



**TÉCNICO**  
LISBOA



## **Catalysed pyrolysis of scrap rubber tyres**

**Łukasz Wojnicki**

Thesis to obtain the Master of Science Degree in

### **Energy Engineering and Management**

Supervisors: Prof. Ana Paula Vieira Soares Pereira Dias

Prof. Teresa Grzybek

#### **Examination Committee**

Chairperson: Professor Francisco Manuel Da Silva Lemos

Supervisor: Prof. Ana Paula Vieira Soares Pereira Dias

Member of the Committee: Professor Ana Filipa da Silva Ferreira

**November 2019**

I declare that this document is an original work of my own authorship and that it fulfils

all the requirements of the Code of Conduct and Good Practices of

Universidade de Lisboa

# Acknowledgements

First and foremost, I would like to thank my supervisor Prof. Dr. Ana Paula Soares Dias for her immeasurable and always kind help. Secondly, I would like to give sincere thanks to my co-supervisor Prof. Dr. Teresa Grzybek for immense number of tips and help that I received from her.

Acknowledgements are due to *Biogoma - Sociedade De Reciclagem De Pneus Lda* for providing me with scrap rubber tyres material used during the laboratory work.

I would also like to thank my sister Basia for her relentless support, motivating me and patience for answering tons of my, sometimes stupid, questions. I can honestly say that I would not be able to complete this thesis without your help. You are the best.

Next, I would like to thank my friends Hamid, Sara, Katerina, Sebastian, Laura and Kuba for their support and encouragement. You are always there for me and I greatly appreciate it.

Additionally, I would like to recognize motivation that I was constantly receiving in different forms (talks, videos, texts) from my friend André that could be summed up in his quote: “just \*\*\*\*\* get it over and done with”. Muito obrigado.

Last but not least, I would like to acknowledge my parents – Andrzej and Agata, the rest of my siblings – Kamil and Karolina, and their partners –Monika, Paweł and Rafał, who were great support for me. You guys are my strength and everyday motivation.

## 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

## List of figures

Figure 1 Tyres production - current and predicted .....	9
Figure 2 Current and predicted number of kilometres made by cars and trucks. ....	10
Figure 3 Waste tyres management in European Union .....	11
Figure 4 Comparison of passenger and truck tyre composition .....	13
Figure 5 Products yield of waste tyres pyrolysis without and with various catalysts. ....	17
Figure 6 Waste tyres samples.....	19
Figure 7 Samples of catalysts mixed with scrap rubber tyres.....	19
Figure 8 Setaram Labsys DSC-TG-DTA thermobalance.....	20
Figure 9 Scheme of the installation for pyrolysis process in a reactor . ....	21
Figure 10 The reactor placed in the oven. ....	22
Figure 11 The sample of tyres mixed with a catalyst before pyrolysis. ....	22
Figure 12 Bio-char after pyrolysis of rubber tyres mixed with a catalyst. ....	23
Figure 13 Apparatus used to perform FTIR analysis. ....	24
Figure 14 The overview of kinetic analysis methods for the decomposition process .....	25
Figure 15 TG curves for waste tyres with different heating rates .....	28
Figure 16 DTG curves for waste tyres with different heating rates.....	29
Figure 17 Regression lines for waste tyres computed by three different methods.....	30
Figure 18 TG curves of waste tyres with different catalysts .....	31
Figure 19 DTG curves of waste tyres with different catalysts.....	32
Figure 20 Products' yields of pyrolysis at 450 °C.....	33
Figure 21 Products' yields of pyrolysis at different temperatures .....	34
Figure 22 Products' yields of pyrolysis with different catalysts .....	35
Figure 23 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber at different temperatures (400 °C to 500 °C) centered between 2800 and 3000 cm <sup>-1</sup> .....	36
Figure 24 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 <sup>-1</sup> .....	37
Figure 25 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber with different catalysts centered between 2800 and 3000 cm <sup>-1</sup> .....	37
Figure 26 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber with different catalysts centered between 1200 and 1800 cm <sup>-1</sup> .....	38

## List of tables

Table 1 Influence of the temperature on product yields with different catalysts. ....	18
Table 2 Activation energy computed by three different methods based on TGA data. ....	30

# Table of contents

<b>ACKNOWLEDGEMENTS</b> .....	<b>2</b>
<b>ABSTRACT</b> .....	<b>4</b>
<b>LIST OF TABLES</b> .....	<b>6</b>
<b>1. INTRODUCTION</b> .....	<b>9</b>
1.1 TYRES GENERATION PROBLEM .....	9
1.2 METHODS OF WASTE TYRES RECYCLING .....	10
1.3 THE PURPOSE OF THE THESIS .....	11
<b>2. PYROLYSIS OF TYRES</b> .....	<b>13</b>
2.1 TYRES COMPOSITION .....	13
2.2 PYROLYSIS OF WASTE TYRES .....	13
2.2.1 <i>Types of pyrolysis</i> .....	14
2.2.2 <i>Waste tyres as feedstock for pyrolysis</i> .....	14
2.2.3 <i>Types of reactors for waste tyres pyrolysis</i> .....	14
2.2.3.1 Fixed bed reactors .....	14
2.2.3.2 Fluidized bed reactors .....	15
2.2.3.3 Screw kiln and rotary kiln reactors .....	16
2.2.4 <i>Catalysts for waste tyres pyrolysis</i> .....	16
2.2.5 <i>Products of waste tyres pyrolysis and their properties</i> .....	18
<b>3. EXPERIMENTAL</b> .....	<b>19</b>
3.1 MATERIALS .....	19
3.2 THERMOGRAVIMETRIC ANALYSIS .....	19
3.3 PYROLYSIS IN THE REACTOR .....	20
3.4 CHARACTERIZATION METHODS .....	24
3.4.1 <i>FTIR</i> .....	24
3.4.2 <i>XRD</i> .....	24
3.5 DETERMINATION OF ACTIVATION ENERGY .....	25
3.5.1 <i>Kissinger-Akahira-Sunose method</i> .....	26
3.5.2 <i>Flynn-Wall-Ozawa method</i> .....	27
3.5.3 <i>Starink method</i> .....	27
<b>4. RESULTS AND DISCUSSION</b> .....	<b>28</b>
4.1 THERMOGRAVIMETRIC ANALYSIS .....	28
4.1.1 <i>Thermogravimetric analysis of scrap rubber tyres for different heating rates</i> .....	28
4.1.2 <i>Determination of activation energy</i> .....	29

4.1.3 Thermogravimetric analysis of scrap rubber tyres with different catalysts .....	30
4.2 PYROLYSIS IN A FIXED BED REACTOR .....	32
4.2.1 Reproducibility of the process.....	32
4.2.2 Influence of the temperature.....	33
4.2.3 Catalysed pyrolysis.....	34
4.3 FTIR OF BIOOILS .....	35
<b>5. CONCLUSIONS .....</b>	<b>39</b>
5.1 FUTURE WORK.....	39
<b>6. REFERENCES .....</b>	<b>40</b>



# 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, 7]

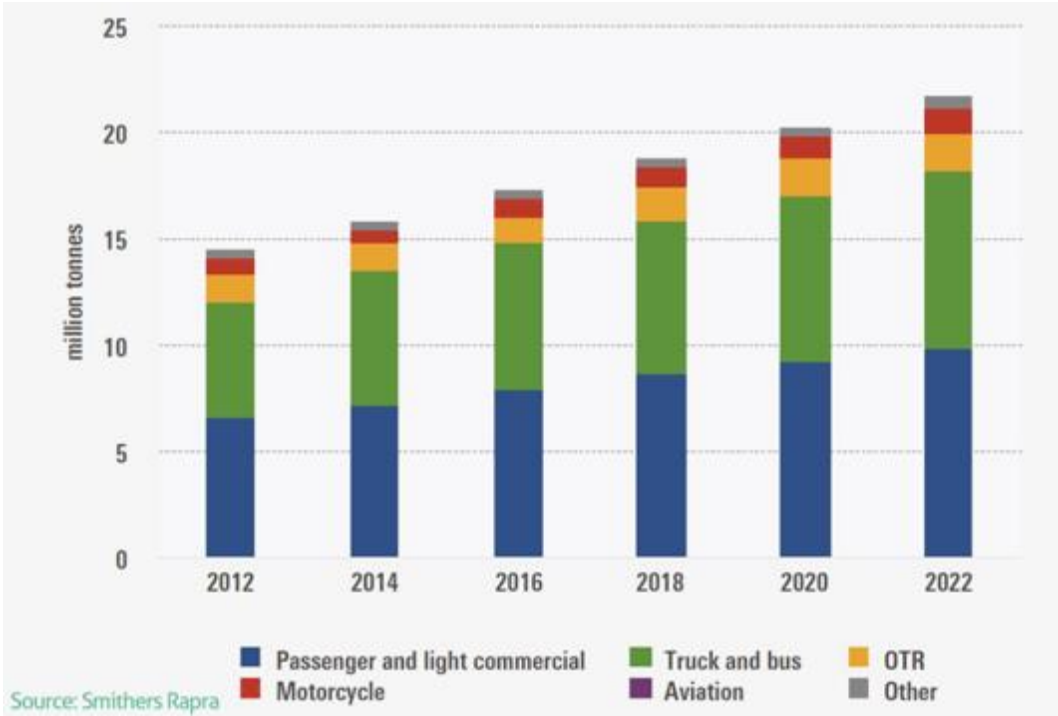


Figure 1 Tyres production - current and predicted [1]

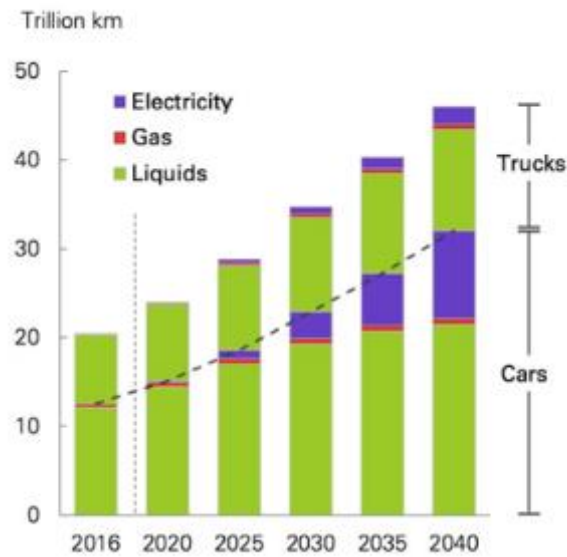


Figure 2 Current and predicted number of kilometres made by cars and trucks. [8]

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, 6, 7].

