Catalysed pyrolysis of scrap rubber tyres

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Abstract

In this work catalysed pyrolysis of scrap rubber tyres was studied. Thermogravimetric analysis of scrap rubber tyres of different sizes was conducted to determine, which size is the best for further research. TGA of waste tyres at different heating rates was performed in order to obtain data that will allow to calculate activation energy. Also TGA of scrap rubber tyres with different catalysts was conducted. Activation energy using three different isoconversional methods (FWO, KAS, Starink) was computed. Mentioned methods gave the following results, respectively 104.722, 98.868 and 99.629 kJ/mol.

Furthermore, pyrolysis of scrap rubber tyres in a fixed bed reactor was performed. Four trials at the same temperature were conducted in order to check reproducibility of the process. Yields of the products turned out to be similar for each trial. Next, pyrolysis of waste tyres at different temperatures was performed, ranging from 400 to 500 °C. Influence of seven different catalysts at pyrolysis yields was studied. FTIR analysis of bio-oils from pyrolysis trials was conducted to study their quality.

Keywords: scrap rubber tyres, waste tyres, pyrolysis, catalytic pyrolysis, thermogravimetry

1. Introduction

1.1 Tyres generation problem

Dependence of our society on fossil fuels and fossil fuel based resources leads to deterioration of environment and climate change. Each year over 1.5 billion of tyres is being produced worldwide and currently 4 billions of them is being held on stockpiles or landfills. All of them are going to eventually end up as waste tyres. This constitutes a significant percentage of total solid waste stream. In European Union approximately 3.3 millions of waste tyres (2010) is produced annually. Considering constant population and economic growth it can be expected that the number of cars will be increasing year by year, which will unavoidably lead to an immense number of end-of-life tyres being produced. This trend is pictured in Figure 1. Not only the number of vehicles will be increasing, but also, as shown in Figure 2, number of kilometres drove by them. [2, 3, 5]

Constantly increasing solid waste production is one of the most important problems of our society. It is estimated that more than 1.34 billion tons of solid waste is produced annually in European Union. What is more, many developing countries lack appropriate infrastructure for waste management. The current legislation forces hierarchical waste management as follows: reduce, reuse, recycle, energy recovery, landfilling. First two options can solve the problem only for a very limited amount of waste tyres. Recycling is not a direct solution for mitigation of waste tyres disposal and landfilling is banned in European Union. Moreover, recycling is also difficult due to the fact that tyres are designed in such a way as to be resistant to bad weather conditions and mechanical stresses. Taking into account these limitations, energy recovery looks like a good perspective. The life span of waste tyres at the landfill is from 80 up to 100 years and keeping them on the landfill increases fire hazard. Tyres have high energy content (calorific value higher than coal) and because of that they are often combusted in cement plants. However, it may be dangerous for the environment, as it increases emission of sulphur dioxide and carbon monoxide. Because of the aforementioned reasons and in order to aim towards decarbonization of the environment alternative ways of handling waste tyres have to be found. Amongst them there is pyrolysis [2, 3, 4, 5].
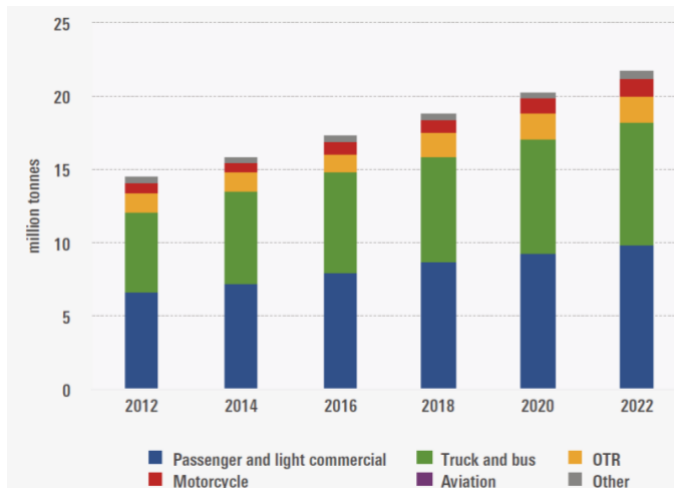
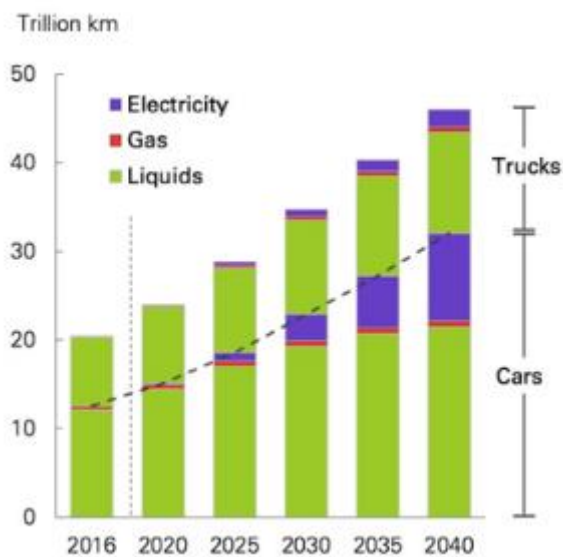*Figure 1 Tyres production - current and predicted [1]*

