Co-Pyrolysis of Estonian Oil Shale with Polymer Wastes
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ABSTRACT: Recycling of polymeric wastes is important for both energy recovery and raw material processing. In light of the EU Green Deal, the oil shale industry is looking for new opportunities to use its production potential. As an intermediate stage, the co-pyrolysis of oil shale with waste plastic and tires will be considered acceptable. The article presents the kinetics of pyrolysis of Estonian oil shale, the main polymer components of municipal waste, and their mixtures with oil shale by the thermogravimetric analysis method. The influence of each component separately on the process of sample weight loss during co-pyrolysis was also studied. It is shown that when plastics are added to oil shale, the experimental and calculated data coincide according to the principle of the additive contribution of each component. Kinetic parameters were calculated according to the Coats−Redfern integral method and show that during the co-pyrolysis of mixtures of oil shale with polymer wastes, the value of the activation energy increases in comparison with the pyrolysis of oil shale. Based on the experimental data, it was determined that there is a manifestation of a synergistic effect in the form of an increase in the yield of liquid products during the co-pyrolysis of oil shale and polymer wastes.

1. INTRODUCTION
In recent years, the topic of reuse of polymer wastes, including plastics and used car tires, has become increasingly important. Annual increase in production of polymer/plastic materials inevitably leads to an increase in the waste produced that requires recycling. According to Statista, more plastic has been produced in the past 15 years than in the 50 years prior.1 In the European Union, only the demand for plastics in 2019 amounted to 50.7 million tones. The most common plastics that are used on a daily basis and are universally applicable are polyethylene (PE-HD and PE-LD) and polypropylene (PP).2 According to PlasticsEurope association in 2019 in Europe, of the collected 29 million tons of plastic wastes, 42.6% went to energy recovery, 32.5% to recycling, and 24.9% was buried in a landfill amounting to roughly 7 million tons.2 In September 2020, ETRMA, the European Tire and Rubber Manufacturers’ Association, reported3 that in 2018, 32 countries (EU28, Norway, Serbia, Switzerland, and Turkey) collected 3.58 million tons of end of life tires from which 193 thousand tons have not been reused. Thus, a fair amount of polymer wastes still needs to be incorporated into sustainable waste management and, by the virtue of it, into circular economy.

On the other hand, according to the “Estonian national energy and climate plan (NECP 2030)”, by 2050, Estonia must strive to reduce carbon emissions to zero.4 To achieve this goal, the Estonian government announced two dates—the exiting of the production of oil shale electricity no later than 2035 and the production of shale oil no later than 2040. During this period, it is planned to reduce the negative impact of oil shale production on the natural environment. For this purpose, oil shale processing enterprises are looking for an opportunity to modernize production and switch to a new type of raw material.

From an environmental and economic point of view, the most rational approach is the use of polymer wastes as an alternative fuel, which contain PE-HD, PE-LD, PP, tire, and other components. However, the use of only polymer wastes as raw material is currently not possible due to the peculiarities of the existing oil shale processing plants. Today, the main technology for processing oil shale in Estonia is the Galoter process, which is pyrolysis of raw materials by the solid heat carrier method. Pyrolysis is the thermal decomposition of organic material in an oxygen-free atmosphere to form gaseous, liquid, and solid products.5 The solid heat carrier in the Galoter process is its own ash, which is returned to the pyrolysis process. Because the ash content of polymer wastes is quite low, therefore, the first step is to replace part of the oil shale with polymer wastes, which, according to estimates, can reach 50%.

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Pyrolysis of plastic wastes components is one of the ways of recycling. The co-pyrolysis of polymer waste with various materials containing organic matter, including oil shale, has been widely investigated. For example, Tiikma et al. have studied the impact of co-pyrolysis of low-density polyethylene with Estonian kukersite oil shale, its semi coke, and Dictyonema shale on the yield and composition of the pyrolysis oil. They noted that yield and chemical group composition of co-pyrolysis oil depend on a certain degree on the oil shale type used. Information about the kinetics of the pyrolysis process is important when designing industrial pyrolysis plants. The kinetics of co-pyrolysis of polymer waste with various materials containing organic matter is well studied. Thus, Aboulkas et al. have studied pyrolysis kinetics of Moroccan oil shale kerogen mixed with high-density polyethylene (PE-HD) using a thermogravimetric analysis (TGA) system at various heating rates of 2, 10, 20, and 50 K/min in the temperature range of 300–1273 K in a nitrogen atmosphere. The thermogravimetric method was extended by the same group to the studies on the pyrolytic behaviors of Moroccan oil shale kerogen, polyethylene terephthalate, and their mixtures. The experiments were carried out dynamically by increasing the temperature from 298 to 1273 K at a heating rate of 2–100 K/min in a nitrogen atmosphere.

