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STUDY OF PYROLYSISIS OF POLYMERS AND COAL AND CO-PYROLYSIS OF THEIR BLENDS, KINETICS OF THE PROCESS

KO-PYROLÝZA VYBRANÝCH POLYMERŮ S UHLÍM

Abstract

Amount of polymer waste increase every year and for this reason upgrading of this waste is a necessity. Nowadays waste disposal and incineration of polymers waste are the most frequently used methods which (i) did not allowed chemical and energy utilization and (ii) are not environmentally friendly. Pyrolysis and co-pyrolysis provide an attractive way to dispose of and convert polymer waste and coal into higher value fuel and the specific benefits of this method potentially include many environmental friendly advantages. Pyrolysis and co-pyrolysis has been studied using termogravimetry apparatus NETZCH TG-DTA STA 409 EP. The pyrolysis of all polymers except for scrap tyres was a one-step process and temperature range was narrower than for coal pyrolysis. The overlapping temperature range for pyrolysis of polymers and coal was 200–600°C. The synergic effect and kinetics of co-pyrolysis of polymers and coal has been studied in the given temperature range. The addition of polymers to coal led to (i) the enhancement of weight loss of brown coal, (ii) the shift of temperature of the max pyrolysis speed and (iii) the slight influence of E_A of coal pyrolysis.

Abstrakt

Množství odpadních polymerů každoročně stoupá a jejich recyklace je velmi důležitá. V dnešní době je největší část těchto odpadů ukládána na skládky nebo spalována. Tyto dvě metody však nejsou příliš vhodné (nedochází k chemickému ani energetickému využití materiálu) a nejsou ani šetrné k životnímu prostředí. Pyrolýza a ko-pyrolýza jsou vhodné recyklační metody umožňující přeměnu odpadních polymerů a uhlí na paliva s vyšším energetickým obsahem a jsou šetrné k životnímu prostředí. Pyrolýza a ko-pyrolýza vybraných polymerních materiálů s hnědým uhlím byla studována pomocí dynamické termogravimetrie na přístroji LECO TG-DTA STA 409 EP firmy NETZCH. Pyrolýza polymerů, kromě odpadních pneumatik, probíhala v jednom stupni a v užším teplotním intervalu než pyrolýza uhlí. Teplotní interval, kdy docházelo k pyrolýze polymeru i uhlí byl 200-600°C. V tomto teplotním intervalu byla rovněž studována kinetika ko-pyrolýzy a synergický efekt studovaných polymerů a hnědého uhlí. Nejvyšší pozitivní synergický efekt vedoucí ke zvýšení hmotnostního úbytku hnědého uhlí a rychlejší pyrolýzy při nižších teplotách měl ze studovaných polymerů polypropylen.

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1 INTRODUCTION

Production, consumption and, consequently, waste of polymers increase very sharply every year because these materials have excellent properties (resistant, light, workable, etc.) and nowadays are irreplaceable from point of view of human life.

Annual consumption of plastic in west Europe is about 60 million tons [1]. OZO Ostrava s.r.o. (Ltd.) company, which deals with cartage and waste disposal from the city of Ostrava (the third biggest city in the Czech Republic) and surrounding villages, manipulated with 86.61 thousand tons of municipal solid waste (MSW) in the year 2009 and plastics formed 17 wt.% of MSW. In this context, there are five main types of plastics in MSW - polyethylene of high and low density, polystyrene, polypropylene, also rubber and other kinds of plastics in lower quantity [2].

Upgrading of polymers waste is a necessity both for environmental protection and for sustainable development, however, nowadays waste disposal and incineration of polymers waste are the most frequently used methods. These two methods are connected with a number of environmental problems. In this time, many environmental problems are formed when stock of scrap tyres burns and dangerous pollutants (f.e. dioxines) and risks of human life and environment rise.

The addition of polymers to the thermal processing of natural organic materials (co-processing) provides an attractive way to dispose of and convert polymer waste and coal into higher value fuel and the specific benefits of this method potentially include: the reduction of the volume of waste, chemical and energy recovery and the replacement of fossil fuels.