Figure 2 Current and predicted number of kilometres made by cars and trucks. [6]

1.2 Methods of waste tyres recycling

Considering legislation mentioned above, there are few ways of waste tyres recycling that are currently being applied such as grinding, retreading, reclaiming, combustion and pyrolysis [7]. In Figure 3 waste tyres management ways in European Union between 2011 and 2015 are presented.
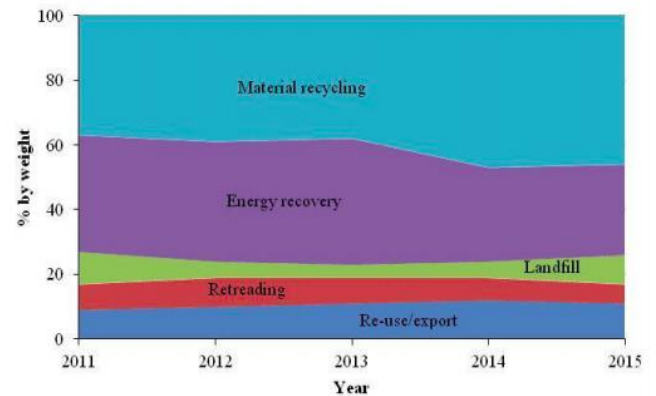

Figure 3 Waste tyres management in European Union

Grinding is basically decreasing the tyre size using various mechanical equipment. In this process ground rubber of different sizes is produced. There are several types of grinding: wet grinding, cryogenic grinding, mechanical grinding and water jet grinding. Material derived from the process of grinding can be used in numerous applications such as sport surfaces, children playgrounds, carpets, asphalts, civil engineering or footwear industry [8].

Another option for waste tyres recycling is retreading, which is highly economic. In this process, using special equipment, new tread is applied on a tyre without removing the old one. It resembles the process of creation of the tyre, but only 30-50% of the material used for production of new tyre is required. Numerous tests proved that proper retreading process makes tyres as safe as new ones. The process is fairly low cost compared to the production of a new tyres but can only be applied to a certain extent of damaged tyres [8].

Reclaiming of scrap rubber is another approach to handle waste tyres disposal problem. It is the transformation of a three dimensionally insoluble, interlinked and infusible strong thermoset polymer into a two-dimensional thermoplastic product that simulates majority of the assets of virgin rubber and is soft and processable. There are two different types of reclaiming process: physical and chemical [9].

High calorific value of waste tyres enables using them as a fuel in incinerators. Combustion of tyres allows for fairly low-cost power production and is environmentally acceptable. On the other hand, it requires specific flue gas cleaning technology, has high operating costs, prevents material recovery and cause substantial CO_2 emission [10].

Alternative way for waste tyres recycling is pyrolysis.

2. Materials and methods

2.1 Materials

For the purpose of the experiment scrap rubber tyres, from a local producer, of 4 different size ranges were prepared: 0.6-0.8mm, 0.8-2.5mm, 2-4mm, 4-6mm. Used rubber comes from end-of-life tyres from passenger cars. During the experiment various catalysts were applied combined with tyres. Catalysts used in the experiment: K_2CO_3, $MgCO_3$, $CaCO_3$, TiO_2, Al_2O_3, SiO_2 and Montmorillonite.

2.2 Thermogravimetric analysis

TGA is one of the methods of thermal analysis and it measures the change of samples mass as a function of time or temperature in controlled conditions. Thermogravimetric analysis is broadly used to study physical phenomena such as absorption, adsorption, phase transition, thermal decomposition etc. In principle, when the sample in the Thermogravimetric Analyzer is heated, its mass changes. Observing this change allows to obtain information about thermal stability of a material or its composition. [11, 12]

Thermogravimetric analysis of waste tyres sample was conducted using TG-DTA/DSC Seteram labsys connected with computer equipped in appropriate software.

Thermogravimetric Analysis (TGA) of samples of all sizes was conducted. After that it was determined that the size 0.6-0.8mm achieved the best performance, hence it was selected as a sample for further experiments. Next, TGA for four different heating rates (40 °C/min, 30 °C/min, 20 °C/min and 10 °C/min) was conducted. After that TGA of tires combined with different catalysts with a 1:1 ratio was performed.

All trials were conducted according to the following step sequence:
1. Placing the sample in the crucible and weighing it.
2. Placing the crucible in the apparatus chamber.
3. Adjusting software settings.
4. Beginning of the trial.
5. Waiting for the sample to cool down after the trial.
6. Removing the crucible from the chamber.

2.3 Pyrolysis in the reactor

For the purpose of pyrolysis, a fixed bed vertical reactor has been used. The reactor was installed in a temperature-controlled oven. The flow of nitrogen through the reactor was maintained during each trial. The reactor is a cylindrical glass column in which, at the bottom, a layer of glass wool is placed, above it there is an inert material (silicon carbide) and then a layer of glass wool again. On top of this, in each trial, the sample of tyres rubber (with or without catalyst) was placed. As a part of the installation, a condenser was connected at the bottom of the reactor and placed in water. [13]

During the process of pyrolysis, the liquid product stays in the inert material and afterwards it is removed with a solvent (acetone). The solid product of pyrolysis, biochar, stays at the place of the sample in a reactor.

