelling of all the chemical steps, involved in the formation of light products, and the physical steps, involved in the evaporation of the products from the pan.

3.7 Deactivation study

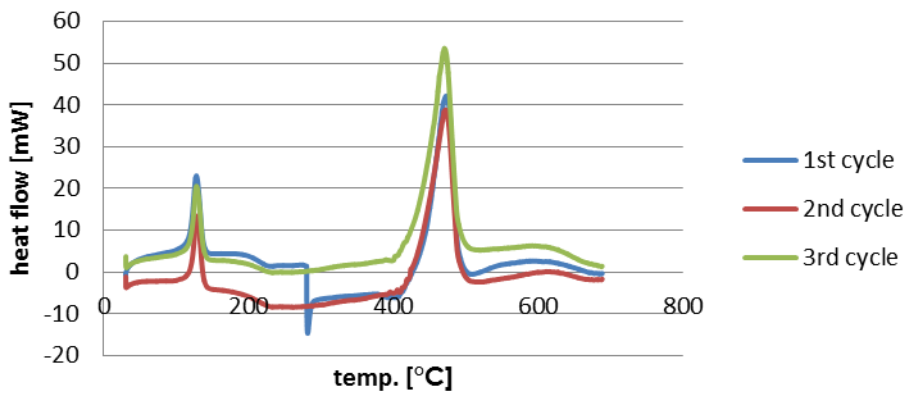
The catalyst deactivation in the waste plastic pyrolysis process is mostly caused by poisoning and coking. For the poisoning of catalyst contaminants, such as heavy metals, play a major role. The formation of deposits is provoked by hydrocarbon reactants and products.

In this study loss in performance causing deactivation is investigated with the focus on the surface blocking phenomena. It is due to the fact that only pure polyethylene is pyrolysed and it does not contain any other compounds, so the poisoning effect is not likely to happen.

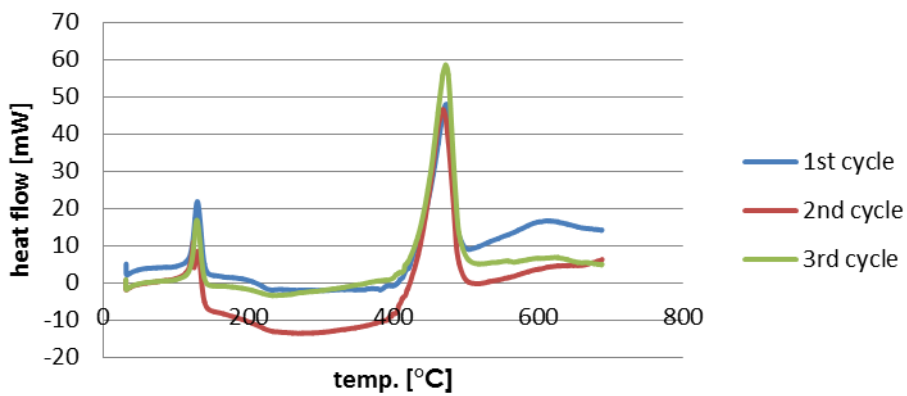
The study of deactivation was carried out for three catalysts which showed the strongest influence on the polyethylene pyrolysis process: MtH90AlCu, K30H90Al, MtH60Al. To test the activity, the procedure explained below was implemented in three attempts for each catalyst in order to avoid obtaining incorrect results. The way of conducting the test is related to the separate issue concerning a careful control of the catalyst hydration state, without which the study would be incorrect.

The experiments were carried out for the 10 mg of polyethylene with 1 mg of the catalyst under the heating rate of 10°C/min. Each experiment consisted of 3 cycles. Each cycle follows the same sequence of steps described in the chapter 3.1. After the first cycle a new, more or less equal, amount of polyethylene was added to the catalyst used in the previous cycle and then the action was repeated for the third cycle. This procedure allowed to check if the catalysts still retained the activity in the following cycles.

a Mth60Al first activation test - DSC analysis



b Mth60Al second activation test - DSC analysis



c Mth60Al third activation test - DSC analysis

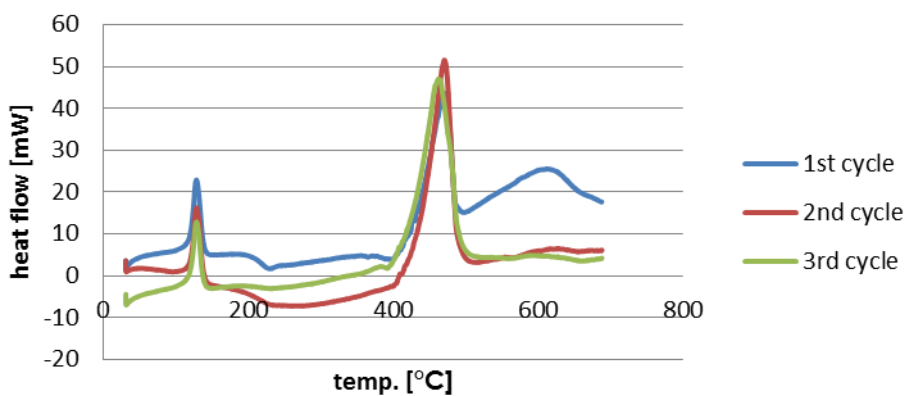
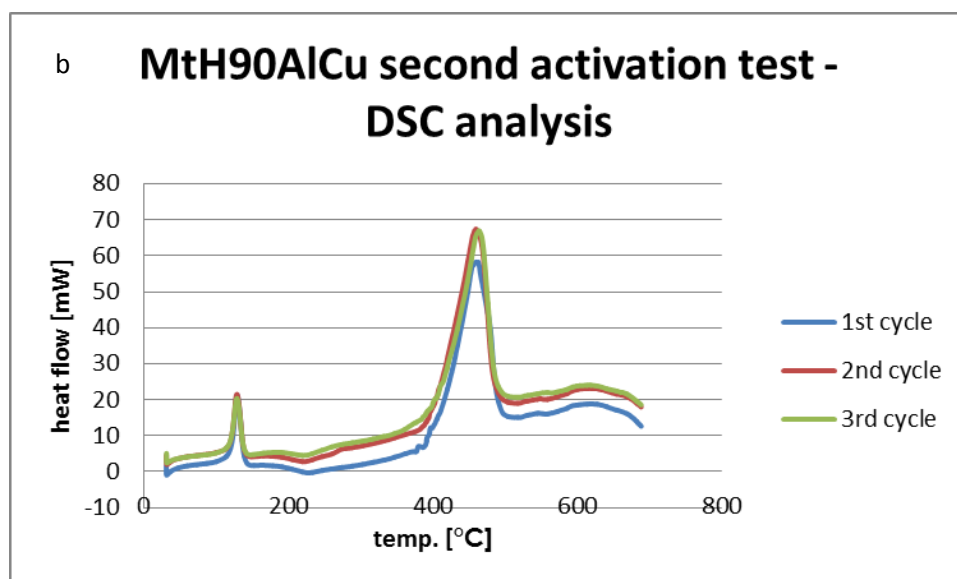
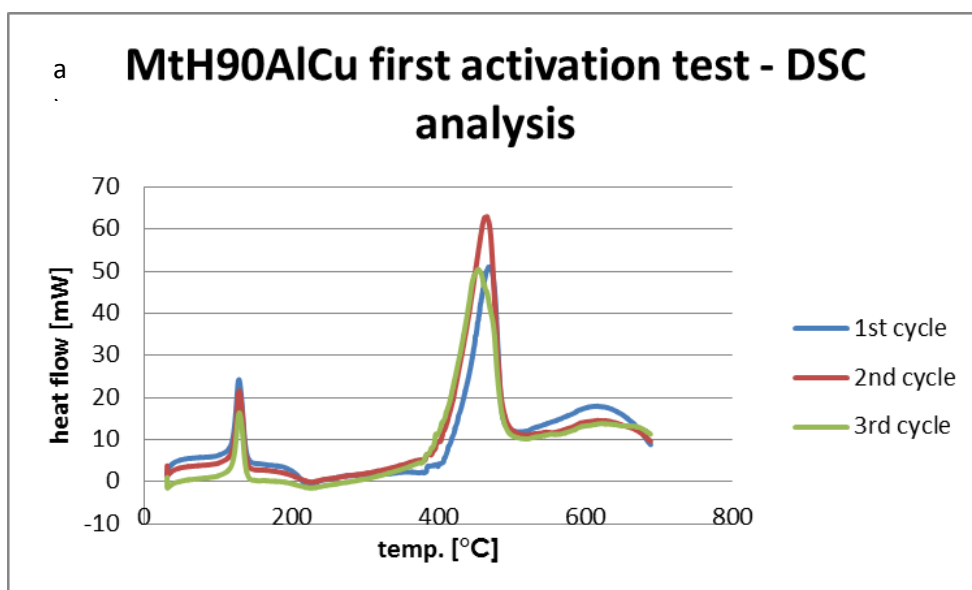


