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I.I.Ishmiev, A.U.Aldangurova, Z.S.Khalikova, S.K.Aldabergenova,
V.N.Fomin, A.V.Dik, P.A.Batkov

Ye.A.Buketov Karaganda State University
(E-mail: vitfomin@mail.ru)

Low-temperature pyrolysis of polyethylene

This article describes the commodity polyethylene pyrolysis at temperatures 300–370 ºC. It was shown that the yield of gaseous products in these conditions increases with increasing temperature and by prolonging the process. Dependencies are described by using stochastic determinated design of experiments. The formal activation energy of the pyrolysis process (7.7 kJ/mol) with producing gaseous components was also determined.

Key words: stochastic determinated design of experiment, polyethylene pyrolysis, one-way ANOVA.

The problem of disposal of domestic and industrial waste plastics today is one of the most important components of the fight against pollution. Widespread using of plastic packaging, utensils and other items with small term of operation leads to the fact that a large number of polymer materials is in the dumps. For example, municipal solid waste (MSW) comprises about 3 % of plastic. When the total amount of solid waste in the CIS countries, about 100 million tons per year emitted 3 million tons of plastic products. In most cases, the plastic waste in the CIS countries are not separately disposed of and sent to landfills, or incinerated with the rest of the garbage. In the US and the EU content of plastics in MSW reaches 11 %, and thanks to a system of separate waste collection is possible for specialized processing of polymers.

For such a popular material like polyethylene terephthalate, there are the developed numerous methods of disposal, including not only getting recycled PET, and chemical recycling, leading to the starting materials for its synthesis. Other polymers such us polyacrylates, styrene copolymers, polyolefins, etc. recycled are usually pretty crude methods such as incineration. Slightly less often these wastes are used as secondary raw materials for the production of plastics or subjected to pyrolysis. The most common product in the world of pyrolysis of waste polymers — is a low-grade fuel oil. Waste polyethylene is sometimes used for paraffin production.

Polyolefins as polyethylene and polypropylene comprise the majority of non-utilized waste polymers. With the general trend towards restricting the use of the packaging of these materials in the developed countries, the problem of pollution of the environment is very acute. It should be collected and disposed waste polyolefins which are already in the environment.

The universal method for the disposal of waste polyolefins might be pyrolysis with obtaining the starting materials — ethylene and propylene.

Currently polyethylene pyrolysis relatively well studied. Different investigators considered pyrolysis of low and high density polyethylene [1, 2], mixtures of these polymers [2], mixtures of polyethylene with other materials [3], in the presence of various catalysts, in various atmospheres. The work has a number of common features. In particular the authors suggest that at temperatures below 300 ºC pyrolysis does not occur, and its speed becomes noticeable only above 360 ºC. In this regard, they learn at a pyrolysis temperature of at least 400 ºC. During process in open reactors rising the temperature impacts negatively generally on the proportion of the gaseous products of pyrolysis. First of all this related to the fact that at high temperatures many pyrolysis products are boiled. Supreme alkenes and alkanes output from the reaction zone. Thus the possibility of further destruction of paraffins to form a low molecular weight products is excluded.

It seemed to us interesting to study pyrolysis of commercial polyethylene (packaging film) at relatively low temperatures in the absence of catalysts. Confirmation of the possible formation of gaseous pyrolysis products in these conditions gives hope to increase their output in further experiments using catalysts.

For the experiments was constructed a simple device consisting of a vertical tube furnace, regulated AC source voltage (LATR) and the thermostat through an electronic thermostat C-400. As disposable reactors during pyrolysis applied thin-walled glass tubes with a diameter of 1 cm, which is placed on the bottom weighed polyethylene. In the middle of tube (6 cm from the bottom) was placed a glass wool tampon height of 1.5–2 cm, necessary to prevent carryover of heavy hydrocarbons in the form of mist. The opening of tube was closed with a rubber stopper with a gas outlet pipe of diameter 0.5 cm and a length of 20 cm, serving as reflux. The tube was immersed in a preheated planned temperature tube furnace at the lower edge of the glass wool to ensure the identity of the pyrolysis conditions. At the end of the scheduled time we determined the mass loss of polyethylene by weighing and calculated the conversion of it into gaseous products α.