The following sequence of activities was applied during each trial:
1. Heating the oven to a set temperature of a trial.
2. Weighing the sample.
3. Placing glass wool, inert material and glass wool again in a reactor.
4. Introducing the sample into the reactor.
5. Implementing nitrogen flow in order to remove oxygen from the bed.
6. Turning off the oven and nitrogen flow and placing the reactor in the oven.
7. Turning on the nitrogen flow and the oven.
8. Starting counting time of the trial when the temperature reached the set one.
9. Turning off the nitrogen flow and the oven once the trial ended.
10. Taking out the reactor from the oven.
11. Waiting for the reactor to cool down.
12. Removing the bio-char from the reactor and weighing it.
13. Extracting bio-oil from the inert material using acetone.
14. Using a rotative separator to separate bio-oil from acetone.

The described procedure was applied to all performed trials. Firstly, four trials for uncatalyzed samples at the temperature of 450 °C were conducted in order to study reproducibility of the process. Next, pyrolysis without a catalyst was performed at different temperatures from 400 to 500 °C. Moreover, pyrolysis of scrap rubber tyres at 450 °C was performed with seven different catalysts. All the experiments were conducted with 15 minutes as trial time. In each trial mass of the tyres sample was 10 g, while in catalysed samples 2.5 g of catalysts was used. The trial for $CaCO_3$ as a catalyst was repeated with 1.25 g.

2.4 Characterization methods

2.4.1 FTIR

Fourier Transform Infrared Spectroscopy is a technique used to detect certain chemical compounds in gas, liquid or solid samples. Infrared radiation is transmitted through the sample, part of this radiation goes through and arrives a detector, the rest is absorbed by the sample. Specifically, light at different frequencies is absorbed by bonds between different elements. The signal received by the detector is called the molecular "fingerprint" of a sample. Apart from chemical, also structural information, can be determined by assessing the capability of a sample to absorb infrared beam.

ATR-FTIR spectroscopy method was applied to characterize biooil samples. The apparatus BOMEN (FTLA2000-100, ABB) with DTGS detector was used to record spectra. Studied wavelength range was 500-4000 cm^{-1}. Kubelka-Munk function was applied to correct the reflectance signal.

2.5 Determination of activation energy

There are many different methods for kinetic analysis of the decomposition process. The major division can be made for "model free kinetics" and "model fitting kinetics". Figure 4 depicts an overview of kinetic analysis methods. [15]
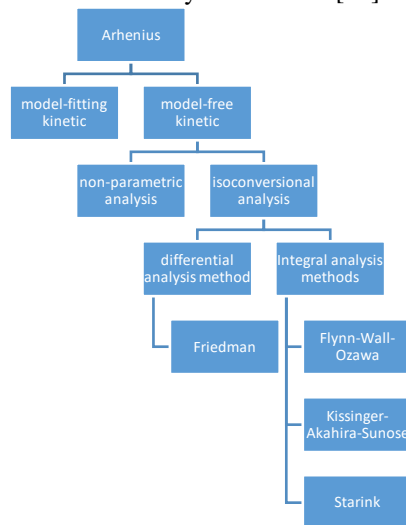

Figure 4 The overview of kinetic analysis methods for the decomposition process

In the model-fitting methods kinetic parameters are forcefully fitted into an equation and a, model that statistically fits the best, is being chosen. However, usually more than one reaction mechanism fits the data, which makes the result ambiguous and effects in Arrhenius parameters varying a lot [15]. Model-free methods do not require to assume any reaction model; they are also simpler and it is easier to avoid errors while using them. To determine activation energy for thermochemical conversion most frequently isoconversional methods are applied and that is the case in this research as well.

In case of this research, to determine activation energy, isoconversional methods have been applied, specifically integral analysis methods. These methods are based on a principle which says that assuming the constant extent of conversion, the reaction rate is a function of a temperature only. This constant extent of conversion may be defined as a stage at which a fixed amount is transformed, so it is an equivalent stage of reaction for different heating rates. Thus, in order to use these methods, data for several heating rates are needed.

The equation for the dynamic analysis of non-isothermal data has a following form [16]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} f(\alpha) e^{-\frac{E_\alpha}{RT}} \qquad (1)$$

Where:
α - conversion
A - pre-exponential factor [s^{-1}]
β - heating rate [K/s]
Eα - activation energy [kJ/mol]
R – universal gas constant [kJ/mol*K]
T – temperature [K]
f(α) – function depending on the conversion

In the integral methods, the integral version of the equation is used and data on T(β) (where β is heating rate) is used to calculate activation energy [17].

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = \frac{A}{\beta} \int_{T_0}^{T_f} \exp\left(-\frac{E}{RT}\right) dT = \left(\frac{A}{\beta}\right) p(x) \quad (2)$$

After the separation of variables, g(α) as conversion integral and p(x) as temperature integral are defined, where x is E/RT.

The temperature integral, (in this case it is p(x)), requires a range of approximation and since there is no exact solution for it, various researchers developed different empirical interpolation formulae. There are two best-known methods – Flynn-Wall-Ozawa (FWO) and Kissinger-Akahira-Sunose (KAS). The latter has a deviation developed by Starink and therefore is called the Starink method.