## 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 [29]. In Figure 3 waste tyres management ways in European Union between 2011 and 2015 are presented.

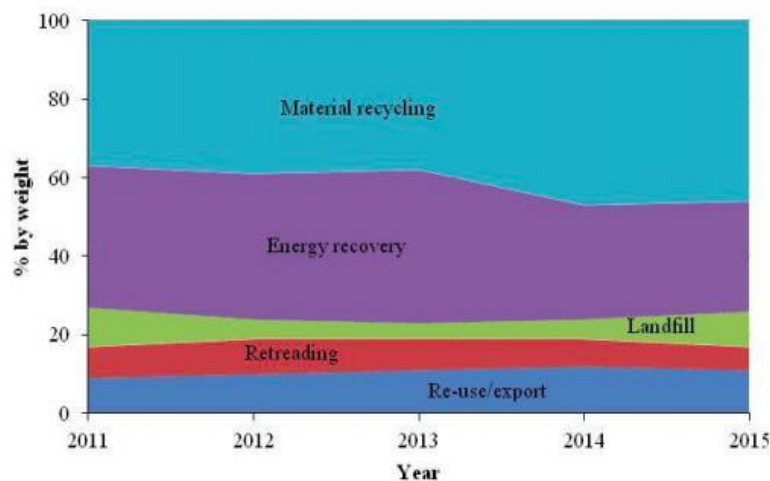


Figure 3 Waste tyres management in European Union

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 [30].

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 [30].

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 [31].

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<sub>2</sub> emission [32].

Alternative way for waste tyres recycling is pyrolysis, which is the subject of this thesis and is described in a following chapter.

### 1.3 The purpose of the thesis

The main aim of the thesis was to conduct kinetic analysis of scrap rubber tyres pyrolysis and based on that determining activation energy using isoconversional integral methods. In the thesis the influence of different catalysts on thermal decomposition of rubber tyres was studied using

thermogravimetric analysis. Furthermore, influence of temperature and different catalysts on the yields of pyrolysis products have been investigated in the reactor.

## 2. Pyrolysis of tyres

### 2.1 Tyres composition

A typical tyre consists of natural rubber, synthetic rubber, tyre cords (steel, rayon, nylon, polyester, glass, glass fiber, aramid), bead wires (steel), plasticizers (oil, resins), fine chemicals (sulphur, zinc oxide, antioxidants, antiozonants) and fillers (carbon black and/or silica). The antioxidants and antiozonants are resistant to degradation. The percentage share of these components depends on the tyre application. For example, passenger car tyres usually have a similar share of natural and synthetic rubber (around 22-24%) while in a truck tyre the share of natural rubber is usually twice as high as synthetic rubber (natural rubber 27-30%, synthetic rubber 14-15%). Given percentages are exemplary and in reality they differ depending on the producer and other factors. Another exemplary tyre composition is illustrated in Figure 4. Rubber in a tyre gives elasticity and resistance while tyre cords and bead wires are responsible for keeping form and resistance. Plasticizers are added in order to improve workability and tackiness. Fine chemicals in tyres enable its vulcanization and protect the tyre from ageing. Carbon black is used to increase resistance of rubber. [4]

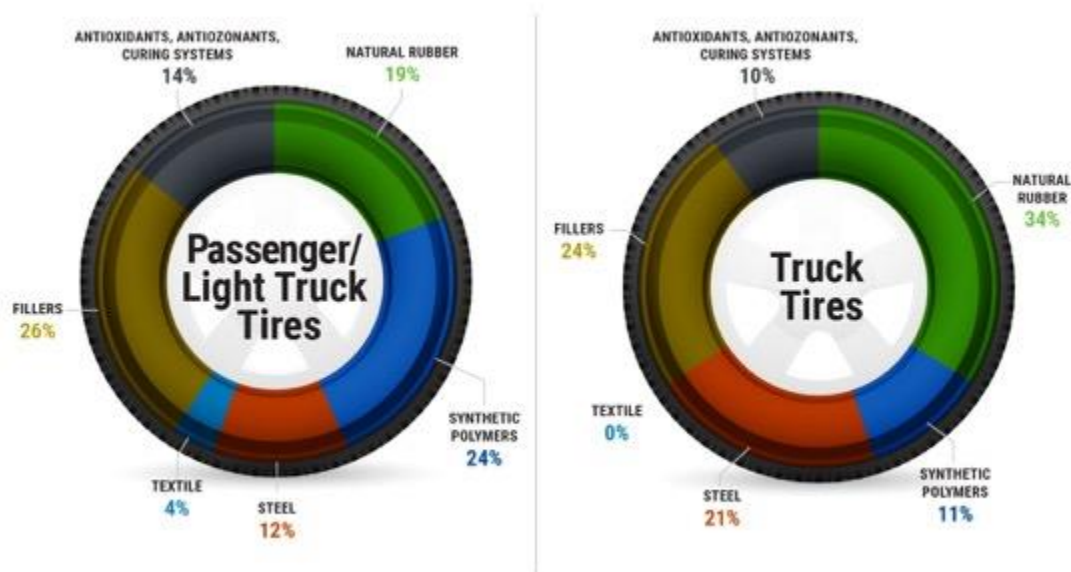


Figure 4 Comparison of passenger and truck tyre composition [5]

### 2.2 Pyrolysis of waste tyres

Pyrolysis is a process of thermo-chemical decomposition of organic polymers in the absence of oxygen. The process is usually conducted in the range of temperatures between 400 and 600 °C. Products of tyres pyrolysis are char, gasses, liquid oil and steel, all of which can be further used in a variety of applications. Char after an appropriate upgrade can be applied as a substitute for activated carbon in different chemical processes. Gasses may be used as energy source to fuel the process itself. Liquid oil from tyres pyrolysis usually have fairly high energy content which enables using it both as a fuel and feedstock for petrochemical processes. [3, 7]

## 2.2.1 Types of pyrolysis

Depending on the temperature, heating rate or volatiles residence time pyrolysis can be divided into certain types. The simplest division is made on slow and fast pyrolysis. Any pyrolytic process with the usage of a catalyst is called catalytic pyrolysis.

Slow thermal decomposition at fairly low temperature is characteristic for slow pyrolysis. In this case the process is conducted with a low heating rate and rather long volatiles residence time, which leads to a bigger share of solid products, such as coke and tar. The main purpose of slow pyrolysis is to obtain char.

Fast pyrolysis, in contrast to the slow one, considers fast pyrolytic decomposition at higher temperature and heating rate. For this kind of pyrolysis an infrastructure that enables a fast vapor removal is needed. Furthermore, fine particle size of feedstock is required. Such conditions favour the production of liquid oil. Fast pyrolysis is mostly conducted in fluidized bed, free-fall, ablative and entrained reactors in which the time of reaction is between milliseconds and seconds. Short volatiles residence time should not exceed 2 seconds, or otherwise secondary reactions will occur.

## 2.2.2 Waste tyres as feedstock for pyrolysis

There are several factors that make tyres a good feedstock for pyrolysis. First of all, they contain a significant share of volatile matter which consists of polymeric compounds. These polymeric compounds originate from synthetic and natural rubber. Additionally, waste tyres have high calorific value reaching 35-40 MJ/kg. It is higher than calorific value of coal used in conventional power plants. Another advantage of tyres over coal is usually lower ash content. [6, 7]

## 2.2.3 Types of reactors for waste tyres pyrolysis

A few different kinds of reactors are used for waste tyres pyrolysis, such as fixed bed, fluidized bed, screw kiln and rotary kiln reactors. Using a certain kind of reactor influences the product yield of the process. [2, 4, 7]

### 2.2.3.1 Fixed bed reactors

Temperature range for pyrolysis in a fixed bed reactor is usually 450-700 °C. Aydın and İlikılıç [9] studied the pyrolysis of waste tyres in the fixed bed reactor with capacity of 1.15 l under nitrogen conditions. Fabric and steel were removed from the feedstock prior to the process. The temperature range applied was 400-700 °C. It was observed that increasing temperature from 400 °C to 500 °C caused the increase in oil yield from 31 wt.% to 40 wt.%, respectively. However, further increase in temperature did not significantly influence oil yield. The influence of nitrogen flow on the product yield was reported to be negligible.

Williams et al. [10] investigated how the change of heating rate (from 5 to 80 °C/min) and temperature (from 300 to 720 °C) influenced the product yield in a small-scale, fixed-bed, batch reactor. In each case around 50 g of waste tyres were processed. The highest oil yield of 54-58.8 wt.% was achieved with temperature between 600 and 720 °C. The increasing heating rate led also to the increase

in gas yield, which at 720 °C and the heating rate 5 °C/min was 6.6 wt.%, while with the heating rate 80 °C/min it was 14.8 wt.%. Cunliffe and Williams [11] used a bigger fixed bed reactor to pyrolyze 1.5 kg of waste tyres at 475 °C and the heating rate equal to 5 °C/min. The obtained product yields were: oil – 58.2 wt.%, char – 37.3 wt.% and gas – 4.5 wt.%.