Despite a significant amount of scientific work in the field of co-pyrolysis of oil shale with various polymer wastes, most of the works investigated the process of pyrolysis of oil shale in a mixture with one or two components, while the real polymer wastes contain a significantly larger number of components. The aim of this work is to study the process of pyrolysis of oil shale in a mixture with all the main polymer components of waste and to determine the kinetic parameters of co-pyrolysis.

2. THEORY OF THE STUDY OF KINETIC PARAMETERS

TGA is a research and analysis method based on the registration of changes in the mass of a sample depending on its temperature or time under certain and controlled conditions of changes in the ambient temperature. TGA is quite accurate and fast, and it is used to study characteristics and kinetics of pyrolysis of materials with complex matrices, such as solid fuels. In pyrolysis kinetics analysis, the activation energy is an important parameter describing the pyrolysis process of a sample. There are a number of methods for calculating the activation energy, based on mathematical processing of the TGA curve. The least time-consuming and most accurate for polymers and oil shale is the double-logarithm method. The condition for the applicability of the Coats–Redfern method is the first order of the decomposition reaction. When calculating the kinetics of oil shale pyrolysis and polymer decomposition, it is usually assumed that these reactions are of the first order.

Arrhenius equation

\[ K = A \cdot e^{-E_a/RT} \]

where \( A \) is the pre-exponential factor, sek\(^{-1}; E_a \) is the activation energy, kJ/mol; \( R \) is the universal gas constant; and \( T \) is the temperature of the test substance, K.

The Coats–Redfern procedure is widely reported in the literature. Following the established procedure for each reaction stage separately, the extent of reaction \( (\alpha) \) is calculated by comparing the mass at time \( \tau \) \((m_i)\) with the initial \((m_0)\) and final \((m_f)\) masses as per eq 2.

\[ \alpha = \frac{m_0 - m_f}{m_0 - m_i} \]

Then, according to the procedure for first-order reactions, the value of the activation energy \( E_a \) can be defined as the tangent of the slope of the linear portion of the curve plotted in coordinates \( \ln(-\ln(1 - \alpha)/T^2) \) against \( 10^3/T \). After analyzing the curves of thermal decomposition, it is possible to select linear sections and approximate them using a linear equation of the type \( y = ax + b \), where the value of the parameter \( a \) corresponds to the value \(-E_a/R\).

3. EXPERIMENTAL SECTION

3.1. Sample Characterization. The oil shale sample used in this study—Estonian oil shale (EOS) from an under-ground mine called Ojamaa. The polyethylene (PE-HD and PE-LD), PP, and the tires used in this study were collected from the Uikala municipal waste dump.

The calorific value was determined in a calorimetric bomb Parr 6300; the net calorific value was calculated using EVS-ISO 1928 and corrected for undecomposed carbonates. Elemental composition was determined using a “vario macro cube” device, fixed carbon determined by calculation. The ash content was determined by the international standard. The data are shown in Table 1.

For all samples, the yield of semi-coking products was determined in accordance with the standard ISO 647. The results were recalculated per apparent organic content. The data are shown in Table 2.

### Table 1. Proximate and Ultimate Analysis Results

| samples | ash (A) | fixed carbon (PC) | net calorific value, MJ/kg | carbon (C) | hydrogen (H) | nitrogen (N) | sulfur (S) |
|---------|---------|-------------------|---------------------------|------------|--------------|--------------|------------|
| EOS     | 50.10   | 2.70              | 8.807                     | 27.50      | 2.70         | 0.07         | 1.60       |
| PE-HD   | 0.40    | <1.00             | 44.575                    | 84.02      | 15.50        | 0.02         | 0.06       |
| PE-LD   | 1.30    | <1.00             | 44.286                    | 83.04      | 15.54        | 0.05         | 0.08       |
| PP      | <0.10   | <1.00             | 44.876                    | 84.09      | 15.77        | 0.01         | 0.03       |
| Tires   | 8.02    | 24.60             | 34.388                    | 78.70      | 7.70         | 0.47         | 1.25       |

In dry basis.