Pyrolysis and co-pyrolysis is a thermal degradation (without oxygen agent) leading char, oil and gas production, which have big potential as useful end products. Co-pyrolysis of coal with polymer waste is the oldest method from a group of co-processing methods which led to (i) the enhancement of gas amount and its gross calorific value, (ii) improvement of thermoplastic properties of coal charge and (iii) improvement of thermomechanical and thermochemical properties of blast furnace cokes. Co-pyrolysis enables possible chemical interaction between polymers and coal leading to some positive changes in the amount (quantity) and quality of the final products [2]. In the temperature range from 400 to 500 °C a certain interaction between polymers and coal can occur. In the given temperature range coal is in a plastic state and the structure of polymers is cleaved to radicals of low hydrocarbons [3]. The mechanism of co-pyrolysis is described as the cleaving of coal structure: R-R → 2R• and the interaction with polymers: polymer-H + R• → polymer• + R-H [4]. The formation and stabilisation of free radicals by hydrogen transport depends on the material and temperature used [3].

Waste rubber and plastics seem to be very suitable materials for co-pyrolysis with coal (especially low-volatile coal) as these materials are a rich source of hydrocarbons and play an active role during coal liquefaction. Dynamic thermogravimetry (with linear temperature increase) is a method widely used to study the thermal degradation of different type of polymers, coal and their blends and to evaluate basic kinetic parameters such as a speed constant (k), activation energy (E), reaction order (n) and a pre-exponential factor (A).

The scientific studies have shown that mixed polymer waste was used as a minor component in coal blends without any detriment to coke quality [4]. Many authors [5,6] studied the thermal decomposition of coal and plastic blends such as high density polyethylene and polypropylene using a thermogravimetric method. It was shown that plastic waste has strong influence on thermoplastic properties of coal as well as the structure and thermal behaviour of the semicoke. Cai et al. [6] studied thermal behaviour of low-volatile coal plastic (low- and high-density polyethylene, polypropylene) and their blends in the ratio of 95 wt. % of coal and 5 wt.% of plastics. Coal was decomposed at a lower temperature than of plastics; temperature range of organic origin volatilisation range is broader for coal than for plastics. This range is more complex for blends than for individual components. Sharypov et al. [7] concluded that synergic effect of polyolefin addition is observed preferentially with low rank coal due to their higher content in thermally unstable C-O bonds. Lignin-derived radicals promote polyolefinic macromolecules degradation, leading to an increase of the amount of distillable liquid fraction. Lignin structure has aromatic units combined with oxygen containing chemical bonds that are less thermally stable than C-C bonds of plastics. For this reason a similar effect can occur during co-pyrolysis of brown coal and plastic blends. Brown coal is characterised by

high concentration of chemical bonds containing oxygen. A synergic effect of waste rubber tyres and coal was observed at the temperature of 430 °C without or with molybdenum catalysts and greater total conversion to liquids was yielded [8]. Two-stage pyrolysis of 75 wt.% coal and 15 wt.% rubber led to the production of gas with high amount of hydrogen and carbon monoxide and to solid phase consisting mainly of carbon [9]. Ishaq et. al. [3] studied co-pyrolysis of polystyrene, low- and high-density polyethylene and polypropylene with coal in the presence of a solvent and catalysts. Among the studied plastics, high-density polyethylene and polypropylene showed higher weight loss.

On the other hand, some articles report no effects or "asynergic" effects of plastics and coal. Sakurovs [10] discovered that polypropylene does not influence fluidity of coal during co-pyrolysis whereas polystyrene decreases fluidity of all types of coking coal above the temperature of 420 °C, in contrast with polyacrilonitrile which increases their fluidity. Domínquez et al. [11] detected slight reduction of fluidity when plastic waste (low- and high-density polyethylene) was added to coal pyrolysis because the products of plastic degradation were hydrogen acceptors. Polystyrene was suggested as a strong hydrogen acceptor because it produces, above all, ethylbenzene a major pyrolysis product. It was blended with coal and pitch [10]. Co-pyrolysis of brown and black coal and acrylonitri-butadiene-styren led to enhancement of liquid pyrolysis phase. It can be explained by higher amount of hydrogen and lower amount of oxygen in this copolymer [2].

We can deduct from the mentioned above facts, that co-pyrolytic behaviour of low-volatile brown coal, chosen polymers and their blends were investigated using thermogravimetric analysis. Thanks to it, we obtain an overall understanding of the interaction between coal and plastics.