Fig. 34 DSC analysis signals obtained for the a) first test, b) second test, c) third test in deactivation study of PE/MtH60Al sample



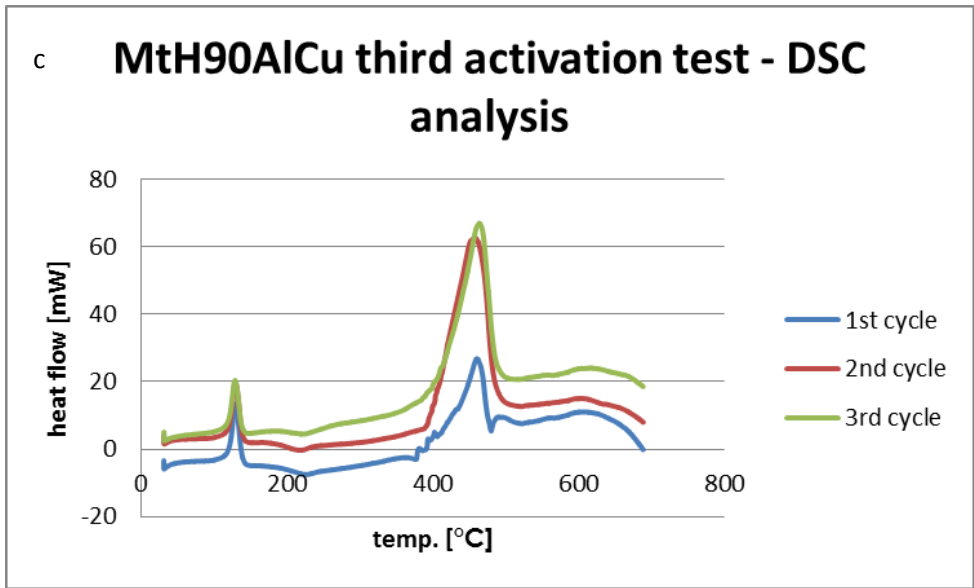
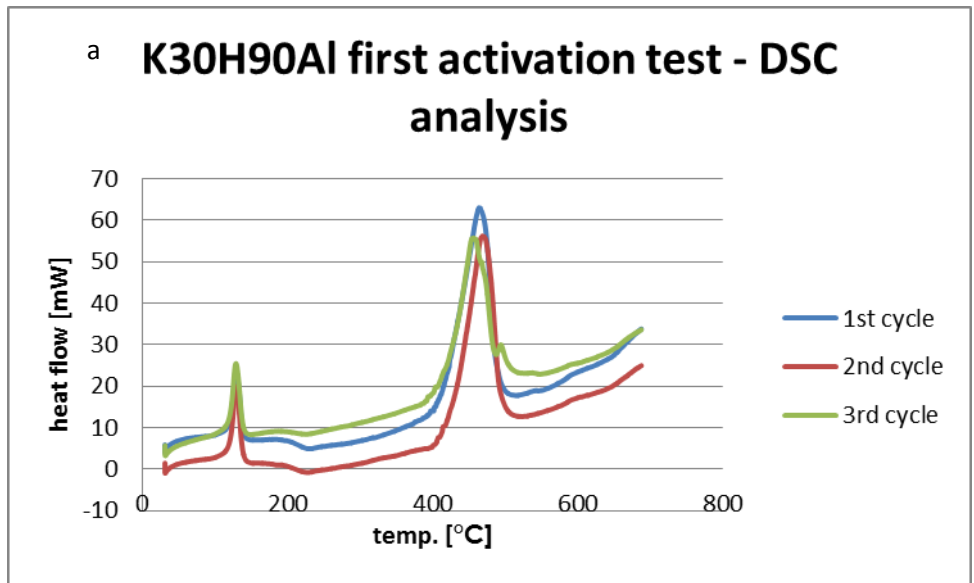


Fig. 35 DSC analysis signals obtained for the a) first test, b) second test, c) third test in deactivation study of PE/MtH90AlCu sample



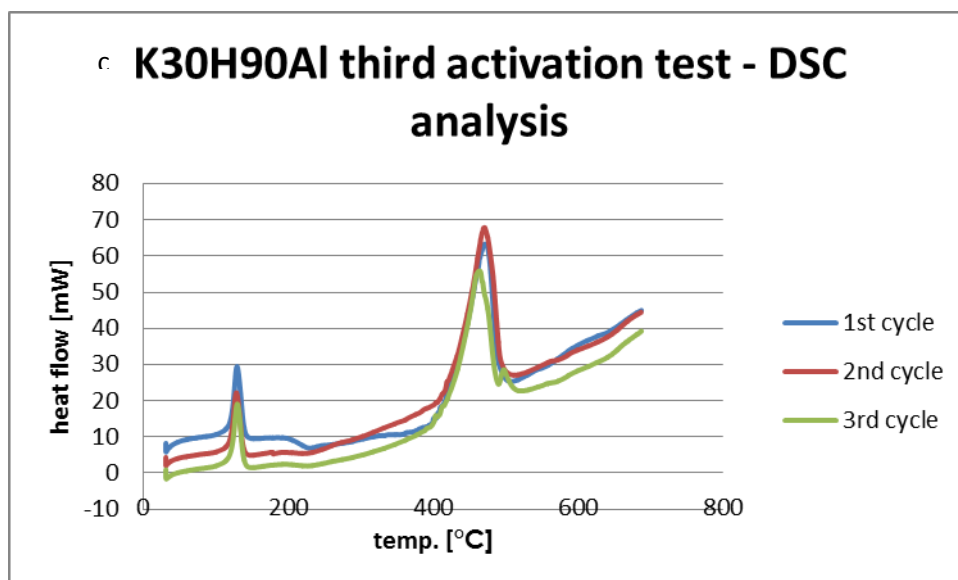
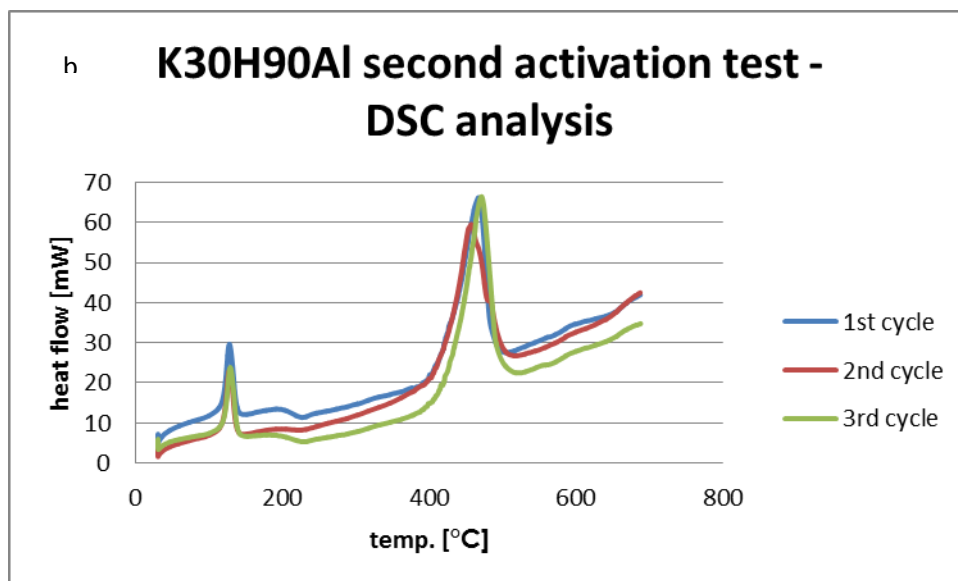


Fig. 36 DSC analysis signals obtained for the a) first test, b) second test, c) third test in deactivation study of PE/K30H90Al sample

As observed in Figure 34 Mth60Al catalyst reduced the temperature of degradation of polyethylene in all three cycles for all three attempts conducted. Obtained peaks show fractional difference in position indicating similar melting and degradation temperatures. This means that deactivation does not take place significantly and the level of activity was maintained in all studied cycles. Also there is little difference in the shape of the peak representing heat demand during in the pyrolysis process.