### Table 2. Yield of Semi-Coking Products

| samples | yield of semi-coking products per apparent organic content, m/m |
|---------|---------------------------------------------------------------|
| EOS     | oil   | semi-coke | pyrogenetic water | gas + loss |
|         | 59.8  | 17.8     | 5.4             | 17.0       |
| PE-LD   | 92.7  | 0.8      | 0.3             | 6.2        |
| PE-HD   | 92.5  | 1.5      | 0.0             | 6.0        |
| PP      | 93.6  | 0.1      | 0.0             | 6.3        |
| Tires   | 58.9  | 33.5     | 0.1             | 7.5        |

Table 2. Yield of Semi-Coking Products
4. RESULTS AND DISCUSSION

4.1. Decomposition of EOS, Polymers, and Mixtures of Polymer Wastes with Oil Shale. Figure 1 shows a simple weight loss (TG) curve of the studied oil shale and polymers and a differential weight loss (DTG) curve.

The curves show that the loss of mass during heating of the oil shale occurs in two stages (there is also a stage of moisture loss, but it is insignificant). The first major stage is the stage of decomposition of the organic part of the oil shale. It occurs in the temperature range from 300 to 550 °C. The second stage is decomposition of the mineral part of the oil shale, which occurs in the temperature range of 670–870 °C.

It can be seen from the graphs that the weight loss during pyrolysis for all polymers occurs in one stage. Thermal decomposition of PE-LD and PE-HD occurs in the temperature range of 400–550 °C with maximum weight loss at 480 °C. In PP, the decomposition of the organic part begins at a lower temperature. This process takes place in the range of 300–520 °C, with a maximum loss of mass at 442 °C. This range (300–550 °C) corresponds to the stage of active pyrolysis, in which thermal decomposition of the initial polymer molecule occurs, accompanied by a weight loss of ~98%. Upon subsequent heating in the temperature range from 500 to 945 °C, the process of passive pyrolysis occurs, accompanied by thermal destruction of stronger bonds in the solid residue and a weight loss of less than 1%. The organic part of tires begins to decompose at a temperature of 250 °C and the decomposition process ends at 550 °C, while the maximum weight loss occurs at 400 °C. A high residual weight at the end of the sample analysis of about 34% indicates a significant amount of filler in the tire composition. Table 3 shows the TGA parameters for EOS and polymers.

Table 3. TGA Parameters for EOS and Polymers

| TGA parameter   | EOS | PE-LD | PE-HD | PP | tires |
|-----------------|-----|-------|-------|----|-------|
| T_onset °C      | 412.8 | 766.0  | 455.6  | 460.5 | 419.5  | 353.6 |
| T_midpoint °C   | 444.7 | 798.8  | 480.7  | 480.4 | 442.3  | 400.3 |
| T_endset °C     | 476.6 | 839.4  | 493.9  | 500.3 | 468.9  | 451.0 |

Table 3 shows that the temperature of the maximum weight loss (T_midpoint) of the organic part of the oil shale is 445 °C. These results show that the values of the highest intensity of destruction of organic matter obtained in this work are very similar to those mentioned in the literature. The temperature of the maximum weight loss (T_midpoint) of the inorganic part of the oil shale is 799 °C. The temperature of the maximum weight loss (T_midpoint) for PE-LD and PE-HD is approximately 480 °C, for PP is 442 °C, and for tires is 400 °C.

To study the kinetics of oil shale decomposition with a mixture of polymer wastes in a 50/50 ratio (50% oil shale, 12.5% PE-HD, 12.5% PE-LD, 12.5% PP, and 12.5% tires), TGA of oil shale was also carried out with each polymer separately in a 50/50 ratio. Figure 2 shows a simple weight loss (TG) curve of the studied test mixtures and a DTG curve.

The curves show that when a mixture of oil shale with polymer wastes is heated, weight loss occurs in two stages; while at the first stage, the weight loss increased significantly because polymer wastes consist mainly of organic matter, the second stage involves the decomposition of the mineral part of the oil shale.

From the data in Table 4, it can be seen that the addition of PE-LD and PE-HD plastics to oil shale leads to the fact that the stage of active decomposition of the organic part and the maximum weight loss of the samples occurs at the same temperatures as in the analysis of each polymer separately. Therefore, the stage of active decomposition of the organic part of the polymer PE-LD occurs in the temperature range.
The onset of decomposition is 455.6–493.9 °C, and for a mixture of PE-LD with oil shale, this range is 456.8–496.3 °C. For PE-HD plastic and a mixture of oil shale with it, these ranges are T_{onset}=T_{endset} 460.5–500.3 and 464.0–499.2 °C, respectively.