2.5.1 Kissinger-Akahira-Sunose method

This method, also known as the generalized Kissinger method, uses the temperature integral approximation according to Coats-Redfern, which looks as follows [17]:

$$p(x) = \frac{e^{-x}}{x^2} \qquad (3)$$

Next, substituting it in the equation (1) and taking the logarithm of both sides, results in the equation:

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E_\alpha g(\alpha)} - \frac{E_\alpha}{RT_{\alpha,i}}\right) \qquad (4)$$

2.5.2 Flynn-Wall-Ozawa method

In the FWO method the temperature integral approximation according to Doyle is used:

$$\int_{T_0}^{T_f} exp\left(-\frac{E}{RT}\right) dT = \left(\frac{E}{R}\right)(0.0484 e^{-1.0516u}) \quad (5)$$

Then, it is substituted into the equation (1) and by taking logarithm of both sides, the result is as follows:

$$ln\beta = ln\frac{AE}{Rg(\alpha)} - 5.331 - 1.052\frac{E}{RT} \qquad (6)$$

2.5.3 Starink method

Based on KAS method, Starink developed the modified equation to the shape that allows to calculate activation energy more accurately.

$$\ln\left(\frac{\beta}{T^{1.8}}\right) = ln\frac{AR}{E_a g(\alpha)} - 1.0037\frac{E_a}{RT_\alpha} \qquad (7)$$

Overall, all the integral analysis methods can be simplified to the following version:

$$\ln\left(\frac{\beta}{T^s}\right) = C - \frac{BE_a}{RT_\alpha} \qquad (8)$$

In the above equation variables "s", "B" and "C" are, depending on the method, equal to:

- KAS: s = 2, B = 1, $C = \ln\left(\frac{AR}{E_a g(\alpha)}\right)$,

- FWO: s = 0, B = 1.052, $C = ln\frac{AE}{Rg(\alpha)} - 5.331$,

- Starink: s = 1.8, B = 1.0037, $C = \ln\left(\frac{AR}{E_\alpha g(\alpha)}\right)$.

In order to calculate activation energy, the left-hand side of the equation (8) has to be plotted versus 1/T. The slope of the obtained straight line gives the value of $\frac{BE_\alpha}{R}$, while the intercept gives the value of the variable "C" from equation (8).

3. Results and discussion

3.1 Thermogravimetric analysis

3.1.1 TGA of scrap rubber tyres for different heating rates

The mass loss thermograms of thermal decomposition of scrap rubber tyres at four different heating rates (10, 20, 30, 40 °C/min) are shown in Figure 5. All the samples of tyres had a size of 0.6-0.8mm and a similar weight of ca. 113 mg.
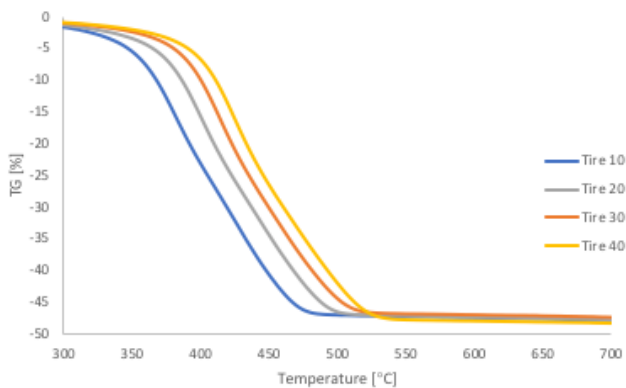

Figure 5 TG curves for waste tyres with different heating rates

The weight loss curves represent the mass loss with the increase of temperature at different heating rates. The curves for all heating rates have a similar shape. The decomposition for each heating rate starts at temperature higher than 300 °C. In the case of the sample with the heating rate of 10 °C/min, the decomposition starts and finishes the earliest. It ends at ca. 490 °C with the weight loss of 47%. The decomposition of the sample with the heating rate of 20 °C/min ends at ca. 510 °C with the weight loss of 47%. For the sample with the heating rate of 30 °C/min the decomposition ends at ca. 530 °C with the weight loss of 47%. When it comes to the sample with the heating rate of 40 °C/min decomposition ends at ca. 555 °C with the weight loss of 48%. In all cases it is a single stage degradation with a single peak. Based on this information, the conclusion can be drawn that the lower the heating rate the earlier the decomposition starts.

The differential mass loss thermograms (DTG) of thermal decomposition of scrap rubber tyres at four different heating rates (10, 20, 30, 40 °C/min) are shown in Figure 6. All the samples of tyres had a size of 0.6-0.8mm and similar weigh of ca. 113 mg.
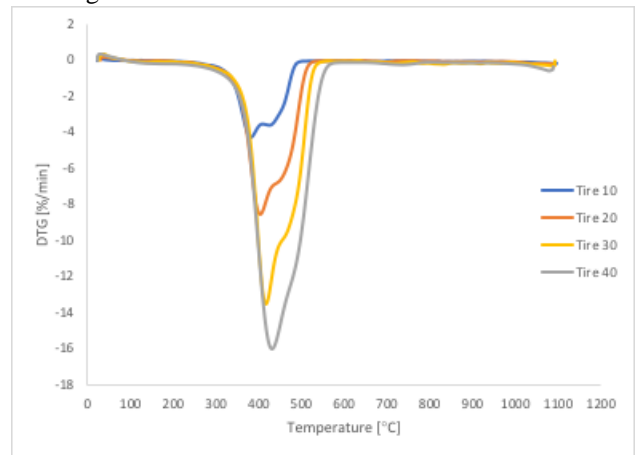