In the research has been used stochastic determinated design of experiments [4]. Since at this stage there are only two factors: the temperature and the processing time, and later there will be three (the mass fraction of the catalyst will be added), was chosen four-factor design matrix of experiment with three levels of varying factors. In the absence of a catalyst the positions of third and fourth factors have been left vacant. Experimental design and results are presented in Table 1.

Table 1

The plan and the results of the experiment by low-temperature pyrolysis of polyethylene

No.	T, K	τ, min	Vac. 1	Vac. 2	α	k, min^{-1}
1	573	180	1	1	0.04546	0.0002585
2	573	120	2	2	0.030505	0.0002582
3	573	60	3	3	0.01505	0.0002527
4	603	180	2	3	0.04955	0.0002823
5	603	120	3	1	0.0306	0.000259
6	603	60	1	2	0.01662	0.0002793
7	643	180	3	2	0.05403	0.0003086
8	643	120	1	3	0.03625	0.00030765
9	643	60	2	1	0.01423	0.0002897

Even without analyzing of experimental results it is evident that conversion degree actually not exceed 5.5 % which agrees with literature data about the low speed of the process in this temperature range. Processing of the data by methods adopted within the framework of stochastic determinated design of experiments has allowed to receive partial depending shown in the Figures 1–4.

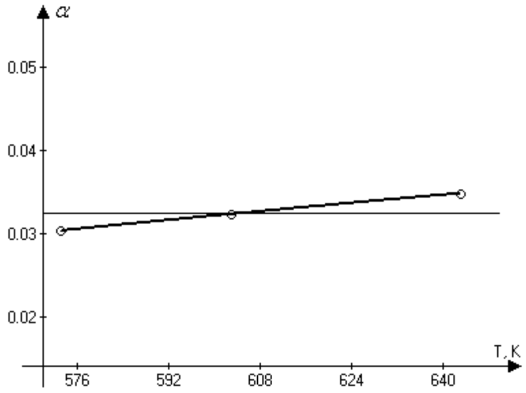

Figure 1. The dependence of conversion degree by the temperature

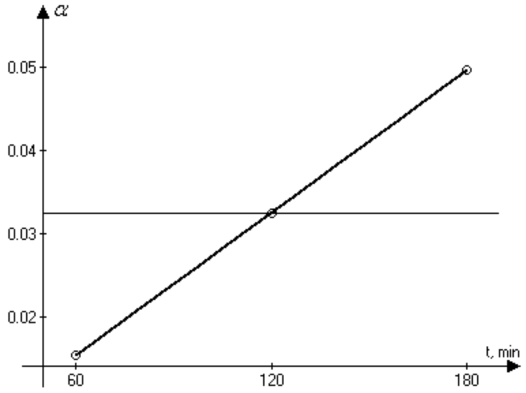

Figure 2. The dependence of conversion degree by the time

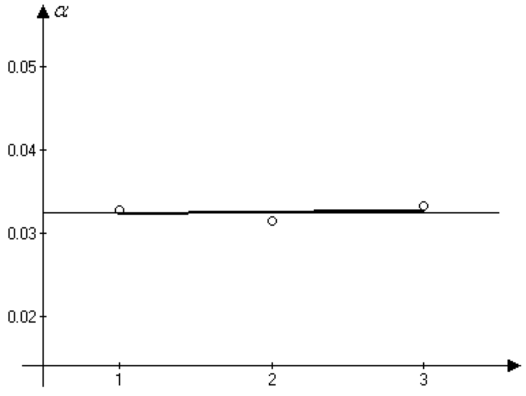

Figure 3. The dependence of conversion degree by the vacant factor 1

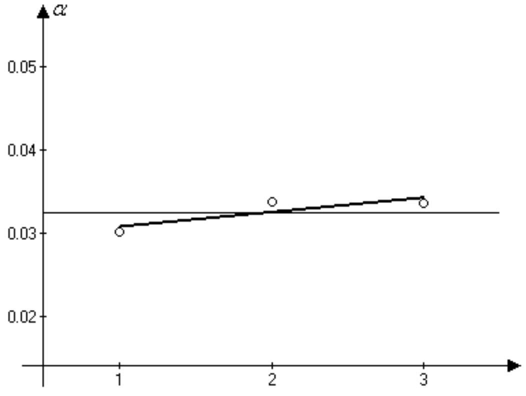

Figure 4. The dependence of conversion degree by the vacant factor 2

The derived formulas and the results of the statistical evaluation are shown in Table 2. Figure 1 shows the partial dependence of output the gaseous products depending the process temperature. This dependence is weak, despite the importance of coefficient of the non-linear multiple correlation (CNMC) exceeding 2 (t_R=∞). One-way ANOVA dispersion analysis depending on output by temperature shows no significance (F=0.01683<<$F_{\text{crit.}}$=5.1432). Given the sufficient of determinacy depending the degree of conversion of the temperature [5] should recognize the need to use obtained partial dependence of depending on the formula in the final.