For PP and tires, the beginning and end of active decomposition of the organic part is shifted by 20 °C toward higher temperature. In this case, the nature of decomposition of the organic part of the oil shale sample with the mixture (50% oil

Table 4. TGA Parameters for Mixtures Oil Shales with Polymer Wastes

| TGA parameter | EOS + PE-LD | EOS + PE-HD | EOS + PP | EOS + tires | EOS + mix |
|---------------|-------------|-------------|----------|-------------|-----------|
| T_{onset}, °C | 456.8       | 464.0       | 446.6    | 378.1       | 456.6     |
| T_{midpoint}, °C | 476.0       | 481.4       | 464.9    | 425.1       | 371.7     |
| T_{endset}, °C | 496.3       | 499.2       | 483.8    | 477.0       | 495.5     |

Figure 2. Simple weight loss (TG) curve of the studied mixtures of EOS with polymer wastes and a DTG curve.

Figure 3. Calculated and experimental curves of weight loss (TG) for mixtures of EOS with polymer wastes.
shale, 12.5% PE-HD, 12.5% PE-LD, 12.5% PP, and 12.5% tires) becomes the same as for PE-HD and PE-LD because their thermal degradation behavior is similar and their total organic matter in the test mixture predominates. The decomposition of the mineral part for all mixtures of oil shale with polymers is shifted toward lower temperature. Perhaps, this is due to the more complete decomposition of oil shale at the first stage of thermal destruction and the weakening of chemical bonds in the solid residue.

4.2. Study of Additivity Based on TG Analysis. To test the principle of additivity in the process of thermal decomposition of multicomponent mixtures, we studied the data on the co-pyrolysis of mixtures of EOS with polymer wastes by the TGA method. On the basis of TG data, graphs were constructed (Figure 3), comparing experimental and calculated data on the principle of the additive contribution of each component.

As seen in Figure 3, the calculated points are in good agreement with the experimental curves both for a mixture of oil shale with individual components of polymer wastes and for a multicomponent mixture. This confirms the legitimacy of using the additivity principle for calculating the mass loss of a mixture of oil shale and polymer wastes. Thus, the data obtained can be used in the future for mathematical modeling of the pyrolysis process of multicomponent mixtures, as well as in the design of pyrolysis plants and to determine the yield of pyrolysis products.

4.3. Study of Additivity Based on the Yield of Co-Pyrolysis Products. To verify the principle of additivity, the calculated data on the yields of pyrolysis products for individual components (Table 2) were compared with experimental data on the yield of pyrolysis products for the mixtures under the study. As an evaluation criterion, the yields of product were chosen based per apparent organic content (Figure 4).

As can be seen from Figure 4, for most mixtures, except for the mixture with tires, a manifestation of a synergistic effect is observed in the form of an increase in the yield of liquid pyrolysis products. The difference in oil yield from the calculated one was 11.1, 8.6, and 10.0% for PE-LD, PE-HD, and PP, respectively. Other authors have also previously reported synergistic effects in co-pyrolysis. Bozkurt et al. reported that in the case of co-

Figure 4. Comparison of experimental and calculated data on the yield of pyrolysis products of a mixture of oil shale with polymer wastes.
pyrolysis of Turkish oil shale with PP, the yield of pyrolysis products increased. Also, during the co-pyrolysis process, PP acted as a hydrogen source and saturated the free radicals formed as a result of breaking the cross-links and made positive contributions to the liquid product yield by creating a positive synergistic effect. Li et al.\(^46\) have studied co-pyrolysis of Fushun and Longkou deposit oil shale with varying ratios of PP and polyethylene in mixtures. They noted that plastics have an obvious synergistic effect that increases the yield of shale oil due to the combined pyrolysis of mixtures of oil shale and plastic, and this effect is more significant with polyethylene. The synergistic effect was interpreted based on the free radical reaction in the theory of pyrolysis. Because the hydrogen content in oil shale was low and the hydrogen content in plastic was high, the hydrogen atoms of the plastic were transferred to free radicals, which increased the yield of liquid products. Sinaj et al.\(^46\) reported that co-pyrolysis of Turkish lignite with PE-LD significantly increased yield of oil, indicating a synergy between lignite and PE-LD. In the case of co-pyrolysis of oil shale and tires, a decrease in the yield of oil is observed, which in turn can be explained by the fact that the rubber contains a significant amount of sulfur, which is bound with alkaline earth metals of the mineral part of oil shale during pyrolysis and leads to an increase in the yield of the solid phase. Despite the negative contribution to the yield of liquid products from tires, the total oil yield for the mixture of all polymer components with oil shale remains 6.5% higher than the calculated values. Thus, it can be stated that the synergistic effect is primarily manifested in the interaction of volatile products of oil shale and polymer wastes in the gas and condensed phases. As a result, the oil yield is higher than expected from the calculated one, and the amount of char and gas for all mixtures, except EOS + tires, decreases.