2 EXPERIMENTAL

2.1 Materials and techniques

The feedstock materials used in this work included a low volatile brown coal (LVC), as well as low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), scrap tyres (ST) and their blends (LVC+LDPE, LVC+HDPE, LVC+PP, LVC+ST) with the addition of polymers of 5 wt.%.

We used shredder commercial granules (under 1mm) of pure LDPE; PP in form of fine powder made in company HP-TREND s.r.o. and shredder shampoo's and soap's bottles (under 1mm) as a HDPE samples. As rubber sample was used shredder scrap tyres (under 1mm) from cars. As low volatile coal we used brown coal (under 0.18 mm) from area Mostecká uhelná a.s. The experiments were carried out with such a small particle size due to elimination of temperature profiles inside the sample. Coal and polymer-based materials blends were homogenized by mixing in appropriate proportion.

The thermal analysis was carried out using simultaneous TG-DTA apparatus NETZSCH STA 409 EP. All the experiments were conducted under the identical conditions: the samples (10^1-10^2 mg in weight) were heated up to 1000 °C in the crucibles (aluminium oxide) in a dynamic inert atmosphere of argon (with the flow rate of 100 $cm^3 min^{-1}$) at the heating rate of 10°C min^{-1}.

Proximate analysis (Table 1) was carried out by thermo gravimetric analyser LECO TGA 601.

2.2 Determination of apparent kinetic parameters

Method of direct non-linear regression [12] was used for calculation of apparent kinetic parameters of pyrolysis processes from thermogravimetric (TG) curves.

The calculation is based on the kinetic equation (1).

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right)(1-\alpha)^n \tag{1}$$

If the time step is set small enough, the derivatives in Eq (1) may be replaced by differences. We assume that the TG curve is composed of very small linear segments of the length Δt, in which the reaction rate is constant:

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$$\Delta\alpha = A\exp\left(-\frac{E}{RT}\right)(1-\alpha)^n\Delta t \tag{2}$$

where:
α - degree of conversion [%],
t - time [s],
T - absolute temperature [K],
R - molar gas constant [8.314 JK^{-1}mol^{-1}],
A - frequency factor $\left[\frac{1}{s}\right]$,

E - activation energy $\left[\frac{J}{mol}\right]$,

n - the reaction order [-].

Assuming the α_0 and t_0 at the beginning of the α vs. t curve, further points of the curve can be calculated from the recurrence relation

$$\alpha_i = \alpha_{i-1} + A\exp\left(-\frac{E}{RT_{i-1}}\right)(1-\alpha_{i-1})^n(t_i - t_{i-1}) \tag{3}$$

If the TG curve consists of p various processes with kinetic parameters A_j, E_{aj} and n_j (j=1 to p), Eq. (3) can be used for calculation of extent of conversion for individual reactions. In this case, the equation describing the whole curve can express as a sum of particular equations:

$$\alpha_i = \sum_j \alpha_{j,i-1} + \sum_j A\exp\left(-\frac{E_j}{RT_{i-1}}\right)(1-\alpha_{j,i-1})^{n_j}(t_i - t_{i-1}) \tag{4}$$

Last equation enables determination of apparent kinetic parameters of multistep reactions by non-linear optimalization.

3 RESULTS AND DISCUSION

3.1 Thermogravimetric study

Some characteristics of used polymers and coal are given in Table 1 and in Table 2. Generally, with increasing amount of volatiles in the sample total pyrolysis weight loss increases.

Tab. 1 Proximate analysis of polymers and coal.

Sample	LVC	LDPE	HDPE	PP	ST	PA	PS	ABS
Moisture/wt.%	7.2	0.1	0.1	0.1	0.7	1.6	0.0	0.2
Volatile/wt.%	44.3	99.9	95.0	98.8	62.3	98.1	99.3	97.7
Fixed C/wt.%	44.0	0.0	0.0	0.0	32.7	0.2	0.7	2.1
Ash/wt.%	5.5	0.1	5.0	1.2	4.3	0.1	0.0	0.0

Tab. 2 Elemental analysis of coal.