Williams et al. [12] conducted pyrolysis of shredded and whole tyres on a larger scale in a batch reactor with the capacity of 1 ton at the temperature of 950 °C. Products yields were quite different from those for batch reactors with a smaller capacity, namely 20.9 wt.% and 23.9 wt.% for oil and gas, respectively. The problem with that kind of large batch reactors is with heat transfer among all the tyres inside. The mentioned temperature of 950 °C was the maximum one applied and it was achieved after the heating period of 8 hours and 40 minutes. Because of the reactor design the tyres in its outer part underwent pyrolysis first, and the gases released from the tyres in the inner part of the reactor underwent secondary cracking reactions resulting in oil decomposition and the increase in gas product yield.

### **2.2.3.2 Fluidized bed reactors**

Kaminsky et al. [15] investigated tyres pyrolysis in a fluidized bed reactor on laboratory, technical and pilot scales with throughputs of 1, 30 and 200 kg/h, respectively. On technical scale tyres were pyrolyzed as a whole. The fluidized bed was heated indirectly by quartz sand bed with radiant heat tubes inside to the temperatures of 500-780 °C. In this system pyrolysis gas, which is the product, was used as a heat source. Screw extractor was used for ash removal in the system. In order to remove particulate matter product gasses were directed through cyclones. Condensed oil was removed from the reactor and then underwent distillation to form two fractions – light and heavy oils. In the next stage, electrostatic precipitators were used to get rid of remaining oil droplets from the gas. Tyres pyrolysis at the lab-scale fluidized bed with throughput of 1 kg/h and temperature of 740 °C gave oil yield of 30.2 wt.%, while pyrolysis at 700 °C at pilot scale with throughput 200 kg/h gave oil yield of 26.8 wt.%. Using steel free basis in the same conditions for the pilot scale gave results similar to the laboratory scale with oil yield equal to 30.9 wt.%.

Williams and Brindle [16] pyrolyzed tyre crumbs on laboratory scale in the fluidized bed reactor at temperature range of 450-600 °C. The applied throughput was 220 g/h and reactor dimensions were: diameter of 7.5 cm and height of 100 cm, the reactor bed was quartz sand. The process was conducted under nitrogen which was previously preheated to the temperature of 400 °C. At the temperature equal to 450 °C the highest oil yield of 55 wt.% was achieved, while at the temperature of 600 °C it was the lowest – 43.5 wt.%. Respective gas yields for these temperatures were 2.5 wt.% and 14 wt.%.

Circulating fluidized bed laboratory-scale reactor was used by X. Dai et al. [17]. The purpose of the experiment was to find out how tyre particle size (0.32 and 0.8 mm), process temperature (360-810 °C) and gas residence time (1-5 s) influence the composition and yields of the products. The dimensions of the reactor were 10 cm in diameter and 290 cm height, the bed was quartz sand. The screw feeder was used to introduce tyres to the reactor. Char and sand entrained from the bed were caught by two cyclones and then reversed to the reactor. Pyrolysis gasses were preheated and then used as fluidizing gas; water cooled condensers were applied to condensate oils. The highest oil yield

(52 wt.%) was achieved at the temperature of 450 °C and it decreased significantly (to 30 wt.%) at 810 °C. Gas yield at these temperatures was respectively 15 wt.% and 40 wt.%. When it comes to particle size, at the same temperature (500 °C) smaller one (0.32 mm) gave higher oil yield equal to 50 wt.%, while bigger one (0.8 mm) gave 41 wt.%. Changing the residence time of gasses in the hot zone of the reactor did not have a big influence on the oil yield. At the temperature of 500 °C with residence time of 1 s oil yield was 52 wt.%, while with residence time of 5 s it was 48 wt.%.

### **2.2.3.3 Screw kiln and rotary kiln reactors**

Apart from fixed bed reactors also moving bed reactors were tested for waste tyres pyrolysis. Aylón et al. [18] researched how pyrolysis temperature (600-800 °C) and tyres mass flow rate influenced product yield and its composition in continuous operating reactors. They used a screw kiln reactor and electrical furnaces to externally heat it. Throughputs of shredded tyres between 3.5 and 8 kg/h were fed to the reactor by screw feeder. The highest oil yield (48.4 wt.%) was achieved with tyre mass flow of 8 kg/h and the temperature of 600 °C. The same research group achieved oil yield of 56.4 wt.% for a fixed bed reactor. The difference was claimed to be due to different gas residence times and heating rates in these two reactors.

Diez et al. [19] conducted pyrolysis in such a way as to produce mainly gas and very little oil. In order to achieve that, fast heating rate and long gas residence time were applied. A screw kiln reactor was used and an electrical furnace was applied to externally heat it. Temperature of the process was 500/600 °C. The achieved product yields were: gas ca. 66.5 wt.% and char ca. 33.5 wt.%.

The impact of pyrolysis temperature on the product yield in a pilot-scale rotary kiln reactor was investigated by Galvagno et al. [20]. The reactor had the diameter of 0.4 m and was rotated with the speed of 3 r.p.m. The applied throughput was 4.8 kg/h and the system was heated externally by electric furnaces. The highest oil yield (38.12 wt.%) was obtained at the temperature of 550 °C, while the highest gas yield (10.75 wt.%) was achieved at the temperature of 680 °C. A similar experiment was conducted by Li et al. [21]. The used rotary kiln reactor had the following dimensions: diameter – 0.3 m and length – 3 m. Rotating speed applied in the experiment was 0.45-0.9 r.p.m.; the reactor was externally heated with electric furnaces. The maximum oil yield of 45.1 wt.% was achieved at 500 °C, whereas the gas yield was 13.6 wt.%. The highest gas yield of 18.3 wt.% was obtained at 650 °C.

### **2.2.4 Catalysts for waste tyres pyrolysis**

Many various catalysts were used in waste tyres pyrolysis process. The purpose of their application was to decrease the temperature of the process or to improve quantity and quality of the products.

Miandad et al. [2] examined the influence of different advanced catalysts, such as zeolite, natural zeolite, activated calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) and activated alumina ( $\text{Al}_2\text{O}_3$ ) on the products of waste tyres pyrolysis. The mass ratio of the catalyst to feedstock was 1:10 - with the samples of 1000 g of tyres and 100 g of catalyst. The applied heating rate was 10 °C/min, increasing the temperature from room temperature to 450 °C, which, based on TGA, was decided to be optimal. The process was



continued at the latter temperature for 75 minutes. The application of the catalysts led to the decrease in the concentration of aromatic compounds in produced oil. The oil from non-catalytic pyrolysis contained 93.3% aromatic compounds, while when using natural zeolite, activated calcium hydroxide and activated alumina it decreased to, respectively, 71, 60.9 and to 71%. On the other hand, synthetic zeolite as catalyst increased the concentration of aromatic compounds to 93.7%. The influence of the catalysts on a product yields is presented in Figure 5.

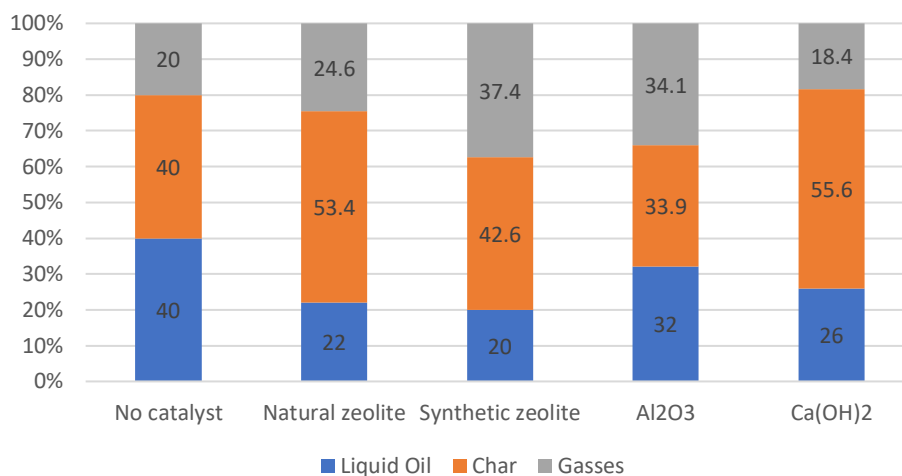


Figure 5 Products yield of waste tyres pyrolysis without and with various catalysts. Adapted from [2]

Aydın and İlkılıç [22] conducted waste tyres pyrolysis with  $\text{Ca}(\text{OH})_2$  as the catalyst. The main purpose was to decrease sulfur content in the liquid products. Three samples were investigated with 5%, 10% and 15% of catalyst, respectively. While the sample with 5% of catalyst led to a decrease in sulfur content, increasing the amount of the catalyst did not have a big influence on further S content decrease. The sample without the catalyst resulted in the liquid product with sulfur content of 1.4 wt.%, whereas for the samples reprocessed with the catalyst the sulfur content was ca. 0.9 wt.%.

The influence of alumina ( $\text{Al}_2\text{O}_3$ ), silica ( $\text{SiO}_2$ ) and their mixture with a 1:1 mass ratio on the yield and the composition of the products of waste tyre pyrolysis was investigated by Shah et al. [23]. The process was conducted at three different temperatures – 300 °C, 350 °C and 400 °C for all catalysts. Increasing the temperature resulted in the increase of gas yield. However, the increase was the most significant when  $\text{Al}_2\text{O}_3$  was used as the catalyst. Table 1 presents products yield for all studied temperatures and catalysts. The highest oil yield of 28.2 wt.% was achieved with  $\text{SiO}_2$  at 400 °C.