### 4.4. Kinetics of Co-Pyrolysis. Activation Energy

To calculate the activation energy from the DTG curve for oil shale, polymer wastes, and their mixtures, a temperature range of 225–515 °C was chosen, which corresponds to the stage of thermal decomposition of the organic part of the materials under the study. Within this interval, a step every 10 °C was chosen. The temperature dependence was transformed, and all temperature values were calculated as 10\(^{\alpha}/T\), where \(T\) is the temperature in K. According to the data obtained, a graph of dependence \(\ln(-\ln(1-\alpha)/T^2)\) on 10\(^{\alpha}/T\) was plotted (Figure 5).

The “breaking point” was determined from the graphs plotted over a wide temperature range for the raw materials. Based on the “breaking point”, the graphs were divided into two zones. Zone 1 is a reaction zone at low temperature, and zone 2 is a reaction zone at higher temperature. For polymers PE-LD, PE-HD, and PP, the presence of a “breaking point” is quite clear, which indicates different rates of decomposition in these zones. For tires and oil shale, the “breaking point” is not so clear. As previously noted by other authors, for oil shale, this is due to various reactions occurring during decomposition, which overlap to some extent and can affect the calculated values.\(^47\)

Tables 5 and 6 shows the kinetic parameters of pyrolysis of the raw materials and mixtures of polymer wastes with oil shale.

### Table 5. Obtained Characteristics of Kinetic Parameters of Pyrolysis of the Raw Materials

| sample | Zone | temperature range, °C | \(R^2\) | activation energy, kJ/mol | log A |
|--------|------|------------------------|--------|--------------------------|------|
| EOS    | zone II 225–365 | 0.99 | 44.38 | 7.42 |
| PE-LD  | zone I 375–515 | 0.99 | 129.33 | 8.29 |
| PE-HD  | zone II 225–405 | 0.98 | 43.72 | 10.96 |
| PP     | zone II 225–315 | 0.99 | 51.60 | 8.08 |
| EOS + tires | zone II 225–315 | 0.99 | 63.48 | 2.62 |
| EOS + mix | zone I 325–515 | 0.98 | 158.08 | 13.36 |

### Table 6. Obtained Characteristics of Kinetic Parameters of Pyrolysis of the Mixtures of Polymer Wastes with Oil Shale

| sample | zone | temperature range, °C | \(R^2\) | activation energy, kJ/mol | log A |
|--------|------|------------------------|--------|--------------------------|------|
| EOS + mix | zone II 225–445 | 0.99 | 59.94 | 4.51 |
| EOS + PE-LD | zone II 225–415 | 0.98 | 234.36 | 24.48 |
| EOS + PE-HD | zone I 415–515 | 0.99 | 46.95 | 8.31 |
| EOS + PP | zone I 425–515 | 0.98 | 233.82 | 24.14 |
| EOS + tires | zone II 225–395 | 0.98 | 46.59 | 5.14 |

The results demonstrate a close linear fitting with \(R^2\) coefficients of determination ranging from 0.90 to 0.99 over the used temperature ranges (Tables 5 and 6). The table also shows the values of the activation energy and the pre-exponential factor. If we compare the kinetic parameters of pyrolysis of individual components of polymer wastes and their mixtures with oil shale, it can be assumed that the value of the activation energy during co-pyrolysis can be influenced by the
structure of the polymer molecule. Thus, for a mixture of oil shale with PE-LD and PP, which have a branched structure, the activation energy value increases by 1.5 times compared to the calculated value for pure components, which indicates a more active course of the decomposition process. This is in good agreement with the above data on the yield of liquid pyrolysis products, where the highest oil yield from the calculated one was obtained also for a mixture of oil shale with PE-LD and PP. In turn, for a mixture of oil shale with tires and PE-HD, the activation energy value is slightly reduced, which indicates a positive effect when these materials are processed together. This decrease can be explained by the influence of the mineral part of oil shale, which can have a catalytic effect on the thermal degradation of these polymers.