Figure 6 DTG curves for waste tyres with different heating rates

The DTG curves are the first derivative of TG curves and they represent the mass loss per time against the temperature increase. As it can be seen at the graph, the noticeable mass loss per minute for each of the heating rates starts at temperature higher than 300 °C and initially follows the same path. All curves have one distinguishable peak, which emerges at higher temperature with increasing the heating rate and second, vague peak which becomes less apparent with increasing temperature. Based on the literature first peak was identified as degradation of styrene-butadiene rubber (SBR), while the second one occurred due to the degradation of polybutadiene rubber (BR). Maximum weigh loss rate for studied heating rates appears at following temperatures: 10 °C/min – 378 °C, 20 °C/min – 395 °C, 30 °C/min – 413 °C, 40 °C/min – 431 °C.

3.1.2 Determination of activation energy

Based on the methodology described in Chapter 2.5, activation energy was calculated using three aforementioned methods. Using the data from TG, left hand side of the equation (8) was plotted versus 1/T for each of the three methods, as it can be seen in Figure 7. Next, trend lines were drawn, which slopes gave the values of $\frac{BE_\alpha}{R}$.
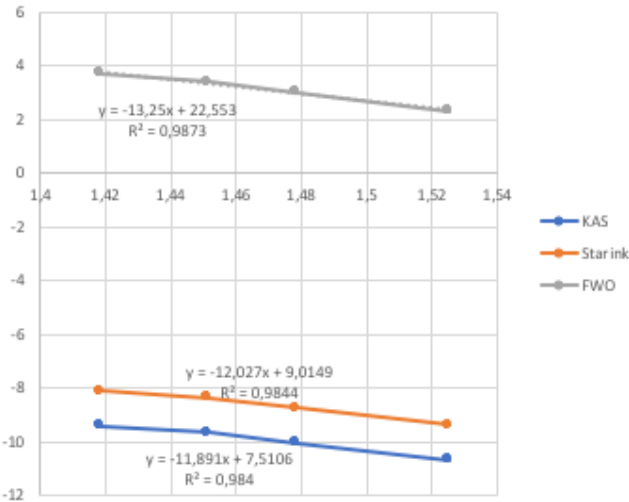

Figure 7 Regression lines for waste tyres computed by three different methods

The values of activation energy calculate by three different methods are summarized in the Table 1.

Table 1 Activation energy computed by three different methods based on TGA data.

	KAS	Starink	FWO
E_a [kJ/mol]	98.9	99.7	104.7

D. I. Aslan et al. [18] performed thermogravimetric analysis of waste tyres and computed activation energy using two isoconversional methods: KAS and FWO. The researchers used waste tyres shredded to the size below 0.25 mm and conducted TGA with samples weigh ca. 10 mg under nitrogen atmosphere. Four different heating rates were studies (5, 10, 20 and 40 °C/min), the samples initially were kept at the temperature 110 °C for 20 minutes in order to get rid of the moisture and later at 800 °C also for 20 minutes to ensure full pyrolytic decomposition of a sample. The results were 161.5 kJ/mol for KAS method and 164.1 kJ/mol for FWO method.

3.1.3 TGA of scrap rubber tyres with different catalysts

The mass loss thermograms of thermal decomposition of scrap rubber tyres with seven different catalysts are shown in Figure 8. All the samples of tyres had a size of 0.6-0.8mm and similar weight of ca. 113 mg.
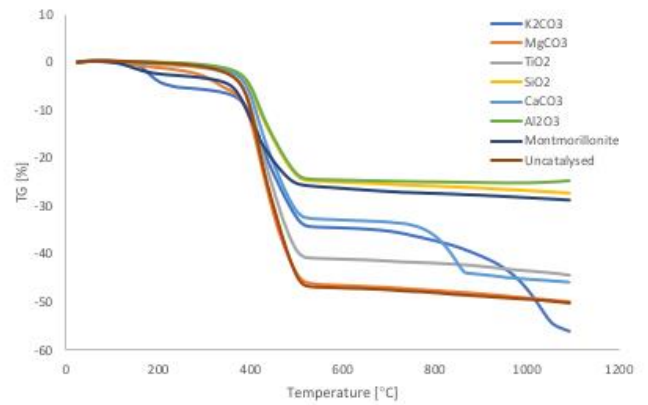

Figure 8 TG curves of waste tyres with different catalysts

As it can be seen from the comparison of the catalysed and uncatalyzed thermal decomposition curves, the addition of catalysts does not have a significant influence on the temperature range of main mass loss. In each case the main mass loss starts at ca. 350 °C and finishes at ca. 550 °C. The addition of the catalysts does not increase the maximum weight loss rate. For uncatalyzed pyrolysis the maximum weight loss rate is ca. 14 %/min whereas for different catalysts the maximum weight loss rate ranges between ca. 6.5 %/min for montmorillonite and 11.7 %/min for MgCO$_3$.