Temperature (°C)	Al <sub>2</sub> O <sub>3</sub>			SiO <sub>2</sub>			Al <sub>2</sub> O <sub>3</sub> + SiO <sub>2</sub>		
	300	350	400	300	350	400	300	350	400
Gas	7.4	16.67	20.93	2.4	8.0	15.46	0.4	1.533	5.0
Oil	3.73	17.53	23.2	1.8	8.07	28.2	1.233	13.13	14.8
Solid	95.5	65.8	55.67	96	84.06	56.26	98.58	85.33	80.13

Table 1 Influence of the temperature on product yields with different catalysts. Adapted from [23]

## 2.2.5 Products of waste tyres pyrolysis and their properties

Products of waste tyres pyrolysis are oil, char, gas and remaining steel. All of them can be used again. Oil is a liquid product of pyrolysis, it has a dark brown colour and after upgrading it may be used in Diesel engines. Depending on process condition it may have fairly high calorific value, even higher than tyres used as a process feed [7]. The solid product is biochar, its composition is determined by process conditions. On the other hand, biochar yield and quality highly influence economic feasibility of pyrolysis process. Gaseous product of pyrolysis is called pyrogas, it can be combusted and used as energy source for a process itself. Process temperature and used raw material have an influence on pyrogas composition. Recovered steel can be used further in a steel industry [7].

## 3. Experimental

### 3.1 Materials

For the purpose of the experiment scrap rubber tyres, from a local producer (Biogoma - Sociedade De Reciclagem De Pneus Lda), of 4 different size ranges were prepared: 0.6-0.8mm, 0.8-2.5mm, 2-4mm, 4-6mm. Samples of all ranges are presented in Figure 6. Used rubber comes from end-of-life tyres from passenger cars. During the experiment various, low cost, commercial 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. Samples of catalysts mixed with scrap rubber tyres are presented in Figure 7.



Figure 6 Waste tyres samples

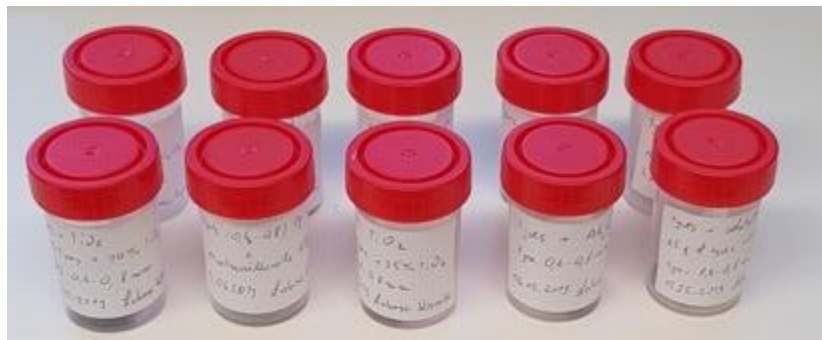


Figure 7 Samples of catalysts mixed with scrap rubber tyres.

### 3.2 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. [13, 14]

Thermogravimetric analysis of waste tyres sample was conducted using TG-DTA/DSC Setaram labsys (Figure 8) connected with computer equipped in appropriate software.



*Figure 8 Setaram Labsys DSC-TG-DTA thermobalance*

Thermogravimetric Analysis (TGA) of samples of all sizes was conducted. After that it was determined that the size 0.6 - 0.8 mm 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 performed under nitrogen atmosphere. The crucible used in the experiment is made of aluminium and it has volume of 0.5 ml. All the samples had a weigh between 100 – 150 mg.

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.

### **3.3 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, as can be seen in Figure 9. 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. Scheme of the installation is presented in Figure 9. [27]

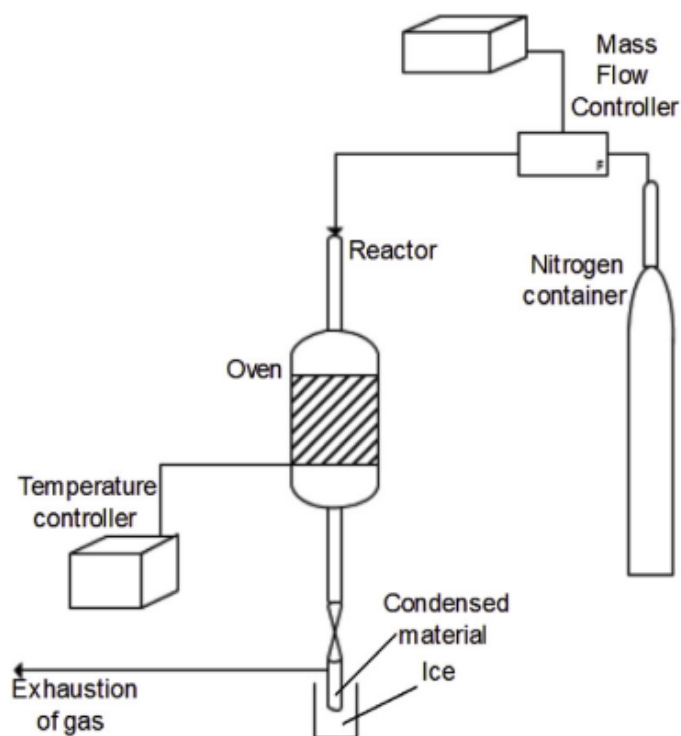


Figure 9 Scheme of the installation for pyrolysis process in a reactor [27].

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.



*Figure 10 The reactor placed in the oven.*



*Figure 11 The sample of tyres mixed with a catalyst before pyrolysis.*



*Figure 12 Bio-char after pyrolysis of rubber tyres mixed with a catalyst.*

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<sub>3</sub> as a catalyst was repeated with 1.25 g.

## 3.4 Characterization methods

### 3.4.1 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.



*Figure 13 Apparatus used to perform FTIR analysis.*

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  $\text{cm}^{-1}$ . Kubelka-Munk function was applied to correct the reflectance signal.



### 3.5 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 14 depicts an overview of kinetic analysis methods. [25]

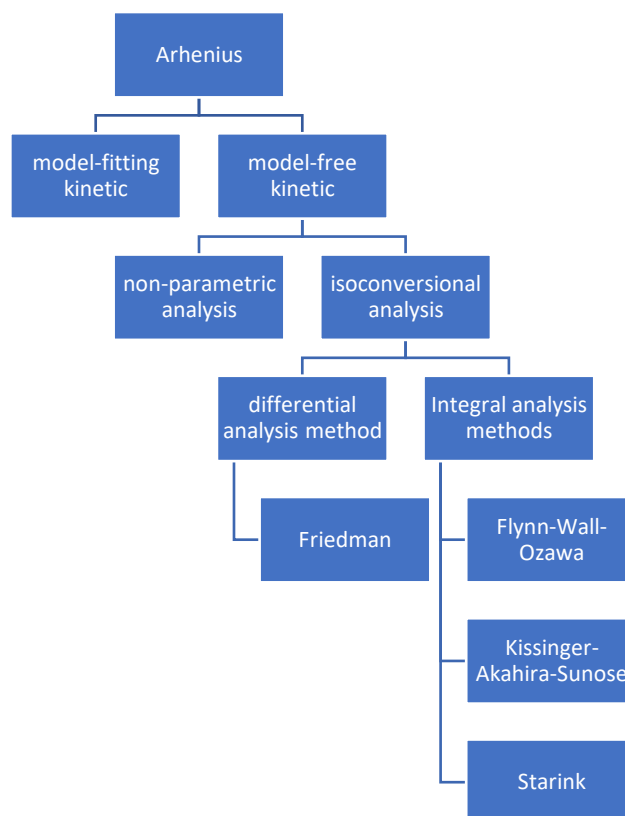


Figure 14 The overview of kinetic analysis methods for the decomposition process

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. [25] 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, isoconversial 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 [28]:

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

Where:

- $\alpha$  - conversion
- A - pre-exponential factor [s<sup>-1</sup>]
- $\beta$  - heating rate [K/s]
- $E_\alpha$  - activation energy [kJ/mol]
- R – universal gas constant [kJ/mol\*K]
- T – temperature [K]
- $f(\alpha)$  – function depending on the conversion

In the integral methods, the integral version of the equation is used and data on T( $\beta$ ) (where  $\beta$  is heating rate) is used to calculate activation energy. [26]

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

After the separation of variables,  $g(\alpha)$  as conversion integral and  $p(x)$  as temperature integral are defined, where  $x$  is  $\frac{E}{RT}$ .

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.

### 3.5.1 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 [26]:

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

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

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

### 3.5.2 Flynn-Wall-Ozawa method

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

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

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

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

### 3.5.3 Starink method

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

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

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

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

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

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

## 4. Results and discussion

### 4.1 Thermogravimetric analysis

#### 4.1.1 Thermogravimetric analysis 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 15. All the samples of tyres had a size of 0.6-0.8mm and a similar weight of ca. 113 mg.