5. CONCLUSIONS

The article presents the results of studying the kinetic parameters of pyrolysis of oil shale from Estonia deposits and mixtures of these oil shales with polymer wastes in a ratio of 50% oil shale, 12.5% PE-HD, 12.5% PE-LD, 12.5% PP, and 12.5% used car tires by the TGA method. The values of the activation energy and the pre-exponential factor were obtained using the Coats–Redfern integral method. It is shown that the activation energy in the temperature range near the maximum decomposition rate of organic matter differs for oil shale and for mixtures of oil shale with polymer wastes. For a mixtures of oil shale with PE-LD and PP, which have a branched structure, the value of the activation energy increases by 1.5 times, which indicates a more active course of the decomposition process. This is in good agreement with the above data on the yield of liquid pyrolysis products, where the highest oil yield from the calculated one was also obtained for a mixture of oil shale with PE-LD and PP. For a mixture of oil shale with tires and PE-HD, the activation energy is slightly reduced, which indicates a positive effect when these materials are processed together. The nature of decomposition of the organic part of the oil shale sample with the mixture (50% oil shale, 12.5% PE-HD, 12.5% PE-LD, 12.5% PP, and 12.5% tires) becomes the same as for PE-HD and PE-LD because their thermal degradation behavior is similar and their total organic matter in the test mixture predominates. On the basis of the data obtained, it can be concluded that in the co-pyrolysis of oil shale and polymer wastes in equal proportions, the kinetic parameters characteristic of the thermal destruction of polymer wastes will play a predominant role. The kinetics of co-pyrolysis depends mainly on plastics and tires, as they make up about 80% of all organic matter.

Also presented are data on the effect of each component of the plastic components separately on the process of weight loss of the sample during co-pyrolysis. It is shown that when plastics are added to oil shale, the experimental and calculated data coincide according to the principle of additivity contribution of each component. Thus, the data obtained can be used in the future for mathematical modeling of the pyrolysis process of multi-component mixtures and in the design of pyrolysis installations for determining the residual amount of the solid phase.

The work shows a synergistic effect in the co-pyrolysis of oil shale with plastics. The difference in oil yield from the calculated one was 8.6, 10.0, and 11.0% for PE-LD, PE-HD, and PP, respectively. For tires, this relationship was not observed. According to experimental data, the yield of oil is less than calculated. Despite the negative contribution to the yield of liquid products from tires, the total oil yield for a mixture of all polymer components with oil shale remains positive and amounts to 6.5% wt above the calculated indicators.

This series of experiments gives ground to the statement that co-pyrolysis is a promising way for the oil shale industry to enter the waste management market. In the course of further development of the process of co-pyrolysis of polymer wastes, it is possible that oil shale will be replaced with another mineral component that provides a catalytic effect.

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Notes

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ABBREVIATIONS

EOS, Estonian oil shale
PE-HD, high-density polyethylene
PE-LD, low-density polyethylene
PP, polypropylene
PET, polyethylene terphthalate
Mix, 50% oil shale, 12.5% PE-HD, 12.5% PE-LD, 12.5% PP, 12.5% tires
TGA, thermogravimetric analysis
ETRMA, European tire and rubber manufacturers’ ELTs, end of life tyres
ISO, International Organization for Standardization
EVS-ISO, Standard of the republic of Estonia-International Organization for Standardization
TG, weight loss curve
DTG, differential weight loss curve
REFERENCES

(1) Production of plastics worldwide from 1950 to 2019 (in million metric tons). https://www.statista.com/statistics/282732/global-production-of-plastics-since-1950/ (accessed Aug 12, 2020).

(2) Plastic—the Facts 2020. https://www.plasticsurope.com/en/resources/publications/4312-plastics-facts-2020. (accessed Nov 27, 2020).

(3) Europe—91% of all End of Life Tyres collected and treated in 2018. https://www.etrma.org/library/europe-91-of-end-of-life-tyres-collected-and-treated-in-2018/. (accessed Decet 28, 2020).

(4) Estonian national energy and climate plan (NECP 2030). https://ec.europa.eu/energy/sites/ener/files/documents/ec_cotures_translation_ee_necep.pdf. (accessed May 28, 2021).

(5) Velghe, E.; Carleer, R.; Yperman, J.; Schreurs, S. Study of the pyrolysis of municipal solid waste for the production of valuable products. J. Anal. Appl. Pyrol. 2011, 92, 366–375.

