

## Pyrolysis of Polymer Waste in the Presence of Metal Chlorides of Iron Subgroup

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In this work investigation of the influence of the polymeric cord of used tires composition on the course of the catalytic pyrolysis presents. It was found that with the collaborative catalytic pyrolysis of rubber and cord in a weight ratio of 1:1 the flow rate of the process and the mass fraction of volatile products are increased, which affects the increase of the efficiency and the decrease of the power consumption of the process. While studying co-pyrolysis process of polymeric cord and biomass it was revealed that the use of iron subgroup metal chlorides as a catalyst allowed decreasing the apparent activation energy in 30 kJ/mol compared to a non-catalytic process. The application of chlorides of iron subgroup metals can lead to the increase in the yield (up to 25 %) of gaseous products with high calorific value.

### 1. Introduction

At present, one of the significant results of anthropogenic influence on nature is the formation of great amount of solid domestic wastes, particularly polymers, which are characterized by the stability to the natural degradation. Polymeric wastes correspond approximately to twelve per cent of total domestic wastes and their amount is constantly growing. The main type of polymeric waste of consumption residue is spring-mounted tires (Laboy-Nieves, 2014). Currently global stocks of used tires constitute about 25 million tons and the number continues to increase (Archer et al., 2004). Currently, share of recycling of used tires by crushing for production of crumb rubber is increasing, though this method is not without drawbacks, as a result of the refining process forms a complex mixture of polymer fibers and rubber crumb (the polymeric cord) which also requires utilization.

In Russia the main method of tires utilization remains the combustion. However this process is conjugated with majority of problems. At tire burning there are formed such chemicals as biphenyl, anthracene, fluorine, pyrene, benz(α)pyrene, which become the main human hazard while going into the atmosphere. Two of these compounds – biphenyl and benz(α)pyrene – regard to carcinogens. Worn or buried automobile tires in natural conditions are decomposing minimum 100 years. The contact of tires with rainfall and ground waters is attended by the leaching of numeral toxic organic compounds: diphenylamine, dibutylphthalate, phenantrene etc., which contaminate the ground. Furthermore rubber is macromolecular substance and remains to thermoreactive polymers which are as distinct from thermoplastics cannot be processed at high temperature. This fact is the key problem of reusing of rubber wastes (Wong et al., 2015).

Among the modern, efficient and flexible forms of recycling of complex mixtures of plastic wastes are particularly important methods of catalytic pyrolysis. Industrial implementation of catalytic pyrolysis methods, which provides use of the various types of polymer wastes as a raw material for energy production, will promote the decision a number of local energy and utilities issues. The last works in the field of thermodestruction of polymeric wastes are devoted to the study of co-pyrolysis of polymers and biomass (Martinez et al., 2014). Industrial implementation of catalytic pyrolysis methods, which provides use of the various types of polymer wastes as a raw material for energy production, will promote the decision a number of local energy and utilities issues (Barbarias et al., 2015). The last works in the field of thermodestruction of

polymeric wastes are devoted to the study of co-pyrolysis of polymers and biomass (Onay and Koca, 2015): in the case of non-catalytic process (Brebu and Nistor, 2014), as well as in the presence of zeolites and Ni-Mo catalysts (Barta-Rajnai et al., 2015), Red Mud and ReUS-Y catalysts (Brebu et al., 2014).

Great significance for the development of the industry of thermal processing of polymer wastes carried by studies aimed at investigating influence of the type and weight ratio of the polymeric material in the polymer composition of the waste on the process and the yield of the pyrolysis products. Recently we studied catalytic co-pyrolysis process of biomass (peat) and oil-containing wastes using both aluminosilicates and metal chlorides (Kosivtsov et al., 2015). In this paper we report the study of polymeric waste co-pyrolysis in the presence of iron subgroup metal chlorides. A study of interference components of the mixture on the pyrolysis process makes a significant contribution to the scientific basis of the method allowing establishing the optimal composition of the polymer mixture, contributes to lower energy consumption the process. It makes possible to selection of an effective catalyst system in the presence of which the process takes place at lower temperatures, with greater reaction rate and selectivity for end products - liquid and gaseous energy resources.