The second catalyst deactivation studies are presented in Figure 35. As in the first case reduction of the degradation temperature was present in all attempts cycles. It can be seen that, introduction of

new portions of polymer in the following cycles has no significant influence, in terms of change of the degradation temperature, on the activity of Mth90AlCu catalyst. While the presence of repeatedly used catalyst keep maintaining the degradation temperature, which proves that the activation state of the catalyst has not changed significantly, the heat demand slightly changes through cycles. In the Figure 36 the results for PE/K30H90Al are presented, and similarly as in the previous examples the degradation temperature was maintained in all cycles. Temperature in comparison with the reference first cycle results has shown very small or none of the difference. This indicates that no deactivation effect was noted.

All degradation temperatures for tested catalysts: Mth60Al, Mth90AlCu and K30H90Al are shown in Table 9, Table 10 and Table 11, respectively.

Mth60Al	first cycle	second cycle	third cycle
first activation test	472	472	470
second activation test	473	468	472
third activation test	471	471	464

Table 9 Degradation temperature for PE with Mth60Al obtained from DSC/TG analysis.

From above table, presenting results for the Mth60Al catalyst, it is clear that, the catalyst has not lost its activity, with succeeding cycles but, on the contrary, albeit slightly, improved its performance. Unfortunately, the temperature improvement is not high. In the best case the degradation temperature was decreased only by 6°C. The increase in catalyst activity in the second and third cycle is quite unusual but it can be related to the fact that the calcination before DSC/TG experiment, which main reason is to stabilize the porous structure or otherwise influenced it, was conducted in 500°C, which is lower than the maximum temperature used in the first cycle of degradation in the deactivation test. There is a possibility that this higher temperature of the experiment led to the structural change of catalyst, influencing its cracking features. It is also possible that for the pillared montmorillonites, the Al pillars are stable only to a certain temperature, which is why heating them three times to 700°C may have resulted in the destruction of pillars. Even though Al pillars undergo degradation at c.a. 750-800°C. Unfortunately, it cannot be uniquely identified, based only on the DSC/TGA analysis, and for further clarification one needs more experiments.

MtH90AlCu	first cycle	second cycle	third cycle
first activation test	466	466	462
second activation test	459	460	463
third activation test	460	458	463

Table 10 Degradation temperature for PE with MtH90AlCu obtained from DSC/TG analysis.

Table 10 is a set of results received from MtH90AlCu testing. The following cycle temperatures slightly increase giving in the worst attempt checked 4°C of the parameter growth. The obtained change is small and the temperature level in the first attempt had dropped. This means that some deactivation took place but certain activity was still maintained. A possible explanation for this deactivation might be caused by decreasing of both total external surface and the number of acidic sites decrease.

K30H90Al	first cycle	second cycle	third cycle
first activation test	464	468	468
second activation test	467	457	471
third activation test	469	469	462

Table 11 Degradation temperature for PE with K30H90Al obtained from DSC/TG analysis.

The Table 11 containing results from K30H90Al deactivation investigation presents that the activity is more or less maintained but no activation is clearly observed. For the first attempt activation decreases, and both temperatures from two next cycles are higher than the reference one. In the second test the performance of the catalyst in the second cycle has significantly increased, decreasing the temperature for 10°C. Surprisingly, the third run for the same catalyst shows deactivation occurrence. In the last attempt the catalyst shows worse result for the second run than for the third one, where the temperature dropped for 7°C. This confusion results might be explained by some reaction occurrence, which influenced catalyst performance.

Unfortunately, temperatures obtained for the reference first cycle are higher compared to results obtained from the first pyrolysis test conducted.

At the very first polyethylene degradation test with the Mth60Al catalyst the degradation temperature equal to 457 °C, in the case of Mth90AlCu 448°C and for the K30H90Al the first obtained temperature was at the level of 454°C.

This is probably due to the loss of original properties of catalysts, caused by the most probable adsorption of molecules from the external environment. These results indicate that these catalysts are extremely sensitive to the environment in which they are stored and careful control of these conditions, for instance if they are stored under constant humidity conditions to protect the surface, this kind of difficulties can be reduced.

3.7.1 Pyrolysis heat demand and internal reactions relation.

It has been observed that although degradation of the polymer is achieved in the same way in each of the test cycles, the need for heating in each run of the process is different. This subsection is devoted to the comparison of differences in energy consumption during the processes and the mass loss effect.

The survey covers three catalysts that showed the best activity in the pyrolysis process of polyethylene. The comparison refers to one activity test consisting of three cycles and the methodology of the tests corresponds to that described in the above section.

Mth60Al DSC/TG analysis:

The pure montmorillonite with cation exchange modification represents third best catalyst, in this study, on the PE pyrolysis performance. It also shows high degree of stability in subsequent tests carried out, but the level of heat flow recorded in the process differs.

To see whether the heat is supplied with no mass loss, indicating bond breaking that leads to heavy molecules weight derivatives were calculated and presented for each of the cycle.

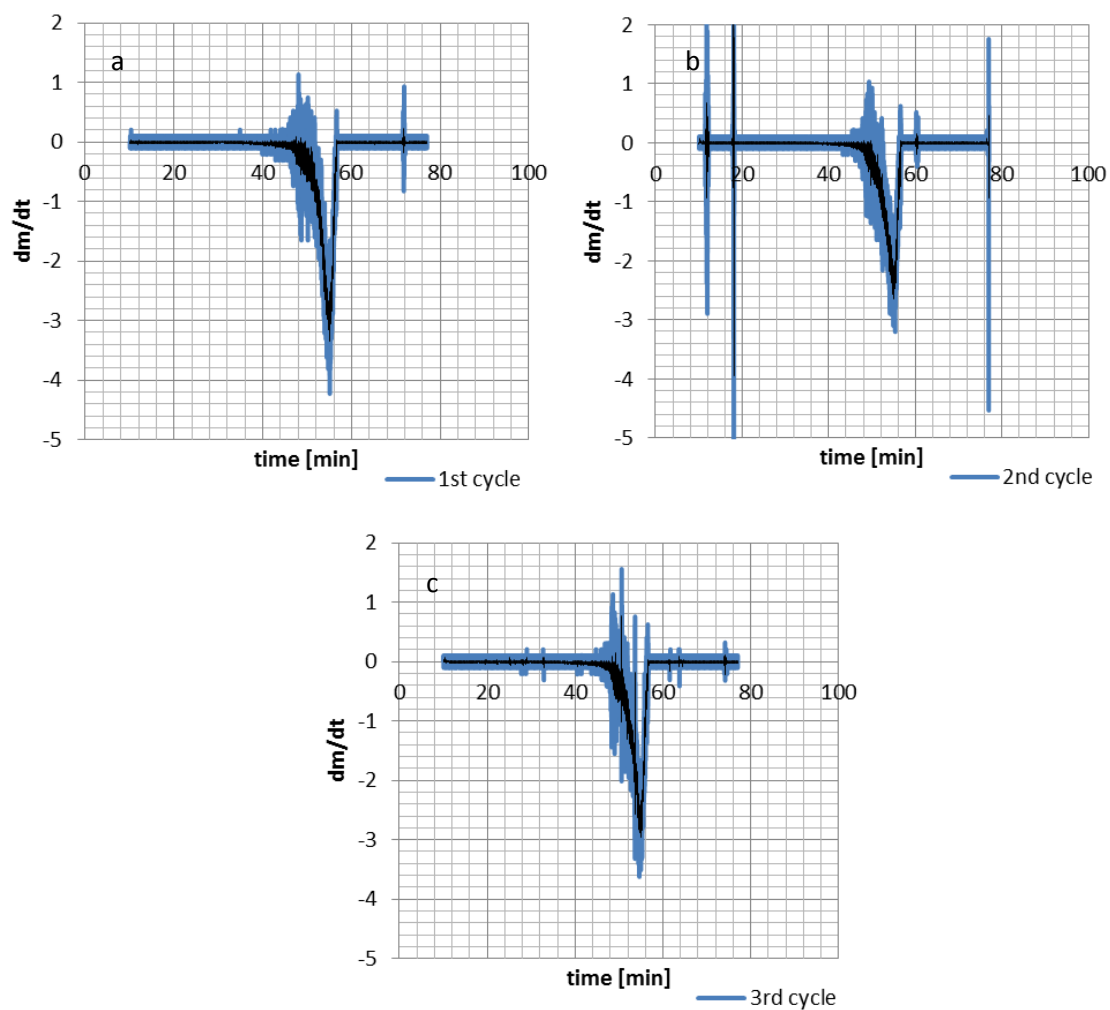


Fig. 37 Mass derivatives obtained for PE/MtH60Al pyrolysis in a) first cycle, b) second cycle, c) third cycle.