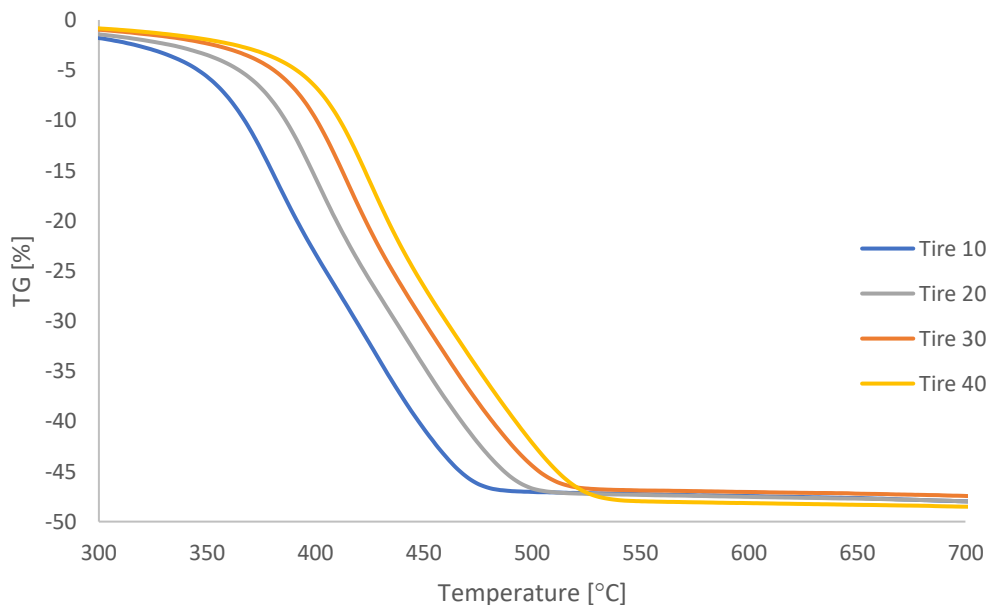


Figure 15 TG curves for waste tyres with different heating rates

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 16. All the samples of tyres had a size of 0.6-0.8mm and similar weigh of ca. 113 mg.

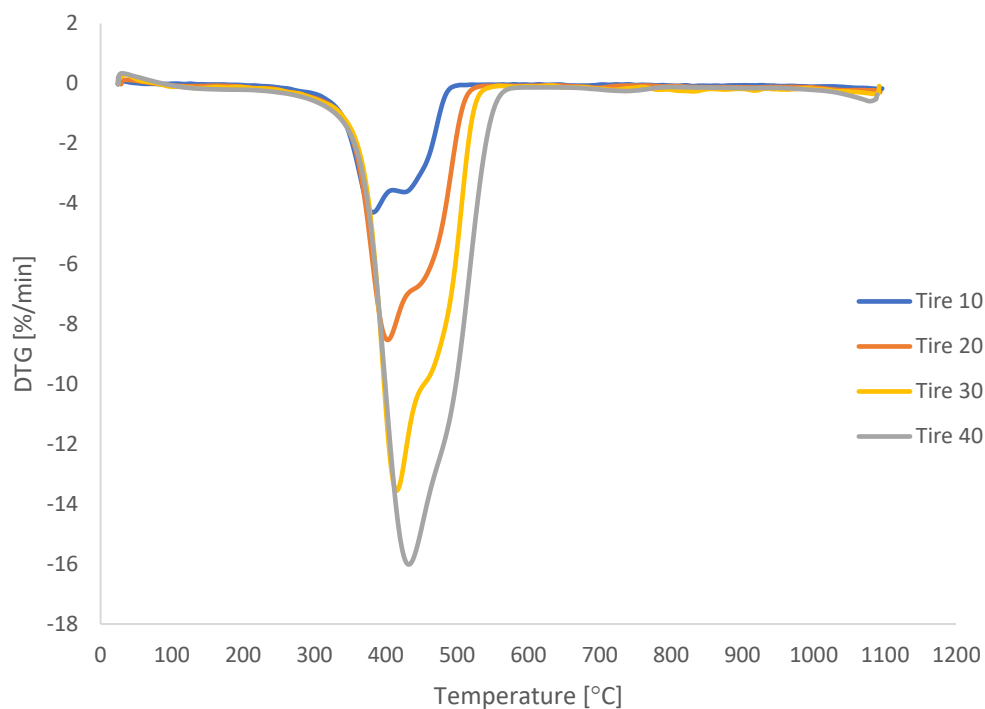


Figure 16 DTG curves for waste tyres with different heating rates

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 [34] 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.

#### 4.1.2 Determination of activation energy

Based on the methodology described in Chapter 3.5, 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 17. Next, trend lines were drawn, which slopes gave the values of  $\frac{BE\alpha}{R}$ .

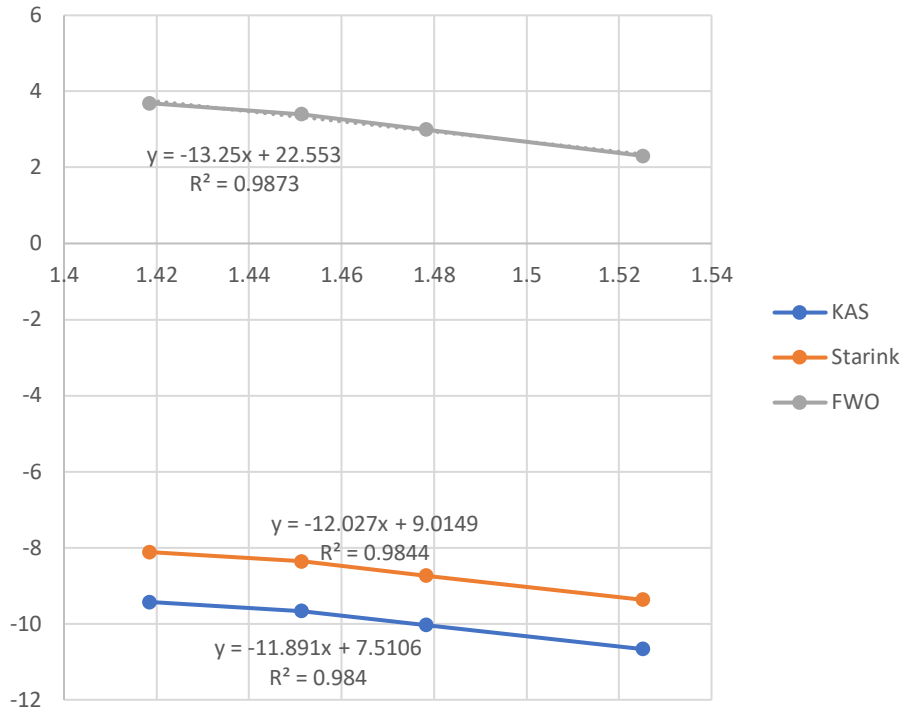


Figure 17 Regression lines for waste tyres computed by three different methods

The values of activation energy calculate by three different methods are summarized in the Table 2.

	KAS	Starink	FWO
E <sub>a</sub> [kJ/mol]	98.868	99.629	104.722

Table 2 Activation energy computed by three different methods based on TGA data.

D. I. Aslan et al. [33] 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.

#### 4.1.3 Thermogravimetric analysis 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 18. All the samples of tyres had a size of 0.6-0.8mm and similar weight of ca. 113 mg.

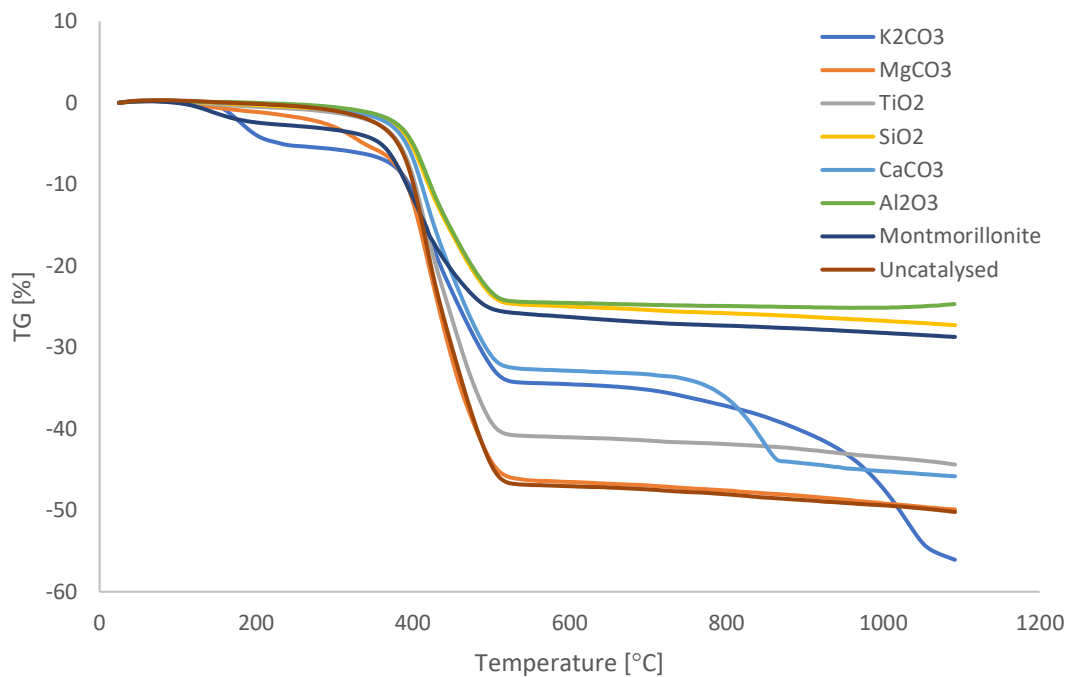


Figure 18 TG curves of waste tyres with different catalysts

As it can be seen from the comparison of the catalysed and uncatalysed 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 uncatalysed 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<sub>3</sub>.