## 2. Experimental

Co-pyrolysis process was carried out in developed laboratory unit consisted of stationary steel-batch reactor (1), electrical heater (2) equipped with heat controller with patch thermocouple (Figure 1).

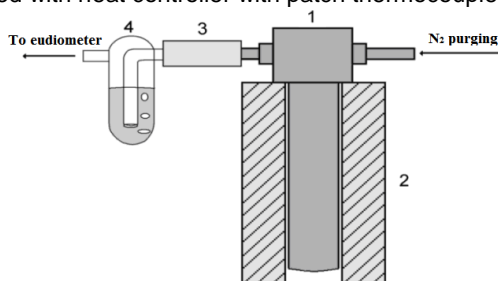


Figure 1: Experimental setup for co-pyrolysis process

Polymeric cord extracted from the secondary tires by mechanical crushing contains in its composition polyester fibers and rubber residues in a weight ratio (1:1). Since tires and polyesters represent different classes of polymers it can cause the influence on the course of the process. To investigate the inner interaction of the polymers pyrolysis process of pure fractions of polymeric fiber cord and rubber was carried out at temperature 450 °C in the presence of  $\text{CoCl}_2$  2 wt. % according to (Kosivtsov et al., 2008). Co-pyrolysis of polymers and peat mixture was studied in a temperature range 350 – 600 °C varying catalyst concentration. During the experiments the masses of solid, liquid and gaseous products were determined; also the qualitative and quantitative analysis of the pyrolysis gaseous products mixture was done. The gaseous products analysis was carried out using analytical complex on the base of gas chromatograph (Kislitz et al., 2004). The catalytic influence of metal chlorides was evaluated using the total amount of the obtained gases and the heat of combustion of the gaseous products.

## 3. Results and Discussion

### 3.1 Polymeric waste pyrolysis

In order to achieve thermodynamic compatibility of plastic masses, systems with low content of one of the component are more favorable than with a mixture in the ratio 1:1, thus an equal weight ratio of the rubber and polyester fraction in the recovering polymer cord should contribute to the thermodynamic instability of the polymer mixture and reduce the heat resistance (Shvartz and Dinzboung, 1972).

Results of the mass distribution of the pyrolysis products of the samples of model mixtures are presented on Figure 2. According to the submitted experimental data, with the sample composition containing polyester and rubber fractions (1:1) showed a maximum decrease in weight of the solid residue and increase in mass of gaseous and liquid products compared with predicted values obtained by calculation using a linear extrapolation method. The given fact indicative of the fact that at collaborative pyrolysis of polyester cord and rubber tires the efficiency of the recycling process is increasing.

The influence of the catalyst on the weight distribution of the pyrolysis products is to increase the yield of gaseous and liquid products by reducing the weight of the solid pyrolysis residue. According to experimental data (Figure 2), the use of cobalt chloride affects both the polyester and the rubber fraction. During the study

of mutual influence of plastics on the conversion into gaseous and liquid products it was revealed that with the mutual pyrolysis of polyesters and rubber yield of gaseous and liquid products is increasing, and cobalt chloride in roughly equal measure increases the conversion to liquid and gaseous products such as polyester and rubber fraction.

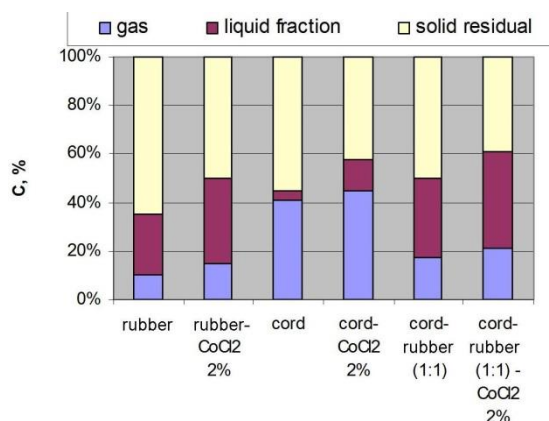


Figure 2: Influence of the polymer composition and the presence of CoCl<sub>2</sub> on the pyrolysis product yield

Collaborative pyrolysis of polyester and rubber fractions also changes the composition of the gaseous fraction. It is expressed in total heat of combustion of gaseous products increasing. The use of cobalt chloride also increases the total heat of combustion of gaseous products (Figure 3).