Table 2

Partial dependences

Factor	Formula	R	t_R	F (F_{crit}=5.1432)
Temp.	$\alpha = 2.905E-9 * e^{-0.002597*X_1} * X_1^{2.779}$	1	∞	0.01683
Time	$\alpha = -0.001933 + 2.867E-4 * X_2$	1	∞	308.5055
Vac. 1	$\alpha = 0.03207 + 2.000E-4 * X_3$	0.6902	1.3181	0.3694
Vac. 2	$\alpha = 0.02897 + 0.00175 * X_4$	0.6762	0.7286	0.1379

The dependence of the degree of pyrolysis by time is expressed very clearly. Its importance is beyond doubt as the value of CNMC (R=1, t_R=∞), and by the Fisher test (F=308.5055>>$F_{\text{crit.}}$=5.1432). Approximating line for the vacant factors (Fig. 3, 4) are close to the line of average values, indicating a satisfactory quality of experiments and calculations. The significance of the second vacant factor for CNMC caused by mathematical reasons, refuted Fisher test value that is consistent with the deterministic component in the framework of SDDE.

Thus, the resulting equation pyrolysis of polyethylene at temperatures 300–370ºC can be represented as:

$$\alpha = 2.905E-9 * e^{-0.002597*X_1} * X_1^{2.779} + 0.001933 - 2.867E\text{-}4 * X_2 - 0.03248\,, \qquad (1)$$

R = 0.9886, t_R = 106.8179.

Calculation by formula (1) shows that the degree of polyethylene conversion into gaseous pyrolysis products increases with increasing temperature and increasing duration of the process. Temperature affects at this less than the time. By using the degree of conversion of the temperature may be obtained rate constants of the formation of the pyrolysis gases:

$$\alpha = 1 - e^{-k\tau}\,; \qquad (2)$$

$$k = -Ln(1-\alpha)/\tau\,. \qquad (3)$$

The values of the rate constants calculated for each experiment by the formula (3) are shown in Table 1. Averaging the values of the constants for each temperature gives values (min^{-1}), by which the conventional method can be calculated seemingly activation energy of process. To this end, coordinates ln(k) – 1/T find the equation of a line approximating the experimental points by method of least squares (Fig. 5). Tangent of the slope the line is $-\dfrac{E_a}{R}$.