| Element/wt.%	C	H	N	S
	66.2	5.6	0.8	3.4

Fig. 1 shows TG curves of pyrolysis of pure polymers and coal. It can be seen that with increasing temperature decreases sample weight (increases loss of sample weight). TG pyrolysis curves of (i) LDPE, HDPE and PP and (ii) ABS and PS are almost identical; this indicates that they have the same pyrolysis behaviors due to similar chemical bonds in their molecular structure [13]. Compared to TG curves of polymers samples, TG curve of LVC is not so sharp and is finished at lower weight loss due to the lowest amount of volatiles (36 wt.%) and the highest amount of ash and fixed carbon in coal.
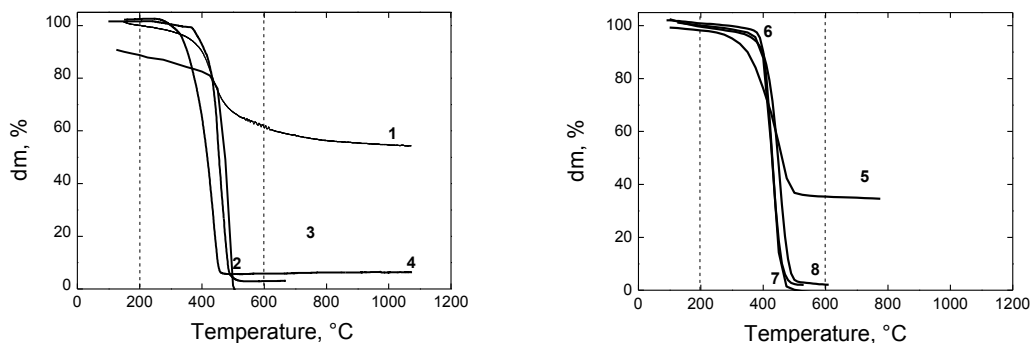
Fig. 1 TG curves of pyrolysis of coal and plastics left: LVC (1), LDPE (2), HDPE (3), PP (4), right: ST (5), ABS (6), PS (7), PA (8).

Weight loss of ST is also lower compared to rest polymers. It is caused by lower amount of volatiles, higher amount of fixed carbon and addition of additives in the ST structure used during manufacturing of tyres. Compared to weight loss of LDPE and PP, total weight loss of HDPE sample is lower due to some pigments and additives used for shampoo and soap bottles.

As for blends with 5 wt.% of polymers, TG curves approach to TG curve for pure LVC. It is probably clarify by low addition of polymers.
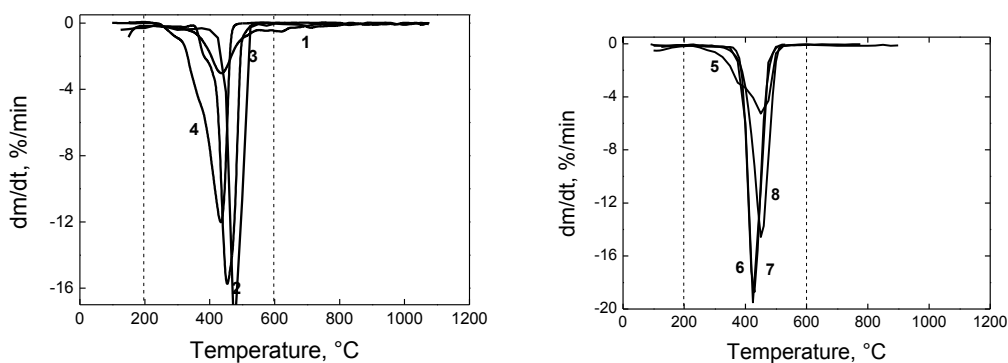
Fig. 2 DTG curves of pyrolysis of coal and plastics left: LVC (1), LDPE (2), HDPE (3), PP (4), right: ST (5), ABS (6), PS (7), PA (8).

The weight losses show that degradation of plastics is almost totally one-step process which illustrates presence of one peak at DTG curves (Fig. 2). On the contrary, thermal degradation of ST proceeds in two stages. First peak at temperature 387 °C corresponds to oils, plasticators and additives vaporization. Second peak at temperature 460 °C fits into rubber decomposition.

Pyrolysis of LVC is also two-stage process. First peak at 118 °C responds to water vaporization and releasing of molecules from micro-structure and the second peak to coal decomposition.

Some characteristic temperatures of pyrolysis and co-pyrolysis process determined from DTG curves are showed in Table 3. There is: temperature of (i) initial weight loss (T_I), (ii) the end of the reaction (T_F) and (iii) maximum pyrolysis speed (T_{max}). T_{max} is related to the material structure and process conditions. Polymers with similar structure have this temperature usually almost identical [6]. In Table 3 there are also weight losses of pure materials and their blends.