The addition of catalysts has a substantial influence on the final mass loss. Whereas for pyrolysis with different heating rates without the catalysts, the final mass loss was basically constant, for pyrolysis with different catalysts it varies from ca. 25% for Al$_2$O$_3$ up to 56% for K$_2$CO$_3$. It is clear that the applied catalyst has a strong influence on the final products distribution.
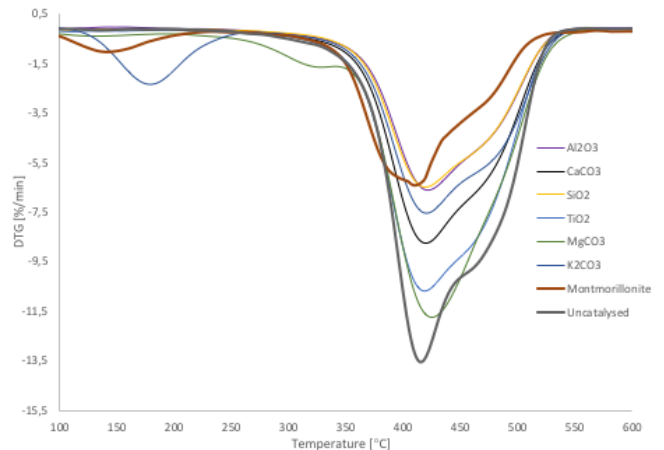

Figure 9 DTG curves of waste tyres with different catalysts

It can be seen from TGA and DTG for K$_2$CO$_3$ and montmorillonite that the addition of these catalysts has an influence on the reaction mechanism of tyre rubber pyrolysis. Thermal decomposition of tyre rubber without catalysts occurs with only one main peak on DTG curve. The addition of K$_2$CO$_3$ results in an additional peak at around 180 °C. In case of montmorillonite the peak occurs at ca. 145 °C.

3.2 Pyrolysis in a fixed bed reactor

3.2.1 Reproducibility of the process

In order to check the reproducibility of the process, four trials of uncatalyzed pyrolysis at the temperature of 450 °C were conducted. The percentage share of products' yields is presented in Figure 10.
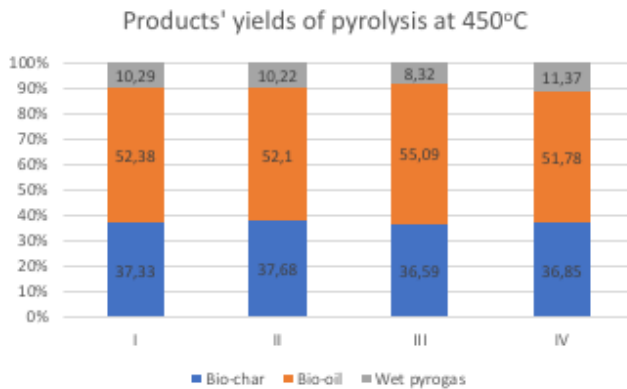

Figure 10 Products' yields of pyrolysis at 450 oC

As it can be seen at the chart above, the results for all four trials are very similar. Yields of wet pyrogas and bio-oil for the third trial are slightly different, which may be the effect of inhomogeneous material.

3.2.2 Influence of the temperature

Pyrolysis of scrap rubber tyres without the catalyst at five different temperatures has been conducted in order to study the influence of the temperature on the products yields. The results are presented in Figure 11.
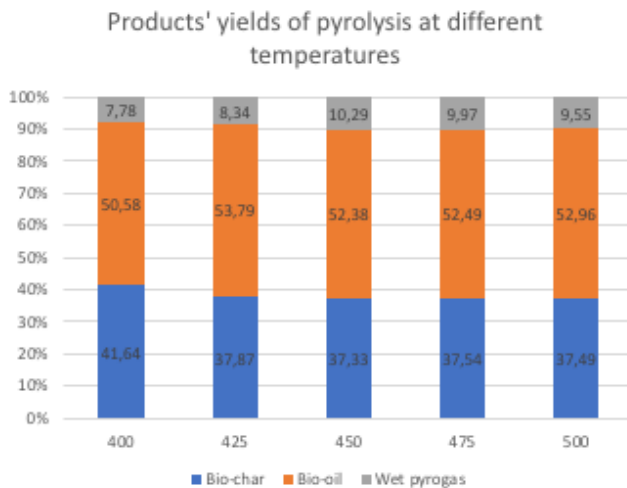

Figure 11 Products' yields of pyrolysis at different temperatures

The highest bio-oil yield of 53.79% was achieved for the temperature of 425 °C. On the other hand, the lowest - 50.58% - for 400 °C. The same temperature gave the highest yield of biochar (41.64%) and the lowest yield of wet pyrogas (7.78%).

Pyrolysis conducted at 450 °C gave the highest yield of wet pyrogas (10.29%) and lowest yield of biochar (37.33%).