Derivatives graphs indicate that the amount of mass subject to degradation in the first cycle is the highest, but the lowest polymer conversion is obtained for the second cycle. Although some changes are noted the effectiveness of the catalyst and the process is unchanged, as it can be seen in the Figure 38.

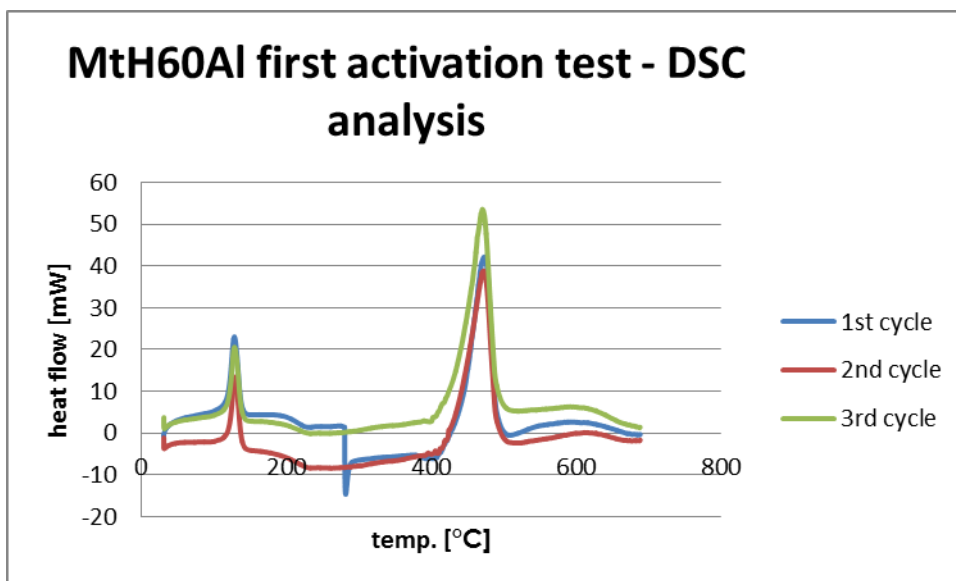
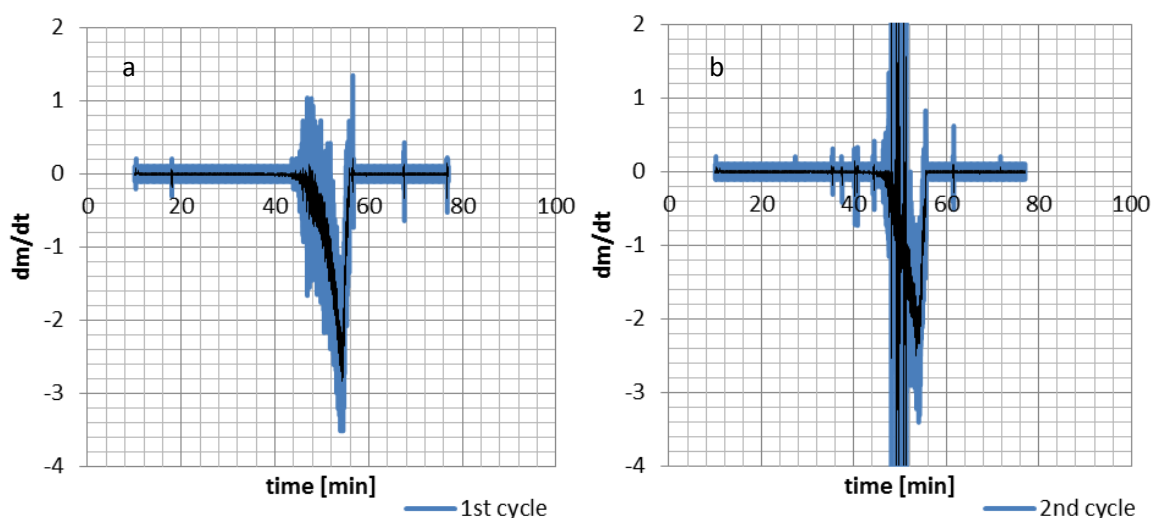


Fig. 38 DSC/TG analysis results for the PE/Mth60Al pyrolysis from the deactivation study.

Mth90AlCu DSC/TG analysis:

Montmorillonite which was acid activated, pillared and impregnated with Cu²⁺ represents the best results in terms of decreasing degradation temperature in polyethylene pyrolysis. On the other hand, it is the most susceptible to deactivation from all catalysts tested in the deactivation study.

The change of mass over time is the highest for the first cycle representation curve and successively lower for next two cycles conducted (Figure 39). It can be clearly observed in Figure 40 that on the heat flow curve representing the first cycle the degradation peak indicate the same temperature as peaks representing two consecutive cycles confirming the lack of decline in effectiveness.



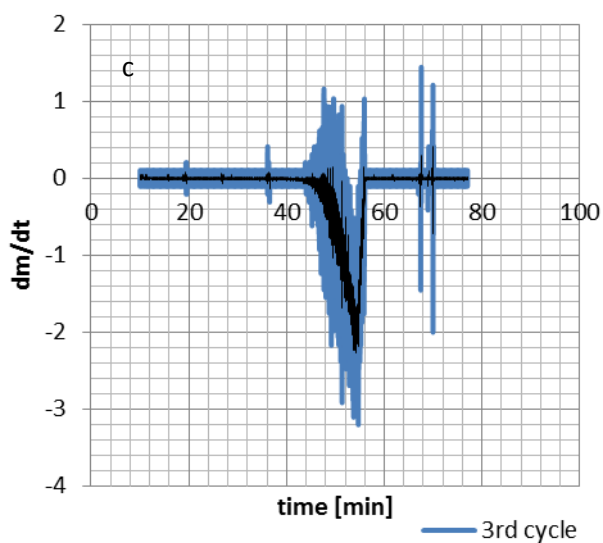


Fig. 39 Mass derivatives obtained for PE/MtH90AlCu pyrolysis in a) first cycle, b) second cycle, c) third cycle

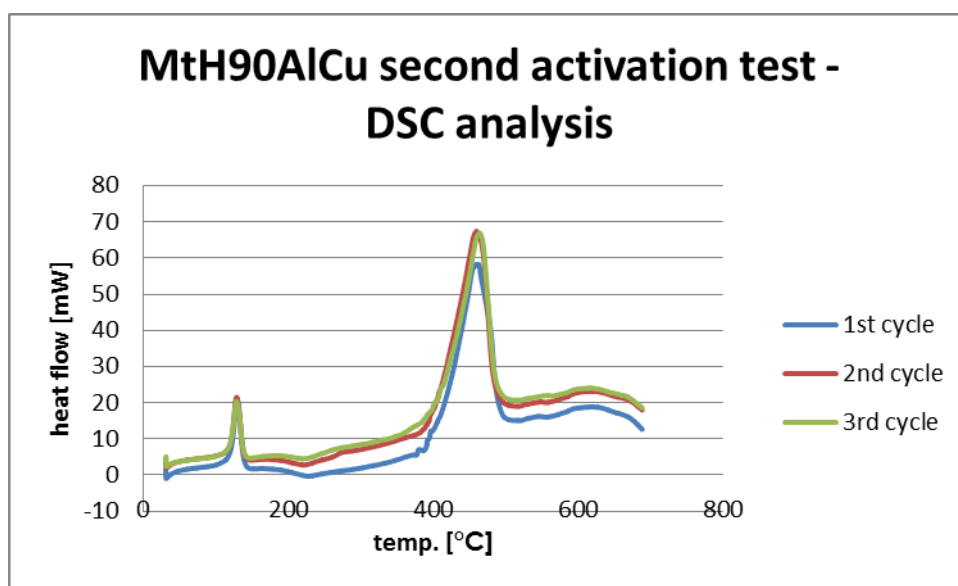


Fig. 40 DSC/TG analysis results for the PE/MtH90AlCu pyrolysis from the deactivation study.