Compared to DTG peak latitude, narrower latitudes were observed for polymers than for LVC. It means that decomposition of LVC is accomplished in broader temperature range and thermal degradation of the studied coal starts at lower temperature (T_I=272 °C) and ends at higher

temperature (T_F=644 °C) than polymers which corresponds with literatures [5, 7]. Temperature range for plastic thermal decomposition varies from T_I=220 (for ST) to T_F=586 °C (for PP) and in this temperature range the highest effect of polymers addition in coal could be occurred [15]. For this reason, synergic effect between polymers and coal was evaluated for temperature range 200 – 600 °C.

TG and DTG curves of blends lie between pure polymers and coal. For this reason they are not demonstrated.

Addition of 5 wt.% or 20 wt.% of all polymers did not shift values of temperatures T_I and T_F. On the other hand, T_{max} was shifted. Addition of LDPE, HDPE and PP shifted T_{max} about 42 °C to higher value. Others polymers slightly shifted T_{max} to lower temperature.

Addition of all polymer enhanced weight loss of LVC. The highest enhancement of LVC weight loss was detected after (i) PS addition which is in discordance with literature [10] and after (ii) ABS addition. Increasing of weight loss after ABS addition is interpreted by higher amount of hydrogen and lower amount of oxygen in copolymer ABS [2].

Tab. 3 Characteristic temperatures and weight loss of sample pyrolysis.

	T_I/°C	T_F/°C	T_{max}/°C	Weight loss/wt.%[1]
LVC	272	644	118;435	36
LDPE	354	533	454	99
5LDPE+LVC	272	644	476	42
20LDPE+LVC	272	644	477	51
HDPE	301	533	484	85
5HDPE+LVC	272	644	476	39
20HDPE+LVC	272	644	480	49
PP	247	586	433	97
5PP+LVC	272	644	445	41
20PP+LVC	272	644	462	52
ST	220	518	387;460	63
5ST+LVC	272	644	431	38
20ST+LVC	272	644	438;484	43
PA	326	508	453	97
5PA+LVC	272	644	431	41
20PA+LVC	272	644	440	49
PS	358	490	430	100
5PS+LVC	272	644	436	43
20PS+LVC	272	644	442	49
ABS	358	512	430	100
5ABS+LVC	272	644	429	43
20ABS+LVC	272	644	433	48

[1]Weight loss in temperature range 200-600 °C

3.2 Kinetic study

Kinetics parameters of pyrolysis of LVC and polymers published in literature varied in wide range due to different process conditions of thermogravimetric measurement and applying differential methods (integral, differentia, approximate or special) [14].

Tab. 4 Apparent kinetic parameters, activation energy and pre-exponential factor.

	Temp./°C	n	$E/\text{kJ.mol}^{-1}$	A/s^{-1}	$*R^2$
LVC	200-550	1.1	75	$7.550.10^2$	0.9969
LDPE	330-530	0.9	165	$6.277.10^9$	0.9993
5LDPE+LVC	200-600	1.1	75	$4.574.10^2$	0.9977
20LDPE+LVC	200-650	1.1	85	$2.217.10^3$	0.9950
HDPE	240-530	0.3	90	$1.645.10^5$	0.9968
5HDPE+LVC	200-650	1.6	100	$7.240.10^3$	0.9987
20HDPE+LVC	200-650	1.1	90	$4.583.10^3$	0.9957
PP	250-475	0.3	70	$1.058.10^4$	0.9997
5PP+LVC	200-600	1.4	80	$6.252.10^2$	0.9959
20PP+LVC	200-650	1.6	115	$9.352.10^4$	0.9939
ST	200-400	1.0	160	$1.799.10^9$	0.9997
	400-520	0.6	60	$3.017.10^2$	0.9994
5ST+LVC	200-600	1.6	85	$7.389.10^2$	0.9971
20ST+LVC	20-600	1.6	90	$1.355.10^3$	0.9975
PA	300-600	1.0	155	$7.836.10^8$	0.9997
5PA+LVC	200-600	1.4	85	$1.191.10^3$	0.9964
20PA+LVC	200-650	1.8	115	$4.356.10^4$	0.9973
PS	300-530	1.5	255	$7.890.10^{15}$	0.9997
5PS+LVC	250-600	1.5	90	$2.027.10^3$	0.9963
20PS+LVC	200-650	2.2	145	$2.870.10^6$	0.9953
ABS	300-530	1.8	280	$1.885.10^{17}$	0.9998
5ABS+LVC	260-600	1.8	105	$1.162.10^4$	0.9976
20ABS+LVC	200-650	2.3	155	$1.056.10^7$	0.9960