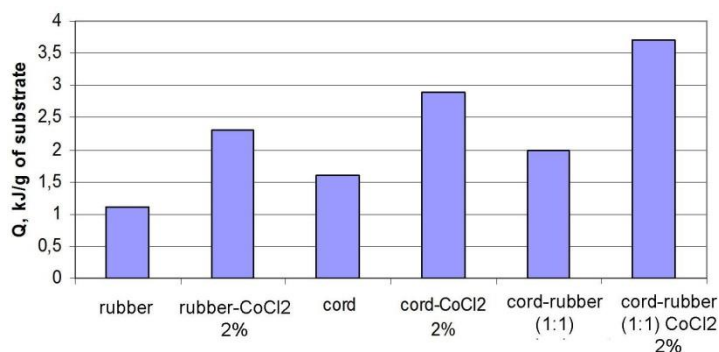


Figure 3: Dependence of total heat value of pyrolysis gaseous products on the composition and the CoCl<sub>2</sub> presence

The increase of the total calorific value of gaseous products of pyrolysis depending on the composition of the sample and the use of the catalyst might be explained by the growth of the formations of combustible gases. During pyrolysis of the cord containing no rubber fraction, main gaseous products were carbon oxides (II) and (IV). Also, in small amounts methane, ethylene and ethane are generated. The composition of pyrolysis cord gaseous products explains the low calorific value of gaseous products. Pyrolysis of rubber fraction is characterized with a huge amount of hydrocarbon component and less concentrations of carbon oxide (II), especially carbon oxide (IV). An increase of hydrocarbon component and carbon dioxides was observed at collaborative pyrolysis of polyester and rubber fractions. An increase of formations of carbon oxides can be explained by presence of polyester fraction. It might be noticed that with collaborative pyrolysis there was found hydrogen in composition of gaseous products, which might be caused, possibly, by polymers interactions and also its special additives and fillers. The use of the catalyst in all cases resulted in the increase of hydrocarbon component volume, the growth of carbon oxide (II) and some reduction in the volume of carbon monoxide (IV). Since the use of cobalt chloride, the growth of hydrogen volumes was observed only in cases when sample contained rubber fraction, thus can be made a conclusion that the use of the catalyst was affected to increase of volumes of formed hydrogen, most likely due to the reactions of dehydrogenation of polymers rubber fractions.

### 3.2 Co-pyrolysis of polymers and biomass

The use of catalysts in the process of temperature decomposition of organic materials is firstly focused on the increase of the yield of liquid and gaseous products used as fuels. The solid carbon-containing residue yield of peat and polymeric cord co-pyrolysis obtained in the temperature range 350 – 600 °C is shown in Figure 4.

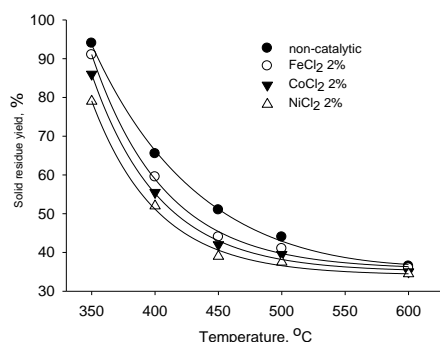


Figure 4: Dependence of co-pyrolysis solid residue yield on the process temperature for the investigated catalysts and non-catalytic process

The catalytic activity of metal chlorides in the peat and polymeric cord co-pyrolysis (regarding the decrease of the solid residue yield) increased in the row FeCl<sub>2</sub> → CoCl<sub>2</sub> → NiCl<sub>2</sub>. However the activity presented does not affect the gaseous hydrocarbons formation. The highest yield of the combustible gases was observed while using cobalt chloride as the catalyst

One of the key parameters which allow estimating the qualitative characteristics of the gaseous fuels is the calorific value of the gaseous mixture. The dependence of volumetric calorific value of co-pyrolysis gaseous products on the catalyst type and temperature is shown in Figure 5.