K30H90Al DSC/TG analysis:

The last catalyst discussed in this chapter is modified with acid and alumina hydroxides montmorillonite K30H90Al. It shows the best performance at the first cycle, while at the two next cycles degradation results are slightly worse.

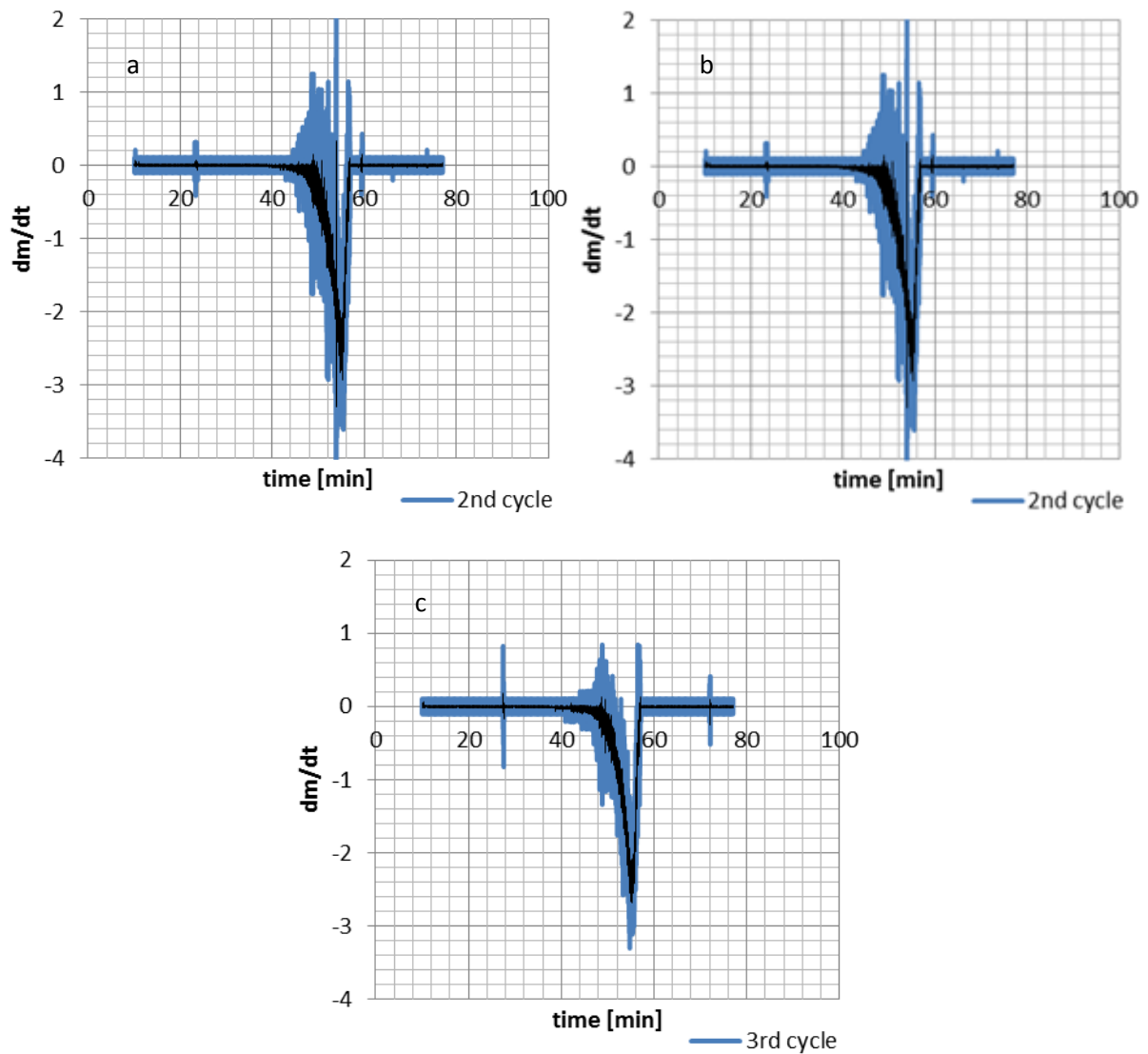


Fig.41 Mass derivatives obtained for PE/K30H90Al pyrolysis in a) first cycle, b) second cycle, c) third cycle.

Looking at the derivative plots it can be noticed that for the lowest degradation temperature received the mass conversion is in average: two units of mass per unit of time. And for higher temperatures of degradation this variation is higher. It shows that even if the activation drops a little, the mass change goes faster in the following cycles. It can be explained by high temperature from the first cycle influencing the structure of the catalyst in a way that the pyrolysis proceeds in a shorter time.

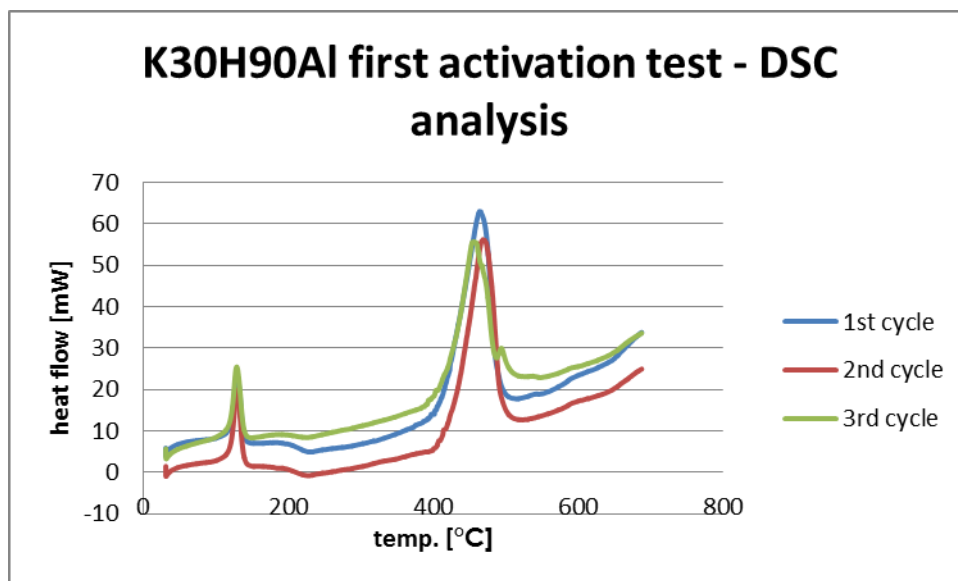


Fig. 42 DSC/TG analysis results for the PE/K30H90Al pyrolysis from the deactivation study.

The DSC/TG signals showing the highest effectiveness in a process for the third run conducted by resulting in degradation temperature slight drop. However, still all results in terms of degradation temperature are very similar.

3.8 Pyrolysis of waste plastics.

This chapter contain the results and summation of the pyrolysis of four different types of waste plastics in the presence of three different catalysts showing the best results in PE pyrolysis process. Namely, they are: Mth60Al, Mth90AlCu and K30H90Al.

Investigated waste plastics are sampled form a group of four plastic materials described as follows:

1. Electric cables containing aluminum cations and flame retardants.
2. Electric cables containing copper cations and flame retardants.
3. Electric cables containing aluminum cations and flame retardants, but obtained from another source than material 1.
4. Three times washed mixture of different plastics (mostly PP and PE materials) containing fibers and water.

Waste plastic materials samples were labeled by the supplier with specified substitute names, which will be used in further description of the study:

- A3 as an electric cables containing aluminum cations and flame retardants sample
- A6 as an electric cables containing copper cations and flame retardants sample
- A5 as an electric cables containing aluminum cations and flame retardants, but obtained from another source than material 1 sample
- A2 as a three times washed mixture of different plastic (mostly PP and PE materials) containing fibers and water sample.