$*R^2$ correlation coefficient

It can be seen that activation energy (E_A) for pyrolysis of pure polymers is much higher than for LVC and slope of straight line in Arrhenius plot is steeper. Activation energies and pre-exponential factors (A) of coal/polymer blends are resembled that suggested that pyrolysis mechanisms for blends is also similar.

Tab. 5 Intersection region of Arrhenius plots of coal and polymers.

Sample	LDPE	HDPE	PP	ST	PA	PS	ABS
Temperature/°C	-	-	-	424	424	450	472

Differences in the kinetics of LVC and polymer pyrolysis are illustrated by Arrhenius plots (Fig. 3). Compared to coal Arrhenius plot, polymer linear dependency of ln k vs. 1/T is shifted to higher values of speed constant at higher temperature. Above temperature of Arrhenius plot crossing (Table 5) speed constant (k) of pyrolysis is higher for polymers than for coal (Fig. 3). Addition of polymers to coal did not distinctly change the slope of straight line (minimal changes in activation energies). Comparable values of activation energies for pyrolysis of coal and blends indicate similar reactivity at different temperatures. Slope of straight line is identity for ABS and PS (Fig. 3 right).
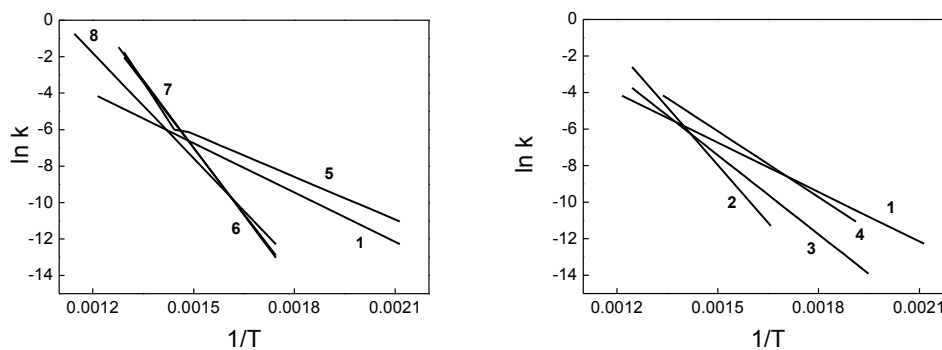
Fig. 3 Arrhenius plots of coal and plastics left LVC (1), LDPE (2), HDPE (3), PP (4), right: ST (5), ABS (6), PS (7), PA (8).

3 CONCLUSIONS

From the thermogravimetric measurement of pyrolysis of coal, seven types of polymers (LDPE, HDPE, PP, scrap tyres (ST), PA, PS and ABS) and co-pyrolysis of their blends can be concluded the following: all polymers except for scrap tyres proved comparable pyrolysis behaviour during the heating in a dynamic inert atmosphere of argon. The different weight losses for the pyrolysis of scrap tyres and coal appeared. It is connected with lower content of volatiles. The pyrolysis process of polymers proceeded in the temperature range from 220 to 586 °C. The temperature range of an organic substance devolatilisation for coal was even broader, i.e.272 – 644 °C.

The aaddition of polymers caused (i) the increase of the total weight loss of coal up to 7 wt. % after the addition of 5 wt.% of polymers and up to 16 wt.% after the addition of 20 wt.% of polymers and (ii) the shift of temperature of maximum pyrolysis speed (T_{max}) to a lower value only for blends containing scrap tyres, PA and ABS.

The apparent kinetic parameters were calculated using the method of direct non-linear regression. The activation energy of pyrolysis for polymers was much higher than for coal. The addition of such polymers to coal had only a slight impact on the activation energy values. Compared to the value of speed constant, at higher temperatures there have been observed higher values for polymers rather than for coal. The situation at lower temperature is contrary.

On the basis of these results, it could be concluded that an interaction between polymers and coal occurred during the thermal treatment.

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