(6) Cunliffe, A. M.; Williams, P. T. Composition of oils derived from the batch pyrolysis of tyres. J. Anal. Appl. Pyrol. 1998, 44, 131–152.

(7) Williams, P. T.; Besler, S.; Taylor, D. T. The pyrolysis of scrap automotive tyres: The influence of temperature and residence time on product composition. Fuel 1990, 69, 1474–1482.

(8) Scheirs, J.; Kaminsky, W. Feedstock recycling and pyrolysis of waste plastics; John Wiley & Sons. Academic Press: New-York, 2006; pp 383–434.

(9) Onwudili, J. A.; Insura, N.; Williams, P. T. Composition of products from the pyrolysis of polyethylene and polypropylene in a closed batch reactor: Effects of temperature and residence time. J. Anal. Appl. Pyrol. 2009, 86, 293–303.

(10) Al-Salem, S. M.; Lettieri, P.; Baeyens, J. Kinetics and product distribution of end of life tyres (ELTs) pyrolysis: A novel approach in polyisoprene and SBR thermal cracking. J. Hazard. Mater. 2009, 172, 1690–1694.

(11) Anene, A.; Fredriksen, S.; Sætre, K.; Tokheim, L.-A. Experimental Study of Thermal and Catalytic Pyrolysis of Plastic Waste Components. Sustainability 2018, 10, 3979.

(12) Al-Salem, S. M.; Lettieri, P. Kinetic study of high density polyethylene (HDPE) pyrolysis. Chem. Eng. Res. Des. 2010, 88, 1599–1606.

(13) Sharuddin, S. D. A.; Abnisa, F.; Daoud, W. M. A. W.; Aroua, M. K. Pyrolysis of plastic waste for liquid fuel production as prospective energy resource. IOP Conf. Ser.: Mater. Sci. Eng. 2018, 334, 012001.

(14) Aydin, H.; İlkılıç, C. Optimization of fuel production from waste vehicle tires by pyrolysis and resembling to diesel fuel by various desulfurization methods. Fuel 2012, 102, 605–612.

(15) Tiktak, L.; Luik, H.; Pryadka, N. Co-Pyrolysis of Estonian Shales With Low-Density Polyethylene. Oil Shale 2004, 21, 75–85.

(16) SencHugh, K.; Kaidalov, A.; Shaparenko, L.; Popov, A.; Kindorkin, B.; Lushnyak, V.; Chikul, V.; Elenurm, A.; Marguste, M. Utilization of rubber waste in mixture with oil shale in destructive thermal processing using the method of solid heat carrier. Oil Shale 1997, 14, 59–66.

(17) Abnisa, F.; Wan Daoud, W. M. A.; Ramalingam, S.; Azemi, M. N. B. M.; Sahu, J. N. Co-pyrolysis of palm kernel oil and polyethylene waste mixtures to synthesis liquid fuel. Fuel 2013, 108, 311–318.

(18) Assumpção, L. C. F. N.; Carbonell, M. M.; Marques, M. R. C. Co-pyrolysis of polyolefin waste with Brazilian heavy oil. J. Environ. Sci. Health, Part A: Toxic/Hazard. Subst. Environ. Eng. 2011, 46, 461–464.

(19) Bernardo, M.; Lapa, N.; Gonçalves, M.; Mendes, B.; Pinto, F.; Fonseca, I.; Lopes, H. Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures. J. Hazard. Mater. 2012, 219–220, 196–202.

(20) Ding, K.; Zhong, Z.; Wang, J.; Zhang, B.; Fan, L.; Liu, S.; Wang, Y.; Liu, Y.; Zhong, D.; Chen, P.; Ruan, R. Improving hydrocarbon yield from catalytic fast co-pyrolysis of hemiclellulose and plastic in the dual-catalyst bed of CaO and HZSM-5. Bioresour. Technol. 2018, 261, 86–92.

(21) Hayashi, J.; Mizuta, H.; Kusakabe, K.; Morooka, S. Flash Copyrolysis of Coal and Polyolefin. Energy Fuels 1994, 8, 1353–1359.

(22) Johannes, I.; Tiekka, L.; Luik, H. Synergy in co-pyrolysis of oil shale and pine sawdust in autoclaves. J. Anal. Appl. Pyrol. 2013, 104, 341–352.

(23) Melendi-Espina, S.; Alvarez, R.; Díez, M. A.; Casal, M. D. Coal and plastic waste co-pyrolysis by thermal analysis mass spectrometry. Fuel Process. Technol. 2015, 137, 351–358.