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<sub>2</sub>O<sub>3</sub> up to 56% for K<sub>2</sub>CO<sub>3</sub>. It is clear that the applied catalyst has a strong influence on the final products distribution.

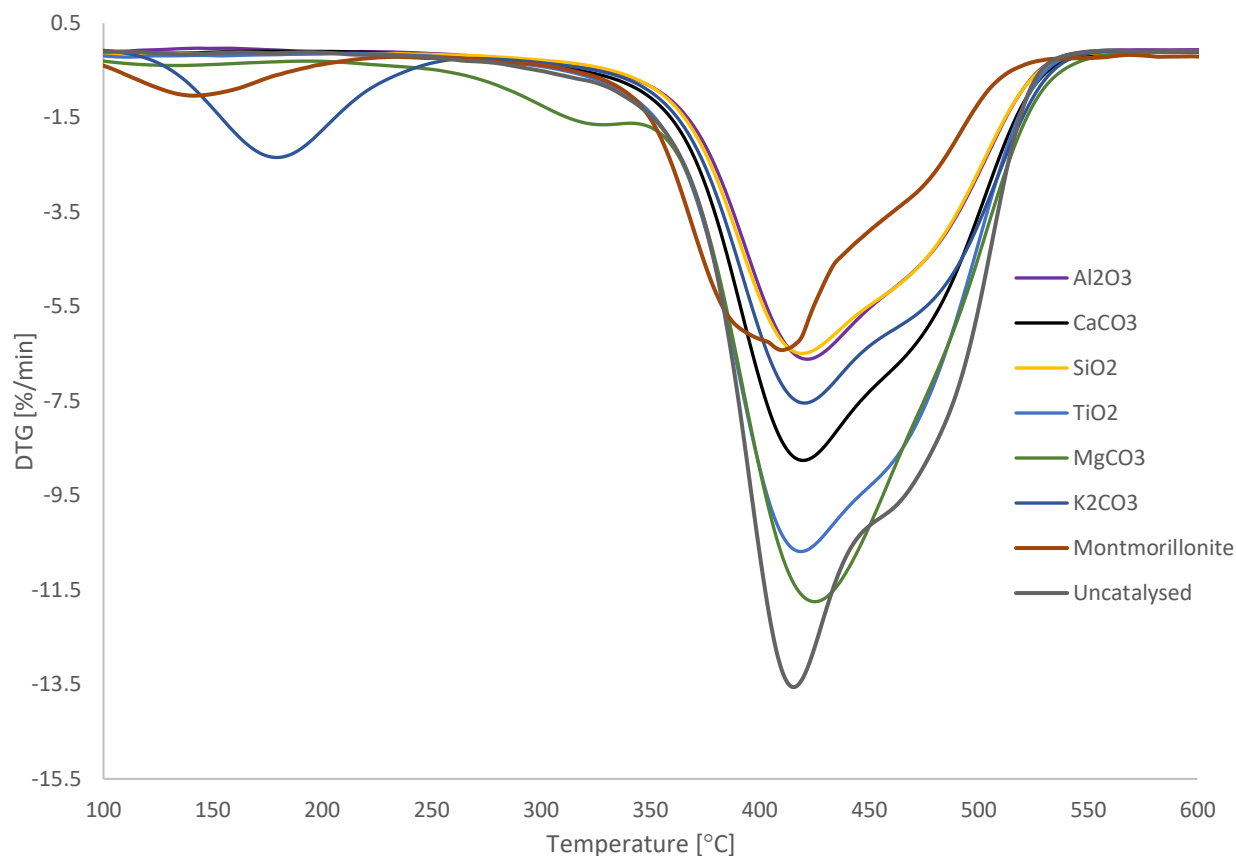


Figure 19 DTG curves of waste tyres with different catalysts

It can be seen from TGA and DTG for  $K_2CO_3$  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  $K_2CO_3$  results in an additional peak at around 180 °C. In case of montmorillonite the peak occurs at ca. 145 °C.

## 4.2 Pyrolysis in a fixed bed reactor

### 4.2.1 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 20.



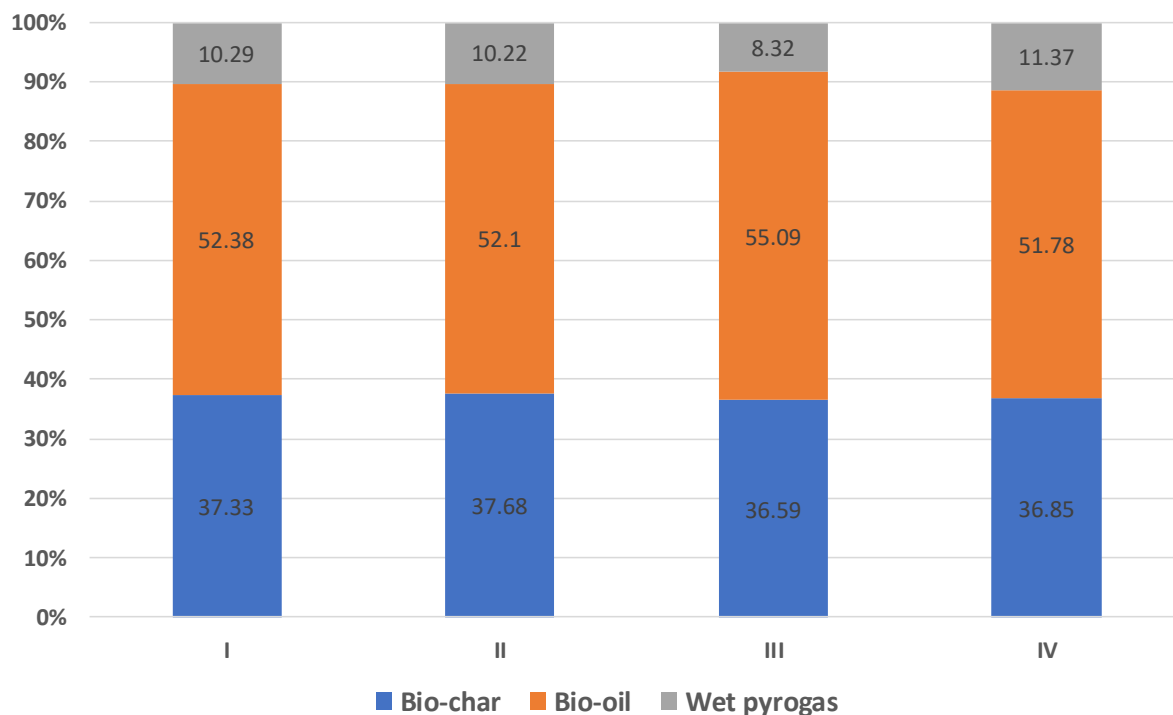


Figure 20 Products' yields of pyrolysis at 450 °C

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.

#### 4.2.2 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 21.

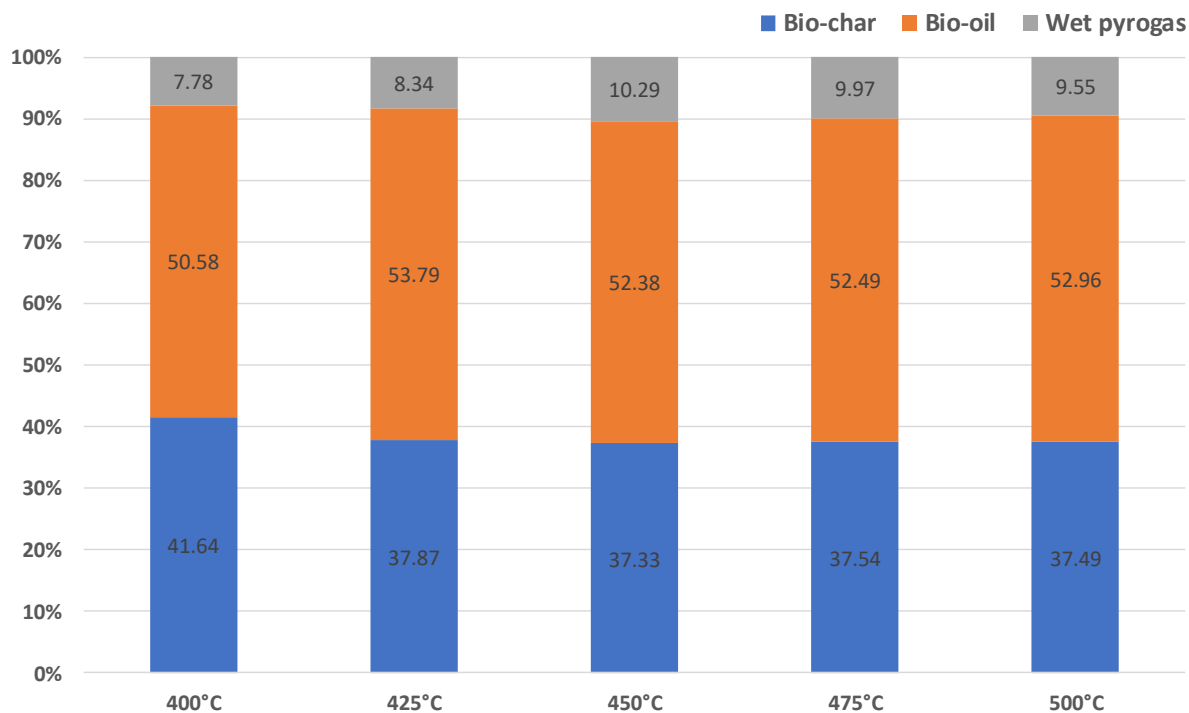


Figure 21 Products' yields of pyrolysis at different temperatures

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%).

### 4.2.3 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 CaCO<sub>3</sub> 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 22.