3.2.3 Catalysed pyrolysis

Pyrolysis of scrap rubber tyres with different catalysts in a fixed bed reactor was conducted in order to observe the influence of these catalysts on the products yields of the process. In each trial 2.5g of catalyst was used, and the trial with CaCO3 was additionally repeated with the amount of 1.25g. The percentage share of biochar, bio-oil and wet pyrogas obtained during each trial is presented in Figure 12.
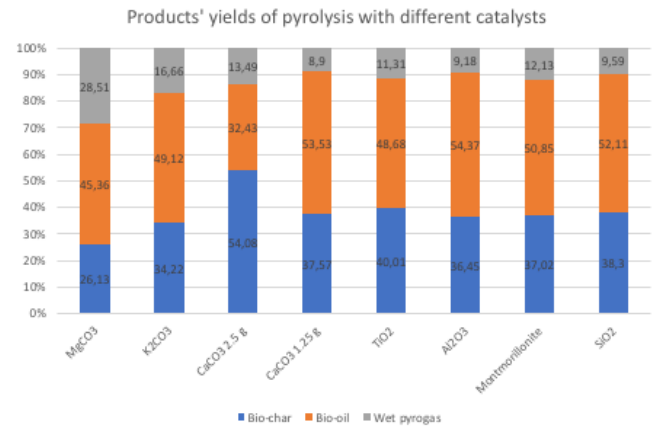

Figure 12 Products' yields of pyrolysis with different catalysts

The highest yield of bio-oil was achieved when Al_2O_3 was used as a catalyst and it was equal to 54.37%. It was slightly lower for 1.25g of $CaCO_3$ – 53.53%. On the other hand, the lowest bio-oil yield was noted for the trial with 2.5g of $CaCO_3$, while giving the highest biochar yield at the same time – 54.08%. Using $MgCO_3$ as a catalyst resulted in the lowest biochar yield (26.13%) and the highest yield of wet pyrogas (28.51%). For the other studied catalysts, the yield of wet pyrogas oscillated between 8.9% and 16.66%.

3.3 FTIR of biooils

In order to characterize biooils obtained during pyrolysis trials Fourier Transform Infrared Spectroscopy was conducted for each sample. Figure 13 shows FTIR spectra of biooils from pyrolysis performed at different temperatures for bands centred between 2800 and 3000 cm^{-1}. The peak at 2920 cm^{-1} was assigned to C-H stretching group. The sharpest peak occurs for the temperature 475 °C.
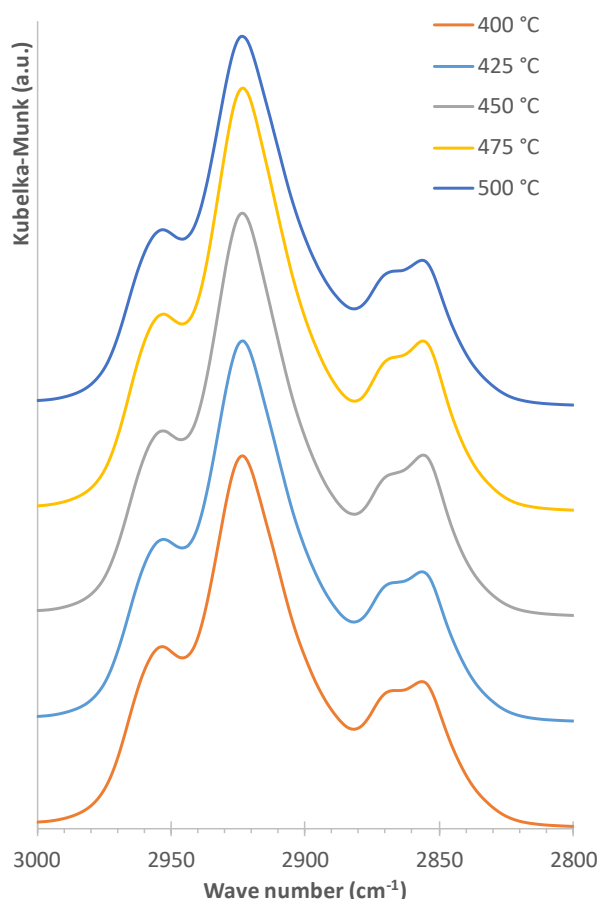
Figure 13 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber at different temperatures (400 °C to 500°C) centred between 2800 and 3000 cm-1
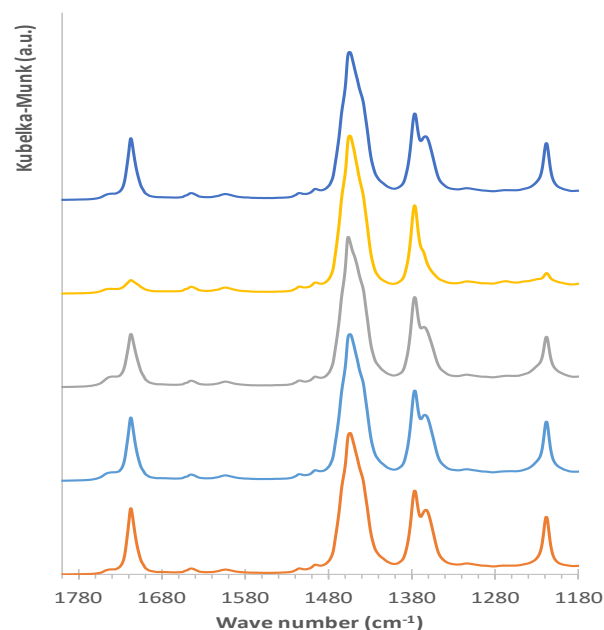

Figure 14 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber at different temperatures (400 °C to 500°C) centered between 1180 and 1800 cm-1