The methods and techniques used to study the degradation of waste plastic materials are the same as described in the chapter dedicated to pyrolysis process investigation.

DSC/TG analysis of A3/catalyst:

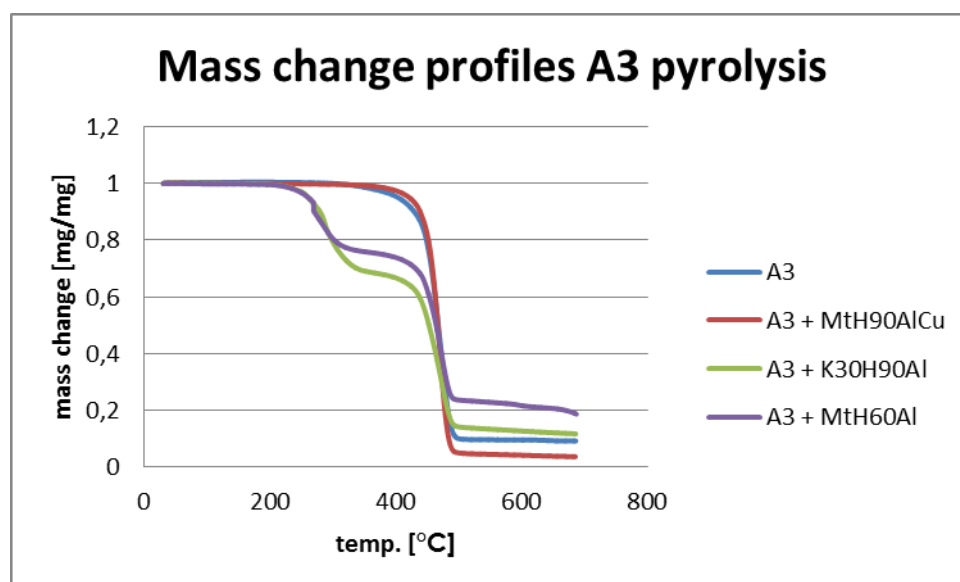


Fig.43 Summary of curves obtained from TG analysis during the pyrolysis of A3 in the presence of various catalysts.

The TG analysis signals of the first waste plastic tested (Figure 43) shows different mass change profiles for each catalyst used on the process. As it can be observed Mth90AlCu catalyst did not achieve the expected results, but, in contrast, slightly increased the degradation temperature (Table 12). However, the presence of the catalyst led to almost no solid residues remained after the reaction. In two other cases represented by green and purple curve on the plot, the degradation of mass seems to proceed in two stages. It is noted that the mass loss started to appear at much lower temperatures, than for the reference blue curve. In presence of K30H90Al one third of the total mass has decreased before reaching 400°C, and in the presence of Mth60Al catalyst, one fourth of mass. The big difference, however, is the mass of solids residues left after the process. While the K30H90Al

cause very similar amount of residues produced as in a case of pure A3 pyrolysis, the MtH60Al presence is responsible for two times bigger amount of residues.

The reason why two-stage mass decreasing phenomena appeared can be related with low homogenized mixture of the investigated waste plastic material.

The DSC analysis results presented on the Figure 44 show much lower heat consumption recorded for all types of catalysts used, in contrast to the pure-A3 pyrolysis. Unfortunately, the catalytic degradation temperature taken from all tests conducted is higher than the temperature obtain in thermal degradation as shown in Table 12.

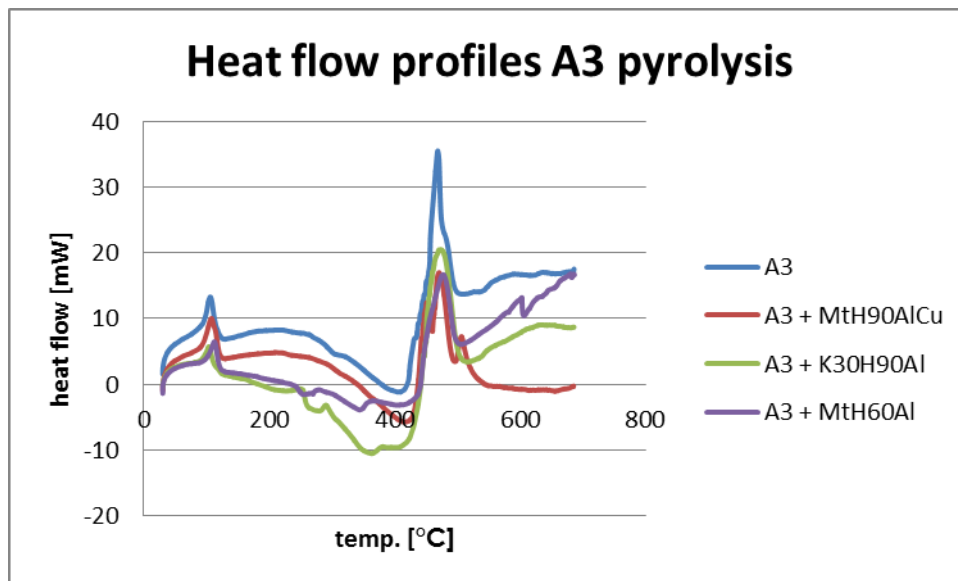


Fig.44 Summary of curves obtained from DSC analysis during the pyrolysis of A3 in the presence of various catalysts.

sample	Tdegradation [°C]
A3	468
A3+MtH90AlCu	472
A3+K30H90Al	481
A3+MtH60Al	482

Table 12 Degradation temperatures obtain in pyrolysis of the A3 material with different catalysts.

Looking at the Table 12 it is clear that the use of the tested catalysts is not appropriate for the pyrolysis of electric cables containing aluminum cations and flame retardants sample.

DSC/TG analysis of A6/catalyst:

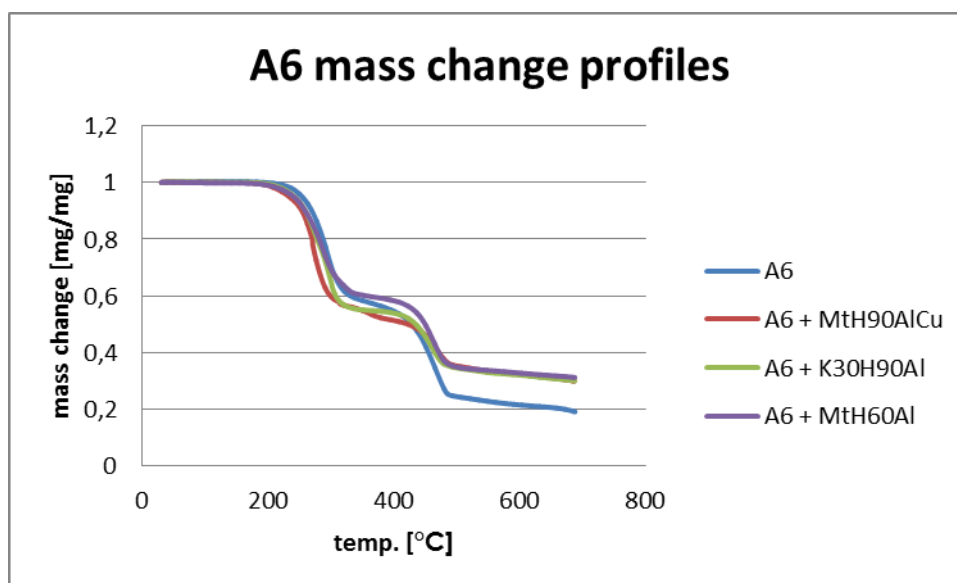


Fig.45 Summary of curves obtained from TG analysis during the pyrolysis of A6 in the presence of various catalysts.

In the case of the second plastic material tested A6, all mass change representation curves show the same trend of two-stage mass degradation. Another common resulting feature is that all catalysts used caused higher solid products formation, than in a case where no catalyst was used. It can be explained by the presence of plastic adjuvants stuck on the surface, as a result of which the catalyst is covered with some solid compounds. In the presence of Mth90AlCu the first stage of weight degradation began faster than in other tests carried out, which can be seen in the Figure 46. However, the second stage of mass degradation is improved not by the Mth90AlCu but K30H90Al used. Consequently, the best impact on the A6 pyrolysis was registered in case of the latter catalyst. The last catalyst tested – Mth60Al – was characterized by the delayed process with the increased temperatures of degradation (Table 13).