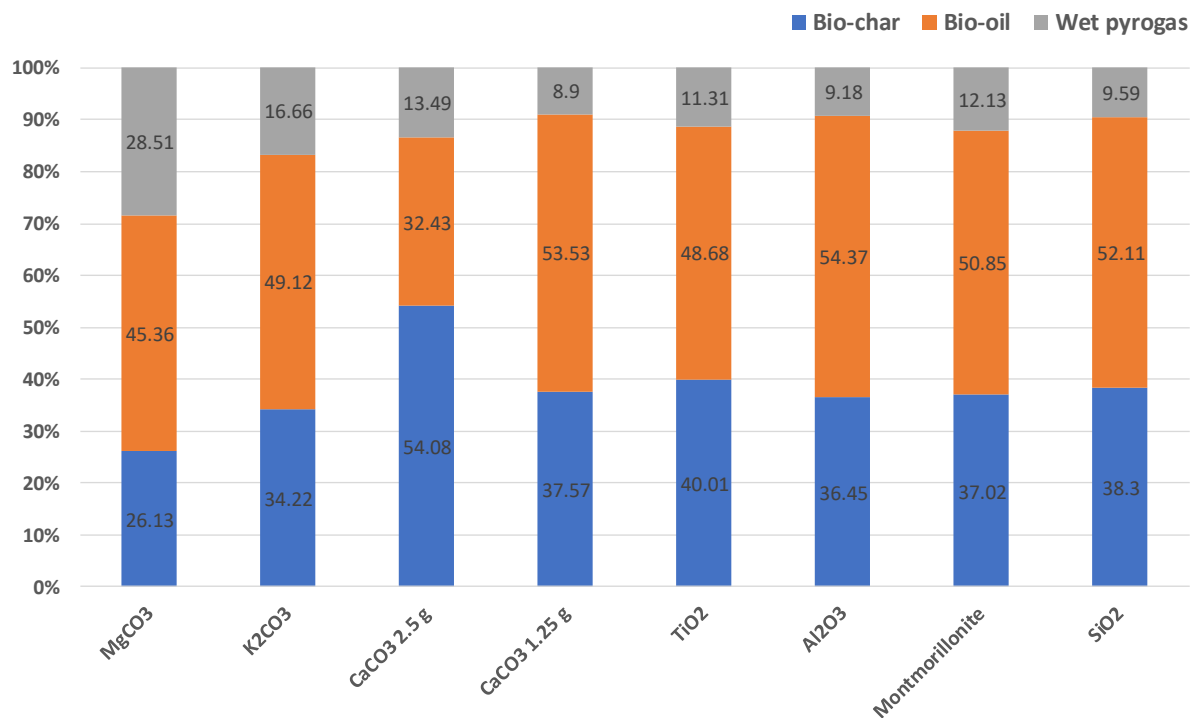


Figure 22 Products' yields of pyrolysis with different catalysts

The highest yield of bio-oil was achieved when Al<sub>2</sub>O<sub>3</sub> was used as a catalyst and it was equal to 54.37%. It was slightly lower for 1.25g of CaCO<sub>3</sub> – 53.53%. On the other hand, the lowest bio-oil yield was noted for the trial with 2.5g of CaCO<sub>3</sub>, while giving the highest biochar yield at the same time – 54.08%. Using MgCO<sub>3</sub> as a catalyst resulted in the lowest bio-char 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%.

### 4.3 FTIR of biooils

In order to characterize biooils obtained during pyrolysis trials Fourier Transform Infrared Spectroscopy was conducted for each sample. Figure 23 shows FTIR spectra of biooils from pyrolysis performed at different temperatures for bands centred between 2800 and 3000 cm<sup>-1</sup>. The peak at 2920 cm<sup>-1</sup> was assigned to C-H stretching group. The sharpest peak occurs for the temperature 475 °C.

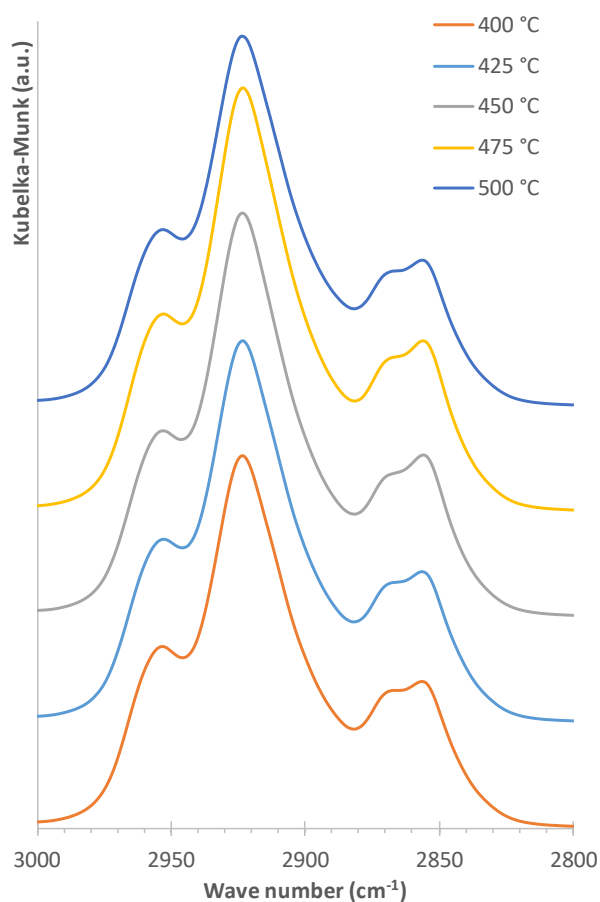


Figure 23 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber at different temperatures (400 °C to 500 °C) centered between 2800 and 3000  $\text{cm}^{-1}$

In Figure 24 FTIR spectra of biooils from pyrolysis performed at different temperatures for bands between 1780 and 1180  $\text{cm}^{-1}$  is presented. The peak at 1450  $\text{cm}^{-1}$  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 25 and 26. First one shows data for bands between 2800 and 3000  $\text{cm}^{-1}$ . The peak at 2920  $\text{cm}^{-1}$  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  $\text{cm}^{-1}$  the highest peak appears at 1450  $\text{cm}^{-1}$  and it was identified as C-H bending groups. The peak is the most intense for Montmorillonite and the least for  $\text{K}_2\text{CO}_3$ .

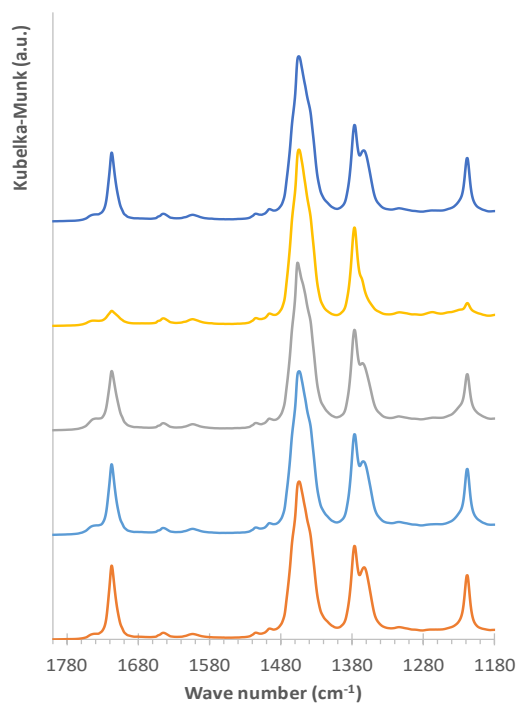


Figure 24 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber at different temperatures (400 °C to 500 °C) centered between 1180 and 1800  $\text{cm}^{-1}$

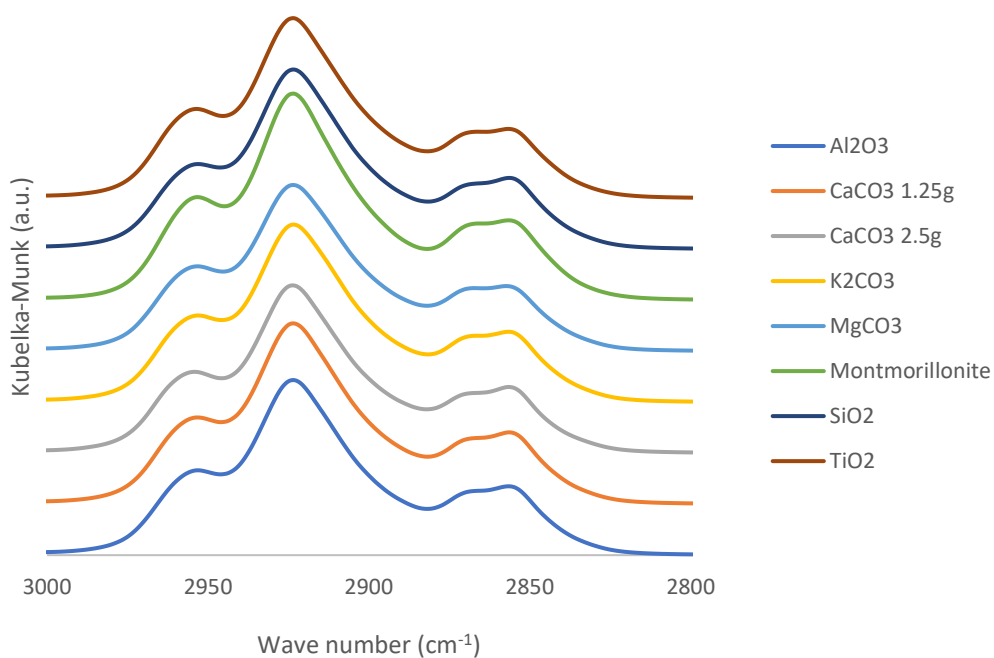


Figure 25 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber with different catalysts centered between 2800 and 3000  $\text{cm}^{-1}$