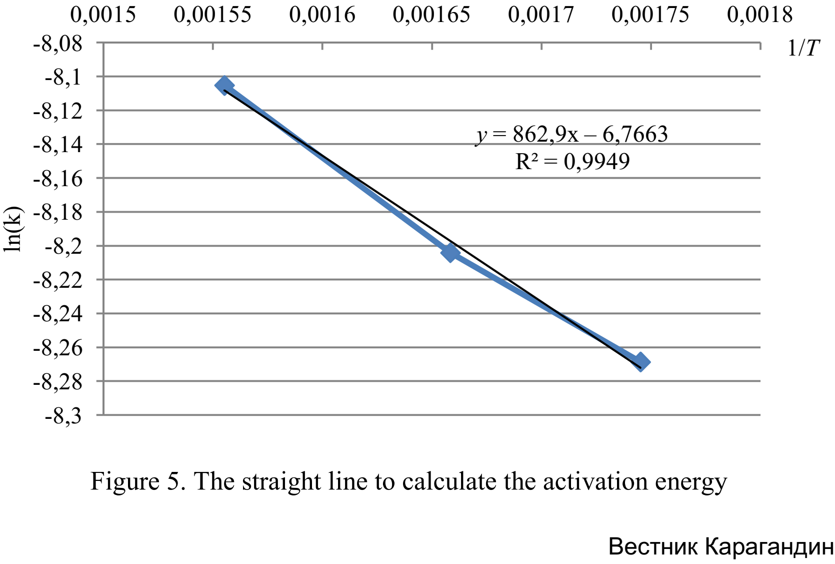

Figure 5. The straight line to calculate the activation energy

The activation energy calculated by this method is only 7.7 kJ/mol. The calculation of the formula

$$E_a = R \times \ln\left[\frac{\tau_2 \ln(1-\alpha_1)}{\tau_1 \ln(1-\alpha_2)}\right] / \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

leads to this same value.

Literature survey reveals that the activation energy of pyrolysis polyethylene depends on the temperature and the type of polymer. However, it is within 190–320 kJ/mol [6]. The approximate calculation of the activation energy based the rules of the van't Hoff formula giving in this case the values of 273–344 kJ/mol, which generally consistent with the literature data. We can conclude that the processes leading to the formation of gaseous products of pyrolysis, are subordinate and occur after the start of degradation of macromolecules resulting from the exothermic process stabilization of radicals and other intermediates.

Summing up we can say that our chosen method of studying the pyrolysis of polyethylene allows to estimate the kinetic parameters of the degradation of polyethylene at temperatures 300–400 ºC and can be used for further study of the catalytic cracking of the polymer.

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И.И.Ишмиев, А.У.Алдангурова, З.С.Халикова, С.К.Алдабергенова,
В.Н.Фомин, А.В.Дик, П.А.Батков

Полиэтиленнің төмен температуралы пиролизі

Мақалада 300–370 ºС температура аралығындағы тауарлы полиэтиленнің пиролизі жайында жазылған. Ұсынылған реакциялық жағдайда газ түріндегі өнімдер шығымының артуы, температураның және үдерістің жалғасуының өсуіне тікелей тәуелділігі көрсетілген. Тәуелділіктер тәжірибелерді ықтималдылық-детерминирленген жобалау арқылы талданды. Газды өнімдердің түзілуімен жүретін, 7,7 кДж/моль-ға тең, пиролиз үдерісінің белсенділік энергиясы анықталды.

И.И.Ишмиев, А.У.Алдангурова, З.С.Халикова, С.К.Алдабергенова,
В.Н.Фомин, А.В.Дик, П.А.Батков

Низкотемпературный пиролиз полиэтилена

В статье описан пиролиз товарного полиэтилена при температурах 300–370 ºС. Показано, что выход газообразных продуктов в этих условиях растет с ростом температуры и при увеличении продолжительности процесса. Зависимости описаны с помощью вероятностно-детерминированного планирования эксперимента. Найдена формальная энергия активации процесса пиролиза с образованием газообразных продуктов, составляющая 7,7 кДж/моль.