(24) Onay, O.; Koca, H. Determination of synergetic effect in co-pyrolysis of lignite and waste tyre. Fuel 2015, 150, 169–174.

(25) Ro, K. S.; Hunt, P. G.; Jackson, M. A.; Compton, D. L.; Yates, S. R.; Cantrell, K.; Chang, S. Co-pyrolysis of swine manure with agricultural plastic waste: Laboratory-scale study. Waste Manag. 2014, 34, 1520–1528.

(26) Zhou, L.; Luo, T.; Huang, Q. Co-pyrolysis characteristics and kinetics of coal and plastic blends. Energy Convers. Manage. 2008, 50, 705–711.

(27) Wu, X.; Wu, Y.; Wu, K.; Chen, Y.; Hu, H.; Yang, M. Study on pyrolytic kinetics and behavior: The co-pyrolysis of microalgae and polypropylene. Bioresour. Technol. 2015, 192, 522–528.

(28) Çepelioğullar, Ö.; Pütün, A. E. Thermal and kinetic behaviors of biomass and plastic wastes in co-pyrolysis. Energy Convers. Manage. 2013, 75, 63–270.

(29) Tang, Y.; Huang, Q.; Sun, K.; Chi, Y.; Yan, J. Co-pyrolysis characteristics and kinetic analysis of organic food waste and plastic. Bioresour. Technol. 2018, 249, 16–23.

(30) Aboulkas, A.; El Harfi, K.; El Bouadi, A.; Benchanaa, M.; Mokhlisse, A.; Outzourit, A. Kinetics of co-pyrolysis of tarfaya (morocco) oil shale with high-density polyethylene. Oil Shale 2007, 24, 15–33.

(31) Aboulkas, A.; El Harfi, K.; El Bouadi, A.; Nadifiyine, M. Study on the pyrolysis of Moroccan oil shale with poly (ethylene terephthalate). J. Therm. Anal. Calorim. 2010, 100, 323–330.

(32) Chi, M.; Xu, X.; Cui, D.; Zhang, H.; Wang, Q. A Tg-Fit Investigation and Kinetic Analysis of Oil Shale Kerogen Pyrolysis Using the Distributed Activation Energy Model. Oil Shale 2016, 33, 228–247.

(33) Foltin, J. P.; Prado, G. N.; Lisbóa, A. C. L. Kinetic analysis of the oil shale pyrolysis using thermogravimetry and differential scanning calorimetry. Chem. Eng. Trans. 2017, 61, 559–564.

(34) Syed, S.; Qadah, R.; Talab, I.; Janajreh, I. Kinetics of pyrolysis and combustion of oil shale sample from thermogravimetric data. Fuel 2011, 90, 1631–1637.

(35) Koptelov, A. A.; Koptelov, I. A.; Rogozina, A. A.; Yushkov, E. S. Potential of thermal analysis as applied to studying the kinetics of thermal degradation of polymers. Russ. J. Appl. Chem. 2016, 89, 1454–1460.

(36) Tiwari, P.; Deo, M. Detailed kinetic analysis of oil shale pyrolysis TGA data. AIChE J. 2012, 58, 505–515.

(37) Coats, A. W.; Redfern, J. P. Kinetic Parameters from Thermogravimetric Data. Nature 1964, 201, 68–69.

(38) Pihl, O.; Tshepelevitsh, M.; Burko, M.; Siirde, A. E. Thermal and kinetic behaviors of oil shales. Oil Shale 1997, 14, 59–66.

(39) Bozkurt, P. A.; Kutlu, N. M.; Canel, M. Co-Pyrolysis of Göynük Oil Shale with Polypropylene and Structural Characterization of Pyrolysis Liquid. J. Turk. Chem. Soc., Sect. A 2016, 3, 247–264.

(40) Li, Y.; He, J. G.; Liu, Y. H. Preparation of shale oil from copyrolysis of oil shale/plastics mixes. Adv. Mater. Res. 2012, 512–515, 2162–2165.
(MKP) Lignite (Turkey) with Low-Density Polyethylene. Energy Fuels 2006, 20, 1609–1613.

(47) Maaten, B.; Loo, L.; Konist, A.; Nešumajev, D.; Pihu, T.; Kulaots, I. Decomposition kinetics of American, Chinese and Estonian Oil Shales Kerogen. Oil Shale 2016, 33, 167–183.