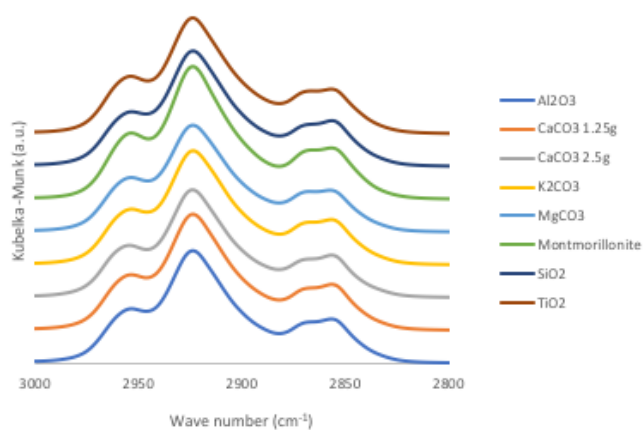In Figure 14 FTIR spectra of biooils from pyrolysis performed at different temperatures for bands between 1780 and 1180 cm-1 is presented. The peak at 1450 cm-1 was assigned to C-H bending groups. The highest and sharpest peak in this range appears for the trial at 475 °C. Intensity of the peak is not increasing with the temperature.

FTIR spectra of biooils from pyrolysis of scrap rubber tires mixed with different catalysts is presented in Figure 15 and 16. First one shows data for bands between 2800 and 3000 cm-1. The peak at 2920 cm-1 was related to C-H stretching groups and it has very similar intensity for each catalyst. It appears to be the sharpest for a sample with Montmorillonite as catalyst. In range 1200-1800 cm-1 the highest peak appears at 1450 cm-1 and it was identified as C - H bending groups. The peak is the most intense for Montmorillonite and the least for K_2CO_3.

Figure 15 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber with different catalysts centred between 2800 and 3000 cm -1
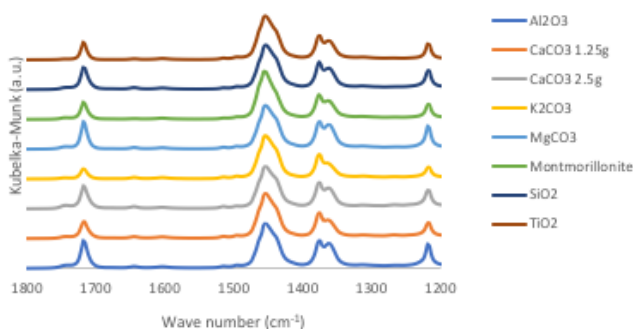
Figure 16 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber with different catalysts centred between 1200 and 1800 cm -1

4. Conclusions

Constant economic growth effecting in increasing number of driven vehicles is a reason of enormous amount of waste tyres being produced day by day. Those tyres constitute a significant part of solid waste stream and have to be managed with minimum hazard for the environment. There are several methods of waste tyres recycling such as grinding, retreading, reclaiming, combustion and pyrolysis. In this dissertation energy recovery by pyrolysis of scrap rubber tyres was studied.

The pyrolysis process of waste tyres with and without catalysts in thermogravimetric analyser was performed in order to study decomposition behaviour. TG and DTG curves obtained from the experiment show the impact of used catalysts on lowering maximum weigh loss rate. It can be observed that catalysts such as $CaCO_3$ are able to decrease the temperature at which maximum decomposition rate is achieved. Thus, pyrolysis at lower temperature could be performed, what would cause energy savings. Thermogravimetric analysis of scrap rubber tyres samples at different heating rates allowed to compute activation energy using three different isconversional integral methods. Obtained results turned out to be lower when compared to similar experiments found in the literature. The disparity may come from the differences in a process' conditions. It may also be caused by the fact that tyres used in both cases had different granulation and were coming from a different source.

Furthermore, pyrolysis of scrap rubber tyres in a fixed bed reactor was performed. Four consecutive trials at the same temperature 450 °C gave similar results when it comes to products' yields. It means that the process is reproducible and maintaining the same process conditions will allow to obtain similar results. Next, five trials with increasing temperature by 25 °C from 400 to 500 °C were conducted. Changing the temperature in this range did not have significant influence on the products' yields of the pyrolysis. Usage of seven different catalysts resulted in various effects on pyrolysis' product yields. Considerably highest bio-oil yield was achieved when using 2.5 g of Al2O3 and 1.25 g of CaCO3 as catalysts. Using MgCO3 as catalyst promotes creation of wet pyrogas, which constitute almost 30% of pyrolysis products in this case. Significantly highest biochar yield was achieved when using 2.5 g of CaCO3 as catalyst. Based on catalyzed process data conclusion can be drawn that different catalysts can be used to control product distribution.

4.1 Future work

Further research could include conducting XRD test for each biochar obtained from the pyrolysis in order to study their composition and quality. What is more, as product distribution for uncatalyzed process at the temperature of 400 and 425 °C was very similar to the one at 450 °C, further trials with catalysts at those temperatures could be conducted. It would lower the energy demand for the process. As it can be observed at DTG data graph, the process continues till the temperature even above 500 °C, it means that further research at higher temperatures could be conducted in order to check if it will increase bio-oil and wet pyrogas yields.

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