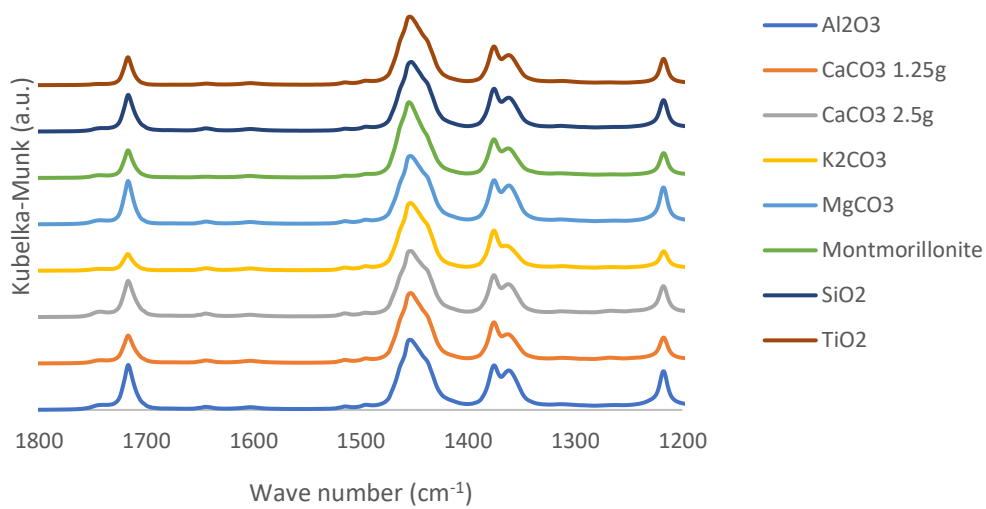


Figure 26 FTIR-ATR spectra of bio-oil phases obtained by scrap tires rubber with different catalysts centered between 1200 and 1800  $\text{cm}^{-1}$

## 5. 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  $\text{CaCO}_3$  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  $450\text{ }^\circ\text{C}$  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  $25\text{ }^\circ\text{C}$  from  $400$  to  $500\text{ }^\circ\text{C}$  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  $2.5\text{ g}$  of  $\text{Al}_2\text{O}_3$  and  $1.25\text{ g}$  of  $\text{CaCO}_3$  as catalysts. Using  $\text{MgCO}_3$  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  $2.5\text{ g}$  of  $\text{CaCO}_3$  as catalyst. Based on catalyzed process data conclusion can be drawn that different catalysts can be used to control product distribution.

### 5.1 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  $425\text{ }^\circ\text{C}$  was very similar to the one at  $450\text{ }^\circ\text{C}$ , 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  $500\text{ }^\circ\text{C}$ , 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.

## 6. References

- [1] <https://www.smithersrapra.com/resources/2017/april/tire-industry-in-boom-cycle>
- [2] P.T. Williams, *Pyrolysis of waste tyres: A review*, Waste Management, 2013, vol. 33, p. 1714-1728
- [3] R. Miandad et al., *Effect of advanced catalysts on tire waste pyrolysis oil*, Process Safety and Environmental Protection, 2018, vol. 116, p. 542-552
- [4] I. Hita et al., *Opportunities and barriers for producing high quality fuels from the pyrolysis of scrap tyres*, Renewable and Sustainable Energy Reviews, 2016, vol. 56, p. 745-759
- [5] <https://www.ustires.org/whats-tire-0>
- [6] J. Nisar et al., *Pyrolysis of waste tire rubber: Influence of temperature on pyrolysates yield*, Journal of Environmental Chemical Engineering, 2018, vol. 6, p. 3469-3473
- [7] J.D. Martinez et al., *Waste tyre pyrolysis – A review*, Renewable and Sustainable Energy Reviews, 2013, vol. 23, p. 179-213
- [8] J. Pyper, *BP Forecast: Shared, Autonomous EVs Will Help Drive to Peak Oil Before 2040*, February 2018, <https://www.greentechmedia.com/articles/read/bp-forecast-autonomous-electric-vehicles-peak-oil?fbclid=IwAR3LsKk8qbLkuMnPb3h3WMzDkaxYyyFC10v-TKiwKmOFwtYYqFAv0tosnbg#gs.gnjfp8> Available on 6.06.2019
- [9] H. Aydın, C. İlkılıç, *Optimization of fuel production from waste vehicle tires by pyrolysis and resembling to diesel fuel by various desulfurization methods*, December 2012, vol. 102, p. 605-612
- [10] P.T. Williams et al., *The pyrolysis of scrap automotive tyres: The influence of temperature and heating rate on product composition*, Fuel, December 1990, vol. 69, p. 1474-1482
- [11] A.M. Cunliffe, P.T. Williams, *Composition of oils derived from the batch pyrolysis of tyres*, Journal of Analytical and Applied Pyrolysis, 1998, vol. 44, p. 131-152
- [12] P.T. Williams, R.P. Bottrill, A.M. Cunliffe, *Combustion of Tyre Pyrolysis Oil*, Process Safety and Environmental Protection, 1998, vol. 76, p. 291-301
- [13] S. Loganathan et al., *Thermogravimetric Analysis for Characterization of Nanomaterials*, Thermal and Rheological Measurement Techniques for Nanomaterials Characterization, 2017, p. 67-108
- [14] S.T.D. Ellingham, T.J.U. Thompson, M. Islam., *Thermogravimetric Analysis of property changes and weight loss in incinerated bone*, Palaeogeography, Palaeoclimatology, Palaeoecology, 2015, vol. 438, p. 239-244
- [15] W. Kaminsky, C. Mennerich, Z. Zhang., *Feedstock recycling of synthetic and natural rubber by pyrolysis in a fluidized bed*, Journal of Analytical and Applied Pyrolysis, 2009, vol. 85, p. 334-337
- [16] P.T. Williams, A.J. Brindle, *Fluidised bed pyrolysis and catalytic pyrolysis of scrap tyres*, Environmental Technology, 2003, vol. 24, p. 921-929



- [17] X. Dai et al., *Pyrolysis of waste tires in a circulating fluidized-bed reactor*, Energy, 2001, vol. 26, p. 385-399
- [18] E. Aylón et al. *Waste Tire Pyrolysis: Comparison between Fixed Bed Reactor and Moving Bed Reactor*, Applied Chemistry, 2008, vol. 47, p. 4029-4033
- [19] C. Diez et al. *Pyrolysis of tyres: A comparison of the results from a fixed-bed laboratory reactor and a pilot plant (rotatory reactor)*, Journal of Analytical and Applied Pyrolysis, 2005, vol.74, p. 254-258
- [20] S. Galvagno et al. *Pyrolysis process for the treatment of scrap tyres: preliminary experimental results*, Waste Management, 2002, vol. 22, p. 917-923.
- [21] S.-Q. Li et al. *Pilot-Scale Pyrolysis of Scrap Tires in a Continuous Rotary Kiln Reactor*, Industrial and Engineering Chemistry Research, 2004, vol. 43, p. 5133-5145
- [22] H. Aydın, C. İlkılıç, *Fuel production from waste vehicle tires by catalytic pyrolysis and its application in a diesel engine*, Fuel Processing Technology, 2011, vol. 92, p. 1129-1135
- [23] J. Shah et al., *Recovery of value-added products from the catalytic pyrolysis of waste tyre*, Energy Conversion and Management, 2009, vol. 50, p. 991-994
- [24] S. Vyazovkin, C. A. Wight, *Model-free and model-fitting approaches to kinetic analysis of isothermal and nonisothermal data*, Termochimica Acta, 1999, vol. 340-341, p. 53-68
- [25] A. Khawam, *Application of solid state-kinetics to desolvation reactions*, Iowa University Doctoral Thesis, 2007
- [26] M.J. Starink, *The determination of activation energy from linear heating rate experiments: a comparison of the accuracy of isoconversion methods*, Termochimica Acta, 2003, vol. 404, p. 163-176
- [27] A.P. Soares Dias et al., *Catalyzed pyrolysis of SRC poplar biomass. Alkaline carbonates and zeolite catalysts*, Energy, 2019, vol. 183, p. 1114-1122
- [28] S. Vyazovkin et al., *ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data*, Termochimica Acta, 2011, vol. 520, p. 1-19
- [29] C. Sathiskumar, S. Karhikeyan, *Recycling of waste tires and its energy storage application of by-products – a review*, Sustainable Materials and Technologies, 2019, vol. 22
- [30] L. Bockstal et al., *Devulcanisation and reclaiming of tires and rubber by physical and chemical processes: A review*, Journal of Cleaner Production, 2019, vol. 236
- [31] B. Adhikari et al., *Reclamation and recycling of waste rubber*, Progress in Polymer Science, 2000, vol. 25, p. 909-948
- [32] S. Singh et al., *Waste tyre rubber as a secondary fuel for power plants*, Fuel, 2009, vol. 88, p. 2473- 2480
- [33] D. I. Aslan et al., *Pyrolysis reaction models of waste tires: Application of Master-Plots method for energy conversion via devolatilization*, Waste Management, 2017, vol. 68, p. 405 – 411

[34] B. Lah et al., *Pyrolysis of natural, butadiene, styrene–butadiene rubber and tyre components: Modelling kinetics and transport phenomena at different heating rates and formulations*, *Chemical Engineering Science*, 2013, vol. 87, p. 1 - 13