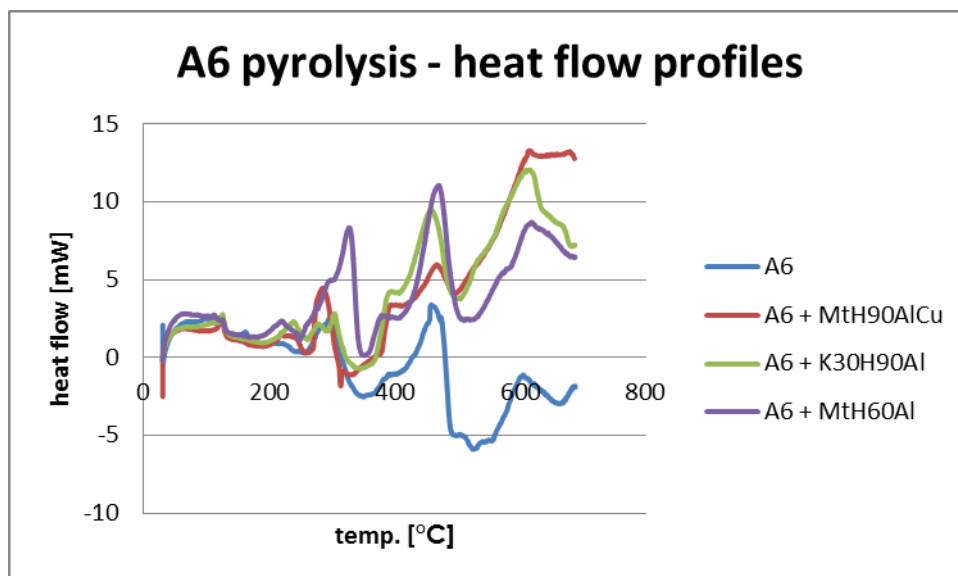


Fig.46 Summary of curves obtained from DSC analysis during the pyrolysis of A6 in the presence of various catalysts.

sample	Tdegradation [°C]	
A6	296	464
A6+MtH90AlCu	287	470
A6+K30H90Al	304	460
A6+MtH60Al	325	471

Table 13 Degradation temperatures obtain in pyrolysis of the A6 material with different catalysts.

As presented in the Table 13 the temperature improvement does not occur for both degradation stages for one catalyst. For MtH90AlCu only the first stage temperature had changed and in a case of K30H90Al only the second stage temperature.

DSC/TG analysis of A5/catalyst:

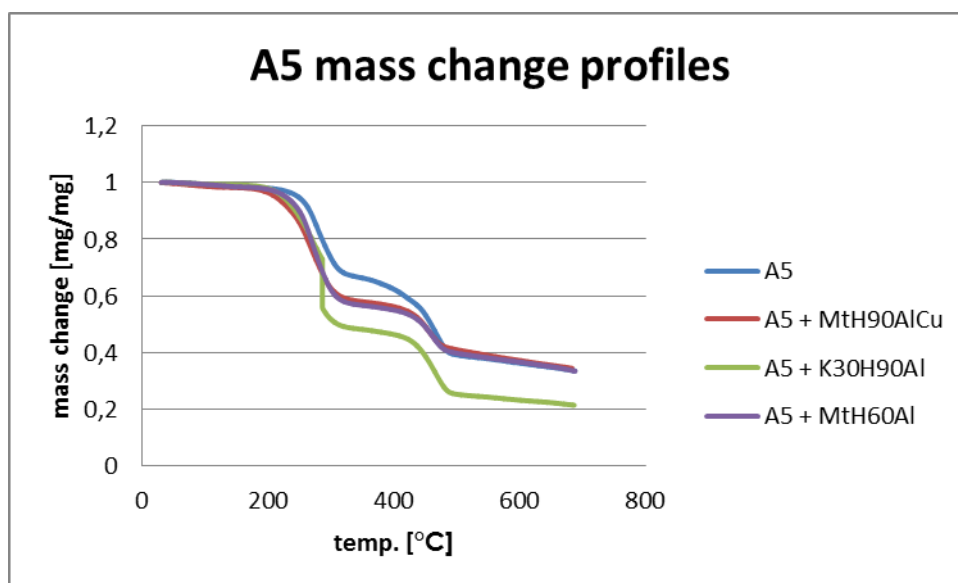


Fig.47 Summary of curves obtained from TG analysis during the pyrolysis of A5 in the presence of various catalysts.

During the test for the next waste plastic sample, again two stage degradation occurred. The A5 pyrolysis process results presented in Figure 47 indicate that all catalysts accelerated the degradation in both stages. It is also important to emphasize that the catalysts influenced solid residues appearance to a different degree. While the MtH90AlCu and MtH60Al catalysts has not affected the amount of solid products, the K30H90Al presence decreased residues mass by 43%. Unfortunately, the green curve shows an experimental problem because there is sudden change in mass around 300° C, which requires further tests to confirm the correct effect on residues.

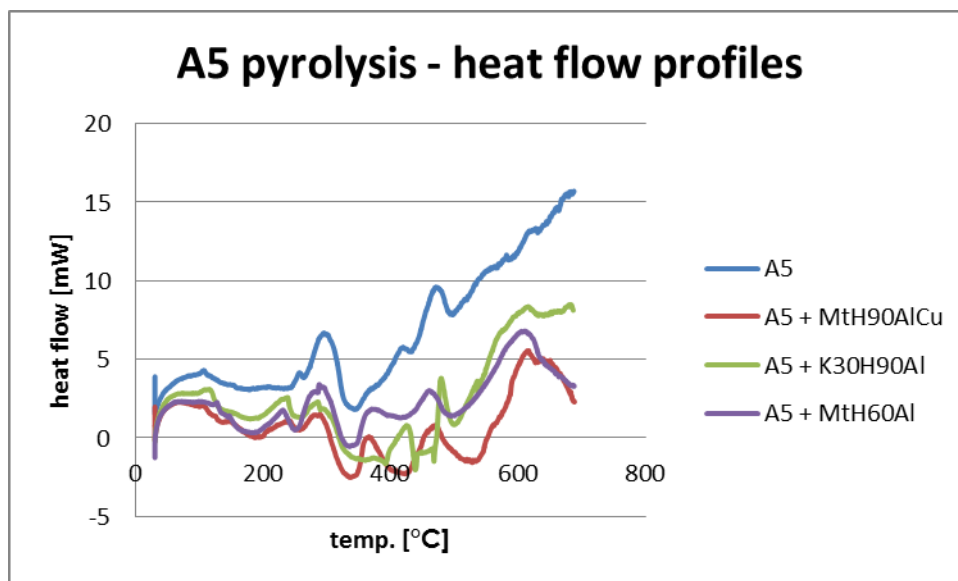


Fig.48 Summary of curves obtained from DSC analysis during the pyrolysis of A5 in the presence of various catalysts.

sample	Tdegradation [°C]	
A5	294	472
A5+MtH90AlCu	283	473
A5+K30H90Al	286	480
A5+MtH60Al	290	460

Table 14 Degradation temperatures obtain in pyrolysis of the A5 material with different catalysts.

The DSC analysis signal curves shown in the Figure 48 present very turbulent heat flow tendencies, which might have been caused by high diversification of the plastic composition. It is interesting to note that the use of catalyst greatly affected the heat consumption in a process, in all tests performed. To properly analyze the DSC curves a further look at the second cycles would be necessary. Nevertheless, the „turbulent” aspect is more likely due to the very heterogeneous nature of the waste material and its interaction with the catalyst. The most „turbulent” curve is the K30H90Al one which as seen in the weight curve has some experimental problem.

The catalysts influence on the degradation temperature is presented in the Table 14, which shows that all first-stage degradation temperatures are improved by the catalysts. Unfortunately, it is not a case with the second-stage degradation temperature, which was decreased by only one catalyst MtH60Al by 12 °C. Oddly enough it means, that only MtH60Al catalyst presence improved the

pyrolysis of the electric cables containing aluminum cations and flame retardants, while for the A3 sample with the same composition but obtained from another source Mth60Al catalyst caused increase in the degradation temperature.