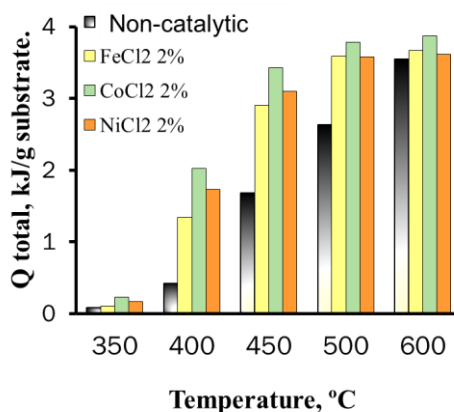


Figure 5: Dependence of calorific value of co-pyrolysis gaseous products on the catalyst type and temperature

While using the chlorides of iron subgroup metals the total calorific value of the gaseous products increased and reached out the constant at a temperature 450 °C. In the case of non-catalytic process the total calorific value of the gaseous products increased with the increase of co-pyrolysis process temperature across the studied temperature range (Figure 5). Basing on the value of the total calorific value of the co-pyrolysis gas in the studied temperature range the experiments can be ranged as the following: CoCl<sub>2</sub> > NiCl<sub>2</sub> > FeCl<sub>2</sub> > non-catalytic process.

The influence of the catalysts on the total calorific value of the co-pyrolysis gases decreases with the increase in the process temperature up to over 500 °C and at 600 °C the difference in the values of the heat of combustion of gaseous products in the case of non-catalytic process is insufficient.

To explain the obtained experimental data on calorific value of gaseous products of peat and used automobile tires polymeric cord co-pyrolysis it is necessary to study the composition of the gaseous products. The dependence of the obtained gaseous mixture components volumes on the temperature of process in the presence of CoCl<sub>2</sub> is shown as a diagram in Figure 6.

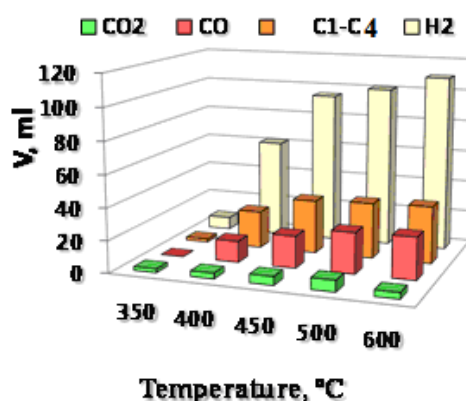


Figure 6: Gas phase composition depending on the temperature in the presence of cobalt chloride (2 % (wt.))

Analyzing the total composition of co-pyrolysis gaseous products composition obtained during catalytic pyrolysis processes it should be noted that the use of cobalt chloride leads to the formation of high volumes of C<sub>1</sub> – C<sub>4</sub> hydrocarbons and carbon monoxide. While using cobalt chloride as the catalyst the significant increase in hydrocarbons, hydrogen and carbon oxide (II) in a temperature range 350 – 450 °C was observed. The further increase in the temperature of the catalytic process over 450 °C did not lead to the significant increase in hydrogen and hydrocarbons volume.

#### 4. Conclusions

Based on the obtained experimental data it can be concluded that the pyrolysis of tires extracted from a polymeric cord proceeds, apparently in two stages. At the first stage preferably occurs cleavage of heterolytic linkages in polyester –C-O and negligible share of cleavage of homogenic linkage –C-C, as evidenced by the increased formation of CO and CO<sub>2</sub> at first 5-7 minutes of process time and relatively low level of aliphatic gaseous products methane, ethane, ethylene, propane. During the second stage of the process there is a significant degree of the liquid fraction formation, also the increase of hydrocarbons concentration in gaseous products, which may indicate the flow of degradation of the polymers backbone included in the polymer mixture. The increased formation hydrogen indicates the occurrence of dehydration reaction of the hydrocarbons molecules with formation of compounds.

The use of the combined pyrolysis process of polymeric waste and biomass allows sufficiently increasing thermodestruction process rate and raising liquid and gaseous products yield. The application of chlorides of iron subgroup metals can lead to the increase in the yield (up to 25 %) of gaseous products with high calorific value. The use of cobalt chloride has an impact on the increase of conversion of polymeric fraction into liquid and gaseous products by reducing the mass of solids.

#### Acknowledgments

The authors thank the Ministry of Education and Science of the Russian Federation (project RFMEFI57414X0075) and Russian Foundation for Basic Research for the financial support.

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