DSC/TG analysis of A2/catalyst:

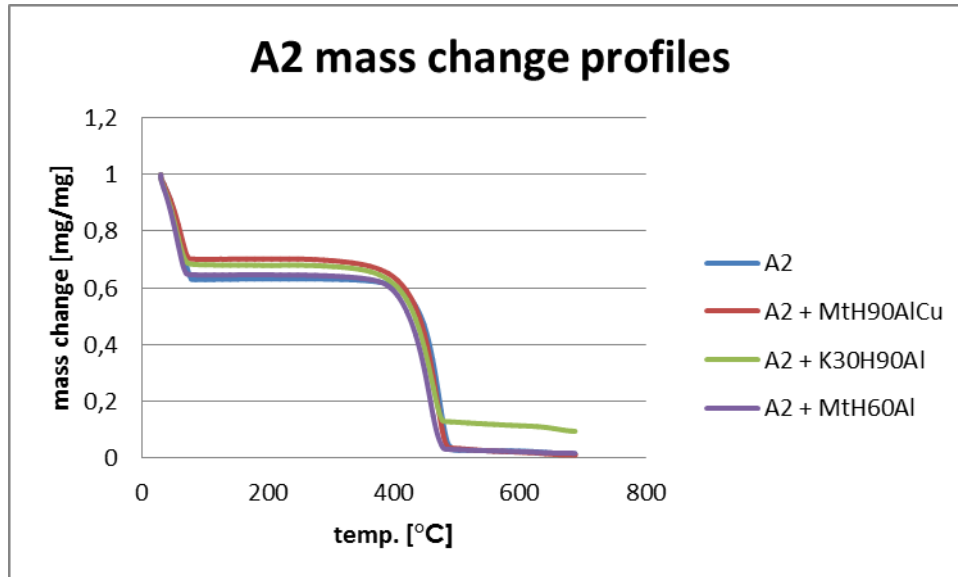


Fig.49 Summary of curves obtained from TG analysis during the pyrolysis of A2 in the presence of various catalysts.

In the pyrolysis of three times washed mixture of different plastic containing fibers and water sample the first drop in weight at the beginning of the process is caused by water evaporation. It leads to mass decrease of around 40% as shown in the Figure 49 and also to high heat consumption presented in the Figure 50. As the TG analysis chart shows the pyrolysis proceeds in one stage mass degradation presenting the same trend for all tests conducted. The only easily seen difference is the solid residues amount. The K30H90Al catalyst inhibited the total degradation, while in other cases almost no solid residues were produced.

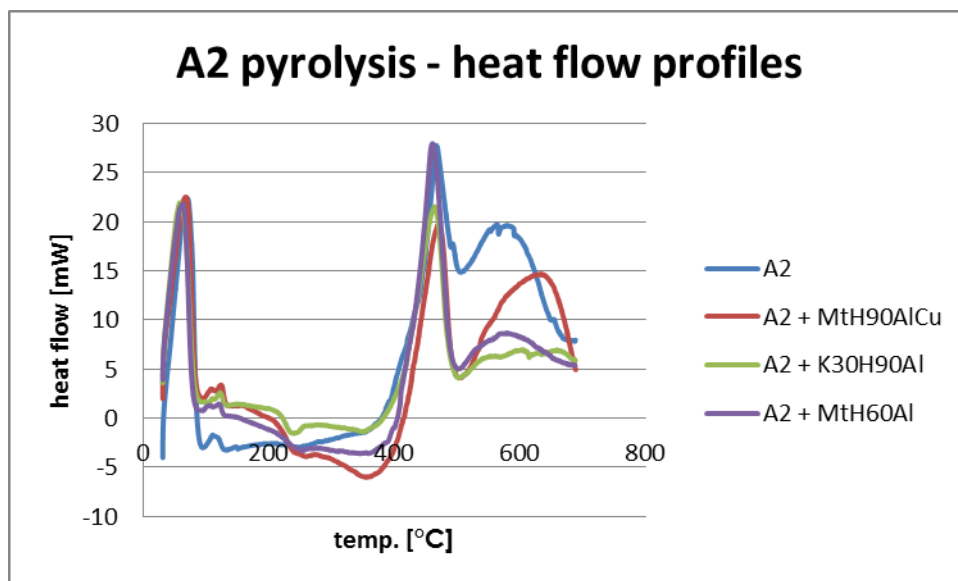


Fig.50 Summary of curves obtained from DSC analysis during the pyrolysis of A2 in the presence of various catalysts.

sample	Tdegradation [°C]
A2	467
A2+MtH90AlCu	470
A2+K30H90Al	464
A2+MtH60Al	461

Table 15 Degradation temperatures obtained in pyrolysis of the A2 material with different catalysts.

As mentioned above, water evaporation is responsible for the first high heat flow peak received for all processes and another peak for the degradation process. As it is shown in Figure 50, all degradation peaks are very similar, differing only slightly in heat flow quantity. As presented in the Table 15, the degradation temperatures obtained from catalytic processes are changed only by a few degrees. The highest temperature drop is equal to 6 °C and it belongs to MtH90Al, while the second highest decrease is 3°C of the MtH90Al catalyst. The only catalyst causing increase in degradation temperature is MtH90AlCu, rising the temperature by 3°C. The very small influence of the catalyst introduction causing negligible temperature changes make their use unfounded, because the efficiency of plastics degradation is concerned. However, the observed mass changes indicate differences in the products, which might be of advantage, in case a certain range of hydrocarbons are obtained. This needs additional studies, possibly under stationary conditions, with the full analysis of the product distribution.

4. Conclusions

The conclusions drawn from this work are as follows:

Calcination results show that different way of modification of the catalysts causes considerable changes in the amount of water adsorbed from the air in investigated montmorillonites. Acid strength distribution investigation proved, that three modification methods used: acid activation, cation intercalation and cation impregnation influences montmorillonites, resulting in similar distribution of acid strengths but different number of acid sites. The optimal time of hydrochloric acid treatment of pure montmorillonite is 60 minutes. However, the modification with Al hydroxycations that run after the acid activation indicate 90 minutes of acid treatment as the most efficient to obtain the highest amount of active sites.

The catalytic pyrolysis of polyethylene for the group of montmorillonites with different time of exposure to hydrochloric acid was investigated using DSC/TGA analysis. From first group catalysts, K30H90 (montmorillonite activated for 90 minutes), has shown the best results in reduction of degradation temperature. Unfortunately, the discussed group did not contribute to decrease the degradation temperature sufficiently. It is highly probable that acid modification which destroyed the structure led to reduction of the porosity.

The second group studied using DSC/TGA analysis presented montmorillonites activated with acid at different times and treated with aluminum hydroxycations. All catalysts show considerable improvement in temperature decrease in comparison to the first group, and the best results were obtained for K30H90Al. Still, the overly delaminated structures of montmorillonites could not be pillared with alumina hydroxycations, so the cations could only create aggregates on the surface. This might explain low efficiency of the second group.

In the last tested group consisting of

- unmodified montmorillonite,
- industrially acid activated montmorillonite treated with aluminum hydroxycations,
- montmorillonite acid activated for 60 minutes and pillared with alumina hydroxide cations,
- montmorillonite acid activated for 90 minutes, pillared with alumina hydroxide cations and promoted with copper cations,

the lowest degradation temperature was obtain for the last listed: M_tH₉₀AlCu. Moreover, this catalyst showed the best results from all catalysts investigated in this work. The high efficiency of the M_tH₉₀AlCu may be explained by the fact that the delamination of the montmorillonite structure allowed to create alumina hydroxycations pillars and additionally the Lewis sites (copper cations) introduction increased overall acidity of the catalyst.

Several catalyst were effective in reducing the degradation temperature of pure HDPE and the deactivation studies have also shown that, when using pure HDPE, several catalysts are capable of maintaining the activity after use. However, when the same catalysts were used to degrade actual plastic waste, the results were, unfortunately, not very encouraging and only a limited activity was observed for some of the catalysts and some of the waste materials tested.

Further work is required to understand what components of the plastic wastes are deleterious to the catalyst activity and how to improve the process so that the effectiveness of the catalysts in pyrolysing PE can be used in actual plastic waste.

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